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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
13/722,585	12/20/2012	Dae-Young KIM	P10904US

CONFIRMATION NO. 8652

86144
LRK Patent Law Firm
1952 Gallows Rd
Suite 200
Vienna, VA 22182

POWER OF ATTORNEY NOTICE

OC000000099202007

Date Mailed: 05/02/2018

NOTICE REGARDING CHANGE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 04/19/2018.

- The Power of Attorney to you in this application has been revoked by the assignee who has intervened as provided by 37 CFR 3.71. Future correspondence will be mailed to the new address of record(37 CFR 1.33).

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/qtran/

UNITED STATES PATENT AND TRADEMARK OFFICE

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Alexandria, Virginia 22313-1450
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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
13/722,585	12/20/2012	Dae-Young KIM	0313070.IPXXX.00003

CONFIRMATION NO. 8652

24573
K&L Gates LLP-Chicago
P.O. Box 1135
CHICAGO, IL 60690

POA ACCEPTANCE LETTER

OC000000099202037

Date Mailed: 05/02/2018

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 04/19/2018.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/qtran/

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82A (07-13)
Approved for use through 01/31/2018. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

TRANSMITTAL FOR POWER OF ATTORNEY TO ONE OR MORE REGISTERED PRACTITIONERS

NOTE: This form is to be submitted with the Power of Attorney by Applicant form (PTO/AIA/82B) to identify the application to which the Power of Attorney is directed, in accordance with 37 CFR 1.5, unless the application number and filing date are identified in the Power of Attorney by Applicant form. If neither form PTO/AIA/82A nor form PTO/AIA82B identifies the application to which the Power of Attorney is directed, the Power of Attorney will not be recognized in the application.

Application Number	13/722,585
Filing Date	12-20-2012
First Named Inventor	Dae-Young KIM
Title	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
Art Unit	1784
Examiner Name	WANG, XIAOBEI
Attorney Docket Number	0313070.IPXXX.00003

SIGNATURE of Applicant or Patent Practitioner

Signature	/Matthew S. Dicke/	Date (Optional)	2018-04-19
Name	Matthew S. Dicke	Registration Number	58,819
Title (if Applicant is a juristic entity)			
Applicant Name (if Applicant is a juristic entity)			

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. If more than one applicant, use multiple forms.

☐ *Total of _____ forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82B (07-13)
Approved for use through 01/31/2018. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

POWER OF ATTORNEY BY APPLICANT

I hereby revoke all previous powers of attorney given in the application identified in either the attached transmittal letter or the boxes below.

Application Number	Filing Date

(Note: The boxes above may be left blank if information is provided on form PTO/AIA/82A.)

☑ I hereby appoint the Patent Practitioner(s) associated with the following Customer Number as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above: 24573

OR

☐ I hereby appoint Practitioner(s) named in the attached list (form PTO/AIA/82C) as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the patent application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above. (Note: Complete form PTO/AIA/82C.)

Please recognize or change the correspondence address for the application identified in the attached transmittal letter or the boxes above to:

☐ The address associated with the above-mentioned Customer Number

OR

☑ The address associated with Customer Number: 24573

OR

☐ Firm or Individual Name					
Address					
City		State		Zip	
Country					
Telephone		Email			

I am the Applicant (if the Applicant is a juristic entity, list the Applicant name in the box):

LS MTRON LTD.

☐ Inventor or Joint Inventor (title not required below)

☐ Legal Representative of a Deceased or Legally Incapacitated Inventor (title not required below)

☑ Assignee or Person to Whom the Inventor is Under an Obligation to Assign (provide signer's title if applicant is a juristic entity)

☐ Person Who Otherwise Shows Sufficient Proprietary Interest (e.g., a petition under 37 CFR 1.46(b)(2) was granted in the application or is concurrently being filed with this document) (provide signer's title if applicant is a juristic entity)

SIGNATURE of Applicant for Patent

The undersigned (whose title is supplied below) is authorized to act on behalf of the applicant (e.g., where the applicant is a juristic entity).

Signature	Ham Jong Geun	Date (Optional)	
Name			
Title	IP Manager , LS MTRON LTD.		

NOTE: Signature - This form must be signed by the applicant in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. If more than one applicant, use multiple forms.

☐ Total of forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Electronic Acknowledgement Receipt	
EFS ID:	32381579
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	86144
Filer:	Matthew S. Dicke/Elias Santiago
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	P10904US
Receipt Date:	19-APR-2018
Filing Date:	20-DEC-2012
Time Stamp:	11:40:50
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Assignee showing of ownership per 37 CFR 3.73	00003_373.pdf	118300 7930fe70c01070976d26033db6ecd07b91d2b824	no	3

Warnings:

Information:					
2	Power of Attorney	00003_POA.pdf	288438 26ff336aa2de1e55393f6677a4ef82819c1a59b0	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	406738	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/AIA/96 (08-12)
Approved for use through 01/31/2013. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

STATEMENT UNDER 37 CFR 3.73(c)

Applicant/Patent Owner: LS MTRON LTD.

Application No./Patent No.: 13/722,585 Filed/Issue Date: 12-20-2012

Titled: COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

LSIS CO., LTD., a corporation

(Name of Assignee) (Type of Assignee, e.g., corporation, partnership, university, government agency, etc.)

states that, for the patent application/patent identified above, it is (choose **one** of options 1, 2, 3 or 4 below):

1. ☑ The assignee of the entire right, title, and interest.

2. ☐ An assignee of less than the entire right, title, and interest (check applicable box):

   ☐ The extent (by percentage) of its ownership interest is _____%. Additional Statement(s) by the owners holding the balance of the interest must be submitted to account for 100% of the ownership interest.

   ☐ There are unspecified percentages of ownership. The other parties, including inventors, who together own the entire right, title and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

3. ☐ The assignee of an undivided interest in the entirety (a complete assignment from one of the joint inventors was made). The other parties, including inventors, who together own the entire right, title, and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

4. ☐ The recipient, via a court proceeding or the like (*e.g.*, bankruptcy, probate), of an undivided interest in the entirety (a complete transfer of ownership interest was made). The certified document(s) showing the transfer is attached.

The interest identified in option 1, 2 or 3 above (not option 4) is evidenced by either (choose **one** of options A or B below):

A. ☑ An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in the United States Patent and Trademark Office at Reel 030038, Frame 0382, or for which a copy thereof is attached.

B. ☐ A chain of title from the inventor(s), of the patent application/patent identified above, to the current assignee as follows:

1. From: _____ To: _____

   The document was recorded in the United States Patent and Trademark Office at

   Reel _____, Frame _____, or for which a copy thereof is attached.

2. From: _____ To: _____

   The document was recorded in the United States Patent and Trademark Office at

   Reel _____, Frame _____, or for which a copy thereof is attached.

This collection of information is required by 37 CFR 3.73(b). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PTO/AIA/96 (08-12)
Approved for use through 01/31/2013. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

STATEMENT UNDER 37 CFR 3.73(c)

3. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

4. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

5. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

6. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

☐ Additional documents in the chain of title are listed on a supplemental sheet(s).

☑ As required by 37 CFR 3.73(c)(1)(i), the documentary evidence of the chain of title from the original owner to the assignee was, or concurrently is being, submitted for recordation pursuant to 37 CFR 3.11.

[NOTE: A separate copy (i.e., a true copy of the original assignment document(s)) must be submitted to Assignment Division in accordance with 37 CFR Part 3, to record the assignment in the records of the USPTO. See MPEP 302.08]

The undersigned (whose title is supplied below) is authorized to act on behalf of the assignee.

/Matthew S. Dicke/	2018-04-19
Signature	Date
Matthew S. Dicke	Registered Attorney, 58,819
Printed or Typed Name	Title or Registration Number

[Page 2 of 2]

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	10/04/2016	9457541	P10904US	8652

86144 7590 09/14/2016

LRK Patent Law Firm
1952 Gallows Rd
Suite 200
Vienna, VA 22182

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 0 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

Dae-Young KIM, Gyeonggi-do, KOREA, REPUBLIC OF;
Byoung-Kwang Lee, Gyeonggi-do, KOREA, REPUBLIC OF;
Seung-Jun Choi, Gyeonggi-do, KOREA, REPUBLIC OF;
LS MTRON LTD., Gyeonggi-do, KOREA, REPUBLIC OF

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The USA offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to encourage and facilitate business investment. To learn more about why the USA is the best country in the world to develop technology, manufacture products, and grow your business, visit SelectUSA.gov.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any changes of address)

86144 7590 06/03/2016
LRK Patent Law Firm
1952 Gallows Rd
Suite 200
Vienna, VA 22182

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission
I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	P10904US	8652

TITLE OF INVENTION: COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$960	$0	$0	$960	09/06/2016

EXAMINER	ART UNIT	CLASS-SUBCLASS
WANG, XIAOBEI	1784	428-522000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).
- ☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
- ☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 LRK Patent Law Firm
2
3

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: LS MTRON LTD.

(B) RESIDENCE: (CITY and STATE OR COUNTRY): ANYANG-CITY, GYEONGGI-DO, REPUBLIC OF KOREA

Please check the appropriate assignee category or categories (will not be printed on the patent): ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. The following fee(s) are submitted:
- ☒ Issue Fee
- ☒ Publication Fee (No small entity discount permitted)
- ☐ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**
- ☐ A check is enclosed.
- ☐ Payment by credit card. Form PTO-2038 is attached.
- ☒ The director is hereby authorized to charge the required fee(s), any deficiency, or credits any overpayment, to Deposit Account Number 50-4875 (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)
- ☐ Applicant certifying micro entity status. See 37 CFR 1.29
  NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
- ☐ Applicant asserting small entity status. See 37 CFR 1.27
  NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
- ☐ Applicant changing to regular undiscounted fee status.
  NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date 9/6/2016
Typed or printed name Taekse Lee Registration No. 61976

PTOL-85 Part B (10-13) Approved for use through 10/31/2013. OMB 0651-0033 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Electronic Patent Application Fee Transmittal

Application Number:	13722585
Filing Date:	20-Dec-2012
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Filer:	Taeksoo Lee
Attorney Docket Number:	P10904US

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Utility Appl Issue Fee	1501	1	960	960

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**960**

Electronic Acknowledgement Receipt	
EFS ID:	26837570
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	86144
Filer:	Taeksoo Lee
Filer Authorized By:	
Attorney Docket Number:	P10904US
Receipt Date:	06-SEP-2016
Filing Date:	20-DEC-2012
Time Stamp:	12:26:03
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$960
RAM confirmation Number	090616INTEFSW12263300
Deposit Account	8990
Authorized User	Paul LEE
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Issue Fee Payment (PTO-85B)	issuefee.pdf	951316 892074a814e603d188a9a7219364b13ac2e5cb44	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30702 4131c235e0ab097673cc88e06314befb745873f3	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	982018		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

86144 7590 06/03/2016

LRK Patent Law Firm
1952 Gallows Rd
Suite 200
Vienna, VA 22182

EXAMINER
WANG, XIAOBEI

ART UNIT	PAPER NUMBER
1784	

DATE MAILED: 06/03/2016

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	P10904US	8652

TITLE OF INVENTION: COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$960	$0	$0	$960	09/06/2016

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

86144 7590 06/03/2016
LRK Patent Law Firm
1952 Gallows Rd
Suite 200
Vienna, VA 22182

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission
I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	P10904US	8652

TITLE OF INVENTION: COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$960	$0	$0	$960	09/06/2016

EXAMINER	ART UNIT	CLASS-SUBCLASS
WANG, XIAOBEI	1784	428-522000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).
- ❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
- ❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.
1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. The following fee(s) are submitted:
- ❑ Issue Fee
- ❑ Publication Fee (No small entity discount permitted)
- ❑ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**
- ❑ A check is enclosed.
- ❑ Payment by credit card. Form PTO-2038 is attached.
- ❑ The director is hereby authorized to charge the required fee(s), any deficiency, or credits any overpayment, to Deposit Account Number _____ (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)
- ❑ Applicant certifying micro entity status. See 37 CFR 1.29 — NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
- ❑ Applicant asserting small entity status. See 37 CFR 1.27 — NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
- ❑ Applicant changing to regular undiscounted fee status. — NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

PTOL-85 Part B (10-13) Approved for use through 10/31/2013. OMB 0651-0033 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	P10904US	8652

86144 7590 06/03/2016

LRK Patent Law Firm
1952 Gallows Rd
Suite 200
Vienna, VA 22182

EXAMINER	
WANG, XIAOBEI	

ART UNIT	PAPER NUMBER
1784	

DATE MAILED: 06/03/2016

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 13/722,585	Applicant(s) KIM ET AL.	
	Examiner Xiaobei Wang	Art Unit 1784	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to *2/18/2016*.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on_____.
2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.
3. ☒ The allowed claim(s) is/are *1,2,5 and 6*. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov .
4. ☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☒ All b) ☐ Some *c) ☐ None of the:
   1. ☒ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).
6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____ .
5. ☐ Examiner's Amendment/Comment
6. ☒ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/Xiaobei Wang/ Examiner, Art Unit 1784	/HUMERA SHEIKH/ Supervisory Patent Examiner, Art Unit 1784

1. The present application is being examined under the pre-AIA first to invent provisions.

DETAILED ACTION

Response to Arguments

2. Applicant's arguments, see Remarks, filed 2/18/2016, with respect to the 35 U.S.C. 103(a) rejection of claims 1, 2, 5 and 6 have been fully considered and are persuasive. The rejection has been withdrawn.

Allowable Subject Matter

1. Claims 1, 2, 5 and 6 are allowed.

2. The following is an examiner's statement of reasons for allowance: The prior art of record does not teach or suggest a copper foil having the claimed texture coefficients so as to prevent wrinkle generation.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Xiaobei Wang whose telephone number is (571)270-5705. The examiner can normally be reached on Monday through Friday 9AM - 5PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Humera Sheikh can be reached on 571-272-0604. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Xiaobei Wang/
Examiner, Art Unit 1784

/HUMERA SHEIKH/
Supervisory Patent Examiner, Art Unit 1784

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	68	(cu copper) near foil and ("111" and "200" and "220") with (crystal crystalline orientation index)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	OR	ON	2016/04/28 13:30
L2	9	1 and wrinkle	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	OR	ON	2016/04/28 13:30

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L3	7	(cu copper) near (sheet.clm. foil.clm.) and ("111".clm. and "200".clm. and "220".clm.) with (crystal crystalline orientation index)	US-PGPUB; USPAT	OR	ON	2016/04/28 13:37
L4	0	3 and 428/522.ccls. and B32B15$.cpc.	US-PGPUB; USPAT	OR	ON	2016/04/28 13:37

4/28/2016 1:38:13 PM
C:\Users\xwang2\Documents\EAST\Workspaces\13722585.wsp

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	**Art Unit**
	XIAOBEI WANG	1784

CPC						
Symbol					**Type**	**Version**
B32B		15	/	01	F	2013-01-01
Y10T		428	/	12431	A	2015-01-15
Y10T		428	/	12229	A	2015-01-15
Y10T		428	/	12472	A	2015-01-15
Y10T		428	/	12993	A	2015-01-15
C22C		9	/	00	I	2013-01-01
C25D		3	/	38	A	2013-01-01
C25D		7	/	0614	I	2013-01-01
H01M		4	/	661	I	2013-01-01
H01M		10	/	052	A	2013-01-01
			/			
			/			
			/			
			/			
			/			

CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
			/					
			/					

/LUCAS WANG/ Examiner.Art Unit 1784	05/17/2016	**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	4	
/HUMERA SHEIKH/ Supervisory Patent Examiner.Art Unit 1784	05/30/2016	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	N/A

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	Art Unit
	XIAOBEI WANG	1784

US ORIGINAL CLASSIFICATION						INTERNATIONAL CLASSIFICATION										
CLASS	SUBCLASS					CLAIMED						NON-CLAIMED				
429	522					H	0	1	M	4 / 64 (2006.0)						
CROSS REFERENCE(S)																
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)															
429	485	517														
428	577	612	687													

/LUCAS WANG/ Examiner.Art Unit 1784 (Assistant Examiner)	05/17/2016 (Date)	**Total Claims Allowed:** 4	
/HUMERA SHEIKH/ Supervisory Patent Examiner.Art Unit 1784 (Primary Examiner)	05/30/2016 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure N/A

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	**Art Unit**
	XIAOBEI WANG	1784

☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☒ T.D. ☐ R.1.47

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1														
2	2														
3	5														
4	6														

/LUCAS WANG/ Examiner.Art Unit 1784	05/17/2016	**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	4	
/HUMERA SHEIKH/ Supervisory Patent Examiner.Art Unit 1784	05/30/2016	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	N/A

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	Art Unit
	Xiaobei Wang	1784

CPC- SEARCHED		
Symbol	Date	Examiner
B32B 15/01	07-30-2014	CL
C22C 9/00	07-30-2014	CL
C25D 3/38, 7/0614	07-30-2014	CL
H01M 4/661, 10/052	07-30-2014	CL

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner
429	522, 485, 517	07-30-2014	CL
428	577, 612, 687	07-30-2014	CL

SEARCH NOTES		
Search Notes	Date	Examiner
Updated EAST Search	7/9/2015	XW
Updated EAST Search	10/21/2015	XW
Updated EAST Search	4/28/2016	XW

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner
429	485, 517, 522	07-30-2014	CL
428	577, 612, 687	07-30-2014	
B32B	15/all	4/28/2016	XW
428	522	4/28/2016	XW

/LUCAS WANG/ Examiner.Art Unit 1784	

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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 13/722,585	Filing Date 12/20/2012	☐ To be Mailed

ENTITY: ☒ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT	02/18/2016	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 4	Minus	** 20	= 0	X $80 =	0
	Independent (37 CFR 1.16(h))	* 1	Minus	***3	= 0	X $420 =	0
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	0

AMENDMENT		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

LIE
/PAMELA v. THERATT/

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	: LS Mtron Ltd.	Group Art Unit: 1784	
Appl. No.	: 13/722,585	Examiner:	Wang, Xiaobei
Filed	: 12/20/2012	Confirmation No. : 8652	

For : COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

AMENDMENT UNDER 37 C.F.R. § 1.111

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In response to the Office action of October 29, 2015, which set a three-month shortened statutory period to expire on January 29, 2016, now February 29, 2016 with a one month Extension of Time, Applicant submits the amendments and remarks as follows for entry in the above-identified patent application and requests reconsideration of the rejections of the application, in due course.

However, if any extension of time is necessary or there are any underpayments or overpayments of fees associated with the filing of this Amendment, this is an express request for any necessary extension of time and authorization to charge any required extension of time fee or any other fees which may be required to preserve the pendency of the present application to Deposit Account No. 50-4895.

Amendments to the Claims are reflected in the listing of claims which begins on page 2 of this paper.

Remarks begin on page 4 of this paper

IN THE CLAIMS

This listing of claims will replace all prior versions, and listings, of claims in the application:

LISTING OF CLAIMS

1. (Currently Amended) A copper foil for a current collector of a lithium secondary battery,

wherein, in a crystalline structure, a ratio of a sum of texture coefficients of a (111) surface and a (200) surface to a total sum of texture coefficients of the (111) surface, the (200) surface and a (220) surface is 60 to 85%, a ratio of a texture coefficient of the (111) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 18 to 38%, a ratio of the texture coefficient of the (200) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 28 to 62%, and a ratio of the texture coefficient of the (220) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 15 to 40%,

wherein the texture coefficient satisfies the following equation:

$$TC(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{n}\Sigma\frac{I(hkl)}{I_0(hkl)}}$$

wherein I(hkl) represents a measured diffraction intensity with respect to a (hkl) surface, and I_0(hkl) represents a standard diffraction intensity of ASTM (American Society of Testing Materials) standard powder-shaped diffraction data,

wherein the copper foil has a weight deviation of 3% or less, and

wherein the copper foil has a tensile strength of 30 to 40 kgf/mm^2,

so as to prevent the generation of wrinkles at a surface of the copper foil.

2. (Original) The copper foil for a current collector of a lithium secondary battery according to claim 1, wherein the copper foil has a surface roughness (Rz-JIS) of 2 μm or less.

3. (Cancelled)

4. (Cancelled)

5. (Original) The copper foil for a current collector of a lithium secondary battery according to claim 1, wherein the copper foil has an elongation of 3 to 20%.

6. (Original) The copper foil for a current collector of a lithium secondary battery according to claim 1, wherein the copper foil has a thickness of 1 to 35 μm.

REMARKS

Claim 1 has been amended. Claims 1, 2, 5 and 6 remain pending in the application. No new matter is believed to be introduced by the present amendments.

Reconsideration of the rejections and allowance of the pending application in view of the above-noted claim amendments and the following remarks are respectfully requested.

Applicant appreciates Examiner Wang spending time on February 8, 2016 to discuss this case during a telephone interview. Claim 1 has been amended in the manner discussed during the interview.

In the Office action, claims 1 and 5 stand rejected under pre-AIA 35 U.S.C. 103(a) as being unpatenable over Hirose et al. (US PGPub 2009/0061326, hereinafter "Hirose") in view of Matsuda et al. (US PGPub 2010/0038115, hereinafter "Matsuda"). Claims 2 and 6 stand rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Hirose and Matsuda and further in view of Nishimoto (US Patent 6,451,441, hereinafter "Nishimoto"). In addition, claims 1 and 5 stand rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Battey et al. (US Patent 4,695,348, hereinafter "Battey") in view of Matsuda. Claims 2 and 6 stand rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Battey and Matsuda and further in view of Nishimoto. Applicant will argue the inapplicability of these rejections to the amended claims.

Independent claim 1 has been amended to include the limitation "so as to prevent the generation of wrinkles at a surface of the copper foil." This limitation is supported in the specification in multiple places. No new matter is believed to be introduced by the present amendment.

Independent claim 1 now recites:

> A copper foil for a current collector of a lithium secondary battery,
>
> wherein, in a crystalline structure, a ratio of a sum of texture coefficients of a (111) surface and a (200) surface to a total sum of texture coefficients of the (111) surface, the (200) surface and a (220) surface is 60 to 85%, a ratio of a texture coefficient of the (111) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 18 to 38%, a ratio of the texture coefficient of the (200) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 28 to 62%, and a ratio of the texture coefficient of the (220) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 15 to 40%,
>
> wherein the texture coefficient satisfies the following equation:
>
> $$TC(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{n}\Sigma\frac{I(hkl)}{I_0(hkl)}}$$
>
> wherein I(hkl) represents a measured diffraction intensity with respect to a (hkl) surface, and I_0(hkl) represents a standard diffraction intensity of ASTM (American Society of Testing Materials) standard powder-shaped diffraction data,
>
> wherein the copper foil has a weight deviation of 3% or less, and
>
> wherein the copper foil has a tensile strength of 30 to 40 kgf/mm^2,
>
> so as to prevent the generation of wrinkles at a surface of the copper foil.

Applicant respectfully submits that the references relied upon in the rejection under 35 U.S.C. 103(a), considered singly or in any proper combination, do not disclose such a combination of features as is now recited in amended claim 1.

The Office Action states that the applicant presents no objective evidence showing that the prior art copper foil contains wrinkles at the surface. The applicant respectfully traverses this allegation based on the points set forth below.

In the previously filed Amendment, the applicant set forth an argument based on the ratio I(200)/I(111) of Hirose for each of Examples and Comparative Examples in Table 1 of this application. Here, among Comparative Examples which do not satisfy the conditions of Claim 1 of this application, some Comparative Examples (i.e., Comparative Examples 1, 5-9) satisfy the condition of the ratio I(200)/I(111) of Hirose. In other words, it shows that the copper foil of Hirose contains wrinkles at the surface.

Therefore, applicant believes that Hirose does not recognize that the texture coefficient ratio is an important factor in relation to the generation of wrinkles at the surface of the copper foil, and thus the applicant presented objective evidence showing that the prior art copper foil contains wrinkles at the surface.

The Office Action states that applicant's data (i.e., Table 1 of Specification) may support a conclusion that the texture coefficients are important to having no wrinkle, but does not appear to support a conclusion that the precise confluence of texture coefficients, tensile strength and weight deviation has critical significance to the lack of wrinkles. The applicant respectfully traverses this allegation based on the points set forth below.

Referring to Table 1 of this application, all Examples 1-7 satisfy the numerical ranges of all conditions, defined in Claim 1 of this application, thereby preventing wrinkles. However, Comparative Example 9 satisfies the numerical range of the tensile strength and four texture coefficient ratios, defined in Claim 1 of this application, but does not satisfy the numerical range of the weight deviation, which results in the generation of wrinkles. In detail, as seen from Comparative Example 9, even though other conditions of Claim 1 are satisfied, if the weight deviation deviates just a little

above the range of Claim 1, wrinkles are generated. In other words, the weight deviation has critical significance to the prevention of wrinkles.

Furthermore, referring to Table 1 of this application, all Examples 1-7 satisfy the numerical ranges of all conditions, defined in Claim 1 of this application, thereby preventing wrinkles. However, Comparative Examples 7 and 8 satisfy the numerical ranges of the weight deviation and four texture coefficient ratios, defined in Claim 1 of this application, but do not satisfy the numerical range of the tensile strength, which results in the generation of wrinkles. In detail, as seen from Comparative Examples 7 and 8, even though the other conditions of Claim 1 are satisfied, if the tensile strength deviates just a little below or above the range of Claim 1, wrinkles are generated. In other words, the tensile strength has critical significance to the prevention of wrinkles.

Therefore, as described above, the applicant believes that applicant's data (i.e., Table 1 of the Specification) may support a conclusion that the precise confluence of texture coefficients, tensile strength and weight deviation has critical significance to the prevention of wrinkles.

In addition, referring to Table 1 of this application, all Examples 1-7 satisfy the numerical ranges of all conditions, defined in Claim 1 of this application, thereby preventing wrinkles. However, Comparative Examples 1 to 6 satisfy the numerical ranges of the tensile strength and the weight deviation, defined in Claim 1 of this application, but do not satisfy at least one of the numerical ranges of four the texture coefficient ratios, which results in the generation of wrinkles. In detail, as seen from Comparative Examples 1 and 2, if the (111) ratio deviates just a little below or above the range of Claim 1, wrinkles are generated even though the other conditions of Claim 1

are satisfied. In addition, as seen from Comparative Examples 3 and 4, if the (200) ratio deviates just a little below or above the range of Claim 1, wrinkles are generated even though the other conditions of Claim 1 are satisfied. Moreover, as seen from Comparative Examples 5 and 6, if the (222) ratio and the (111)+(200) ratio deviate just a little below or above the ranges of Claim 1, wrinkles are generated even though the other conditions of Claim 1 are satisfied. In other words, the texture coefficient ratios have critical significance to the prevention of wrinkles.

The instant application is directed to preventing the generation of wrinkles at a surface of the copper foil. As will be explained in detail below, the cited prior art fails to disclose the prevention of wrinkles at a surface of the copper foil.

Referring to Table 1 in the specification of this application, the factors which prevent wrinkles from being generated at the surface of a copper foil are a texture coefficient ratio, a tensile strength and a weight deviation.

Comparative Examples 7-9 in Table 1 satisfy the texture coefficient ratio defined in Claim 1. In other words, a ratio of a sum of texture coefficients of a (111) surface and a (200) surface to a total sum of texture coefficients of the (111) surface, the (200) surface and a (220) surface is 60 to 85%; a ratio of a texture coefficient of the (111) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 18 to 38%; a ratio of the texture coefficient of the (200) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 28 to 62%; and a ratio of the texture coefficient of the (220) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 15 to 40%.

However, the number of generated wrinkles in Comparative Examples 7 and 8 is 2, and the number of generated wrinkles in Comparative Example 9 is 5. In other words, in order to prevent wrinkles from being generated at the surface of the copper foil, all conditions of the texture coefficient ratio, the tensile strength and the weight deviation should be satisfied.

In detail, as defined in Claim 1, not only the texture coefficient ratio should be satisfied, but also the copper foil should have a weight deviation of 3% or less and the copper foil should have a tensile strength of 30 to 40 kgf/mm^2. In Examples 1 to 7 of Table 1, the texture coefficient ratio, the tensile strength and the weight deviation are entirely satisfied so that the number of generated wrinkles is 0 (zero).

Meanwhile, the prior art references (Hirose, Battey, Matsuda and Nishimoto) all fail to teach or suggest the distinctive feature of the subject invention which is directed to preventing the generation of wrinkles at a surface of the copper foil.

First, Hirose is directed to improving the cycle characteristic. For this, Hirose only discloses that a current collector containing copper has a ratio I(200)/I(111) in the range from 0.5 to 1.5, and does not disclose the tensile strength and the weight deviation.

Referring to Table 1 in the specification of this application, among Examples of the subject invention satisfying the conditions of Claim 1 of this application, some examples satisfy the condition of the ratio I(200)/I(111) of Hirose and the other examples do not satisfy the condition. In addition, among Comparative Examples which do not satisfy the conditions of Claim 1 of this application, some comparative examples satisfy the condition of the ratio I(200)/I(111) of Hirose and the other comparative

examples do not satisfy the condition. Please see the followings for more details.

First, the ratio I(200)/I(111) of Hirose can be calculated as follows by using the data of Table 1 of this application.

$$TC : \textit{Texture Coeffciient}$$

$$\frac{(200)ratio}{(111)ratio} = \frac{\dfrac{TC(200)}{TC(111)+TC(200)+TC(220)}}{\dfrac{TC(111)}{TC(111)+TC(200)+TC(220)}} = \frac{TC(200)}{TC(111)}$$

$$= \frac{\dfrac{\dfrac{I(200)}{I_0(200)}}{\dfrac{1}{3}\left(\dfrac{I(111)}{I_0(111)}+\dfrac{I(200)}{I_0(200)}+\dfrac{I(220)}{I_0(220)}\right)}}{\dfrac{\dfrac{I(111)}{I_0(111)}}{\dfrac{1}{3}\left(\dfrac{I(111)}{I_0(111)}+\dfrac{I(200)}{I_0(200)}+\dfrac{I(220)}{I_0(220)}\right)}} = \frac{\dfrac{I(200)}{I_0(200)}}{\dfrac{I(111)}{I_0(111)}} = \frac{I_0(111)}{I_0(200)} \times \frac{I(200)}{I(111)}$$

$$\Rightarrow \textit{JCPDS CARD } 04-0836 : I_0(111) = 100,\ I_0(200) = 46$$

$$\frac{(200)ratio}{(111)ratio} = \frac{100}{46} \times \frac{I(200)}{I(111)}$$

$$\Rightarrow \quad \frac{I(200)}{I(111)} = 0.46 \times \frac{(200)ratio}{(111)ratio}$$

By using this method, the ratio I(200)/I(111) of each example and comparative example of Table 1 of this application can be calculated as follows.

	(111)+(200) ratio	111) ratio	200) ratio	220) ratio	(200) ratio / (111) ratio	I(200)/I(111)	0.5 ≤ I(200)/I(111) ≤ 1.5
Example 1	76	6	0	4	1.9231	0.8846	Y
Example 2	62	1	1	8	1.0000	0.4600	N
Example 3	83	2	1	7	1.5938	0.7331	Y
Example 4	70	0	0	0	2.5000	1.1500	Y
Example 5	72	5	6	9	1.0286	0.4731	N
Example 6	81	2	9	9	2.6818	1.2336	Y
Example 7	66	6	0	4	0.8333	0.3833	N
Comparative Example 1	64	6	8	6	3.0000	1.3800	Y
Comparative Example 2	73	1	2	7	0.7805	0.3590	N
Comparative Example 3	62	7	5	8	0.6757	0.3108	N

Comparative Example 4	83	9	4	7	3.3684	1.5495	N
Comparative Example 5	87	4	3	3	1.5588	0.7171	Y
Comparative Example 6	57	6	1	3	1.1923	0.5485	Y
Comparative Example 7	80	0	9	1	1.6333	0.7513	Y
Comparative Example 8	75	3	1	6	2.2174	1.0200	Y
Comparative Example 9	76	5	0	5	2.0000	0.9200	Y

As discussed above, among Examples satisfying the conditions of Claim 1 of this application, some examples satisfy the condition of the ratio I(200)/I(111) of Hirose and the other examples do not satisfy the condition. In addition, among Comparative Examples which do not satisfy the conditions of Claim 1 of this application, some comparative examples satisfy the condition of the ratio I(200)/I(111) of Hirose and the other comparative examples do not satisfy the condition.

In other words, even though the copper foil satisfies the ratio I(200)/I(111) disclosed in Hirose, wrinkles can be generated at the surface of the copper foil. Therefore, Hirose does not recognize that the texture coefficient ratio is an important

factor in relation to the prevention of wrinkles at the surface of the copper foil.

Further, in the subject invention, the prevention of wrinkles at the surface of the copper foil depends not only on the texture coefficient ratio but also on the tensile strength and the weight deviation, but Hirose fails to teach or suggest the tensile strength and the weight deviation.

In relation to the tensile strength, the Office Action compares the tensile strength taught by Matsuda with the tensile strength of the subject invention. As indicated in the Office Action, Paragraph [0051] of Matsuda discloses that the electrodeposited copper foil has a tensile strength of more than 30 kgf/mm^2. However, Matsuda is directed to providing an electrodeposited copper foil which has a lower profile and a higher gloss than low-profile electrodeposited copper foil conventionally supplied in markets. Furthermore, Paragraph [0012] Matsuda discloses:

"*the copper foil expansion/ contraction behavior* cannot follow the current collector expansion/ contraction, whereby *a phenomenon of the breakage thereof occurs*. Therefore, mechanical properties of copper foil as current collecting material, *for bearing the repeated expansion/contraction behavior*, are required to have a favorable balance between the tensile strength and elongation."

In other words, the tensile strength taught by Matsuda is not a property of preventing the generation of wrinkles at the surface of the copper foil but rather a property of preventing the breakage of the copper foil. However, the tensile strength, defined in Claim 1 of this application, is a property of preventing the generation of wrinkles at the surface of the copper foil.

In relation to the weight deviation, the Office Action states that Hirose does not

discuss a weight deviation and thus it is presumed to be 0%. However, the applicant respectfully traverses this. The electrodeposited copper foil is prepared by laminating copper by an electric current flowing to an electrolyte. In this process, it is required for controlling a concentration of the electrolyte and a current density, but a weight deviation inevitably occurs in the width or length direction of the copper foil, and generally the weight deviation is great. Copper foils currently available on the market have weight deviation, and there is no copper foil in which the weight deviation is 0. Moreover, it is not easy to reduce the weight deviation. In addition, in the related art, it is known that the weight deviation of the copper foil may cause a fault in fabrication of PCB, but it is not known in the art at all that the weight deviation of the copper foil gives an influence on the generation of wrinkles at the surface of the copper foil, which is different from the subject invention. Therefore, it is not reasonable in the art to presume that the weight deviation of the copper foil of Hirose is 0%. The electrodeposited copper foil has a weight deviation as discussed above, but Hirose has no disclosure in relation to the weight deviation, and thus Hirose fails to teach or suggest the weight deviation in relation to the generation of wrinkles at the surface of the copper foil.

As discussed above, Hirose does not recognize that the texture coefficient ratio is an important factor in relation to the generation of wrinkles at the surface of the copper foil, and Matsuda does not recognize that the tensile strength is an important factor in relation to the generation of wrinkles at the surface of the copper foil. In addition, Hirose and Matsuda do not disclose that the weight deviation is an important factor in relation to the generation of wrinkles at the surface of the copper foil. Therefore, though

one of ordinary skill in the art considers the texture coefficient ratio taught by Hirose and the tensile strength taught by Matsuda together, the numerical ranges of four texture coefficient ratios, the tensile strength and the weight deviation, defined in Claim 1 of this application, cannot be easily derived and is not shown in the cited prior art.

In addition, Battey is directed to a copper etching process, in which anisotropic etching is achieved consistently. Battey teaches that the anisotropy of the etching is dependent upon the crystal structure of the copper foil. In other words, Battey is directed to "consistent anisotropy of etching", but the subject invention is directed to "preventing the generation of wrinkles at the surface of the copper foil". Battey just recognizes that the crystal structure of the copper foil affects the anisotropy of the etching but does not recognize that the crystal structure of the copper foil affects the generation of wrinkles at the surface of the copper foil. In addition, in the subject invention, the prevention of wrinkles at the surface of the copper foil depends not only on the texture coefficient ratio but also on the tensile strength and the weight deviation, but Battey fails to teach or suggest the tensile strength and the weight deviation.

In relation to the tensile strength, the Office Action compares the tensile strength taught by Matsuda with the tensile strength of the subject invention. However, as discussed above, the tensile strength taught by Matsuda is not a property of preventing the generation of wrinkles at the surface of the copper foil but rather a property of preventing the breakage of the copper foil. However, the tensile strength, defined in Claim 1 of this application, is a property for preventing the generation of wrinkles at the surface of the copper foil.

In relation to the weight deviation, the Office Action states that Battey does not

discuss a weight deviation and thus it is presumed to be 0%. However, the applicant respectfully traverses this. The electrodeposited copper foil is prepared by laminating copper by an electric current flowing to an electrolyte. In this process, it is required for controlling a concentration of the electrolyte and a current density, but a weight deviation inevitably occurs in the width or length direction of the copper foil, and generally the weight deviation is great. Copper foils currently available on the market have weight deviation, and there is no copper foil in which weight deviation is 0. Moreover, it is not easy to reduce the weight deviation. In addition, in the related art, it is known that the weight deviation of the copper foil may cause a fault in fabrication of PCB, but it is not known in the art at all that the weight deviation of the copper foil gives an influence on the generation of wrinkles at the surface of the copper foil, which is different from the subject invention. Therefore, it is not reasonable in the art to presume that the weight deviation of the copper foil of Hirose is 0%. The electrodeposited copper foil has a weight deviation as discussed above, but Battey has no disclosure in relation to the weight deviation, and thus Battey fails to teach or suggest the weight deviation in relation to the prevention of wrinkles at the surface of the copper foil.

Therefore, though one of ordinary skill in the art considers the crystal structure taught by Battey and the tensile strength taught by Matsuda together, the numerical ranges of four texture coefficient ratios, the tensile strength and the weight deviation, defined in Claim 1 of this application, cannot be easily derived and is not disclosed by the cited prior art.

In addition, Nishimoto is directed to attaching a metal foil to a resin film by

using an adhesive. Nishimoto is not directed to preventing the generation of wrinkles at the surface of the metal foil, and fails to teach or suggest the numerical ranges of four texture coefficient ratios, the tensile strength and the weight deviation, defined in Claim 1 of this application. Therefore, Claim 1 cannot be derived by those skilled in the art from any combination of cited prior art references.

Wrinkles are not generated at the surface of the copper foil only when all conditions of the texture coefficient ratio, the tensile strength and the weight deviation, defined in Claim 1 of this application, are satisfied. However, the prior art references fail to teach or suggest all of these conditions.

In addition, referring to Table 1 of this application, Comparative Examples 1 to 6 satisfy the numerical ranges of the tensile strength and the weight deviation, defined in Claim 1 of this application, but do not satisfy at least one of the numerical ranges of four the texture coefficient ratios, which results in generation of wrinkles. In detail, as seen from Comparative Examples 1 and 2, if the (111) ratio deviates just a little below or above the range of Claim 1, wrinkles are generated even though the other conditions of Claim 1 are satisfied. In addition, as seen from Comparative Examples 3 and 4, if the (200) ratio deviates just a little below or above the range of Claim 1, wrinkles are generated even though the other conditions of Claim 1 are satisfied. Moreover, as seen from Comparative Examples 5 and 6, if the (222) ratio and the (111)+(200) ratio deviate just a little below or above the ranges of Claim 1, wrinkles are generated even though the other conditions of Claim 1 are satisfied.

In addition, Comparative Examples 7 and 8 satisfy the numerical ranges of the weight deviation and four texture coefficient ratios, defined in Claim 1 of this

application, but do not satisfy the numerical range of the tensile strength, resulting in the generation of wrinkles. In detail, as seen from Comparative Examples 7 and 8, if the tensile strength deviates just a little below or above the range of Claim 1, wrinkles are generated even though the other conditions of Claim 1 are satisfied.

Moreover, Comparative Example 9 satisfies the numerical range of the tensile strength and four texture coefficient ratios, defined in Claim 1 of this application, but does not satisfy the numerical range of the weight deviation, resulting in the generation of wrinkles. In detail, as seen from Comparative Example 9, if the weight deviation deviates just a little above the range of Claim 1, wrinkles are generated even though the other conditions of Claim 1 are satisfied.

Meanwhile, Examples 1 to 7 satisfy the numerical ranges of all conditions, defined in Claim 1 of this application, and no wrinkles are created. Therefore, the numerical ranges of four texture coefficient ratios, the tensile strength and the weight deviation, defined in Claim 1 of this application, are critical to the prevention of wrinkles.

Independent claim 1 is now in condition for allowance in view of the above-noted remarks. Dependent claims 2, 5 and 6 are also submitted to be in condition for allowance in view of their dependence from the allowable base claim and also at least based upon their recitations of additional features of the present invention.

Any amendments to the claims which have been made in this amendment, and which have not been specifically noted to overcome a rejection based on prior art, should be considered to have been made for a purpose unrelated to patentability, and no estoppel should be deemed to be attached thereto.

Based on the above, it is respectfully submitted that this application is now in condition for allowance, and a Notice of Allowance is respectfully requested.

Should the Examiner have any questions or comments regarding this response, or the present application, the Examiner is invited to contact the undersigned at the below-listed telephone number.

Respectfully submitted,

/Taeksoo Lee/
Taeksoo Lee
Reg. No. 61,976

February 18, 2016
LRK Patent Law Firm
1952 Gallows Rd. Suite 200
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(703) 854-1331

Electronic Patent Application Fee Transmittal	
Application Number:	13722585
Filing Date:	20-Dec-2012
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Filer:	Taeksoo Lee
Attorney Docket Number:	P10904US
Filed as Large Entity	
Filing Fees for Utility under 35 USC 111(a)	

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension - 1 month with $0 paid	1251	1	200	200
Miscellaneous:				
		Total in USD ($)		**200**

Electronic Acknowledgement Receipt	
EFS ID:	24950764
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	86144
Filer:	Taeksoo Lee
Filer Authorized By:	
Attorney Docket Number:	P10904US
Receipt Date:	18-FEB-2016
Filing Date:	20-DEC-2012
Time Stamp:	14:28:11
Application Type:	Utility under 35 USC 111(a)

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Payment was successfully received in RAM	$200
RAM confirmation Number	792
Deposit Account	
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	P10904_trl.pdf	293660 6567dea91673624b038317395da690557b28f11d	no	2
Warnings:					
Information:					
2		P10904_A03.pdf	6235062 5b0e4b10bd7ad4f5127a0afab817058c6bd30a2c	yes	19

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Amendment/Req. Reconsideration-After Non-Final Reject	1	3
	Applicant Arguments/Remarks Made in an Amendment	4	19

Warnings:					
Information:					
3	Fee Worksheet (SB06)	fee-info.pdf	30950 a4062c7cdf4d2a34b6a4a0c6b5ac9556d219bf74	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	6559672		

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New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc Code: TRAN.LET

Document Description: Transmittal Letter

PTO/SB/21 (07-09)
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TRANSMITTAL FORM

(to be used for all correspondence after initial filing)

Total Number of Pages in This Submission

Application Number	13/722,585
Filing Date	12/20/2012
First Named Inventor	Dae-Young KIM
Art Unit	1784
Examiner Name	Wang, Xiaobei
Attorney Docket Number	P10904US

ENCLOSURES (*Check all that apply*)

- ☑ Fee Transmittal Form
  - ☑ Fee Attached
- ☑ Amendment/Reply
  - ☐ After Final
  - ☐ Affidavits/declaration(s)
- ☑ Extension of Time Request
- ☐ Express Abandonment Request
- ☐ Information Disclosure Statement
- ☐ Certified Copy of Priority Document(s)
- ☐ Reply to Missing Parts/ Incomplete Application
  - ☐ Reply to Missing Parts under 37 CFR 1.52 or 1.53
- ☐ Drawing(s)
- ☐ Licensing-related Papers
- ☐ Petition
- ☐ Petition to Convert to a Provisional Application
- ☐ Power of Attorney, Revocation Change of Correspondence Address
- ☐ Terminal Disclaimer
- ☐ Request for Refund
- ☐ CD, Number of CD(s) _____
  - ☐ Landscape Table on CD
- ☐ After Allowance Communication to TC
- ☐ Appeal Communication to Board of Appeals and Interferences
- ☐ Appeal Communication to TC **(Appeal Notice, Brief, Reply Brief)**
- ☐ Proprietary Information
- ☐ Status Letter
- ☐ Other Enclosure(s) (please Identify below):

Remarks

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

Firm Name	LRK Patent Law Firm		
Signature	/Taeksoo Lee/		
Printed name	Taeksoo Lee		
Date	February 18, 2016	Reg. No.	61976

CERTIFICATE OF TRANSMISSION/MAILING

I hereby certify that this correspondence is being facsimile transmitted to the USPTO or deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on the date shown below:

Signature			
Typed or printed name		Date	

This collection of information is required by 37 CFR 1.5. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and1.14. This collection is estimated to 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	P10904US	8652

86144 7590 02/08/2016

LRK Patent Law Firm
1952 Gallows Rd
Suite 200
Vienna, VA 22182

EXAMINER
WANG, XIAOBEI

ART UNIT	PAPER NUMBER
1784	

NOTIFICATION DATE	DELIVERY MODE
02/08/2016	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

e_oa@lrkpatent.com
plee@lrkpatent.com

Applicant-Initiated Interview Summary	**Application No.** 13/722,585	**Applicant(s)** KIM ET AL.	
	Examiner Xiaobei Wang	**Art Unit** 1784	

All participants (applicant, applicant's representative, PTO personnel):

(1) *Xiaobei Wang*. (3)_____.

(2) *Stephen Paine*. (4)_____.

Date of Interview: *2/4/2016*.

Type: ☒ Telephonic ☐ Video Conference
☐ Personal [copy given to: ☐ applicant ☐ applicant's representative]

Exhibit shown or demonstration conducted: ☐ Yes ☒ No.
If Yes, brief description: _____.

Issues Discussed ☐101 ☐112 ☐102 ☐103 ☒Others
(For each of the checked box(es) above, please describe below the issue and detailed description of the discussion)

Claim(s) discussed: *1*.

Identification of prior art discussed: _____.

Substance of Interview
(For each issue discussed, provide a detailed description and indicate if agreement was reached. Some topics may include: identification or clarification of a reference or a portion thereof, claim interpretation, proposed amendments, arguments of any applied references etc...)

Discussed proposed amendment to claim 1 introducing the limitation "decrease wrinkle generation". I suggested the use of language such as "prevent wrinkle generation" to more clearly delineate what was meant by the wording, and more accurately reflect data presented in Table 1 of the Specification in order to advance prosecution. Full consideration will be given to Applicant's officially filed response.

Applicant recordation instructions: The formal written reply to the last Office action must include the substance of the interview. (See MPEP section 713.04). If a reply to the last Office action has already been filed, applicant is given a non-extendable period of the longer of one month or thirty days from this interview date, or the mailing date of this interview summary form, whichever is later, to file a statement of the substance of the interview

Examiner recordation instructions: Examiners must summarize the substance of any interview of record. A complete and proper recordation of the substance of an interview should include the items listed in MPEP 713.04 for complete and proper recordation including the identification of the general thrust of each argument or issue discussed, a general indication of any other pertinent matters discussed regarding patentability and the general results or outcome of the interview, to include an indication as to whether or not agreement was reached on the issues raised.

☐ Attachment

/Xiaobei Wang/ Examiner, Art Unit 1784	

Summary of Record of Interview Requirements

Manual of Patent Examining Procedure (MPEP), Section 713.04, Substance of Interview Must be Made of Record
A complete written statement as to the substance of any face-to-face, video conference, or telephone interview with regard to an application must be made of record in the application whether or not an agreement with the examiner was reached at the interview.

Title 37 Code of Federal Regulations (CFR) § 1.133 Interviews
Paragraph (b)

In every instance where reconsideration is requested in view of an interview with an examiner, a complete written statement of the reasons presented at the interview as warranting favorable action must be filed by the applicant. An interview does not remove the necessity for reply to Office action as specified in §§ 1.111, 1.135. (35 U.S.C. 132)

37 CFR §1.2 Business to be transacted in writing.
All business with the Patent or Trademark Office should be transacted in writing. The personal attendance of applicants or their attorneys or agents at the Patent and Trademark Office is unnecessary. The action of the Patent and Trademark Office will be based exclusively on the written record in the Office. No attention will be paid to any alleged oral promise, stipulation, or understanding in relation to which there is disagreement or doubt.

The action of the Patent and Trademark Office cannot be based exclusively on the written record in the Office if that record is itself incomplete through the failure to record the substance of interviews.

It is the responsibility of the applicant or the attorney or agent to make the substance of an interview of record in the application file, unless the examiner indicates he or she will do so. It is the examiner's responsibility to see that such a record is made and to correct material inaccuracies which bear directly on the question of patentability.

Examiners must complete an Interview Summary Form for each interview held where a matter of substance has been discussed during the interview by checking the appropriate boxes and filling in the blanks. Discussions regarding only procedural matters, directed solely to restriction requirements for which interview recordation is otherwise provided for in Section 812.01 of the Manual of Patent Examining Procedure, or pointing out typographical errors or unreadable script in Office actions or the like, are excluded from the interview recordation procedures below. Where the substance of an interview is completely recorded in an Examiners Amendment, no separate Interview Summary Record is required.

The Interview Summary Form shall be given an appropriate Paper No., placed in the right hand portion of the file, and listed on the "Contents" section of the file wrapper. In a personal interview, a duplicate of the Form is given to the applicant (or attorney or agent) at the conclusion of the interview. In the case of a telephone or video-conference interview, the copy is mailed to the applicant's correspondence address either with or prior to the next official communication. If additional correspondence from the examiner is not likely before an allowance or if other circumstances dictate, the Form should be mailed promptly after the interview rather than with the next official communication.

The Form provides for recordation of the following information:
- Application Number (Series Code and Serial Number)
- Name of applicant
- Name of examiner
- Date of interview
- Type of interview (telephonic, video-conference, or personal)
- Name of participant(s) (applicant, attorney or agent, examiner, other PTO personnel, etc.)
- An indication whether or not an exhibit was shown or a demonstration conducted
- An identification of the specific prior art discussed
- An indication whether an agreement was reached and if so, a description of the general nature of the agreement (may be by attachment of a copy of amendments or claims agreed as being allowable). Note: Agreement as to allowability is tentative and does not restrict further action by the examiner to the contrary.
- The signature of the examiner who conducted the interview (if Form is not an attachment to a signed Office action)

It is desirable that the examiner orally remind the applicant of his or her obligation to record the substance of the interview of each case. It should be noted, however, that the Interview Summary Form will not normally be considered a complete and proper recordation of the interview unless it includes, or is supplemented by the applicant or the examiner to include, all of the applicable items required below concerning the substance of the interview.

A complete and proper recordation of the substance of any interview should include at least the following applicable items:
1) A brief description of the nature of any exhibit shown or any demonstration conducted,
2) an identification of the claims discussed,
3) an identification of the specific prior art discussed,
4) an identification of the principal proposed amendments of a substantive nature discussed, unless these are already described on the Interview Summary Form completed by the Examiner,
5) a brief identification of the general thrust of the principal arguments presented to the examiner,
   (The identification of arguments need not be lengthy or elaborate. A verbatim or highly detailed description of the arguments is not required. The identification of the arguments is sufficient if the general nature or thrust of the principal arguments made to the examiner can be understood in the context of the application file. Of course, the applicant may desire to emphasize and fully describe those arguments which he or she feels were or might be persuasive to the examiner.)
6) a general indication of any other pertinent matters discussed, and
7) if appropriate, the general results or outcome of the interview unless already described in the Interview Summary Form completed by the examiner.

Examiners are expected to carefully review the applicant's record of the substance of an interview. If the record is not complete and accurate, the examiner will give the applicant an extendable one month time period to correct the record.

Examiner to Check for Accuracy

If the claims are allowable for other reasons of record, the examiner should send a letter setting forth the examiner's version of the statement attributed to him or her. If the record is complete and accurate, the examiner should place the indication, "Interview Record OK" on the paper recording the substance of the interview along with the date and the examiner's initials.

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	P10904US	8652

86144 7590 10/29/2015

LRK Patent Law Firm
1952 Gallows Rd
Suite 200
Vienna, VA 22182

EXAMINER
WANG, XIAOBEI

ART UNIT	PAPER NUMBER
1784	

NOTIFICATION DATE	DELIVERY MODE
10/29/2015	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

e_oa@lrkpatent.com
plee@lrkpatent.com

Office Action Summary	Application No. 13/722,585	Applicant(s) KIM ET AL.	
	Examiner Xiaobei Wang	Art Unit 1784	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *10/18/2015*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5)☒ Claim(s) *1,2,5 and 6* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1,2,5 and 6* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☒ All b)☐ Some** c)☐ None of the:

1.☒ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)

2) ☐ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

1. The present application is being examined under the pre-AIA first to invent provisions.

DETAILED ACTION

Response to Arguments

2. Applicant's arguments, see Remarks, filed 10/18/2015, with respect to the rejection(s) of claim(s) 1-6 under 35 U.S.C. 103(a) over Hirose (US PGPub 2009/0061326) and Battey (US Patent 4,695,348) have been fully considered and are persuasive. The rejections are withdrawn, as none of Hirose, Battey or the secondary reference Nishimoto (US Patent 6,451,441) teaches the claimed tensile strength. However, upon further search and consideration, a new ground of rejection is entered in view of Matsuda et al. (US PGPub 2010/0038115). Applicant's other arguments are addressed below.

3. Applicant argues that the teachings and suggestions of Hirose and Battey do not arrive at the claimed invention because the prior art references do not teach or suggest having zero wrinkles at the surface of the copper foil. To begin, it is noted that the features upon which applicant relies (i.e., the lack of wrinkles on the surface of the copper foil) are not recited in the rejected claims. Therefore, Applicant's arguments regarding the prior art and the lack of recognition between the texture coefficients and the lack of wrinkles are not persuasive. Although the claims are interpreted in light of the specification, limitations from the specification are not read into the claims. See *In re Van Geuns*, 988 F.2d 1181, 26 USPQ2d 1057 (Fed. Cir. 1993).

4. Furthermore, in Applicant's discussion of wrinkles, Applicant argues that the precise confluence of texture coefficient ratios, tensile strength, and weight deviation have critical significance as to the lack of wrinkles (p. 7 of Remarks). Applicant also argues that the prior art copper foil has wrinkles. However, the prior art references do not appear to discuss wrinkles and Applicant presents no objective evidence showing that the prior art copper foil contains wrinkles at the surface. Moreover, Applicant's data (see Table 1 of Specification) may support a conclusion that the texture coefficients are important to having no wrinkles, but does not appear to support a conclusion that the precise confluence of texture coefficients, tensile strength and weight deviation has critical significance to the lack of wrinkles. For instance, each example in Table 1 has a weight deviation within the claimed range, and most are within the claimed range for tensile strength. The only consistent difference between the inventive and comparative examples that appears to account for the presence of wrinkles is the texture coefficient values being outside the claimed ranges for the comparative examples.

Claim Rejections - 35 USC § 103

5. The text of those sections of Title 35, U.S. Code not included in this action can be found in a prior Office action.

6. **Claim 1 and 5 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Hirose et al. (US PGPub 2009/0061326) in view of Matsuda et al. (US PGPub 2010/0038115).**

7. Regarding claim 1, Hirose discloses a copper foil (¶ 145) used in lithium battery current collectors (¶ 3-4). Hirose teaches that an ideal ratio between the (200) and (111)

planes should be between 0.5 and 1.5 (¶ 12) in order to improve the contact characteristics and cycle characteristics of a battery (¶ 15). Hirose also teaches the (220) plane should not be a primary orientation (¶ 155, see Figs. 11A and 11B). Hirose therefore recognizes that these crystal planes are important characteristics for a copper foil in a battery, and thus, the relative abundance or scarcity of these crystal planes, and by corollary, any measure of the intensity of these planes in the copper foil, are result effective variables. *See* MPEP 2144.05 II. One of ordinary skill in the art therefore would have been motivated, based on the teachings of Hirose, to obtain the ideal amounts of these crystal planes in a copper foil through routine optimization and thereby also arrive at the claimed ratios of texture coefficients (i.e., a ratio of crystal planes). As to weight deviation, Hirose does not discuss a weight deviation, thus it is presumed to be 0% absent objective evidence to the contrary. *See* MPEP 2112.

8. Hirose does not expressly teach a tensile strength or an elongation. Matsuda teaches a copper foil suitable for use in collecting materials on lithium ion batteries (¶ 52). These copper foils ideally have a tensile strength of more than 30 kg-f/mm2 and an elongation of at least 8% (¶ 51). It would have been obvious at the time of invention for one of ordinary skill in the art to create the copper foil of Hirose having the properties as taught by Matsuda because Matsuda teaches these mechanical properties are ideal for various electronic applications of copper foil (¶ 51). The ranges taught by Matsuda overlap the claimed ranges, creating a prima facie case of obviousness.

9. **Claims 2 and 6 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Hirose et al. (US PGPub 2009/0061326) in view of Matsuda et al.**

(US PGPub 2010/0038115), as applied to claim 1, further in view of Nishimoto (US Patent 6,451,441).

10. Regarding claims 2 and 6, the limitations of claim 1 have been addressed above. Hirose does not expressly teach the claimed properties of the copper foil. Nishimoto teaches a metal foil which is bonded to a resin film to form a laminate structure (see col. 1, lines 5-11). The copper foil of Hirose is similarly part of a laminate (see ¶ 97). The metal foil can be a copper foil and has a thickness of from 5 to 50 µm (col 5, lines 5-11). See MPEP 2144.05 I. The metal foil is coarsened to have a surface roughness of about 0.2 µm to about 0.7 µm (col 5, lines 26-32). It would have been obvious for one of ordinary skill in the art to apply the teachings of Nishimoto regarding the properties of the copper foil to the copper foil of Hirose because Nishimoto discloses conventional characteristics known to result in a working copper laminate and therefore there is a high expectation of success in adopting the same properties.

11. **Claim 1 and 5 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Battey et al. (US Patent 4,695,348) in view of Matsuda et al. (US PGPub 2010/0038115).**

12. Regarding claim 1, Battey teaches a copper foil used in the manufacture of electronic circuit boards (col. 1, lines 8-17). The crystal orientation of the copper foil is described as being predominantly in the (111) and (200) orientations with relatively little (220) orientation in order to improve etching (col. 2, lines 1-10). Battey gives several examples of copper foils and X-ray diffraction analysis of the crystal structure, concluding that at least 70% of the orientation should be in the (111) and (200) planes,

with no more than 15% in the (220) planes (col. 4, lines 1-35). Battey therefore recognizes that these crystal planes are important characteristics for a copper foil, and thus, the relative abundance or scarcity of these crystal planes, and by corollary, any measure of the intensity of these planes in the copper foil, are result effective variables. *See* MPEP 2144.05 II. One of ordinary skill in the art therefore would have been motivated, based on the teachings of Battey, to obtain the ideal amounts of these crystal planes in a copper foil through routine optimization and thereby arrive at the claimed ratios of texture coefficients (i.e., a ratio of crystal planes). As to weight deviation, Battey does not discuss a weight deviation, thus it is presumed to be 0% absent objective evidence to the contrary. *See* MPEP 2112.

13. Battey does not expressly teach a tensile strength or an elongation. Matsuda teaches a copper foil suitable for use in flexible circuit boards and collecting materials on lithium ion batteries (¶ 52). These copper foils ideally have a tensile strength of more than 30 kg-f/mm2 and an elongation of at least 8% (¶ 51). It would have been obvious at the time of invention for one of ordinary skill in the art to create the copper foil of Hirose having the properties as taught by Matsuda because Matsuda teaches these mechanical properties are ideal for various electronic applications of copper foil (¶ 51). The ranges taught by Matsuda overlap the claimed ranges, creating a prima facie case of obviousness.

14. **Claims 2 and 6 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Battey et al. (US Patent 4,695,348) in view of Matsuda et al. (US**

PGPub 2010/0038115), as applied to claim 1, further in view of Nishimoto (US Patent 6,451,441).

15. Regarding claims 2 and 6, the limitations of claim 1 have been addressed above. Battey does not expressly teach the claimed properties of the copper foil. Nishimoto teaches a metal foil which is bonded to a resin film to form a laminate structure (see col. 1, lines 5-11). The copper foil of Battey is similarly used in a laminate (see col. 1, lines 4-17). The metal foil can be a copper foil and has a thickness of from 5 to 50 µm (col 5, lines 5-11). This range overlaps the claimed range, creating a prima facie case of obviousness. See MPEP 2144.05 I. The metal foil is coarsened to have a surface roughness of about 0.2 µm to about 0.7 µm (col 5, lines 26-32). It would have been obvious for one of ordinary skill in the art to apply the teachings of Nishimoto regarding the properties of the copper foil to the copper foil of Battey because Nishimoto discloses conventional characteristics known to result in a working copper laminate and therefore there is a high expectation of success in adopting the same properties.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Xiaobei Wang whose telephone number is (571)270-5705. The examiner can normally be reached on Monday through Friday 9AM - 5PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Humera Sheikh can be reached on 571-272-0604. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Xiaobei Wang/
Examiner, Art Unit 1784

Notice of References Cited	Application/Control No. 13/722,585	Applicant(s)/Patent Under Reexamination KIM ET AL.	
	Examiner Xiaobei Wang	Art Unit 1784	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
*	A	US-2010/0038115 A1	02-2010	Matsuda; Mitsuyoshi	C25D1/04	174/254
	B	US-				
	C	US-				
	D	US-				
	E	US-				
	F	US-				
	G	US-				
	H	US-				
	I	US-				
	J	US-				
	K	US-				
	L	US-				
	M	US-				

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	42	(cu copper) near foil and ("111" and "200" and "220") with (crystal crystalline orientation index)	US-PGPUB; USPAT; USOCR	OR	ON	2015/10/21 11:42
L2	5	1 and wrinkle	US-PGPUB; USPAT; USOCR	OR	ON	2015/10/21 11:42
L3	23	(cu copper) near foil and ("111" and "200" and "220") with (crystal crystalline orientation index)	FPRS; EPO; JPO; DERWENT	OR	ON	2015/10/21 11:43

EAST Search History (Interference)

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10/ 21/ 2015 11:45:04 AM
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Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	Art Unit
	CATHY LAM	1784

CPC- SEARCHED		
Symbol	Date	Examiner
B32B 15/01	07-30-2014	CL
C22C 9/00	07-30-2014	CL
C25D 3/38, 7/0614	07-30-2014	CL
H01M 4/661, 10/052	07-30-2014	CL

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner
429	522, 485, 517	07-30-2014	CL
428	577, 612, 687	07-30-2014	CL

SEARCH NOTES		
Search Notes	Date	Examiner
Updated EAST Search	7/9/2015	XW
Updated EAST Search	10/21/2015	XW

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner
429	485, 517, 522	07-30-2014	CL
428	577, 612, 687	07-30-2014	

	/C.L./ Primary Examiner.Art Unit 1784

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	: LS Mtron Ltd.	Group Art Unit: 1784	
Appl. No.	: 13/722,585	Examiner:	Wang, Xiaobei
Filed	: 12/20/2012	Confirmation No. : 8652	

For : COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

AMENDMENT UNDER 37 C.F.R. § 1.111

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In response to the Office action of July 21, 2015, which set a three-month shortened statutory period to expire on October 21, 2015, Applicant submits the amendments and remarks as follows for entry in the above-identified patent application and requests reconsideration of the rejections of the application, in due course.

However, if any extension of time is necessary or there are any underpayments or overpayments of fees associated with the filing of this Amendment, this is an express request for any necessary extension of time and authorization to charge any required extension of time fee or any other fees which may be required to preserve the pendency of the present application to Deposit Account No. 50-4895.

Amendments to the Claims are reflected in the listing of claims which begins on page 2 of this paper.

Remarks begin on page 4 of this paper

IN THE CLAIMS

This listing of claims will replace all prior versions, and listings, of claims in the application:

LISTING OF CLAIMS

1. (Currently Amended) A copper foil for a current collector of a lithium secondary battery,

wherein, in a crystalline structure, a ratio of a sum of texture coefficients of a (111) surface and a (200) surface to a total sum of texture coefficients of the (111) surface, the (200) surface and a (220) surface is 60 to 85%, a ratio of a texture coefficient of the (111) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 18 to 38%, a ratio of the texture coefficient of the (200) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 28 to 62%, and a ratio of the texture coefficient of the (220) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 15 to 40%, ~~and~~

wherein the texture coefficient satisfies the following equation:

$$TC(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{n}\Sigma\frac{I(hkl)}{I_0(hkl)}}$$

wherein I(hkl) represents a measured diffraction intensity with respect to a (hkl) surface, and I_0(hkl) represents a standard diffraction intensity of ASTM (American Society of Testing Materials) standard powder-shaped diffraction data,

wherein the copper foil has a weight deviation of 3% or less, and

wherein the copper foil has a tensile strength of 30 to 40 kgf/mm^2.

2. (Original) The copper foil for a current collector of a lithium secondary battery according to claim 1, wherein the copper foil has a surface roughness (Rz-JIS) of 2 μm or less.

3. (Cancelled)

4. (Cancelled)

5. (Original) The copper foil for a current collector of a lithium secondary battery according to claim 1, wherein the copper foil has an elongation of 3 to 20%.

6. (Original) The copper foil for a current collector of a lithium secondary battery according to claim 1, wherein the copper foil has a thickness of 1 to 35 μm.

REMARKS

Claims 3 and 4 have been canceled without prejudice or disclaimer of the subject matter thereof. Hence, claims claims 1, 2, 5 and 6 remain pending in the application. Claim 1 is hereby amended. No new matter is believed to be introduced by the present amendments.

Reconsideration of the rejections and allowance of the pending application in view of the above-noted claim amendments and the following remarks are respectfully requested.

In the Office action, claim 1 stands rejected under pre-AIA 35 U.S.C. 103(a) as being unpatenable over Hirose et al. (US PGPub 2009/0061326, hereinafter "*Hirose*"). Claims 2-6 stand rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over *Hirose* further in view of Nishimoto (US Patent 6,451,441, hereinafter "*Nishimoto*"). In addition, claim 1 stands rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Battey et al. (US Patent 4,695,348, hereinafter "*Battey*"). Claims 2-6 stand rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over *Battey* further in view of *Nishimoto*. This rejection is respectfully traversed.

Independent claim 1 has been amended to include the limitations of claims 3 and 4 by further reciting "wherein the copper foil has a weight deviation of 3% or less, and wherein the copper foil has a tensile strength of 30 to 40 kgf/mm^2." (Emphasis added) No new matter is believed to be introduced by the present amendment.

Independent claim 1 now recites:

> A copper foil for a current collector of a lithium secondary battery,
> wherein, in a crystalline structure, a ratio of a sum of texture coefficients of a (111) surface and a (200) surface to a

total sum of texture coefficients of the (111) surface, the (200) surface and a (220) surface is 60 to 85%, a ratio of a texture coefficient of the (111) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 18 to 38%, a ratio of the texture coefficient of the (200) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 28 to 62%, and a ratio of the texture coefficient of the (220) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 15 to 40%,

wherein the texture coefficient satisfies the following equation:

$$TC(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{n}\Sigma\frac{I(hkl)}{I_0(hkl)}}$$

wherein I(hkl) represents a measured diffraction intensity with respect to a (hkl) surface, and I_0(hkl) represents a standard diffraction intensity of ASTM (American Society of Testing Materials) standard powder-shaped diffraction data,

wherein the copper foil has a weight deviation of 3% or less, and

wherein the copper foil has a tensile strength of 30 to 40 kgf/mm^2.

Applicant respectfully submits that the references relied upon in the rejection under 35 U.S.C. 103(a), considered singly or in any proper combination, do not disclose such a combination of features.

The Office action asserts regarding the original claim 1 that "*Hirose teaches that an ideal ratio between the (200) and (111) planes should be between 0.5 and 1.5 in order to improve the contact characteristics and cycle characteristics of a battery... Hirose therefore recognizes that these crystal planes are important characteristics for a copper foil in a battery and thus the relative abundance or scarcity of these crystal planes, and by corollary, any measure of the intensity of these planes in the copper foil, are result effective variables...*", and that "*Battey teaches a copper foil used in the manufacture of*

electronic circuit boards. The crystal orientation of the copper foil is described as being predominantly in the (111) and (200) orientations with relatively little (220) orientation in order to improve etching. Battey gives several examples of copper foils and X-ray diffraction analysis of the crystal structure, concluding that at least 70% of the orientation should be in the (111) and (200) planes, with no more than 15% I the (220) planes..." In addition, the Office action further asserts regarding the original claims 3 and 4 that "*Nishimoto teaches a metal foil which is bonded to a resin film to for a laminate... The metal foil that bonded to a resin film, has an adhesive force (or bond strength) of from 50 to 700 g/20mm... As to the weight deviation, neither prior art reference discusses a weight deviation, thus it is presumed to be 0% absent objective evidence to the contrary...*" This assertion is respectfully traversed.

The embodiment of the present invention is directed to decreasing the generation of wrinkles at a surface of the copper foil. Specifically, referring to Table 1 in the specification of the instant application, factors which make the number of wrinkles generated at the surface of a copper foil into 0 (zero) are a texture coefficient ratio, a tensile strength and a weight deviation. Comparative Examples 7-9 in Table 1 satisfy the texture coefficient ratio defined in Claim 1. In other words, a ratio of a sum of texture coefficients of a (111) surface and a (200) surface to a total sum of texture coefficients of the (111) surface, the (200) surface and a (220) surface is 60 to 85%; a ratio of a texture coefficient of the (111) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 18 to 38%; a ratio of the texture coefficient of the (200) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 28 to 62%; and a ratio of the texture

coefficient of the (220) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 15 to 40%. However, the number of generated wrinkles in Comparative Examples 7 and 8 is "2", and the number of generated wrinkles in Comparative Example 9 is "5". In other words, in order to make the number of wrinkles generated at the surface of the copper foil into 0 (zero), all conditions of the texture coefficient ratio, the tensile strength and the weight deviation should be satisfied. In detail, as defined in the amended Claim 1, not only should the texture coefficient ratio be satisfied, but the copper foil should also have a weight deviation of 3% or less and the copper foil should also have a tensile strength of 30 to 40 kgf/mm^2. In Examples 1 to 7 of Table 1, the texture coefficient ratio, the tensile strength and the weight deviation are entirely satisfied so that the number of generated wrinkles is 0 (zero). Therefore, the numerical ranges of four texture coefficient ratios, the tensile strength and the weight deviation, defined in Claim 1 of the instant application, have the critical significance. The above feature is not disclosed in *Hirose*, *Battey*, and *Nishimoto*.

Hirose is directed to improving the cycle characteristic. Specifically, *Hirose* discloses that a current collector containing copper has a ratio I(200)/I(111) in the range from 0.5 to 1.5. However, referring to Table 1 in the specification of the instant application, among Examples of the present embodiment satisfying the conditions of Claim 1 of the instant application, some examples satisfy the condition of the ratio I(200)/I(111) of *Hirose*, but the other examples do not satisfy the condition. In addition, among Comparative Examples which do not satisfy the conditions of Claim 1 of the instant application, some comparative examples satisfy the condition of the ratio I(200)/I(111) of *Hirose*, but the other comparative examples do not satisfy the condition.

More specifically, the ratio I(200)/I(111) of *Hirose* can be calculated as follows by using the data of Table 1 of the instant application.

$$TC : Texture\ Coeffcilent$$

$$\frac{(200)ratio}{(111)ratio} = \frac{\frac{TC(200)}{TC(111)+TC(200)+TC(220)}}{\frac{TC(111)}{TC(111)+TC(200)+TC(220)}} = \frac{TC(200)}{TC(111)}$$

$$= \frac{\frac{\frac{I(200)}{I_0(200)}}{\frac{1}{3}\left(\frac{I(111)}{I_0(111)}+\frac{I(200)}{I_0(200)}+\frac{I(220)}{I_0(220)}\right)}}{\frac{\frac{I(111)}{I_0(111)}}{\frac{1}{3}\left(\frac{I(111)}{I_0(111)}+\frac{I(200)}{I_0(200)}+\frac{I(220)}{I_0(220)}\right)}} = \frac{\frac{I(200)}{I_0(200)}}{\frac{I(111)}{I_0(111)}} = \frac{I_0(111)}{I_0(200)} \times \frac{I(200)}{I(111)}$$

$$\Rightarrow\ JCPDS\ CARD\ 04-0836 : I_0(111)=100,\ I_0(200)=46$$

$$\frac{(200)ratio}{(111)ratio} = \frac{100}{46} \times \frac{I(200)}{I(111)}$$

$$\Rightarrow \quad \frac{I(200)}{I(111)} = 0.46 \times \frac{(200)ratio}{(111)ratio}$$

By using this method, the ratio I(200)/I(111) of each example and comparative example of Table 1 of the instant application can be calculated as follows.

	(111)+(200) ratio	(111) ratio	(200) ratio	(220) ratio	(200) ratio /(111) ratio	I(200)/I(111)	0.5 ≤ I(200)/I(111) ≤ 1.5
Example 1	76	26	50	24	1.9231	0.8846	Y

Example 2	62	31	31	38	1.0000	0.4600	N
Example 3	83	32	51	17	1.5938	0.7331	Y
Example 4	70	20	50	30	2.5000	1.1500	Y
Example 5	72	35	36	29	1.0286	0.4731	N
Example 6	81	22	59	19	2.6818	1.2336	Y
Example 7	66	36	30	34	0.8333	0.3833	N
Comparative Example 1	64	16	48	36	3.0000	1.3800	Y
Comparative Example 2	73	41	32	27	0.7805	0.3590	N
Comparative Example 3	62	37	25	38	0.6757	0.3108	N
Comparative Example 4	83	19	64	17	3.3684	1.5495	N
Comparative Example 5	87	34	53	13	1.5588	0.7171	Y
Comparative Example 6	57	26	31	43	1.1923	0.5485	Y
Comparative Example 7	80	30	49	21	1.6333	0.7513	Y
Comparative Example 8	75	23	51	26	2.2174	1.0200	Y
Comparative Example 9	76	25	50	25	2.0000	0.9200	Y

As discussed above, among Examples satisfying the conditions of Claim 1 of the instant application, some examples satisfy the condition of the ratio I(200)/I(111) of *Hirose*, but the other examples do not satisfy the condition. In addition, among Comparative Examples which do not satisfy the conditions of Claim 1 of the instant

application, some comparative examples satisfy the condition of the ratio I(200)/I(111) of *Hirose*, but the other comparative examples do not satisfy the condition. In other words, even though the copper foil satisfies the ratio I(200)/I(111) disclosed in *Hirose*, wrinkles are generated at the surface of the copper foil in *Hirose*. Therefore, *Hirose* does not recognize that the texture coefficient ratio is an important factor in relation to the generation of wrinkles at the surface of the copper foil. At least in view of the above, *Hirose* cannot properly be relied upon for disclosing the above feature of the present embodiment.

Battey is directed to a copper etching process, in which anisotropic etching is achieved consistently. Here, *Battey* teaches that the anisotropy of the etching is dependent upon the crystal structure of the copper foil. In other words, *Battey* is directed to "consistent anisotropy of etching", while the embodiment of the present invention is directed to "decreasing the generation of wrinkles at the surface of the copper foil". That is, *Battey* just recognizes that the crystal structure of the copper foil affects the anisotropy of the etching, but does not recognize that the crystal structure of the copper foil affects wrinkles at the surface of the copper foil. At least in view of the above, *Battey* cannot properly be relied upon for disclosing the above feature of the present embodiment. In addition, in the embodiment of the present invention, the generation of wrinkles at the surface of the copper foil depends not only on the texture coefficient ratio but also on the tensile strength and the weight deviation. *Battey* fails to teach or suggest the tensile strength and the weight deviation. Wrinkles are not generated at the surface of the copper foil only if all conditions of the texture coefficient ratio, the tensile strength and the weight deviation, defined in Claim 1 of the instant application, are satisfied. However,

the prior art references fail to teach or suggest all of these conditions. In addition, referring to Table 1 of the instant application, Comparative Examples 1 to 6 satisfy the numerical ranges of the tensile strength and the weight deviation, defined in Claim 1 of the instant application, but do not satisfy at least one of the numerical ranges of four the texture coefficient ratios, resulting in generation of wrinkles. In detail, as seen from Comparative Examples 1 and 2, even though other conditions of Claim 1 are satisfied, if the (111) ratio deviates just a little below or above the range of Claim 1, wrinkles are generated. In addition, as seen from Comparative Examples 3 and 4, even though other conditions of Claim 1 are satisfied, if the (200) ratio deviates just a little below or above the range of Claim 1, wrinkles are generated. Moreover, as seen from Comparative Examples 5 and 6, even though other conditions of Claim 1 are satisfied, if the (222) ratio and the (111)+(200) ratio deviate just a little below or above the ranges of Claim 1, wrinkles are generated. In addition, Comparative Examples 7 and 8 satisfy the numerical ranges of the weight deviation and four texture coefficient ratios, defined in Claim 1 of the instant application, but do not satisfy the numerical range of the tensile strength, resulting in generation of wrinkles. In detail, as seen from Comparative Examples 7 and 8, even though other conditions of Claim 1 are satisfied, if the tensile strength deviates just a little below or above the range of Claim 1, wrinkles are generated. Moreover, Comparative Example 9 satisfies the numerical range of the tensile strength and four texture coefficient ratios, defined in Claim 1 of the instant application, but do not satisfy the numerical range of the weight deviation, resulting in generation of wrinkles. In detail, as seen from Comparative Example 9, even though other conditions of Claim 1 are satisfied, if the weight deviation deviates just a little above the range of Claim 1, wrinkles

are generated. Meanwhile, Examples 1 to 7 satisfy the numerical ranges of all conditions, defined in Claim 1 of the instant application, thereby causing no wrinkle. At least in view of the above, *Battey* cannot properly be relied upon for disclosing the above feature of the present embodiment.

The Office action further asserts that "*Nishimoto teaches a metal foil which is bonded to a resin film to for a laminate... The metal foil that bonded to a resin film, has an adhesive force (or bond strength) of from 50 to 700 g/20mm... As to the weight deviation, neither prior art reference discusses a weight deviation, thus it is presumed to be 0% absent objective evidence to the contrary...*" This assertion is respectfully traversed. With regard to the tensile strength, the examiner compares the adhesive force taught by *Nishimoto* with the tensile strength of the present embodiment, while comparing the metal foil of *Nishimoto* with the copper foil of the present embodiment. However, the adhesive force taught by *Nishimoto* is not an adhesive force of the metal foil, but an adhesive force of the adhesive layer. This can be understood from lines 47-49, col. 8 of *Nishimoto*, i.e., "*The thus obtained film with metal foil of the invention exhibits an adhesive force of the adhesive layer of, usually, from 50 to 700 g/20 mm (about 0.5 to 7.0 N/20 mm)*" In the embodiment of the present invention, however, the tensile strength is a characteristic of the copper foil. In addition, the tensile strength and the adhesive force are different parameters from each other. The adhesive force refers to the ability of an adhesive to stick to a surface and bond two surfaces together. As disclosed in lines 53-55, col. 8 of *Nishimoto*, the adhesive force of the adhesive layer is measured in compliance with 180° peeling strength at the time of peeling the resin film off. However, the tensile strength is the maximum stress that a material can withstand

while being stretched or pulled before failing or breaking. In addition, *Nishimoto* is directed to attaching a metal foil to a resin film by using an adhesive. That is, *Nishimoto* fails to teach or suggest an object of preventing the generation of wrinkles at the surface of the metal foil.

At least in view of the above, even assuming, *arguendo*, that the teachings of *Hirose* or *Battey* in view of *Nishimoto* can be properly combined, the asserted combination of *Hirose* or *Battey* in view of *Nishimoto* would not result in the embodiment as recited in the independent claim 1. Accordingly, favorable reconsideration and withdrawal of the rejection under 35 U.S.C. §103(a) are respectfully requested.

Independent claim 1 is now in condition for allowance in view of the above-noted remarks. Dependent claims 2, 5 and 6 are also submitted to be in condition for allowance in view of their dependence from the allowable base claim and also at least based upon their recitations of additional features of the present invention.

Any amendments to the claims which have been made in this amendment, and which have not been specifically noted to overcome a rejection based on prior art, should be considered to have been made for a purpose unrelated to patentability, and no estoppel should be deemed to be attached thereto.

Based on the above, it is respectfully submitted that this application is now in condition for allowance, and a Notice of Allowance is respectfully requested.

Should the Examiner have any questions or comments regarding this response, or the present application, the Examiner is invited to contact the undersigned at the below-listed telephone number.

Respectfully submitted,

/Taeksoo Lee/
Taeksoo Lee
Reg. No. 61,976

October 18, 2015
LRK Patent Law Firm
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Electronic Acknowledgement Receipt

EFS ID:	23815645
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	86144
Filer:	Taeksoo Lee
Filer Authorized By:	
Attorney Docket Number:	P10904US
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Time Stamp:	19:16:07
Application Type:	Utility under 35 USC 111(a)

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Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	P10904_trl.pdf	293670 0875bdf6c52aa03fb0e77d50c8ec414af54cfb66	no	2
Warnings:					
Information:					

2		P10904_A02.pdf	4592373 4e17a9ddff52c174bbe993720e456a7180b12e83	yes	14

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Amendment/Req. Reconsideration-After Non-Final Reject	1	3
	Applicant Arguments/Remarks Made in an Amendment	4	14

Warnings:	
Information:	
Total Files Size (in bytes):	4886043

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New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc Code: TRAN.LET

Document Description: Transmittal Letter

PTO/SB/21 (07-09)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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TRANSMITTAL FORM

(to be used for all correspondence after initial filing)

Total Number of Pages in This Submission

Application Number	13/722,585
Filing Date	12/20/2012
First Named Inventor	Dae-Young KIM
Art Unit	1784
Examiner Name	Wang, Xiaobei
Attorney Docket Number	P10904US

ENCLOSURES (*Check all that apply*)

- ☐ Fee Transmittal Form
  - ☐ Fee Attached
- ☑ Amendment/Reply
  - ☐ After Final
  - ☐ Affidavits/declaration(s)
- ☐ Extension of Time Request
- ☐ Express Abandonment Request
- ☐ Information Disclosure Statement
- ☐ Certified Copy of Priority Document(s)
- ☐ Reply to Missing Parts/ Incomplete Application
  - ☐ Reply to Missing Parts under 37 CFR 1.52 or 1.53
- ☐ Drawing(s)
- ☐ Licensing-related Papers
- ☐ Petition
- ☐ Petition to Convert to a Provisional Application
- ☐ Power of Attorney, Revocation Change of Correspondence Address
- ☐ Terminal Disclaimer
- ☐ Request for Refund
- ☐ CD, Number of CD(s) _____
  - ☐ Landscape Table on CD
- ☐ After Allowance Communication to TC
- ☐ Appeal Communication to Board of Appeals and Interferences
- ☐ Appeal Communication to TC **(Appeal Notice, Brief, Reply Brief)**
- ☐ Proprietary Information
- ☐ Status Letter
- ☐ Other Enclosure(s) (please Identify below):

Remarks

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

Firm Name	LRK Patent Law Firm		
Signature	/Taeksoo Lee/		
Printed name	Taeksoo Lee		
Date	October 16, 2015	Reg. No.	61976

CERTIFICATE OF TRANSMISSION/MAILING

I hereby certify that this correspondence is being facsimile transmitted to the USPTO or deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on the date shown below:

Signature			
Typed or printed name		Date	

This collection of information is required by 37 CFR 1.5. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and1.14. This collection is estimated to 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
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Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 13/722,585	Filing Date 12/20/2012	☐ To be Mailed

ENTITY: ☒ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

	(Column 1)	(Column 2)		
FOR	NUMBER FILED	NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT		(Column 1)		(Column 2)	(Column 3)		
	10/18/2015	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 4	Minus	** 20	= 0	X $80 =	0
	Independent (37 CFR 1.16(h))	* 1	Minus	***3	= 0	X $420 =	0
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	0

AMENDMENT		(Column 1)		(Column 2)	(Column 3)		
		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

LIE
/LYNNELL JOHNSON/

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	P10904US	8652

86144 7590 07/21/2015

LRK Patent Law Firm
1952 Gallows Rd
Suite 200
Vienna, VA 22182

EXAMINER
WANG, XIAOBEI

ART UNIT	PAPER NUMBER
1784	

NOTIFICATION DATE	DELIVERY MODE
07/21/2015	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

e_oa@lrkpatent.com
plee@lrkpatent.com

Office Action Summary	Application No. 13/722,585	Applicant(s) KIM ET AL.	
	Examiner Xiaobei Wang	Art Unit 1784	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *4/15/2015*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5)☒ Claim(s) *1-6* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-6* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☒ The drawing(s) filed on *12/20/2012* is/are: a)☒ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☒ All b)☐ Some** c)☐ None of the:

1.☒ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)

2) ☐ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

1. The present application is being examined under the pre-AIA first to invent provisions.

2. Applicant is requested to take notice that the Examiner in Charge of this Application has changed.

DETAILED ACTION

Response to Arguments

3. Applicant's arguments, see Remarks, filed 4/15/2015, with respect to the rejection(s) of claim(s) 1-6 under 35 U.S.C. 103(a) over "The Properties & Market Status of Copper Foil for Li 2nd Battery" have been fully considered and are persuasive, as the reference is not prior art in view of the effective filing date for this application. Therefore, the rejection has been withdrawn. However, upon further consideration, a new ground(s) of rejection is made in view of Hirose (US PGPub 2009/0061326) and Battey (US Patent 4,695,348).

Claim Rejections - 35 USC § 103

4. The following is a quotation of pre-AIA 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

5. **Claim 1 is rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Hirose et al. (US PGPub 2009/0061326)**.

6. Regarding claim 1, Hirose discloses a copper foil (¶ 145). Hirose teaches that an ideal ratio between the (200) and (111) planes should be between 0.5 and 1.5 (¶ 12) in

order to improve the contact characteristics and cycle characteristics of a battery (¶ 15). Hirose also teaches the (220) plane should not be a primary orientation (¶ 155, see Figs. 11A and 11B). Hirose therefore recognizes that these crystal planes are important characteristics for a copper foil in a battery, and thus, the relative abundance or scarcity of these crystal planes, and by corollary, any measure of the intensity of these planes in the copper foil, are result effective variables. *See* MPEP 2144.05 II. One of ordinary skill in the art therefore would have been motivated, based on the teachings of Hirose, to obtain the ideal amounts of these crystal planes in a copper foil through routine optimization and thereby arrive at the claimed ratios of texture coefficients.

7. **Claims 2-6 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Hirose et al. (US PGPub 2009/0061326), as applied to claim 1, further in view of Nishimoto (US Patent 6,451,441)**.

8. Regarding claims 2-6, the limitations of claim 1 have been addressed above. Hirose does not expressly teach the claimed properties of the copper foil. Nishimoto teaches a metal foil which is bonded to a resin film to form a laminate. The metal foil can be a copper foil and has a thickness of from 5 to 50 µm (col 5, lines 5-11). The metal foil is coarsened to have a surface roughness of about 0.2 µm to about 0.7 µm (col 5, lines 26-32). The metal foil that bonded to a resin film, has an adhesive force (or bond strength) of from 50 to 700 g/20mm (or 25 N/m to 350 N/m) (col. 8, lines 47-56). As to the elongation, given that the copper foil of Hirose is substantially similar to the claimed copper foil, one of ordinary skill in the art would expect the same properties, absent objective evidence to the contrary. *See* MPEP 2112. As to weight deviation,

neither prior art reference discusses a weight deviation, thus it is presumed to be 0% absent objective evidence to the contrary. *See* MPEP 2112. It would have been obvious for one of ordinary skill in the art to apply the teachings of Nishimoto regarding the properties of the copper foil to the copper foil of Hirose because Nishimoto discloses conventional characteristics known to result in a working copper laminate and therefore there is a high expectation of success in adopting the same properties.

9. **Claim 1 is rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Battey et al. (US Patent 4,695,348)**.

10. Regarding claim 1, Battey teaches a copper foil used in the manufacture of electronic circuit boards (col. 1, lines 8-17). The crystal orientation of the copper foil is described as being predominantly in the (111) and (200) orientations with relatively little (220) orientation in order to improve etching (col. 2, lines 1-10). Battey gives several examples of copper foils and X-ray diffraction analysis of the crystal structure, concluding that at least 70% of the orientation should be in the (111) and (200) planes, with no more than 15% in the (220) planes (col. 4, lines 1-35). Battey therefore recognizes that these crystal planes are important characteristics for a copper foil, and thus, the relative abundance or scarcity of these crystal planes, and by corollary, any measure of the intensity of these planes in the copper foil, are result effective variables. *See* MPEP 2144.05 II. One of ordinary skill in the art therefore would have been motivated, based on the teachings of Battey, to obtain the ideal amounts of these crystal planes in a copper foil through routine optimization and thereby arrive at the claimed ratios of texture coefficients.

11. **Claims 2-6 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Battey et al. (US Patent 4,695,348), as applied to claim 1, further in view of Nishimoto (US Patent 6,451,441)**.

12. Regarding claims 2-6, the limitations of claim 1 have been addressed above. Battey does not expressly teach the claimed properties of the copper foil. Nishimoto teaches a metal foil which is bonded to a resin film to form a laminate. The metal foil can be a copper foil and has a thickness of from 5 to 50 µm (col 5, lines 5-11). The metal foil is coarsened to have a surface roughness of about 0.2 µm to about 0.7 µm (col 5, lines 26-32). The metal foil that bonded to a resin film, has an adhesive force (or bond strength) of from 50 to 700 g/20mm (or 25 N/m to 350 N/m) (col. 8, lines 47-56). As to the elongation, given that the copper foil of Battey is substantially similar to the claimed copper foil, one of ordinary skill in the art would expect the same properties, absent objective evidence to the contrary. *See* MPEP 2112. As to weight deviation, neither prior art reference discusses a weight deviation, thus it is presumed to be 0% absent objective evidence to the contrary. *See* MPEP 2112. It would have been obvious for one of ordinary skill in the art to apply the teachings of Nishimoto regarding the properties of the copper foil to the copper foil of Battey because Nishimoto discloses conventional characteristics known to result in a working copper laminate and therefore there is a high expectation of success in adopting the same properties.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Xiaobei Wang whose telephone number is (571)270-5705. The examiner can normally be reached on Monday through Friday 9AM - 5PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Humera Sheikh can be reached on 571-272-0604. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/David Sample/
Primary Examiner, Art Unit 1784

/Xiaobei Wang/
Examiner, Art Unit 1784

Notice of References Cited	Application/Control No. 13/722,585	Applicant(s)/Patent Under Reexamination KIM ET AL.	
	Examiner Xiaobei Wang	Art Unit 1784	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-2009/0061326	03-2009	Hirose et al.	429/338
*	B	US-4,695,348	09-1987	Battey et al.	216/20
*	C	US-6,451,441	09-2002	Nishimoto et al.	428/461
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	41	(cu copper) near foil and ("111" and "200" and "220") with (crystal crystalline orientation index)	US-PGPUB; USPAT; USOCR	OR	ON	2015/07/09 14:32

EAST Search History (Interference)

< This search history is empty>

7/9/2015 4:23:24 PM
C:\Users\xwang2\Documents\EAST\Workspaces\13722585.wsp

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	Art Unit
	CATHY LAM	1784

CPC- SEARCHED		
Symbol	Date	Examiner
B32B 15/01	07-30-2014	CL
C22C 9/00	07-30-2014	CL
C25D 3/38, 7/0614	07-30-2014	CL
H01M 4/661, 10/052	07-30-2014	CL

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner
429	522, 485, 517	07-30-2014	CL
428	577, 612, 687	07-30-2014	CL

SEARCH NOTES		
Search Notes	Date	Examiner
Updated EAST Search	7/9/2015	XW

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner
429	485, 517, 522	07-30-2014	CL
428	577, 612, 687	07-30-2014	

	/C.L./ Primary Examiner.Art Unit 1784

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	: LS Mtron Ltd.	Group Art Unit: 1784
Appl. No.	: 13/722,585	Examiner: LAM, Cathy Fong Fong
Filed	: 12/20/2012	Confirmation No. : 8652

For : COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

REPLY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In response to the Office Action of February 12, 2015, which set a three-month shortened statutory period to expire on May 12, 2015, Applicant submits the remarks as follows for entry in the above-identified patent application and requests reconsideration of the rejections of the application, in due course. However, if any extension of time is necessary, this is an express request for any necessary extension of time and authorization to charge any required extension of time fee or any other fees which may be required to preserve the pendency of the present application to Deposit Account No. 50-4895.

Remarks begin on page 2 of this paper.

REMARKS

As an initial matter, Applicant thanks the Examiner for the telephonic interview of April 3, 2015 and the Interview Summary of April 8, 2015. Applicant confirms that the telephonic interview was conducted on April 3, 2015 between Cathy LAM, Examiner, and Taeksoo Lee, Applicant's representative. Applicant further confirms that in the interview Applicant's representative informed the Examiner that the prior art of record should not have been used against the claims because this application is a continuation of application 13/029,656, which has an earlier filing date than the prior art of record.

Claims 1-6 are pending in the application.

Reconsideration of the rejections and allowance of the pending application in view of the following remarks are respectfully requested.

In the Office action claims 1-6 were rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over The Properties & Market Status of Copper Foil for Li 2nd Battery (Industrial materials journal vol 310, Oct. 05, 2012), hereinafter "prior art of record". This rejection is respectfully traversed.

As informed in the Interview of April 3, 2015, the prior art of record does not qualify as a prior art against the claims of the present application. Specifically, since the present application is a continuation of application No. 13/029,656, filed on **February 17, 2011**, now Pat. No. 8,349,518, the effective filing date of the present application is earlier than the publication date of the prior art of record which is **October 5, 2012**; therefore, the prior art of record does not qualify as a prior art against the claims of the present application. Accordingly, the §103(a) rejection is now moot. Favorable reconsideration and withdrawal of the rejection under 35 U.S.C. 103(a) are respectfully requested.

Independent claim 1 is now in condition for allowance in view of the above-noted remarks. Dependent claims 2-6 are also submitted to be in condition for allowance in view of their dependence from the allowable base claim.

Based on the above, it is respectfully submitted that this application is now in condition for allowance, and a Notice of Allowance is respectfully requested.

Should the Examiner have any questions or comments regarding this response, or the present application, the Examiner is invited to contact the undersigned at the below-listed telephone number.

Respectfully submitted,

/Taeksoo Lee/
Taeksoo Lee
Reg. No. 61,976

LRK Patent Law Firm
1952 Gallows Rd. Suite 200
Vienna, VA 22181
(703) 854-1331

Electronic Acknowledgement Receipt

EFS ID:	22072061
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	86144
Filer:	Taeksoo Lee
Filer Authorized By:	
Attorney Docket Number:	P10904US
Receipt Date:	15-APR-2015
Filing Date:	20-DEC-2012
Time Stamp:	16:13:50
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	P10904_trl.pdf	293707 e36710ad2ccbfb490c1b73389947ff2fc1bf82ec	no	2

Warnings:

Information:

2		P10904_A01.pdf	822211 269f7f2f0305ea5ffe8f49d9e09728cea284cddd	yes	3

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Amendment/Req. Reconsideration-After Non-Final Reject	1	1
	Applicant Arguments/Remarks Made in an Amendment	2	3

Warnings:	
Information:	
Total Files Size (in bytes):	1115918

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc Code: TRAN.LET

Document Description: Transmittal Letter

PTO/SB/21 (07-09)
Approved for use through 07/31/2012. OMB 0651-0031
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TRANSMITTAL FORM

(to be used for all correspondence after initial filing)

Application Number	13/722,585
Filing Date	12/20/2012
First Named Inventor	Dae-Young KIM
Art Unit	1784
Examiner Name	LAM, Cathy Fong Fong
Attorney Docket Number	P10904US

Total Number of Pages in This Submission

ENCLOSURES (*Check all that apply*)

- ☐ Fee Transmittal Form
  - ☐ Fee Attached
- ☑ Amendment/Reply
  - ☐ After Final
  - ☐ Affidavits/declaration(s)
- ☐ Extension of Time Request
- ☐ Express Abandonment Request
- ☐ Information Disclosure Statement
- ☐ Certified Copy of Priority Document(s)
- ☐ Reply to Missing Parts/ Incomplete Application
  - ☐ Reply to Missing Parts under 37 CFR 1.52 or 1.53
- ☐ Drawing(s)
- ☐ Licensing-related Papers
- ☐ Petition
- ☐ Petition to Convert to a Provisional Application
- ☐ Power of Attorney, Revocation Change of Correspondence Address
- ☐ Terminal Disclaimer
- ☐ Request for Refund
- ☐ CD, Number of CD(s) _____
  - ☐ Landscape Table on CD
- ☐ After Allowance Communication to TC
- ☐ Appeal Communication to Board of Appeals and Interferences
- ☐ Appeal Communication to TC **(Appeal Notice, Brief, Reply Brief)**
- ☐ Proprietary Information
- ☐ Status Letter
- ☐ Other Enclosure(s) (please Identify below):

Remarks

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

Firm Name	LRK Patent Law Firm		
Signature	/Taeksoo Lee/		
Printed name	Taeksoo Lee		
Date	April 15, 2015	Reg. No.	61976

CERTIFICATE OF TRANSMISSION/MAILING

I hereby certify that this correspondence is being facsimile transmitted to the USPTO or deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on the date shown below:

Signature			
Typed or printed name		Date	

This collection of information is required by 37 CFR 1.5. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and1.14. This collection is estimated to 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The **Privacy Act of 1974** (**P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	P10904US	8652

86144 7590 04/08/2015

LRK Patent Law Firm
1952 Gallows Rd
Suite 200
Vienna, VA 22182

EXAMINER
LAM, CATHY FONG FONG

ART UNIT	PAPER NUMBER
1784	

NOTIFICATION DATE	DELIVERY MODE
04/08/2015	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

e_oa@lrkpatent.com
plee@lrkpatent.com

Applicant-Initiated Interview Summary	Application No.	Applicant(s)	
	13/722,585	KIM ET AL.	
	Examiner	Art Unit	
	CATHY LAM	1784	

All participants (applicant, applicant's representative, PTO personnel):

(1) *CATHY LAM*. (3)_____.

(2) *Atty: Taeksoo Lee*. (4)_____.

Date of Interview: *03 April 2015*.

Type: ☒ Telephonic ☐ Video Conference
☐ Personal [copy given to: ☐ applicant ☒ applicant's representative]

Exhibit shown or demonstration conducted: ☐ Yes ☒ No.
If Yes, brief description: _____.

Issues Discussed ☐101 ☐112 ☐102 ☐103 ☐Others
(For each of the checked box(es) above, please describe below the issue and detailed description of the discussion)

Claim(s) discussed: _____.

Identification of prior art discussed: *of record*.

Substance of Interview
(For each issue discussed, provide a detailed description and indicate if agreement was reached. Some topics may include: identification or clarification of a reference or a portion thereof, claim interpretation, proposed amendments, arguments of any applied references etc...)

Applicant's representative informed the examiner that the prior art of record should not have been used against the claims, because this application is a continuation of application 13/029656, which has a earlier filing date than the prior art of record .

Applicant recordation instructions: The formal written reply to the last Office action must include the substance of the interview. (See MPEP section 713.04). If a reply to the last Office action has already been filed, applicant is given a non-extendable period of the longer of one month or thirty days from this interview date, or the mailing date of this interview summary form, whichever is later, to file a statement of the substance of the interview

Examiner recordation instructions: Examiners must summarize the substance of any interview of record. A complete and proper recordation of the substance of an interview should include the items listed in MPEP 713.04 for complete and proper recordation including the identification of the general thrust of each argument or issue discussed, a general indication of any other pertinent matters discussed regarding patentability and the general results or outcome of the interview, to include an indication as to whether or not agreement was reached on the issues raised.

☐ Attachment

/CATHY LAM/ Primary Examiner, Art Unit 1784	

Summary of Record of Interview Requirements

Manual of Patent Examining Procedure (MPEP), Section 713.04, Substance of Interview Must be Made of Record
A complete written statement as to the substance of any face-to-face, video conference, or telephone interview with regard to an application must be made of record in the application whether or not an agreement with the examiner was reached at the interview.

Title 37 Code of Federal Regulations (CFR) § 1.133 Interviews
Paragraph (b)

In every instance where reconsideration is requested in view of an interview with an examiner, a complete written statement of the reasons presented at the interview as warranting favorable action must be filed by the applicant. An interview does not remove the necessity for reply to Office action as specified in §§ 1.111, 1.135. (35 U.S.C. 132)

37 CFR §1.2 Business to be transacted in writing.
All business with the Patent or Trademark Office should be transacted in writing. The personal attendance of applicants or their attorneys or agents at the Patent and Trademark Office is unnecessary. The action of the Patent and Trademark Office will be based exclusively on the written record in the Office. No attention will be paid to any alleged oral promise, stipulation, or understanding in relation to which there is disagreement or doubt.

The action of the Patent and Trademark Office cannot be based exclusively on the written record in the Office if that record is itself incomplete through the failure to record the substance of interviews.

It is the responsibility of the applicant or the attorney or agent to make the substance of an interview of record in the application file, unless the examiner indicates he or she will do so. It is the examiner's responsibility to see that such a record is made and to correct material inaccuracies which bear directly on the question of patentability.

Examiners must complete an Interview Summary Form for each interview held where a matter of substance has been discussed during the interview by checking the appropriate boxes and filling in the blanks. Discussions regarding only procedural matters, directed solely to restriction requirements for which interview recordation is otherwise provided for in Section 812.01 of the Manual of Patent Examining Procedure, or pointing out typographical errors or unreadable script in Office actions or the like, are excluded from the interview recordation procedures below. Where the substance of an interview is completely recorded in an Examiners Amendment, no separate Interview Summary Record is required.

The Interview Summary Form shall be given an appropriate Paper No., placed in the right hand portion of the file, and listed on the "Contents" section of the file wrapper. In a personal interview, a duplicate of the Form is given to the applicant (or attorney or agent) at the conclusion of the interview. In the case of a telephone or video-conference interview, the copy is mailed to the applicant's correspondence address either with or prior to the next official communication. If additional correspondence from the examiner is not likely before an allowance or if other circumstances dictate, the Form should be mailed promptly after the interview rather than with the next official communication.

The Form provides for recordation of the following information:
- Application Number (Series Code and Serial Number)
- Name of applicant
- Name of examiner
- Date of interview
- Type of interview (telephonic, video-conference, or personal)
- Name of participant(s) (applicant, attorney or agent, examiner, other PTO personnel, etc.)
- An indication whether or not an exhibit was shown or a demonstration conducted
- An identification of the specific prior art discussed
- An indication whether an agreement was reached and if so, a description of the general nature of the agreement (may be by attachment of a copy of amendments or claims agreed as being allowable). Note: Agreement as to allowability is tentative and does not restrict further action by the examiner to the contrary.
- The signature of the examiner who conducted the interview (if Form is not an attachment to a signed Office action)

It is desirable that the examiner orally remind the applicant of his or her obligation to record the substance of the interview of each case. It should be noted, however, that the Interview Summary Form will not normally be considered a complete and proper recordation of the interview unless it includes, or is supplemented by the applicant or the examiner to include, all of the applicable items required below concerning the substance of the interview.

A complete and proper recordation of the substance of any interview should include at least the following applicable items:
1) A brief description of the nature of any exhibit shown or any demonstration conducted,
2) an identification of the claims discussed,
3) an identification of the specific prior art discussed,
4) an identification of the principal proposed amendments of a substantive nature discussed, unless these are already described on the Interview Summary Form completed by the Examiner,
5) a brief identification of the general thrust of the principal arguments presented to the examiner,
   (The identification of arguments need not be lengthy or elaborate. A verbatim or highly detailed description of the arguments is not required. The identification of the arguments is sufficient if the general nature or thrust of the principal arguments made to the examiner can be understood in the context of the application file. Of course, the applicant may desire to emphasize and fully describe those arguments which he or she feels were or might be persuasive to the examiner.)
6) a general indication of any other pertinent matters discussed, and
7) if appropriate, the general results or outcome of the interview unless already described in the Interview Summary Form completed by the examiner.

Examiners are expected to carefully review the applicant's record of the substance of an interview. If the record is not complete and accurate, the examiner will give the applicant an extendable one month time period to correct the record.

Examiner to Check for Accuracy

If the claims are allowable for other reasons of record, the examiner should send a letter setting forth the examiner's version of the statement attributed to him or her. If the record is complete and accurate, the examiner should place the indication, "Interview Record OK" on the paper recording the substance of the interview along with the date and the examiner's initials.

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Doc Code: M865 or FAI.REQ.INTV

PTOL-413A (08-10)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

Applicant Initiated Interview Request Form

Application No.: 13/722,585 First Named Applicant: Dae-Young KIM
Examiner: LAM, Cathy Fong Fong Art Unit: 1784 Status of Application: Non-final Rejection Mailed

Tentative Participants:
(1) Taeksoo Lee (2) _____
(3) _____ (4) _____

Proposed Date of Interview: April 1~3, 2015 **Proposed Time:** 11am~12pm (AM/PM)

Type of Interview Requested:
(1) [✓] Telephonic (2) [ ] Personal (3) [ ] Video Conference

Exhibit To Be Shown or Demonstrated: [ ] YES [✓] NO
If yes, provide brief description: _____

Issues To Be Discussed

Issues (Rej., Obj., etc)	Claims/ Fig. #s	Prior Art	Discussed	Agreed	Not Agreed
(1) 103(a) rejection	1		[ ]	[ ]	[ ]
(2)			[ ]	[ ]	[ ]
(3)			[ ]	[ ]	[ ]
(4)			[ ]	[ ]	[ ]

[ ] Continuation Sheet Attached [ ] Proposed Amendment or Arguments Attached
Brief Description of Arguments to be Presented: _____

An interview was conducted on the above-identified application on _____

NOTE: This form should be completed and filed by applicant in advance of the interview (see MPEP § 713.01). If this form is signed by a registered practitioner not of record, the Office will accept this as an indication that he or she is authorized to conduct an interview on behalf of the principal (37 CFR 1.32(a)(3)) pursuant to 37 CFR 1.34. This is not a power of attorney to any above named practitioner. See the Instruction Sheet for this form, which is incorporated by reference. By signing this form, applicant or practitioner is certifying that he or she has read the Instruction Sheet. After the interview is conducted, applicant is advised to file a statement of the substance of this interview (37 CFR 1.133(b)) as soon as possible. This application will not be delayed from issue because of applicant's failure to submit a written record of this interview.

/Taeksoo Lee/
Applicant/Applicant's Representative Signature

Examiner/SPE Signature

Taeksoo Lee
Typed/Printed Name of Applicant or Representative

61976
Registration Number, if applicable

This collection of information is required by 37 CFR 1.133. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 24 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

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The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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3/27/2015

From:	Paul T. Lee
Phone:	703-854-1331
Fax:	703-854-1332
Company Name:	LRK Patent Law Firm
To:	LAM, Cathy Fong Fong
Phone:	571-272-1538
Fax:	571-273-8300
Company Name:	USPTO

Enclosures:

Applicant Initiated Interview Request Form

☐ Urgent ☐ For Review ☐ Please Comment ☒ Please Reply ☐ Please Recycle

PAGE 1/3 * RCVD AT 3/27/2015 2:15:38 PM [Eastern Daylight Time] * SVR:W-PTOFAX-002/8 * DNIS:2738300 * CSID: * DURATION (mm-ss):01-22

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United States Patent and Trademark Office
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www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
13/722,585	12/20/2012	Dae-Young KIM	P10904US

CONFIRMATION NO. 8652

86144
LRK Patent Law Firm
1952 Gallows Rd
Suite 200
Vienna, VA 22182

POA ACCEPTANCE LETTER

OC000000073497427

Date Mailed: 02/20/2015

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 02/11/2015.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

/zretta/

Office of Data Management, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
13/722,585	12/20/2012	Dae-Young KIM	001333-0037

CONFIRMATION NO. 8652

26610
STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

POWER OF ATTORNEY NOTICE

OC000000073497423

Date Mailed: 02/20/2015

NOTICE REGARDING CHANGE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 02/11/2015.

- The Power of Attorney to you in this application has been revoked by the applicant. Future correspondence will be mailed to the new address of record(37 CFR 1.33).

/zretta/

Office of Data Management, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	001333-0037	8652

26610 7590 02/12/2015
STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

EXAMINER	
LAM, CATHY FONG FONG	

ART UNIT	PAPER NUMBER
1784	

MAIL DATE	DELIVERY MODE
02/12/2015	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No. 13/722,585	Applicant(s) KIM ET AL.	
	Examiner CATHY LAM	Art Unit 1784	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *Nov. 20, 2014*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5)☒ Claim(s) *1-6* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-6* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☒ All b)☐ Some** c)☐ None of the:

1.☒ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☒ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date *11-20-2014*.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

DETAILED ACTION

1. The present application is being examined under the pre-AIA first to invent provisions.

Information Disclosure Statement

2. The information disclosure statement (IDS) submitted on Nov. 20, 2014 was filed after the mailing date of the Notice of Allowability on Aug. 27, 2014. The submission is in compliance with the provisions of 37 CFR 1.97. Accordingly, the information disclosure statement is being considered by the examiner.

Claim Rejections - 35 USC § 103

3. The following is a quotation of pre-AIA 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 1-6 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over The Properties & Market Status of Copper Foil for Li 2nd Battery (Industrial materials journal vol 310,Oct. 05, 2012).

The prior art provided by Applicant teaches an electrolytic copper foil that is used in a lithium secondary battery.

The prior art teaches that a *conventional* copper foil has a surface roughness of ≤ 1.9 µm , a tensile strength of 30.8 to 55.8 kgf/mm^2, an elongation of 4.8-9.2% and a thickness of from 8-10 µm (see the 1st paragraph of page 1).

The copper foil in the prior art meets the present invention except for ratios of the different crystalline plane structures and the weight deviation.

In view of the prior art teaching, it would have been obvious for one to use the conventional copper foil for the lithium battery because the conventional copper foil possesses the same physical characteristic and would likely perform the same job.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CATHY LAM whose telephone number is (571)272-1538. The examiner can normally be reached on 9am-6pm.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Humera Sheikh can be reached on (571) 272-0604. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CATHY LAM/
Primary Examiner, Art Unit 1784

Receipt date: 11/20/2014

INFORMATION DISCLOSURE STATEMENT

FOR	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY IMPROVED IN WRINKLE CHARACTERISTICS		
Application No.	13/722,585	Filing Date	December 20, 2012
Applicant	LS Mtron Ltd.	Inventor(s)	KIM, Dae-Young, et al.
Our Ref.	OVP123760US	Your Ref.	2010F-0043USC1

U.S. PATENT DOCUMENTS

Document No.	Date (mm/dd/yyyy)	Inventors	U.S. Class	U.S. Subclass	Remarks

FOREIGN PATENT DOCUMENTS

Document No.	Date (mm/dd/yyy)	Country	Class	Subclass	Translation of Abstract		Remarks
					Yes	No	

OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, etc.)

/C.L./ KONDO KAZUO, 『FIRST STEP IN LEARNING MICROPLATING TECHNOLOGY – PIONEERING VARIOUS APPLICATION FIELDS』, published by Shintani Shigeki, June 15, 2004, pages 56~57, printed in Japan

/C.L./ C.Y.Chiu, J.C.Oung, D.T.Shieh, H.L.Lu, 「The Properties and Market Status of Copper Foil for Lithium Secondary Battery」(Industrial materials journal, Vol 310, October 5, 2012, printed in Taiwan, published by Material and Chemical Research Laboratories of Industrial Technology Research Institute), pages 170~178

/Cathy Lam/ 02/05/2015

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	Art Unit
	CATHY LAM	1784

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☒ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	08/14/2013	07/30/2014	02/09/2015						
	1	✓	=	✓						
	2	✓	=	✓						
	3	✓	=	✓						
	4	✓	=	✓						
	5	✓	=	✓						
	6	✓	=	✓						

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82A (07-13)
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NOTE: This form is to be submitted with the Power of Attorney by Applicant form (PTO/AIA/82B) to identify the application to which the Power of Attorney is directed, in accordance with 37 CFR 1.5, unless the application number and filing date are identified in the Power of Attorney by Applicant form. If neither form PTO/AIA/82A nor form PTO/AIA82B identifies the application to which the Power of Attorney is directed, the Power of Attorney will not be recognized in the application.

Application Number	13/722,585
Filing Date	2012-12-20
First Named Inventor	Dae-Young KIM
Title	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
Art Unit	1784
Examiner Name	LAM, Cathy Fong Fong
Attorney Docket Number	P10904US

SIGNATURE of Applicant or Patent Practitioner

Signature	/Taeksoo Lee/	Date (Optional)	
Name	Taeksoo Lee	Registration Number	61976
Title (if Applicant is a juristic entity)			
Applicant Name (if Applicant is a juristic entity)			

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. If more than one applicant, use multiple forms.

☐ *Total of _____ forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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POWER OF ATTORNEY BY APPLICANT

I hereby revoke all previous powers of attorney given in the application identified in either the attached transmittal letter or the boxes below.

Application Number	Filing Date

(Note: The boxes above may be left blank if information is provided on form PTO/AIA/82A.)

☑ I hereby appoint the Patent Practitioner(s) associated with the following Customer Number as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above: 86144

OR

☐ I hereby appoint Practitioner(s) named in the attached list (form PTO/AIA/82C) as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the patent application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above. (Note: Complete form PTO/AIA/82C.)

Please recognize or change the correspondence address for the application identified in the attached transmittal letter or the boxes above to:

☑ The address associated with the above-mentioned Customer Number

OR

☐ The address associated with Customer Number:

OR

Firm or Individual Name					
Address					
City		State		Zip	
Country					
Telephone		Email			

I am the Applicant (if the Applicant is a juristic entity, list the Applicant name in the box):

LS Mtron Ltd.

☐ Inventor or Joint Inventor (title not required below)

☐ Legal Representative of a Deceased or Legally Incapacitated Inventor (title not required below)

☑ Assignee or Person to Whom the Inventor is Under an Obligation to Assign (provide signer's title if applicant is a juristic entity)

☐ Person Who Otherwise Shows Sufficient Proprietary Interest (e.g., a petition under 37 CFR 1.46(b)(2) was granted in the application or is concurrently being filed with this document) (provide signer's title if applicant is a juristic entity)

SIGNATURE of Applicant for Patent

The undersigned (whose title is supplied below) is authorized to act on behalf of the applicant (e.g., where the applicant is a juristic entity).

Signature	/Young	Date (Optional)	Feb. 10, 2011
Name	Kim, YoungHwan		
Title	IP Team Leader		

NOTE: Signature - This form must be signed by the applicant in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. If more than one applicant, use multiple forms.

☐ Total of forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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STATEMENT UNDER 37 CFR 3.73(c)

Applicant/Patent Owner: Dae-Young KIM et al.

Application No./Patent No.: 13/722,585 Filed/Issue Date: 12/20/2012

Titled: COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

LS Mtron Ltd., a corporation

(Name of Assignee) (Type of Assignee, e.g., corporation, partnership, university, government agency, etc.)

states that, for the patent application/patent identified above, it is (choose **one** of options 1, 2, 3 or 4 below):

1. ☑ The assignee of the entire right, title, and interest.

2. ☐ An assignee of less than the entire right, title, and interest (check applicable box):

   ☐ The extent (by percentage) of its ownership interest is _____%. Additional Statement(s) by the owners holding the balance of the interest must be submitted to account for 100% of the ownership interest.

   ☐ There are unspecified percentages of ownership. The other parties, including inventors, who together own the entire right, title and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

3. ☐ The assignee of an undivided interest in the entirety (a complete assignment from one of the joint inventors was made). The other parties, including inventors, who together own the entire right, title, and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

4. ☐ The recipient, via a court proceeding or the like (*e.g.*, bankruptcy, probate), of an undivided interest in the entirety (a complete transfer of ownership interest was made). The certified document(s) showing the transfer is attached.

The interest identified in option 1, 2 or 3 above (not option 4) is evidenced by either (choose **one** of options A or B below):

A. ☑ An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in the United States Patent and Trademark Office at Reel 030038, Frame 0382, or for which a copy thereof is attached.

B. ☐ A chain of title from the inventor(s), of the patent application/patent identified above, to the current assignee as follows:

   1. From: _____ To: _____

      The document was recorded in the United States Patent and Trademark Office at

      Reel _____, Frame _____, or for which a copy thereof is attached.

   2. From: _____ To: _____

      The document was recorded in the United States Patent and Trademark Office at

      Reel _____, Frame _____, or for which a copy thereof is attached.

This collection of information is required by37 CFR3.73(b). The information is required toobtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentialityis governed by35 U.S.C. 122and 37 CFR1.11 and1.14. Thiscollection is estimated to take 12 minutes to complete, including gathering, preparing, and submittingthe completed application form to the USPTO.Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent tothe Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS.**SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450**

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STATEMENT UNDER 37 CFR 3.73(c)

3. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

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5. From: _____ To: _____

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6. From: _____ To: _____

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☐ Additional documents in the chain of title are listed on a supplemental sheet(s).

☐ As required by 37 CFR 3.73(c)(1)(i), the documentary evidence of the chain of title from the original owner to the assignee was, or concurrently is being, submitted for recordation pursuant to 37 CFR 3.11.

[NOTE: A separate copy (i.e., a true copy of the original assignment document(s)) must be submitted to Assignment Division in accordance with 37 CFR Part 3, to record the assignment in the records of the USPTO. See MPEP 302.08]

The undersigned (whose title is supplied below) is authorized to act on behalf of the assignee.

/Taeksoo Lee/	February 11, 2015
Signature	Date
Taeksoo Lee	61976
Printed or Typed Name	Title or Registration Number

[Page 2 of 2]

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The informationprovided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the informationin order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an InternationalApplication filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, arecord may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from thissystem of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt

EFS ID:	21468773
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	26610
Filer:	Taeksoo Lee
Filer Authorized By:	
Attorney Docket Number:	001333-0037
Receipt Date:	11-FEB-2015
Filing Date:	20-DEC-2012
Time Stamp:	15:21:00
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	P10904_trl.pdf	294616 c1b4ef052cf32f4786d961cdf1d33c5288023670	no	2

Warnings:	
Information:	

2	Power of Attorney	P10904_poa.pdf	1805661 ada7c0dafd8345f6ab6f4215472636ad496e9db9	no	3
Warnings:					
Information:					
3	Assignee showing of ownership per 37 CFR 3.73.	aia0096.pdf	134880 779e4b6df408f4881c9fd235515cb97108b1ff02	no	3
Warnings:					
Information:					
		Total Files Size (in bytes):	2235157		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc Code: TRAN.LET

Document Description: Transmittal Letter

PTO/SB/21 (07-09)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

TRANSMITTAL FORM

(to be used for all correspondence after initial filing)

Total Number of Pages in This Submission	

Application Number	13/722,585
Filing Date	2012-12-20
First Named Inventor	Dae-Young KIM
Art Unit	1784
Examiner Name	LAM, Cathy Fong Fong
Attorney Docket Number	P10904US

ENCLOSURES (*Check all that apply*)

- ☐ Fee Transmittal Form
  - ☐ Fee Attached
- ☐ Amendment/Reply
  - ☐ After Final
  - ☐ Affidavits/declaration(s)
- ☐ Extension of Time Request
- ☐ Express Abandonment Request
- ☐ Information Disclosure Statement
- ☐ Certified Copy of Priority Document(s)
- ☐ Reply to Missing Parts/ Incomplete Application
  - ☐ Reply to Missing Parts under 37 CFR 1.52 or 1.53
- ☐ Drawing(s)
- ☐ Licensing-related Papers
- ☐ Petition
- ☐ Petition to Convert to a Provisional Application
- ☑ Power of Attorney, Revocation Change of Correspondence Address
- ☐ Terminal Disclaimer
- ☐ Request for Refund
- ☐ CD, Number of CD(s) _____
  - ☐ Landscape Table on CD
- ☐ After Allowance Communication to TC
- ☐ Appeal Communication to Board of Appeals and Interferences
- ☐ Appeal Communication to TC **(Appeal Notice, Brief, Reply Brief)**
- ☐ Proprietary Information
- ☐ Status Letter
- ☑ Other Enclosure(s) (please Identify below):
  Statement Under 37 CFR 3.73(c)

Remarks

Applicant respectfully submits Power of Attorney and statement required by 37 CFR 3.73(c).

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

Firm Name	LRK Patent Law Firm		
Signature	/Taeksoo Lee/		
Printed name	Taeksoo Lee		
Date	February 11, 2015	Reg. No.	61976

CERTIFICATE OF TRANSMISSION/MAILING

I hereby certify that this correspondence is being facsimile transmitted to the USPTO or deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on the date shown below:

Signature			
Typed or printed name		Date	

This collection of information is required by 37 CFR 1.5. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and1.14. This collection is estimated to 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The **Privacy Act of 1974** (**P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Doc code: RCEX
Doc description: Request for Continued Examination (RCE)

PTO/SB/30EFS (07-09)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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REQUEST FOR CONTINUED EXAMINATION(RCE)TRANSMITTAL
(Submitted Only via EFS-Web)

Application Number	13/722,585	Filing Date	2012-12-20	Docket Number (if applicable)	001333/0037	Art Unit	1784
First Named Inventor	Kim, Dae-Young et al.			Examiner Name	Cathy F.F. Lam		

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application.
Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. The Instruction Sheet for this form is located at WWW.USPTO.GOV

SUBMISSION REQUIRED UNDER 37 CFR 1.114

Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

- ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____
- ☐ Other _____

☒ Enclosed

- ☐ Amendment/Reply
- ☒ Information Disclosure Statement (IDS)
- ☐ Affidavit(s)/ Declaration(s)
- ☐ Other _____

MISCELLANEOUS

☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of months _____
(Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)

☐ Other _____

FEES

☒ **The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.**
The Director is hereby authorized to charge any underpayment of fees, or credit any overpayments, to Deposit Account No 194709

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED

☒ Patent Practitioner Signature

☐ Applicant Signature

PTO/SB/30EFS (07-09)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Signature of Registered U.S. Patent Practitioner			
Signature	/Brian M. Rothery/	Date (YYYY-MM-DD)	2014-11-20
Name	Brian M. Rothery	Registration Number	35340

This collection of information is required by 37 CFR 1.114. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Patent Application Fee Transmittal	
Application Number:	13722585
Filing Date:	20-Dec-2012
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Filer:	Brian M. Rothery/ERICA GODLEWSKI
Attorney Docket Number:	001333-0037
Filed as Large Entity	

Utility under 35 USC 111(a) Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
Request for Continued Examination	1801	1	1200	1200
Submission- Information Disclosure Stmt	1806	1	180	180
		Total in USD ($)		**1380**

Electronic Acknowledgement Receipt	
EFS ID:	20751920
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	26610
Filer:	Brian M. Rothery/ERICA GODLEWSKI
Filer Authorized By:	Brian M. Rothery
Attorney Docket Number:	001333-0037
Receipt Date:	20-NOV-2014
Filing Date:	20-DEC-2012
Time Stamp:	12:41:09
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	$1380
RAM confirmation Number	10889
Deposit Account	194709
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: Charge any Additional Fees required under 37 C.F.R. Section 1.16 (National application filing, search, and examination fees) Charge any Additional Fees required under 37 C.F.R. Section 1.17 (Patent application and reexamination processing fees)	

Charge any Additional Fees required under 37 C.F.R. Section 1.19 (Document supply fees) Charge any Additional Fees required under 37 C.F.R. Section 1.20 (Post Issuance fees) Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)					
File Listing:					
Document Number	**Document Description**	**File Name**	**File Size(Bytes)/ Message Digest**	**Multi Part /.zip**	**Pages (if appl.)**
1	Transmittal Letter	IDStranmsittla112014.pdf	256480 f7dd1ad4040b1e96e9a6a23d8696b9279b8134f3	no	3
Warnings:					
Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	0037IDSlist112014.pdf	180854 a31970a39990aad18183f165d21407a6426801b0	no	1
Warnings:					
Information:					
This is not an USPTO supplied IDS fillable form					
3	Request for Continued Examination (RCE)	RCE1120.pdf	79502 83ccde4d5e710ad681a9b3986f2ce3c32838e23f	no	3
Warnings:					
This is not a USPTO supplied RCE SB30 form.					
Information:					
4	Non Patent Literature	Kazuo.pdf	293563 dd98f838741a51aea94d6194bb9f2de1a02cf87e	no	9
Warnings:					
Information:					
5	Non Patent Literature	Chiu.pdf	5205461 838db25e71a5a08d27b08aa15902110f4a55f3f4	no	23
Warnings:					
Information:					
6	Fee Worksheet (SB06)	fee-info.pdf	32180 ba52831c406bacf85a4ed0c78dd4f295651d0373	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	6048040		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
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National Stage of an International Application under 35 U.S.C. 371
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New International Application Filed with the USPTO as a Receiving Office
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Docket No.
001333-0037

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: **KIM, Dae-Young** Group Art Unit: **1784**

Application No.: **13/722,585** Examiner: **Lam, Cathy F.F.**

Filed: **December 20, 2012**

For: **COPPER FOIL FOR CURERNT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS**

Date: **November 20, 2014**

INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In compliance with the duty of disclosure under 37 C.F.R. § 1.56 and in accordance with the practice under 37 C.F.R. §§ 1.97 and 1.98, the Examiner's attention is directed to the documents listed on the enclosed Information Disclosure Statement by Applicant form (PTO/SB/08A and/or B, PTO-1449, or equivalent).

The following checked sections apply to this Information Disclosure Statement:

☐ In accordance with 37 C.F.R. § 1.98(a)(2)(ii) as revised at 69 Fed. Reg. 56481 (September 21, 2004), copies of the cited U.S. patent application publication(s) and/or U.S. patent(s) have not been submitted.

☐ The cited reference(s) were called to Applicant'(s) attention in a counterpart foreign patent application. A copy of the official communication in that counterpart foreign patent application citing the reference(s) is submitted herewith, and the Examiner is respectfully directed thereto for a concise explanation of the relevance of the cited art.

☐ At least some of the cited references are not (or the cited reference is not) in English, and so English abstracts of those references (that reference) are provided, if available.

☒ At least some of the cited references are not (or the cited reference is not) in English, and so machine English translations of those references (that reference) are provided, where available.

☐ This Information Disclosure Statement is being filed (1) within three months of the filing date of a national application other than a continued prosecution application under Sec. 1.53(d), (2) within three months of the date of entry of the national stage as set forth in Sec. 1.491 in an international application, (3) before the mailing of a first Office action on the merits, or (4) before the mailing of a first Office action after the filing of a Request for Continued Examination under 37 C.F.R. § 1.114. Accordingly, neither a fee nor Statement under 37 C.F.R. § 1.97(e) is due.

☐ This Information Disclosure Statement is being filed before the mailing date of any of a final action under 37 C.F.R. § 1.113, a Notice of Allowance under 37 C.F.R. § 1.311, or an action that otherwise closes prosecution in the application, and so is accompanied by one of:

(1) A Statement under 37 C.F.R. § 1.97(e), which follows; **or**

(2) The fee set forth in 37 C.F.R. § 1.17(p), authorization for which follows.

☒ This Information Disclosure Statement is being filed either (1) on or after the mailing date of a final action under 37 C.F.R. § 1.113, or (2) on or before payment of the issue fee, and is accompanied by:

(1) A Statement under 37 C.F.R. § 1.97(e), which follows; **and**

(2) The fee set forth in 37 C.F.R. § 1.17(p), authorization for which follows.

☒ Fee Under 37 C.F.R. § 1.17(p)

The Commissioner is authorized to charge the fee under 37 C.F.R. § 1.17(p) ($180) to Deposit Account No. 19-4709.

☒ Statement Under 37 C.F.R. § 1.97(e)

Each item of information contained in this Information Disclosure Statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the Information Disclosure Statement; or

No item of information contained in the Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in Sec. 1.56(c) more than three months prior to the filing of the Information Disclosure Statement.

☐ Additional Comments

Applicant(s) have the following additional comments:

It is respectfully requested that the above information be considered by the Examiner and that an initialed copy of the accompanying Information Disclosure Statement by Applicant form (PTO/SB/08A and/or B, PTO-1449, or equivalent) be returned to the undersigned indicating that such information has been considered.

Other than any fees mentioned above, no fees are believed to be due in connection with this Information Disclosure Statement. Nevertheless, the Commissioner is authorized to charge any fees which are deemed to be now or hereafter due in connection with this paper to Deposit Account No. 19-4709.

Favorable consideration and prompt allowance of this application is respectfully requested. In the event that there are any questions, or should additional information be required, please contact Applicant'(s) attorney at the number listed below.

Respectfully submitted,

/Brian M. Rothery/

Brian M. Rothery
Reg. No. **35,340**
Attorney for Applicant(s)
Stroock & Stroock & Lavan, LLP
180 Maiden Lane
New York, New York 10038
(212) 806-5400

INFORMATION DISCLOSURE STATEMENT

FOR	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY IMPROVED IN WRINKLE CHARACTERISTICS		
Application No.	13/722,585	Filing Date	December 20, 2012
Applicant	LS Mtron Ltd.	Inventor(s)	KIM, Dae-Young, et al.
Our Ref.	OVP123760US	Your Ref.	2010F-0043USC1

U.S. PATENT DOCUMENTS

Document No.	Date (mm/dd/yyyy)	Inventors	U.S. Class	U.S. Subclass	Remarks

FOREIGN PATENT DOCUMENTS

Document No.	Date (mm/dd/yyy)	Country	Class	Subclass	Translation of Abstract		Remarks
					Yes	No	

OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, etc.)

KONDO KAZUO, 『FIRST STEP IN LEARNING MICROPLATING TECHNOLOGY – PIONEERING VARIOUS APPLICATION FIELDS』, published by Shintani Shigeki, June 15, 2004, pages 56~57, printed in Japan

C.Y.Chiu, J.C.Oung, D.T.Shieh, H.L.Lu, 「The Properties and Market Status of Copper Foil for Lithium Secondary Battery」(Industrial materials journal, Vol 310, October 5, 2012, printed in Taiwan, published by Material and Chemical Research Laboratories of Industrial Technology Research Institute), pages 170~178

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	001333-0037	8652

26610 7590 10/08/2014
STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

EXAMINER	
LAM, CATHY FONG FONG	
ART UNIT	**PAPER NUMBER**
1784	
MAIL DATE	**DELIVERY MODE**
10/08/2014	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Supplemental Notice of Allowability	**Application No.** 13/722,585	**Applicant(s)** KIM ET AL.	
	Examiner CATHY LAM	**Art Unit** 1784	**AIA (First Inventor to File) Status** No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to *the IDS filed on August 21, 2014*.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on_____.
2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.
3. ☐ The allowed claim(s) is/are _____. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov .
4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:
   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____.

Applicant has **THREE MONTHS FROM THE** "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).
6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☒ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date 08-21-2014
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____ .
5. ☐ Examiner's Amendment/Comment
6. ☐ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/CATHY LAM/ Primary Examiner, Art Unit 1784	

Receipt date: 08/21/2014

INFORMATION DISCLOSURE STATEMENT

FOR	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY IMPROVED IN WRINKLE CHARACTERISTICS		
Application No.	13/722,585	Filing Date	December 20, 2012
Applicant	LS Mtron Ltd.	Inventor(s)	KIM, Dae-Young, et al.
Our Ref.	OVP123760US	Your Ref.	001333-0037

U.S. PATENT DOCUMENTS

Document No.	Date (mm/dd/yyyy)	Inventors	U.S. Class	U.S. Subclass	Remarks
US 2004/0104117 A1	Jun. 3, 2004	Jeom-Sik Yang, et al.			
US 5,326,455 B	Jul. 5, 1994	Toyoshige Kubo, et al			
US 2006/0166032 A1	Jul. 27, 2006	Masashi Kumagai, et al			

/C.L./

FOREIGN PATENT DOCUMENTS

Document No.	Date (mm/dd/yyy)	Country	Class	Subclass	Translation of Abstract		Remarks
					Yes	No	
JP 1997-143785 A	Jun. 3, 1997	JP					US 5,834,140 B1
JP 2006-052441 A	Feb. 23, 2006	JP			V		
JP 2004-256879 A	Sep. 16, 2004	JP			V		
JP 1997-306504 A	Nov. 28, 1997	JP			V		
JP 2007-200871 A	Aug. 9, 2007	JP					US 2010/0015514 A1
JP 2004-263289 A	Sep. 24, 2004	JP					US 2006/0191798 A1
KR 10-2008-0103438	Nov. 27, 2008	KR					US 2009/0061326 A1
JP 4,413,552 B	Nov. 27, 2009	JP					US 2004/0029006 A1
JP 4,017,628 B	Sep. 28, 2007	JP					US 5,834,140 B1
JP 3,742,144 B	Nov. 18, 2005	JP			V		
JP 2001-11684 A	Jan. 16, 2001	JP			V		
JP 2004-107786 A	Apr. 8, 2004	JP					US 2004/0149583 A1

/C.L./

OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, etc.)

~~FIRST STEP IN LEARNING MICROPLATING TECHNOLOGY - PIONEERING VARIOUS APPLICATION FIELDS~~ (Written and edited by KONDO KAZUO) No date given

2008 NEW BATTERY TECHNOLOGY OUTLOOK, Lithium-ion Rechargeable Electric Double Layer Capacitor Fuel Cell, Electronic Journal

2007 ECB Technology Outlook, Section 7 Material for electric circuit board

Effect of hard particle perturbation on microstructure and property of electroformed copper (The China Journal of

/C.L./

Receipt date: 08/21/2014

/C.L./	Nonferrous Metals, Vol. 16 No.9, 2006, pages 1558-1562)
	Influence of K4Fe(CN)6 on Electorless Copper Plating using Hypophosphite as Reducing Agent (The China Journal of Material Engineer, No.4, 2009, pages 39-44)
	FURUKAWA CIRCUIT FOIL CO., LTD (Catalog) (FURUKAWA ELECTRIC CO., LTD, May 20, 2009)
	The Properties and Market Status of Copper Foil for Lithium Secondary Battery, C.Y.Chiu, J.C.Oung, D.T.Shieh, H.L.Lu No date given
/C.L./	Industrial Technology Research Institute No.195, Sec.4, Chung Hsing Rd., Chutung Hsinchu, 31040, Taiwan, R.O.C.9 (Nov.14, 2012)
	Electrolytic Deposit Copper Foil for Printed Circuits, KS C 2211:1987
	Copper foil for printed wiring boards, KS C 6249-5-1:2000
	Nonferrous Metals Processing, Feb, 2008, Vol.37, Vo.1
	Chinese Journal of Pare Metals, Dec. 2005, Vol.29, No.6

/Cathy Lam/ 09/26/2014

Docket No.
001333/0037

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventors: **Kim, Dae-Young et al.** Group Art Unit: **1784**

Application No.: **13/722,585** Examiner: **Lam, Cathy F.F.**

Filed **December 20, 2012** Confirmation No.: **8652**

For: **Copper Foil For Current Collector of Lithium secondary battery With Improved Wrinkle Characteristics**

REQUEST FOR CONSIDERATION OF PREVIOUSLY-SUBMITTED INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

On August 21, 2014, an Information Disclosure Statement ("IDS") was filed in the above-captioned case. The IDS was filed after the non-final rejection dated March 14, 2014 but before the Notice of Allowance dated August 27, 2014. The IDS was filed with the fee set forth in 37 CFR 1.17(p) and thus was timely pursuant to 37 CFR 1.97(c).

The Notice of Allowance did not include any form indicating that the IDS had been considered by the Office. The Applicant therefore requests that the references cited in the IDS be considered by the Office and a notification of such be entered into the record for this case.

Further, this application is a continuation of United States Patent Application No. 13/029,656, which has since issued as United States Patent No. 8,349,518. When considering the references cited in the IDS the Office should be aware that none of these references were

disclosed in the parent application No. 13/029,656 and that examination and consideration of these references that were not disclosed nor considered during prosecution of the parent application No. 13/029,656 may be required and is respectfully requested. The references cited in the IDS arose from Office Actions in corresponding counterpart foreign applications and an opposition against a Korean Patent corresponding to the parent application No. 13/029,656.

Respectfully submitted,

Date: September 2, 2014

Mord M. Lewis
Registration No. 50,478, on behalf of:
Brian M. Rothery
Registration No. 35,340
Attorneys for Applicant
Stroock & Stroock & Lavan LLP
180 Maiden Lane
New York, New York 10038
(212) 806-5400

Electronic Acknowledgement Receipt

EFS ID:	20024649
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	26610
Filer:	Brian M. Rothery/Rachel Dorazio
Filer Authorized By:	Brian M. Rothery
Attorney Docket Number:	001333-0037
Receipt Date:	02-SEP-2014
Filing Date:	20-DEC-2012
Time Stamp:	17:30:19
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Miscellaneous Incoming Letter	Request_Consideration.pdf	1320509 69731a8d3385afff32c467a56e996a9a5d2615d4	no	2

Warnings:	
Information:	

Total Files Size (in bytes):	1320509

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

26610 7590 08/27/2014

STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

EXAMINER
LAM, CATHY FONG FONG

ART UNIT	PAPER NUMBER
1784	

DATE MAILED: 08/27/2014

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	001333-0037	8652

TITLE OF INVENTION: COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$960	$0	$0	$960	11/28/2014

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

26610 7590 08/27/2014
STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission
I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	001333-0037	8652

TITLE OF INVENTION: COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$960	$0	$0	$960	11/28/2014

EXAMINER	ART UNIT	CLASS-SUBCLASS
LAM, CATHY FONG FONG	1784	428-522000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).
- ❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
- ❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.
1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. The following fee(s) are submitted:
- ❑ Issue Fee
- ❑ Publication Fee (No small entity discount permitted)
- ❑ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**
- ❑ A check is enclosed.
- ❑ Payment by credit card. Form PTO-2038 is attached.
- ❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credits any overpayment, to Deposit Account Number _____ (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)
- ❑ Applicant certifying micro entity status. See 37 CFR 1.29
  NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
- ❑ Applicant asserting small entity status. See 37 CFR 1.27
  NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
- ❑ Applicant changing to regular undiscounted fee status.
  NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

PTOL-85 Part B (10-13) Approved for use through 10/31/2013. OMB 0651-0033 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	001333-0037	8652

26610 7590 08/27/2014

STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

EXAMINER	
LAM, CATHY FONG FONG	

ART UNIT	PAPER NUMBER
1784	

DATE MAILED: 08/27/2014

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 13/722,585	Applicant(s) KIM ET AL.	
	Examiner CATHY LAM	Art Unit 1784	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to *the Terminal Disclaimer filed on Aug 11, 2014*.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on_____.
2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.
3. ☒ The allowed claim(s) is/are *1-6*. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov .
4. ☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☒ All b) ☐ Some *c) ☐ None of the:
   1. ☒ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____.

Applicant has **THREE MONTHS FROM THE** "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
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5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
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Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____ .
5. ☐ Examiner's Amendment/Comment
6. ☐ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/CATHY LAM/
Primary Examiner, Art Unit 1784

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	Art Unit
	CATHY LAM	1784

CPC- SEARCHED		
Symbol	Date	Examiner
B32B 15/01	07-30-2014	CL
C22C 9/00	07-30-2014	CL
C25D 3/38, 7/0614	07-30-2014	CL
H01M 4/661, 10/052	07-30-2014	CL

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner
429	522, 485, 517	07-30-2014	CL
428	577, 612, 687	07-30-2014	CL

SEARCH NOTES		
Search Notes	Date	Examiner

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner
429	485, 517, 522	07-30-2014	CL
428	577, 612, 687	07-30-2014	

	/C.L./ Primary Examiner.Art Unit 1784

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CONFIRMATION NO. 8652

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
13/722,585	12/20/2012	428	1784	001333-0037

APPLICANTS
LS MTRON LTD., Gyeonggi-do, KOREA, REPUBLIC OF

INVENTORS
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Byoung-Kwang Lee, Gyeonggi-do, KOREA, REPUBLIC OF;
Seung-Jun Choi, Gyeonggi-do, KOREA, REPUBLIC OF;

**** CONTINUING DATA ***************************
This application is a CON of 13/029,656 02/17/2011 PAT 8349518

**** FOREIGN APPLICATIONS ***************************
JAPAN 2010-161088 07/15/2010

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED ****
01/18/2013

Foreign Priority claimed ☑ Yes ☐ No 35 USC 119(a-d) conditions met ☑ Yes ☐ No Verified and Acknowledged /CATHY FONG FONG LAM/ Examiner's Signature	☐ Met after Allowance Initials	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
		KOREA, REPUBLIC OF	1	6	1

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NEW YORK, NY 10038
UNITED STATES

TITLE
COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

FILING FEE RECEIVED		
1400	FEES: Authority has been given in Paper No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other _____ ☐ Credit

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	Art Unit
	CATHY LAM	1784

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☒ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	08/14/2013	07/30/2014							
	1	✓	=							
	2	✓	=							
	3	✓	=							
	4	✓	=							
	5	✓	=							
	6	✓	=							

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	**Art Unit**
	CATHY LAM	1784

CPC							
Symbol						**Type**	**Version**
C25D		3	/	38		A	2013-01-01
C25D		7	/	0614		I	2013-01-01
C22C		9	/	00		I	2013-01-01
H01M		4	/	661		I	2013-01-01
H01M		10	/	052		A	2013-01-01
B32B		15	/	01		F	2013-01-01
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CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
			/					
			/					

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 6	
/CATHY LAM/ Primary Examiner.Art Unit 1784 (Primary Examiner)	07-30-2014 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure N/A

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
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US ORIGINAL CLASSIFICATION		INTERNATIONAL CLASSIFICATION										
CLASS	SUBCLASS	CLAIMED					NON-CLAIMED					
429	522	H	0	1	M	4 / 64 (2006.01.01)						

CROSS REFERENCE(S)					
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)				
429	485	517			
428	577	612	687		

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	6	
/CATHY LAM/ Primary Examiner.Art Unit 1784	07-30-2014	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	N/A

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
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	CATHY LAM	1784

☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☒ T.D. ☐ R.1.47

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
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NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 6	
/CATHY LAM/ Primary Examiner.Art Unit 1784 (Primary Examiner)	07-30-2014 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure N/A

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INFORMATION DISCLOSURE STATEMENT

FOR	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY IMPROVED IN WRINKLE CHARACTERISTICS		
Application No.	13/722,585	Filing Date	December 20, 2012
Applicant	LS Mtron Ltd.	Inventor(s)	KIM, Dae-Young, et al.
Our Ref.	OVP123760US	Your Ref.	001333-0037

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Application Number:	13722585
Filing Date:	20-Dec-2012
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Filer:	Brian M. Rothery/ERICA GODLEWSKI
Attorney Docket Number:	001333-0037
Filed as Large Entity	

Utility under 35 USC 111(a) Filing Fees

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Petition:				
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Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
Submission- Information Disclosure Stmt	1806	1	180	180
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Information:					
2	Non Patent Literature	d2.pdf	293565 40c8fb872ab25003112200fed16212d385073214	no	9
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3	Foreign Reference	d5.pdf	257708 c2b9e2a9bc019449bf948b61d7d025a4be887889	no	9
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<u>New International Application Filed with the USPTO as a Receiving Office</u>
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US005834140A

United States Patent [19]

Wolski et al.

[11] **Patent Number: 5,834,140**

[45] **Date of Patent: Nov. 10, 1998**

[54] **ELECTRODEPOSITED COPPER FOIL FOR FINE PATTERN AND METHOD FOR PRODUCING THE SAME**

[75] Inventors: **Adam M. Wolski**, Edgewater Park, N.J.; **Michel Streel**, Houffalize, Belgium; **Akitoshi Suzuki**; **Hideo Otsuka**, both of Imaichi, Japan

[73] Assignee: **Circuit Foil Japan Co., Ltd.**, Tokyo, Japan

[21] Appl. No.: **715,104**

[22] Filed: **Sep. 18, 1996**

[30] **Foreign Application Priority Data**

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Apr. 26, 1996 [JP] Japan 8-106743

[51] **Int. Cl.**[6] **C25D 1/04**

[52] **U.S. Cl.** **429/220**; 205/57; 205/77; 205/296; 428/606; 428/607; 428/612; 428/675; 428/687; 428/935; 429/122; 429/245

[58] **Field of Search** 205/50, 76, 77, 205/57, 296; 428/606, 607, 612, 675, 687, 935; 429/122, 220, 245

[56] **References Cited**

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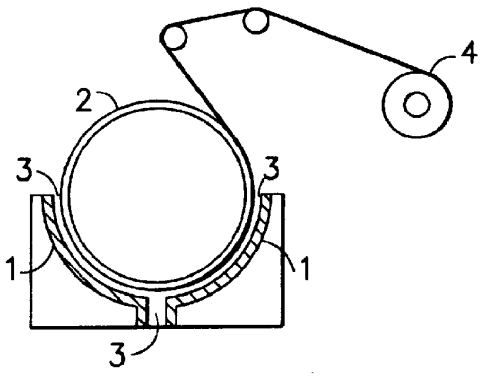
41 26 502 2/1993 Germany .

Primary Examiner—Kathryn L. Gorgos
Assistant Examiner—William T. Leader
Attorney, Agent, or Firm—Frishauf. Holtz, Goodman, Langer & Chick, P.C.

[57] **ABSTRACT**

The present invention is an electrodeposited copper foil characterised in that roughening treatment is performed on a matte side of an untreated copper foil wherein the surface roughness R_z of the matte side of the untreated copper foil is the same as or less than the surface roughness R_z of the shiny side of this untreated copper foil. The electrodeposited copper foil is made by electrodepositing copper onto a drum from an electrolyte which contains 0.05 to 5 ppm 3-mercapto 1-propanesulfonate; at least one organic compound selected from 0.1 to 15 ppm of a polysaccharide which is a carbohydrate such as starches, celluloses and vegetable rubbers, and 0.3 to 35 ppm of a low molecular weight glue having a weight average molecular weight of 10,000 or less; and 10 to 60 ppm of a chloride ion. The copper foil may be used in making a printed circuit board or as a component of a secondary battery cell.

15 Claims, 1 Drawing Sheet



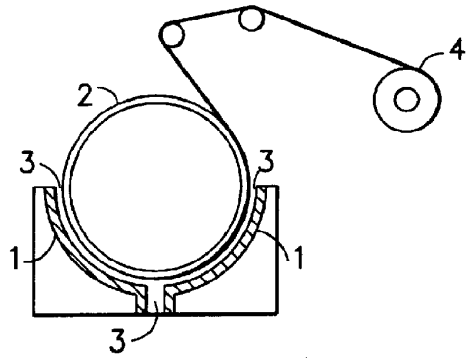


FIG.1

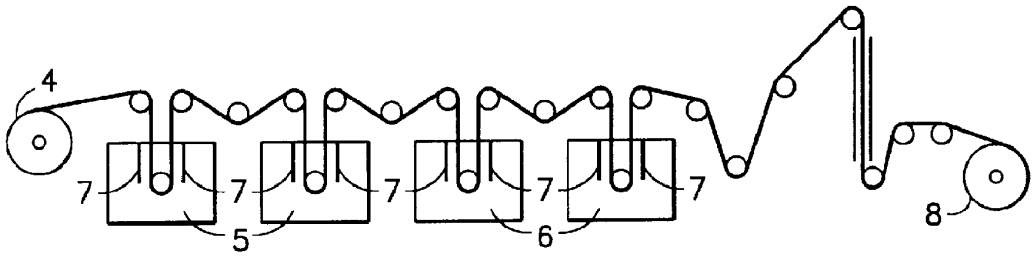


FIG.2

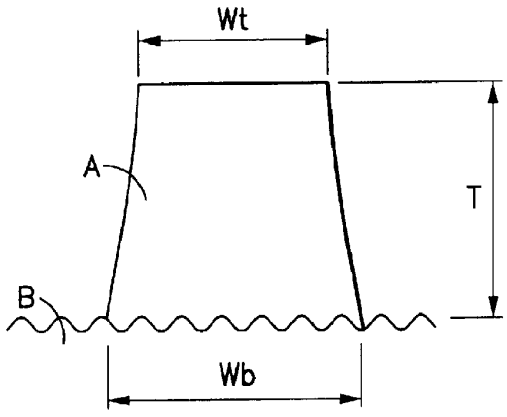


FIG.3

ELECTRODEPOSITED COPPER FOIL FOR FINE PATTERN AND METHOD FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an electrodeposited copper foil which is capable of making a fine pattern and capable of obtaining a high etching factor, a method for producing the same, and a copper-clad laminated board and a printed-wiring board (printed circuit) using the same.

Also, the untreated copper foil according to the present invention has flatter surfaces on both surfaces as compared with the conventional ones so that it can be used as an electrode material for a secondary battery, a flat cable, a shielding material for covering cables and others, but use of the electrodeposited copper foil of the present invention is not limited thereto.

2. Prior Art

An electrodeposited copper foil for a printed circuit has been produced industrially by filling a gap between an insoluble electrode such as a lead electrode or a titanium electrode covered with a platinum group metal and a rotating cathode drum which is made of stainless steel or titanium and opposed to the insoluble electrode, with an electrolyte of a copper sulfate aqueous solution, passing electricity to these electrodes to electrodeposit copper on the rotating cathode drum and peeling off the electrodeposited copper continuously.

In general, when an aqueous solution containing only a copper ion and a sulfuric acid ion is used as an electrolyte, pinhole or microporosity is generated on the copper foil due to dust or oils inevitably existing in the equipments and causes serious problems in practical use. Also, the mountain-valley shape of a surface (a matte side) of the copper foil which contacts with the electrolyte is deformed so that sufficieut strength cannot be obtained when the copper foil is adhered to an insulating substrate material in a later stage. When roughness of the matte side is large, there are caused problems that insulation resistance between layers and circuit conductivity of a multilayer printed-wiring board (printed circuit) are lowered, or at pattern etching after adhering the copper foil to a substrate material, transfer of copper to the substrate or undercutting of a circuit portion occurs, whereby various characteristics as a circuit substrate are damaged.

In order to prevent the pinhole or the like, a chloride ion is added to the electrolyte, or the electrolyte is passed through a filter containing activated carbon to remove dust and oils. In order to prevent microporosity and adjust the mountain-valley shape of the matte side, glue has heretofore been added to the electrolyte, and it has been also proposed to add various organic materials and inorganic materials as additives other than glue. Technology of producing an electrodeposited copper foil for a printed-wiring board is based on plating technology as can be understood from the point that electrodes are provided in a solution containing a metal salt and electricity is passed to the electrodes to electrodeposit a metal on a cathode. As an additive for producing the electrodeposited copper foil for a printed-wiring board, an additive for copper plating can be diverted in many cases. Glue, thiourea and molasses have heretofore been known as a brightener for copper plating, and when the above additives are added to the electrolyte, it can be expected to exhibit a so-called brightening effect, i.e., an effect of making roughness of the matte side smaller with

respect to the electrodeposited copper foil for a printed-wiring board. In U.S. Pat. No. 5,171,417, there has been disclosed a method of producing an electrodeposited copper foil, in which activated sulfur such as thiourea is used as an additive. However, the electrodeposited copper foil for a printed-wiring board is produced with current density which is higher than that of common plating in order to improve productivity, etc.; in recent years, characteristics required for the electrodeposited copper foil for a printed-wiring board have been heightened significantly; and in particular, there has been demanded strongly a copper foil in which roughness of the matte side is suppressed without impairing mechanical characteristics such as elongation, whereby satisfactory characteristics cannot be obtained under the present circumstances even when the above additives for plating are used as such as additives for the electrodeposited copper foil for a printed-wiring board.

On the other hand, in recent years, developments in electronic circuit technology including a semiconductor and an integrated circuit are remarkable. As a matter of course, further technological innovation has been demanded even in a printed-wiring board which is a forming portion or a mounting portion thereof. These demands are to develop a highly multilayered and finely patterned printed circuit board.

Characteristics required for the electrodeposited copper foil for a printed-wiring board in order to satisfy these demands are good insulation property between layers and patterns, low profiling of a matte side (lowering in roughness) in order to prevent undercutting at etching, improved high temperature elongation characteristic in order to prevent crack due to thermal stress and also high tensile strength for dimensional stability of the printed-wiring board. A demand for further low profiling for fine patterning has been particularly strong.

Low profiling of the matte side can be accomplished by, for example, adding a large amount of glue or thiourea to the electrolyte as described above, but accompanied with increase in its amount added, both of ordinary temperature elongation and high temperature elongation are lowered abruptly. On the other hand, a copper foil obtained from an electrolyte to which no additive is added has extremely high values of ordinary temperature elongation and high temperature elongation, but the shape of the matte side is deformed, roughness is enlarged, high tensile strength cannot be maintained, and further it is impossible to produce an electrodeposited copper foil in which these characteristics are stable. When electrolysis current density is suppressed to a lower value, as compared with an electrodeposited foil prepared with high current density, roughness of the matte side is lowered and elongation and tensile strength are improved, but lowering in productivity is not preferred from an economical view.

As described above, it is not easy to realize further low profiling, good room temperature elongation, good high temperature elongation and high tensile strength which have been demanded for a recent electrodeposited copper foil for a printed-wiring board.

As the reason why fine pattern cannot be produced by the conventional electrodeposited copper foil, there may be mentioned that a surface roughness of the foil is rough.

An electrodeposited copper foil can be generally produced by firstly using an electroforming cell as shown in FIG. 1 to produce a copper foil which is called to as an untreated copper foil and then using a treater as shown in FIG. 2, the produced copper foil is subjected to bond

enhancing treatment and stain proofing treatment to prepare a surface treated copper foil.

In the electroforming cell, an electrolyte **3** is passed through an apparatus comprising a drum-shaped cathode **2** (the surface of which is made of SUS (stainless steel) or titanium) which is rotating and an anode **1** (a lead electrode or a titanium electrode covered by a noble metal oxide) provided to a concentric circle shape to said cathode **2**, and an electric current is passed through both electrodes to deposit copper on the surface of said cathode with a desired thickness and then the copper foil is peeled off from the surface of said cathode. The thus prepared foil is called to as an untreated copper foil.

Thereafter, in order to provide characteristics necessary for a copper-clad laminated board, the untreated copper foil **4** is passed through the treater as shown in FIG. **2** to carry out an electrochemical or chemical surface treatment continuously. Among these treatments, there is a process of depositing copper modules on the surface of the foil for enhancing bonding strength of the foil when it is laminated to an insulating resin substrate. This process is called to as a bond enhancing treatment. The copper foil subjected to the above treatments is called a treated copper foil **8** and can be used for a copper-clad laminated board.

Mechanical characteristics of the electrodeposited copper foil can be determined by the characteristics of the untreated copper foil **4**, and an etching characteristic of a copper foil, i.e. an etching rate and uniform dissolution property are also determined in a large part by the characteristics of the untreated foil.

A main factor which affects an etching characteristic among the characteristics of a copper foil is a surface roughness of the foil. An effect of a roughness of the surface which is subjected to the bond enhancing treatment and to be laminated to an insulating resin substrate is remarkable. Factors which affect the roughness of the copper foil can be roughly divided into two. One of which is a surface roughness of the untreated copper foil and the other is a manner of copper nodules to be deposited to the surface subjected to the bond enhancing treatment of the foil. When the surface roughness of the untreated copper foil which is a raw foil is rough, the roughness of the copper foil after the bond enhancing treatment becomes rough. Also, generally speaking, when a deposited amount of copper nodules to the foil is a large, the roughness of the copper foil after the bond enhancing treatment becomes rough. The deposited amount of copper nodules at the bond enhancing treatment can be controlled by the amount of the electric current to be flown at the time of the treatment while the surface roughness of the untreated copper foil is almost determined by the electrolysis conditions when copper is deposited on the drum-shaped cathode as mentioned above, particularly by an additive to be added to an electrolyte.

In general, in the untreated copper foil, the so-called shiny side which is a surface at the side contacting with the drum has a relatively smooth surface, but at the reverse surface called a matte side, unevenness is relatively remarkable. In order to smooth the matte side, some attempts have been made until now. For example, there is a method for producing an electrodeposited copper foil prepared by using an active sulfur such as thiourea, etc., as an additive as disclosed in the above-mentioned U.S. Pat. No. 5,171,417. However, in this case, while the roughened surface can be smoothened as compared with the case where a conventional additive such as glue is used, it is still rough as compared with the shiny side and the effect is not yet complete.

Also, since the shiny side is relatively smooth so that, as disclosed in Japanese Provisional Patent Publication No. 270331/1994, an attempt has been made that copper nodules are deposited to the shiny side whereby laminating it with a resin substrate. However, in this case, there is a disadvantage that it must adhere a dry film or a resist to the usual matte side whereby adhesive force to the copper foil lowers due to unevenness of the surface and the film or the resist easily peels off from the foil.

SUMMARY OF THE INVENTION

The present invention has been made in order to cancel the problems of the prior art techniques, and an object thereof is to provide a copper foil which has a high etching factor without lowering peeling resistance and acomplishes fine pattern without remaining copper particles at the root of the circuit pattern, and also has a large high temperature elongation and high tensile strength.

Here, the measure of the fine pattern can be generally shown by the etching factor (=2T/(Wb−Wt)) shown in FIG. **3**. If the value is larger, the shape of the section of a circuit becomes more sharp.

The present invention is an electrodeposited copper foil which comprises a copper foil having a shiny side and a matte side and said matte side which has a surface roughness R_z measured by JIS B 0601-1994 of substantially the same as that of the shiny side or less being subjected to a surface roughening treatment. Surface roughness R_z means R_z as specified by the definition of JIS B 0601-1994 "Indication of definition of surface roughness" 5.1, i.e. 10-point mean roughness (R_z).

This untreated copper foil can be obtained by electrolysis using an electrolyte to which has been added a chemical compound having a mercapto group and apart from this at least one type of organic compound and chloride ions.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a sectional view showing the structure of an electroforming cell wherein the reference numeral **1** is an anode of an electroforming cell, **2** is a cathode of an electroforming cell, **3** is an electrolyte of an electroforming cell and **4** is an untreated copper foil.

FIG. **2** is a sectional view showing the structure of a treater wherein the reference numeral **4** is the same as in FIG. **1**, **5** is an electrolyte of a treater, **6** is an electrolyte of a treater, **7** is an anode of a treater, and **8** is a surface-treated copper foil.

FIG. **3** is a schematic view showing a calculating method of an etching factor wherein A is a cross-section of copper foil, B is an insulating board, Wt is a top width of copper foil cross-section, Wb is a bottom width of copper foil cross-section and T is a thickness of a copper foil.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

An electrodeposited copper foil of the present invention comprises an untreated copper foil having a shiny side and a matte side, and a surface roughness R_z of the matte side is the same as a surface roughness R_z of the shiny side or less and the matte side is subjected to a surface bond enhancing treatment. Here, the surface roughness R_z means a ten-point mean roughness (R_z) defined at the paragraph 5.1 of "Definition and Designation of Surface Roughness" according to "JIS B 0601-1994".

In the present invention, an additive which is a base of a combination is 3-mercapto 1-propanesulfonate as a com-

pound having a mercapto group. 3-Mercapto 1-propanesulfonate is a compound representatively shown by $HS(CH_2)_3SO_3R$ or the like, wherein R represents an alkali metal atom such as lithium, sodium, potassium, etc. Among these, sodium is particularly preferred as an alkali metal atom. This compound does not have a strong effect of making copper crystal fine when it is used alone. However, by using the compound in combination with other organic compound, copper crystal can be made fine and a plating surface having less unevenness can be obtained. Detailed action and mechanism thereof have not yet been clarified, but it is estimated that a molecule of the compound is reacted with a copper ion in a copper sulfate electrolyte to be converted into a complex, or the compound acts on a plating interface to elevate overvoltage, whereby copper crystal can be made fine and a plating surface having less unevenness can be formed.

One organic compound other than the compound having a mercapto group to be used in combination is a high molecular weight polysaccharide. The high molecular weight polysaccharide is a carbohydrate such as a starch, a cellulose and a vegetable rubber and generally becomes colloid in water. As a polysaccharide produced industrially and inexpensively, there may be meutioned edible starch, starch for industrial use and dextrin as a starch; water-soluble cellulose ether as disclosed in Japanese Provisional Patent Publication No. 182890/1990, i.e., sodium carboxymethyl cellulose and carboxymethylhydroxyethyl cellulose ether as a cellulose; and gum arabic and tragacanth gum as a vegetable rubber.

By using the above organic compound in combination with 3-mercapto 1-propanesulfonate, copper crystal can be made fine and a plating surface having less unevenness can be obtained. In addition to the action of making copper crystal fine, the organic compound has an action of preventing a produced copper foil from being fragile. The organic compound alleviates inner stress accumulated in the copper foil so that the organic compound not only prevents breaking and curling of the copper foil occurring when the copper foil is wound from a cathode drum, but also improves elongations at room temperature and high temperature.

The other organic compound to be used in combination of the present invention is a low molecular weight glue. The low molecular weight glue is a glue or gelatin a molecular weight of which is made small by decomposing a generally produced glue or gelatin with an enzyme, an acid or an alkali. The low molecular weight glue is commercially available as, for example, "PBF" (trade name) produced by Nippi Gelatin Co. in Japan and "PCRA" (trade name) produced by Peter-Cooper Co. in U.S.A. These commercially available products have weight average molecular weights (Mw) of 10,000 or less and are characterized in that jelly strength is extremely low due to the low molecular weights.

Common glue and gelatin have effects of preventing microporosity and controlling roughness of a matte side to improve a shape thereof, but they have a problem of lowering elongation characteristics. However, it has been found that by using a glue having a molecular weight which is smaller than those of commercially available common glue and gelatin, it is possible to obtain effects of preventing microporosity and controlling roughness of a matte side to improve a shape thereof without greatly impairing elongation and other characteristics.

When the high molecular weight polysaccharide and the low molecular weight glue are simultaneously added to 3-mercapto 1-propanesulfonate, elongation at high temperature is further improved and also it is possible to prevent microporosity and obtain a fine and uniform uneven surface as compared with the case of adding the high molecular weight polysaccharide or the low molecular weight glue alone.

An amount of 3-mercapto 1-propanesulfonate to be added to the electrolyte is preferably in the range of 0.05 to 5 ppm by weight, an amount of the high molecular weight polysaccharide of 0.1 to 15 ppm by weight, and an amount of the low molecular weight glue of 0.3 to 35 ppm by weight, respectively.

Further, in addition to the above organic additive, a chloride ion is added to the electrolyte. When no chloride ion exists in the electrolyte, the desired copper foil having a matte side which is low-profiled cannot be obtained. Its amount to be added may be several ppm by which the effects exhibit, but in order to produce a low-profiled copper foil in a broad current density range stably, it is preferred to keep the amount in a range of 10 to 60 ppm. Even when the amount exceeds 60 ppm, low profiling can be effected. However, the effect of low profiling is not increased significantly accompanied with increase in the amount, and when the amount is excessive, dendritic electrodeposition occurs or limiting current density is lowered. As the method of adding the chloride ion, hydrochloric acid or sodium chloride is dissolved in water and the aqueous solution is added to the electrolyte.

As described above, by adding 3-mercapto 1-propanesulfonate in combination of the high molecular weight polysaccharide and/or the low molecular weight glue and a minute amount of the chloride ion to the electrolyte, various characteristics required for a low-profiled copper foil for fine patterning can be realized at a high level.

Further, the surface roughness R_z at the matte side of the untreated copper foil of the present invention is the same or smaller thau the surface roughness R_z at the shiuy side of said untreated copper foil so that the surface treated copper foil after subjecting to bond enhancing treatment onto the matte side becomes more low-profiled one as compared with the conventional foil whereby it becomes a foil having a large etching factor.

EXAMPLES

In the following, the present invention is described in more detail by referring to Examples, but the present invention is not limited by these Examples.

Examples 1 to 4

(1) Foil preparation

Electrolytes having compositions shown in Table 1 (copper sulfate-sulfuric acid solutions before additives were added) were cleaned by passing them through activated carbon filters. Then, to the electrolytes were added sodium 3-mercapto 1-propanesulfonate, hydroxyethyl cellulose as a high molecular weight polysaccharide, a low molecular weight glue (molecular weight: 3,000) and a chloride ion so as to have concentrations shown in Table 1, respectively, whereby electrolytes for foil preparation were prepared. All of the concentrations of the chloride ion were adjusted to 30 ppm, but the present invention is not limited by this concentration. By using the electrolytes thus prepared and using a noble metal oxide-coated titanium electrode as an anode and a rotating drum made of titanium as a cathode, untreated

copper foils each having a thickness of 18 μm were prepared by electroforming preparation under electrolysis conditions shown in Table 1.

(2) Evaluation of matte side roughness and mechanical characteristics

With respect to the untreated copper foils of the respective Examples obtained in (1), surface roughnesses R_z and R_a were measured by using a surface roughness meter (SE-3C model produced by Kosaka Kenkyujo, Japan). Here, the surface roughnesses R_z and R_a are R_z and R_a defined in "Definitions and Designation of Surface Roughness" of JIS B 0601-1994. That is, R_z is a ten-point mean roughness expressed in micrometer (μm) which is the value of difference between the mean value of altitudes of peaks from the highest to the 5th, measured in the direction of vertical magnification from a straight line that is parallel to the mean line and that does not intersect the profile, and the mean value of altitudes of valleys from the deepest to the 5th, within a sampled portion, of which length corresponds to the reference length, from the profile, and R_a is a center-line mean roughness expressed in micrometer (μm) which is the value, when the roughness curve has been expressed by y=f(x), obtained from the following formula, extracting a part of measuring length l in the direction of its center-line from the roughness curve, and taking the centerline of this extracted part as X-axis and the direction of vertical magnification as Y-axis.

$$R_a = \frac{1}{l}\int_0^l |f(x)|dx$$

Incidentally, a reference length: l is 2.5 mm when the matte side is measured and 0.8 mm when the shiny side is measured. Also, elongation after holding the copper foils for 5 minutes in the longitudinal direction at room temperature and a temperature of 180° C. and also tensile strength at the respective temperatures were measured by using a tensile tester (1122 model produced by Instron Co., England), respectively. The results are shown in Table 2.

Comparative Examples 1 and 2

With respective to copper foils prepared in the same manner as in Examples except for carrying out electrolysis by using electrolytes having compositions shown in Table 1 under electrolysis conditions shown in Table 1, matte side roughness and mechanical characteristics were evaluated. The results are shown in Table 2.

TABLE 1

Examples or Comparative examples	Electrolyte compositions and electrolysis conditions: Additives MPS (ppm)	HEC (ppm)	Glue (ppm)	Thio-urea (ppm)	Cl^- (ppm)	Electrolysis conditions: Current density (A/dm^2)	Temperature (°C.)
Example 1	1.5	10.0	—	—	30	50	58
Example 2	0.5	—	3.0	—			
Example 3	0.5	3.0	6.0	—			
Example 4	1.0	5.0	5.0	—			
Comparative example 1	—	—	1.5	0.4			
Comparative example 2	—	—	4.0	—			

Electrolyte is copper sulfate/sulfuric acid solution and the concentrations are 90 g/l of copper and 110 g/l of sulfuric acid.

MPS: Sodium 3-mercapto 1-propanesulfonate

HEC: Hydroxyethyl cellulose

Glue: The low molecular weight glue (molecular weight Mw: 3,000) was used in Examples 2 to 4 and common glue (molecular weight Mw: 60,000) was used in Comparative examples 1 and 2.

TABLE 2

	Surface roughness and mechanical characteristics of untreated copper foil							
	Matte side		Shiny side		Room temperature (25° C.)		High temperature (180° C.)	
	roughness (μm)		roughness (μm)		Tensile strength	Elongation	Tensile strength	Elongation
	R_z	R_a	R_z	R_a	(kgf/mm^2)	(%)	(kgf/mm^2)	(%)
Example 1	1.3	0.30	2.0	0.40	37.2	18.1	18.6	26.7
Example 2	2.1	0.32	2.1	0.35	33.6	11.7	19.5	19.7
Example 3	1.1	0.20	1.8	0.35	35.3	19.8	19.0	24.6
Example 4	0.6	0.14	1.4	0.23	33.8	14.4	18.7	25.8
Comparative example 1	3.3	0.40	2.0	0.37	36.8	9.0	20.3	8.0
Comparative example 2	4.8	0.70	2.1	0.32	33.7	9.5	20.5	2.0

In Example 1 in which sodium 3- mercapto 1-propanesulfonate and hydroxyethyl cellulose were added and in Example 2 in which sodium 3-mercapto 1-propanesulfonate and the low molecular weight glue were added, matte side roughnesses (surface roughnesses at matte sides) are sufficiently small, and high temperature elongation characteristics are excellent.

In Examples 3 and 4 in which hydroxyethyl cellulose and the low molecular weight glue were added to sodium 3-mercapto 1-propanesulfonate, matte side roughnesses become smaller as compared with those of Examples 1 and 2.

To the contrary, in Comparative example 1 in which thiourea and glue were added, whereas the roughness of the matte side becomes small as compared with the conventional untreated copper foil, it is rougher than the untreated copper foil of the present invention and only an untreated copper foil having a matte side with a larger roughness than that of the shiny side is obtained. Also, in the case of the untreated copper foil, high temperature elongation is small.

In Comparative example 2, characteristics of an electrodeposited copper foil prepared by using common glue are shown for reference as Prior art copper foil example.

Next, bond enhancing treatment was carried out onto the matte sides of the untreated copper foils shown in Examples 1 to 4 and Comparative examples 1 and 2, respectively. Also, the same bond enhancing treatment was carried out onto the shiny side of the untreated copper foil shown in Comparative example 2. Bath composition and conditions for the treatment are as mentioned below. After the bond enhancing treatment, stain proofing was further carried out to the foil to prepare a treated copper foil. The surface roughness of the copper foil was measured by using a surface roughness meter (SE-3C model produced by Kosaka Kenkyujo, Japan). The results are shown in Table 3. In Table 3, Examples 1 to 4 and Comparative examples 1 and 2 each correspond to copper foils in which untreated copper foils of Examples 1 to 4 and Comparative examples 1 and 2 in Table 2 are subjected to bond enhancing treatment onto their matte sides, respectively, and Comparative example 3 in Table 3 is a foil in which the untreated copper foil of Comparative example 2 in Table 2 is subjected to bond enhancing treatment onto its shiny side.

1. Copper plating conditions of First layer

Bath composition	
Metal copper	20 g/l
Sulfuric acid	100 g/l
Bath temperature	25 °C.
Current density	30 A/dm^2
Plating time	10 seconds

2. Copper plating conditions of Second layer

Bath composition	
Metal copper	60 g/l
Sulfuric acid	100 g/l
Bath temperature	60 °C.
Current density	15 A/dm^2
Plating time	10 seconds

The resulting copper foils are each laminated to one surface of a glass epoxy resin FR-4 (trade name) substrate to prepare copper-clad laminated boards, respectively. Further, evaluation of etching property was carried out by the following "evaluation method".

Evaluation Method

Evaluation of the etching property was carried out by the following method. That is, after washing the surface of each copper-clad laminated board, a liquid resist was uniformly coated with a thickness of 5 μm on said surface and dried. Next, a circuit pattern for testing was placed on the resist and ultraviolet ray was irradiated with 200 mJ/cm^2 by using an exposure machine. The test pattern comprises ten parallel lines with a line width of 100 μm, a space width of 100 μm and a length of 5 cm. Immediately after irradiation, development, washing and drying were carried out.

Thus, to the respective copper-clad laminated boards in which a circuit was formed by the resist, etching was carried out by using an etching evaluation device. The etching evaluation device is to inject an etching solution to the vertically standing copper-clad laminated board sample from a right angle direction with a single nozzle. As the etching solution, a solution in which ferric chloride and hydrochloric acid were mixed ($FeCl_3$: 2 mole/l, HCl: 0.5

mole/l) was used. Etching was carried out at a solution temperature of 50° C., an injection pressure of 0.16 MPa, a solution flow amount of 1 l/min and a distance of the sample and the nozzle of 15 cm. An injection time was made 55 seconds. Immediately after injection, washing was carried out and the resist was removed by using acetone to obtain a printed circuit pattern.

To the resulting respective printed circuit patterns, an etching factor at a bottom width of 70 μm was measured. At the same time, peeling strength (peeling resistance) was also measured. The results are shown in Table 3.

TABLE 3

Examples or Comparative examples	Surface roughness and etching property after bond enhancing treatment: Roughness of bond enhancing treated surface (μm) R_z	R_a	Etching factor	Peeling strength* (kgf/cm)
Example 1	1.8	0.3	3.9	1.14
Example 2	2.2	0.5	3.8	1.17
Example 3	1.6	0.3	3.9	1.16
Example 4	1.1	0.3	4.1	1.13
Comparative example 1	3.7	0.5	3.2	1.06
Comparative example 2	7.3	1.1	2.3	1.64
Comparative example 3	4.6	0.7	3.5	1.13

*measured by using FR-4 substrate.

When a etching factor value is large, etching characteristics can be judged to be good. As can be seen from Table 3, the etching factors of Examples 1 to 4 are markedly larger than those of Comparative examples 1 to 3.

In Comparative examples 1 and 2, roughnesses of the matte sides of the untreated copper foils are large as compared with those of Examples 1 to 4 so that roughnesses after bond enhancing treatment are large whereby etching factors are not good. Incidentally, the roughness of the matte side of the untreated copper foil of Example 2 and that of the shiny side of the uutreated copper foil of Comparative example **3** are substantially the same. However, although these foils are treated under the same conditions, the surface roughness after bond enhancing treatment of Example 2 is smaller than that of Comparative example 3 which is a conventional example. The reason of the above can be considered that, since the shiny side is a surface directly contacted with a titanium drum, a flaw in the drum is transferred as such and when the bond enhancing treatment is carried out thereon, roughened copper grains become likely rough and large and finally the surface roughness after the bond enhancing treatment becomes large. On the other hand, the matte side of the copper foil according to the present invention is extremely dense due to mirror surface-state electrodeposition, and when a bond enhancing treatment is carried out thereon, roughened copper grains become finer and the surface roughness after the bond enhancing treatment becomes finally smaller. This is more remarkable in Examples 1, 3 and 4 where each of the surface roughness of a matte side of the untreated copper foil is further small, whereby their roughnesses of the surfaces subjected to bond enhancing treatment become extremely small and etching factors thereof are large. The reason why the peeling strengths of Examples 1 to 4 are substantially the same as that of Comparative example 3 irrespective of having extremely small roughness of the treated surface can be considered that roughened copper grains become finer by the bond enhancing treatment so that the surface area becomes large whereby peeling strength becomes large in spite of small roughness.

Although the value of the etching factor of Comparative example 3 shows a value closer to that of Examples 1 to 4, it is inferior to Examples 1 to 4 in terms of the traces left behind at the time of etching because the roughness of the roughening treatment is larger in Comparative example 3 than it is in the case of Examples 1 to 4.

As described above, according to the present invention, low profiling of an electrodeposited copper foil can be realized easily, and also an electrodeposited copper foil having excellent elongations at room temperature and high temperature and also high tensile strength can be obtained. The electrodeposited copper foil thus obtained can be used suitably as an inner or outer layer copper foil for a high density printed-wiring board and further as an electrodeposited copper foil for a flexible substrate because of improvement in flexibility.

Further, as compared with a conventional untreated copper foil, both surfaces of the untreated copper foil obtained by the present invention are flat, whereby the foil obtained by the present invention can be used as an electrode for a secondary battery, a flat cable, a material for electric cable-covering and shielding material or the like.

We claim:

1. An electroplated copper foil formed by electrodeposition of copper onto a drum and which comprises a copper foil having a shiny side formed in contact with the drum and a matte side wherein, without surface treatment, said matte side has a surface roughness Rz measured by JIS B 0601-1994 substantially the same as or less than that of the shiny side formed as a result of the electrodeposition of the copper foil using an electrolyte containing 0.05 to 5 ppm by weight 3-mercapto 1-propanesulfonate; at least one organic compound selected from the group consisting of 0.1 to 15 ppm by weight of a polysaccharide which is a carbohydrate selected from the group consisting of starches, celluloses and vegetable rubbers, and 0.3 to 35 ppm by weight of a low molecular weight glue having a weight average molecular weight of 10,000 or less; and 10 to 60 ppm of a chloride ion.

2. The foil according to claim **1**, wherein the 3-mercapto 1-propanesulfonate is sodium 3-mercapto 1-propanesulfonate.

3. The foil according to claim **1**, wherein the organic compound is the polysaccharide.

4. The foil according to claim **1**, wherein the organic compound is the low molecular weight glue having the weight average molecular weight of 10,000 or less.

5. The foil according to claim **1**, wherein the organic compound is a mixture of the polysaccharide and the low molecular weight glue having a weight average molecular weight of 10,000 or less.

6. The foil according to claim **1**, wherein the foil is subjected to a surface bond enhancing treatment.

7. The foil according to claim **6**, wherein the surface bond enhancing treatment is carried out by electrodeposition.

8. A copper-clad laminated board comprising an electrodeposited copper foil according to claim **1**.

9. A printed circuit board comprising an electrodeposited copper foil according to claim **1**.

10. A secondary battery cell including a component comprising an electrodeposited copper foil according to claim **1**.

11. An improved method for electrolytically producing a copper foil formed by electrodeposition of copper onto a

drum, the copper foil having a shiny side formed in contact with the drum and a matte side, the improvement wherein the method produces a copper foil wherein, without treatment, the matte side has a surface roughness Rz measured by JIS B 0601-1994 substantially the same as or less than that of the shiny side, said method comprising carrying out electrolysis with an electrolyte comprising 0.05 to 5 ppm by weight 3-mercapto 1-propanesulfonate; at least one organic compound selected from the group consisting of 0.1 to 15 ppm by weight of a polysaccharide which is a carbohydrate selected from the group consisting of starches, celluloses and vegetable rubbers, and 0.3 to 35 ppm by weight of a low molecular weight glue having a weight average molecular weight of 10,000 or less; and 10 to 60 ppm of a chloride ion.

12. The method according to claim **11**, wherein the 3-mercapto 1-propanesulfonate is sodium 3-mercapto 1-propanesulfonate.

13. The method according to claim **11**, wherein the organic compound is the polysaccharide.

14. The method according to claim **11**, wherein the organic compound is the low molecular weight glue having the weight average molecular weight of 10,000 or less.

15. The method according to claim **11**, wherein the organic compound is a mixture of the polysaccharide and the low molecular weight glue having a weight average molecular weight of 10,000 or less.

* * * * *

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(54)【発明の名称】　ファインパターン用電解銅箔とその製造方法

(57)【要約】

【課題】　本発明は、引き剥し強さを低下させることなく、高いエッチングファクターを持ち、配線パターンの根元に銅粒子が残ることなく、ファインパターンを達成できる銅箔であると共に大きな高温伸び率及び高い引張り強さを有する銅箔を提供することを目的とする。

【解決手段】　本発明は、電解銅箔であって、未処理銅箔の析出面の表面粗度R_zが該未処理銅箔の光沢面の表面粗度R_zと同じか、それより小さい箔の析出面上に粗化処理を施したことを特徴とする。

【特許請求の範囲】
【請求項１】　未処理銅箔の析出面の表面粗度R_zが該未処理銅箔の光沢面の表面粗度R_zと同じか、それより小さい箔の析出面上に粗化処理を施したことを特徴とする電解銅箔。
【請求項２】　電解銅箔の製造方法であって、未処理銅箔の製造を、メルカプト基を持つ化合物並びにそれ以外の少なくとも１種以上の有機化合物及び塩化物イオンを添加した電解液を用いた電解にて行うことを特徴とする方法。
【請求項３】　前記のメルカプト基を持つ化合物が３－メルカプト１－プロパンスルホン酸塩である請求項２に記載の方法。
【請求項４】　前記の有機化合物が高分子多糖類である請求項３に記載の方法。
【請求項５】　前記の有機化合物が低分子量膠である請求項３に記載の方法。
【請求項６】　前記の有機化合物が高分子多糖類及び低分子量膠である請求項３に記載の方法。

【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、ファインパターン化が可能な電解銅箔、すなわち高いエッチングファクターが得られる電解銅箔、この電解銅箔を使用した銅張積層板並びにプリント配線板に関する。また、本発明による未処理銅箔は、従来に比べ両面がフラットなため、二次電池用電極やフラットケーブル、電線被覆シールド材等にも使用可能である。しかし、本発明による電解銅箔はこれらに限られるものではない。
【０００２】
【従来の技術】プリント回路用電解銅箔は、工業的には硫酸銅水溶液の電解液を、鉛や白金族を被覆したチタン電極などの不溶性電極と、これに対向して設けられたステンレスやチタン製の陰極回転ドラムの隙間に満たしてこれら電極に通電し、陰極回転ドラムの上に銅を析出させ、これを連続的に巻取ることにより製造されている。
【０００３】一般に銅イオンと硫酸イオンだけを含む水溶液を電解液として用いると、設備上混入が避けられないゴミや油類によって銅箔にピンホールやマイクロポロシティーが発生して実用上重大な欠陥となったり、該銅箔の電解液と接する側の面（粗面）が持つ山谷の形状が崩れてしまい、後にこの銅箔を絶縁基板材料と接合する際に十分な強度が得られなかったり、該粗面の粗さが大きい場合には多層プリント配線板の層間絶縁抵抗や回路導電率が低下したり、基板材料に接合後のパターンエッチング時に基板への残銅現象或いは回路部のアンダーカット現象を引き起こし、回路基板として種々の性能を劣化させてしまうという問題を生じる。
【０００４】このピンホール等の防止のため電解液に塩化物イオンを添加したり、電解液を活性炭等を含むフィルターに通してゴミや油類を除去している。またマイクロポロシティー防止及び粗面の山谷形状を整えるために、古くから膠を電解液に添加する事が行われており、膠以外にも種々の有機物や無機物を添加剤として用いることが提案されてきた。プリント配線板用電解銅箔の製造技術は銅塩を含む溶液に電極を設け、これに通電して、カソードに銅を析出させるという点から分かるように、めっき技術を基礎としており、プリント配線板用電解銅箔製造用の添加剤としては銅めっき用添加剤を転用出来る場合が多い。膠、チオ尿素、糖蜜などは古くから銅めっき用の光沢剤として知られており、このことから電解液にこれら添加剤を添加した場合にはいわゆる光沢作用、プリント配線板用電解銅箔に関しては粗面の粗さを小さくする効果の発現が期待出来、米国特許５，１７１，４１７号明細書には、チオ尿素などの活性イオウを添加剤として用いた電解銅箔の製造方法が開示されている。しかしながら、プリント配線板用電解銅箔は、生産性の向上などを目的として、通常のめっきより高い電流密度で生産されている点や、近年プリント配線板用電解銅箔に要求される性能が著しく高度になったこと、特に伸びなどの機械的性能を損なうことなく、粗面の粗さを低く抑えた銅箔に対する要求が強くなったことなどから、これらめっき用の添加剤をそのままプリント配線板用電解銅箔の添加剤として使用しても満足できる特性が得られないのが現状である。
【０００５】一方、近年、半導体、集積回路をはじめとした電子回路技術の発達はめざましく、当然のことながら、その部品の形成部あるいは搭載部であるプリント配線板においても尚一層の技術革新が求められている。プリント配線板の高多層化、ファインパターン化の要求等がそれである。
【０００６】これらの要求を満足させるためにプリント配線板用電解銅箔に求められる性能は、層間及びパターン間の絶縁性、エッチング時のアンダーカット防止のための粗面（析出面。以下、同様）のローブロファイル化（粗さの低下）及び熱応力によるクラック防止のための高温伸び特性の向上、さらにはプリント配線板の寸法安定性のための高い引張り強さが求められている。特にファインパターン化のための更なるローブロファイル化の要求が強い。
【０００７】粗面のローブロファイル化は、例えば前述の様に膠やチオ尿素を多量に電解液に添加すれば達成されるが、反面、その添加量の増加に伴って常温伸び率、高温伸び率とも急激に低下してしまう。一方、添加剤を添加しない電解液から得られる銅箔は、常温伸び率、高温伸び率ともに非常に高いものになるが、粗面の形状が乱れ、粗さが大きくなったり、高い引張り強さを維持出来なくなり、さらにはこれら性能が安定したものを製造すると言った点では無理がある。電解電流密度を低く抑えた場合、高電流密度での電解箔に比べ、粗面の粗さは

低くなり、伸び率や引張り強さも向上するが、生産性の低下は経済上好ましくない。

【０００８】このように、近年のプリント配線板用電解銅箔に要求される、更なるローブロファイル化、良好な常温伸び率、高温伸び率及び高い引張り強さを実現することは容易ではない。

【０００９】従来の電解銅箔がファインパターン化できない理由の大きな要因として、表面粗さが粗いことをあげることができる。電解銅箔は、通常、図１に示すような電解製箔装置により製箔された銅箔に、図２に示す表面処理装置により密着性向上のための粗化処理、防錆処理を施して製造される。電解製箔装置は回転するドラム状のカソード（表面はＳＵＳ又はチタン製）２と該カソードに対して同心円状に配置されたアノード１（鉛又は貴金属酸化物被覆チタン電極）からなる装置に、電解液３を流通させつつ両極間に電流を流して、該カソード表面に所定の厚さに銅を析出させ、その後該カソード表面から銅をはぎ取る。この段階の箔を未処理銅箔という。

【００１０】この後、銅張積層板に必要とされる性能を付与するため、図２に示すような表面処理装置に未処理銅箔４を通し、電気化学的あるいは化学的な表面処理を連続的に行う。この処理のうち、絶縁樹脂基板と接着させるときの密着性を高めるために、粒状の銅を析出させる工程がある。これを粗化処理と呼んでいる。これらの表面処理した後の銅箔を表面処理銅箔８と呼び、銅張積層板に使用される。

【００１１】電解銅箔の機械的性能は未処理銅箔４の性能によって決定されるが、銅箔のエッチング特性、すなわちエッチング速度と均一溶解性も、この未処理銅箔の性能によって多くが決定される。

【００１２】銅箔の性能でエッチング性に大きな影響のある要因は表面の粗さである。粗化処理を施して絶縁樹脂基板と接着する面の粗さの影響が大きい。銅箔の粗さに影響する要因には大きく分けて２つある。ひとつは未処理銅箔の表面粗さであり、もうひとつは粗化処理の粒状の銅の付き方である。元箔である未処理銅箔の表面粗さが粗いと粗化処理後の銅箔の粗さは粗くなる。また、一般的に粒状の銅の付着量が多いと粗化処理後の銅箔の粗さは粗くなる。粗化処理時の粒状の銅の付着量は処理時に流す電流により調節が可能であるが、未処理銅箔の表面粗さは、前述のドラム状のカソードに銅を析出させる時の電解条件、特に電解液に加える添加剤によって決まるところが大きい。

【００１３】一般的には、未処理箔は光沢面と呼ぶドラムに接触していた側の面は比較的平滑であるが、逆の面である粗面は凹凸を有する。粗面を平滑化するために、過去幾つかの試みがなされている。例えば前述の米国特許第５，１７１，４１７号の明細書に開示された、チオ尿素などの活性イオウを添加剤として用いた電解銅箔の製造方法がそれである。しかし、この場合は従来のニカワ等の添加剤を用いた場合に比較して粗面は平滑化されるが、光沢面に比較すると未だ粗く、効果は完全ではない。

【００１４】また、光沢面は比較的平滑であることから、特開平６－２７０３３１号公報に開示されているように、光沢面側に粒状の銅を付着させ樹脂基板と接着させる試みもなされている。しかしこの場合は、回路のエッチング時に、通常の粗面側にドライフィルムやレジストをはらなければならず、表面の凹凸のために銅箔との接着力が低くなり、剥離しやすいという欠点がある。

【００１５】

【発明が解決しようとする課題】本発明はこのような従来技術の問題点を解消すべくなされたものであり、引き剥し強さを低下させることなく、高いエッチングファクターを持ち、配線パターンの根元に銅粒子が残ることなく、ファインパターンを達成できる銅箔であると共に大きな高温伸び率及び高い引張り強さを有する銅箔を提供するものである。ここで、ファインパターン化の尺度は、一般的には図３に示すエッチングファクター（＝２Ｔ／（Ｗｂ－Ｗｔ）によってあらわすことができる。この値が大きいほど回路断面はシャープな形状となる。

【００１６】

【課題を解決するための手段】本発明は、電解銅箔であって、未処理銅箔の析出面の表面粗度R_zが該未処理銅箔の光沢面の表面粗度R_zと同じか、それより小さい箔の析出面上に粗化処理を施したことを特徴とする。ここで、表面粗度R_zとは、ＪＩＳ　Ｂ　０６０１$^{-1994}$「表面粗さの定義と表示」の５．１十点平均粗さ（R_z）の定義に規定されたR_zをいう。前記の未処理銅箔は、メルカプト基を持つ化合物並びにそれ以外の少なくとも１種以上の有機化合物及び塩化物イオンを添加した電解液を用いた電解にて得ることができる。

【００１７】本発明における、組み合わせのベースとなる添加剤は、３－メルカプト１－プロパンスルホン酸塩である。３－メルカプト１－プロパンスルホン酸塩は、ＨＳ（CH_2）$_3$ ＳＯ$_3$ Ｎａ等で代表して示される化合物である。この化合物は、単独では銅の結晶を微細化する効果はそれほどないが、他の有機化合物と組み合わせて用いることにより、銅の結晶を微細化し、凹凸の少ないめっき表面を得ることができる。その詳しい作用機構は不明であるが、当該分子が硫酸銅電解液中の銅イオンと反応し、錯体となる事により、あるいはめっき界面に作用して過電圧を上昇させる事によって、銅の結晶を微細化し、凸凹の少ないめっき面の形成を可能ならしめるのではないかと推定される。

【００１８】組み合わせる有機化合物の一つ目は、高分子多糖類である。高分子多糖類とは、デンプン、セルロース、植物ゴムなどの炭水化物であり、一般に水中でコロイドとなる。工業的に安価に製造されているものとして、デンプンでは食用デンプン、工業用デンプン、デキ

ストリン、セルロースとしては特開平２－１８２８９０号公報に開示されているような水溶性セルロースエーテル、すなわち、カルボキシメチルセルロースナトリウム、カルボキシメチルヒドロキシエチルセルロースエーテルなどがある。植物ゴムとしてはアラビアゴムやトラカンドゴムがある。

【００１９】これらの有機化合物は、３－メルカプト１－プロパンスルホン酸塩と組み合わせることにより、銅の結晶を微細化し、凹凸のないめっき面を得ることができるが、結晶の微細化に加えて、これらの有機化合物には、製造された銅箔の脆化を防止する働きがある。これらの有機化合物は銅箔に蓄積される内部応力を緩和するため、陰極ドラムから巻き取られる際の破れや銅箔が丸まってしまう現象を防止するばかりでなく、常温及び高温の伸び率も改善する。

【００２０】本発明における組み合わせにかかるもう一つの有機化合物は、低分子量膠である。低分子量膠とは一般に製造されている膠、ゼラチンを酵素や酸もしくはアルカリで分解し、その分子量を小さくしたものである。例えばニッピゼラチン社製の“ＰＢＦ”や米国Ｐｅｔｅｒ－Ｃｏｏｐｅｒ社製の“ＰＣＲＡ”として市販されている。これらの分子量は１万以下で、低分子量のためゼリー強度が著しく低いのが特徴である。

【００２１】通常の膠やゼラチンは、マイクロポロシティーの防止や粗面の粗さを抑え形状を整える効果があるが、伸び特性を低下させるという弊害がある。しかしながら通常の膠やゼラチンとして市販されているものよりも分子量の小さい膠を使用すれば、伸び特性などを大きく犠牲にせず、マイクロポロシティーの防止や粗面の粗さを抑え形状を整える効果があることが分かった。尚、３－メルカプト１－プロパンスルホン酸塩に高分子多糖類と低分子量膠を同時に加えると、それぞれを単独で加えるよりも、高温の伸び率が改善されるとともに、マイクロポロシティーの防止や細かな均一な凸凹面を得ることが可能である。

【００２２】更に、上記の有機添加剤に加え塩化物イオンを電解液に添加する。電解液中に塩化物イオンがまったく存在しないと、所望される粗面がローブプロファイル化された銅箔を得ることができないからである。その添加量としては、数ｐｐｍで効果が出てくるが、広い電流密度範囲で安定してローブプロファイル銅箔を製造するためには、１０～６０ｐｐｍの範囲に保つことが好ましい。６０ｐｐｍを越える添加量でもローブプロファイル化されるが、添加量を増加したほどにはその効果に著しい増進が認められず、逆に添加量が過剰になると、樹枝状の電析が起こったり限界電流密度が低下するので好ましくない。

【００２３】以上述べた通り、電解液に３－メルカプト１－プロパンスルホン酸塩と高分子多糖類及び／又は低分子量膠と微量の塩化物イオンを併用添加することにより、ファインパターン化のためのローブプロファイル銅箔に求められる種々の特性を高いレベルで実現させることが可能となった。さらには、本発明による未処理銅箔の析出面の表面粗度R_zは該未処理銅箔の光沢面の表面粗度R_zと同程度か、それより小さい箔となるため、析出面上に粗化処理を施した後の表面処理銅箔は従来のものに比較して更にローブプロファイルとなり、大きなエッチングファクターを持った箔となる。

【００２４】

【発明の実施の形態】以下に本発明を実施例に基づいて更に詳しく説明するが、本発明はこれらに限定されるものではない。

【００２５】実施例１～５

（１）製箔

表１に示す組成の電解液（添加剤を添加する前の硫酸銅－硫酸溶液）を、活性炭フィルターに通して清浄処理した。ついで、この電解液に３－メルカプト１－プロパンスルホン酸ナトリウムと、高分子多糖類としてヒドロキシエチルセルロース及び低分子量膠（分子量３，０００）と、塩化物イオンを表１に示す濃度となるように、それぞれ添加して製箔用電解液を調製した。尚、塩化物イオン濃度を全て３０ｐｐｍに調整したが、本発明はこの濃度に限定されるものではない。このようにして調製した電解液を用い、アノードには貴金属酸化物被覆チタン電極、陰極にはチタン製回転ドラムを用いて表１に示す電解条件の下に、１８μm厚みの　未処理銅箔を電解製箔によって製造した。

【００２６】（２）粗面粗さ及び機械的特性の評価

（１）で得られた各実施例の未処理銅箔の表面粗さR_z、R_aを表面粗さ計（小坂研究所製ＳＥ－３Ｃ型）を用いて測定した（ここで、表面粗さR_z、R_aとは、ＪＩＳ　Ｂ　０６０１$^{-1994}$「表面粗さの定義と表示」に規定されたR_z、R_aである。尚、基準長さ：ｌは、粗面測定時２．５㎜、光沢面測定時０．８㎜である）。そして幅方向の常温での、及び１８０℃の温度における５分間保持後での伸び率並びに各々の温度での引張り強さを引張り試験機（インストロン社製１１２２型）を用いて、それぞれ測定した。結果を、表２に示す。

【００２７】比較例１～２

表１に示す組成の電解液及び電解条件の下に電解した以外、実施例と同様に製箔して得られた銅箔の表面粗さ及び機械的特性を評価した。結果を表２に示す。

【００２８】

【表１】

表１　電解液組成と電解条件

実施例又は比較例	添加剤					電解条件	
	MPS (ppm)	HEC (ppm)	膠 (ppm)	チオ尿素 (ppm)	Cl^- (ppm)	電流密度 (A/dm^2)	液温 (℃)
実施例１	1.5	10.0	-	-	30	50	58
実施例２	0.5	-	3.0	-			
実施例３	0.8	3.0	6.0	-			
実施例４	1.0	5.0	5.0	-			
比較例１	-	-	1.5	0.4			
比較例２	-	-	4.0	-			

電解液は、硫酸銅／硫酸溶液。その濃度は、銅：90g/l,硫酸：110g/l

ＭＰＳ：３－メルカプト１－プロパンスルホン酸ナトリウム

ＨＥＣ：ヒドロキシエチルセルロース

膠：実施例２～４は、低分子量膠（分子量３，０００）

比較例１～２は、通常の膠（分子量６０，０００）

【００２９】　　【表２】

表２　未処理銅箔の表面粗さ及び機械特性

実施例又は比較例	粗面粗さ (μm)		光沢面粗さ (μm)		常温		高温(180℃)	
	R_z	R_a	R_z	R_a	引張り強さ (kgf/mm^2)	伸び (%)	引張り強さ (kgf/mm^2)	伸び (%)
実施例１	1.3	0.30	2.0	0.40	37.2	18.1	18.6	26.7
実施例２	2.1	0.32	2.1	0.35	33.6	11.7	19.5	19.7
実施例３	1.1	0.20	1.8	0.35	35.3	19.8	19.0	24.6
実施例４	0.6	0.14	1.4	0.23	33.8	14.4	18.7	25.8
比較例１	3.3	0.40	2.0	0.37	36.8	9.0	20.3	8.0
比較例２	4.8	0.70	2.1	0.32	33.7	9.5	20.5	2.0

【００３０】３－メルカプト１－プロパンスルホン酸ナトリウム及びヒドロキシエチルセルロースを添加した実施例１、３－メルカプト１－プロパンスルホン酸ナトリウム及び低分子量膠を添加した実施例２では、粗面粗さ（粗面の表面粗さ）は充分に小さく、高温伸び特性が優れている。３－メルカプト１－プロパンスルホン酸ナトリウムにヒドロキシエチルセルロースと低分子量膠を添加した実施例３及び実施例４では、実施例２及び３に比較してさらに粗面粗さが小さくなっている。

【００３１】これに対して、チオ尿素と通常膠を加えた比較例１では、従来の未処理銅箔に比較すると粗面の粗さは小さくなるが本発明の未処理銅箔に比較すると粗く、光沢面に比較して大きな粗度の粗面を持つ未処理銅箔しか得ることができない。しかも、この未処理銅箔の場合、高温伸びが小さい。尚、比較例２には、従来の銅の例として通常膠を用いて製箔した未処理銅の性能を参考までに示した。

【００３２】次いで、実施例１～４及び比較例１～２に示した未処理銅箔の粗面に粗化処理を行った。また比較例２に示した未処理箔の光沢面に同様な粗化処理を行った。粗化のための浴組成と条件は下記の通りである。粗化処理後、更に防錆処理を施して表面処理銅箔を製造した。この銅箔の表面粗さを表面粗さ計（小坂研究所製ＳＥ－３Ｃ型）を用いて測定した。結果を表３に示した。尚、表３において、実施例１～４及び比較例１～２は、それぞれ表２の実施例１～４及び比較例１～２の未処理銅箔の粗面に粗化処理を行ったものであり、比較例３は表２の比較例２の未処理銅箔の光沢面に粗化処理を行っ

たものである。

【００３３】

１．第１層目の銅めっき条件

浴組成	金属銅	２０g/l
	硫酸	１００g/l
	浴温度	２５℃
	電流密度	３０A/dm^2
	処理時間	１０秒

【００３４】

２．第２層目の銅めっき条件

浴組成	金属銅	６０g/l
	硫酸	１００g/l
	浴温度	６０℃
	電流密度	１５A/dm^2
	処理時間	１０秒

【００３５】得られた銅箔をガラスエポキシ樹脂ＦＲ－４基板の片面に熱融着して銅張積層板を作成した。更に、下記の「評価法」によりエッチング性の評価を行った。

【００３６】評価法

エッチング特性の評価は次に示す方法で行った。各銅張積層板表面を洗浄後、該表面に液レジストを５μm の厚みで均一に塗布して乾燥した。次にレジストに試験用回路パターンを重ね、露光機を用いて２００mJ/cm^{2}で紫外線照射した。テストパターンは線幅１００μm 、線間１００μm 、長さ５cmの平行直線を１０本並べたものである。照射後直ちに現像し、水洗、乾燥した。

【００３７】このように、レジストによる回路が形成された各銅張積層板のそれぞれに対し、エッチング評価装置によりエッチングした。エッチング評価装置は単ノズルで、垂直に立てた試料の銅張積層板に対して直角方向からエッチング液を噴射するものである。エッチング液には塩化第二鉄と塩酸を混合した液($FeCl_3$:2mol/l,HCl:0.5mol/l) を使用し、液温５０℃、噴射圧０．１６MPa 、液流量１l/min 、試料とノズルの距離１５cmにて行った。噴射時間は５５秒とした。噴射後直ちに水洗し、アセトンにてレジストを剥離してプリント回路パターンを得た。

【００３８】得られた各々のプリント回路パターンに対し、ボトム幅７０μm の時のエッチングファクターを測定した。また同時に引き剥し強さも測定した。その結果を表３に示す。エッチングファクター値が大きいほどエッチング特性が良好と判断できるが、実施例１～４は比較例１～３よりもエッチングファクターが格段に大きい。

【００３９】比較例１～２は、実施例１～４に比し未処理銅箔の粗面の粗度が大きいため、粗化処理後の粗度も大きくエッチングファクターは良くない。これに対し実施例２の未処理銅箔の粗面と、比較例３の未処理銅箔の光沢面の粗度はほぼ等しい。しかし、同条件で処理したにもかかわらず粗化処理後の表面粗度は実施例２の方が小さく、従来例２の方が大きい。これは、光沢面の場合は、チタンドラムに接していた面であるため、ドラムの傷がそのまま転写されており、そのうえに粗化処理がなされると粗化の銅粒が粗大化しやすく最終的に粗化処理後の表面粗度は大きくなってしまう、一方、本発明による銅箔の粗面は鏡面状態の電析で非常に緻密であるため、その上に粗化処理がなされると粗化の銅粒が微細化し、最終的に粗化処理後の表面粗度は小さくなるものと思われる。これは未処理銅箔の粗面の表面粗度がさらに小さい実施例１、実施例３及び実施例４の場合さらに顕著になり、粗化処理面の粗さは非常に小さくなり、エッチングファクターも大きくなっている。粗化処理面の粗さが非常に小さいにもかかわらず比較例３と同程度の引き剥し強さとなるのは、粗化処理において粗化の銅粒が微細化する結果、表面積が大きくなり、粗さが小さいにもかかわらず引き剥し強さが大きくなるからと考えられる。尚、比較例３は、粗化処理面の粗さが実施例１～４のそれに比較して大きくなるため、エッチングファクターの値では比較例１～２のそれより実施例１～４のそれに近い値を示すが、エッチング時の足残りの点で実施例１～４に比べて劣る（高温伸びが良くないという理由ではなく、上記の理由で劣る）。

【００４０】

【表３】

表３　粗化処理後の表面粗さ及びエッチング性

実施例又は比較例	粗化処理面粗さ（μm）		エッチングファクター	引き剥し強さ※（kgf/cm）
	R_z	R_a		
実施例１	1.8	0.3	3.9	1.14
実施例２	2.2	0.5	3.8	1.17
実施例３	1.6	0.3	3.9	1.16
実施例４	1.1	0.3	4.1	1.13
比較例１	3.7	0.5	3.2	1.06
比較例２	7.3	1.1	2.3	1.64
比較例３	4.6	0.7	3.5	1.13

※ＦＲ－４基材にて測定

【００４１】

【発明の効果】上述の通り、本発明によれば、電解銅箔のローブロファイル化を容易に実現でき、しかも常温及び高温における伸び率が優れ、かつ高い引張り強さを有する電解銅箔を得ることができる。このようにして得られる電解銅箔は、高密度プリント配線板用の内外層銅箔に、更には耐折性の向上からフレキシブル基板用電解銅箔にも適用することができるものである。また、従来の未処理銅箔に比し両面がフラットなため、本発明により得られる未処理銅箔は、二次電池用電極やフラットケーブル、電線被覆シールド材等にも使用することが可能である。

【図面の簡単な説明】

【図１】電解製箔装置の構造を示す断面図である。

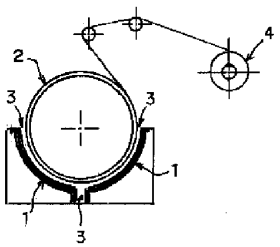
【図２】表面処理装置の構成を示す断面図である。

【図３】エッチングファクターの求め方を示す模式図である。

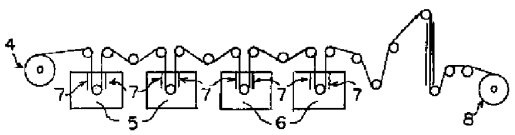
【符号の説明】

Ａ　銅箔の断面
Ｂ　絶縁板
Ｗｔ　銅箔断面のトップ幅
Ｗｂ　銅箔断面のボトム幅
Ｔ　銅箔の厚さ
１　電解製箔装置のアノード
２　電解製箔装置のカソード
３　電解製箔装置の電解液
４　未処理銅箔
５　表面処理装置の電解液
６　表面処理装置の電解液
７　表面処理装置のアノード
８　表面処理銅箔

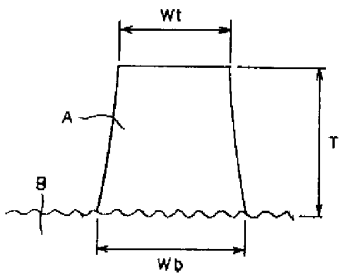
【図１】



【図２】



【図３】



フロントページの続き

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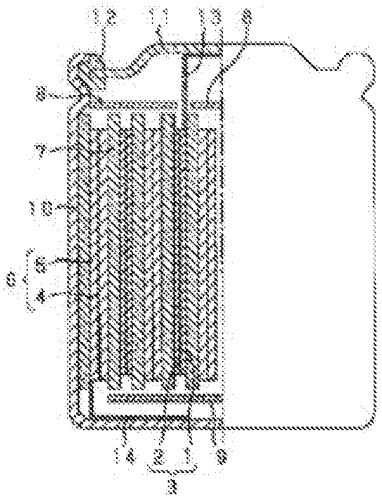
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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery, wherein a collector can be sufficiently deformed along an active material surface, the contact between an active material and the collector can be properly kept, excellent in a charging/discharging cycle, and inexpensive.

SOLUTION: Negative electrodes 6, consisting of an electrode constituting material layer 5, are provided on both surfaces of plane-like collectors 4 of the negative electrodes 6 are composed of electrolyte metallic foil formed of the electrolyte deposit of metal. In the electrolyte metallic foil, the surface roughness of one side main surface is smaller than 3.0μm in terms of a mean roughness of 10 points, and the difference of the surface roughness, between this and the other side main surfaces is smaller than 2.5μm in terms of a mean roughness of 10 points.



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Ｈ０１Ｍ	4/66			Ｈ０１Ｍ	4/66	Ａ	
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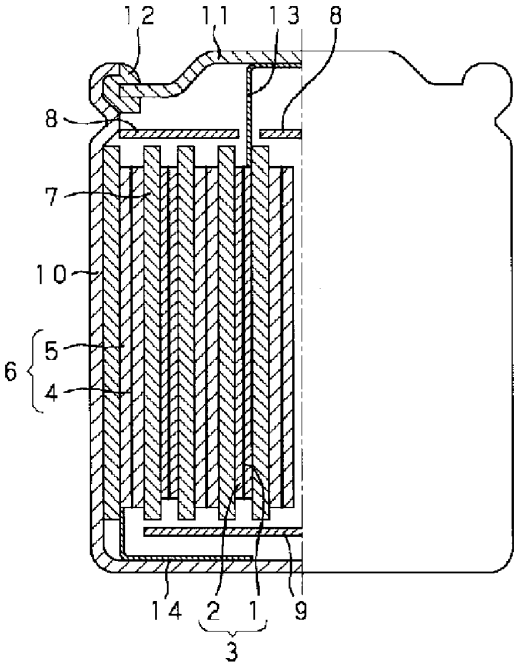
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(54)【発明の名称】　非水電解液二次電池

(57)【要約】

【課題】　活物質表面に沿って集電体が十分に変形し、活物質と集電体の接触性を良好に保って、充放電サイクルに優れた安価な非水電解液二次電池の提供する。

【解決手段】　平面状集電体４の両面に電極構成物質層５が形成されてなる負極６を備え、上記負極６の平面状集電体４は、金属の電解析出から形成される電解金属箔からなり、上記電解金属箔は、一方の主面の表面粗さが１０点平均粗さにして３．０μｍより小さく、この主面と他方の主面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さい。



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【特許請求の範囲】
【請求項１】　平面状集電体の表面に電極構成物質層が形成されてなる正極及び負極を備える非水電解液二次電池において、
正極及び負極の平面状集電体の少なくとも一方は、金属の電解析出から形成される電解金属箔からなり、
上記電解金属箔は、一方の主面の表面粗さが１０点平均粗さにして３．０μｍより小さく、この主面と他方の主面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さいことを特徴とする非水電解液二次電池。
【請求項２】　正極の電極構成物質が、少なくともリチウムを含む金属酸化物からなり、負極の電極構成物質が、リチウムをドープ及び脱ドープ可能な物質とからなることを特徴とする請求項１に記載の非水電解液二次電池。
【請求項３】　上記電解金属箔が銅からなることを特徴とする請求項１に記載の非水電解液二次電池。
【請求項４】　上記電解金属箔の少なくとも一方の面が、防錆被膜によって被覆されていることを特徴とする請求項１に記載の非水電解液二次電池。
【請求項５】　上記電解金属箔の少なくとも一方の面が、シランカップリング剤によって被覆されていることを特徴とする請求項１記載の非水電解液二次電池。

【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、平面状集電体の表面に電極構成物質層が形成されてなる電極を備える非水電解液二次電池に関し、特に平面状集電体の改良に関するものである。
【０００２】
【従来の技術】近年の電子技術のめざましい進歩により、電子機器の小型化、軽量化、高性能化が進み、これら電子機器には、エネルギー密度の高い二次電池が要求されている。従来、これら電子機器に使用される二次電池としてニッケル・カドミウム電池や鉛電池などが挙げられるが、これら電池では、エネルギー密度が高い電池を得るという点で不十分であった。
【０００３】このような状況下で、正極としてリチウムコバルト複合酸化物などのリチウム複合酸化物を使用し、負極として炭素材料などのようなリチウムイオンをドープ及び脱ドープ可能な物質を使用した非水電解液二次電池、いわゆるリチウムイオン二次電池の研究・開発が行われている。このリチウムイオン二次電池は、高エネルギー密度を有し、自己放電も少なく、サイクル特性に優れ、かつ軽量という優れた特性を有する。
【０００４】ところで、上記リチウムイオン二次電池の集電体としては、一般に金属箔が使用されている。特に、銅からなる金属箔は、リチウム金属と合金を形成しない、電気伝導性が良い、低コストといった特徴を有するため、負極集電体として多用されている。この銅箔には、一般に、銅板を機械的にローラ圧延した、いわゆる厚み１０～３０μｍの圧延銅箔が使用されている。しかしながら、圧延銅箔は、圧延装置のサイズの規制から、幅の広いものを得るのが難しい。
【０００５】一方、銅の電解析出によって形成される、いわゆる電解銅箔は、圧延銅箔に比べ比較的幅の広いものも容易に得られる。また、この電解銅箔をリチウムイオン二次電池の負極集電体に使用した場合には、生産性が飛躍的に向上し、電池生産のコストを大幅に下げることができる。
【０００６】
【発明が解決しようとする課題】しかしながら、市販の電解銅箔を負極集電体に使用したリチウムイオン二次電池においては、電池特性、特に充放電でのサイクル特性が悪く、使用することができなかった。
【０００７】そこで、本発明者らが鋭意検討を重ねた結果、上述した問題は、電解金属箔の一方の主面に大きな凹凸が形成されて、電解金属箔の両主面の表面粗さの差が大きすぎるために生じていることがわかった。
【０００８】これまで電解金属箔は、一般にその用途が主にプリント基板、フレキシブル基板であり、プラスチックとの密着性を良くするために（アンカー効果をねらうために）、その主面に大きな凹凸を形成していた。そのため、この電解金属箔を非水電解液二次電池の集電体に用いた場合には、活物質表面に沿った変形が十分に起こらないため、活物質と集電体の接触が悪く、容量の劣化やサイクル特性の低下が生じていた。
【０００９】本発明は、上述のような問題点を解決するために提案されたものであり、活物質表面に沿って集電体が十分に変形し、活物質と集電体の接触性を良好に保って、充放電サイクルに優れた安価な非水電解液二次電池の提供を目的とする。
【００１０】
【課題を解決するための手段】本発明に係る非水電解液二次電池は、平面状集電体の表面に電極構成物質層が形成されてなる正極及び負極を備え、上記正極及び負極の平面状集電体の少なくとも一方は、金属の電解析出から形成される電解金属箔からなり、上記電解金属箔は、一方の主面の表面粗さが１０点平均粗さにして３．０μｍより小さく、この主面と他方の主面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さいことを特徴とする。
【００１１】本発明に係る非水電解液二次電池においては、上記平面状集電体の少なくとも一方が、金属の電解析出から形成される電解金属箔からなることから、製造上の大きさの制約がなく、電池生産のコストを下げることができる。
【００１２】また、本発明に係る非水電解液二次電池においては、集電体である電解金属箔の一方の主面の表面粗さが１０点平均粗さにして３．０μｍより小さく、こ

の主面と他方の主面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さいことから、集電体と活物質との接触性が良く、電気伝導度が大きくなって、充放電サイクルに優れたものとなる。

【００１３】一般に、平面状集電体の表面に電極構成物質層が形成されてなる電極は、活物質とバインダーとを含有する電極構成物質層が集電体の表面に塗布され、その後ロール圧延等でプレスされて作製される。このプレス工程は、電極を所定の密度に圧縮する作用と、適切な導電性を有するように活物質粒子間を接近させる作用とを有する。プレス工程を経た電極は、活物質粒子間、及び活物質と集電体との接触性が良くなり、電気伝導度が大きくなる。

【００１４】さらに、十分な電池特性を得るには、活物質粒子間、及び活物質と集電体の距離を小さくすると共に、集電体の形状が活物質表面の形状に沿って変形することが重要である。活物質表面に沿って集電体が変形した場合には、活物質と集電体との接触性がさらに良くなり、電気伝導度がさらに大きくなり、望ましい電池特性が得られる。

【００１５】しかし、活物質表面に沿って集電体が変形しない場合には、活物質と集電体の接触部分が少なくなり、電気伝導度が小さい。また、集電体表面の凹凸が大きい場合には、活物質と集電体の接触点も少ない。このような接触抵抗が大きい電極は、充放電を繰り返すと、活物質の充放電に伴う膨張収縮によるストレスや、接着剤であるバインダーの電解液への溶解などによって、集電体と活物質との距離が段々と大きくなり、一部の活物質が充放電に利用できない電気伝導度になって容量の劣化が起きる。

【００１６】したがって、この電解金属箔の一方の面の表面粗さが１０点平均粗さにして３．０μｍより大きい場合、或いはこの主面と他方の主面主面との表面粗さとの差が１０点平均粗さにして２．５μｍより大きい場合には、活物質が集電体に塗布されてプレスされる際に、集電体が活物質の表面に沿った変形が十分起こらず、また、表面の凹凸が大きいために活物質との接触点が少なく、充放電に伴って容量の劣化が起きて十分な電池特性が得られない。

【００１７】

【発明の実施の形態】本発明に係る非水電解液二次電池は、平面状集電体の表面に電極構成物質層が形成されてなる電極を備えて構成され、上記平面状集電体の少なくとも一方が金属の電解析出から形成される電解金属箔からなる。そして、この電解金属箔は、一方の主面であるマット面の表面粗さが１０点平均粗さにして３．０μｍより小さく、このマット面と他方の主面である光沢面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さく形成される。

【００１８】なお、一般に、電解金属箔は、所定の金属を含有する水溶液を電解液とし、回転ドラムを電極として、ドラム表面に形成される。この時、形成された電解金属箔は、ドラム側の主面を光沢面と称し、電解液側のもう一方の主面をマット面と称す。

【００１９】上記電解銅箔は、表面の凹凸が小さく、マット面と光沢面との表面粗さの差が小さいため、プレス工程時に活物質表面に沿った変形が十分に起こり、活物質との接触性が良好に保たれる。

【００２０】なお、上述する表面粗さは、ＪＩＳ規格Ｂ０６０１において、１０点平均線粗さ（R_Z）についての定義がなされている。１０点平均粗さ（R_Z）は、図１に示すように、断面曲線から基準長さＬだけだけ抜き取った部分の平均線から縦倍率の方向に測定した、最も高い山頂から５番目までの山頂の標高（Y_p）の絶対値の平均値（$|Y_{p1}+Y_{p2}+Y_{p3}+Y_{p4}+Y_{p5}|/5$）と、最も低い谷底から５番目までの谷底の標高（$Y_v$）の絶対値の平均値（$|Y_{v1}+Y_{v2}+Y_{v3}+Y_{v4}+Y_{v5}|/5$）との和を求めたものである。

【００２１】本発明は、電池を構成する物質について特に限定するものではないが、正極が少なくともリチウムを含む金属酸化物からなり、負極がリチウムをドープ及び脱ドープ可能な負極とからなるようないわゆるリチウムイオン二次電池において好適である。

【００２２】また、リチウムイオン二次電池においては、上記電解金属箔が銅からなることが好ましい。電解銅箔は、リチウム金属と合金を形成することがなく、電気伝導性が良く、低コストで生産できるなどの種々の利点を有している。

【００２３】上記電解金属箔の少なくとも一方の面には、金属箔の酸化を抑制するために、防錆被膜が被覆されていてもよい。また、上記電解金属箔の少なくとも一方の面には、金属箔表面と活物質との吸着性を向上させるために、シランカップリング剤からなる膜が被覆されていてもよい。

【００２４】なお、上記リチウムイオン二次電池において、正極活物質としては、Li_xMO_2（但し、Ｍは、１種類以上の遷移金属を表す。ｘは、リチウムの組成比である。）を含んだ活物質が使用可能である。かかる活物質としては、Li_xCoO_2、Li_xNiO_2、$Li_xMn_2O_4$、Li_xMnO_3、$Li_xNi_yCo_{(1-y)}O_2$などの複合酸化物が挙げられる。

【００２５】上記複合酸化物は、例えば、リチウム、コバルト、ニッケルの炭酸塩を出発原料とし、これら炭酸塩を組成に応じて混合し、酸素存在雰囲気下６００℃～１０００℃の温度範囲で焼成することにより得られる。また、出発原料は、炭酸塩に限定されず、水酸化物、酸化物からも同様に合成可能である。

【００２６】一方、負極活物質としては、リチウムをドープ及び脱ドープ可能なものであれば良く、熱分解炭素類、コークス類（ピッチコークス、ニードルコークス、

石油コークスなど）、グラファイト類、ガラス状炭素類、有機高分子化合物焼成体（フェノール樹脂、フラン樹脂などを適当な温度で焼成し炭素化したもの）、炭素繊維、活性炭などの炭素質材料、あるいは、金属リチウム、リチウム合金（例えば、リチウムーアルミ合金）の他、ポリアセチレン、ポリピロールなどのポリマーも使用可能である。

【００２７】電解液には、リチウム塩を電解質とし、これを有機溶媒に溶解させた電解液が用いられる。ここで有機溶媒としては、特に限定されるものではないが、例えば、プロピレンカーボネート、エチレンカーボネート、１，２ージメトキシエタン、γーブチロラクトン、テトラヒドロフラン、２ーメチルテトラヒドロフラン、１，３ージオキソラン、スルホラン、アセトニトリル、ジエチルカーボネート、ジプロピルカーボネートなどの単独もしくは２種類以上の混合溶媒の使用が可能である。

【００２８】電解質には、$LiClO_4$、$LiAsF_6$、$LiPF_6$、$LiBF_4$、$LiB(C_6H_5)_4$、ＬｉＣｌ、ＬｉＢｒ、CH_3SO_3Li、CF_3SO_3Liなどの使用が可能である。

【００２９】

（組成１）

硫酸銅（$CuSO_4 \cdot 5H_2O$）	３５０ｇ／ｌ
硫酸（H_2SO_4）	１１０ｇ／ｌ
チオ尿素	０．４ｐｐｍ
アラビアゴム	０．８ｐｐｍ
低分子量膠（分子量５０００）	０．４ｐｐｍ
Cl^-	３０ｐｐｍ

次いで、この電解銅箔をCrO_3；１ｇ／ｌ水溶液に５秒間浸漬して、クロメート処理を施し、水洗後乾燥させた。なお、ここでは、クロメート処理を行ったが、ベンゾトリアゾール系処理、或いはシランカップリング剤処理、又はクロメート処理後にシランカップリング剤処理を行ってもよいことは勿論である。

【００３３】そして、負極６は次のようにして作製した。負極活物質５としては、出発原料として石油ピッチを用い、これを焼成して粗粒状のピッチコークスを得た。この粗粒状ピッチコークスを粉砕して平均粒径２０μｍの粉末とし、この粉末を不活性ガス中、１０００℃にて焼成して不純物を除去し、コークス材料粉末を得た。

【００３４】このようにして得られたコークス材料粉末を９０重量部、結着材としてポリフッ化ビニリデンを１０重量部の割合で混合して負極合剤を調整した。次いで、この負極合剤を溶剤であるＮーメチルピロリドンに分散させてスラリーにした。そして、このスラリーを上述した厚さ１０μｍの帯状の電解銅箔である負極集電体４の両面に塗布し、乾燥後ローラプレス機で圧縮形成して、帯状負極６を得た。この帯状負極６は、成形後の負極合剤の膜厚が両面共に９０μｍで同一であり、その幅が５５．６ｍｍ、長さが５５１．５ｍｍに形成される。

【００３５】次に、正極３は、次にようにして作製した。正極活物質（$LiCoO_2$）２は、炭酸リチウム０．５モルと炭酸コバルト１モルと混合し、空気中で９００℃、５時間焼成して$LiCoO_2$を得た。

【００３６】このようにして得られた正極活物質（$LiCoO_2$）２を９１重量％、導電剤としてグラファイトを６重量％、結着剤としてポリフッ化ビニリデンを３重量％の割合で混合して正極合材を作製し、これをＮーメチルー２ピロリドンに分散してスラリー状とした。次に、このスラリーを厚み２０μｍの帯状のアルミニウムからなる正極集電体の両面に均一に塗布し、乾燥後ローラープレス機で圧縮成形して厚み１６０μｍの帯状正極３を得た。この帯状正極３は、成形後の正極合剤の膜厚が表面共に７０μｍであり、その幅が５３．６ｍｍ、長さが５２３．５ｍｍに形成される。

【００３７】このようにして作製された帯状正極３と、帯状負極６と、厚さが２５μｍ、幅が５８．１ｍｍの微多孔性ポリプロピレンフィルムよりなるセパレータ７とを、上述したように積層し、これを積層電極体とした。

【実施例】以下、本発明を適用した非水電解液二次電池について、好適な実施例を図面を参照しながら説明する。なお、本発明は、本実施例に限定されるものではないことは言うまでもない。

【００３０】実施例１

本実施例で作製したリチウムイオン二次電池は、図１に示すように、正極集電体１に正極活物質２を塗布してなる正極３と、負極集電体４に負極活物質５を塗布してなる負極６とから構成される。そして、この非水電解液二次電池は、正極３、セパレータ７、負極６、セパレータ７をこの順に積層して積層電極体とし、この積層電極体を多数回巻回されてなる渦巻式電極体の上下に絶縁体８、９を配置した状態で電池缶１０に収納してなるものである。

【００３１】先ず始めに、電解銅箔からなる負極集電体４は、次のようにして作製した。組成１で示される硫酸銅溶液を電解液として、貴金属酸化物被覆チタンを陽極に、チタン製回転ドラムを陰極として、電流密度５０Ａ／dm^2、液温５０℃の条件で電解することによって、厚み１２μｍの電解銅箔を得た。

【００３２】

この積層電極体は、その長さ方向に沿って負極６を内側にして渦巻型に多数回巻回され、最外周セパレータの最終端部をテープで固定されて、渦巻式電極体となる。この渦巻式電極体の中空部分は、その内径が、３．５ｍｍ、外形が１７ｍｍに形成される。

【００３８】上述のように作製された渦巻式電極体を、その上下両面に絶縁板８、９が設置された状態で、ニッケルメッキが施された鉄製の電池缶１０に収納した。そして、正極３及び負極６の集電を行うために、アルミニウム製の正極リード１３を正極集電体１から導出して電池蓋１１に接続し、ニッケル製の負極リード１４を負極集電体４から導出して電池缶１０に接続した。

【００３９】そして、この渦巻式電極体が収納された電池缶１０に、プロピレンカーボネイトとジエチルカーボネイトとの等容量混合溶媒中に$LiPF_6$を１モル／ｌの割合で溶解した非水電解液５．０ｇを注入した。次いで、アスファルトで表面を塗布された絶縁封口ガスケット１２を介して電池缶１０をかしめることにより、電池蓋１１を固定し、電池缶１０内の気密性を保持させた。

【００４０】以上のようにして、直径１８ｍｍ、高さ６５ｍｍの円筒形非水電解液二次電池（実施例１）を作製した。

【００４１】実施例２

先ず始めに、電解銅箔からなる負極集電体４は次のようにして作製した。組成２で示される硫酸銅溶液を電解液として、貴金属酸化物被覆チタンを陽極に、チタン製回転ドラムを陰極として、電流密度５０Ａ／ｄｍ^2、液温５０℃の条件で電解することによって、厚み１２μｍの電解銅箔を得た。そして、この電解箔にクロメート処理を行った。

【００４２】

（組成２）

硫酸銅（$CuSO_4 \cdot 5H_2O$）	３５０ｇ／ｌ
硫酸（H_2SO_4）	１１０ｇ／ｌ
１－メルカプト３－プロパンスルホン酸ナトリウム	１ｐｐｍ
ヒドロキシエチルセルロース	４ｐｐｍ
低分子量膠（分子量３０００）	４ｐｐｍ
Cl^-	３０ｐｐｍ

上述した電解金属箔を使用した以外は、実施例１と同様にして円筒形非水電解液二次電池（実施例２）を作製した。

【００４３】実施例３

先ず始めに、電解銅箔からなる負極集電体４は次のようにして作製した。組成３で示される硫酸銅溶液を電解液として、貴金属酸化物被覆チタンを陽極に、チタン製回転ドラムを陰極として、電流密度５０Ａ／ｄｍ^2、液温５８℃の条件で電解することによって、厚み９μｍの電解銅箔を得た。

【００４４】

（組成３）

硫酸銅（$CuSO_4 \cdot 5H_2O$）	３５０ｇ／ｌ
硫酸（H_2SO_4）	１１０ｇ／ｌ
膠（分子量６００００）	２ｐｐｍ
Cl^-	３０ｐｐｍ

この電解銅箔の表面粗さは、後述する測定方法により、光沢面がR_z＝２．００μｍ、マット面がR_z＝３．５２μｍであった。

【００４５】次いで、この電解銅箔に、組成４で示される電解液からなる銅電解浴を用いて、電流密度６Ａ／ｄｍ^2、液温５８℃でマット面に光沢銅メッキを施した。そして、この銅メッキが施された電解銅箔に同様にクロメート処理を施した。

【００４６】

（組成４）

硫酸銅（$CuSO_4 \cdot 5H_2O$）	２４０ｇ／ｌ
硫酸（H_2SO_4）	６０ｇ／ｌ
膠	２ｐｐｍ
日本シェーリング（株）製カバシラド２１０	
メイキャップ剤	１０ｃｃ／ｌ
光沢剤（Ａ）	０．５ｃｃ／ｌ
光沢剤（Ｂ）	補充にのみ使用
Cl^-	３０ｐｐｍ

光沢剤の補充は、電流量１０００Ａｈに対して光沢剤（Ａ）及び光沢剤（Ｂ）を各々３００ｃｃ添加した。

【００４７】上述した電解銅箔を使用した以外は、実施例１と同様にして円筒形非水電解液二次電池（実施例

３）を作製した。

【００４８】比較例１

先ず始めに、電解銅箔からなる負極集電体４は次のようにして作製した。組成５で示される硫酸銅溶液を電解液として、貴金属酸化物被覆チタンを陽極に、チタン製回転ドラムを陰極として、電流密度５０Ａ／ｄｍ^2、液温５８℃の条件で電解することによって、厚み１２μｍの電解銅箔を得た。そして、この電解銅箔にクロメート処理を行った。

【００４９】

（組成５）

硫酸銅（$CuSO_4 \cdot 5H_2O$）	３５０ｇ／ｌ
硫酸（H_2SO_4）	１１０ｇ／ｌ
膠	２ｐｐｍ
Cl^-	３０ｐｐｍ

上述した電解銅箔を使用した以外は、実施例１と同様にして円筒形非水電解液二次電池（比較例１）を作製した。

【００５０】そして、実施例１～実施例３及び比較例１で得られた電解銅箔において、その表面粗さ（１０点平均粗さR_Z）を表面粗さ計（株式会社小坂研究所製ＳＥ－３Ｃ型）で調べた。この結果を表１に示す。なお、光沢面の表面粗さを測定する際には、基準長さＬを０．８ｍｍとし、マット面の表面粗さを測定する際には、基準長さＬを２．５ｍｍとした。

【００５１】

【表１】

		表面粗さ(μm)
実施例１	光沢面	1.58
	マット面	2.10
実施例２	光沢面	1.60
	マット面	1.32
実施例３	光沢面	2.00
	マット面	0.70
比較例１	光沢面	1.93
	マット面	3.7

【００５２】また、それぞれの電解銅箔を負極集電体に用いた実施例１～実施例３及び比較例１の円筒形非水電解液二次電池について、１００サイクル後の容量維持率を調べた。その結果を図３、図４及び表２に示す。

【００５３】さらに、それぞれの電解銅箔を負極集電体に用いた実施例１～実施例３及び比較例１の円筒形非水電解液二次電池について、１００サイクル前後のインピーダンスの変化を調べた。その結果を図５、図６及び表２に示す。

【００５４】

【表２】

	100サイクル後の容量維持率(%)	インピーダンス (mΩ) 100サイクル前/後
実施例１	85	108/190
実施例２	90	105/183
実施例３	70	112/220
比較例１	60	119/242

【００５５】図３、図５及び表２に示すように、マット面の表面粗さが３μｍ以上になると容量維持率が大幅に低下し、インピーダンスの変化が大きくなるため、マット面の表面粗さは、３μｍ未満が好ましい。また、図４及び図６に示すように、マット面と光沢面との表面粗さの差が大きくなるほど容量維持率が低くなり、インピーダンスが大きくなっている。このことから、マット面と光沢面との表面粗さの差は、２．５μｍ未満であることが好ましい。

【００５６】また、電解銅箔の表面粗さは、実施例１及び実施例２のように、最初の電解条件によって規制してもよいし、実施例３のように、銅メッキを後から施して規制してもよい。

【００５７】以上のことから、上述した非水電解液二次電池においては、圧延銅箔に比べ製造上大きさの制約がなく、生産性が高い電解銅箔を負極集電体に用いていることから、生産性が向上し、電池生産コストを大幅に下げることができる。

【００５８】さらに、上述した非水電解液二次電池においては、集電体である電解金属箔の一方の面であるマット面の表面粗さが３．０μｍより小さく、光沢面とマット面との表面粗さとの差が２．５μｍより小さいことから、集電体と活物質との接触性が良く、電気伝導度が大きくなって、充放電サイクルに優れたものとなる。

【００５９】

【発明の効果】以上の説明からも明らかなように、本発明に係る非水電解液二次電池は、集電体に金属の電解析出から形成される電解金属箔を用いてなることから、電池の生産性を向上させ、電池生産のコストを下げることができる。

【００６０】また、この電解金属箔は、一方の面であるマット面の表面粗さが１０点平均粗さにして３．０μｍより小さく、この主面と他方の主面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さく形成される。このことから、本発明に係る非水電解液二次電池においては、集電体と活物質との接触性が良く、電気伝導度が大きくなって、充放電サイクルに優れたものとなる。

【図面の簡単な説明】

【図１】１０点平均粗さ（R_Z）の定義を説明するための断面図である。

【図２】本発明を適用した円筒形非水電解液二次電池の概略断面図である。

【図３】上記円筒形非水電解液二次電池において、電解銅箔のマット面の表面粗さと容量維持率との関係を示す特性図である。

【図４】上記円筒形非水電解液二次電池において、電解銅箔のマット面と光沢面との表面粗さの差と、容量維持率との関係を示す特性図である。

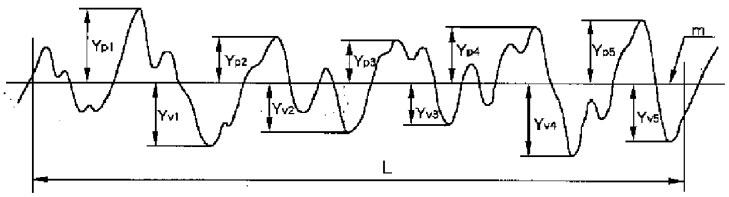
【図５】上記円筒形非水電解液二次電池において、電解銅箔のマット面の表面粗さと１００サイクル後のインピーダンスとの関係を示す特性図である。

【図６】上記円筒形非水電解液二次電池において、電解銅箔のマット面と光沢面との表面粗さの差と、１００サイクル後のインピーダンスとの関係を示す特性図である。

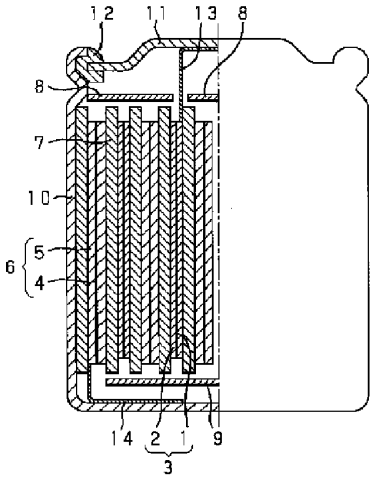
【符号の説明】

１　正極集電体、２　正極活物質、３　正極、４　負極集電体、５　負極活物質、６　負極、７　セパレータ、８　絶縁体、９　絶縁体、１０　電池缶、１１電池蓋、１２　絶縁封口ガスケット、１３　正極リード、１４　負極リード、

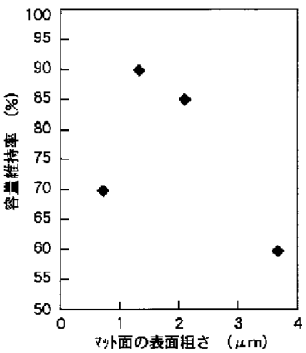
【図１】



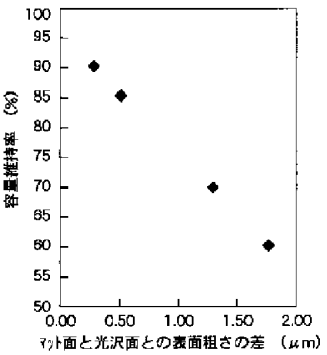
【図２】



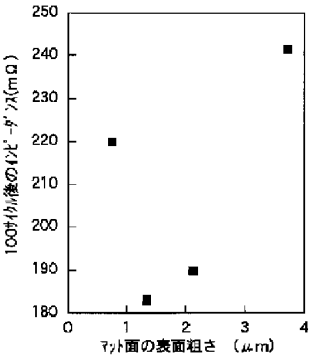
【図３】



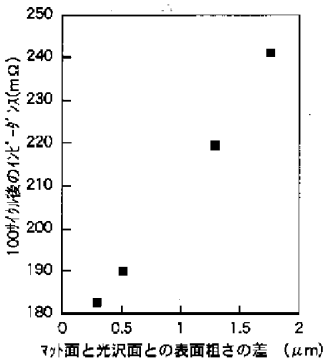
【図４】



【図５】



【図６】



フロントページの続き

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(54) **CURRENT COLLECTOR, ANODE, AND BATTREY**

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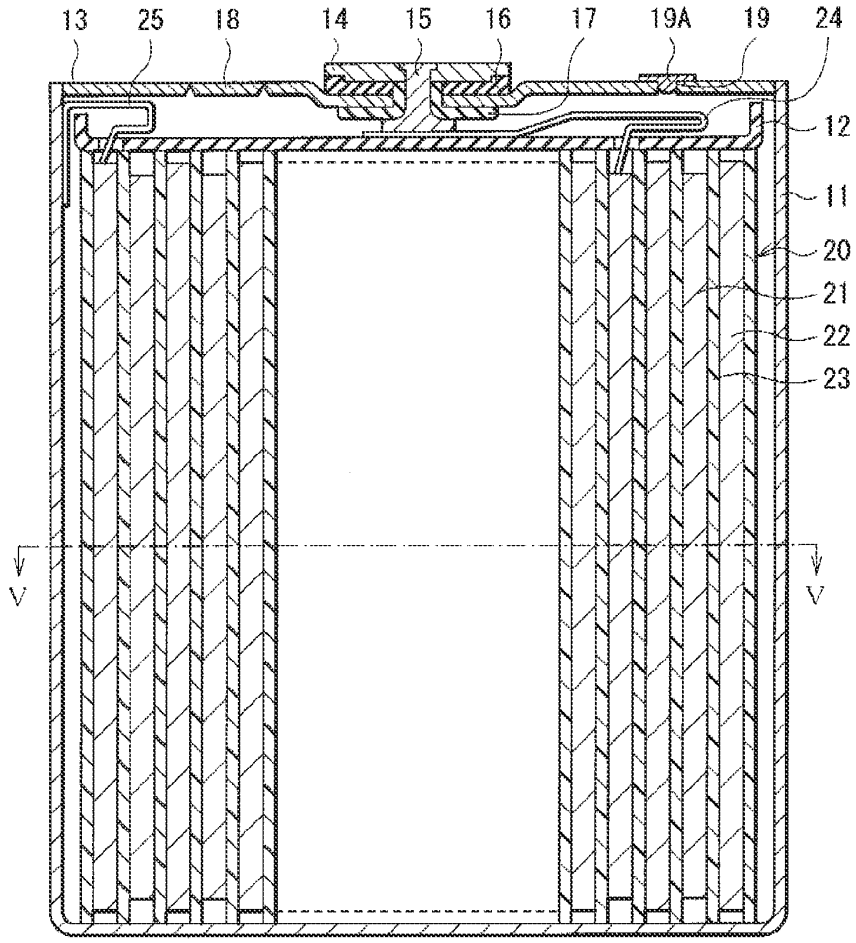
(51) **Int. Cl.**

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C22C 9/00	(2006.01)
H01M 6/02	(2006.01)

(52) **U.S. Cl.** **429/338**; 420/469; 429/209; 429/218.1; 429/221; 429/223; 429/220; 429/336; 429/337; 429/199

(57) **ABSTRACT**

A battery capable of improving the cycle characteristics is provided. A current collector containing copper (Cu), in which ratio I(200)/I(111) between intensity I (200) of a peak originated in (200) crystal plane of copper obtained by X-ray diffraction and intensity I (111) of a peak originated in (111) crystal plane thereof is in the range from 0.5 to 1.5.



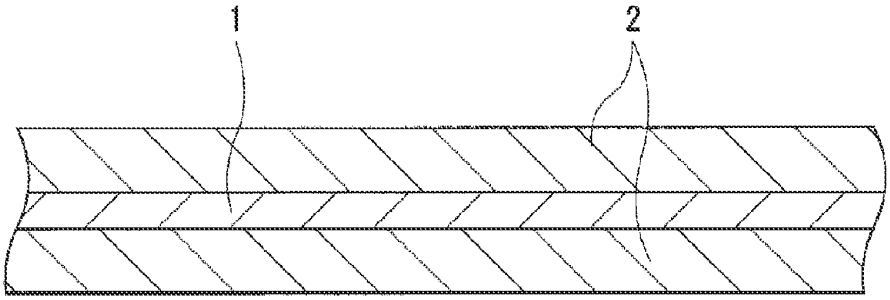


FIG. 1

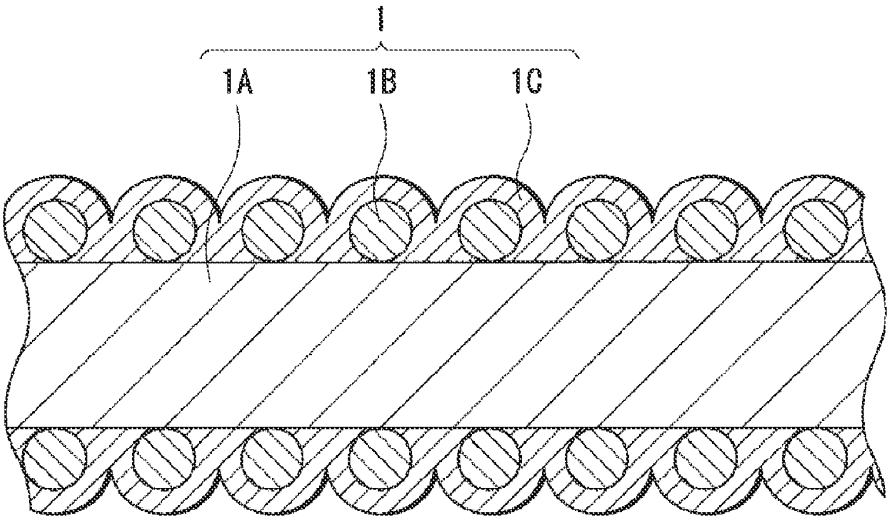


FIG. 2

FIG. 3A

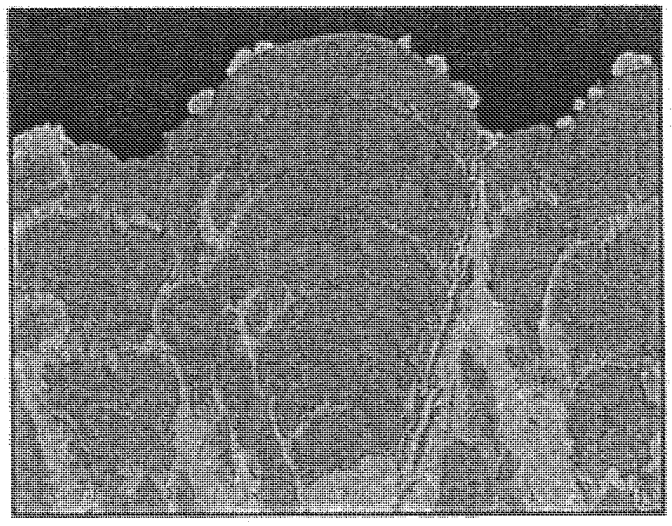
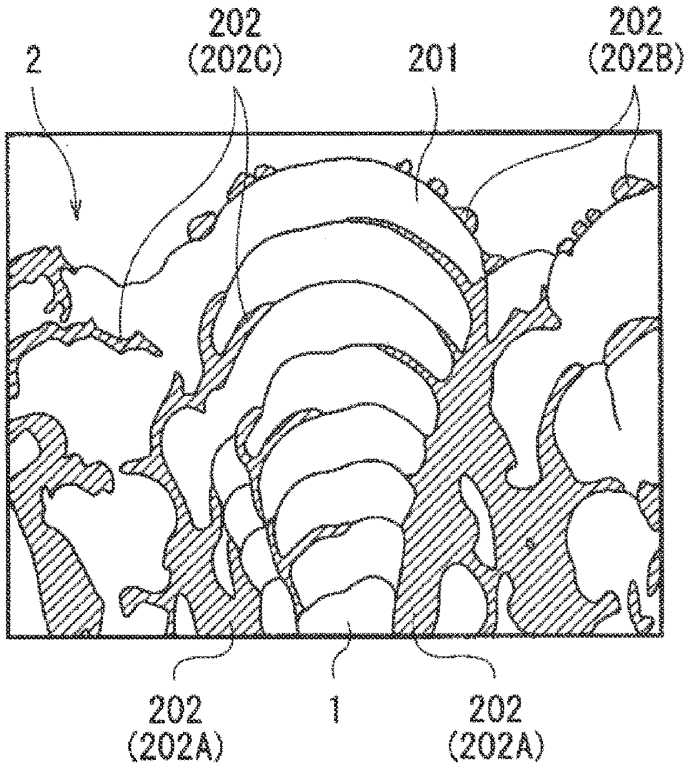


FIG. 3B



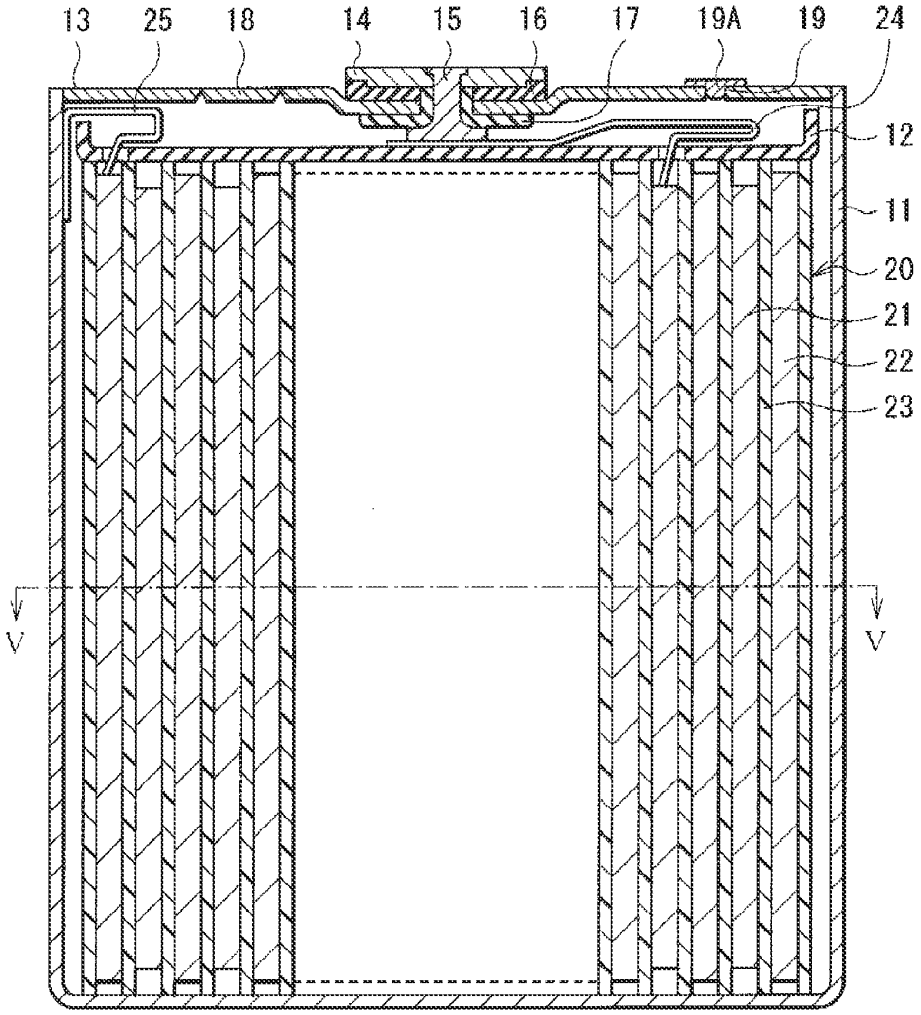


FIG. 4

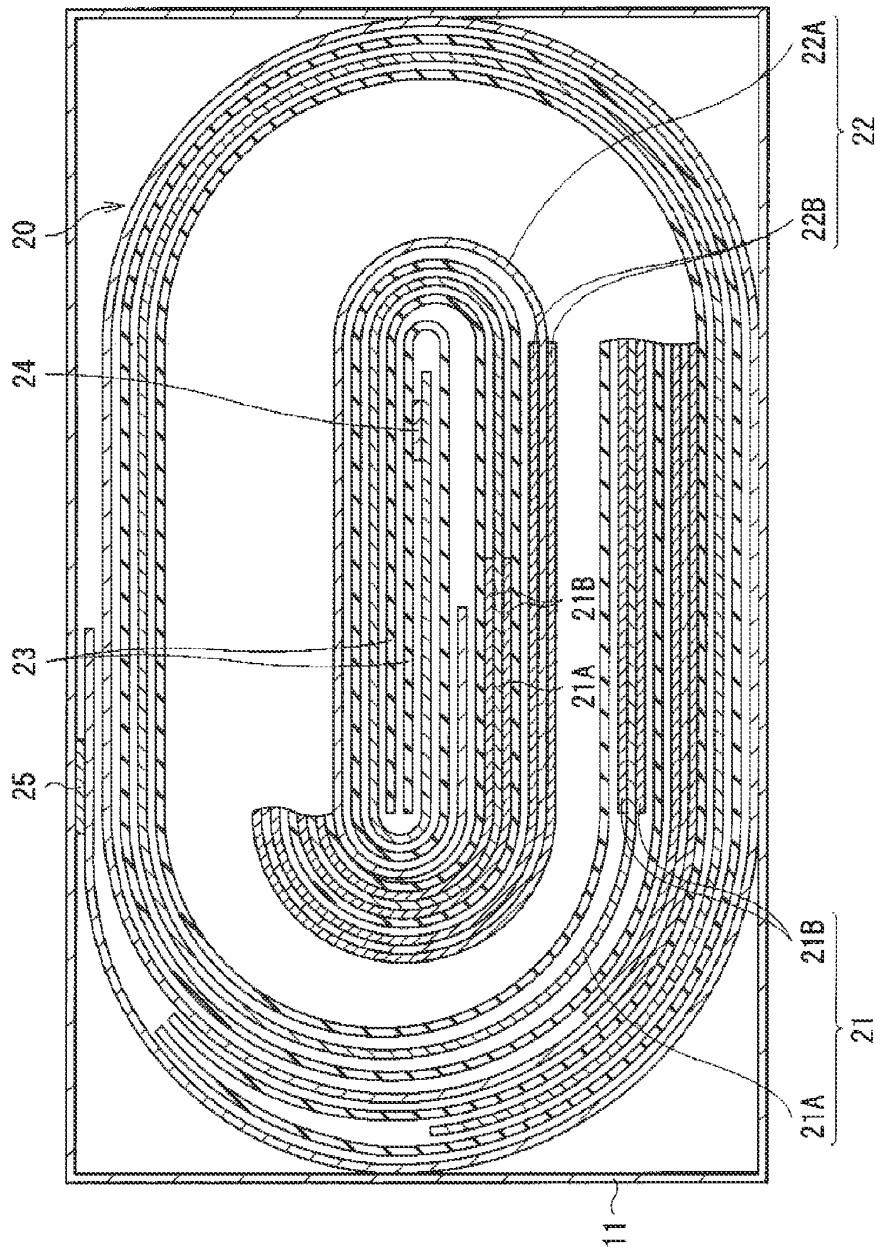


FIG. 5

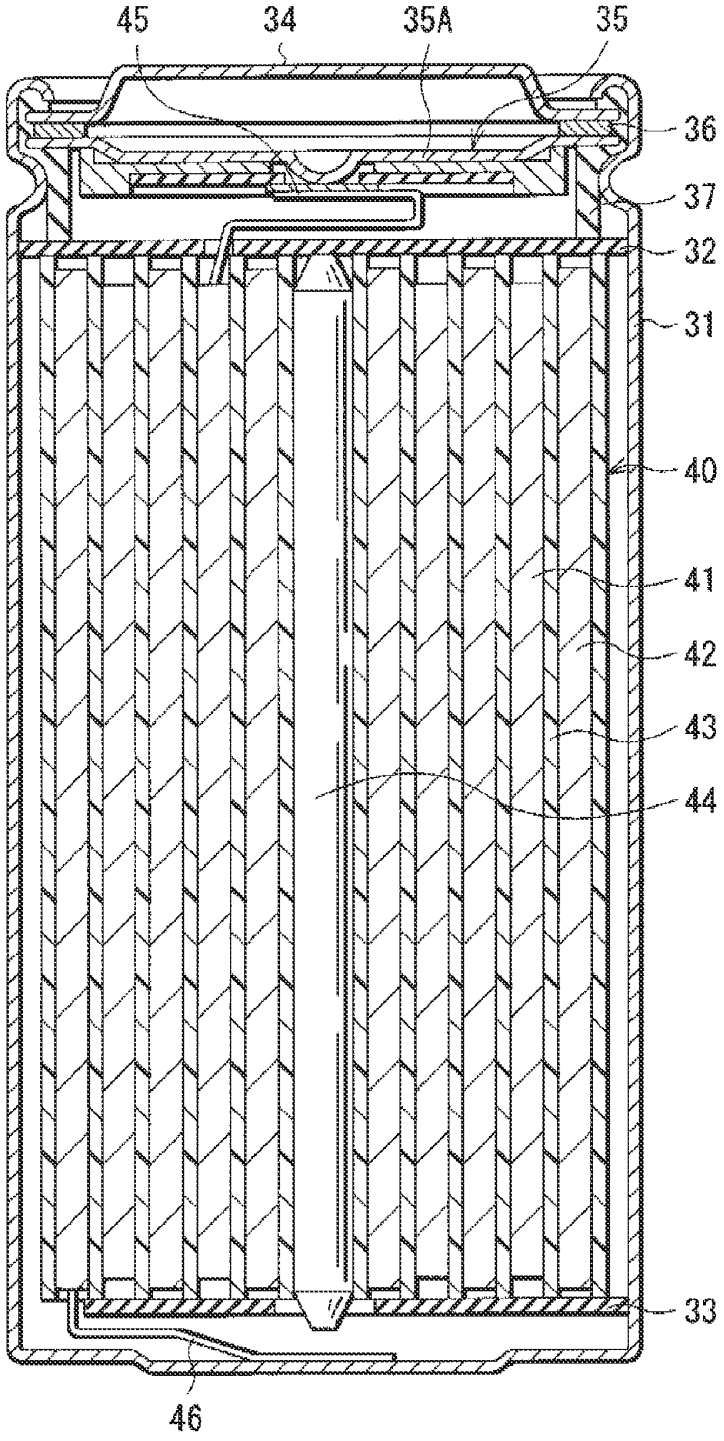


FIG. 6

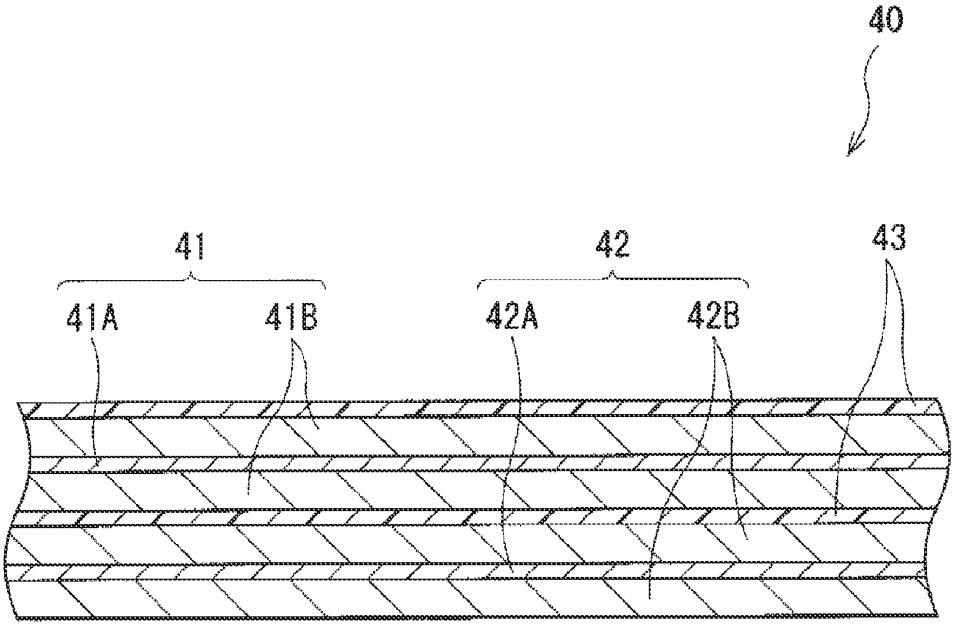


FIG. 7

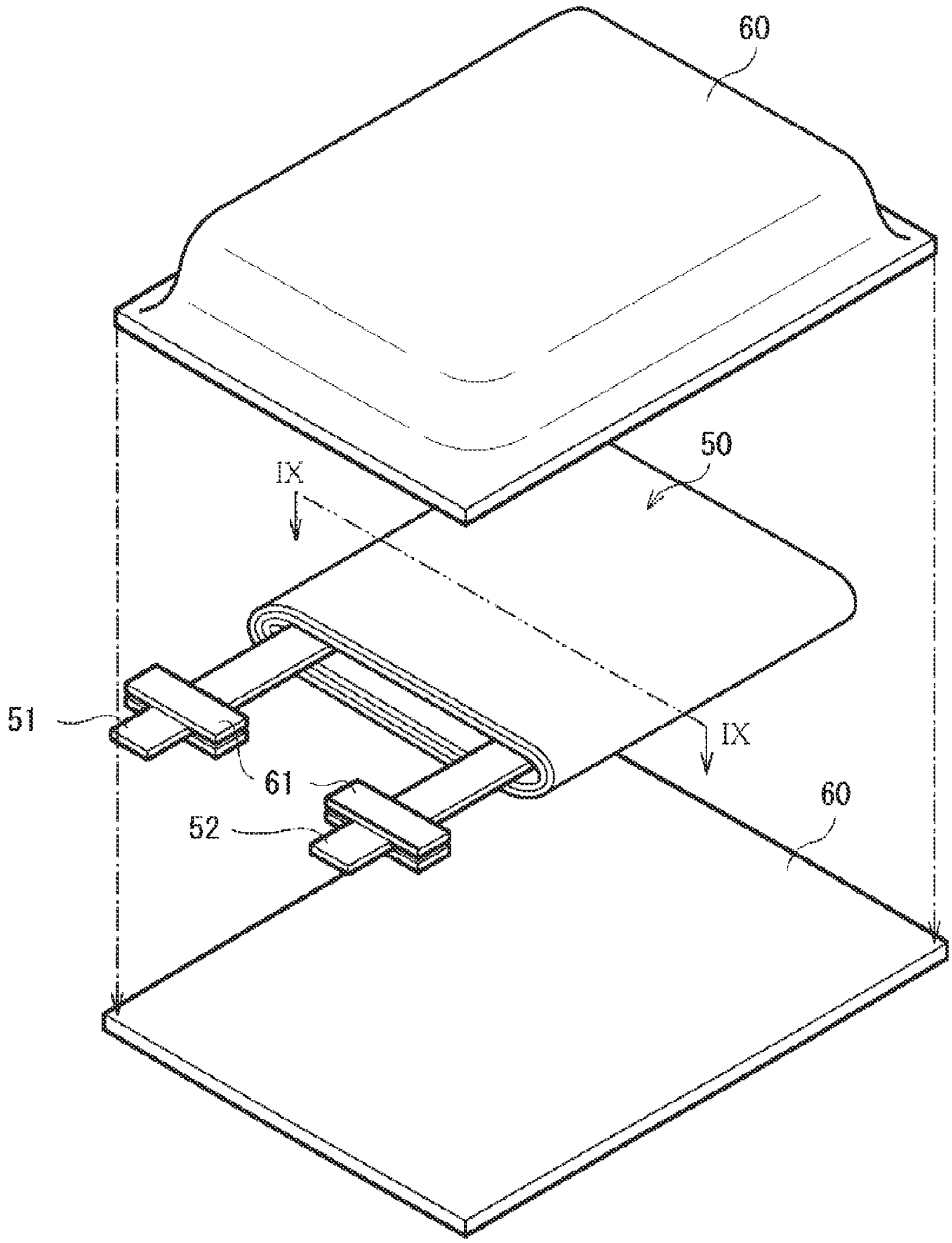


FIG. 8

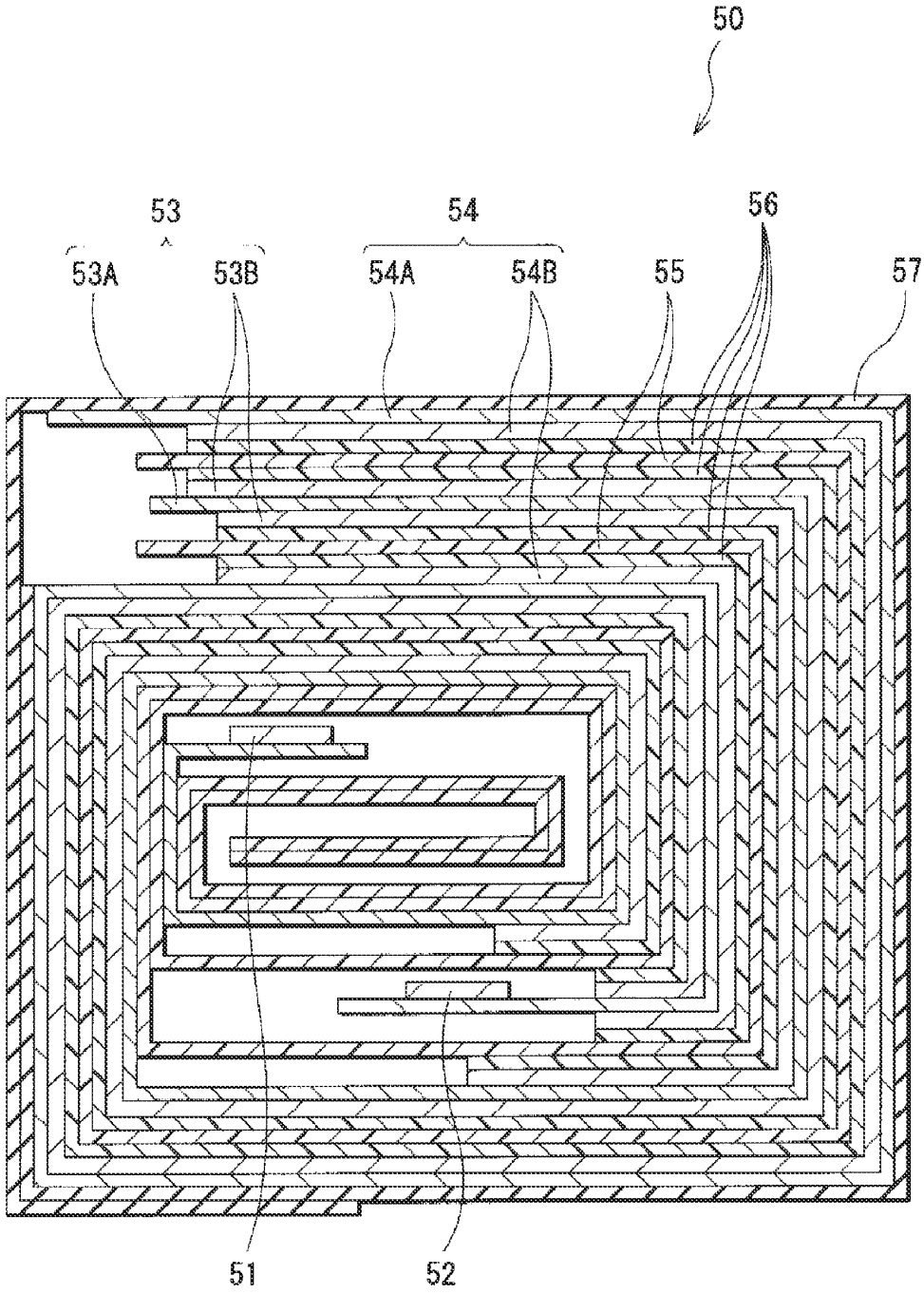


FIG. 9

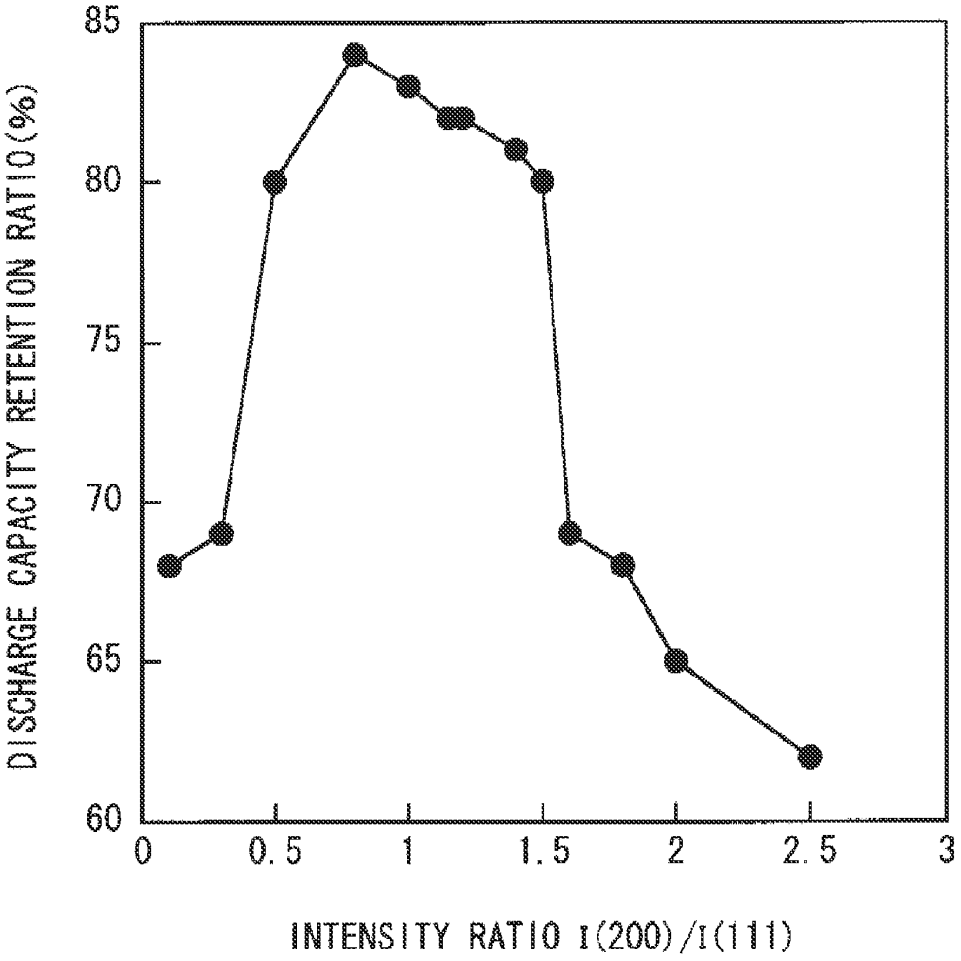

85
80
75
70
65
60
0
0.5
1
1.5
2
2.5
3
DISCHARGE CAPACITY RETENTION RATIO(%)
INTENSITY RATIO I(200)/I(111)

FIG. 10

FIG. 11A

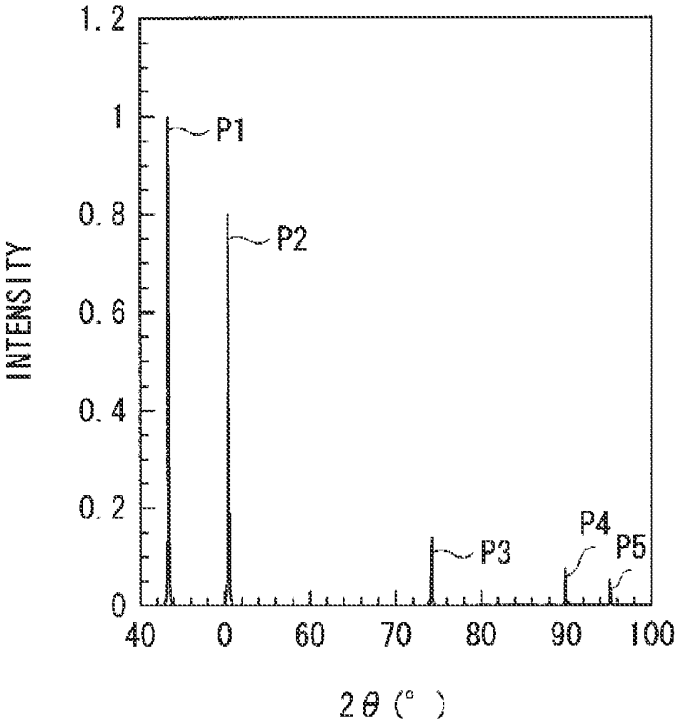
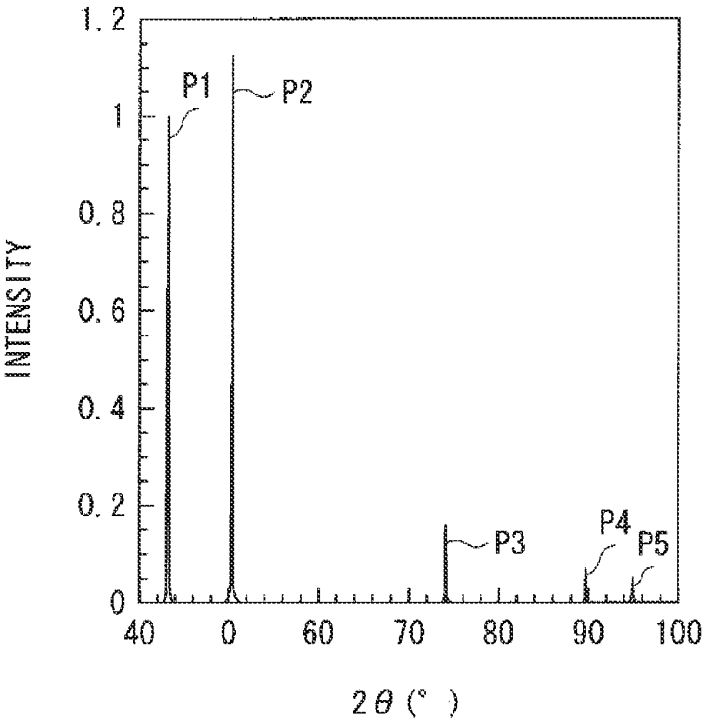


FIG. 11B



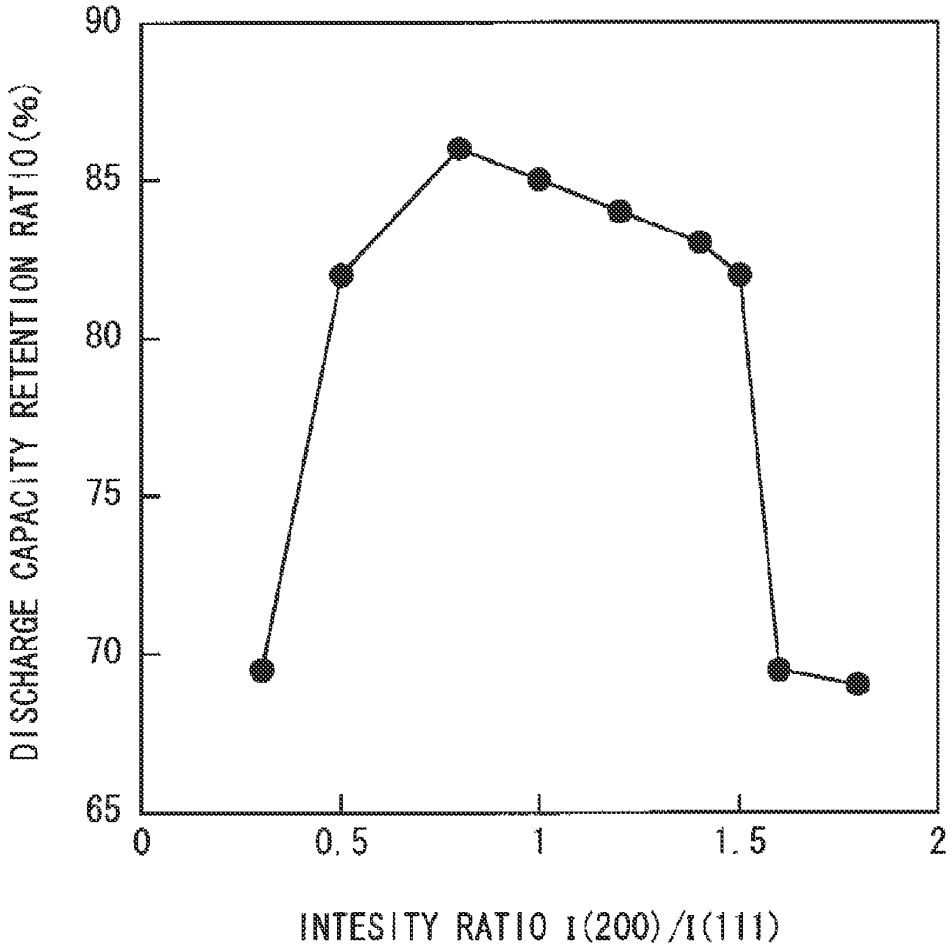

90
85
80
75
70
65
0
0.5
1
1.5
2
DISCHARGE CAPACITY RETENTION RATIO(%)
INTESITY RATIO I(200)/I(111)

FIG. 12

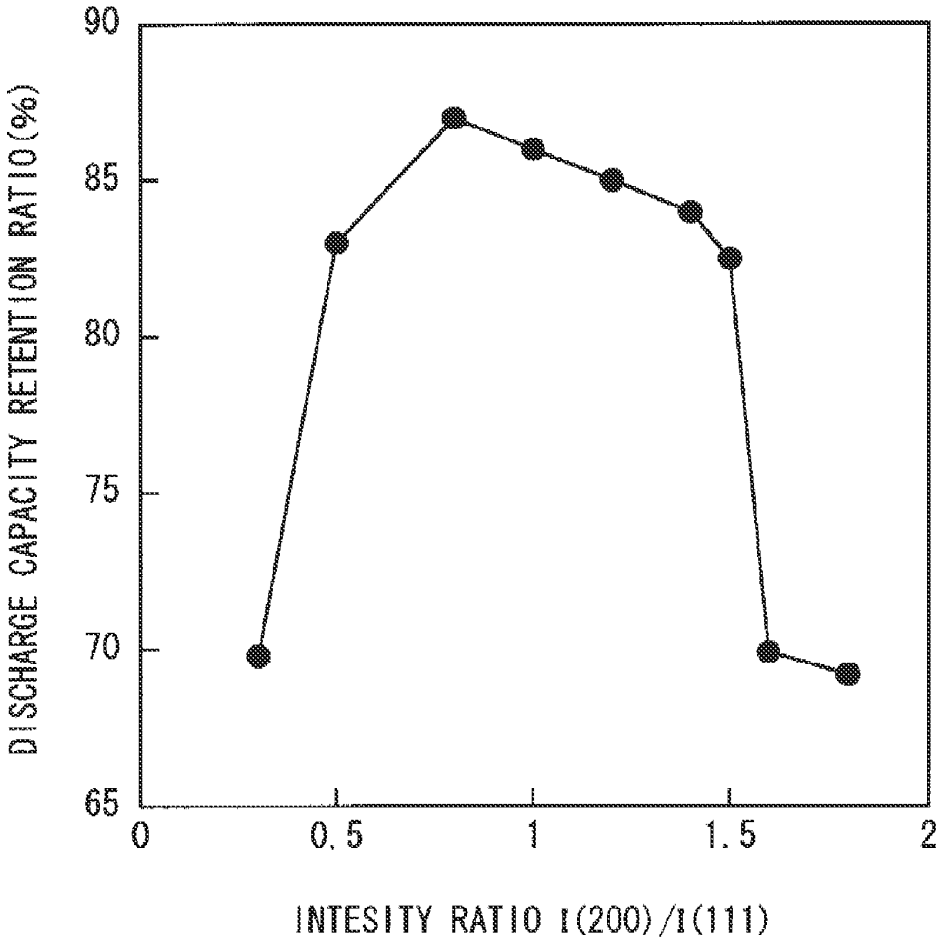

90
85
80
75
70
65
0
0.5
1
1.5
2
DISCHARGE CAPACITY RETENTION RATIO(%)
INTESITY RATIO I(200)/I(111)

FIG. 13

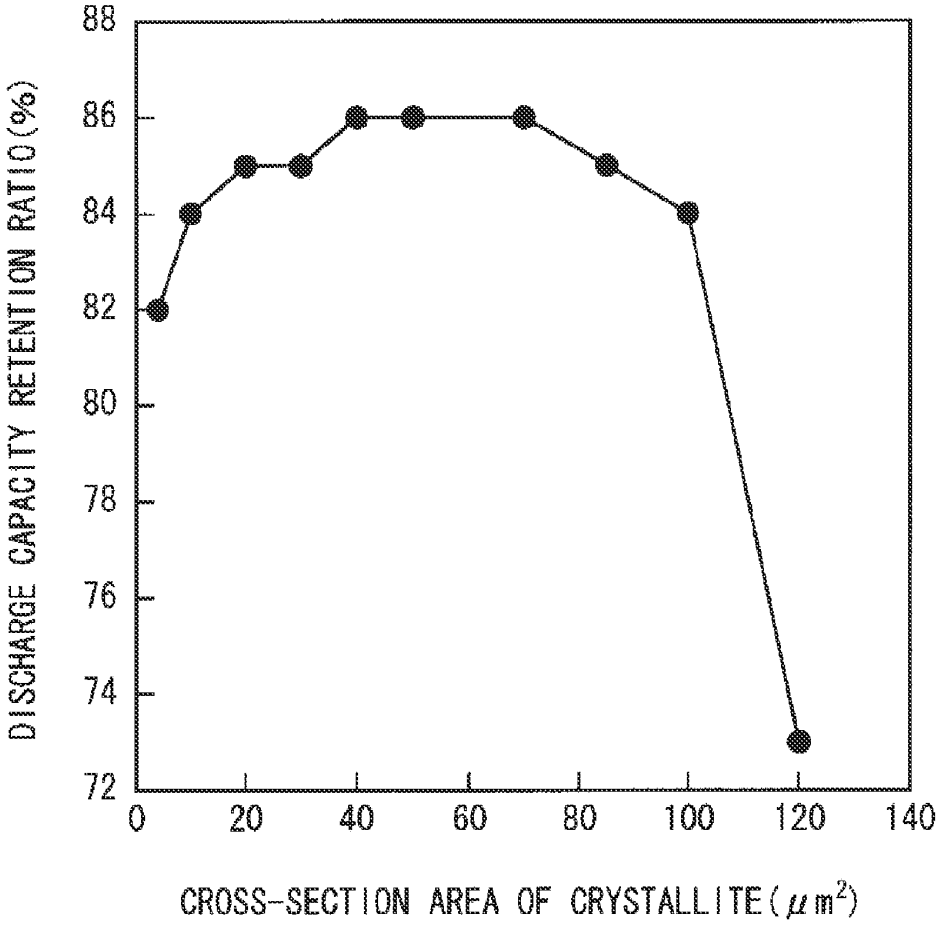

DISCHARGE CAPACITY RETENTION RATIO(%)
88
86
84
82
80
78
76
74
72
0
20
40
60
80
100
120
140
CROSS-SECTION AREA OF CRYSTALLITE(μm²)

FIG. 14

FIG. 15A

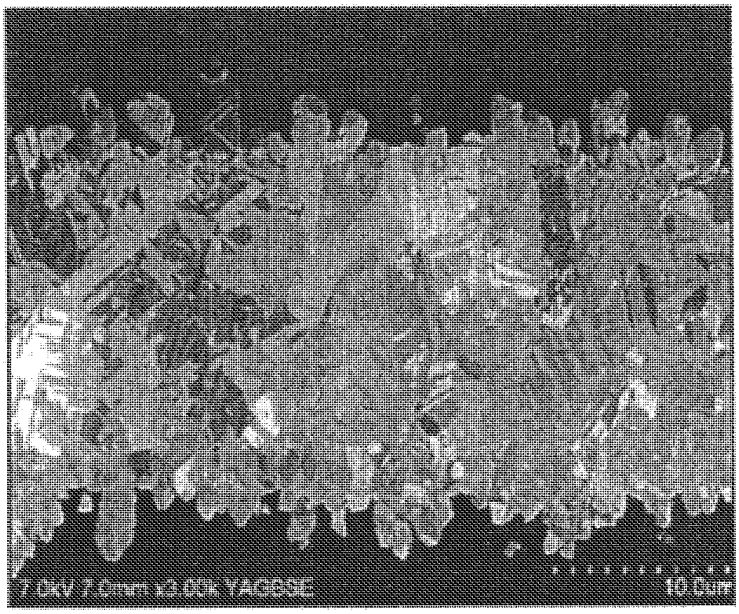
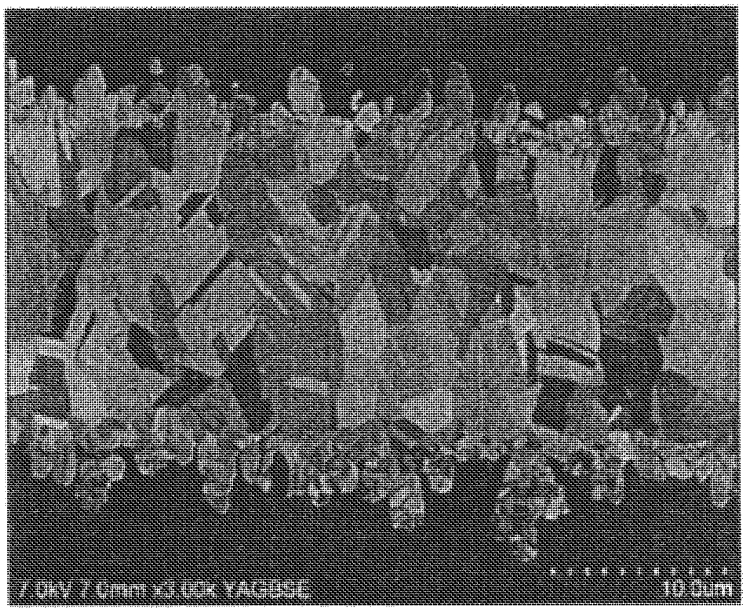


FIG. 15B



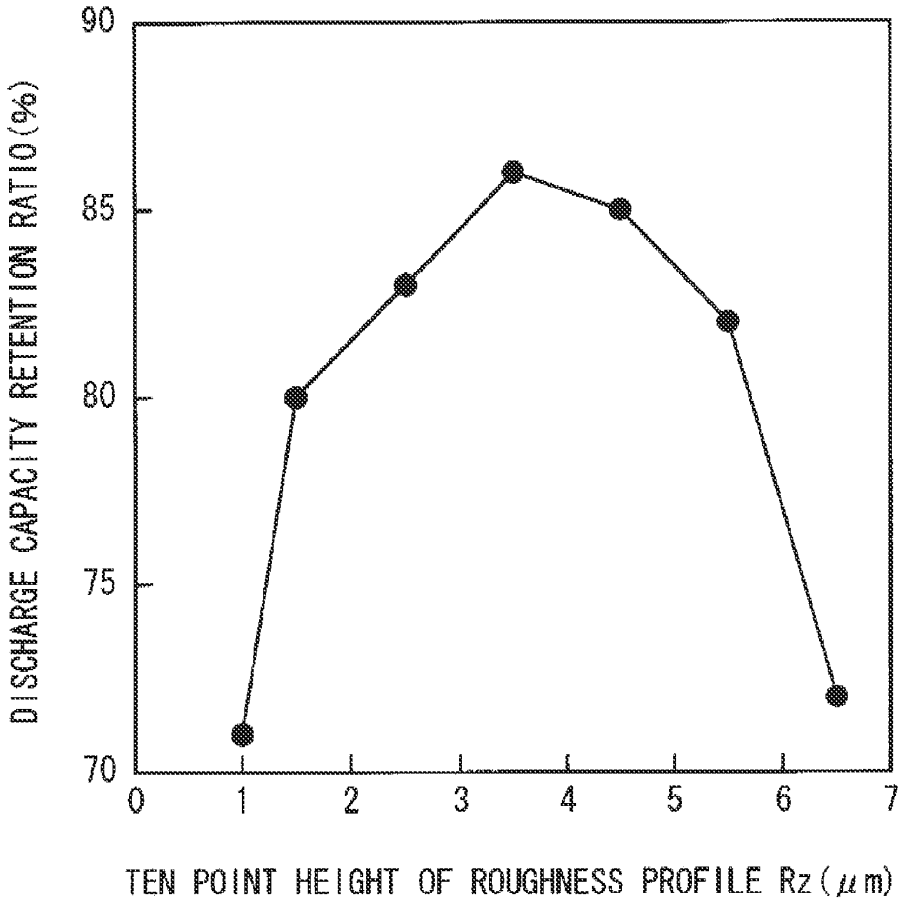

90
85
80
75
70
0
1
2
3
4
5
6
7
DISCHARGE CAPACITY RETENTION RATIO(%)
TEN POINT HEIGHT OF ROUGHNESS PROFILE Rz(μm)

FIG. 16

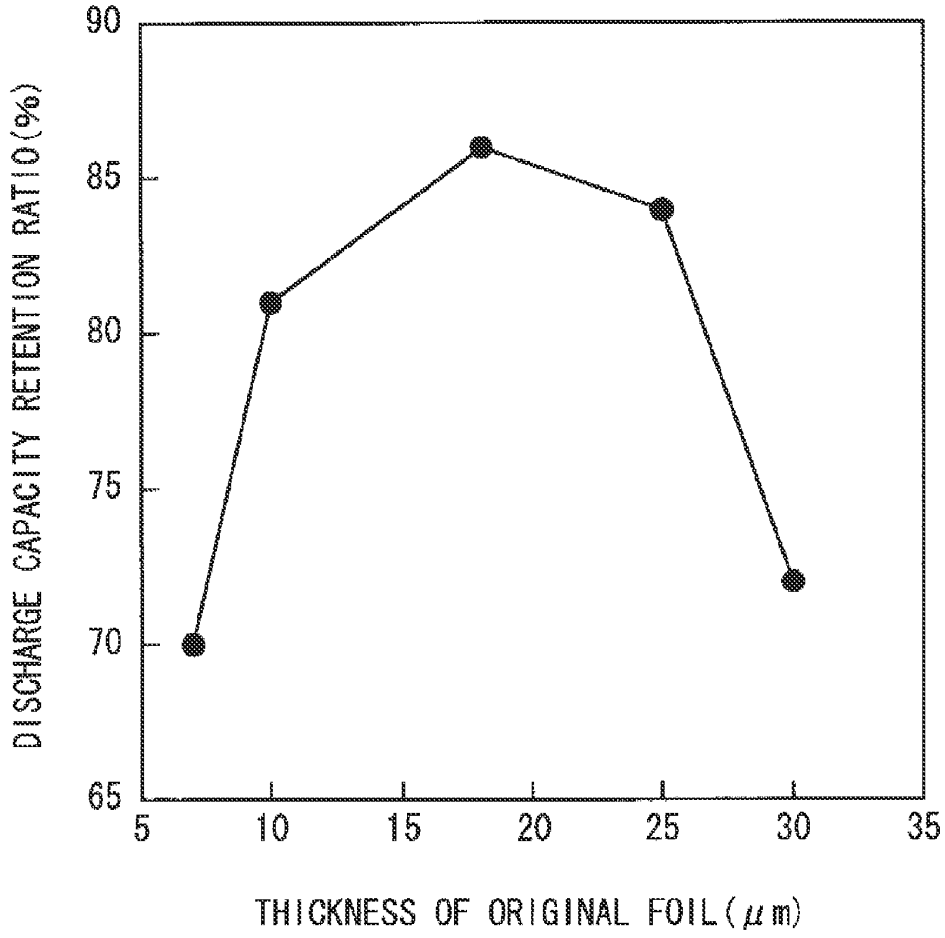

90
85
80
75
70
65
DISCHARGE CAPACITY RETENTION RATIO(%)
5
10
15
20
25
30
35
THICKNESS OF ORIGINAL FOIL(μm)

FIG. 17

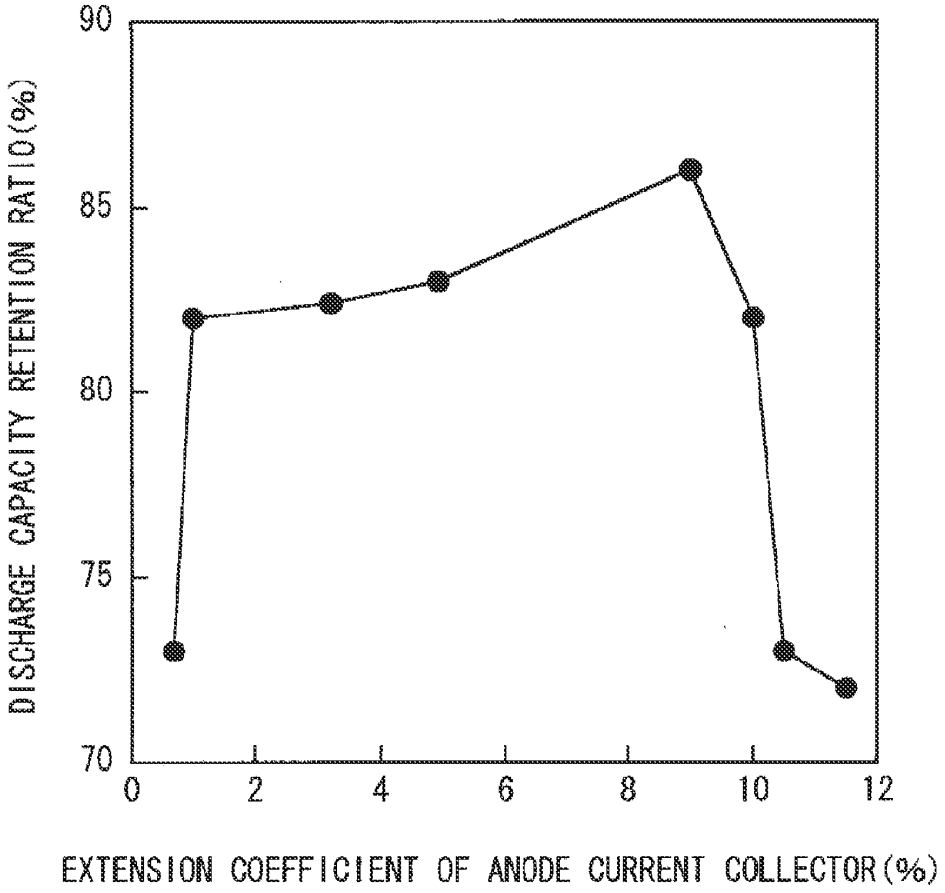

90
85
80
75
70
0
2
4
6
8
10
12
DISCHARGE CAPACITY RETENTION RATIO(%)
EXTENSION COEFFICIENT OF ANODE CURRENT COLLECTOR(%)

FIG. 18

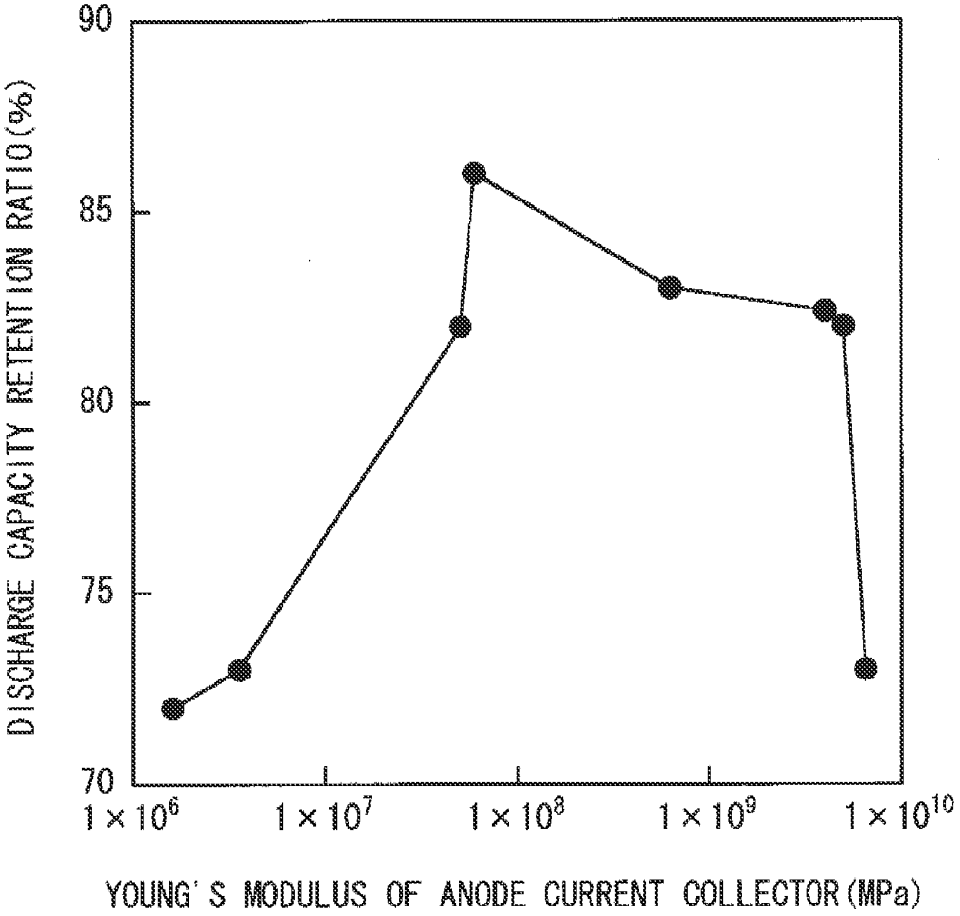

90
85
80
75
70
DISCHARGE CAPACITY RETENTION RATIO (%)
1 × 10^6
1 × 10^7
1 × 10^8
1 × 10^9
1 × 10^10
YOUNG'S MODULUS OF ANODE CURRENT COLLECTOR (MPa)

FIG. 19

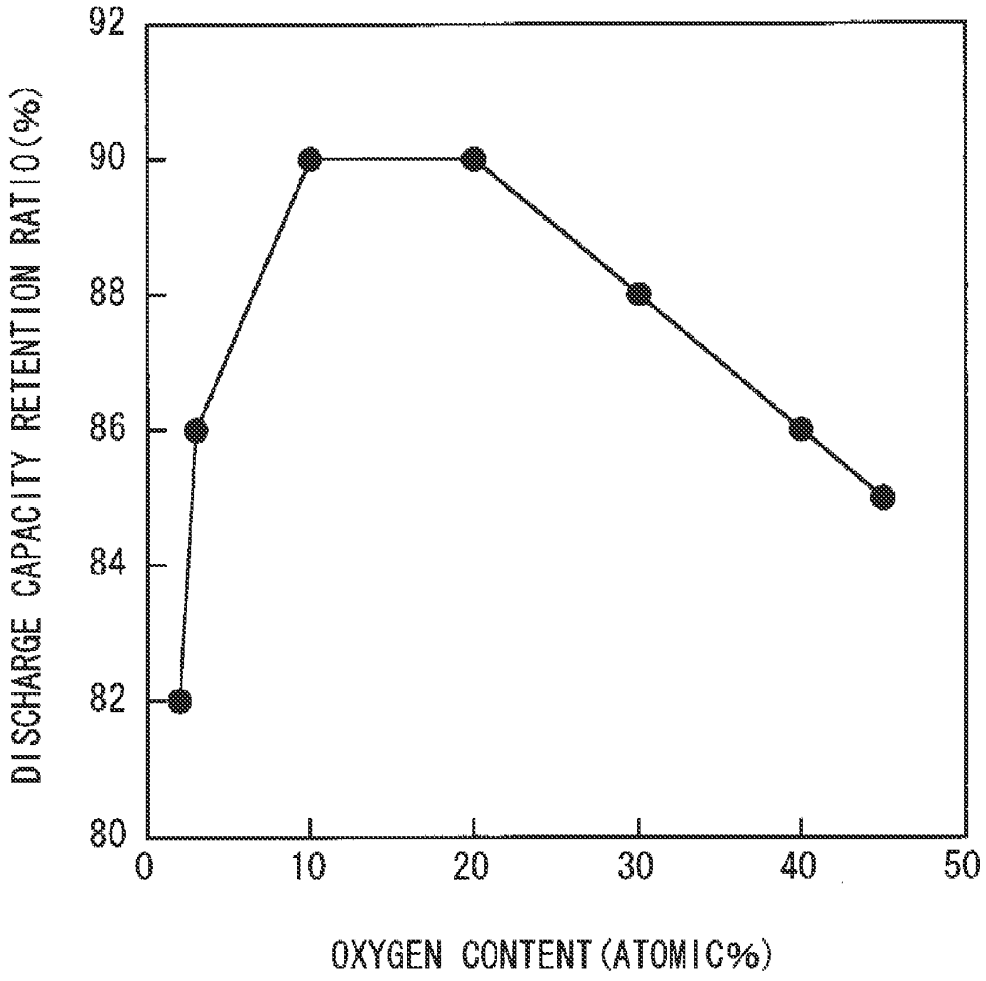

92
90
88
86
84
82
80
0
10
20
30
40
50
DISCHARGE CAPACITY RETENTION RATIO(%)
OXYGEN CONTENT(ATOMIC%)

FIG. 20

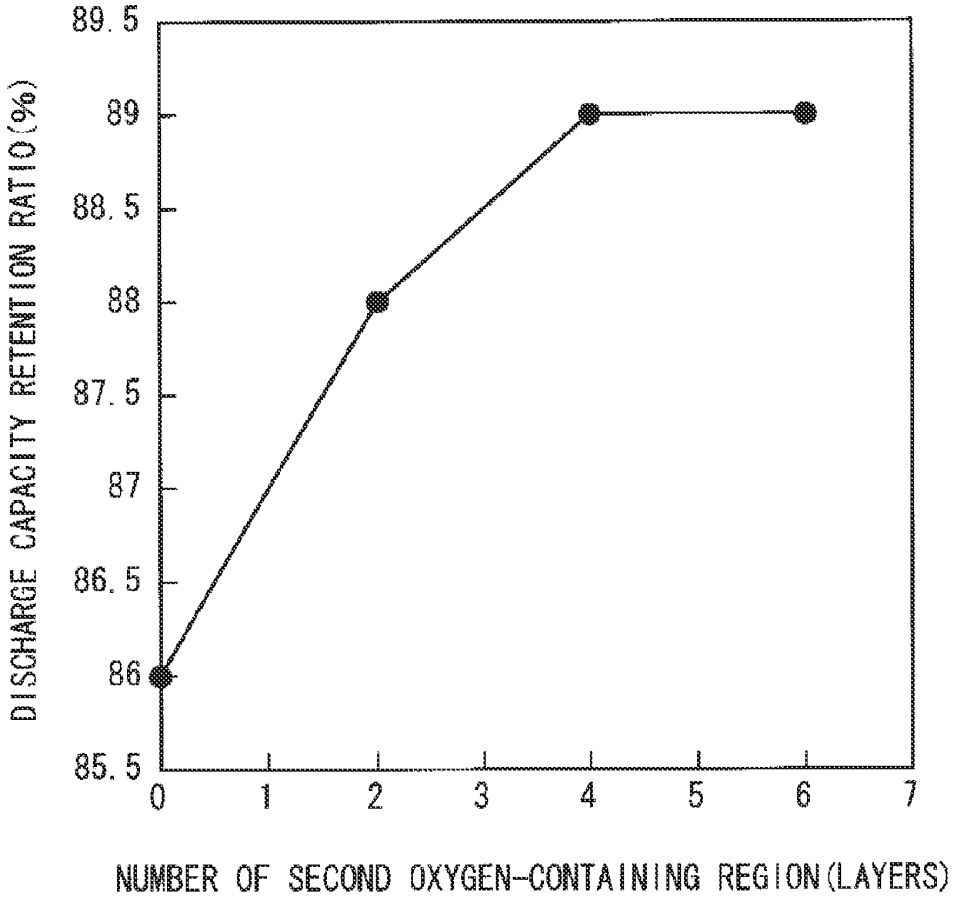

89.5
89
88.5
88
87.5
87
86.5
86
85.5
DISCHARGE CAPACITY RETENTION RATIO(%)
0
1
2
3
4
5
6
7
NUMBER OF SECOND OXYGEN-CONTAINING REGION(LAYERS)

FIG. 21

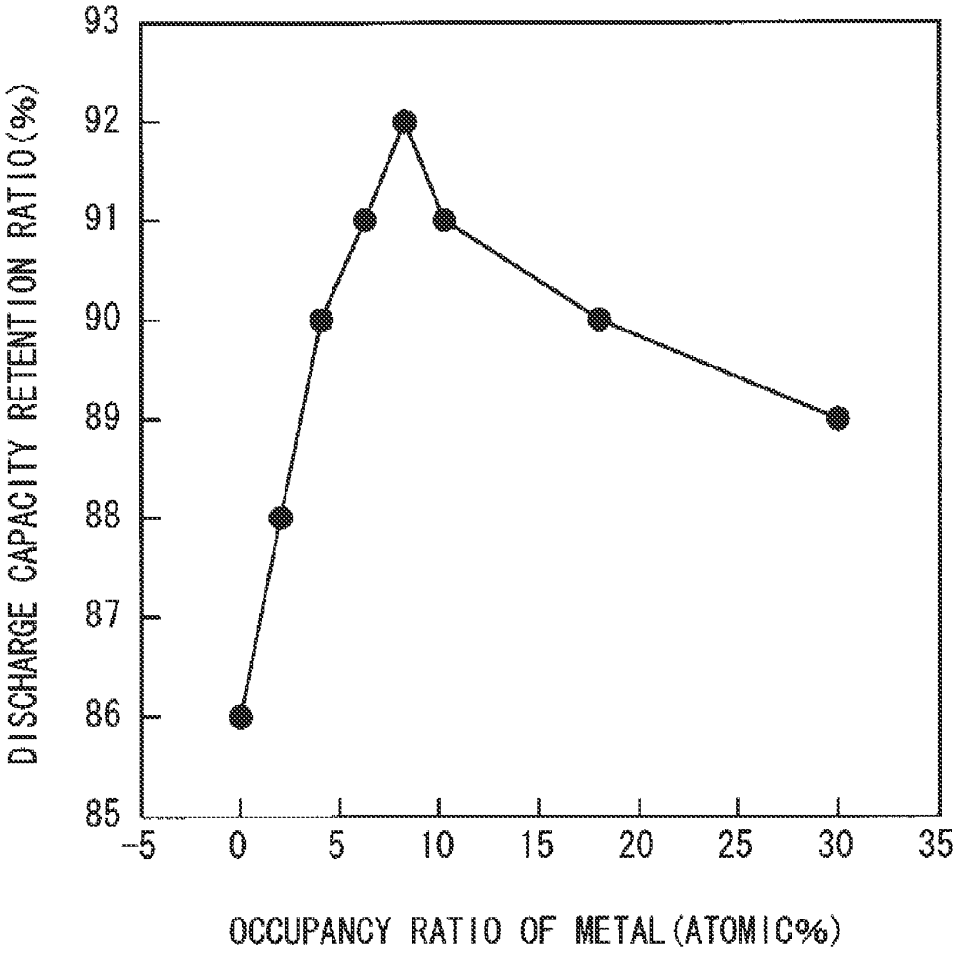

DISCHARGE CAPACITY RETENTION RATIO(%)
93
92
91
90
89
88
87
86
85
-5
0
5
10
15
20
25
30
35
OCCUPANCY RATIO OF METAL(ATOMIC%)

FIG. 22

FIG. 23A

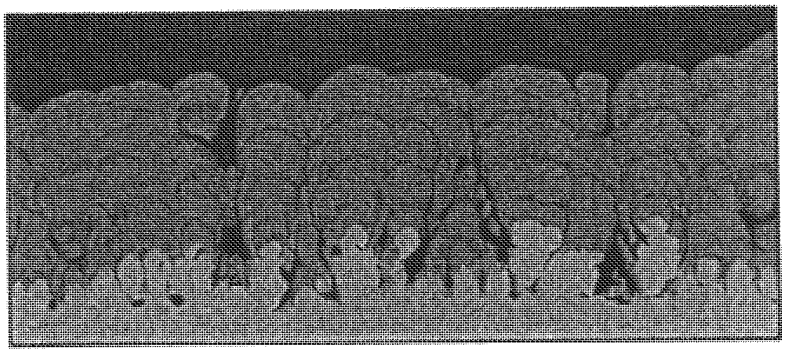
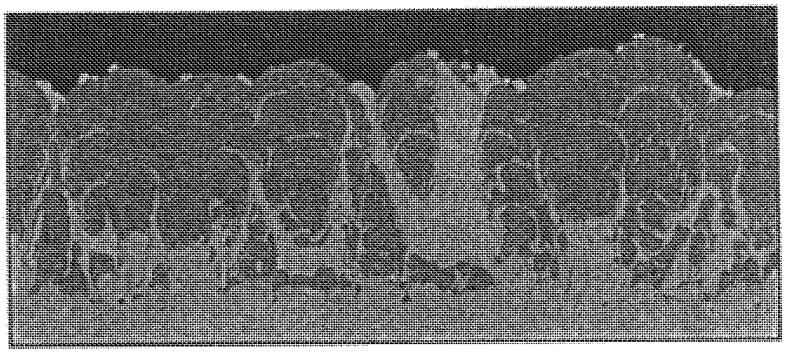


FIG. 23B



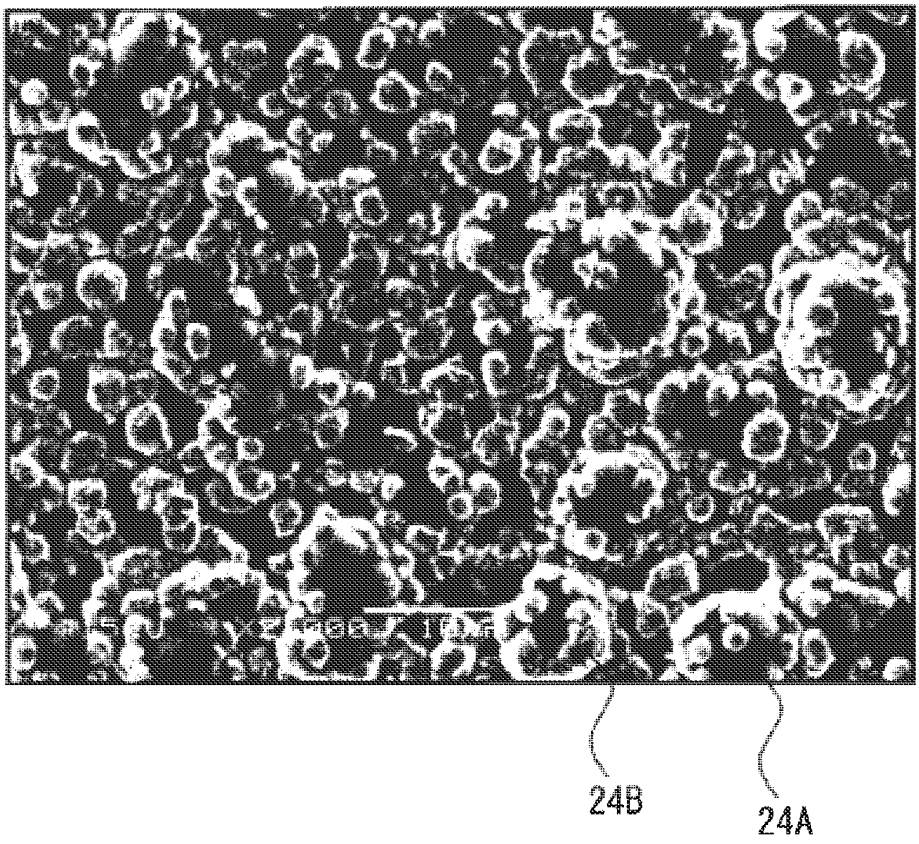
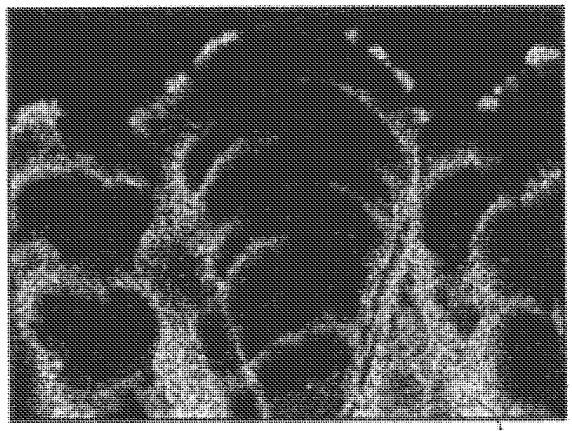


FIG. 24

FIG. 25A



FIG. 25B



CURRENT COLLECTOR, ANODE, AND BATTREY

CROSS REFERENCES TO RELATED APPLICATIONS

[0001] The present invention contains subject matter related to Japanese Patent Application JP 2007-136815 filed in the Japanese Patent Office on May 23, 2008, the entire contents of which being incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a current collector containing copper, and an anode and a battery using it.

[0004] 2. Description of the Related Art

[0005] In recent years, portable electronic devices such as combination cameras (videotape recorder), mobile phones, and notebook personal computers have been widely used, and it is strongly demanded to reduce their size and weight and to achieve their long life. Accordingly, as a power source for the portable electronic devices, a battery, in particular a light-weight secondary batter capable of providing a high energy density has been developed.

[0006] Specially, a secondary battery using insertion and extraction of lithium for charge and discharge reaction (so-called lithium ion secondary battery) is extremely prospective, since such a secondary battery provides a higher energy density compared to a lead battery and a nickel cadmium battery.

[0007] The lithium ion secondary battery has a cathode, an anode, and an electrolytic solution. The anode has a structure in which an active material layer is provided on a current collector. The active material layer contains an active material contributing to electrode reaction. As the active material of the anode, a carbon material has been widely used. However, in recent years, as the high performance and the multi functions of the portable electronic devices are developed, further improvement in the battery capacity is demanded. Thus, it has been considered to use silicon instead of the carbon material. Since the theoretical capacity of silicon (4199 mAh/g) is significantly higher than the theoretical capacity of graphite (372 mAh/g), it is prospected that the battery capacity is thereby highly improved.

[0008] However, when silicon as an active material is deposited by vapor-phase deposition method, the active material layer tends to be hardly contacted with the current collector. Thus, according to the contact degree, the active material layer may be separated from the current collector when charge and discharge are repeated. If the active material layer is separated, electrode reaction of the anode is inhibited by lowering of the current collection characteristics or the like. In the result, the cycle characteristics as important characteristics of secondary batteries are lowered.

[0009] Therefore, to improve the cycle characteristics even when silicon is used as the active material of the anode, various devices have been invented. Specifically, a technique using a current collector having an extension coefficient of 13% or more (for example, refer to Japanese Unexamined Patent Application Publication No. 2005-135856), a technique using a current collector having arithmetic average roughness Ra of from 0.01 μm to 1 μm (for example, refer to Japanese Patent No. 3733066), a technique using a current collector having a tensile strength of 3.82 N/mm or more and having arithmetic average roughness Ra of from 0.01 μm to 1 μm (for example, refer to International Publication No. WO 01/29912) and the like have been proposed.

SUMMARY OF THE INVENTION

[0010] The recent portable electronic devices increasingly tend to become small, and the high performance and the multi functions tend to be increasingly developed. Accordingly, there is a tendency that charge and discharge of the secondary battery are frequently repeated, and thus the cycle characteristics are easily lowered. In particular, in the lithium ion secondary battery in which silicon is used as the active material of the anode to attain a high capacity, the active material layer is easily separated from the current collector due to expansion and shrinkage of the active material in charge and discharge as well, and accordingly the cycle characteristics are easily lowered significantly. Thus, further improvement of the cycle characteristics of the secondary battery is aspired.

[0011] In view of the foregoing, in the invention, it is desirable to provide a current collector, an anode, and a battery capable of improving the cycle characteristics.

[0012] According to an embodiment of the invention, there is provided a current collector containing copper. In the current collector, ratio I(200)/I (111) between intensity I (200) of a peak originated in (200) crystal plane of copper obtained by X-ray diffraction and intensity I (111) of a peak originated in (111) crystal plane thereof is in the range from 0.5 to 1.5.

[0013] According to an embodiment of the invention, there is provided an anode including a current collector and an active material layer provided thereon. In the anode, the current collector contains copper, and ratio I (200)/I(111) between intensity I (200) of a peak originated in (200) crystal plane of copper obtained by X-ray diffraction and intensity I (111) of a peak originated in (111) crystal plane thereof is in the range from 0.5 to 1.5.

[0014] According to an embodiment of the invention, there is provided a battery including a cathode, an anode, and an electrolytic solution. The anode includes a current collector and an active material layer provided thereon. In the battery, the current collector contains copper, and ratio I(200)/I(111) between intensity I (200) of a peak originated in (200) crystal plane of copper obtained by X-ray diffraction and intensity I (111) of a peak originated in (111) crystal plane thereof is in the range from 0.5 to 1.5.

[0015] According to the current collector and the anode of the embodiment of the invention, the current collector contains copper, and the intensity ratio I(200)/I(111) between the intensities of the peaks originated in the crystal planes of copper obtained by X-ray diffraction is in the range from 0.5 to 1.5. Thus, the contact characteristics between the current collector and the active material layer are improved. Therefore, according to the battery using the current collector or the anode of the embodiment of the invention, the cycle characteristics may be improved.

[0016] Other and further objects, features and advantages of the invention will appear more fully from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1 is a cross section showing a structure of an anode using a current collector according to an embodiment of the invention;

[0018] FIG. **2** is a schematic cross section showing enlarged part of the anode current collector shown in FIG. **1**;

[0019] FIGS. **3**A and **3**B are an SEM photograph showing a cross sectional structure of the anode shown in FIG. **1** and a schematic view thereof;

[0020] FIG. **4** is a cross section showing a structure of a first battery including the anode according to the embodiment of the invention;

[0021] FIG. **5** is a cross section taken along line V-V of the first battery shown in FIG. **4**;

[0022] FIG. **6** is a cross section showing a structure of a second battery including the anode according to the embodiment of the invention;

[0023] FIG. **7** is a cross section showing an enlarged part of the spirally wound electrode body shown in FIG. **6**;

[0024] FIG. **8** is a cross section showing a structure of a third battery including the anode according to the embodiment of the invention;

[0025] FIG. **9** is a cross section taken along line IX-IX of the spirally wound electrode body shown in FIG. **8**;

[0026] FIG. **10** is a diagram showing a correlation between an intensity ratio and a discharge capacity retention ratio;

[0027] FIGS. **11**A and **11**B are XRD analysis results of anodes (Examples 1-2 and 1-4);

[0028] FIG. **12** is a diagram showing another correlation between an intensity ratio and a discharge capacity retention ratio;

[0029] FIG. **13** is a diagram showing still another correlation between an intensity ratio and a discharge capacity retention ratio;

[0030] FIG. **14** is a diagram showing a correlation between a cross-section area of a crystallite and a discharge capacity retention ratio;

[0031] FIGS. **15**A and **15**B are SEM photographs showing cross sectional structures of anode current collectors (Examples 2-2 and 4-1);

[0032] FIG. **16** is a diagram showing a correlation between ten point height of roughness profile Rz and a discharge capacity retention ratio;

[0033] FIG. **17** is a diagram showing a correlation between a thickness of an original foil and a discharge capacity retention ratio;

[0034] FIG. **18** is a diagram showing a correlation between an extension coefficient of an anode current collector and a discharge capacity retention ratio;

[0035] FIG. **19** is a diagram showing a correlation between a Young's modulus of an anode current collector and a discharge capacity retention ratio;

[0036] FIG. **20** is a diagram showing a correlation between an oxygen content and a discharge capacity retention ratio;

[0037] FIG. **21** is a diagram showing a correlation between the number of second oxygen-containing regions and a discharge capacity retention ratio;

[0038] FIG. **22** is a diagram showing a correlation between a metal occupancy ratio and a discharge capacity retention ratio;

[0039] FIGS. **23**A and **23**B are SEM photographs showing cross sectional structures of anodes (Examples 2-2 and 13-4);

[0040] FIG. **24** is an SEM photograph showing a surface structure of the anode (Example 13-4); and

[0041] FIGS. **25**A and **25**B are EDX element distribution analysis results of a cross section of the anode (Example 13-4).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0042] An embodiment of the invention will be hereinafter described in detail with reference to the drawings.

[0043] FIG. **1** shows a cross sectional structure of an anode using a current collector according to an embodiment of the invention. The anode is used, for example, for an electrochemical device such as a battery. The anode has an anode current collector **1** having a pair of opposed faces and an anode active material layer **2** provided thereon.

[0044] The anode current collector **1** is made of a metal material having favorable electrochemical stability, a favorable electric conductivity, and a favorable mechanical strength, and contains copper. The anode current collector **1** contains copper for the following reasons. Firstly, copper has a high electric conductivity among metal materials, and a high electric conductivity is thereby obtained. Secondary, when an electrode reactant (for example, lithium) is a material not forming an intermetallic compound with copper, lowering of the current collectivity characteristics and separation of the anode active material layer **2** is prevented even on the case that the anode active material layer **2** is expanded or shrunk when an electrochemical device is operated (for example, a battery is charged and discharged). Thirdly, when the anode active material layer **2** is a material being alloyed with copper, the contact characteristics between the anode current collector **1** and the anode active material layer **2** are improved, and thus separation of the anode active material layer **2** is prevented.

[0045] The anode current collector **1** may contain other metal element together with copper. The other types of metal elements may be voluntarily selected according to conditions such as a purpose of the anode. In this case, the current collector **1** is not limited to simple substance of copper, but may be an alloy or other compound.

[0046] The anode current collector **1** may have a single layer structure or a multilayer structure. In the case where the anode current collector **1** has the multilayer structure, it is preferable that the layer adjacent to the anode active material layer **2** is made of a metal material being alloyed with the anode active material layer **2**, and layers not adjacent to the anode active material layer **2** are made of other metal material.

[0047] In particular, in the anode current collector **1**, ratio (intensity ratio) I(200)/I(111) between intensity I (200) of the peak originated in (200) crystal plane of copper obtained by X-ray diffraction and intensity I (111) of the peak originated in (111) crystal plane thereof is in the range from 0.5 to 1.5. In this case, the contact characteristics between the anode current collector **1** and the anode active material layer **2** are improved more than in the case that the intensity ratio I(200)/I(111) is out of the foregoing range, and therefore separation of the anode active material layer **2** is suppressed. In this case, in particular, even when the anode active material layer **2** contains silicon formed by vapor-phase deposition method, sufficient contact characteristics may be obtained. The intensity ratio I(200)/I(111) is calculated by analyzing the anode current collector **1** with the use of X-ray diffraction (XRD) device and measuring two intensities I(200) and I(111).

[0048] The anode current collector **1** has a plurality of copper crystallites. The crystallites are identified by, for example, observing a cross section of the anode current collector **1** with the use of a scanning electron microscope (SEM) or the like. The cross-section area of each crystallite is preferably 100 μm^2 or less. Thereby, the contact characteristics between the anode current collector **1** and the anode active material layer **2** are more improved. "The cross-section area of each crystallite" means a cross-section area occupied by each crystallite when, for example, the plurality of copper crystallites are identified in an SEM photograph (secondary electron image). The cross-section area is measured by, for example, exposing a cross section of the anode current collector **1** by a cross section polisher, and then observing the cross section with the use of a low-accelerated voltage SEM.

[0049] In the case that the anode active material layer **2** is expanded or shrunk when an electrochemical device is operated, the extension (flexibility) of the anode current collector **1** is extremely important. From this view, the extension coefficient of the anode current collector **1** is preferably in the range from 1% to 10%. In the case that the extension coefficient is smaller than 1%, the stress generated when the anode active material layer **2** is expanded and shrunk is hardly relaxed by the flexibility of the anode current collector **1**, and thus the anode active material layer **2** may be separated. In the case that the extension coefficient is larger than 10%, a wrinkle may be generated in the anode current collector **1** when the anode active material layer **2** is expanded and shrunk. In addition, the Young's modulus of the anode current collector **1** is preferably in the range from 5×10^7 MPa to 5×10^9 MPa, because the contact characteristics between the anode current collector **1** and the anode active material layer **2** are thereby improved.

[0050] The surface of the anode current collector **1** is preferably roughened. Thereby, due to the so-called anchor effect, the contact characteristics between the anode current collector **1** and the anode active material layer **2** are improved. In this case, it is enough that at least the surface of the anode current collector **1** opposed to the anode active material layer **2** is roughened. As a roughening method, for example, a method of forming fine particles by electrolytic treatment and the like is cited. The electrolytic treatment is a method of providing concavity and convexity by forming fine particles on the surface of a metal by electrolytic method in an electrolytic bath. When the metal is a copper foil, the copper foil provided with the electrolytic treatment is generally called "electrolytic copper foil."

[0051] Ten point height of roughness profile Rz of the surface of the anode current collector **1** is preferably in the range from 1.5 μm to 5.5 μm. If the ten point height of roughness profile Rz is smaller than 1.5 μm, the contact characteristics between the anode current collector **1** and the anode active material layer **2** may be lowered. Meanwhile, if the ten point height of roughness profile Rz is larger than 5.5 μm, there is a possibility that a favorable particle shape is not able to be obtained when the anode active material is deposited. The definition of the ten point height of roughness profile Rz is based on JIS B 0601.

[0052] FIG. **2** is a schematic view of an enlarged part of the anode current collector **1** shown in FIG. **1**. In the case where the anode current collector **1** is made of an electrolytic copper foil, the anode current collector **1** has, for example, a metal foil (so-called original foil) **1**A and a plurality of fine particles **1**B formed on the surface (for example, the both faces) thereof. In this case, the plurality of fine particles **1**B may be fixed to the original foil **1**A by being covered with a plated film **1**C. Thereby, a plurality of projections are provided for every position of the fine particle **1**B on the surface of the anode current collector **1**. The plated film **1**C is formed by, for example, covering plating or burn plating.

[0053] The thickness of the original foil **1**A is preferably in the range from 10 μm to 25 μm. If the thickness is smaller than 10 μm, the ratio occupied by the anode active material layer **2** is large in the case where the volume of the entire anode is constant and thus such a thickness is preferable to improve the anode performance, while there is a possibility that the anode is subject to thermal damage when forming the anode active material layer **2** by using evaporation method or the like associated with high heat. Meanwhile, if the thickness is larger than 25 μm, the flexibility of the entire anode is lowered and thus the anode performance may be lowered.

[0054] The anode active material layer **2** contains a plurality of anode active material particles containing silicon as an anode active material capable of inserting and extracting an electrode reactant. Silicon has the high ability to insert and extract the electrode reactant, and thereby provides a high energy density. The anode active material particle may be the simple substance, an alloy, or a compound of silicon; or a material having one or more phases thereof at least in part. One thereof may be used singly, or two or more thereof may be used by mixing. In the invention, "alloys" also include an alloy containing one or more metal elements and one or more metalloid elements, in addition to an alloy composed of two or more metal elements. It is needless to say that the "alloy" may contain a nonmetallic element. The texture thereof may be a solid solution, a eutectic crystal (eutectic mixture), an intermetallic compound, or a texture in which two or more of the foregoing textures coexist.

[0055] As the alloy of silicon, for example, an alloy having at least one selected from the group consisting of tin (Sn), nickel, copper, iron, cobalt, manganese (Mn), zinc, indium (In), silver (Ag), titanium, germanium (Ge), bismuth (Bi), antimony (Sb), and chromium as an element other than silicon is cited

[0056] As the compound of silicon, for example, a compound having oxygen and carbon (C) as an element other than silicon is cited. The compound of silicon may contain, for example, one or more of elements described for the alloy of silicon as an element other than silicon.

[0057] The anode active material particle is linked to the anode current collector **1**. The anode active material particle is grown from the surface of the anode current collector **1** in the thickness direction of the anode active material layer **2**. In this case, it is preferable that the anode active material particle is formed by vapor-phase deposition method, and at least part of the interface between the anode current collector **1** and the anode active material layer **2** is alloyed as described above. Specifically, at the interface thereof, the element of the anode current collector **1** may be diffused in the anode active material particle, or the element of the anode active material particle may be diffused in the anode current collector **1**, or both elements may be diffused therein each other. Thereby, breakage due to expansion and shrinkage of the anode active material layer **2** hardly occurs when the electrochemical device is operated, and the electron conductivity between the anode current collector **1** and the anode active material layer **2** is improved.

[0058] As the foregoing vapor-phase deposition method, for example, physical deposition method or chemical deposition method is cited. More specifically, vacuum evaporation method, sputtering method, ion plating method, laser ablation method, thermal chemical vapor deposition (CVD) method, plasma CVD method and the like are cited.

[0059] The anode active material particle may have a single layer structure by being formed through a single deposition step. Otherwise, the anode active material particle may have a multilayer structure in the particle by being formed through a plurality of deposition steps. However, to prevent the anode current collector **1** from being excessively damaged thermally in the case where the anode active material particle is deposited by evaporation method or the like associated with high heat in the deposition step, the anode active material particle preferably has the multilayer structure. In the case where the deposition step of the anode active material particle is divided into several steps (the anode active material particles are sequentially deposited and layered), time that the anode current collector **1** is exposed at high heat is reduced compared to a case that the anode active material particle is deposited by a single deposition step.

[0060] The anode active material particle preferably contains oxygen together with silicon, since thereby expansion and shrinkage of the anode active material layer **2** are prevented. In this case, at least part of oxygen is preferably bonded to part of silicon. The bonding state may be in the form of silicon monoxide, silicon dioxide, or in the form of other metastable state.

[0061] The oxygen content in the anode active material particle is preferably in the range from 3 atomic % to 40 atomic %, since thereby higher effects may be obtained. More specifically, if the oxygen content is smaller than 3 atomic %, there is a possibility that expansion and shrinkage of the anode active material layer **2** are not sufficiently prevented. Meanwhile, if the oxygen content is larger than 40 atomic %, the resistance may be excessively increased. In the case where the anode is used together with an electrolytic solution in an electrochemical device, the anode active material particle does not include a coat formed by decomposition reaction of the electrolytic solution and the like. That is, when the oxygen content in the anode active material particle is calculated, oxygen in such a coat described above is not included in the calculation.

[0062] The anode active material particle containing oxygen is formed by continuously introducing oxygen gas into a chamber when the anode active material particle is formed by vapor-phase deposition method. In particular, when a desired oxygen content is not obtained only by introducing the oxygen gas, a liquid (for example, moisture vapor or the like) may be introduced into the chamber as a supply source of oxygen.

[0063] Further, the anode active material particle may contain a metal element together with silicon. Thereby, expansion and shrinkage of the anode active material layer **2** are prevented. As the metal element, for example, at least one metal element selected from the group consisting of iron, cobalt, nickel, titanium, chromium, and molybdenum is cited. The content of metal element in the anode active material particle may be voluntarily set. However, in the case of using the anode for a battery, an excessively high content of the metal element is not practical, since in such a case, the thickness of the anode active material layer **2** should be increased to obtain a desired battery capacity, and thereby separation and cracks of the anode active material layer **2** may be easily caused.

[0064] The anode active material particle having the foregoing metal element may be formed by, for example, using an evaporation source mixed with the metal element or using multiple evaporation sources when the anode active material particle is formed by evaporation method as vapor-phase deposition method.

[0065] Further, the anode active material particle preferably has an oxygen-containing region in which the anode active material particle contains oxygen together with silicon in the thickness direction, and the oxygen content in the oxygen-containing region is preferably larger than the oxygen content in the other regions. Thereby, expansion and shrinkage of the anode active material layer **2** are prevented. It is possible that the regions other than the oxygen-containing region also contains oxygen, or do not contain oxygen. It is needless to say that in the case where the regions other than the oxygen-containing region also contain oxygen, the oxygen content thereof is lower than the oxygen content in the oxygen-containing region.

[0066] In this case, to further prevent expansion and shrinkage of the anode active material layer **2**, the regions other than the oxygen-containing region preferably also contain oxygen, and the anode active material particle preferably includes a first oxygen-containing region (region having the lower oxygen content) and a second oxygen-containing region having the higher oxygen content than that of the first oxygen-containing region (region having the higher oxygen content). In particular, it is preferable that the second oxygen-containing region is sandwiched between the first oxygen-containing regions. It is more preferable that the first oxygen-containing region and the second oxygen-containing region are alternately and repeatedly layered. Thereby, higher effects may be obtained. The oxygen content in the first oxygen-containing region is preferably small as much as possible. The oxygen content in the second oxygen-containing region is, for example, similar to the oxygen content in the case that the anode active material particle contains oxygen described above.

[0067] The anode active material particle including the first oxygen-containing region and the second oxygen-containing region may be formed, for example, by intermittently introducing oxygen gas into a chamber when the anode active material particle is formed by vapor-phase deposition method. It is needless to say that when a desired oxygen content is not able to be obtained only by introducing the oxygen gas, liquid (for example, moisture vapor or the like) may be introduced into the chamber.

[0068] It is possible that the oxygen content of the first oxygen-containing region is clearly different from the oxygen content of the second oxygen-containing region, or the oxygen content of the first oxygen-containing region is not clearly different from the oxygen content of the second oxygen-containing region. In particular, in the case where the introduction amount of the foregoing oxygen gas is continuously changed, the oxygen content may be continuously changed. In the case where the introduction amount of the oxygen gas is intermittently changed, the first oxygen-containing region and the second oxygen-containing region become so-called "layers." Meanwhile, in the case where the introduction amount of the oxygen gas is continuously changed, the first oxygen-containing region and the second

oxygen-containing region become "lamellar state" rather than "layers." In the latter case, the oxygen content in the anode active material particle is distributed with repeated increase and decrease. In this case, it is preferable that the oxygen content is gradually or continuously changed between the first oxygen-containing region and the second oxygen-containing region. If the oxygen content is changed drastically, the ion diffusion characteristics may be lowered, or the resistance may be increased.

[0069] In particular, the anode active material layer **2** preferably contains a metal containing a metal element not being alloyed with the electrode reactant together with the anode active material particle. Since each anode active material particle is bound to each other through the metal, expansion and shrinkage of the anode active material layer **2** are prevented. "Metal" is a comprehensive term, and thus the metal may be one of a simple substance, an alloy, and a compound, as long as the metal contains a metal element not being alloyed with the electrode reactant. In this case, in particular, even when the anode active material particle is formed by vapor-phase deposition method or the like, high binding characteristics may be obtained. Examples of the metal elements include, for example, at least one selected from the group consisting of iron, cobalt, nickel, zinc, and copper.

[0070] As described above, the metal is provided in a gap between adjacent anode active material particles, in the case that the anode active material particle is grown from the surface of the anode current collector **1** in the thickness direction of the anode active material layer **2**. Further, for example, the metal covers at least part of the exposed face of the anode active material particle, that is, at least part of the surface of the anode active material particle not adjacent to other anode active material particle. Furthermore, when the anode active material particle has a multilayer structure in the particle, the metal is provided in a gap in the particle.

[0071] FIGS. **3**A and **3**B show an enlarged part of the anode shown in FIG. **1**. FIG. **3**A is an SEM photograph, and FIG. **3**B is a schematic drawing of the SEM image shown in FIG. **3**A. In FIG. **3**A, the non-hatched section in FIG. **3**B is an anode active material particle **201**, and the hatched section in FIG. **3**B is a metal **202**. FIGS. **3**A and **3**B show a case that the anode active material particle **201** has the multilayer structure in the particle.

[0072] As shown in FIGS. **3**A and **3**B, the anode active material particle **201** deposited several times on the surface of the anode current collector **1** has the multilayer structure in the particle. In this case, the surface of the anode current collector **1** is roughened (a plurality of projections exist on the surface of the anode current collector **1**). Thus, the anode active material particle **201** is gradually grown in the thickness direction for every projection. For example, the metal material **202** is provided in the gap between adjacent anode active material particles **201** (metal **202**A), the metal **202** partly covers the exposed face of the anode active material particle **201** (metal **202**B), and the metal **202** is provided in the gap in the anode active material particle **201** (metal **202**C).

[0073] The metal **202**A fills the gap between adjacent anode active material particles to improve the binding characteristics of the anode active material layer **2**. More specifically, in the case where the anode active material particle **201** is formed by vapor-phase deposition method or the like, the anode active material particles **201** are grown for every projection existing on the surface of the anode current collector **1** as described above, and thus the gap is generated between the adjacent anode active material particles **201**. The gap causes lowering of the binding characteristics of the anode active material layer **2**. Therefore, to improve the binding characteristics, the metal **202**A fills in the foregoing gap. In this case, it is enough that part of the gap is filled therewith, but the larger filling amount is preferable, since thereby the binding characteristics of the anode active material layer **2** are more improved. The filling amount of the metal material **202**A is preferably 20% or more, more preferably 40% or more, and much more preferably 80% or more.

[0074] To prevent a fibrous minute projection (not shown) generated on the exposed face of the uppermost layer of the anode active material particle **201** from adversely affecting the performance of the electrochemical device, the metal **202**B covers such a projection. More specifically, in the case where the anode active material particle **201** is formed by vapor-phase deposition method or the like, the fibrous minute projections are generated on the surface thereof, and thus a void is generated between the projections. The void causes increase of the surface area of the anode active material particle **201**, and accordingly the amount of an irreversible coat formed on the surface is also increased, possibly resulting in lowering of progression of the electrode reaction. Therefore, to avoid the lowering of progression of the electrode reaction, the foregoing void is filled with the metal **202**B. In this case, it is enough at minimum that part of the void is filled therewith, but the larger filling amount is preferable, since thereby the lowering of progression of the electrode reaction is more suppressed. In FIGS. **3**A and **3**B, the metal **202**B is dotted on the surface of the uppermost layer of the anode active material particle **201**, which means that the foregoing minute projection exists in the location where the metal **202**B is dotted.

[0075] The metal **202**C intrudes into the gap in the anode active material particle **201** to improve the biding characteristics of the anode active material layer **2**. More specifically, in the case where the anode active material particle **201** has a multilayer structure, a gap is generated between each layer. The gap may cause lowering of the biding characteristics of the anode active material layer **2** as well as the foregoing gap between adjacent anode active material particles **201** may do. Therefore, to improve the biding characteristics, the foregoing gap is filled with the metal **202**C. In this case, it is enough that part of the gap is filled therewith, but the larger filling amount is preferable, since thereby the binding characteristics of the anode active material layer **2** are more improved.

[0076] In particular, the metal material **202**C has a function similar to that of the metal **202**B. More specifically, in the case where the anode active material particle **201** is deposited several times and thereby layered, the foregoing minute projection is generated on the surface of the anode active material particle **201** for every deposition. Therefore, the metal **202**C fills in not only the gap in the anode active material particle **201**, but also the foregoing minute void.

[0077] The metal is formed by, for example, at least one selected from the group consisting of vapor-phase deposition method and liquid-phase deposition method. Specially, the metal is preferably formed by liquid-phase deposition method. Thereby, the gap described with reference to FIGS. **3**A and **3**B is easily filled with the metal. In addition, in this case, the metal easily fills in the void.

[0078] Examples of the foregoing vapor-phase deposition method include, for example, a method similar to that used in forming the anode active material particle. Examples of the liquid-phase deposition method include, for example, plating

method such as electrolytic plating method and electroless plating method. Specially, as the liquid-phase deposition method, electrolytic plating method is more preferable than electroless plating method. Thereby, higher effects may be obtained.

[0079] The ratio (molar ratio) M2/M1 between the number of moles M1 per unit area of the anode active material particle and the number of moles M2 per unit area of the metal is preferably in the range from 1/15 to 3/1. The ratio of the number of atoms occupied by the metal (occupancy ratio of the metal) on the surface of the anode is preferably in the range from 2 atomic % to 30 atomic %. Thereby, expansion and shrinkage of the anode active material layer **2** are prevented. The occupancy ratio of the metal may be measured by, for example, performing element analysis of the anode surface with the use of, for example, energy dispersive X-ray fluorescence spectroscopy (EDX).

[0080] Further, the metal may have oxygen, since thereby expansion and shrinkage of the anode active material layer **2** are more suppressed. The oxygen content in the metal may be voluntarily set. The metal containing oxygen may be formed, for example, by a procedure similar to that used in forming the anode active material particle containing oxygen.

[0081] The anode is formed, for example, by the following procedure.

[0082] First, the anode current collector **1** containing copper is prepared. After that, the plurality of anode active material particles containing silicon are formed on the anode current collector **1** by using vapor-phase deposition method or the like. The anode current collector **1** may be prepared by providing electrolytic treatment for the original foil **1**A to form the plurality of fine particles **1**B and the plated film **1**C. Further, the anode active material particle may be formed into a single layer structure by one time deposition step, or a multilayer structure by a plurality of deposition steps. After that, the metal that has a metal element not being alloyed with the electrode reactant is formed by liquid-phase deposition method or the like. Thereby, the metal intrudes into a gap between adjacent anode active material particles, and thus the anode active material layer **2** is formed. In this case, for example, at least part of the exposed face of the anode active material particle is covered with the metal. Meanwhile, for example, in the case where the anode active material particle is formed into the multilayer structure, the metal intrudes into a gap in the anode active material particle.

[0083] In particular, when the anode is manufactured, by heating (so-called annealing) the anode current collector **1** in a given step, the intensity ratio I(200)/I(111) between the intensities of the peaks originated in the copper crystal planes obtained by X-ray diffraction is set in the range from 0.5 to 1.5. In this case, annealing may be performed before or after the anode active material layer **2** is formed. Annealing temperatures of the anode current collector **1** may be voluntarily set according to the value of the foregoing intensity ratio I(200)/I(111).

[0084] Further, it is preferable that the original foil **1**A having a thickness of from 10 μm to 25 μm is used, and the anode current collector having an extension coefficient of from 1% to 10% and Young's modulus of from 5×10^7 MPa to 5×10^9 MPa is used. In this case, it is preferable that the original foil **1**A is annealed to set the cross-section area of each copper crystallite to 100 μm^2 or less. Annealing temperature of the original foil **1**A may be voluntarily set according to the foregoing value of the cross-section area.

[0085] According to the anode using the current collector, the anode current collector **1** contains copper, and the intensity ratio I(200)/I(111) between the intensities of the peaks originated in the copper crystal planes obtained by X-ray diffraction is in the range from 0.5 to 1.5. Therefore, the contact characteristics between the anode current collector **1** and the anode active material layer **2** are improved more than in the case that the intensity ratio I(200)/I(111) is out of the foregoing range. Thereby, the anode active material layer **2** is prevented from being separated from the anode current collector **1**. In this case, if the anode current collector **1** is made of the electrolytic copper foil, in the case that the contact characteristics between the anode current collector **1** (plated film **1**C) and the anode active material layer **2** are sufficient, the plated film **1**C is prevented from being separated from the original foil **1**A and the fine particle **1**B, and the fine particle **1**B and the plated film **1**C are prevented from being separated from the original foil **1**A as well. Accordingly, the electric characteristics such as the electric conductivity may be improved. In particular, if the anode active material particle of the anode active material layer **2** contains silicon and the anode active material particle is deposited by vapor-phase deposition method, the contact characteristics are easily lowered due to expansion and shrinkage of the anode active material layer **2**. In this case, the anode using the anode current collector is used, significant effects may be obtained.

[0086] Further, when the cross-section area of the copper crystallite is 100 μm^2 or less, or the thickness of the original foil **1**A is in the range from 10 μm to 25 μm, or the extension coefficient of the anode current collector **1** is in the range from 1% to 10% and the Young's modulus thereof is in the range from 5×10^7 MPa to 5×10^9 MPa, or the ten point height of roughness profile Rz of the surface of the anode current collector **1** is in the range from 1.5 μm to 5.5 μm, higher effects may be obtained. In addition, at least part of the interface between the anode current collector **1** and the anode active material layer **2** is alloyed, higher effects may be obtained.

[0087] Further, in the case that the anode active material layer **2** has the plurality of anode active material particles containing silicon, if the anode active material particles further contain oxygen and the oxygen content in the anode active materials is in the range from 3 atomic % to 40 atomic %, or if the anode active material particles further have the oxygen-containing region containing oxygen in the thickness direction and the oxygen content in the oxygen-containing region is higher than that of the other regions, higher effects may be obtained.

[0088] Further, if the anode active material layer **2** has the metal containing the metal element not being alloyed with the electrode reactant in the gap between the anode active material particles, each anode active material particle is bound to each other through the metal, and thus pulverization and falling of the anode active material layer **2** may be prevented. In particular, if the metal covers at least part of the exposed face of the anode active material particle, the adverse effect by the fibrous minute projection generated on the exposed face may be prevented. Further, in the case that the anode active material particle has the multilayer structure in the particle, if the anode active material layer **2** has the metal in the gap in the particle, pulverization and falling of the anode active material layer **2** may be prevented as in the case that the anode active material layer **2** has the metal in the gap between the anode active material particles as described above. In this case,

when the molar ratio M2/M1 between the anode active material particle and the metal is in the range from 1/15 to 3/1, or the occupancy ratio of the metal on the surface of the anode active material layer **2** is in the range from 2 atomic % to 30 atomic %, higher effects may be obtained. Further, when the metal is formed by liquid-phase deposition method, the metal easily intrudes into the gap between each anode active material particle and a gap in the anode active material particle, and the metal easily fills in a void between the fibrous minute projections, and thus higher effects may be obtained.

[0089] Next, a description will be hereinafter given of a usage example of the foregoing anode. As an example of the electrochemical devices, batteries are herein taken. The anode is used for the batteries as follows.

First Battery

[0090] FIG. **4** and FIG. **5** show a cross sectional structure of a first battery. FIG. **5** shows a cross section taken along line V-V shown in FIG. **4**. The battery herein described is, for example, a lithium ion secondary battery in which the capacity of an anode **22** is expressed based on insertion and extraction of lithium as an electrode reactant.

[0091] The secondary battery contains a battery element **20** having a flat spirally wound structure inside a battery can **11**.

[0092] The battery can **11** is, for example, a square package member. The battery structure including the battery can **11** is the so-called square structure. As shown in FIG. **5**, the square package member has a shape with the cross section in the longitudinal direction of a rectangle or an approximate rectangle (including curved lines in part). The battery can **11** structures not only a square battery in the shape of a rectangle, but also a square battery in the shape of an oval. That is, the square package member means a rectangle vessel-like member with the bottom or an oval vessel-like member with the bottom, which respectively has an opening in the shape of a rectangle or in the shape of an approximate rectangle (oval shape) formed by connecting circular arcs by straight lines. FIG. **5** shows a case that the battery can **11** has a rectangular cross sectional shape.

[0093] The battery can **11** is made of, for example, a metal material containing iron, aluminum (Al), or an alloy thereof. The battery can **11** may have a function as an anode terminal as well. In this case, to inhibit the secondary battery from being swollen by using the rigidity (hardly deformable characteristics) of the battery can **11** when charged and discharged, the battery can **11** is preferably made of rigid iron (or the alloy thereof) than aluminum. When the battery can **11** is made of iron, for example, the iron may be plated by nickel (Ni) or the like.

[0094] The battery can **11** also has a hollow structure in which one end of the battery can **11** is closed and the other end thereof is opened. At the open end of the battery can **11**, an insulating plate **12** and a battery cover **13** are attached, and thereby inside of the battery can **11** is hermetically closed. The insulating plate **12** is located between the battery element **20** and the battery cover **13**, is arranged perpendicularly to the spirally wound circumferential face of the battery element **20**, and is made of, for example, polypropylene or the like. The battery cover **13** is, for example, made of a material similar to that of the battery can **11**, and also has a function as an anode terminal as the battery can **11** does.

[0095] Outside of the battery cover **13**, a terminal plate **14** as a cathode terminal is arranged. The terminal plate **14** is electrically insulated from the battery cover **13** with an insulating case **16** in between. The insulating case **16** is made of, for example, polybutylene terephthalate or the like. In the approximate center of the battery cover **13**, a through-hole is provided. A cathode pin **15** is inserted in the through-hole so that the cathode pin **15** is electrically connected to the terminal plate **14** and is electrically insulated from the battery cover **13** with a gasket **17** in between. The gasket **17** is made of, for example, an insulating material, and the surface thereof is coated with asphalt.

[0096] In the vicinity of the rim of the battery cover **13**, a cleavage valve **18** and an injection hole **19** are provided. The cleavage valve **18** is electrically connected to the battery cover **13**. When the internal pressure of the battery becomes a certain level or more by internal short circuit, external heating or the like, the cleavage valve **18** is separated from the battery cover **13** to release the internal pressure. The injection hole **19** is sealed by a sealing member **19**A made of, for example, a stainless ball.

[0097] The battery element **20** is formed by layering a cathode **21** and the anode **22** with a separator **23** in between and then spirally winding the resultant laminated body. The battery element **20** is flat according to the shape of the battery can **11**. A cathode lead **24** made of aluminum or the like is attached to an end of the cathode **21** (for example, the internal end thereof). An anode lead **25** made of nickel or the like is attached to an end of the anode **22** (for example, the outer end thereof). The cathode lead **24** is electrically connected to the terminal plate **14** by being welded to an end of the cathode pin **15**. The anode lead **25** is welded and electrically connected to the battery can **11**.

[0098] In the cathode **21**, for example, a cathode active material layer **21**B is provided on the both faces of a strip-shaped cathode current collector **21**A. The cathode current collector **21**A is made of, for example, a metal material such as aluminum, nickel, and stainless. The cathode active material layer **21**B contains a cathode active material, and if necessary, may also contain a binder, a conductive material and the like.

[0099] The cathode active material contains one or more cathode materials capable of inserting and extracting lithium as an electrode reactant. As the cathode material, for example, a lithium complex oxide such as lithium cobalt oxide, lithium nickel oxide, a solid solution containing them ($Li(Ni_xCo_yMn_z)O_2$, values of x, y, and z are respectively expressed as $0<x<1$, $0<y<1$, $0<z<1$, and $x+y+z=1$), lithium manganese oxide having a spinel structure ($LiMn_2O_4$), and a solid solution thereof ($Li(Mn_{2-v}Ni_v)O_4$, a value of v is expressed as $v<2$). Further, as the cathode material, for example, a phosphate compound having an olivine structure such as lithium iron phosphate ($LiFePO_4$) is cited. Thereby, a high energy density may be obtained. In addition, as the cathode material, for example, an oxide such as titanium oxide, vanadium oxide, and manganese dioxide; a disulfide such as iron disulfide, titanium disulfide, and molybdenum sulfide; sulfur; a conductive polymer such as polyaniline and polythiophene is cited.

[0100] The anode **22** has a structure similar to that of the anode using the foregoing current collector. For example, in the anode **22**, an anode active material layer **22**B is provided on the both faces of a strip-shaped anode current collector **22**A. The structures of the anode current collector **22**A and the anode active material layer **22**B are respectively similar to the structures of the anode current collector **1** and the anode active material layer **2**. The charge capacity of the anode

active material capable of inserting and extracting lithium is preferably larger than the charge capacity of the cathode.

[0101] The separator **23** separates the cathode **21** from the anode **22**, and passes ions as an electrode reactant while preventing current short circuit due to contact of the both electrodes. The separator **23** is made of, for example, a porous film made of a synthetic resin such as polytetrafluoroethylene, polypropylene, and polyethylene, or a ceramic porous film. The separator **23** may have a structure in which two or more porous films as the foregoing porous films are layered.

[0102] An electrolytic solution as a liquid electrolyte is impregnated in the separator **23**. The electrolytic solution contains, for example, a solvent and an electrolyte salt dissolved therein.

[0103] The solvent contains, for example, one or more nonaqueous solvents such as an organic solvent. The nonaqueous solvents include, for example, an ester-based carbonate solvent such as ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, and methylpropyl carbonate. Thereby, superior capacity characteristics, superior storage characteristics, and superior cycle characteristics are obtained. One thereof may be used singly, or two or more thereof may be used by mixing. Specially, as the solvent, a mixture of a high-viscosity solvent such as ethylene carbonate and propylene carbonate and a low-viscosity solvent such as dimethyl carbonate, ethyl methyl carbonate, and diethyl carbonate is preferable. Thereby, the dissociation property of the electrolyte salt and the ion mobility are improved, and thus higher effects may be obtained.

[0104] In particular, the solvent preferably contains halogenated ester carbonate, since thereby a stable coat is formed on the surface of the anode **22**, and thus the decomposition reaction of the electrolytic solution is prevented and the cycle characteristics are improved. As the halogenated ester carbonate, fluorinated ester carbonate is preferable, and difluoroethylene carbonate is more preferable, since thereby higher effects may be obtained. As difluoroethylene carbonate, for example, 4,5-difluoro-1,3-dioxolane-2-one or the like is cited.

[0105] Further, the solvent preferably contains a cyclic ester carbonate having an unsaturated bond, since thereby the cycle characteristics are improved. As the cyclic ester carbonate having an unsaturated bond, for example, vinylene carbonate, vinyl ethylene carbonate and the like are cited.

[0106] Further, the solvent preferably contains sultone, since thereby the cycle characteristics are improved, and the secondary battery is prevented from being swollen. As the sultone, for example, 1,3-propenesultone or the like is cited.

[0107] The electrolyte salt contains, for example, one or more light metal salts such as a lithium salt. As the lithium salt, for example, lithium hexafluorophosphate ($LiPF_6$), lithium perchlorate ($LiClO_4$), lithium hexafluoroarsenate ($LiAsF_6$) or the like is cited. Thereby, superior capacity characteristics, superior storage characteristics, and superior cycle characteristics are obtained. One thereof may be used singly, or two or more thereof may be used by mixing. Specially, as the electrolyte salt, lithium hexafluorophosphate is preferable, since the internal resistance is lowered, and thus higher effects may be obtained.

[0108] In particular, the electrolyte salt preferably contains a compound having boron and fluorine, since thereby the cycle characteristics are improved. As the compound having boron and fluorine, for example, lithium tetrafluoroborate or the like is cited.

[0109] The content of the electrolyte salt in the solvent is preferably in the range from 0.3 mol/kg to 3.0 mol/kg, since thereby superior capacity characteristics may be obtained.

[0110] The secondary battery is manufactured, for example, by the following procedure.

[0111] First, the cathode **21** is formed. First, a cathode active material, a binder, and an electrical conductor are mixed to prepare a cathode mixture, which is dispersed in an organic solvent to form paste cathode mixture slurry. Subsequently, the both faces of the cathode current collector **21**A are uniformly coated with the cathode mixture slurry by using a doctor blade, a bar coater or the like, which is dried. Finally, the resultant is compression-molded by a rolling press machine or the like while being heated if necessary to form the cathode active material layer **21**B. In this case, the resultant may be compression molded over several times.

[0112] Next, the anode **22** is formed by forming the anode active material layer **22**B on the both faces of the anode current collector **22**A by the same procedure as that of forming the anode described above.

[0113] Further, the battery element **20** is formed by using the cathode **21** and the anode **22**. First, the cathode lead **24** and the anode lead **25** are respectively attached to the cathode current collector **21**A and the anode current collector **22**A by welding or the like. Subsequently, the cathode **21** and the anode **22** are layered with the separator **23** in between, and spirally wound in the longitudinal direction. After that, the resultant is formed in the flat shape, and thereby the battery element **20** is formed.

[0114] Finally, the secondary battery is assembled. That is, after the battery element **20** is contained in the battery can **11**, the insulating plate **12** is arranged on the battery element **20**. Subsequently, the cathode lead **24** and the anode lead **25** are respectively connected to the cathode pin **15** and the battery can **11** by welding or the like. After that, the battery cover **13** is fixed on the open end of the battery can **11** by laser welding or the like. Finally, the electrolytic solution is injected into the battery can **11** from the injection hole **19**, and impregnated in the separator **23**. After that, the injection hole **19** is sealed by the sealing member **19**A. The secondary battery shown in FIG. **4** and FIG. **5** is thereby completed.

[0115] In the secondary battery, when charged, for example, lithium ions are extracted from the cathode **21**, and are inserted in the anode **22** through the electrolytic solution impregnated in the separator **23**. Meanwhile, when discharged, for example, lithium ions are extracted from the anode **22**, and are inserted in the cathode **21** through the electrolytic solution impregnated in the separator **23**.

[0116] According to the square secondary battery, since the anode **22** has the structure similar to that of the foregoing anode, the contact characteristics between the anode current collector **22**A and the anode active material layer **22**B are improved. Accordingly, the cycle characteristics may be improved. In this case, the cycle characteristics are improved if the anode **22** contains silicon advantageous for obtaining a high capacity. Thus, higher effects may be thereby obtained compared to a case in which the anode contains other anode material such as a carbon material. Effects of the secondary battery other than the foregoing effects are similar to those of the foregoing anode.

Second Battery

[0117] FIG. **6** and FIG. **7** show a cross sectional structure of a second battery. FIG. **7** shows an enlarged part of a spirally

wound electrode body **40** shown in FIG. **6**. The battery is a lithium ion secondary battery as the foregoing first battery. The second battery contains the spirally wound electrode body **40** in which a cathode **41** and an anode **42** are spirally wound with a separator **43** in between, and a pair of insulating plates **32** and **33** inside a battery can **31** in the shape of an approximately hollow cylinder. The battery structure including the battery can **31** is a so-called cylindrical secondary battery.

[0118] The battery can **31** is made of, for example, a metal material similar to that of the battery can **11** in the foregoing first battery. One end of the battery can **31** is closed, and the other end thereof is opened. The pair of insulating plates **32** and **33** is arranged to sandwich the spirally wound electrode body **40** in between and to extend perpendicularly to the spirally wound periphery face.

[0119] At the open end of the battery can **31**, a battery cover **34**, and a safety valve mechanism **35** and a PTC (Positive Temperature Coefficient) device **36** provided inside the battery cover **34** are attached by being caulked with a gasket **37**. Inside of the battery can **31** is thereby hermetically sealed. The battery cover **34** is made of, for example, a material similar to that of the battery can **31**. The safety valve mechanism **35** is electrically connected to the battery cover **34** through the PTC device **36**. In the safety valve mechanism **35**, when the internal pressure becomes a certain level or more by internal short circuit, external heating or the like, a disk plate **35**A flips to cut the electric connection between the battery cover **34** and the spirally wound electrode body **40**. When temperature rises, the PTC device **36** increases the resistance and thereby limits a current to prevent abnormal heat generation resulting from a large current. The gasket **37** is made of, for example, an insulating material and its surface is coated with asphalt.

[0120] For example, a center pin **44** is inserted in the center of the spirally wound electrode body **40**. In the spirally wound electrode body **40**, a cathode lead **45** made of aluminum or the like is connected to the cathode **41**, and an anode lead **46** made of nickel or the like is connected to the anode **42**. The cathode lead **45** is electrically connected to the battery cover **34** by being welded to the safety valve mechanism **35**. The anode lead **46** is welded and thereby electrically connected to the battery can **31**.

[0121] The cathode **41** has a structure in which, for example, a cathode active material layer **41**B is provided on the both faces of a strip-shaped cathode current collector **41**A. The anode **42** has a structure similar to that of the foregoing anode, for example, a structure in which an anode active material layer **42**B is provided on the both faces of a strip-shaped anode current collector **42**A. The structures of the cathode current collector **41**A, the cathode active material layer **41**B, the anode current collector **42**A, the anode active material layer **42**B, and the separator **43** and the composition of the electrolytic solution are respectively similar to the structures of the cathode current collector **21**A, the cathode active material layer **21**B, the anode current collector **22**A, the anode active material layer **22**B, and the separator **23**, and the composition of the electrolytic solution in the foregoing first battery.

[0122] The secondary battery is manufactured, for example, as follows.

[0123] First, for example, the cathode **41** in which the cathode active material layer **41**B is provided on the both faces of the cathode current collector **41**A is formed and the anode **42** in which the anode active material layer **42**B is provided on the both faces of the anode current collector **42**A is formed by respective procedures similar to the procedures of forming the cathode **21** and the anode **22** in the foregoing first battery. Subsequently, the cathode lead **45** is attached to the cathode **41**, and the anode lead **46** is attached to the anode **42**. Then, the cathode **41** and the anode **42** are spirally wound with the separator **43** in between, and thereby the spirally wound electrode body **40** is formed. The end of the cathode lead **45** is welded to the safety valve mechanism **35**, and the end of the anode lead **46** is welded to the battery can **31**. After that, the spirally wound electrode body **40** is sandwiched between the pair of insulating plates **32** and **33**, and contained in the battery can **31**. Subsequently, the electrolytic solution is injected into the battery can **31** and impregnated in the separator **43**. Finally, at the open end of the battery can **31**, the battery cover **34**, the safety valve mechanism **35**, and the PTC device **36** are fixed by being caulked with the gasket **37**. The secondary battery shown in FIG. **6** and FIG. **7** is thereby fabricated.

[0124] In the secondary battery, when charged, for example, lithium ions are extracted from the cathode **41** and inserted in the anode **42** through the electrolytic solution. Meanwhile, when discharged, for example, lithium ions are extracted from the anode **42**, and inserted in the cathode **41** through the electrolytic solution.

[0125] According to the cylindrical secondary battery, the anode **42** has the structure similar to that of the foregoing anode. Thus, the cycle characteristics may be improved. Effects of the secondary battery other than the foregoing effects are similar to those of the first battery.

Third Battery

[0126] FIG. **8** shows an exploded perspective structure of a third battery. FIG. **9** shows an exploded cross section taken along line IX-IX shown in FIG. **8**. In the battery, a spirally wound electrode body **50** on which a cathode lead **51** and an anode lead **52** are attached is contained in a film package member **60**. The battery structure including the package member **60** is a so-called laminated film structure.

[0127] The cathode lead **51** and the anode lead **52** are respectively directed from inside to outside of the package member **60** in the same direction, for example. The cathode lead **51** is made of, for example, a metal material such as aluminum, and the anode lead **52** is made of, for example, a metal material such as copper, nickel, and stainless. The cathode lead **51** and the anode lead **52** are in the shape of a thin plate or mesh.

[0128] The package member **60** is made of an aluminum laminated film in which, for example, a nylon film, an aluminum foil, and a polyethylene film are bonded together in this order. The package member **60** has, for example, a structure in which the respective outer edges of two pieces of rectangle aluminum laminated films are bonded to each other by fusion bonding or an adhesive so that the polyethylene film and the spirally wound electrode body **50** are opposed to each other.

[0129] An adhesive film **61** to protect from the entering of outside air is inserted between the package member **60** and the cathode lead **51**, the anode lead **52**. The adhesive film **61** is made of a material having contact characteristics to the cathode lead **51** and the anode lead **52**. Examples of such a material include, for example, a polyolefin resin such as polyethylene, polypropylene, modified polyethylene, and modified polypropylene.

[0130] The package member **60** may be made of a laminated film having other lamination structure, a polymer film such as polypropylene, or a metal film, instead of the foregoing aluminum laminated film.

[0131] In the spirally wound electrode body **50**, a cathode **53** and an anode **54** are layered with a separator **55** and an electrolyte **56** in between and then spirally wound. The outermost periphery thereof is protected by a protective tape **57**.

[0132] The cathode **53** has a structure in which, for example, a cathode active material layer **53**B is provided on the both faces of a cathode current collector **53**A having a pair of opposed faces. The anode **54** has a structure similar to that of the foregoing anode, for example, has a structure in which an anode active material layer **54**B is provided on the both faces of a strip-shaped anode current collector **54**A. The structures of the cathode current collector **53**A, the cathode active material layer **53**B, the anode current collector **54**A, the anode active material layer **54**B, and the separator **55** are respectively similar to those of the cathode current collector **21**A, the cathode active material layer **21**B, the anode current collector **22**A, the anode active material layer **22**B, and the separator **23** of the foregoing first battery.

[0133] The electrolyte **56** is a so-called gel electrolyte, containing an electrolytic solution and a polymer compound that holds the electrolytic solution. The gel electrolyte is preferable, since high ion conductivity (for example, 1 mS/cm or more at room temperature) may be obtained and liquid leakage may be prevented. The electrolyte **56** is provided, for example, between the cathode **53** and the separator **55**, and between the anode **54** and the separator **55**.

[0134] As the polymer compound, for example, polyacrylonitrile, polyvinylidene fluoride, a copolymer of polyvinylidene fluoride and polyhexafluoropropylene, polytetrafluoroethylene, polyhexafluoropropylene, polyethylene oxide, polypropylene oxide, polyphosphazene, polysiloxane, polyvinyl acetate, polyvinyl alcohol, polymethacrylate, polyacrylic acid, polymethacrylic acid, styrene-butadiene rubber, nitrile-butadiene rubber, polystyrene, polycarbonate or the like is cited. One of these polymer compounds may be used singly, or two or more thereof may be used by mixing. Specially, polyacrylonitrile, polyvinylidene fluoride, polyhexafluoropropylene, polyethylene oxide or the like is preferably used as the polymer compound, since thereby the electrochemical stability may be obtained.

[0135] The composition of the electrolytic solution is similar to the composition of the electrolytic solution in the first battery. However, in this case, the solvent means a wide concept including not only the liquid solvent but also a solvent having ion conductivity capable of dissociating the electrolyte salt. Therefore, when the polymer compound having ion conductivity is used, the polymer compound is also included in the solvent.

[0136] Instead of the gel electrolyte **56** in which the electrolytic solution is held by the polymer compound, the electrolytic solution may be directly used. In this case, the electrolytic solution is impregnated in the separator **55**.

[0137] The battery including the gel electrolyte **56** is manufactured, for example, as follows.

[0138] First, the cathode **53** in which the cathode active material layer **53**B is provided on the both faces of the cathode current collector **53**A is formed and the anode **54** in which the anode active material layer **54**B is provided on the both faces of the anode current collector **54**A is formed by respective procedures similar to the foregoing procedures of forming the cathode **21** and the anode **22** in the foregoing first battery. Subsequently, a precursor solution containing an electrolytic solution, a polymer compound, and a solvent is prepared. Then, the cathode **53** and the anode **54** are respectively coated with the precursor solution. After that, the solvent is volatilized to form the gel electrolyte **56**. Subsequently, the cathode lead **51** is attached to the cathode current collector **53**A, and the anode lead **52** is attached to the anode current collector **54**A. Subsequently, the cathode **53** and the anode **54** formed with the electrolyte **56** are layered with the separator **55** in between to obtain a laminated body. After that, the laminated body is spirally wound in the longitudinal direction, the protective tape **57** is adhered to the outermost periphery thereof to form the spirally wound electrode body **50**. Subsequently, for example, the spirally wound electrode body **50** is sandwiched between the package members **60**, and outer edges of the package members **60** are contacted by thermal fusion bonding or the like to enclose the spirally wound electrode body **50**. At this time, the adhesive film **61** is inserted between the cathode lead **51**/the anode lead **52** and the package member **60**. Thereby, the secondary battery shown in FIG. **8** and FIG. **9** is fabricated.

[0139] Otherwise, the foregoing battery may be manufactured as follows. First, the cathode lead **51** and the anode lead **52** are respectively attached on the cathode **53** and the anode **54**. After that, the cathode **53** and the anode **54** are layered with the separator **55** in between and spirally wound. The protective tape **57** is adhered to the outermost periphery thereof, and a spirally wound body as a precursor of the spirally wound electrode body **50** is formed. Subsequently, the spirally wound body is sandwiched between the package members **60**, the peripheral edges other than one side of the peripheral edges are contacted by thermal fusion-bonding or the like to obtain a pouched state, and the spirally wound body is contained in the pouched-like package member **60**. Subsequently, a composition of matter for electrolyte containing the electrolytic solution, a monomer as a raw material for a polymer compound, a polymerization initiator, and if necessary other material such as a polymerization inhibitor is prepared, which is injected into the pouched-like package member **60**. After that, the opening of the package member **60** is hermetically sealed by, for example, thermal fusion bonding or the like. Finally, the monomer is thermally polymerized to obtain a polymer compound. Thereby, the gel electrolyte **56** is formed. Consequently, the secondary battery shown in FIG. **8** and FIG. **9** is fabricated.

[0140] According to the laminated film secondary battery, the anode **54** has the structure similar to that of the foregoing anode. Thus, the cycle characteristics may be improved. Effects of the secondary battery other than the foregoing effects are similar to those of the first battery.

[0141] In the foregoing first to third batteries, it is possible to check whether the intensity ratio I(200)/I(111) is within the appropriate range (from 0.5 to 1.5) or not both before and after charge and discharge. More specifically, as an anode structure, in some cases the anode active material layer is provided to cover the entire surface of the anode current collector, and in the other cases the anode active material layer is provided to cover only part of the surface thereof (for example, the region opposed to the cathode active material layer). Meanwhile, as a cathode structure, it is general that the cathode active material layer is provided to cover only part of the surface of the cathode current collector. Thereby, the anode current collector includes the region opposed to the

cathode active material layer and the region not opposed to the cathode active material layer. In the region opposed to the cathode active material layer, electrode reaction between the cathode active material layer and the anode active material layer proceeds, and the battery is charged and discharged. Thus, even if the intensity ratio I(200)/I(111) is set to within the appropriate range before charge and discharge, the intensity ratio I(200)/I(111) may be changed due to the effect of charge and discharge. Meanwhile, in the region not opposed to the cathode active material layer, regardless of whether or not the anode active material layer is provided in such a region, the intensity ratio I(200)/I(111) is not affected by charge and discharge, and thus the intensity ratio I(200)/I(111) before charge and discharge is not changed after charge and discharge. Therefore, when the intensity ratio I(200)/I(111) is examined in the region not opposed to the cathode active material layer, it is possible to check whether or not the intensity ratio I(200)/I(111) is within the appropriate range with good reproducibility regardless of presence of charge and discharge.

EXAMPLES

[0142] Examples of the invention will be described in detail.

Example 1-1

[0143] The laminated film secondary battery shown in FIG. **8** and FIG. **9** was fabricated by the following procedure. The secondary battery was fabricated as a lithium ion secondary battery in which the capacity of the anode **54** was expressed based on insertion and extraction of lithium.

[0144] First, the cathode **53** was formed. That is, lithium carbonate (Li_2CO_3) and cobalt carbonate ($CoCO_3$) were mixed at a molar ratio of 0.5:1. After that, the mixture was fired in the air at 900 deg C. for 5 hours. Thereby, lithium cobalt complex oxide ($LiCoO_2$) was obtained. Subsequently, 91 parts by weight of the lithium cobalt complex oxide as a cathode active material, 6 parts by weight of graphite as an electrical conductor, and 3 parts by weight of polyvinylidene fluoride as a binder were mixed to obtain a cathode mixture. After that, the cathode mixture was dispersed in N-methyl-2-pyrrolidone to obtain paste cathode mixture slurry. Finally, the both faces of the cathode current collector **53**A made of a strip-shaped aluminum foil having a thickness of 12 μm were uniformly coated with the cathode mixture slurry, which was dried. After that, the resultant was compression-molded by a roll pressing machine to form the cathode active material layer **53**B. After that, the cathode lead **51** made of aluminum was welded to one end of the cathode current collector **53**A.

[0145] Next, the anode **54** was formed. First, a copper foil having a thickness of 18 μm was prepared as an original foil. After that, the original foil was annealed. The annealing temperature of the original foil was 300 deg C., and the maximum value of the cross-section area of the copper crystallite was 50 μm^2. The cross-section area of the crystallite was measured by exposing a cross section of the original foil with the use of a cross section polisher, and then observing the cross section with the use of a low-accelerated voltage SEM. Subsequently, the anode current collector **54**A made of an electrolytic copper foil was prepared by providing electrolytic treatment for the surface of the original foil to form fine particles and a plated film. The ten point height roughness profile Rz of the surface of the anode current collector **54**A was 3.5 μm. For the ten point height roughness profile Rz, with the use of sensing pin type profilometer Dektak 3 (manufactured by Ulvac Equipment Sales, Inc.), pin scanning was performed in the direction perpendicular to the spirally wound direction of the anode current collector **54**A in a subsequent step, and thereby the average value of measured values that were randomly selected was obtained. When the extension coefficient and the Young's modulus of the anode current collector **54**A were measured, the extension coefficient was 9% and the Young's modulus was 5.93×10^7 MPa. Subsequently, silicon was deposited on the both faces of the anode current collector **54**A by electron beam evaporation method using a deflecting electron beam evaporation source while continuously introducing oxygen gas into a chamber and if necessary introducing moisture vapor into the chamber, so that the anode active particle had a single layer structure. Thereby, the anode active material layer **54**B was formed. Silicon with the purity of 99% was used as the evaporation source, the deposition rate was 10 nm/sec, and the oxygen content in the anode active material particle was 3 atomic %. Finally, the anode current collector **54**A formed with the anode active material layer **54**B was annealed under the reduced pressure atmosphere of 10^{-3} Pa or less. The annealing temperature of the anode current collector **54**A was 150 deg C., and the intensity ratio I(200)/I(111) between the intensities of the peaks originated in the copper crystal planes obtained by X-ray diffraction was set to 0.5. The intensity ratio I(200)/I(111) was measured as follows. The formed anode **54** was cut into a piece being 5 mm×5 mm in size. After that, measurement was performed by analysis with the use of an XRD diffracting device (manufactured by Rigaku Co., Ltd.). CuKa was used as a tube, θ-2θ method was used as a scanning method, the X-ray tube voltage was 40 kV, the tube current was 40 mA, and the measurement range was in the range from 40 degree to 100 degree.

[0146] For the formed anode **54**, a cross section was exposed by focused ion beam etching (FIB), and then local element analysis was performed by auger electron spectrometer (AES). In the result, it was confirmed that the element of the anode current collector **54**A and the element of the anode active material layer **54**B were diffused into each other at the interface between the anode current collector **54**A and the anode active material layer **54**B, and the both elements are alloyed.

[0147] Next, the cathode **53**, a three-layer polymer separator **55** (thickness: 23 μm) in which a porous polyethylene film was sandwiched between porous polypropylene films, the anode **54**, and the foregoing polymer separator **55** were layered in this order. The resultant laminated body was spirally wound in the longitudinal direction, the end section of the spirally wound body was fixed by the protective tape **57** made of an adhesive tape, and thereby a spirally wound body as a precursor of the spirally wound electrode body **50** was formed. Subsequently, the spirally wound body was sandwiched between the package members **60** made of a three-layer laminated film (total thickness: 100 μm) in which nylon (thickness: 30 μm), aluminum (thickness: 40 μm), and non-stretched polypropylene (thickness: 30 μm) were layered from the outside. After that, outer edges other than an edge of one side of the package members **60** were thermally fusion-bonded to each other. Thereby, the spirally wound body was contained in the package members **60** in a pouched state. Subsequently, an electrolytic solution was injected through the opening of the package member **60**, the electrolytic solu-

tion was impregnated in the separator **55**, and thereby the spirally wound electrode body **50** was formed.

[0148] When preparing the electrolytic solution, a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) as a solvent was used, and lithium hexafluorophosphate ($LiPF_6$) was used as an electrolyte salt. The composition of the mixed solvent (EC:DEC) was 50:50 at a weight ratio. The concentration of the electrolyte salt was 1 mol/kg.

[0149] Finally, the opening of the package member **60** was thermally fusion bonded and sealed in the vacuum atmosphere. Thereby, the laminated film secondary battery was fabricated.

Examples 1-2 to 1-7

[0150] A procedure was performed in the same manner as that of Example 1-1, except that the intensity ratio I(200)/I(111) was changed to 0.8 (200 deg C.: Example 1-2), 1 (250 deg C.: Example 1-3), 1.15 (300 deg C.: Example 1-4), 1.2 (350 deg C.: Example 1-6), 1.4 (400 deg C.: Example 1-6), or 1.5 (450 deg C.: Example 1-7), instead of 0.5. The temperatures shown in parentheses are annealing temperatures of the anode current collector **54**A set to obtain the foregoing respective values of the intensity ratio I(200)/I(111).

Comparative Examples 1-1 to 1-6

[0151] A procedure was performed in the same manner as that of Example 1-1, except that the intensity ratio I(200)/I(111) was changed to 0.1 (25 deg C.: Comparative example 1-1), 0.3 (100 deg C.: Comparative example 1-2), 1.6 (500 deg C.: Comparative example 1-3), 1.8 (525 deg C.: Comparative example 1-4), 2 (550 deg C.: Comparative example 1-6), or 2.5 (575 deg C.: Comparative example 1-6), instead of 0.5.

[0152] When the cycle characteristics of the secondary batteries of Examples 1-1 to 1-7 and Comparative examples 1-1 to 1-6 were examined, the results shown in Table 1 and FIG. **10** were obtained. In Table 1, the maximum value is shown as a cross section of the crystallite. The same is similarly applied to the following tables.

[0153] In examining the cycle characteristics, a cycle test was performed by the following procedure, and thereby the discharge capacity retention ratio was obtained. First, to stabilize the battery state, after charge and discharge were performed 1 cycle in the atmosphere at 23 deg C., charge and discharge were performed again. Thereby, the discharge capacity at the second cycle was measured. Subsequently, the secondary battery was charged and discharged 99 cycles in the same atmosphere, and thereby the discharge capacity at the 101st cycle was measured. Finally, the discharge capacity retention ratio (%)=(discharge capacity at the 101st cycle/discharge capacity at the second cycle)×100 was calculated. The charge condition was as follows. That is, after charge was performed at the constant current density of 3 mA/cm^2 until the battery voltage reached 4.2 V, charge was continuously performed at the constant voltage of 4.2 V until the battery density reached 0.3 mA/cm^2. The discharge conditions were as follows. That is, discharge was performed at the constant current density of 3 mA/cm^2 until the battery voltage reached 2.5 V. The procedure and the conditions for examining the cycle characteristics are similarly applied to the following examples and comparative examples.

TABLE 1

Anode active material particle: silicon (electron beam evaporation method)
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm
Oxygen content in the anode active material particle = 3 atomic %

	Anode active material layer	Anode current collector		
	Number of anode active material particle layers (layer)	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Discharge capacity retention ratio (%)
Example 1-1	1	0.5	50	80
Example 1-2		0.8		84
Example 1-3		1		83
Example 1-4		1.15		82
Example 1-5		1.2		82
Example 1-6		1.4		81
Example 1-7		1.5		80
Comparative example 1-1	1	0.1	50	68
Comparative example 1-2		0.3		69
Comparative example 1-3		1.6		69
Comparative example 1-4		1.8		68
Comparative example 1-5		2		65
Comparative example 1-6		2.5		62

[0154] As shown in Table 1 and FIG. **10**, in Examples 1-1 to 1-7 in which the intensity ratio I(200)/I(111) was in the range from 0.5 to 1.5, the discharge capacity retention ratio was largely higher than those of Comparative examples 1-1 to 1-6 in which the intensity ratio I(200)/I(111) was out of the range. That is, the discharge capacity retention ratio was changed in an upward convex curve as the intensity ratio I(200)/I(111) was increased. In particular, when the intensity ratio I(200)/I(111) was smaller than 0.5 or larger than 1.5, the discharge capacity retention ratio was extremely lowered. Accordingly, it was confirmed that in the secondary battery of the invention, the cycle characteristics were improved in the case where the intensity ratio I(200)/I(111) was in the range from 0.5 to 1.5.

[0155] As a representative of Examples 1-1 to 1-7 described above, when the anodes **54** used for the secondary batteries of Examples 1-2 and 1-4 were analyzed by an XRD device, the results shown in FIGS. **11**A and **11**B were obtained. FIG. **11**A and FIG. **11**B respectively show Examples 1-2 and 1-4. The horizontal axis and the vertical axis respectively show 2θ (degree) and a normalized X-ray intensity. As shown in FIGS. **11**A and **11**B, in both Examples 1-2 and 1-4, five peaks identifying the copper crystal condition were confirmed. The five peaks include peak P1 originated in (111) crystal plane, peak P2 originated in (200) crystal plane, peak **3** originated in (220) crystal plane, peak P4 originated in (311) crystal plane, and peak P5 originated in (222) crystal plane. When the intensities of the peaks P1 to P5 were compared to each other, the intensities of the peaks P1 and P2 were significantly larger than those of the peaks P3 to P5. In this case, in Example 1-2, as shown in FIG. **11**A, the intensity of peak P2 was smaller than that of peak P1. Thus, the intensity ratio I(200)/I(111) was smaller than 1. Meanwhile, in Example 1-4, as shown in FIG. **11**B, the intensity of

peak P2 was larger than that of peak P1. Thus, the intensity ratio I(200)/I(111) was larger than 1. Accordingly, it was confirmed that in the secondary battery of the invention, the intensities of the two peaks originated in (111) crystal plane and (200) crystal plane were sufficiently larger than the intensities of the other peaks, and therefore the copper crystal state was determined with a good reproducibility based on the intensity ratio of the two peaks, and the cycle characteristics were changed according to the intensity ratio.

[0156] Though a specific analytical result is not herein shown, when Comparative examples 1-3 to 1-6 in which the intensity ratio I(200)/I(111) was larger than 1.5 were analyzed by the XRD device, a peak showing existence of Cu_3Si was confirmed. Such a result showed that element diffusion excessively proceeded at the interface between the anode current collector **54**A (Cu) and the anode active material particle (Si), and thus Cu_3Si was generated at the interface thereof. In the result, in Comparative examples 1-3 to 1-6, the contact characteristics between the anode current collector **54**A and the anode active material particle were lowered, and thus sufficient cycle characteristics were not obtained.

Examples 2-1 to 2-6

[0157] A procedure was performed in the same manner as that of Examples 1-1 to 1-3 and Examples 1-5 to 1-7, except that the anode active material particle was formed into six-layer structure by depositing silicon six times. The deposition rate was 100 nm/sec.

Comparative Examples 2-1 to 2-3

[0158] A procedure was performed in the same manner as that of Comparative examples 1-2 to 1-4, except that the anode active material particle was formed into six-layer structure as in Examples 2-1 to 2-6.

[0159] When the cycle characteristics of the secondary batteries of Examples 2-1 to 2-6 and Comparative examples 2-1 to 2-3 were examined, the results shown in Table 2 and FIG. **12** were obtained.

TABLE 2

Anode active material particle: silicon (electron beam evaporation method)
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm
Oxygen content in the anode active material particle = 3 atomic %

	Anode active material layer	Anode current collector		
	Number of anode active material particle layers (layer)	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Discharge capacity retention ratio (%)
Example 2-1	6	0.5	50	82
Example 2-2		0.8		86
Example 2-3		1		85
Example 2-4		1.2		84
Example 2-5		1.4		83
Example 2-6		1.5		82
Comparative example 2-1	6	0.3	50	69.5
Comparative example 2-2		1.6		69.5
Comparative example 2-3		1.8		69

[0160] As shown in Table 2 and FIG. **12**, in Examples 2-1 to 2-6 in which the intensity ratio I(200)/I(111) was in the range from 0.5 to 1.5, the discharge capacity retention ratio was largely higher than those of Comparative examples 2-1 to 2-3 in which the intensity ratio I(200)/I(111) was out of the range. Accordingly, it was confirmed that in the secondary battery of the invention, in the case where the number of the anode active material particle layers was six, the cycle characteristics were improved as well.

Examples 3-1 to 3-6

[0161] A procedure was performed in the same manner as that of Examples 1-1 to 1-3 and Examples 1-5 to 1-7, except that the anode active material particle was formed into 12-layer structure by depositing silicon 12 times.

Comparative Examples 3-1 to 3-3

[0162] A procedure was performed in the same manner as that of Comparative examples 1-2 to 1-4, except that the anode active material particle was formed into 12-layer structure as in Examples 3-1 to 3-6.

[0163] When the cycle characteristics of the secondary batteries of Examples 3-1 to 3-6 and Comparative examples 3-1 to 3-3 were examined, the results shown in Table 3 and FIG. **13** were obtained.

TABLE 3

Anode active material particle: silicon (electron beam evaporation method)
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm
Oxygen content in the anode active material particle = 3 atomic %

	Anode active material layer	Anode current collector		
	Number of anode active material particle layers (layer)	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Discharge capacity retention ratio (%)
Example 3-1	12	0.5	50	83
Example 3-2		0.8		87
Example 3-3		1		86
Example 3-4		1.2		85
Example 3-5		1.4		84
Example 3-6		1.5		82.5
Comparative example 3-1	12	0.3	50	69.8
Comparative example 3-2		1.6		69.9
Comparative example 3-3		1.8		69.2

[0164] As shown in Table 3 and FIG. **13**, in Examples 3-1 to 3-6 in which the intensity ratio I(200)/I(111) was in the range from 0.5 to 1.5, the discharge capacity retention ratio was largely higher than those of Comparative examples 3-1 to 3-3 in which the intensity ratio I(200)/I(111) was out of the range. Accordingly, it was confirmed that in the secondary battery of the invention, in the case where the number of the anode active material particle layers was 12, the cycle characteristics were improved as well.

[0165] From the results shown in Table 1 to Table 3, it was confirmed that in the secondary battery of the invention, the cycle characteristics were improved when the intensity ratio I(200)/I(111) was in the range from 0.5 to 1.5, both in the case that the anode active material particle is formed into the single

layer structure and in the case that the anode active material particle is formed into the multilayer structure. In this case, in particular, as evidenced by the result obtained by comparison among Examples 1-1, 2-1, 3-1 and the like under the same conditions except for the number of the anode active material particle layers as the number of layers was larger, the discharge capacity retention ratio tended to be higher. Accordingly, it was confirmed that in the case that the anode active material particle was formed into the multilayer structure, when the number of layers was increased, higher effects were obtained.

Examples 4-1 to 4-9

[0166] A procedure was performed in the same manner as that of Example 2-2, except that the maximum value of the cross-section area of the copper crystallite was changed to 4 μm^2 (25 deg C.: Example 4-1), 10 μm^2 (100 deg C.: Example 4-2), 20 μm^2 (160 deg C.: Example 4-3), 30 μm^2 (200 deg C.: Example 4-4), 40 μm^2 (250 deg C.: Example 4-5), 70 μm^2 (350 deg C.: Example 4-6), 85 μm^2 (400 deg C.: Example 4-7), 100 μm^2 (450 deg C.: Example 4-8), or 120 μm^2 (500 deg C.: Example 4-9), instead of 50 μm^2. The temperatures shown in parentheses are annealing temperatures of the original foil set to obtain the foregoing respective values of the cross-section areas of the crystallite.

[0167] When the cycle characteristics of the secondary batteries of Examples 4-1 to 4-9 were examined, the results shown in Table 4 and FIG. **14** were obtained. In Table 4, the results of Example 2-2 and Comparative examples 2-1 to 2-3 are shown together.

TABLE 4

Anode active material particle: silicon (electron beam evaporation method)
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm
Oxygen content in the anode active material particle = 3 atomic %

	Anode active material layer	Anode current collector		
	Number of anode active material particle layers (layer)	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Discharge capacity retention ratio (%)
Example 4-1	6	0.8	4	82
Example 4-2			10	84
Example 4-3			20	85
Example 4-4			30	85
Example 4-5			40	86
Example 2-2			50	86
Example 4-6			70	86
Example 4-7			85	85
Example 4-8			100	84
Example 4-9			120	73
Comparative example 2-1	6	0.3	50	69.5
Comparative example 2-2		1.6		69.5
Comparative example 2-3		1.8		69

[0168] As shown in Table 4 and FIG. **14**, in Examples 2-2 and 4-1 to 4-9 in which the intensity ratio I(200)/I(111) was in the range from 0.5 to 1.5, the discharge capacity retention ratio was largely higher than those of Comparative examples 2-1 to 2-3 even in the case where the cross-section area of the crystallite was changed. In this case, the discharge capacity retention ratio was changed in an upward convex curve as the cross-section area of the crystallite was increased. In particular, when the cross-section area was larger than 100 μm^2, the discharge capacity retention ratio tended to be extremely lowered. Accordingly, it was confirmed that in the secondary battery of the invention, the cycle characteristics were improved not depending on the cross-section area of the copper crystallite. Further, it was confirmed that when the cross-section area was 100 μm^2 or less, higher effects were obtained.

[0169] As a representative of Examples 2-2 and 4-1 to 4-9 described above, when cross sections of the anode current collectors **54** used for the secondary batteries of Examples 2-2 and 4-1 were observed by a field emission (FE) SEM, the results shown in FIGS. **15**A and **15**B were obtained. FIG. **15**A and FIG. **15**B are SEM photographs showing the cross sectional structures of the anode current collector **54**A. FIG. **15**A and FIG. **15**B respectively show observation results of Examples 4-1 and 2-2. As shown in FIGS. **15**A and **15**B, in both Examples 2-2 and 4-1, a plurality of copper crystallites were observed. That is, when matching the schematic drawing of FIG. **2** with the SEM photographs of FIGS. **15**A and **15**B, in the electrolytic copper foil composing the anode current collector **64**A, a larger crystallite composing the original foil **1**A was observed in the center, and a smaller crystallite composing the fine particle **1**B and the plated film **1**C was observed in the upper side and the lower side to sandwich the larger crystallite. In this case, when the crystallite area composing the original foil of Example 2-2 was compared to that of Example 4-1, there was a large difference. That is, in Example 4-1, as shown in FIG. **16**A, the crystallite area was small. Meanwhile, in Example 2-2, as shown in FIG. **15**B, the crystallite area was large. Accordingly, in the secondary battery of the invention, it was confirmed that the cycle characteristics were changed according to the cross-section area of the copper crystallite composing the anode current collector **54**A.

Examples 5-1 to 5-6

[0170] A procedure was performed in the same manner as that of Example 2-2, except that the ten point height of roughness profile Rz of the surface of the anode current collector **54**A was changed to 1 μm (Example 6-1), 1.5 μm (Example 5-2), 2.5 μm (Example 5-3), 4.5 μm (Example 5-4), 5.5 μm (Example 5-5), or 6.5 μm (Example 5-6), instead of 3.5 μm. The ten point height of roughness profile Rz was changed by adjusting electrolytic conditions using plating bath such as the current ratio, the bath temperature, the treatment times, and the bath composition.

[0171] When the cycle characteristics of the secondary batteries of Examples 5-1 to 5-6 were examined, the results shown in Table 5 and FIG. **16** were obtained. In Table 5, the results of Example 2-2 and Comparative examples 2-1 to 2-3 were shown together.

TABLE 5

Anode active material particle: silicon (electron beam evaporation method)
Thickness of original foil = 18 μm
Oxygen content in the anode active material particle = 3 atomic %

	Anode active material layer	Anode current collector			
	Number of anode active material particle layers (layer)	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Ten point height of roughness profile Rz (μm)	Discharge capacity retention ratio (%)
Example 5-1	6	0.8	50	1	71
Example 5-2				1.5	80
Example 5-3				2.5	83
Example 2-2				3.5	86
Example 5-4				4.5	85
Example 5-5				5.5	82
Example 5-6				6.5	72
Comparative example 2-1	6	0.3	50	3.5	69.5
Comparative example 2-2		1.6			69.5
Comparative example 2-3		1.8			69

[0172] As shown in Table 5 and FIG. **16**, in Examples 2-2 and 5-1 to 5-6 in which the intensity ratio I(200)/I(111) was in the range from 0.5 to 1.5, the discharge capacity retention ratio was higher than those of Comparative examples 2-1 to 2-3 as well when the ten point height of roughness profile Rz was changed. In this case, the discharge capacity retention ratio was changed in an upward convex curve as the ten point height of roughness profile Rz was increased. In particular, when the ten point height of roughness profile Rz was smaller than 1.5 μm or larger than 5.5 μm, the discharge capacity retention ratio tended to be extremely lowered. Accordingly, it was confirmed that in the secondary battery of the invention, the cycle characteristics were improved not depending on the ten point height of roughness profile Rz of the surface of the anode current collector **54**A. Further, it was confirmed that when the ten point height of roughness profile Rz was in the range from 1.5 μm to 5.5 μm, higher effects were obtained.

Examples 6-1 to 6-4

[0173] A procedure was performed in the same manner as that of Example 2-2, except that the thickness of the original foil was changed to 7 μm (Example 6-1), 10 μm (Example 6-2), 25 μm (Example 6-3), or 30 μm (Example 6-4), instead of 18 μm.

[0174] When the cycle characteristics of the secondary batteries of Examples 6-1 to 6-4 were examined, the results shown in Table 6 and FIG. **17** were obtained. In Table 6, the results of Example 2-2 and Comparative examples 2-1 to 2-3 were shown together.

TABLE 6

Anode active material particle: silicon (electron beam evaporation method)
Ten point height of roughness profile Rz = 3.5 μm
Oxygen content in the anode active material particle = 3 atomic %

	Anode active material layer	Anode current collector			
	Number of anode active material particle layers (layer)	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Thickness of original foil (μm)	Discharge capacity retention ratio (%)
Example 6-1	6	0.8	50	7	70
Example 6-2				10	81
Example 2-2				18	86
Example 6-3				25	84
Example 6-4				30	72
Comparative example 2-1	6	0.3	50	18	69.5
Comparative example 2-2		1.6			69.5
Comparative example 2-3		1.8			69

[0175] As shown in Table 6 and FIG. **17**, in Examples 2-2 and 6-1 to 6-4 in which the intensity ratio I(200)/I(111) was in the range from 0.5 to 1.5, the discharge capacity retention ratio was higher than those of Comparative examples 2-1 to 2-3 as well when the thickness of the original foil was changed. In this case, the discharge capacity retention ratio was changed in an upward convex curve as the thickness of the original foil was increased. In particular, when the thickness of the original foil was smaller than 10 μm or larger than 25 μm, the discharge capacity retention ratio tended to be extremely lowered. Accordingly, it was confirmed that in the secondary battery of the invention, the cycle characteristics were improved not depending on the thickness of the original foil. Further, it was confirmed that if the thickness of the original foil was in the range from 10 μm to 25 μm, higher effects were obtained.

Examples 7-1 to 7-7

[0176] A procedure was performed in the same manner as that of Example 2-2, except that the extension coefficient and the Young's modulus of the anode current collector **54**A were changed. In this case, the extension coefficient and the Young's modulus were respectively 0.7% and 6.53×10^9 MPa (Example 7-1), 1% and 5.00×10^9 MPa (Example 7-2), 3.2% and 4.01×10^9 MPa (Example 7-3), 4.9% and 6.32×10^8 MPa (Example 7-4), 10% and 5.00×10^7 MPa (Example 7-5), 10.5% and 3.61×10^6 MPa (Example 7-6), or 11.5% and 1.61×10^6 MPa (Example 7-7).

[0177] When the cycle characteristics of the secondary batteries of Examples 7-1 to 7-7 were examined, the results shown in Table 7 and FIGS. **18** and **19** were obtained. In Table 7, the results of Example 2-2 and Comparative examples 2-1 to 2-3 were shown together.

[0178] As shown in Table 7, FIG. **18**, and FIG. **19**, in Examples 2-2 and 7-1 to 7-7 in which the intensity ratio I(200)/I(111) was in the range from 0.5 to 1.5, the discharge capacity retention ratio was higher than those of Comparative examples 2-1 to 2-3 as well when the extension coefficient and the Young's modulus of the anode current collector **54**A were changed. In this case, the discharge capacity retention ratio was changed in an upward convex curve as the extension coefficient was increased and the Young's modulus was decreased. In particular, when the extension coefficient was smaller than 1% and the Young's modulus was larger than 5×10^9 MPa, or when the extension coefficient was larger than 10% and the Young's modulus was smaller than 5×10^7 MPa, the discharge capacity retention ratio was extremely lowered. Accordingly, it was confirmed that in the secondary battery of the invention, the cycle characteristics were improved not depending on the extension coefficient and the Young's modulus of the anode current collector. Further, it was confirmed that when the extension coefficient was in the range from 1% to 10% and the Young's modulus was in the range from 5×10^7 MPa to 5×10^9 MPa, higher effects were obtained.

Examples 8-1 to 8-6

[0179] A procedure was performed in the same manner as that of Example 2-2, except that the oxygen content in the anode active material particle was changed to 2 atomic % (Example 8-1), 10 atomic % (Example 8-2), 20 atomic % (Example 8-3), 30 atomic % (Example 8-4), 40 atomic % (Example 8-5), or 45 atomic % (Example 8-6) instead of 3 atomic %.

[0180] When the cycle characteristics of the secondary batteries of Examples 8-1 to 8-6 were examined, the results shown in Table 8 and FIG. **20** were obtained. In Table 8, the results of Example 2-2 and Comparative examples 2-1 to 2-3 were shown together.

TABLE 7

Anode active material particle: silicon (electron beam evaporation method)
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm
Oxygen content in the anode active material particle = 3 atomic %

	Anode active material layer	Anode current collecter				
	Number of anode active material particle layers (layer)	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Extension coefficient of original foil (%)	Young's modulus (MPa)	Discharge capacity retention ratio (%)
Example 7-1	6	0.8	50	0.7	6.53×10^9	73
Example 7-2				1	5.00×10^9	82
Example 7-3				3.2	4.01×10^9	82.4
Example 7-4				4.9	6.32×10^8	83
Example 2-2				9	5.93×10^7	86
Example 7-5				10	5.00×10^7	82
Example 7-6				10.5	3.61×10^6	73
Example 7-7				11.5	1.61×10^6	72
Comparative example 2-1	6	0.3	50	9	5.93×10^7	69.5
Comparative example 2-2		1.6				69.5
Comparative example 2-3		1.8				69

TABLE 8

Anode active material particle: silicon (electron beam evaporation method)
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm

	Anode active material layer		Anode current collector		
	Number of anode active material particle layers (layer)	Oxygen content (atomic %)	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Discharge capacity retention ratio (%)
Example 8-1	6	2	0.8	50	82
Example 2-2		3			86
Example 8-2		10			90
Example 8-3		20			90
Example 8-4		30			88
Example 8-5		40			86
Example 8-6		45			85
Comparative example 2-1	6	3	0.3	50	69.5
Comparative example 2-2			1.6		69.5
Comparative example 2-3			1.8		69

[0181] As shown in Table 8 and FIG. **20**, in Examples 2-2 and 8-1 to 8-6 in which the intensity ratio I(200)/I(111) was in the range from 0.5 to 1.5, the discharge capacity retention ratio was higher than those of Comparative examples 2-1 to 2-3 as well when the oxygen content was changed. In this case, the discharge capacity retention ratio was changed in an upward convex curve as the oxygen content was increased. In particular, when the oxygen content was smaller than 3 atomic %, the discharge capacity retention ratio was extremely lowered. However, when the oxygen content was larger than 40 atomic %, the silicon content in the anode active material particle was relatively smaller and thus the battery capacity tended to be largely lowered. Accordingly, it was confirmed that in the secondary battery of the invention, the cycle characteristics were improved not depending on the oxygen content in the anode active material. Further, it was confirmed that if the oxygen content was in the range from 3 atomic % to 40 atomic %, the cycle characteristics were improved and the battery capacity was secured.

Examples 9-1 to 9-3

[0182] A procedure was performed in the same manner as that of Example 2-2, except that the anode active material particle was formed so that a first oxygen-containing region and a second oxygen-containing region having a higher oxygen content than that of the first oxygen-containing region were alternately layered by depositing silicon while intermittently introducing oxygen gas into the chamber, instead that oxygen was contained in the anode active material particle by depositing silicon while continuously introducing oxygen gas or the like into the chamber. The oxygen content in the second oxygen-containing region was 3 atomic %, and the number thereof was 2 (Example 9-1), 4 (Example 9-2), or 6 (Example 9-3).

[0183] When the cycle characteristics of the secondary batteries of Examples 9-1 to 9-3 were examined, the results shown in Table 9 and FIG. **21** were obtained. In Table 9, the results of Example 2-2 and Comparative examples 2-1 to 2-3 are shown together.

TABLE 9

Anode active material particle: silicon (electron beam evaporation method)
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm

	Anode active material layer		Anode current collector		
	Number of anode active material particle layers (layer)	Number of second oxygen-containing regions	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Discharge capacity retention ratio (%)
Example 2-2	6		0.8	50	86
Example 9-1		2			88

TABLE 9-continued

Anode active material particle: silicon (electron beam evaporation method)
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm

	Anode active material layer		Anode current collector		
	Number of anode active material particle layers (layer)	Number of second oxygen-containing regions	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Discharge capacity retention ratio (%)
Example 9-2		4			89
Example 9-3		6			89

[0184] As shown in Table 9 and FIG. **21**, in Examples 9-1 to 9-3 in which the anode active material particle had the first and the second oxygen-containing regions, the discharge capacity retention ratio was higher than that of Example 2-2 in which the anode active material particle did not have the first and the second oxygen-containing regions. In this case, as the number of the second oxygen-containing regions was increased, the discharge capacity retention ratio tended to be higher. Accordingly, it was confirmed that in the secondary battery of the invention, when the anode active material particle had the first and the second oxygen-containing regions, the cycle characteristics were improved. Further, it was confirmed that as the number of the second oxygen-containing regions was increased, higher effects were obtained.

Example 10-1

[0185] A procedure was performed in the same manner as that of Example 2-2, except that the anode active material particle was formed by depositing silicon by using RF sputtering method instead of electron beam evaporation method. At that time, silicon with purity of 99.99% was used as a target, and the deposition rate was 0.5 nm/sec.

Example 10-2

[0186] A procedure was performed in the same manner as that of Example 2-2, except that the anode active material particle was formed by depositing silicon by using CVD method instead of electron beam evaporation method. As a raw material and excitation gas, silane (SiH_4) and argon (Ar) were used, respectively, and the deposition rate and the substrate temperature were respectively 1.5 nm/sec and 200 deg C.

Comparative Example 10-1

[0187] A procedure was performed in the same manner as that of Comparative example 2-1, except that the anode active material particle was formed by using RF sputtering method as in Example 10-1.

Comparative Example 10-2

[0188] A procedure was performed in the same manner as that of Comparative example 2-1, except that the anode active material particle was formed by using CVD method as in Example 10-2.

[0189] When the cycle characteristics of the secondary batteries of Examples 10-1 and 10-2 and Comparative examples 10-1 and 10-2 were examined, the results shown in Table 10 were obtained. In Table 10, the results of Example 2-2 and Comparative examples 2-2 are shown together.

TABLE 10

Anode active material particle: silicon
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm
Oxygen content in the anode active material particle = 3 atomic %

	Anode active material layer		Anode current collector		
	Number of anode active material particle layers (layer)	Forming method	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Discharge capacity retention ratio (%)
Example 2-2	6	Electron beam evaporation method	0.8	50	86
Example 10-1		Sputtering method			84
Example 10-2		CVD method			83
Comparative example 2-1	6	Electron beam evaporation method	9.3	50	69.5
Comparative example 10-1		Sputtering method			65
Comparative example 10-2		CVD method			64

[0190] As shown in Table 10, in Examples 10-1 and 10-2 in which sputtering method or CVD method was used as a method of forming the anode active material particle, the discharge capacity retention ratio equal to that of Example 2-2 using electron beam evaporation method was obtained. In this case, when each method of forming the anode active material particle was compared to each other, the discharge capacity retention ratio tended to be increased in the order of CVD method, sputtering method, and electron beam evaporation method. It is needless to say that in Examples 2-2, 10-1, and 10-2 in which the intensity ratio I(200)/I(111) was in the range from 0.5 to 1.5, the discharge capacity retention ratio was higher than those of Comparative examples 2-1, 10-1, and 10-2 in which the intensity ratio I(200)/I(111) was out of the range. Accordingly, it was confirmed that in the secondary battery of the invention, the cycle characteristics were improved not depending on the method of forming the anode active material particle. Further, it was confirmed that the effect was improved in the order of CVD method, sputtering method, and electron beam evaporation method as the method of forming the anode active material particle.

Example 11-1

[0191] A procedure was performed in the same manner as that of Example 2-2, except that the square secondary battery shown in FIG. **4** and FIG. **5** was fabricated instead of the laminated film secondary battery by the following procedure.

[0192] First, the cathode **21** and the anode **22** were formed. After that, the cathode lead **24** made of aluminum and the anode lead **25** made of nickel were respectively welded to the cathode current collector **21**A and the anode current collector **22**A. Subsequently, the cathode **21**, the separator **23**, and the anode **22** were layered in this order, and spirally wound in the longitudinal direction, and formed in the flat shape. Thereby, the battery element **20** was formed. Subsequently, the battery element **20** was contained inside the battery can **11** made of aluminum. After that, the insulating plate **12** was arranged on the battery element **20**. Subsequently, the cathode lead **24** and the anode lead **25** were respectively welded to the cathode pin **15** and the battery can **11**. After that, the battery cover **13** was fixed to the open end of the battery can **11** by laser welding. Finally, the electrolytic solution was injected into the battery can **11** through the injection hole **19**. After that, the injection hole **19** was sealed by the sealing member **19**A, and thereby the square battery was fabricated.

Example 11-2

[0193] A procedure was performed in the same manner as that of Example 11-1, except that the battery can **11** made of iron was used instead of the battery can **11** made of aluminum.

[0194] When the cycle characteristics of the secondary batteries of Examples 11-1 and 11-2 were examined, the results shown in Table 11 were obtained. Table 11 shows the result of Example 2-2 together.

TABLE 11

Anode active material particle: silicon (electron beam evaporation method)
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm
Oxygen content in the anode active material particle = 3 atomic %

	Anode active material layer	Anode current collector			
	Number of anode active material particle layers (layer)	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Battery structure	Discharge capacity retention ratio (%)
Example 2-2	6	0.8	50	Laminated film	86
Example 11-1				Square (aluminum)	89
Example 11-2				Square (iron)	92

[0195] As shown in Table 11, in Examples 11-1 and 11-2 in which the battery structure was square, the discharge capacity retention ratio was higher than that of Example 2-2 in which the battery structure was the laminated film type. That is, when each material of the battery can **11** was compared to each other, the discharge capacity retention ratio tended to be higher in the case that iron was used than in the case that aluminum was used. Accordingly, it was confirmed that in the secondary battery of the invention, the cycle characteristics were improved not depending the battery structure. Further, it was confirmed that when the battery structure was square, higher effects were obtained in the case that the battery can **11** made of iron was used than in the case that the battery can **11** made aluminum was used. Though no specific examples for a cylindrical secondary battery in which the package member is made of a metal material have been herein given, it is evident that similar effects is obtained in such a cylindrical secondary battery since the cycle characteristics were improved in the square secondary battery including the package member made of the metal than in the laminated film secondary battery including the film package member.

Examples 12-1

[0196] A procedure was performed in the same manner as that of Example 2-2, except that 4-fluoro-1,3-dioxolane-2-one (FEC) as fluorinated ester carbonate (monofluoroethylene carbonate) was used instead of EC as a solvent.

Example 12-2

[0197] A procedure was performed in the same manner as that of Example 2-2, except that 4,5-difluoro-1,3-dioxolane-

2-one (DFEC) as fluorinated ester carbonate (difluoroethylene carbonate) was added as a solvent, and the composition of the mixed solvent (EC:DFEC:DEC) was 25:5:70 at a weight ratio.

Examples 12-3 and 12-4

[0198] A procedure was performed in the same manner as that of Example 12-1, except that vinylene carbonate (VC: Example 12-3) or vinylethylene carbonate (VEC: Example 12-4) that was a cyclic carbonate having an unsaturated bond was added as a solvent to the electrolytic solution. The contents of VC or VEC in the electrolytic solution was 10 wt %.

Example 12-5

[0199] A procedure was performed in the same manner as that of Example 12-1, except that 1,3-propenesultone (PRS) as sultone was added as a solvent to the electrolytic solution. The concentration of PRS in the electrolytic solution was 1 wt %.

Example 12-6

[0200] A procedure was performed in the same manner as that of Example 12-1, except that lithium tetrafluoroborate ($LiBF_4$) that was a compound having boron and fluorine was added as an electrolyte salt to the electrolytic solution. The concentration of $LiBF_4$ in the electrolytic solution was 0.1 mol/kg.

[0201] When the cycle characteristics were examined for the secondary batteries of Examples 12-1 to 12-6, the results shown in Table 12 were obtained. Table 12 shows the result of Example 2-2 together.

[0202] For the secondary batteries of Examples 2-2 and 12-5, not only the cycle characteristics but also the swollenness characteristics were examined. When the swollenness characteristics were examined, the swollenness ratio was obtained by charging the secondary battery by the following procedure. First, to stabilize the battery state, after charge and discharge were performed 1 cycle in the atmosphere at 23 deg C., the thickness before charge at the second cycle was measured. Subsequently, charge was performed again in the same atmosphere. After that, the thickness after charge at the second cycle was measured. Finally, the swollenness ratio (%)=[(thickness after charge−thickness before charge)/thickness before charge]×100 was calculated. The charge condition was similar to the case examining the cycle characteristics.

TABLE 12

Anode active material particle: silicon (electron beam evaporation method)
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm
Oxygen content in the anode active material particle = 3 atomic %

	Anode active material layer	Anode current collector		Electrolytic solution					Discharge capacity	
	Number of anode active material particle layers (layer)	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Solvent (wt %) EC	FEC	DFEC	DEC	Others	retention ratio (%)	Swollenness ratio (%)
Example 2-2	6	0.8	50	50			50		86	3.01
Example 12-1					50		50		90	
Example 12-2				25	----	5	70		91	----
Example 12-3				----	50	----	50	VC	92	----
Example 12-4								VEC	93	----
Example 12-5								PRS	92	0.30
Example 12-6								$LiBF_4$	91	—

[0203] As shown in Table 12, in Examples 12-1 to 12-6 in which the fluorinated ester carbonate (FEC or DFEC) was added to a solvent, or the cyclic ester carbonate or the like having an unsaturated bond as a solvent o (VC, VEC, PRS, or $LiBF_4$) was added to the electrolytic solution, the discharge capacity retention ratio was higher than that of Example 2-2 in which the foregoing was not added. In this case, the discharge capacity retention ratio of Example 12-2 in which the solvent contained DFEC as difluoroethylene carbonate tended to be higher than that of Example 12-1 in which the solvent contained FEC as monofluoroethylene carbonate. Further, the discharge capacity retention ratio of Examples 12-3 to 12-6 containing VC or the like tended to be higher than that of Example 12-1 not containing VC or the like. More specifically, the discharge capacity retention ratio of Examples 12-3 and 12-4 in which the solvent contained VC or VEC was higher than that of Examples 12-5 and 12-6 in which the solvent contained PRS or $LiBF_4$. Further, the discharge capacity retention ratio of Example 12-4 in which the solvent contained VEC was higher than that of Example 12-3 in which the solvent contained VC. Accordingly, it was confirmed that in the secondary battery of the invention, the cycle characteristics were improved not depending on the composition of the solvent and the electrolytic solution. Further, it was confirmed that when the solvent contained the fluorinated ester carbonate, the cyclic ester carbonate having an unsaturated bond, sultone, or the electrolyte salt containing boron and fluorine, higher effects were obtained. In particular, to obtain higher effects, difluoroethylene carbonate was more preferable than monofluoroethylene carbonate as the fluorinated ester carbonate, and vinylethylene carbonate was more

preferable than vinylene carbonate as the cyclic ester carbonate having an unsaturated bond.

[0204] Further, in Example 12-5 in which the solvent contained PRS, the swollenness ratio was largely lowered than that of Example 2-2 in which the solvent did not contain PRS. Thereby, it was confirmed that in the secondary battery of the invention, when the solvent contained sultone, the swollenness characteristics were improved.

Example 13-1

[0205] A procedure was performed in the same manner as that of Example 2-2, except that a metal was formed after the anode active material particle was formed. The metal was formed by depositing cobalt by electrolytic plating method on the both faces of the anode current collector **54**A formed with the anode active material particle, and thereby the anode active material layer **54**B was formed to contain the metal together with the anode active material particle. As a plating solution, a cobalt plating solution (Nippon Kojundo Kagaku Co., Ltd. make) was used. The current density was in the range from 2 A/dm^2 to 5 A/dm^2, and the plating rate was 10 nm/sec. Further, the ratio (molar ratio) M2/M1 between the number of moles M1 per unit area of the anode active material particle and the number of moles M2 per unit area of the metal was 1/15.

Examples 13-2 to 13-7

[0206] A procedure was performed in the same manner as that of Example 13-1, except that the molar ratio M2/M1 was 1/10 (Example 13-2), 1/5 (Example 13-3), 1/2 (Example 13-4), 1/1 (Example 13-5), 2/1 (Example 13-6), or 3/1 (Example 13-7) instead of 1/15.

Examples 13-8 to 13-11

[0207] A procedure was performed in the same manner as that of Example 13-4, except that an iron plating solution (Example 13-8), a nickel plating solution (Example 13-9), a zinc plating solution (Example 13-10), or a copper plating solution (Example 13-11) was used instead of the cobalt plating solution as a plating solution. The current density was in the range from 2 A/dm^2 to 5 A/dm^2 in the case of using the iron plating solution, in the range from 2 A/dm^2 to 10 A/dm^2 in the case of using the nickel plating solution, in the range from 1 A/dm^2 to 3 A/dm^2 in the case of using the zinc plating solution, and in the range from 2 A/dm^2 to 8 A/dm^2 in the case of using the copper plating solution. All the foregoing plating solutions were made by Nippon Kojundo Kagaku Co., Ltd.

[0208] When the cycle characteristics of the secondary batteries of Examples 13-1 to 13-11 were examined, the results shown in Table 13 and FIG. **22** were obtained. Table 13 shows the result of Example 2-2 together.

[0209] For the secondary batteries of Examples 13-1 to 13-11, to examine not only the cycle characteristics but also the relation between a metal amount and the cycle characteristics, the ratio of the number of atoms occupied by the metal (occupancy ratio of the metal) on the surface of the anode **54** was also examined. To examine the occupancy ratio of the metal, the surface of the anode **54** was provided with element analysis with the use of an EDX, and thereby the metal existence ratio on the surface was measured.

TABLE 13

Anode active material particle: silicon (electron beam evsporation method)
Thickness of original foil = 18 μm
Ten point height of roughness profile Rz = 3.5 μm
Oxygen content in the anode active material particle = 3 atomic %

	Anode active material layer				Anode current collector		
	Number of anode active material particle layers (layer)	Metal type	Molar ratio M2/M1	Occupancy ratio of metal (atomic %)	Intensity ratio I (200)/I (111)	Cross-section area of crystallite (μm^2)	Discharge capacity retention ratio (%)
Example 2-2	6	—	—	—	0.8	50	86
Example 13-1		Co	1/15	2			88
Example 13-2			1/10	4.1			90
Example 13-3			1/5	6.3			91
Example 13-4			1/2	8.3			92
Example 13-5			1/1	10.3			91
Example 13-6			2/1	18			90
Example 13-7			3/1	30			89
Example 13-8		Fe	1/2	11.2			91
Example 13-9		Ni		9.5			90
Example 13-10		Zn		8.5			90
Example 13-11		Cu		8.9			90

[0210] As shown in Table 13 and FIG. **22**, in Examples 13-1 to 13-11 in which the metal was formed, when the molar ratio M2/M1 was in the range from 1/15 to 3/1 and the occupancy ratio of the metal was in the range from 2 atomic % to 30 atomic %, the discharge capacity retention ratio thereof was higher than that of Example 2-2 in which the metal was not formed. In this case, Examples 13-4, 13-8 to 13-11 having the different metal types were compared to each other, the discharge capacity retention ratio was higher in the case of using iron than in the case of using copper, zinc, and nickel as the metal; and still higher in the case of using cobalt. Thereby, it was confirmed that in the secondary battery of the invention, when the metal having the metal element not reacting with the electrode reactant was formed after the anode active material particle was formed, the cycle characteristics were improved. It was also confirmed that in this case, when cobalt was used as the metal, higher effects were obtained.

[0211] As a representative of Examples 2-2 and 13-1 to 13-11 described above, when cross sections of the anodes **54**

in the secondary batteries of Examples 2-2 and 13-4 were observed, the results shown in FIG. **23**A to FIG. **25**B were obtained.

[0212] FIGS. **23**A and **23**B are SEM photographs showing the cross sectional structures of the anode **54** before a cycle test. FIG. **23**A and FIG. **23**B respectively show observation results of Examples 2-2 and 13-4. FIG. **24** is an SEM photograph showing the surface structure of the anode **54** of Example 13-4 before the cycle test. As shown in FIGS. **23**A and **23**B, in both Examples 2-2 and 13-4, in the anode active material layer **54**B formed on the roughened surface of the anode current collector **54**A, a state that the anode active material particle was grown on the surface with six-layer structure was observed. However, in Example 2-2, as shown in FIG. **23**A, a gap was generated between each anode active material particle and in the anode active material particle. Meanwhile, in Example 13-4, as shown in FIG. **23**B, the metal intrudes into the foregoing gap, and each anode active material particle was bound to each other through the metal. In particular, in Example 13-4, part of the exposed face of the anode active material particle was coated with the metal. Such a state that the metal intruded into the foregoing gap is also evident from FIG. **24**. In FIG. **24**, the high-contrast part shown by **24**A is the anode active material particle, and the low-contrast part shown by **24**B is the metal. Thereby, it was confirmed that in the secondary battery of the invention, the binding characteristics of the anode active material layer **54**B were improved by the metal.

[0213] FIGS. **25**A and **25**B are results obtained by performing element distribution analysis by an EDX (so-called mapping of element distribution) for the cross section of the anode **54** of Example 13-4 shown in FIG. **23**B. In FIG. **25**A, the low-contrast part shown by **25**A is the silicon distribution range. In FIG. **25**B, the low-contrast part shown by **25**B is the cobalt distribution range. As shown in FIGS. **25**A and **25**B, the range where silicon as the anode active material particle did not exist (the portion surrounded by **25**A in FIG. **25**A) corresponded with the range where cobalt as the metal existed (the portion surrounded by **25**B in FIG. **25**B). Such a range was the gap between adjacent anode active material particles and the gap in the anode active material particle. In particular, in Example 13-4, the metal was dotted on the exposed face of the anode active material particle as well. Accordingly, it was confirmed that in the secondary battery of the invention, the metal intruded into the gap between the anode active material particles and the gap in the anode active material particle, and part of the exposed face of the anode active material particle was coated with the metal.

[0214] The invention has been described with reference to the embodiment and the examples. However, the invention is not limited to the aspects described in the foregoing embodiment and the foregoing examples, and various modifications may be made. For example, the current collector and the anode of the invention are not limitedly applied to the battery, but may be applied to other electrochemical device other than the battery. For example, the current collector and the anode of the invention may be applied to a capacitor or the like.

[0215] Further, in the foregoing embodiment and the foregoing examples, the descriptions have been given of the lithium ion secondary battery in which the anode capacity is expressed based on insertion and extraction of lithium as a battery type. However, the battery of the invention is not limited thereto. The invention is similarly applicable to a secondary battery in which the anode capacity includes the capacity based on insertion and extraction of lithium and the capacity based on precipitation and dissolution of lithium, and the anode capacity is expressed as the sum of these capacities, by setting the charge capacity of the anode material capable of inserting and extracting lithium to a smaller value than that of the charge capacity of the cathode.

[0216] Further, in the foregoing embodiment and the foregoing examples, the description has been given with the specific examples of the square, cylindrical, or laminated film secondary battery as a battery structure, and with the specific example of the battery in which the battery element has the spirally wound structure. However, the invention is similarly applicable to a battery having other structure such as a coin type battery and a button type battery, or a battery in which the battery element has other structure such as a lamination structure. The battery of the invention is similarly applicable to other type of battery such as a primary battery in addition to the secondary battery.

[0217] Further, in the foregoing embodiment and the foregoing examples, the description has been given of the case using lithium as an electrode reactant. However, as an electrode reactant, other Group **1**A element such as sodium (Na) and potassium (K), a Group **2**A element such as magnesium (Mg) and calcium (Ca), or other light metal such as aluminum may be used. In this case, the anode material described in the foregoing embodiment may be used as an anode active material as well.

[0218] Further, in the foregoing embodiment and the foregoing examples, regarding the intensity ratio I(200)/I(111) in the current collector of the invention, the numerical value range thereof derived from the results of the examples has been described as the appropriate range. However, such a description does not totally eliminate the possibility that the intensity ratio may be out of the foregoing range. That is, the foregoing appropriate range is the range particularly preferable for obtaining the effects of the invention. Therefore, as long as effects of the invention may be obtained, the intensity ratio may be out of the foregoing range in some degrees. The same is applied to the cross section of the copper crystallite, the ten point height of roughness profile Rz of the current collector, the extension coefficient, the Young's modulus, the thickness of the original foil and the like, in addition to the foregoing intensity ratio.

[0219] It should be understood by those skilled in the art that various modifications, combinations, sub-combinations and alternations may occur depending on design requirements and other factors insofar as they are within the scope of the appended claims or the equivalents thereof.

What is claimed is:

1. A current collector containing copper (Cu), wherein ratio I(200)/I(111) between intensity I (200) of a peak originated in (200) crystal plane of copper obtained by X-ray diffraction and intensity I (111) of a peak originated in (111) crystal plane thereof is in the range from 0.5 to 1.5.

2. The current collector according to claim **1** having a plurality of copper crystallites, wherein a cross-section area of each crystallite is 100 μm^2 or less.

3. The current collector according to claim **1**, wherein ten point height of roughness profile Rz of a surface is in the range from 1.5 μm to 5.5 μm.

4. The current collector according to claim **1** having an original foil and a plurality of fine particles formed on a surface of the original foil, wherein a thickness of the original foil is in the range from 10 μm to 25 μm.

5. The current collector according to claim 1, wherein an extension coefficient is in the range from 1% to 10%, and a Young's modulus is in the range from 5×10^7 MPa to 5×10^9 MPa.

6. An anode comprising:
a current collector; and
an active material layer provided on the current collector, wherein
the current collector contains copper, and ratio I(200)/I (111) between intensity I (200) of a peak originated in (200) crystal plane of copper obtained by X-ray diffraction and intensity I (111) of a peak originated in (111) crystal plane thereof is in the range from 0.5 to 1.5.

7. The anode according to claim 6, wherein the current collector has a plurality of copper crystallites, and a cross-section area of each crystallite is 100 μm^2 or less.

8. The anode according to claim 6, wherein ten point height of roughness profile Rz of a surface of the current collector is in the range from 1.5 μm to 5.5 μm.

9. The anode according to claim 6, wherein the current collector has an original foil and a plurality of fine particles formed on a surface thereof, and a thickness of the original foil is in the range from 10 μm to 25 μm.

10. The anode according to claim 6, wherein an extension coefficient of the current collector is in the range from 1% to 10%, and a Young's modulus is in the range from 5×10^7 MPa to 5×10^9 MPa.

11. The anode according to claim 6, wherein the current collector and the active material layer are alloyed in at least part of an interface therebetween.

12. The anode according to claim 6, wherein the active material layer includes a plurality of active material particles containing silicon (Si).

13. The anode according to claim 12, wherein the active material particles further contain oxygen (O), and a content of the oxygen in the active material particles is in the range from 3 atomic % to 40 atomic %.

14. The anode according to claim 12, wherein the active material particles further have an oxygen-containing region containing oxygen in a thickness direction, and a content of the oxygen in the oxygen-containing region is higher than a content of oxygen in other regions.

15. The anode according to claim 12, wherein the active material layer includes a metal containing a metal element not being alloyed with an electrode reactant in a gap between the active material particles.

16. The anode according to claim 15, wherein the active material layer includes the metal in at least part of an exposed face of the active material particles.

17. The anode according to claim 15, wherein the active material particles have a multilayer structure in the particles, and the active material layer includes the metal in a gap in the active material particles.

18. The anode according to claim 15, wherein the metal element is at least one selected from the group consisting of iron (Fe), cobalt (Co), nickel (Ni), zinc (Zn), and copper (Cu).

19. The anode according to claim 15, wherein ratio M2/M1 between the number of moles M1 per unit area of the active material particles and the number of moles M2 per unit area of the metal is in the range from 1/15 to 3/1.

20. The anode according to claim 15, wherein a ratio of the number of atoms occupied by the metal on a surface of the active material layer is in the range from 2 atomic % to 30 atomic %.

21. The anode according to claim 12, wherein the active material particles are formed by vapor-phase deposition method.

22. The anode according to claim 15, wherein the metal is formed by liquid-phase deposition method.

23. A battery comprising:
a cathode;
an anode; and
an electrolytic solution,
wherein the anode has a current collector and an active material layer provided thereon, and
the current collector contains copper, and ratio I(200)/I (111) between intensity I (200) of a peak originated in (200) crystal plane of copper obtained by X-ray diffraction and intensity I (111) of a peak originated in (111) crystal plane thereof is in the range from 0.5 to 1.5.

24. The battery according to claim 23, wherein the current collector has a plurality of copper crystallites, and a cross-section area of each crystallite is 100 μm^2 or less.

25. The battery according to claim 23, wherein ten point height of roughness profile Rz of a surface of the current collector is in the range from 1.5 μm to 5.5 μm.

26. The battery according to claim 23, wherein the current collector has an original foil and a plurality of fine particles formed on a surface thereof, and a thickness of the original foil is in the range from 10 μm to 25 μm.

27. The battery according to claim 23, wherein an extension coefficient of the current collector is in the range from 1% to 10%, and a Young's modulus is in the range from 5×10^7 MPa to 5×10^9 MPa.

28. The battery according to claim 23, wherein the current collector and the active material layer are alloyed in at least part of an interface therebetween.

29. The battery according to claim 23, wherein the active material layer contains a plurality of active material particles containing silicon.

30. The battery according to claim 29, wherein the active material particles further contain oxygen, and a content of the oxygen in the active material particles is in the range from 3 atomic % to 40 atomic %.

31. The battery according to claim 29, wherein the active material particles further have an oxygen-containing region containing oxygen in a thickness direction, and a content of the oxygen in the oxygen-containing region is higher than a content of oxygen in other regions.

32. The battery according to claim 29, wherein the active material layer includes a metal containing a metal element not being alloyed with an electrode reactant in a gap between the active material particles.

33. The battery according to claim 32, wherein the active material layer includes the metal in at least part of an exposed face of the active material particles.

34. The battery according to claim 32, wherein the active material particles have a multilayer structure in the particles, and the active material layer includes the metal in a gap in the active material particles.

35. The battery according to claim 32, wherein the metal element is at least one selected from the group consisting of iron, cobalt, nickel, zinc, and copper.

36. The battery according to claim 32, wherein ratio M2/M1 between the number of moles M1 per unit area of the active material particles and the number of moles M2 per unit area of the metal is in the range from 1/15 to 3/1.

37. The battery according to claim **32**, wherein a ratio of the number of atoms occupied by the metal on a surface of the active material layer is in the range from 2 atomic % to 30 atomic %.

38. The battery according to claim **29**, wherein the active material particles are formed by vapor-phase deposition method.

39. The battery according to claim **32**, wherein the metal is formed by liquid-phase deposition method.

40. The battery according to claim **23**, wherein the electrolytic solution contains a solvent containing sultone.

41. The battery according to claim **40**, wherein the sultone is 1,3-propanesultone.

42. The battery according to claim **23**, wherein the electrolytic solution contains a solvent containing a cycle ester carbonate having an unsaturated bond.

43. The battery according to claim **42**, wherein the cycle ester carbonate having an unsaturated bond is vinylene carbonate or vinylethylene carbonate.

44. The battery according to claim **23**, wherein the electrolytic solution includes a solvent containing fluorinated ester carbonate.

45. The battery according to claim **42**, wherein the fluorinated ester carbonate is difluoroethylene carbonate.

46. The battery according to claim **23**, wherein the electrolytic solution includes an electrolyte salt containing boron (B) and fluorine (F).

47. The battery according to claim **46**, wherein the electrolyte salt is lithium tetrafluoroborate ($LiBF_4$).

48. The battery according to claim **23**, wherein the cathode, the anode, and the electrolytic solution are contained in a cylindrical or square package member.

49. The battery according to claim **48**, wherein the package member contains iron or an iron alloy.

* * * * *

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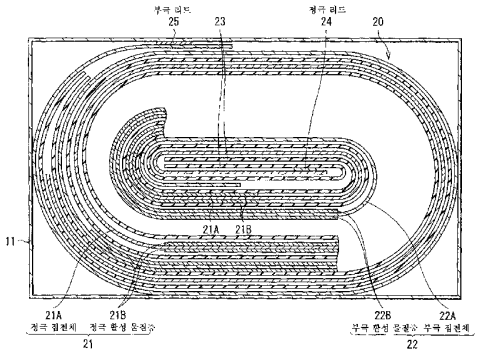
(54) 집전체, 부극 및 전지

(57) 요 약

본 발명은 사이클 특성을 향상시키는 것이 가능한 전지를 제공한다.

정극 (21) 및 부극 (22)와 함께 전해액을 구비하고, 정극 (21)과 부극 (22) 사이에 설치된 세퍼레이터 (23)에 전해액이 함침되어 있다. 부극 (22)는 부극 집전체 (22A) 및 그것에 설치된 부극 활성 물질층 (22B)를 가지고 있다. 이 부극 집전체 (22A)는 구리를 함유하고, X선 회절에 의해 얻어지는 구리의 (200) 결정면에서 기인하는 피크 강도 I(200)과 (111) 결정면에서 기인하는 피크 강도 I(111)과의 비 I(200)/I(111)은 0.5 이상 1.5 이하이다. 강도비 I(200)/I(111)이 상기한 범위밖인 경우보다 부극 집전체 (22A)와 부극 활성 물질층 (22B) 사이의 밀착성이 향상된다.

대 표 도



특허청구의 범위

청구항 1

구리(Cu)를 함유하는 집전체로서,

X선 회절에 의해 얻어지는 구리의 (200) 결정면에서 기인하는 피크 강도 I(200)과 (111) 결정면에서 기인하는 피크 강도 I(111)과의 비 I(200)/I(111)은 0.5 이상 1.5 이하인 것을 특징으로 하는 집전체.

청구항 2

제1항에 있어서, 복수개의 구리 결정자를 가지며, 각 결정자의 단면적이 100 μm^2 이하인 것을 특징으로 하는 집전체.

청구항 3

제1항에 있어서, 표면의 십점 평균 조도 Rz는 1.5 ㎛ 이상 5.5 ㎛ 이하인 것을 특징으로 하는 집전체.

청구항 4

제1항에 있어서, 원박(原箔)과 그의 표면에 형성된 복수개의 미립자를 가지며, 상기 원박의 두께가 10 ㎛ 이상 25 ㎛ 이하인 것을 특징으로 하는 집전체.

청구항 5

제1항에 있어서, 신장률이 1 % 이상 10 % 이하, 영률이 5×10^7 MPa 이상 5×10^9 MPa 이하인 것을 특징으로 하는 집전체.

청구항 6

집전체와 그것에 설치된 활성 물질층을 포함하는 부극으로서,

상기 집전체가 구리를 함유하고, X선 회절에 의해 얻어지는 구리의 (200) 결정면에서 기인하는 피크 강도 I(200)과 (111) 결정면에서 기인하는 피크 강도 I(111)과의 비 I(200)/I(111)은 0.5 이상 1.5 이하인 것을 특징으로 하는 부극.

청구항 7

제6항에 있어서, 상기 집전체가 복수개의 구리 결정자를 가지며, 각 결정자의 단면적이 100 μm^2 이하인 것을 특징으로 하는 부극.

청구항 8

제6항에 있어서, 상기 집전체 표면의 십점 평균 조도 Rz가 1.5 ㎛ 이상 5.5 ㎛ 이하인 것을 특징으로 하는 부극.

청구항 9

제6항에 있어서, 상기 집전체가 원박과 그의 표면에 형성된 복수개의 미립자를 가지며, 상기 원박의 두께가 10 ㎛ 이상 25 ㎛ 이하인 것을 특징으로 하는 부극.

청구항 10

제6항에 있어서, 상기 집전체의 신장률이 1 % 이상 10 % 이하, 영률이 5×10^7 MPa 이상 5×10^9 MPa 이하인 것을 특징으로 하는 부극.

청구항 11

제6항에 있어서, 상기 집전체와 상기 활성 물질층이 계면의 적어도 일부에서 합금화되어 있는 것을 특징으로 하

는 부극.

청구항 12

제6항에 있어서, 상기 활성 물질층이 규소(Si)를 함유하는 복수개의 활성 물질 입자를 포함하는 것을 특징으로 하는 부극.

청구항 13

제12항에 있어서, 상기 활성 물질 입자가 산소(O)를 더 함유하고, 상기 활성 물질 입자 중에서의 산소 함유량이 3 원자수% 이상 40 원자수% 이하인 것을 특징으로 하는 부극.

청구항 14

제12항에 있어서, 상기 활성 물질 입자가 두께 방향에서 산소를 더 함유하는 산소 함유 영역을 가지며, 상기 산소 함유 영역에서의 산소 함유량이 그 이외의 영역에서의 산소 함유량보다 높은 것을 특징으로 하는 부극.

청구항 15

제12항에 있어서, 상기 활성 물질층이 상기 활성 물질 입자 사이의 간극에 전극 반응 물질과 합금화되지 않는 금속 원소를 함유하는 금속을 갖는 것을 특징으로 하는 부극.

청구항 16

제15항에 있어서, 상기 활성 물질층이 상기 활성 물질 입자의 노출면의 적어도 일부에 상기 금속을 갖는 것을 특징으로 하는 부극.

청구항 17

제15항에 있어서, 상기 활성 물질 입자가 입자 내에 다층 구조를 가지며, 상기 활성 물질층이 상기 활성 물질 입자 내의 간극에 상기 금속을 갖는 것을 특징으로 하는 부극.

청구항 18

제15항에 있어서, 상기 금속 원소가 철(Fe), 코발트(Co), 니켈(Ni), 아연(Zn) 및 구리(Cu)로 이루어지는 군 중 1종 이상인 것을 특징으로 하는 부극.

청구항 19

제15항에 있어서, 상기 활성 물질 입자의 단위 면적당 몰수 M1과 상기 금속의 단위 면적당 몰수 M2와의 비 M2/M1이 1/15 이상 3/1 이하인 것을 특징으로 하는 부극.

청구항 20

제15항에 있어서, 상기 활성 물질층의 표면에서 상기 금속이 차지하는 원자수의 비율이 2 원자수% 이상 30 원자수% 이하인 것을 특징으로 하는 부극.

청구항 21

제12항에 있어서, 상기 활성 물질 입자가 기상법에 의해 형성되어 있는 것을 특징으로 하는 부극.

청구항 22

제15항에 있어서, 상기 금속이 액상법에 의해 형성되어 있는 것을 특징으로 하는 부극.

청구항 23

정극 및 부극과 함께 전해액을 구비한 전지로서,

상기 부극은 집전체와 그것에 설치된 활성 물질층을 포함하고,

상기 집전체는 구리를 함유하며, X선 회절에 의해 얻어지는 구리의 (200) 결정면에서 기인하는 피크 강도

I(200)과 (111) 결정면에서 기인하는 피크 강도 I(111)과의 비 I(200)/I(111)은 0.5 이상 1.5 이하인 것을 특징으로 하는 전지.

청구항 24

제23항에 있어서, 상기 집전체가 복수개의 구리 결정자를 가지며, 각 결정자의 단면적이 100 μm^2 이하인 것을 특징으로 하는 전지.

청구항 25

제23항에 있어서, 상기 집전체 표면의 십점 평균 조도 Rz가 1.5 ㎛ 이상 5.5 ㎛ 이하인 것을 특징으로 하는 전지.

청구항 26

제23항에 있어서, 상기 집전체가 원박과 그의 표면에 형성된 복수개의 미립자를 가지며, 상기 원박의 두께가 10 ㎛ 이상 25 ㎛ 이하인 것을 특징으로 하는 전지.

청구항 27

제23항에 있어서, 상기 집전체의 신장률이 1 % 이상 10 % 이하, 영률이 5×10^7 MPa 이상 5×10^9 MPa 이하인 것을 특징으로 하는 전지.

청구항 28

제23항에 있어서, 상기 집전체와 상기 활성 물질층이 계면의 적어도 일부에서 합금화되어 있는 것을 특징으로 하는 전지.

청구항 29

제23항에 있어서, 상기 활성 물질층이 규소를 함유하는 복수개의 활성 물질 입자를 포함하는 것을 특징으로 하는 전지.

청구항 30

제29항에 있어서, 상기 활성 물질 입자가 산소를 더 함유하며, 상기 활성 물질 입자 중에서의 산소 함유량이 3 원자수% 이상 40 원자수% 이하인 것을 특징으로 하는 전지.

청구항 31

제29항에 있어서, 상기 활성 물질 입자가 두께 방향에서 산소를 더 함유하는 산소 함유 영역을 가지며, 상기 산소 함유 영역에서의 산소 함유량이 그 이외의 영역에서의 산소 함유량보다 높은 것을 특징으로 하는 전지.

청구항 32

제29항에 있어서, 상기 활성 물질층이 상기 활성 물질 입자 사이의 간극에 전극 반응 물질과 합금화되지 않는 금속 원소를 함유하는 금속을 갖는 것을 특징으로 하는 전지.

청구항 33

제32항에 있어서, 상기 활성 물질층이 상기 활성 물질 입자의 노출면의 적어도 일부에 상기 금속을 갖는 것을 특징으로 하는 전지.

청구항 34

제32항에 있어서, 상기 활성 물질 입자가 입자 내에 다층 구조를 가지며, 상기 활성 물질층이 상기 활성 물질 입자 내의 간극에 상기 금속을 갖는 것을 특징으로 하는 전지.

청구항 35

제32항에 있어서, 상기 금속 원소가 철, 코발트, 니켈, 아연 및 구리로 이루어지는 군 중 1종 이상인 것을 특징

으로 하는 전지.

청구항 36

제32항에 있어서, 상기 활성 물질 입자의 단위 면적당 몰수 M1과 상기 금속의 단위 면적당 몰수 M2와의 비 M2/M1이 1/15 이상 3/1 이하인 것을 특징으로 하는 전지.

청구항 37

제32항에 있어서, 상기 활성 물질층의 표면에서 상기 금속이 차지하는 원자수의 비율이 2 원자수% 이상 30 원자수% 이하인 것을 특징으로 하는 전지.

청구항 38

제29항에 있어서, 상기 활성 물질 입자가 기상법에 의해 형성되어 있는 것을 특징으로 하는 전지.

청구항 39

제32항에 있어서, 상기 금속이 액상법에 의해 형성되어 있는 것을 특징으로 하는 전지.

청구항 40

제23항에 있어서, 상기 전해액이 술톤을 함유하는 용매를 포함하는 것을 특징으로 하는 전지.

청구항 41

제40항에 있어서, 상기 술톤이 1,3-프로펜술톤인 것을 특징으로 하는 전지.

청구항 42

제23항에 있어서, 상기 전해액이 불포화 결합을 갖는 환상 탄산에스테르를 함유하는 용매를 포함하는 것을 특징으로 하는 전지.

청구항 43

제42항에 있어서, 상기 불포화 결합을 갖는 환상 탄산에스테르가 탄산비닐렌 또는 탄산비닐에틸렌인 것을 특징으로 하는 전지.

청구항 44

제23항에 있어서, 상기 전해액이 불소화 탄산에스테르를 함유하는 용매를 포함하는 것을 특징으로 하는 전지.

청구항 45

제44항에 있어서, 상기 불소화 탄산에스테르가 탄산디플루오로에틸렌인 것을 특징으로 하는 전지.

청구항 46

제23항에 있어서, 상기 전해액이 붕소(B) 및 불소(F)를 갖는 전해질염을 포함하는 것을 특징으로 하는 전지.

청구항 47

제46항에 있어서, 상기 전해질염이 사불화붕산리튬($LiBF_4$)인 것을 특징으로 하는 전지.

청구항 48

제23항에 있어서, 상기 정극, 상기 부극 및 상기 전해액이 원통형 또는 각형 외장 부재의 내부에 수납되어 있는 것을 특징으로 하는 전지.

청구항 49

제48항에 있어서, 상기 외장 부재가 철 또는 철 합금을 함유하는 것을 특징으로 하는 전지.

명 세 서

발명의 상세한 설명

기 술 분 야

<1> 본 발명은 구리를 함유하는 집전체 및 그것을 이용한 부극 및 전지에 관한 것이다.

배 경 기 술

<2> 최근 카메라 일체형 VTR(비디오 테이프 리코더), 휴대 전화 또는 노트북 등의 휴대용 전자 기기가 널리 보급되었고, 그의 소형화, 경량화 및 장기 수명화가 강하게 요구되었다. 이에 따라서, 휴대용 전자 기기의 전원으로서, 전지, 특히 경량이며 고에너지 밀도가 얻어지는 이차 전지의 개발이 진행되고 있다.

<3> 그 중에서도 충방전 반응에 리튬의 흡장 및 방출을 이용하는 이차 전지(소위 리튬 이온 이차 전지)는, 납 전지나 니켈 카드뮴 전지보다 큰 에너지 밀도가 얻어지기 때문에 크게 기대되고 있다.

<4> 리튬 이온 이차 전지는 정극 및 부극과 함께 전해액을 구비한다. 이 부극은, 집전체에 활성 물질층이 설치된 구성을 가지고, 그의 활성 물질층은 전극 반응에 기여하는 활성 물질을 포함한다. 부극 활성 물질로서는, 탄소 재료가 널리 이용되고 있지만, 최근에는 휴대용 전자 기기의 고성능화 및 다기능화에 따라서 전지 용량의 한층 더 향상이 요구되고 있기 때문에, 탄소 재료 대신에 규소를 이용하는 것이 검토되고 있다. 규소의 이론 용량(4199 mAh/g)은 흑연의 이론 용량(372 mAh/g)보다 각별히 커서 전지 용량의 대폭적인 향상이 기대되기 때문이다.

<5> 그런데, 기상법에 의해 활성 물질로서 규소를 퇴적시킨 경우에는, 활성 물질층이 집전체에 밀착되기 어려운 경향이 있기 때문에, 그의 밀착 정도에 따라서는 충방전을 반복하였을 때에 활성 물질층이 집전체로부터 박리될 가능성이 있다. 활성 물질층이 박리되면, 집전성의 저하 등에서 기인하여 부극의 전극 반응이 저해되기 때문에, 이차 전지의 중요한 특성인 사이클 특성이 저하되어 버린다.

<6> 따라서, 부극 활성 물질로서 규소를 이용한 경우에도 사이클 특성을 향상시키기 위해서 각종 고안이 이루어졌다. 구체적으로는, 신장률이 13 % 이상인 집전체를 이용하는 기술(예를 들면, 특허 문헌 1 참조)나, 산술 평균 조도 Ra가 0.01 ㎛ 이상 1 ㎛ 이하인 집전체를 이용하는 기술(예를 들면, 특허 문헌 2 참조)이나, 인장 강도가 3.82 N/㎟ 이상임과 동시에 산술 평균 조도 Ra가 0.01 ㎛ 이상 1 ㎛ 이하인 집전체를 이용하는 기술(예를 들면, 특허 문헌 3 참조) 등이 제안되어 있다.

<7> [특허 문헌 1] 일본 특허 공개 제2005-135856호 공보

<8> [특허 문헌 2] 일본 특허 제3733066호 명세서

<9> [특허 문헌 3] 국제 공개 제01/29912호 공보

발명의 내용

해결 하고자하는 과제

<10> 최근 휴대용 전자 기기는 점점 소형화, 고성능화 및 다기능화되었고, 그에 따라서 이차 전지의 충방전이 빈번하게 반복되는 경향이 있기 때문에, 사이클 특성이 저하되기 쉬운 상황에 있다. 특히 고용량화를 위해서 부극 활성 물질로서 규소를 이용한 리튬 이온 이차 전지에서는, 충방전시에서의 활성 물질의 팽창 및 수축에 의해서도 활성 물질층이 집전체로부터 박리되기 쉽기 때문에, 사이클 특성이 현저히 저하되기 쉽다. 이 때문에, 이차 전지 사이클 특성에 대해서도 한층 더 향상이 요망되었다.

<11> 본 발명은 이러한 문제점을 감안하여 이루어진 것으로, 그의 목적은 사이클 특성을 향상시킬 수 있는 집전체, 부극 및 전지를 제공하는 것에 있다.

과제 해결수단

<12> 본 발명의 집전체는 구리를 함유하는 집전체이다. 이 집전체에서는, X선 회절에 의해 얻어지는 구리의 (200) 결정면에서 기인하는 피크 강도 I(200)과 (111) 결정면에서 기인하는 피크 강도 I(111)과의 비 I(200)/I(111)이

0.5 이상 1.5 이하이다.

<13> 본 발명의 부극은 집전체와 그것에 설치된 활성 물질층을 포함하는 부극이다. 이 부극에서는, 집전체가 구리를 함유하고, X선 회절에 의해 얻어지는 구리의 (200) 결정면에서 기인하는 피크 강도 I(200)과 (111) 결정면에서 기인하는 피크 강도 I(111)과의 비 I(200)/I(111)이 0.5 이상 1.5 이하이다.

<14> 본 발명의 전지는 정극 및 부극과 함께 전해액을 구비한 전지이며, 부극이 집전체와 그것에 설치된 활성 물질층을 포함한다. 이 전지에서는, 집전체가 구리를 함유하고, X선 회절에 의해 얻어지는 구리의 (200) 결정면에서 기인하는 피크 강도 I(200)과 (111) 결정면에서 기인하는 피크 강도 I(111)과의 비 I(200)/I(111)이 0.5 이상 1.5 이하이다.

효 과

<15> 본 발명에 의한 집전체 또는 부극에 따르면, 집전체가 구리를 함유하고, X선 회절에 의해 얻어지는 구리의 결정면에서 기인하는 피크 강도비 I(200)/I(111)이 0.5 이상 1.5 이하이기 때문에, 집전체와 활성 물질층 사이의 밀착성이 향상된다. 따라서, 본 발명의 집전체 또는 부극을 이용한 전지에 따르면, 사이클 특성을 향상시킬 수 있다.

발명의 실시를 위한 구체적인 내용

<16> 이하, 본 발명의 실시 형태에 대하여 도면을 참조하여 상세히 설명한다.

<17> 도 1은 본 발명의 한 실시 형태에 따른 집전체를 이용한 부극의 단면 구성을 나타낸다. 이 부극은, 예를 들면 전지 등의 전기 화학 디바이스에 이용되는 것이며, 대향하는 한쌍의 면을 갖는 부극 집전체 (1)과 그것에 설치된 부극 활성 물질층 (2)를 포함한다.

<18> 부극 집전체 (1)은 양호한 전기 화학적 안정성, 전기 전도성 및 기계적 강도를 갖는 금속 재료에 의해 구성되어 있고, 구리를 함유한다. 이 부극 집전체 (1)이 구리를 함유하는 것은 이하의 이유에 의한다. 첫째로, 구리는 금속 재료 중에서도 높은 전기 전도성을 가지고 있기 때문에, 높은 도전율이 얻어진다. 둘째로, 전극 반응 물질(예를 들면 리튬 등)이 구리와 금속간 화합물을 형성하지 않는 것이면, 전기 화학 디바이스의 동작시(예를 들면 전지의 충방전시)에 부극 활성 물질층 (2)가 팽창 및 수축하더라도, 집전성의 저하나 부극 활성 물질층 (2)의 박리가 억제된다. 셋째로, 부극 활성 물질층 (2)가 구리와 합금화되는 것이면, 부극 집전체 (1)과 부극 활성 물질층 (2) 사이의 밀착성이 향상되기 때문에, 그 부극 활성 물질층 (2)의 박리가 억제된다.

<19> 이 부극 집전체 (1)은 구리와 함께 다른 금속 원소를 함유할 수도 있다. 이 외의 금속 원소의 종류는 부극의 용도 등의 조건에 따라서 임의로 선택 가능하다. 이 경우에는, 부극 집전체 (1)이 구리 단체로 한정되지 않고, 합금이나 다른 화합물일 수도 있다.

<20> 또한, 부극 집전체 (1)은 단층 구조를 가질 수도 있고, 다층 구조를 가질 수도 있다. 다층 구조를 갖는 경우에는, 부극 활성 물질층 (2)와 인접하는 층이 그것과 합금화하는 금속 재료에 의해 구성되어 있고, 인접하지 않는 층이 다른 금속 재료에 의해 구성되어 있는 것이 바람직하다.

<21> 특히, 부극 집전체 (1)에서는, X선 회절에 의해 얻어지는 구리의 (200) 결정면에서 기인하는 피크 강도 I(200)과 (111) 결정면에서 기인하는 피크 강도 I(111)과의 비(강도비) I(200)/I(111)이 0.5 이상 1.5 이하이다. 강도비 I(200)/I(111)이 상기한 범위밖인 경우보다 부극 집전체 (1)과 부극 활성 물질층 (2) 사이의 밀착성이 향상되므로, 그 부극 활성 물질층 (2)의 박리가 억제되기 때문이다. 이 경우에는, 특히 부극 활성 물질층 (2)가 기상법에 의해 형성된 규소를 함유하는 경우에도, 충분한 밀착성이 얻어진다. 이 강도비 I(200)/I(111)은, X선 회절(X-ray diffraction: XRD) 장치를 이용하여 부극 집전체 (1)을 분석하고, 2개의 강도 I(200), I(111)을 측정함으로써 산출 가능하다.

<22> 이 부극 집전체 (1)은 복수개의 구리 결정자를 가지고 있다. 이 결정자에 대해서는, 예를 들면 주사형 전자 현미경(scanning electron microscope: SEM) 등을 이용하여 부극 집전체 (1)의 단면을 관찰함으로써 확인 가능하다. 각 결정자의 단면적은 100 μm^2 이하인 것이 바람직하다. 부극 집전체 (1)과 부극 활성 물질층 (2) 사이의 밀착성이 보다 향상되기 때문이다. 이 「결정자의 단면적」이란, 예를 들면 SEM 사진(이차 전자상) 내에 복수개의 구리 결정자가 확인된 경우에, 각 결정자가 차지하는 단면의 면적이다. 이 단면적은, 예를 들면 크로스섹션 폴리셔(crosssection polisher)에 의해 부극 집전체 (1)의 단면을 노출시킨 후, 저가속 전압 SEM을 이용하여

단면을 관찰함으로써 측정 가능하다.

<23> 전기 화학 디바이스의 동작시에 부극 활성 물질층 (2)가 팽창 및 수축하는 경우에는, 부극 집전체 (1)의 신장(유연성)이 매우 중요하다. 이러한 관점에서, 부극 집전체 (1)의 신장률은 1 % 이상 10 % 이하인 것이 바람직하다. 신장률이 1 %보다 작으면, 부극 활성 물질층 (2)가 팽창 및 수축하였을 때에 생기는 응력을 부극 집전체 (1)의 유연성에 의해 완화시키기 어렵기 때문에, 부극 활성 물질층 (2)가 박리될 가능성이 있기 때문이다. 또한, 신장률이 10 %보다 크면, 부극 활성 물질층 (2)가 팽창 및 수축하였을 때에 부극 집전체 (1)에 주름이 생길 가능성이 있기 때문이다. 이 외, 부극 집전체 (1)의 영(Young)률은 5×10^{7} MPa 이상 5×10^{9} MPa 이하인 것이 바람직하다. 부극 집전체 (1)과 부극 활성 물질층 (2) 사이의 밀착성이 보다 향상되기 때문이다.

<24> 부극 집전체 (1)의 표면은 조면화되어 있는 것이 바람직하다. 소위 앵커 효과에 의해, 부극 집전체 (1)과 부극 활성 물질층 (2) 사이의 밀착성이 향상되기 때문이다. 이 경우에는, 적어도 부극 활성 물질층 (2)와 대향하는 부극 집전체 (1)의 표면이 조면화되어 있으면 좋다. 조면화 방법으로서는, 예를 들면 전해 처리에 의해 미립자를 형성하는 방법 등을 들 수 있다. 이 전해 처리는, 전해조 중에서 전해법에 의해서 금속 표면에 미립자를 형성함으로써 요철을 설치하는 방법이다. 이 금속이 동박인 경우, 전해 처리가 실시된 동박은 일반적으로 「전해 동박」이라 불린다.

<25> 부극 집전체 (1)의 표면의 십점 평균 조도 Rz는 1.5 ㎛ 이상 5.5 ㎛ 이하인 것이 바람직하다. 십점 평균 조도 Rz가 1.5 ㎛보다 작으면, 부극 집전체 (1)과 부극 활성 물질층 (2) 사이의 밀착성이 저하될 가능성이 있고, 5.5 ㎛보다 크면, 부극 활성 물질의 퇴적시에 양호한 입자 형상이 얻어지지 않을 가능성이 있기 때문이다. 이 십점 평균 조도 Rz의 정의는 JIS B 0601에 준거한다.

<26> 도 2는 도 1에 나타낸 부극 집전체 (1)의 일부를 확대하여 모식적으로 나타낸다. 부극 집전체 (1)이 전해 동박으로 이루어지는 경우, 그 부극 집전체 (1)은, 예를 들면 금속박(소위 원박) (1A)와, 그의 표면(예를 들면 양면)에 형성된 복수개의 미립자 (1B)를 가지고 있다. 이 경우에는, 복수개의 미립자 (1B)가 도금막 (1C)에 의해서 피복됨으로써 원박 (1A)에 고정될 수도 있다. 이에 따라, 부극 집전체 (1)의 표면에는, 미립자 (1B)의 위치마다 복수개의 돌기부가 설치되어 있다. 또한, 도금막 (1C)는, 예를 들면 커버링 도금 처리 또는 베이킹 도금 처리에 의해 형성되어 있다.

<27> 원박 (1A)의 두께는 10 ㎛ 이상 25 ㎛ 이하인 것이 바람직하다. 두께가 10 ㎛보다 얇으면, 부극 전체의 부피를 일정하게 한 경우에 부극 활성 물질층 (2)가 차지하는 비율이 커져 부극의 성능을 향상시키기 때문에 바람직하지만, 그의 한편, 고열을 수반하는 증착법 등을 이용하여 부극 활성 물질층 (2)를 형성하는 경우에는 열적 손상을 받을 가능성이 있기 때문이다. 또한, 두께가 25 ㎛보다 두꺼우면, 부극 전체의 유연성이 저하되기 때문에, 부극의 성능이 저하될 가능성이 있기 때문이다.

<28> 부극 활성 물질층 (2)는, 전극 반응 물질을 흡장 및 방출하는 것이 가능한 부극 활성 물질로서, 규소를 함유하는 복수개의 부극 활성 물질 입자를 포함한다. 규소는 전극 반응 물질을 흡장 및 방출하는 능력이 크기 때문에, 높은 에너지 밀도가 얻어지기 때문이다. 이 부극 활성 물질 입자는 규소의 단체, 합금 또는 화합물일 수도 있고, 이들 중 1종 또는 2종 이상의 상을 적어도 일부에 갖는 것일 수도 있다. 이들은 단독으로 이용될 수도 있고, 복수종이 혼합되어 이용될 수도 있다. 또한, 본 발명에 있어서의 「합금」에는, 2종 이상의 금속 원소로 이루어지는 것뿐 아니라, 1종 이상의 금속 원소와 1종 이상의 반금속 원소를 함유하는 것도 포함된다. 물론 「합금」은 비금속 원소를 포함할 수도 있다. 그의 조직에는, 고용체, 공정(공융 혼합물), 금속간 화합물 또는 이들의 2종 이상이 공존하는 것도 있다.

<29> 규소의 합금으로서는, 예를 들면 규소 이외의 구성 원소로서, 주석(Sn), 니켈, 구리, 철, 코발트, 망간(Mn), 아연, 인듐(In), 은(Ag), 티탄, 게르마늄(Ge), 비스무스(Bi), 안티몬(Sb) 및 크롬으로 이루어지는 군 중 1종 이상을 갖는 것 등을 들 수 있다.

<30> 규소의 화합물로서는, 예를 들면 규소 이외의 구성 원소로서, 산소 및 탄소(C)를 갖는 것 등을 들 수 있다. 또한, 규소의 화합물은, 예를 들면 규소 이외의 구성 원소로서, 규소의 합금에 대하여 설명한 일련의 원소 중 1종 또는 2종 이상을 포함할 수도 있다.

<31> 부극 활성 물질 입자는 부극 집전체 (1)에 연결되어 있고, 그 부극 집전체 (1)의 표면에서 부극 활성 물질층 (2)의 두께 방향으로 성장한다. 이 경우에는, 부극 활성 물질 입자가 기상법에 의해 형성되고, 상기한 바와 같이 부극 집전체 (1)과 부극 활성 물질층 (2)의 계면의 적어도 일부에서 합금화되어 있는 것이 바람직하다. 구체적으로는, 양자의 계면에 있어서 부극 집전체 (1)의 구성 원소가 부극 활성 물질 입자로 확산될 수도 있고,

부극 활성 물질 입자의 구성 원소가 부극 집전체 (1)로 확산될 수도 있고, 양자의 구성 원소가 서로 확산될 수도 있다.

<32> 전기 화학 디바이스의 동작시에 부극 활성 물질층 (2)의 팽창 및 수축에 기인하여 파손되기 어려워짐과 동시에, 부극 집전체 (1)과 부극 활성 물질층 (2) 사이에서 전자 전도성이 향상되기 때문이다.

<33> 상기한 기상법으로서는, 예를 들면 물리 퇴적법 또는 화학 퇴적법, 보다 구체적으로는 진공 증착법, 스퍼터법, 이온 플레이팅법, 레이저 박리법, 열 화학 기상 성장(chemical vapor deposition: CVD)법 또는 플라즈마 화학 기상 성장법 등을 들 수 있다.

<34> 이 부극 활성 물질 입자는 1회의 퇴적 공정을 거쳐 형성됨으로써 단층 구조를 가질 수도 있고, 복수회의 퇴적 공정을 거쳐 형성됨으로써 입자 내에 다층 구조를 가질 수도 있다. 단, 퇴적시에 고열을 수반하는 증착법 등에 의해 부극 활성 물질 입자를 퇴적시키는 경우에, 부극 집전체 (1)이 열적 손상을 지나치게 받는 것을 억제하기 위해서는, 다층 구조를 갖는 것이 바람직하다. 부극 활성 물질 입자의 퇴적 공정을 복수회로 분할하여 행함으로써(부극 활성 물질 입자를 차례로 퇴적시켜 적층함으로써), 그 퇴적 공정을 1회에 행하는 경우보다 부극 집전체 (1)이 고열에 노출되는 시간이 짧아지기 때문이다.

<35> 부극 활성 물질 입자는 규소와 함께 산소를 더 함유하는 것이 바람직하다. 부극 활성 물질층 (2)의 팽창 및 수축이 억제되기 때문이다. 이 경우에는, 적어도 일부의 산소가 일부의 규소와 결합되어 있는 것이 바람직하다. 또한, 결합 상태는 일산화규소 또는 이산화규소일 수도 있고, 다른 준안정 상태일 수도 있다.

<36> 부극 활성 물질 입자 중에서의 산소 함유량은 3 원자수% 이상 40 원자수% 이하인 것이 바람직하다. 보다 높은 효과가 얻어지기 때문이다. 상세하게는 산소 함유량이 3 원자수%보다 적으면, 부극 활성 물질층 (2)의 팽창 및 수축이 충분히 억제되지 않을 가능성이 있고, 40 원자수%보다 많으면, 저항이 너무 증대될 가능성이 있기 때문이다. 또한, 전기 화학 디바이스에 있어서 부극이 전해액과 함께 이용되는 경우에는, 그 전해액의 분해 반응에 의해 형성되는 피막 등은 부극 활성 물질 입자에 포함시키지 않는 것으로 한다. 즉, 부극 활성 물질 입자 중에서의 산소 함유량을 산출하는 경우에는, 상기한 피막 중의 산소는 포함시키지 않는다.

<37> 산소를 함유하는 부극 활성 물질 입자는, 기상법에 의해 부극 활성 물질 입자를 형성할 때에, 챔버 내에 연속적으로 산소 가스를 도입함으로써 형성 가능하다. 특히, 산소 가스를 도입하는 것만으로는 원하는 산소 함유량이 얻어지지 않는 경우에는, 챔버 내에 산소 공급원으로서 액체(예를 들면 수증기 등)을 도입할 수도 있다.

<38> 또한, 부극 활성 물질 입자는 규소와 함께 금속 원소를 더불어 함유할 수도 있다. 부극 활성 물질층 (2)의 팽창 및 수축이 억제되기 때문이다. 이 금속 원소로서는, 예를 들면 철, 코발트, 니켈, 티탄, 크롬 및 몰리브덴으로 이루어지는 군 중 1종 이상 등을 들 수 있다. 부극 활성 물질 입자 중에서의 금속 원소의 함유량은 임의로 설정 가능하다. 단, 부극이 전지에 이용되는 경우에는, 금속 원소의 함유량이 너무 많아지면 원하는 전지 용량을 얻기 위해서 부극 활성 물질층 (2)를 두껍게 해야만 하고, 부극 활성 물질층 (2)의 박리나 균열이 발생하기 쉬워질 가능성이 있다.

<39> 상기한 금속 원소를 함유하는 부극 활성 물질 입자는, 예를 들면 기상법으로서 증착법에 의해 부극 활성 물질 입자를 형성할 때에, 금속 원소를 혼합시킨 증착원 또는 다원계 증착원 등을 이용함으로써 형성 가능하다.

<40> 또한, 부극 활성 물질 입자는 그의 두께 방향에서 규소와 함께 산소를 더불어 함유하는 산소 함유 영역을 가지고, 그 산소 함유 영역에서의 산소 함유량은 그 이외의 영역에서의 산소 함유량보다 높아진 것이 바람직하다. 부극 활성 물질층 (2)의 팽창 및 수축이 억제되기 때문이다. 이 산소 함유 영역 이외의 영역은 산소를 함유할 수도 있고, 함유하지 않을 수도 있다. 물론, 산소 함유 영역 이외의 영역도 산소를 함유하는 경우에는, 그 산소 함유량이 산소 함유 영역에서의 산소 함유량보다 낮은 것은 물론이다.

<41> 이 경우에는, 부극 활성 물질층 (2)의 팽창 및 수축을 보다 억제하기 위해서, 산소 함유 영역 이외의 영역도 산소를 함유하며, 부극 활성 물질 입자가 제1 산소 함유 영역(보다 낮은 산소 함유량을 갖는 영역) 및 그보다 높은 산소 함유량을 갖는 제2 산소 함유 영역(보다 높은 산소 함유량을 갖는 영역)을 포함하는 것이 바람직하다. 특히, 제1 산소 함유 영역에 의해 제2 산소 함유 영역이 사이에 끼워진 것이 바람직하고, 이들이 교대로 반복하여 적층된 것이 보다 바람직하다. 보다 높은 효과가 얻어지기 때문이다. 제1 산소 함유 영역에서의 산소 함유량은 가능한 한 적은 것이 바람직하고, 제2 산소 함유 영역에서의 산소 함유량은, 예를 들면 상기한 부극 활성 물질 입자가 산소를 함유하는 경우의 함유량과 동일하다.

<42> 제1 및 제2 산소 함유 영역을 포함하는 부극 활성 물질 입자는, 예를 들면 기상법에 의해 부극 활성 물질 입자

를 형성할 때에, 챔버 내에 간헐적으로 산소 가스를 도입함으로써 형성 가능하다. 물론, 산소 가스를 도입하는 것만으로는 원하는 산소 함유량이 얻어지지 않는 경우에는, 챔버 내에 액체(예를 들면 수증기 등)을 도입할 수도 있다.

<43> 또한, 제1 및 제2 산소 함유 영역 사이에서는, 산소 함유량이 명확하게 상이할 수도 있고, 명확하게 상이하지 않을 수도 있다. 특히, 상기한 산소 가스의 도입량을 연속적으로 변화시킨 경우에는, 산소 함유량이 연속적으로 변화될 수도 있다. 제1 및 제2 산소 함유 영역은 산소 가스의 도입량을 간헐적으로 변화시킨 경우에는 소위 「층」이 되고, 한편 산소 가스의 도입량을 연속적으로 변화시킨 경우에는 「층」이라고 하기 보다 오히려 「층상」이 된다. 후자의 경우에는, 부극 활성 물질 입자 중에서 산소 함유량이 고저를 반복하면서 분포한다. 이 경우에는, 제1 및 제2 산소 함유 영역 사이에서, 산소 함유량이 단계적 또는 연속적으로 변화되는 것이 바람직하다. 산소 함유량이 급격히 변화되면, 이온 확산성의 저하나 저항의 증대를 초래할 가능성이 있기 때문이다.

<44> 특히, 부극 활성 물질층 (2)는 부극 활성 물질 입자와 함께, 전극 반응 물질과 합금화되지 않는 금속 원소를 함유하는 금속을 더불어 포함하는 것이 바람직하다. 이 금속을 통해 부극 활성 물질 입자끼리 결착되므로, 부극 활성 물질층 (2)의 팽창 및 수축이 억제되기 때문이다. 이 「금속」이란, 광의의 의미이고, 전극 반응 물질과 합금화되지 않는 금속 원소를 함유하면, 단체, 합금 또는 화합물 중 어느 것일 수도 있다. 이 경우에는, 특히 기상법 등에 의해 부극 활성 물질 입자를 형성한 경우에도 높은 결착성이 얻어진다. 이 금속 원소로서는, 예를 들면 철, 코발트, 니켈, 아연 및 구리로 이루어지는 군 중 1종 이상 등을 들 수 있다.

<45> 이 금속은, 상기한 바와 같이 부극 활성 물질 입자가 부극 집전체 (1)의 표면에서 부극 활성 물질층 (2)의 두께 방향으로 성장된 경우에, 인접하는 부극 활성 물질 입자 사이의 간극에 설치되어 있다. 또한, 금속은, 예를 들면 부극 활성 물질 입자의 노출면, 즉 다른 부극 활성 물질 입자와 인접하지 않은 표면의 적어도 일부를 피복한다. 또한, 금속은, 예를 들면 부극 활성 물질 입자가 입자 내에 다층 구조를 갖는 경우에, 그 입자 내의 간극에 설치되어 있다.

<46> 도 3은 도 1에 나타낸 부극의 일부를 확대하여 나타내었고, (A)는 SEM 사진, (B)는 (A)에 나타낸 SEM상의 모식도를 각각 나타낸다. 도 3에서는, (A)에 있어서 (B)에서 해칭이 부여되지 않은 부분이 부극 활성 물질 입자 (201)이고, 해칭이 부여된 부분이 금속 (202)이다. 또한, 도 3에서는, 부극 활성 물질 입자 (201)이 입자 내에 다층 구조를 갖는 경우를 나타낸다.

<47> 도 3에 나타낸 바와 같이, 부극 집전체 (1)의 표면에 복수회에 걸쳐 퇴적된 부극 활성 물질 입자 (201)은, 그 입자 내에 다층 구조를 갖는다. 이 경우에는, 부극 집전체 (1)의 표면이 조면화되어 있기 때문에(부극 집전체 (1)의 표면에 복수개의 돌기가 존재함), 부극 활성 물질 입자 (201)이 돌기부마다 두께 방향으로 단계적으로 성장한다. 금속 (202)는, 예를 들면 인접하는 부극 활성 물질 입자 (201) 사이의 간극에 설치되어 있고(금속 (202A)), 부극 활성 물질 입자 (201)의 노출면이 부분적으로 피복되어 있으며(금속 (202B)), 부극 활성 물질 입자 (201)의 입자 내 간극에 설치되어 있다(금속 (202C)).

<48> 금속 (202A)는 부극 활성 물질층 (2)의 결착성을 높이기 위해서, 인접하는 부극 활성 물질 입자 사이의 간극에 들어가 있다. 상세하게는 기상법 등에 의해 부극 활성 물질 입자 (201)이 형성되는 경우에는, 상기한 바와 같이 부극 집전체 (1)의 표면에 존재하는 돌기부마다 부극 활성 물질 입자 (201)이 성장하기 때문에, 인접하는 부극 활성 물질 입자 (201) 사이에 간극이 생긴다. 이 간극은 부극 활성 물질층 (2)의 결착성을 저하시키는 원인이 되기 때문에, 그 결착성을 높이기 위해서, 상기한 간극에 금속 (202A)가 충전되어 있다. 이 경우에는, 간극의 일부라도 충전되어 있으면 좋지만, 그 충전량이 많을수록 바람직하다. 부극 활성 물질층 (2)의 결착성이 보다 향상되기 때문이다. 금속 (202A)의 충전량은 20 % 이상인 것이 바람직하고, 40 % 이상인 것이 보다 바람직하고, 80 % 이상인 것이 더욱 바람직하다.

<49> 금속 (202B)는, 최상층의 부극 활성 물질 입자 (201)의 노출면에 생기는 수염 형상의 미세한 돌기부(도시하지 않음)가 전기 화학 디바이스의 성능에 악영향을 미치는 것을 방지하기 위해서, 그 돌기부를 피복하고 있다. 상세하게는 기상법 등에 의해 부극 활성 물질 입자 (201)이 형성되는 경우에는, 그 표면에 수염 형상의 미세한 돌기부가 생기기 때문에, 돌기부 사이에 공극이 생긴다. 이 공극은 부극 활성 물질 입자 (201)의 표면적의 증가를 초래하고, 그 표면에 형성되는 불가역성의 피막량도 증가시키기 때문에, 전극 반응의 진행도를 저하시키는 원인이 될 가능성이 있다. 따라서, 전극 반응 진행도의 저하를 방지하기 위해서, 상기한 공극이 금속 (202B)에 의해 매립된다. 이 경우에는, 공극의 일부라도 매립되어 있으면 좋지만, 그 매립량이 많을수록 바람직하다. 전극 반응 진행도의 저하가 보다 억제되기 때문이다. 도 3에 있어서, 최상층의 부극 활성 물질 입자 (201)의 표면에 금속 (202B)가 점재된 것은, 그 점재 개소에 상기한 미세한 돌기부가 존재하는 것을 나타낸다.

<50> 금속 (202C)는 부극 활성 물질층 (2)의 결착성을 높이기 위해서 부극 활성 물질 입자 (201) 내의 간극에 들어가 있다. 상세하게는, 부극 활성 물질 입자 (201)이 다층 구조를 갖는 경우에는, 각 계층 사이에 간극이 생긴다. 이 간극은, 상기한 인접하는 부극 활성 물질 입자 (201) 사이의 간극과 동일하게, 부극 활성 물질층 (2)의 결착성을 저하시키는 원인이 되기 때문에, 그 결착성을 높이기 위해서 상기한 간극에 금속 (202C)가 충전된다. 이 경우에는, 간극의 일부라도 충전되어 있으면 좋지만, 그 충전량이 많을수록 바람직하다. 부극 활성 물질층 (2)의 결착성이 보다 향상되기 때문이다.

<51> 특히, 금속 (202C)는 금속 (202B)와 동일한 기능도 담당한다. 상세하게는, 부극 활성 물질 입자 (201)이 복수회에 걸쳐 퇴적됨으로써 적층되는 경우에는, 그 퇴적시마다 부극 활성 물질 입자 (201)의 표면에 상기한 미세한 돌기부가 생긴다. 이로부터, 금속 (202C)는 부극 활성 물질 입자 (201) 내의 간극에 충전될 뿐만 아니라, 상기한 미세한 공극도 매립된다.

<52> 이 금속은, 예를 들면 기상법 및 액상법으로 이루어지는 군 중 1종 이상의 방법에 의해 형성되어 있다. 그 중에서도 금속은 액상법에 의해 형성되어 있는 것이 바람직하다. 도 3을 참조하여 설명한 간극에 금속이 충전되기 쉬움와 동시에, 동일하게 공극에 금속이 매립되기 쉽기 때문이다.

<53> 상기한 기상법으로서는, 예를 들면 부극 활성 물질 입자의 형성 방법과 동일한 방법을 들 수 있다. 또한, 액상법으로서는, 예를 들면 전해 도금법 또는 무전해 도금법 등의 도금법을 들 수 있다. 그 중에서도, 액상법으로서는, 무전해 도금법보다 전해 도금법이 바람직하다. 보다 높은 효과가 얻어지기 때문이다.

<54> 부극 활성 물질 입자의 단위 면적당 몰수 M1과 금속의 단위 면적당 몰수 M2와의 비(몰비) M2/M1은 1/15 이상 3/1 이하인 것이 바람직하다. 또한, 부극 표면에서 금속이 차지하는 원자수의 비율(금속의 점유 비율)은 2 원자수% 이상 30 원자수% 이하인 것이 바람직하다. 부극 활성 물질층 (2)의 팽창 및 수축이 억제되기 때문이다. 이 금속의 점유 비율은, 예를 들면 부극의 표면을 에너지 분산형 형광 X선 분석(energy dispersive x-ray fluorescence spectroscopy: EDX)으로 원소 분석함으로써 측정 가능하다.

<55> 또한, 금속은 산소를 함유할 수도 있다. 부극 활성 물질층 (2)의 팽창 및 수축이 보다 억제되기 때문이다. 금속 중에서의 산소 함유량은 임의로 설정 가능하다. 산소를 함유하는 금속은, 예를 들면 산소를 함유하는 부극 활성 물질 입자와 동일한 절차에 의해 형성 가능하다.

<56> 이 부극은, 예를 들면 이하의 절차에 의해 제조된다.

<57> 우선, 구리를 함유하는 부극 집전체 (1)을 준비한 후, 기상법 등을 이용하여 부극 집전체 (1) 상에 규소를 함유하는 복수개의 부극 활성 물질 입자를 형성한다. 이 부극 집전체 (1)을 준비하는 경우에는, 원박 (1A)에 전해 처리를 실시하여 복수개의 미립자 (1B) 및 도금막 (1C)를 형성함으로써 얻을 수도 있다. 또한, 부극 활성 물질 입자를 형성하는 경우에는, 1회의 퇴적 공정에 의해 단층 구조가 되도록 할 수도 있고, 복수회의 퇴적 공정에 의해 다층 구조가 되도록 할 수도 있다. 이 후, 액상법 등을 이용하여 전극 반응 물질과 합금화되지 않는 금속 원소를 갖는 금속을 형성한다. 이에 의해, 인접하는 부극 활성 물질 입자 사이의 간극에 금속이 들어가서 부극 활성 물질층 (2)가 형성된다. 이 경우에는, 예를 들면 부극 활성 물질 입자의 노출면의 적어도 일부가 금속에 의해 피복된다. 또한, 예를 들면 부극 활성 물질 입자를 다층 구조가 되도록 형성한 경우에는, 부극 활성 물질 입자 내의 간극에 금속이 들어간다.

<58> 특히, 부극을 제조할 때는, 어느 하나의 공정에서 부극 집전체 (1)을 가열(소위 어닐링)함으로써, X선 회절에 의해 얻어지는 구리의 결정면에서 기인하는 피크 강도비 I(200)/I(111)이 0.5 이상 1.5 이하가 되도록 한다. 이 경우에는, 부극 활성 물질층 (2)의 형성 전에 어닐링할 수도 있고, 그 형성 후에 어닐링할 수도 있다. 이 부극 집전체 (1)의 어닐링 온도는 상기한 강도비 I(200)/I(111)의 값에 따라서 임의로 설정 가능하다.

<59> 또한, 두께가 10 ㎛ 이상 25 ㎛ 이하인 원박 (1A)를 이용함과 동시에, 신장률이 1 % 이상 10 % 이하, 영률이 5×10^{7} MPa 이상 5×10^{9} MPa 이하인 부극 집전체 (1)을 이용하는 것이 바람직하다. 이 경우에는, 원박 (1A)를 어닐링하여 구리의 각 결정자의 단면적이 100 μm^{2} 이하가 되도록 하는 것이 바람직하다. 이 원박 (1A)의 어닐링 온도는 상기한 단면적의 값에 따라서 임의로 설정 가능하다.

<60> 이 집전체를 이용한 부극에 따르면, 부극 집전체 (1)이 구리를 함유하고, X선 회절에 의해 얻어지는 구리의 결정면에서 기인하는 피크 강도비 I(200)/I(111)이 0.5 이상 1.5 이하이기 때문에, 그 강도비 I(200)/I(111)이 상기한 범위밖인 경우보다 부극 집전체 (1)과 부극 활성 물질층 (2) 사이의 밀착성이 향상된다. 이에 따라, 부극 활성 물질층 (2)가 부극 집전체 (1)로부터 박리되는 것이 억제된다. 이 경우에는, 부극 집전체 (1)이 전해

동박이면, 부극 집전체 (1)(도금막 (1C))과 부극 활성 물질층 (2)와의 밀착성이 충분한 경우에, 도금막 (1C)가 원박 (1A) 및 미립자 (1B)로부터 박리되거나, 미립자 (1B) 및 도금막 (1C)가 원박 (1A)로부터 박리되는 것도 억제된다. 따라서, 전기 전도성 등의 전기적 특성을 향상시킬 수 있다. 특히, 부극 활성 물질층 (2)의 부극 활성 물질 입자가 규소를 함유하고, 그 부극 활성 물질 입자가 기상법에 의해 퇴적되어 있으면, 부극 활성 물질층 (2)의 팽창 및 수축에서 기인하여 밀착성이 저하되기 쉽기 때문에, 현저한 효과를 얻을 수 있다.

<61> 또한, 구리 결정자의 단면적이 100 μm^2 이하이거나, 또는 원박 (1A)의 두께가 10 ㎛ 이상 25 ㎛ 이하이거나, 또는 부극 집전체 (1)의 신장률이 1 % 이상 10 % 이하, 영률이 5×10^7 MPa 이상 5×10^9 MPa 이하이거나, 또는 부극 집전체 (1)의 표면의 십점 평균 조도 Rz가 1.5 ㎛ 이상 5.5 ㎛ 이하이면, 보다 높은 효과를 얻을 수 있다. 이 외, 부극 집전체 (1) 및 부극 활성 물질층 (2)가 계면의 적어도 일부에서 합금화되어 있으면, 보다 높은 효과를 얻을 수 있다.

<62> 또한, 부극 활성 물질층 (2)가 규소를 함유하는 복수개의 부극 활성 물질 입자를 갖는 경우에, 그 부극 활성 물질 입자가 산소를 더 함유하고, 부극 활성 물질 입자 중에서의 산소 함유량이 3 원자수% 이상 40 원자수% 이하이거나, 또는 부극 활성 물질 입자가 두께 방향에서 산소를 더 함유하는 산소 함유 영역을 가지고, 산소 함유 영역에서의 산소 함유량이 그 이외의 영역에서의 산소 함유량보다 높아지면, 보다 높은 효과를 얻을 수 있다.

<63> 또한, 부극 활성 물질층 (2)가 부극 활성 물질 입자 사이의 간극에 전극 반응 물질과 합금화되지 않는 금속 원소를 함유하는 금속을 가지고 있으면, 그 금속을 통해 부극 활성 물질 입자끼리 결착되기 때문에, 부극 활성 물질층 (2)의 분쇄 및 붕락을 억제할 수 있다. 특히, 금속이 부극 활성 물질 입자의 노출면의 적어도 일부를 피복하고 있으면, 그 노출면에 생기는 수염 형상의 미세한 돌기부에 의한 악영향을 억제할 수 있다. 또한, 부극 활성 물질 입자가 입자 내에 다층 구조를 갖는 경우에, 그 입자 내의 간극에 금속을 가지고 있으면, 상기한 부극 활성 물질 입자 사이의 간극에 금속을 갖는 경우와 동일하게, 부극 활성 물질층 (2)의 분쇄 및 붕락을 억제할 수 있다. 이 경우에는, 부극 활성 물질 입자와 금속과의 몰비 M2/M1이 1/15 이상 3/1 이하이거나, 부극 활성 물질층 (2)의 표면에서의 금속의 점유 비율이 2 원자수% 이상 30 원자수% 이하이면, 보다 높은 효과를 얻을 수 있다. 또한, 금속이 액상법에 의해 형성되어 있으면, 부극 활성 물질 입자 사이의 간극 및 부극 활성 물질 입자 내의 간극에 금속이 들어가기 쉬워짐과 동시에, 수염 형상의 미세한 돌기부 사이의 공극에 금속이 매립되기 쉬워지기 때문에, 보다 높은 효과를 얻을 수 있다.

<64> 다음에, 상기한 부극의 사용예에 대하여 설명한다. 여기서, 전기 화학 디바이스의 일례로서 전지를 예로 들면, 부극은 이하와 같이 하여 전지에 이용된다.

<65> (제1 전지)

<66> 도 4 및 도 5는 제1 전지의 단면 구성을 나타내고, 도 5에서는 도 4에 나타낸 V-V선에 따른 단면을 나타낸다. 여기서 설명하는 전지는, 예를 들면 부극 (22)의 용량이 전극 반응 물질인 리튬의 흡장 및 방출에 기초하여 표시되는 리튬 이온 이차 전지이다.

<67> 이 이차 전지는, 전지캔 (11)의 내부에, 편평한 권회 구조를 갖는 전지 소자 (20)이 수납된 것이다.

<68> 전지캔 (11)은, 예를 들면 각형 외장 부재이다. 이 전지캔 (11)을 포함하는 전지 구조는 소위 각형이라 불린다. 이 각형 외장 부재란, 도 5에 나타낸 바와 같이, 길이 방향에 있어서의 단면이 직사각형 또는 대략 직사각형(일부에 곡선을 포함함)의 형상을 갖는 것이고, 직사각형의 각형 전지뿐만 아니라 타원 형상의 각형 전지도 구성하는 것이다. 즉, 각형 외장 부재란, 직사각형 또는 원호를 직선으로 연결한 대략 직사각형(타원 형상)의 개구부를 갖는 유저 직사각형 형태 또는 유저 타원 형상 형태의 그릇형 부재이다. 또한, 도 5에서는, 전지캔 (11)이 직사각형의 단면 형상을 갖는 경우를 나타낸다.

<69> 이 전지캔 (11)은, 예를 들면 철, 알루미늄(Al) 또는 이들의 합금을 함유하는 금속 재료에 의해 구성되어 있고, 전극 단자로서의 기능을 갖는 것도 가능하다. 이 경우에는, 충방전시에 전지캔 (11)의 단단함(변형되기 어려움)을 이용하여 이차 전지의 팽창을 억제하기 위해서, 알루미늄보다 단단한 철(그의 합금을 포함함)이 바람직하다. 전지캔 (11)이 철에 의해 구성되는 경우에는, 예를 들면 니켈(Ni) 등의 도금이 실시될 수도 있다.

<70> 또한, 전지캔 (11)은 한 단부 및 다른 단부가 각각 폐쇄 및 개방된 중공 구조를 가지며, 그 개방 단부에 절연판 (12) 및 전지 뚜껑 (13)이 부착되어 밀폐되어 있다. 절연판 (12)는 전지 소자 (20)과 전지 뚜껑 (13) 사이에, 그 전지 소자 (20)의 권회 주위면에 대하여 수직으로 배치되어 있고, 예를 들면 폴리프로필렌 등에 의해 구성되어 있다. 전지 뚜껑 (13)은, 예를 들면 전지캔 (11)과 동일한 재료에 의해 구성되어 있고, 그와 함께 부극 단

자로서의 기능도 가지고 있다.

<71> 전지 뚜껑 (13)의 외측에는, 정극 단자가 되는 단자판 (14)가 설치되어 있고, 그 단자판 (14)는 절연 케이스 (16)을 통해 전지 뚜껑 (13)으로부터 전기적으로 절연되어 있다. 이 절연 케이스 (16)은, 예를 들면 폴리부틸렌테레프탈레이트 등에 의해 구성되어 있다. 또한, 전지 뚜껑 (13)의 거의 중앙에는 관통 구멍이 설치되어 있고, 그 관통 구멍에는 단자판 (14)와 전기적으로 접속됨과 동시에 가스켓 (17)을 통해 전지 뚜껑 (13)으로부터 전기적으로 절연되도록 정극 핀 (15)가 삽입되어 있다. 이 가스켓 (17)은, 예를 들면 절연 재료에 의해 구성되어 있고, 그 표면에는 아스팔트가 도포되어 있다.

<72> 전지 뚜껑 (13)의 주연부 부근에는, 열개 밸브 (18) 및 주입 구멍 (19)이 설치되어 있다. 열개 밸브 (18)은 전지 뚜껑 (13)과 전기적으로 접속되어 있고, 내부 단락 또는 외부에서의 가열 등에서 기인하여 전지의 내압이 일정 이상이 된 경우에, 전지 뚜껑 (13)으로부터 분리되어 내압을 개방하도록 되어 있다. 주입 구멍 (19)는, 예를 들면 스테인레스강 볼로 이루어지는 밀봉 부재 (19A)에 의해 밀폐되어 있다.

<73> 전지 소자 (20)은 세퍼레이터 (23)을 개재하여 정극 (21) 및 부극 (22)가 적층된 후에 권회된 것이고, 전지캔 (11)의 형상에 따라서 편평형으로 되어 있다. 정극 (21)의 단부(예를 들면 내종단부)에는, 알루미늄 등에 의해 구성된 정극 리드 (24)가 부착되어 있고, 부극 (22)의 단부(예를 들면 외종단부)에는, 니켈 등에 의해 구성된 부극 리드 (25)가 부착되어 있다. 정극 리드 (24)는 정극 핀 (15)의 한 단부에 용접되어 단자판 (14)와 전기적으로 접속되어 있고, 부극 리드 (25)는 전지캔 (11)에 용접되어 전기적으로 접속되어 있다.

<74> 정극 (21)은, 예를 들면 벨트형 정극 집전체 (21A)의 양면에 정극 활성 물질층 (21B)가 설치된 것이다. 이 정극 집전체 (21A)는, 예를 들면 알루미늄, 니켈 또는 스테인레스 등의 금속 재료에 의해 구성되어 있다. 정극 활성 물질층 (21B)는 정극 활성 물질을 포함하고, 필요에 따라서 결착제나 도전제 등을 포함할 수도 있다.

<75> 정극 활성 물질은 전극 반응 물질인 리튬을 흡장 및 방출하는 것이 가능한 정극 재료 중 어느 1종 또는 2종 이상을 포함한다. 이 정극 재료로서는, 예를 들면 코발트산리튬, 니켈산리튬 또는 이들을 포함하는 고용체 ($Li(Ni_xCo_yMn_z)O_2$; x, y 및 z의 값은 각각 0<x<1, 0<y<1, 0<z<1, x+y+z=1이다.)나, 스피넬 구조를 갖는 망간산리튬($LiMn_2O_4$) 또는 그의 고용체($Li(Mn_{2-v}Ni_v)O_4$; v의 값은 v<2이다.) 등의 리튬 복합 산화물을 들 수 있다. 또한, 정극 재료로서는, 예를 들면 인산철리튬($LiFePO_4$) 등의 올리빈 구조를 갖는 인산 화합물도 들 수 있다. 높은 에너지 밀도가 얻어지기 때문이다. 또한, 정극 재료는 상기 외, 예를 들면 산화티탄, 산화바나듐 또는 이산화망간 등의 산화물이나, 이황화철, 이황화티탄 또는 황화몰리브덴 등의 이황화물이나, 황이나, 폴리아닐린 또는 폴리티오펜 등의 도전성 고분자일 수도 있다.

<76> 부극 (22)는 상기한 집전체를 이용한 부극과 동일한 구성을 가지고, 예를 들면 벨트형 부극 집전체 (22A)의 양면에 부극 활성 물질층 (22B)가 설치된 것이다. 부극 집전체 (22A) 및 부극 활성 물질층 (22B)의 구성은 각각 부극 집전체 (1) 및 부극 활성 물질층 (2)의 구성과 동일하다. 리튬을 흡장 및 방출하는 것이 가능한 부극 활성 물질의 충전 용량은 정극의 충전 용량보다 커져 있는 것이 바람직하다.

<77> 세퍼레이터 (23)은 정극 (21)과 부극 (22)를 격리시키고, 양극의 접촉에서 기인하는 전류의 단락을 방지하면서 전극 반응 물질의 이온을 통과시키는 것이다. 이 세퍼레이터 (23)은, 예를 들면 폴리테트라플루오로에틸렌, 폴리프로필렌 또는 폴리에틸렌 등의 합성 수지로 이루어지는 다공질막이나, 세라믹으로 이루어지는 다공질막 등에 의해 구성되어 있고, 이들 중 2종 이상의 다공질막이 적층된 것일 수도 있다.

<78> 이 세퍼레이터 (23)에는, 액상 전해질로서 전해액이 함침되어 있다. 이 전해액은 용매 및 그것에 용해된 전해질염을 포함한다.

<79> 용매는, 예를 들면 유기 용제 등의 비수용매 중 1종 또는 2종 이상을 함유한다. 이 비수용매로서는, 예를 들면 탄산에틸렌, 탄산프로필렌, 탄산부틸렌, 탄산디메틸, 탄산디에틸, 탄산에틸메틸 또는 탄산메틸프로필 등의 탄산에스테르계 용매를 들 수 있다. 우수한 용량 특성, 보존 특성 및 사이클 특성이 얻어지기 때문이다. 이들은 단독으로 이용될 수도 있고, 복수종이 혼합되어 이용될 수도 있다. 그 중에서도, 용매로서는, 탄산에틸렌 또는 탄산프로필렌 등의 고점도 용매와, 탄산디메틸, 탄산에틸메틸 또는 탄산디에틸 등의 저점도 용매를 혼합한 것이 바람직하다. 전해질염의 해리성 및 이온의 이동도가 향상되기 때문에, 보다 높은 효과가 얻어지기 때문이다.

<80> 특히, 용매는 할로겐화 탄산에스테르를 함유하는 것이 바람직하다. 부극 (22)의 표면에 안정한 피막이 형성되어 전해액의 분해 반응이 억제되기 때문에, 사이클 특성이 향상되기 때문이다. 이 할로겐화 탄산에스테르로서는, 불소화 탄산에스테르가 바람직하고, 탄산디플루오로에틸렌이 보다 바람직하다. 보다 높은 효과가 얻어지기

때문이다. 이 탄산디플루오로에틸렌으로서는, 예를 들면 4,5-디플루오로-1,3-디옥솔란-2-온 등을 들 수 있다.

<81> 또한, 용매는 불포화 결합을 갖는 환상 탄산에스테르를 함유하는 것이 바람직하다. 사이클 특성이 향상되기 때문이다. 이 불포화 결합을 갖는 환상 탄산에스테르로서는, 예를 들면 탄산비닐렌 또는 탄산비닐에틸렌 등을 들 수 있다.

<82> 또한, 용매는 술톤을 함유하는 것이 바람직하다. 사이클 특성이 향상됨과 동시에 이차 전지의 팽창이 억제되기 때문이다. 이 술톤으로서는, 예를 들면 1,3-프로펜술톤 등을 들 수 있다.

<83> 전해질염은, 예를 들면 리튬염 등의 경금속염 중 1종 또는 2종 이상을 포함한다. 이 리튬염으로서는, 예를 들면 육불화인산리튬($LiPF_6$), 과염소산리튬($LiClO_4$) 또는 육불화비소산리튬($LiAsF_6$) 등을 들 수 있다. 우수한 용량 특성, 보존 특성 및 사이클 특성이 얻어지기 때문이다. 이들은 단독으로 이용될 수도 있고, 복수종이 혼합되어 이용될 수도 있다. 그 중에서도, 전해질염으로서는 육불화인산리튬이 바람직하다. 내부 저항이 저하되므로, 보다 높은 효과가 얻어지기 때문이다.

<84> 특히, 전해질염은 붕소 및 불소를 갖는 화합물을 포함하는 것이 바람직하다. 사이클 특성이 향상되기 때문이다. 이 붕소 및 불소를 갖는 화합물로서는, 예를 들면 사불화붕산리튬 등을 들 수 있다.

<85> 용매 중에서의 전해질염의 함유량은 0.3 몰/kg 이상 3.0 몰/kg 이하인 것이 바람직하다. 우수한 용량 특성이 얻어지기 때문이다.

<86> 이 이차 전지는, 예를 들면 이하의 절차에 의해 제조된다.

<87> 최초로, 정극 (21)을 제조한다. 우선, 정극 활성 물질, 결착제 및 도전제를 혼합하여 양극 합제로 만든 후, 유기 용제에 분산시킴으로써 페이스트형 정극 합제 슬러리로 만든다. 계속해서, 닥터 블레이드 또는 바 코터 등을 이용하여 정극 집전체 (21A)의 양면에 정극 합제 슬러리를 균일하게 도포하여 건조시킨다. 마지막으로, 필요에 따라서 가열하면서 롤 프레스기 등을 이용하여 압축 성형함으로써 정극 활성 물질층 (21B)를 형성한다. 이 경우에는, 압축 성형을 복수회에 걸쳐 반복할 수도 있다.

<88> 다음에, 상기한 부극의 제조 절차와 동일한 절차에 의해서 부극 집전체 (22A)의 양면에 부극 활성 물질층 (22B)를 형성함으로써 부극 (22)를 제조한다.

<89> 또한, 정극 (21) 및 부극 (22)를 이용하여 전지 소자 (20)을 제조한다. 우선, 용접 등에 의해 정극 집전체 (21A) 및 부극 집전체 (22A)에 각각 정극 리드 (24) 및 부극 리드 (25)를 부착시킨다. 계속해서, 세퍼레이터 (23)을 개재하여 정극 (21) 및 부극 (22)를 적층시킨 후, 길이 방향에서 권회시킨다. 그 후, 편평한 형상이 되도록 성형함으로써 전지 소자 (20)을 형성한다.

<90> 마지막으로, 이차 전지를 조립한다. 우선, 전지캔 (11)의 내부에 전지 소자 (20)을 수납한 후, 그 전지 소자 (20) 상에 절연판 (12)를 배치한다. 계속해서, 용접 등에 의해 정극 리드 (24) 및 부극 리드 (25)를 각각 정극 핀 (15) 및 전지캔 (11)에 접속시킨 후, 레이저 용접 등에 의해 전지캔 (11)의 개방 단부에 전지 뚜껑 (13)을 고정시킨다. 그 후, 주입 구멍 (19)로부터 전지캔 (11)의 내부에 전해액을 주입하여 세퍼레이터 (23)에 함침시킨 후, 그 주입 구멍 (19)를 밀봉 부재 (19A)로 막는다. 이에 따라, 도 4 및 도 5에 나타낸 이차 전지가 완성된다.

<91> 이 이차 전지에서는, 충전을 행하면, 예를 들면 정극 (21)로부터 리튬 이온이 방출되고, 세퍼레이터 (23)에 함침된 전해액을 통해 부극 (22)에 흡장된다. 한편, 방전을 행하면, 예를 들면 부극 (22)로부터 리튬 이온이 방출되고, 세퍼레이터 (23)에 함침된 전해액을 통해 정극 (21)에 흡장된다.

<92> 이 각형 이차 전지에 따르면, 부극 (22)가 상기한 부극과 동일한 구성을 가지고 있기 때문에, 부극 집전체 (22A)와 부극 활성 물질층 (22B)와의 밀착성이 향상된다. 따라서, 사이클 특성을 향상시킬 수 있다. 이 경우에는, 부극 (22)가 고용량화에 유리한 규소를 함유하는 경우에 사이클 특성이 향상되기 때문에, 탄소 재료 등의 다른 부극 재료를 포함하는 경우보다도 높은 효과를 얻을 수 있다. 이 이차 전지에 따른 상기 이외의 효과는 상기한 부극과 동일하다.

<93> (제2 전지)

<94> 도 6 및 도 7은 제2 전지의 단면 구성을 나타내고, 도 7에서는 도 6에 나타낸 권회 전극체 (40)의 일부를 확대하여 나타낸다. 이 전지는, 예를 들면 상기한 제1 전지와 같이 리튬 이온 이차 전지이며, 거의 중공 원주형 전지캔 (31)의 내부에, 정극 (41) 및 부극 (42)가 세퍼레이터 (43)을 개재하여 권회된 권회 전극체 (40) 및 한쌍

의 절연판 (32), (33)이 수납된 것이다. 이 전지캔 (31)을 포함하는 전지 구조는 소위 원통형이라 불린다.

<95> 전지캔 (31)은, 예를 들면 상기한 제1 전지에 있어서의 전지캔 (11)과 동일한 금속 재료에 의해 구성되어 있고, 그의 한 단부 및 다른 단부는 각각 폐쇄 및 개방되어 있다. 한쌍의 절연판 (32), (33)은 권회 전극체 (40)을 사이에 끼워, 그 권회 주위면에 대하여 수직으로 연장되도록 배치되어 있다.

<96> 전지캔 (31)의 개방 단부에는, 전지 뚜껑 (34)와, 그의 내측에 설치된 안전 밸브 기구 (35) 및 열감 저항 소자 (Positive Temperature Coefficient: PTC 소자) (36)가 가스켓 (37)을 통해 코킹됨으로써 부착되어 있다. 이에 따라, 전지캔 (31)의 내부는 밀폐되어 있다. 전지 뚜껑 (34)는, 예를 들면 전지캔 (31)과 동일한 재료에 의해 구성되어 있다. 안전 밸브 기구 (35)는 열감 저항 소자 (36)을 통해 전지 뚜껑 (34)와 전기적으로 접속되어 있다. 이 안전 밸브 기구 (35)에서는, 내부 단락 또는 외부에서의 가열 등에서 기인하여 내압이 일정 이상이 된 경우에, 디스크 판 (35A)가 반전하여 전지 뚜껑 (34)와 권회 전극체 (40) 사이의 전기적 접속이 절단되도록 되어 있다. 열감 저항 소자 (36)은 온도의 상승에 따라서 저항이 증대됨으로써 전류를 제한하고, 대전류에서 기인하는 이상한 발열을 방지하는 것이다. 가스켓 (37)은, 예를 들면 절연 재료에 의해 구성되어 있고, 그 표면에는 아스팔트가 도포되어 있다.

<97> 권회 전극체 (40)의 중심에는, 예를 들면 센터핀 (44)가 삽입될 수도 있다. 이 권회 전극체 (40)에서는, 알루미늄 등에 의해 구성된 정극 리드 (45)가 정극 (41)에 접속되어 있고, 니켈 등에 의해 구성된 부극 리드 (46)이 부극 (42)에 접속되어 있다. 정극 리드 (45)는 안전 밸브 기구 (35)에 용접됨으로써 전지 뚜껑 (34)와 전기적으로 접속되어 있고, 부극 리드 (46)은 전지캔 (31)에 용접되어 전기적으로 접속되어 있다.

<98> 정극 (41)은, 예를 들면 벨트형 정극 집전체 (41A)의 양면에 정극 활성 물질층 (41B)가 설치된 것이다. 부극 (42)는 상기한 부극과 동일한 구성을 가지고 있고, 예를 들면 벨트형 부극 집전체 (42A)의 양면에 부극 활성 물질층 (42B)가 설치된 것이다. 정극 집전체 (41A), 정극 활성 물질층 (41B), 부극 집전체 (42A), 부극 활성 물질층 (42B) 및 세퍼레이터 (43)의 구성, 및 전해액의 조성은 각각 상기한 제1 전지에 있어서의 정극 집전체 (21A), 정극 활성 물질층 (21B), 부극 집전체 (22A), 부극 활성 물질층 (22B) 및 세퍼레이터 (23)의 구성, 및 전해액의 조성과 동일하다.

<99> 이 이차 전지는, 예를 들면 이하와 같이 하여 제조된다.

<100> 우선, 예를 들면 상기한 제1 전지에 있어서의 정극 (21) 및 부극 (22)의 제조 절차와 동일한 절차에 의해, 정극 집전체 (41A)의 양면에 정극 활성 물질층 (41B)가 설치된 정극 (41)을 제조함과 동시에, 부극 집전체 (42A)의 양면에 부극 활성 물질층 (42B)가 설치된 부극 (42)를 제조한다. 계속해서, 정극 (41)에 정극 리드 (45)를 부착시킴과 동시에, 부극 (42)에 부극 리드 (46)을 부착시킨다. 계속해서, 정극 (41) 및 부극 (42)를 세퍼레이터 (43)을 개재하여 권회시킴으로써 권회 전극체 (40)을 형성하고, 정극 리드 (45)의 선단부를 안전 밸브 기구 (35)에 용접시킴과 동시에 부극 리드 (46)의 선단부를 전지캔 (31)에 용접시킨 후, 권회 전극체 (40)을 한쌍의 절연판 (32), (33) 사이에 끼우면서 전지캔 (31)의 내부에 수납한다. 계속해서, 전지캔 (31)의 내부에 전해액을 주입하여 세퍼레이터 (43)을 함침시킨다. 마지막으로, 전지캔 (31)의 개구 단부에 전지 뚜껑 (34), 안전 밸브 기구 (35) 및 열감 저항 소자 (36)을 가스켓 (37)을 통해 코킹함으로써 고정시킨다. 이에 따라, 도 6 및 도 7에 나타낸 이차 전지가 완성된다.

<101> 이 이차 전지에서는, 충전을 행하면, 예를 들면 정극 (41)로부터 리튬 이온이 방출되고, 전해액을 통해 부극 (42)에 흡장된다. 한편, 방전을 행하면, 예를 들면 부극 (42)로부터 리튬 이온이 방출되고, 전해액을 통해 정극 (41)에 흡장된다.

<102> 이 원통형 이차 전지에 따르면, 부극 (42)가 상기한 부극과 동일한 구성을 가지고 있기 때문에, 사이클 특성을 향상시킬 수 있다. 이 이차 전지에 따른 상기 이외의 효과는 제1 전지와 동일하다.

<103> (제3 전지)

<104> 도 8은 제3 전지의 분해 사시 구성을 나타내고, 도 9는 도 8에 나타낸 IX-IX선에 따른 단면을 확대하여 나타낸다. 이 전지는, 정극 리드 (51) 및 부극 리드 (52)가 부착된 권회 전극체 (50)이 필름형 외장 부재 (60)의 내부에 수납된 것이다. 이 외장 부재 (60)을 포함하는 전지 구조는 소위 라미네이트 필름형이라 불린다.

<105> 정극 리드 (51) 및 부극 리드 (52)는, 예를 들면 외장 부재 (60)의 내부에서 외부를 향해 동일 방향으로 도출되어 있다. 정극 리드 (51)은, 예를 들면 알루미늄 등의 금속 재료에 의해 구성되어 있고, 부극 리드 (52)는, 예를 들면 구리, 니켈 또는 스테인레스 등의 금속 재료에 의해 구성되어 있다. 이들은, 예를 들면 박판형 또는

메쉬형으로 되어 있다.

<106> 외장 부재 (60)은, 예를 들면 나일론 필름, 알루미늄박 및 폴리에틸렌 필름이 이 순서대로 접합된 알루미늄 라미네이트 필름에 의해 구성되어 있다. 이 외장 부재 (60)은, 예를 들면 폴리에틸렌 필름이 권회 전극체 (50)과 대향하도록, 2매의 직사각형 알루미늄 라미네이트 필름의 외연부끼리 융착 또는 접착제에 의해 서로 접착된 구조를 가지고 있다.

<107> 외장 부재 (60)과 정극 리드 (51) 및 부극 리드 (52) 사이에는, 외기의 침입을 방지하기 위해서 밀착 필름 (61)이 삽입되어 있다. 이 밀착 필름 (61)은 정극 리드 (51) 및 부극 리드 (52)에 대하여 밀착성을 갖는 재료에 의해 구성되어 있다. 이러한 종류의 재료로서는, 예를 들면 폴리에틸렌, 폴리프로필렌, 변성 폴리에틸렌 또는 변성 폴리프로필렌 등의 폴리올레핀 수지를 들 수 있다.

<108> 또한, 외장 부재 (60)은 상기한 알루미늄 라미네이트 필름 대신에, 다른 적층 구조를 갖는 라미네이트 필름에 의해 구성될 수도 있고, 폴리프로필렌 등의 고분자 필름 또는 금속 필름 등에 의해 구성될 수도 있다.

<109> 전극 권회체 (50)은, 정극 (53) 및 부극 (54)가 세퍼레이터 (55) 및 전해질 (56)을 개재하여 적층된 후에 권회된 것이고, 그의 최외주부는 보호 테이프 (57)에 의해 보호되어 있다.

<110> 정극 (53)은, 예를 들면 대향하는 한쌍의 면을 갖는 정극 집전체 (53A)의 양면에 정극 활성 물질층 (53B)가 설치된 것이다. 부극 (54)는 상기한 부극과 동일한 구성을 가지고 있고, 예를 들면 벨트형 부극 집전체 (54A)의 양면에 부극 활성 물질층 (54B)가 설치된 것이다. 정극 집전체 (53A), 정극 활성 물질층 (53B), 부극 집전체 (54A), 부극 활성 물질층 (54B) 및 세퍼레이터 (55)의 구성은 각각 상기한 제1 전지에 있어서의 정극 집전체 (21A), 정극 활성 물질층 (21B), 부극 집전체 (22A), 부극 활성 물질층 (22B) 및 세퍼레이터 (23)의 구성과 동일하다.

<111> 전해질 (56)은 전해액 및 그것을 유지하는 고분자 화합물을 포함하는 소위 겔 전해질이다. 겔 전해질은 높은 이온 전도율(예를 들면 실온에서 1 mS/cm 이상)이 얻어짐과 동시에 누액이 방지되기 때문에 바람직하다. 이 전해질 (56)은, 예를 들면 정극 (53)과 세퍼레이터 (55) 사이 및 부극 (54)와 세퍼레이터 (55) 사이에 설치되어 있다.

<112> 고분자 화합물로서는, 예를 들면 폴리아크릴로니트릴, 폴리불화비닐리덴, 폴리불화비닐리덴과 폴리헥사플루오로프로필렌과의 공중합체, 폴리테트라플루오로에틸렌, 폴리헥사플루오로프로필렌, 폴리에틸렌옥시드, 폴리프로필렌옥시드, 폴리포스파젠, 폴리실록산, 폴리아세트산비닐, 폴리비닐알코올, 폴리메타크릴산메틸, 폴리아크릴산, 폴리메타크릴산, 스티렌-부타디엔 고무, 니트릴-부타디엔 고무, 폴리스티렌 또는 폴리카르보네이트 등을 들 수 있다. 이들은 단독으로 이용될 수도 있고, 복수종이 혼합되어 이용될 수도 있다. 그 중에서도 고분자 화합물로서는, 폴리아크릴로니트릴, 폴리불화비닐리덴, 폴리헥사플루오로프로필렌 또는 폴리에틸렌옥시드가 바람직하다. 전기 화학적으로 안정하기 때문이다.

<113> 전해액의 조성은 제1 전지에 있어서의 전해액의 조성과 동일하다. 단, 이 경우의 용매란, 액상 용매뿐만 아니라 전해질염을 해리시키는 것이 가능한 이온 전도성을 갖는 것까지 포함하는 넓은 개념이다. 따라서, 이온 전도성을 갖는 고분자 화합물을 이용하는 경우에는, 그 고분자 화합물도 용매에 포함된다.

<114> 또한, 전해액을 고분자 화합물에 유지시킨 겔상 전해질 (56) 대신에, 전해액이 그대로 이용될 수도 있다. 이 경우에는, 전해액이 세퍼레이터 (55)에 함침된다.

<115> 이 겔상 전해질 (56)을 구비한 전지는, 예를 들면 이하와 같이 하여 제조된다.

<116> 우선, 상기한 제1 전지에 있어서의 정극 (21) 및 부극 (22)의 제조 절차와 동일한 절차에 의해, 정극 집전체 (53A)의 양면에 정극 활성 물질층 (53B)가 설치된 정극 (53)을 제조함과 동시에, 부극 집전체 (54A)의 양면에 부극 활성 물질층 (54B)가 설치된 부극 (54)를 제조한다. 계속해서, 전해액, 고분자 화합물 및 용제를 포함하는 전구 용액을 제조하고, 정극 (53) 및 부극 (54)의 각각에 도포한 후에 용제를 휘발시킴으로써 겔상 전해질 (56)을 형성한다. 계속해서, 정극 집전체 (53A)에 정극 리드 (51)를 부착시킴과 동시에 부극 집전체 (54A)에 부극 리드 (52)를 부착시킨다. 계속해서, 전해질 (56)이 형성된 정극 (53) 및 부극 (54)를 세퍼레이터 (55)를 개재하여 적층시킨 후, 길이 방향으로 권회시킴과 동시에 최외주부에 보호 테이프 (57)을 접착시킴으로써 권회 전극체 (50)을 형성한다. 계속해서, 예를 들면 외장 부재 (60) 사이에 권회 전극체 (50)을 끼우고, 그 외장 부재 (60)의 외연부끼리 열 융착 등으로 밀착시킴으로써 권회 전극체 (50)을 봉입한다. 그 때, 정극 리드 (51) 및 부극 리드 (35)와 외장 부재 (60) 사이에 밀착 필름 (61)을 삽입한다. 이에 따라, 도 8 및 도 9에 나타낸

이차 전지가 완성된다.

<117> 또한, 상기한 전지는 이하와 같이 하여 제조될 수도 있다. 우선, 정극 (53) 및 부극 (54)에 각각 정극 리드 (51) 및 부극 리드 (52)를 부착시킨 후, 이들의 정극 (53) 및 부극 (54)를 세퍼레이터 (55)를 개재하여 적층 및 권회시킴과 동시에 최외주부에 보호 테이프 (57)을 접착시킴으로써 권회 전극체 (50)의 전구체인 권회체를 형성한다. 계속해서, 외장 부재 (60) 사이에 권회체를 끼우고, 열 융착 등에 의해 1변의 외연부를 제외한 나머지 외연부를 밀착시킴으로써 주머니형 외장 부재 (60)의 내부에 수납한다. 계속해서, 전해액, 고분자 화합물의 원료인 단량체, 중합 개시제, 및 필요에 따라서 중합 금지제 등의 다른 재료를 포함하는 전해질용 조성물을 제조하고, 주머니형 외장 부재 (60)의 내부에 주입한 후, 외장 부재 (60)의 개구부를 열 융착 등으로 밀봉시킨다. 마지막으로, 단량체를 열 중합시켜 고분자 화합물로 함으로써 겔상 전해질 (56)을 형성한다. 이에 따라, 도 8 및 도 9에 나타낸 이차 전지가 완성된다.

<118> 이 라미네이트 필름형 이차 전지에 따르면, 부극 (54)가 상기한 부극과 동일한 구성을 가지고 있기 때문에 사이클 특성을 향상시킬 수 있다. 이 이차 전지에 따른 상기 이외의 효과는 제1 전지와 동일하다.

<119> 또한, 상기한 제1 내지 제3 전지에서는, 충방전 전 및 충방전 후 중 어느 것에서도 강도비 I(200)/I(111)이 적정 범위 내(0.5 이상 1.5 이하)로 되어 있는지를 확인 가능하다. 상세하게는 부극의 구성으로서는, 부극 집전체의 표면 전부를 피복하도록 부극 활성 물질층이 설치되는 경우도 있다면 그 표면의 일부(예를 들면 정극 활성 물질층에 대향하는 영역)만을 피복하도록 부극 활성 물질층이 설치되는 경우도 있다. 이에 대하여, 정극의 구성으로서는, 정극 집전체의 표면 일부만을 피복하도록 정극 활성 물질층이 설치되는 것이 일반적이다. 이에 따라, 부극 집전체는 정극 활성 물질층에 대향하는 영역 및 그것에 대향하지 않는 영역을 포함한다. 정극 활성 물질층에 대향하는 영역에서는, 그 정극 활성 물질층과 부극 활성 물질층 사이에서 전극 반응이 진행되어 전지가 충방전되기 때문에, 그 충방전 전의 단계에서 강도비 I(200)/I(111)이 적정 범위 내에 설정되었다고 해도, 충방전의 영향을 받아 강도비 I(200)/I(111)이 변화될 수 있다. 이에 대하여, 정극 활성 물질층에 대향하지 않는 영역에서는, 그 영역에 부극 활성 물질층의 설치 여부에 관계없이, 강도비 I(200)/I(111)이 충방전의 영향을 받지 않기 때문에, 그 강도비 I(200)/I(111)은 충방전의 전후에서 유지된다. 따라서, 정극 활성 물질층에 대향하지 않는 영역에서 강도비 I(200)/I(111)을 조사하면, 충방전의 유무에 관계없이, 그 강도비 I(200)/I(111)이 적정 범위 내로 되어 있는지의 여부를 양호한 재현성으로 확인할 수 있다.

<120> <실시예>

<121> 본 발명의 실시예에 대하여 상세히 설명한다.

<122> (실시예 1-1)

<123> 이하의 절차에 의해, 도 8 및 도 9에 나타낸 라미네이트 필름형 이차 전지를 제조하였다. 이 때, 부극 (54)의 용량이 리튬의 흡장 및 방출에 기초하여 표시되는 리튬 이온 이차 전지가 되도록 하였다.

<124> 우선, 정극 (53)을 제조하였다. 최초로, 탄산리튬(Li_2CO_3)과 탄산코발트($CoCO_3$)를 0.5:1의 몰비로 혼합한 후, 공기 중에서 900 ℃에서 5 시간 소성시킴으로써 리튬·코발트 복합 산화물($LiCoO_2$)을 얻었다. 계속해서, 정극 활성 물질로서 리튬·코발트 복합 산화물 91 중량부와 도전제로서 흑연 6 중량부, 및 결착제로서 폴리불화비닐리덴 3 중량부를 혼합하여 정극 합제로 만든 후, N-메틸-2-피롤리돈에 분산시킴으로써 페이스트형 정극 합제 슬러리로 만들었다. 마지막으로, 벨트형 알루미늄박(두께=12 ㎛)으로 이루어지는 정극 집전체 (53A)의 양면에 정극 합제 슬러리를 균일하게 도포하여 건조시킨 후, 롤 프레스기로 압축 성형함으로써 정극 활성 물질층 (53B)를 형성하였다. 이 후, 정극 집전체 (53A)의 한 단부에 알루미늄제 정극 리드 (51)를 용접하여 부착시켰다.

<125> 다음에, 부극 (54)를 제조하였다. 최초로, 원박으로서 동박(두께=18 ㎛)를 준비한 후, 그 원박을 어닐링하였다. 이 때, 원박의 어닐링 온도를 300 ℃로 하고, 구리 결정자의 단면적 최대값을 50 $㎛^2$로 하였다. 이 결정자의 단면적에 대해서는, 크로스섹션 폴리셔에 의해 원박 단면을 노출시킨 후, 저가속 전압 SEM을 이용하여 단면 관찰하여 결정자의 단면적을 측정하였다. 계속해서, 원박 표면에 전해 처리를 실시하여 미립자 및 도금막을 형성함으로써, 전해 동박으로 이루어지는 부극 집전체 (54A)를 얻었다. 이 때, 부극 집전체 (54A) 표면의 십점 평균 조도 Rz를 3.5 ㎛로 하였다. 이 십점 평균 조도 Rz에 대해서는, 울백 이에스 가부시끼가이샤 제조의 침 접촉식 표면 형상 측정기 덱탁(Dektak)3을 이용하여, 후속 공정에 있어서의 부극 집전체 (54A)의 권회 방향과 교차하는 방향으로 바늘을 주사시킴으로써 임의로 추출한 5점의 측정값의 평균값을 구하였다. 이 부극 집전체 (54A)의 신장률 및 영률을 측정한 결과, 신장률은 9 %이고, 영률은 5.93×10^7 MPa였다. 계속해서,

챔버 내에 연속적으로 산소 가스 및 필요에 따라서 수증기를 도입하면서, 편향식 전자 빔 증착원을 이용한 전자 빔 증착법에 의해서 부극 집전체 (54A)의 양면에 규소를 퇴적시켜 부극 활성 물질 입자를 단층 구조가 되도록 형성함으로써 부극 활성 물질층 (54B)를 형성하였다. 이 때, 증착원으로서 순도 99 %의 규소를 이용하고, 퇴적 속도를 10 nm/초로 하여 부극 활성 물질 입자 중에서의 산소 함유량을 3 원자수%로 하였다. 마지막으로 10^{-3} Pa 이하의 감압 분위기 중에서 부극 활성 물질층 (54B)가 형성된 부극 집전체 (54A)를 어닐링하였다. 이 때, 부극 집전체 (54A)의 어닐링 온도를 150 ℃로 하고, X선 회절에 의해 얻어지는 구리의 결정면에서 기인하는 피크 강도비 I(200)/I(111)을 0.5로 하였다. 강도비 I(200)/I(111)에 대해서는, 완성된 부극 (54)를 5 mm×5 mm의 크기로 잘라낸 후, 리가꾸 덴끼 가부시끼가이샤 제조의 XRD 회절 장치를 이용하여 분석함으로써 측정하였다. 또한, 관구로서 CuKa, 스캔 방법으로서 θ-2θ법을 이용하고, 관 전압을 40 kV, 관 전류를 40 mA, 측정 범위를 40° 이상 100° 이하로 하였다.

<126> 완성된 부극 (54)에 대하여, 수속 이온 빔 에칭(focused ion beam etching: FIB)에 의해 단면을 노출시킨 후, 오우거 전자 분광법(auger electron spectrometer: AES)에 의해 국소 원소 분석한 결과, 부극 집전체 (54A)와 부극 활성 물질층 (54B)와의 계면에 있어서 구성 원소가 확산되어 있고, 양자가 합금화되어 있는 것이 확인되었다.

<127> 다음에, 정극 (53), 다공성 폴리프로필렌을 주성분으로 하는 필름에 의해 다공성 폴리에틸렌을 주성분으로 하는 필름이 사이에 끼워진 3층 구조의 중합체 세퍼레이터 (55)(두께=23 ㎛), 부극 (54), 및 상기한 중합체 세퍼레이터 (55)를 이 순서대로 적층하고, 길이 방향에 있어서 권회시킨 후, 점착 테이프로 이루어지는 보호 테이프 (57)로 권취 종료 부분을 고정시킴으로써, 권회 전극체 (50)의 전구체인 권회체를 형성하였다. 계속해서, 외측으로부터 나일론(두께=30 ㎛), 알루미늄(두께=40 ㎛) 및 무연신 폴리프로필렌(두께=30 ㎛)가 적층된 3층 구조의 라미네이트 필름(총 두께=100 ㎛)로 이루어지는 외장 부재 (60) 사이에 권회체를 끼운 후, 1변을 제외한 외연부끼리 열 융착시킴으로써, 주머니형 외장 부재 (60)의 내부에 권회체를 수납하였다. 계속해서, 외장 부재 (60)의 개구부에서 전해액을 주입하여 세퍼레이터 (55)에 함침시킴으로써 권회 전극체 (50)을 형성하였다.

<128> 이 전해액을 제조할 때는, 용매로서 탄산에틸렌(EC)과 탄산디에틸(DEC)를 혼합한 혼합 용매를 이용하고, 전해질염으로서 육불화인산리튬($LiPF_6$)을 이용하였다. 이 때, 혼합 용매의 조성을 중량비로 EC:DEC=50:50으로 하고, 전해질염의 농도를 1 몰/kg로 하였다.

<129> 마지막으로, 진공 분위기 중에서 외장 부재 (60)의 개구부를 열 융착시켜 밀봉함으로써 라미네이트 필름형 이차 전지가 완성되었다.

<130> (실시예 1-2 내지 1-7)

<131> 강도비 I(200)/I(111)을 0.5 대신에, 0.8(200 ℃: 실시예 1-2), 1(250 ℃: 실시예 1-3), 1.15(300 ℃: 실시예 1-4), 1.2(350 ℃: 실시예 1-5), 1.4(400 ℃: 실시예 1-6) 또는 1.5(450 ℃: 실시예 1-7)로 한 것을 제외하고, 실시예 1-1과 같은 절차를 거쳤다. 괄호 내의 온도는 강도비 I(200)/I(111)을 상기한 각각의 값으로 하기 위해서 설정한 부극 집전체 (54A)의 어닐링 온도이다.

<132> (비교예 1-1 내지 1-6)

<133> 강도비 I(200)/I(111)을 0.5 대신에, 0.1(25 ℃: 비교예 1-1), 0.3(100 ℃: 비교예 1-2), 1.6(500 ℃: 비교예 1-3), 1.8(525 ℃: 비교예 1-4), 2(550 ℃: 비교예 1-5) 또는 2.5(575 ℃: 비교예 1-6)로 한 것을 제외하고, 실시예 1-1과 같은 절차를 거쳤다.

<134> 이들 실시예 1-1 내지 1-7 및 비교예 1-1 내지 1-6의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 1 및 도 10에 나타낸 결과가 얻어졌다. 또한, 표 1에서는, 결정자의 단면적으로서 최대값을 나타내고, 그에 대한 표시는 이후의 일련의 표에 있어서도 동일하다.

<135> 사이클 특성을 조사할 때는, 이하의 절차로 사이클 시험을 행함으로써 방전 용량 유지율을 구하였다. 우선, 전지 상태를 안정화시키기 위해서 23 ℃의 분위기 중에서 1 사이클 충방전시킨 후, 다시 충방전시킴으로써 2 사이클째 방전 용량을 측정하였다. 계속해서, 동일한 분위기 중에서 99 사이클 충방전시킴으로써 101 사이클째 방전 용량을 측정하였다. 마지막으로, 방전 용량 유지율(%)=(101 사이클째 방전 용량/2 사이클째 방전 용량)×100을 산출하였다. 이 때, 충전 조건으로서는, 3 mA/cm^2의 정전류 밀도로 전지 전압이 4.2 V에 도달할 때까지 충전한 후, 계속해서 4.2 V의 정전압으로 전류 밀도가 0.3 mA/cm^2에 도달할 때까지 충전하였다. 또한, 방전 조

건으로서는, 3 mA/cm^{2}의 정전류 밀도로 전지 전압이 2.5 V에 도달할 때까지 방전하였다. 이 사이클 특성을 조사할 때의 절차 및 조건은, 이후의 일련의 실시예 및 비교예에 대해서도 동일하다.

표 1

부극 활성 물질 입자: 규소(전자 빔 증착법)
원박의 두께=18 μm, 십점 평균 조도 Rz=3.5 μm,
부극 활성 물질 입자 중의 산소 함유량= 3 원자수%

	부극 활성 물질층	부극 집전체		방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	강도비 I(200)/I(111)	결정자의 단면적 (μm^2)	
실시예 1-1	1	0.5	50	80
실시예 1-2		0.8		84
실시예 1-3		1		83
실시예 1-4		1.15		82
실시예 1-5		1.2		82
실시예 1-6		1.4		81
실시예 1-7		1.5		80
비교예 1-1	1	0.1	50	68
비교예 1-2		0.3		69
비교예 1-3		1.6		69
비교예 1-4		1.8		68
비교예 1-5		2		65
비교예 1-6		2.5		62

<136>

<137> 표 1 및 도 10에 나타낸 바와 같이, 강도비 I(200)/I(111)이 0.5 이상 1.5 이하인 실시예 1-1 내지 1-7에서는, 그 범위밖인 비교예 1-1 내지 1-6보다 방전 용량 유지율이 대폭 높아졌다. 즉, 방전 용량 유지율은 강도비 I(200)/I(111)이 커짐에 따라서 상향 볼록형 곡선을 그리도록 변화되고, 특히 강도비 I(200)/I(111)이 0.5보다 작아지거나 1.5보다 커지면 극단적으로 저하되었다. 이로부터, 본 발명의 이차 전지에서는 강도비 I(200)/I(111)이 0.5 이상 1.5 이하인 것에 의해, 사이클 특성이 향상되는 것이 확인되었다.

<138> 여기서, 상기한 실시예 1-1 내지 1-7을 대표하여 실시예 1-2, 1-4의 이차 전지에 이용한 부극 (54)의 결정 상태를 XRD 장치로 분석한 결과, 도 11에 나타낸 결과가 얻어졌다. 도 11 중, (A) 및 (B)는 각각 실시예 1-2, 1-4를 나타내고, 횡축 및 종축은 각각 2Θ(°) 및 규격화한 X선의 강도를 나타낸다. 도 11에 나타낸 바와 같이 실시예 1-2, 1-4 중 어느 것도 구리의 결정 상태를 특정짓는 5개의 피크가 확인되었다. 이 5개의 피크란, (111) 결정면에서 기인하는 피크 P1, (200) 결정면에서 기인하는 피크 P2, (220) 결정면에서 기인하는 피크 P3, (311) 결정면에서 기인하는 피크 P4 및 (222) 결정면에서 기인하는 피크 P5이다. 이들 피크 P1 내지 P5 사이에서 강도를 비교하면, 그 강도는 피크 P3 내지 P5보다 피크 P1, P2에서 현저히 커졌다. 이 경우에는, 실시예 1-2에서는, 도 11(A)에 나타낸 바와 같이 피크 P1보다 피크 P2에 있어서 강도가 작기 때문에, 강도비 I(200)/I(111)이 1보다 작아졌다. 한편, 실시예 1-4에서는, 도 11(B)에 나타낸 바와 같이 피크 P1보다 피크 P2에 있어서 강도가 크기 때문에, 강도비 I(200)/I(111)이 1보다 커졌다. 이로부터, 본 발명의 이차 전지에서는 (111) 결정면 및 (200) 결정면에서 기인하는 2개의 피크의 강도가 다른 피크의 강도보다 충분히 크기 때문에, 그 2개의 피크 강도비에 기초하여 구리의 결정 상태를 양호한 재현성으로 특정지을 수 있음과 동시에, 그 강도비에 따라서 사이클 특성이 변화되는 것이 확인되었다.

<139> 또한, 여기서는 구체적인 분석 결과를 나타내지 않았지만, 강도비 I(200)/I(111)이 1.5보다 큰 비교예 1-3 내지 1-6에 대해서도 동일하게 XRD 장치로 분석한 결과, Cu_3Si의 존재를 나타내는 피크가 확인되었다. 이 결과는, 부극 집전체 (54A)(Cu)와 부극 활성 물질 입자(Si)와의 계면에 있어서 원소 확산이 너무 진행되었기 때문에, 그 계면에 Cu_3Si가 생긴 것을 나타낸다. 이에 따라, 비교예 1-3 내지 1-6에서는, 부극 집전체 (54A)와 부극 활성 물질 입자 사이의 밀착성이 저하되기 때문에, 충분한 사이클 특성이 얻어지지 않는다.

<140> (실시예 2-1 내지 2-6)

<141> 6회에 걸쳐 규소를 퇴적시켜 적층함으로써, 부극 활성 물질 입자를 6층 구조가 되도록 형성한 것을 제외하고, 실시예 1-1 내지 1-3, 1-5 내지 1-7과 같은 절차를 거쳤다. 이 때, 퇴적 속도를 100 nm/초로 하였다.

<142> (비교예 2-1 내지 2-3)

<143> 실시예 2-1 내지 2-6과 동일하게 부극 활성 물질 입자를 6층 구조가 되도록 형성한 것을 제외하고, 비교예 1-2 내지 1-4와 같은 절차를 거쳤다.

<144> 이들 실시예 2-1 내지 2-6 및 비교예 2-1 내지 2-3의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 2 및 도 12에 나타낸 결과가 얻어졌다.

표 2

부극 활성 물질 입자: 규소(전자 빔 증착법)
원박의 두께=18 μm, 십점 평균 조도 Rz=3.5 μm,
부극 활성 물질 입자 중의 산소 함유량= 3 원자수%

	부극 활성 물질층	부극 집전체		방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	강도비 I(200)/I(111)	결정자의 단면적 (μm^2)	
실시예 2-1	6	0.5	50	82
실시예 2-2		0.8		86
실시예 2-3		1		85
실시예 2-4		1.2		84
실시예 2-5		1.4		83
실시예 2-6		1.5		82
비교예 2-1	6	0.3	50	69.5
비교예 2-2		1.6		69.5
비교예 2-3		1.8		69

<145>

<146> 표 2 및 도 12에 나타낸 바와 같이, 강도비 I(200)/I(111)이 0.5 이상 1.5 이하인 실시예 2-1 내지 2-6에서는, 그 범위밖인 비교예 2-1 내지 2-3보다 방전 용량 유지율이 대폭 높아졌다. 이로부터, 본 발명의 이차 전지에서는 부극 활성 물질 입자의 층수를 6층으로 한 경우에도 사이클 특성이 향상되는 것이 확인되었다.

<147> (실시예 3-1 내지 3-6)

<148> 12회에 걸쳐 규소를 퇴적시켜 적층함으로써, 부극 활성 물질 입자를 12층 구조가 되도록 형성한 것을 제외하고, 실시예 1-1 내지 1-3, 1-5 내지 1-7과 같은 절차를 거쳤다.

<149> (비교예 3-1 내지 3-3)

<150> 실시예 3-1 내지 3-6과 동일하게 부극 활성 물질 입자를 12층 구조가 되도록 형성한 것을 제외하고, 비교예 1-2 내지 1-4와 같은 절차를 거쳤다.

<151> 이들 실시예 3-1 내지 3-6 및 비교예 3-1 내지 3-3의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 3 및 도 13에 나타낸 결과가 얻어졌다.

표 3

부극 활성 물질 입자: 규소(진자 빔 증착법)
원박의 두께=18 μm, 심점 평균 조도 Rz=3.5 μm,
부극 활성 물질 입자 층의 산소 함유량= 3 원자수%

	부극 활성 물질층	부극 집전체		방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	강도비 I(200)/I(111)	결정자의 단면적 (μm^2)	
실시예 3-1	12	0.5	50	83
실시예 3-2		0.8		87
실시예 3-3		1		86
실시예 3-4		1.2		85
실시예 3-5		1.4		84
실시예 3-6		1.5		82.5
비교예 3-1	12	0.3	50	69.8
비교예 3-2		1.6		69.9
비교예 3-3		1.8		69.2

<152>

<153> 표 3 및 도 13에 나타낸 바와 같이, 강도비 I(200)/I(111)이 0.5 이상 1.5 이하인 실시예 3-1 내지 3-6에서는, 그 범위밖인 비교예 3-1 내지 3-3보다 방전 용량 유지율이 대폭 높아졌다. 이로부터, 본 발명의 이차 전지에서는 부극 활성 물질 입자의 층수를 12층으로 한 경우에 있어서도 사이클 특성이 향상되는 것이 확인되었다.

<154> 표 1 내지 표 3에 나타낸 일련의 결과로부터, 본 발명의 이차 전지에서는 강도비 I(200)/I(111)이 0.5 이상 1.5 이하이면, 부극 활성 물질 입자를 단층 구조 또는 다층 구조 중 어느 것으로 한 경우에도 사이클 특성이 향상되는 것이 확인되었다. 이 경우에는, 특히 부극 활성 물질 입자의 층수가 다른 것을 제외하고 동일한 조건인 실시예 1-1, 2-1, 3-1 등의 비교 결과로부터 분명한 바와 같이, 그 층수가 증가함에 따라서 방전 용량 유지율이 높아지는 경향을 나타내었다. 이로부터, 부극 활성 물질 입자를 다층 구조로 한 경우에는, 그 층수가 증가하면 보다 높은 효과가 얻어지는 것이 확인되었다.

<155> (실시예 4-1 내지 4-9)

<156> 구리 결정자의 단면적 최대값을 50 μm^2 대신에, 4 μm^2(25 ℃: 실시예 4-1), 10 μm^2(100 ℃: 실시예 4-2), 20 μm^2(150 ℃: 실시예 4-3), 30 μm^2(200 ℃: 실시예 4-4), 40 μm^2(250 ℃: 실시예 4-5), 70 μm^2(350 ℃: 실시예 4-6), 85 μm^2(400 ℃: 실시예 4-7), 100 μm^2(450 ℃: 실시예 4-8) 또는 120 μm^2(500 ℃: 실시예 4-9)로 한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다. 괄호 내의 온도는 결정자의 단면적을 상기한 각각의 값으로 하기 위해서 설정한 원박의 어닐링 온도이다.

<157> 이들 실시예 4-1 내지 4-9의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 4 및 도 14에 나타낸 결과가 얻어졌다. 또한, 표 4에는, 실시예 2-2 및 비교예 2-1 내지 2-3의 결과도 더불어 나타낸다.

표 4

부극 활성 물질 입자: 규소(전자 빔 증착법)
원박의 두께=18 μm, 십점 평균 조도 Rz=3.5 μm,
부극 활성 물질 입자 중의 산소 함유량= 3 원자수%

	부극 활성 물질층	부극 집전체		방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	강도비 I(200)/I(111)	결정자의 단면적 (μm^2)	
실시예 4-1	6	0.8	4	82
실시예 4-2			10	84
실시예 4-3			20	85
실시예 4-4			30	85
실시예 4-5			40	86
실시예 2-2			50	86
실시예 4-6			70	86
실시예 4-7			85	85
실시예 4-8			100	84
실시예 4-9			120	73
비교예 2-1	6	0.3	50	69.5
비교예 2-2		1.6		69.5
비교예 2-3		1.8		69

<158>

<159> 표 4 및 도 14에 나타낸 바와 같이, 강도비 I(200)/I(111)이 0.5 이상 1.5 이하인 실시예 2-2, 4-1 내지 4-9에서는, 결정자의 단면적을 변화시킨 경우에도, 비교예 2-1 내지 2-3보다 방전 용량 유지율이 대폭 높아졌다. 이 경우에는, 결정자의 단면적이 커짐에 따라서 방전 용량 유지율이 상향 볼록형 곡선을 그리도록 변화되고, 특히 단면적이 100 μm^2보다 커지면 극단적으로 저하되는 경향을 나타내었다. 이로부터, 본 발명의 이차 전지에서는 구리 결정자의 단면적에 의존하지 않고 사이클 특성이 향상됨과 동시에, 그 단면적이 100 μm^2 이하이면 보다 높은 효과가 얻어지는 것이 확인되었다.

<160> 여기서, 상기한 실시예 2-2, 4-1 내지 4-9를 대표하여 실시예 2-2, 4-1의 이차 전지에 이용한 부극 집전체 (54A)의 단면을 전계 방사형(field emission: FE) SEM에서 관찰한 결과, 도 15에 나타낸 결과가 얻어졌다. 도 15는 부극 집전체 (54A)의 단면 구조를 나타내는 SEM 사진이고, (A) 및 (B)는 각각 실시예 4-1, 2-2의 관찰 결과를 나타낸다. 도 15에 나타낸 바와 같이 실시예 2-2, 4-1 중 어는 것도 복수개의 구리 결정자가 관찰되었다. 즉, 도 2의 모식도와 도 15의 SEM 사진을 대조하면, 부극 집전체 (54A)를 구성하는 전해 동박에서는, 중앙에 원박 (1A)를 구성하는 큰 결정자가 보이고, 그것을 사이에 두고 상하로 미립자 (1B) 및 도금막 (1C)를 구성하는 작은 결정자가 보였다. 이 경우에는, 실시예 2-2, 4-1 사이에서 원박을 구성하는 결정자의 면적을 비교하면, 그 면적에는 큰 차가 있었다. 즉, 실시예 4-1에서는 도 15(A)에 나타낸 바와 같이 결정자의 면적이 작은 것에 대하여, 실시예 2-2에서는 도 15(B)에 나타낸 바와 같이 결정자의 면적이 컸다. 이로부터, 본 발명의 이차 전지에서는 부극 집전체 (54A)를 구성하는 구리 결정자의 단면적에 따라서 사이클 특성이 변화되는 것이 확인되었다.

<161> (실시예 5-1 내지 5-6)

<162> 부극 집전체 (54A)의 표면의 십점 평균 조도 Rz를 3.5 μm 대신에, 1 μm(실시예 5-1), 1.5 μm(실시예 5-2), 2.5 μm(실시예 5-3), 4.5 μm(실시예 5-4), 5.5 μm(실시예 5-5) 또는 6.5 μm(실시예 5-6)로 한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다. 이 때, 도금욕을 이용한 전해 처리의 조건으로서, 전류비, 욕 온도, 처리 횟수 및 욕 조성 등을 조정함으로써 십점 평균 조도 Rz를 변화시켰다.

<163> 이들 실시예 5-1 내지 5-6의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 5 및 도 16에 나타낸 결과가 얻어졌다. 또한, 표 5에는, 실시예 2-2 및 비교예 2-1 내지 2-3의 결과도 더불어 나타낸다.

표 5

부극 활성 물질 입자: 규소(전자 빔 증착법)
원박의 두께 =18 μm, 부극 활성 물질 입자 중의 산소 함유량=3원자수%

	부극 활성 물질층	부극 집전체			방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	강도비 I(200)/I(111)	결정자의 단면적 (μm²)	십점 평균 조도 Rz (μm)	
실시예 5-1	6	0.8	50	1	71
실시예 5-2				1.5	80
실시예 5-3				2.5	83
실시예 2-2				3.5	86
실시예 5-4				4.5	85
실시예 5-5				5.5	82
실시예 5-6				6.5	72
비교예 2-1	6	0.3	50	3.5	69.5
비교예 2-2		1.6			69.5
비교예 2-3		1.8			69

<164>

<165> 표 5 및 도 16에 나타낸 바와 같이, 강도비 I(200)/I(111)이 0.5 이상 1.5 이하인 실시예 2-2, 5-1 내지 5-6에서는, 십점 평균 조도 Rz를 변화시킨 경우에도 비교예 2-1 내지 2-3보다 방전 용량 유지율이 높아졌다. 이 경우에는, 십점 평균 조도 Rz가 커짐에 따라서 방전 용량 유지율이 상향 볼록형 곡선을 그리도록 변화되고, 특히 십점 평균 조도 Rz가 1.5 μm보다 작아지거나 1.5보다 커지면 극단적으로 저하되는 경향을 나타내었다. 이로부터, 본 발명의 이차 전지에서는 부극 집전체 (54A)의 표면의 십점 평균 조도 Rz에 의존하지 않고 사이클 특성이 향상됨과 동시에, 그 십점 평균 조도 Rz가 1.5 μm 이상 5.5 μm 이하이면 보다 높은 효과가 얻어지는 것이 확인되었다.

<166> (실시예 6-1 내지 6-4)

<167> 원박의 두께를 18 μm 대신에, 7 μm(실시예 6-1), 10 μm(실시예 6-2), 25 μm(실시예 6-3) 또는 30 μm(실시예 6-4)로 한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다.

<168> 이들 실시예 6-1 내지 6-4의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 6 및 도 17에 나타낸 결과가 얻어졌다. 또한, 표 6에는, 실시예 2-2 및 비교예 2-1 내지 2-3의 결과도 더불어 나타낸다.

표 6

부극 활성 물질 입자: 규소(전자 빔 증착법)
십점 평균 조도 Rz=3.5 μm, 부극 활성 물질 입자 중의 산소 함유량=3원자수%

	부극 활성 물질층	부극 집전체			방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	강도비 I(200)/I(111)	결정자의 단면적 (μm²)	원박의 두께 (μm)	
실시예 6-1	6	0.8	50	7	70
실시예 6-2				10	81
실시예 2-2				18	86
실시예 6-3				25	84
실시예 6-4				30	72
비교예 2-1	6	0.3	50	18	69.5
비교예 2-2		1.6			69.5
비교예 2-3		1.8			69

<169>

<170> 표 6 및 도 17에 나타낸 바와 같이, 강도비 I(200)/I(111)이 0.5 이상 1.5 이하인 실시예 2-2, 6-1 내지 6-4에서는 원박의 두께를 변화시킨 경우에도, 비교예 2-1 내지 2-3보다 방전 용량 유지율이 높아졌다. 이 경우에는,

원박의 두께가 두꺼워짐에 따라서 방전 용량 유지율이 상향 볼록형 곡선을 그리도록 변화되고, 특히 두께가 10 ㎛보다 얇아지거나 25 ㎛보다 두꺼워지면 극단적으로 저하되었다. 이로부터, 본 발명의 이차 전지에서는 원박의 두께에 의존하지 않고 사이클 특성이 향상됨과 동시에, 그 두께가 10 ㎛ 이상 25 ㎛ 이하이면 보다 높은 효과가 얻어지는 것이 확인되었다.

<171> (실시예 7-1 내지 7-7)

<172> 부극 집전체 (54A)의 신장률 및 영률을 변경한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다. 이 경우에서의 신장률 및 영률은 각각 0.7 %, 6.53×10^{9} MPa(실시예 7-1), 1 %, 5.00×10^{9} MPa(실시예 7-2), 3.2 %, 4.01×10^{9} MPa(실시예 7-3), 4.9 %, 6.32×10^{8} MPa(실시예 7-4), 10 %, 5.00×10^{7} MPa(실시예 7-5), 10.5 %, 3.61×10^{6} MPa(실시예 7-6) 또는 11.5 %, 1.61×10^{6} MPa(실시예 7-7)였다.

<173> 이들 실시예 7-1 내지 7-7의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 7, 도 18 및 도 19에 나타낸 결과가 얻어졌다. 또한, 표 7에는 실시예 2-2 및 비교예 2-1 내지 2-3의 결과도 더불어 나타낸다.

표 7

부극 활성 물질 입자: 규소(전자 빔 증착법)

원박의 두께=18 ㎛, 십점 평균 조도 Rz=3.5 ㎛, 부극 활성 물질 입자 중의 산소 함유량= 3원자수%

	부극 활성 물질층	부극 집전체				방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	강도비 I(200)/I(111)	결정자의 단면적 (μm^2)	원박의 신장률 (%)	원박의 영률 (MPa)	
실시예 7-1	6	0.8	50	0.7	6.53×10^{9}	73
실시예 7-2				1	5.00×10^{9}	82
실시예 7-3				3.2	4.01×10^{9}	82.4
실시예 7-4				4.9	6.32×10^{8}	83
실시예 2-2				9	5.93×10^{7}	86
실시예 7-5				10	5.00×10^{7}	82
실시예 7-6				10.5	3.61×10^{6}	73
실시예 7-7				11.5	1.61×10^{6}	72
비교예 2-1	6	0.3	50	9	5.93×10^{7}	69.5
비교예 2-2		1.6				69.5
비교예 2-3		1.8				69

<174>

<175> 표 7, 도 18 및 도 19에 나타낸 바와 같이, 강도비 I(200)/I(111)이 0.5 이상 1.5 이하인 실시예 2-2, 7-1 내지 7-7에서는, 부극 집전체 (54A)의 신장률 및 영률을 변화시킨 경우에도 비교예 2-1 내지 2-3보다 방전 용량 유지율이 높아졌다. 이 경우에는, 신장률이 커짐과 함께 영률이 작아짐에 따라서 방전 용량 유지율이 상향 볼록형 곡선을 그리도록 변화되고, 특히 신장률이 1 %보다 작아짐과 함께 영률이 5×10^{9} MPa보다 커지거나, 신장률이 10 %보다 커짐과 함께 영률이 5×10^{7} MPa보다 작아지면 극단적으로 저하되었다. 이로부터, 본 발명의 이차 전지에서는 부극 집전체의 신장률 및 영률에 의존하지 않고 사이클 특성이 향상됨과 동시에, 신장률이 1 % 이상 10 % 이하임과 함께 영률이 5×10^{7} MPa 이상 5×10^{9} MPa 이하이면 보다 높은 효과가 얻어지는 것이 확인되었다.

<176> (실시예 8-1 내지 8-6)

<177> 부극 활성 물질 입자 중에서의 산소 함유량을 3 원자수% 대신에, 2 원자수%(실시예 8-1), 10 원자수%(실시예 8-2), 20 원자수%(실시예 8-3), 30 원자수%(실시예 8-4), 40 원자수%(실시예 8-5) 또는 45 원자수%(실시예 8-6)로 한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다.

<178> 이들 실시예 8-1 내지 8-6의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 8 및 도 20에 나타낸 결과가 얻어졌다. 또한, 표 8에는, 실시예 2-2 및 비교예 2-1 내지 2-3의 결과도 더불어 나타낸다.

표 8

부극 활성 물질 입자: 규소(전자 빔 증착법)
원박의 두께=18 μm, 십점 평균 조도 Rz=3.5 μm

	부극 활성 물질층		부극 집전체		방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	산소 함유량 (원자수%)	강도비 I(200)/I(111)	결정자의 단면적 (μm²)	
실시예 8-1	6	2	0.8	50	82
실시예 2-2		3			86
실시예 8-2		10			90
실시예 8-3		20			90
실시예 8-4		30			88
실시예 8-5		40			86
실시예 8-6		45			85
비교예 2-1	6	3	0.3	50	69.5
비교예 2-2			1.6		69.5
비교예 2-3			1.8		69

<179>

<180> 표 8 및 도 20에 나타낸 바와 같이, 강도비 I(200)/I(111)이 0.5 이상 1.5 이하인 실시예 2-2, 8-1 내지 8-6에서는, 산소 함유량을 변화시킨 경우에도 비교예 2-1 내지 2-3보다 방전 용량 유지율이 높아졌다. 이 경우에는, 산소 함유량이 많아짐에 따라서 방전 용량 유지율이 상향 볼록형 곡선을 그리도록 변화되고, 특히 산소 함유량이 3 원자수%보다 적어지면 극단적으로 저하되었다. 즉, 산소 함유량이 40 원자수%보다 많아지면, 부극 활성 물질 입자 중에서의 규소의 함유량이 상대적으로 적어지기 때문에, 전지 용량이 대폭 저하되기 쉬워진다. 이로부터, 본 발명의 이차 전지에서는 부극 활성 물질 중에서의 산소 함유량에 의존하지 않고 사이클 특성이 향상되는 것이 확인되었다. 또한, 산소 함유량이 3 원자수% 이상 40 원자수% 이하이면, 사이클 특성이 보다 향상됨과 동시에 전지 용량이 확보되는 것도 확인되었다.

<181> (실시예 9-1 내지 9-3)

<182> 챔버 내에 연속적으로 산소 가스 등을 도입하면서 규소를 퇴적시킴으로써 부극 활성 물질 입자에 산소를 함유시키는 대신에, 챔버 내에 간헐적으로 산소 가스를 도입하면서 규소를 퇴적시킴으로써 제1 산소 함유 영역과 그보다 산소 함유량이 높은 제2 산소 함유 영역이 교대로 적층되도록 부극 활성 물질 입자를 형성한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다. 이 때, 제2 산소 함유 영역 중에서의 산소 함유량을 3 원자수%로 하고, 그 수를 2(실시예 9-1), 4(실시예 9-2) 또는 6(실시예 9-3)으로 하였다.

<183> 이들 실시예 9-1 내지 9-3의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 9 및 도 21에 나타낸 결과가 얻어졌다. 또한, 표 9에는, 실시예 2-2 및 비교예 2-1 내지 2-3의 결과도 더불어 나타낸다.

표 9

부극 활성 물질 입자: 규소(전자 빔 증착법)
원박의 두께=18 μm, 십점 평균 조도 Rz=3.5 μm

	부극 활성 물질층		부극 집전체		방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	제2 산소 함유 영역의 수	강도비 I(200)/I(111)	결정자의 단면적 (μm²)	
실시예 2-2	6	—	0.8	50	86
실시예 9-1		2			88
실시예 9-2		4			89
실시예 9-3		6			89

<184>

<185> 표 9 및 도 21에 나타낸 바와 같이, 부극 활성 물질 입자가 제1 및 제2 산소 함유 영역을 갖는 실시예 9-1 내지

9-3에서는, 이들을 갖지 않는 실시예 2-2보다 방전 용량 유지율이 높아졌다. 이 경우에는, 제2 산소 함유 영역의 수가 증가함에 따라서 방전 용량 유지율이 높아지는 경향을 나타내었다. 이로부터, 본 발명의 이차 전지에서는 부극 활성 물질 입자가 제1 및 제2 산소 함유 영역을 갖는 것에 의해 사이클 특성이 향상됨과 동시에, 그 제2 산소 함유 영역의 수가 증가함에 따라서 높은 효과가 얻어지는 것이 확인되었다.

<186> (실시예 10-1)

<187> 전자 빔 증착법 대신에 RF 스퍼터링법을 이용하여 규소를 퇴적시킴으로써 부극 활성 물질 입자를 형성한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다. 이 때, 순도 99.99 %의 규소를 타겟으로서 이용하고, 퇴적 속도를 0.5 nm/초로 하였다.

<188> (실시예 10-2)

<189> 전자 빔 증착법 대신에 CVD법을 이용하여 규소를 퇴적시킴으로써 부극 활성 물질 입자를 형성한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다. 이 때, 원재료 및 여기 가스로서 실란(SiH_4) 및 아르곤(Ar)을 각각 이용하고, 퇴적 속도 및 기판 온도를 각각 1.5 nm/초 및 200 ℃로 하였다.

<190> (비교예 10-1)

<191> 실시예 10-1과 동일하게 RF 스퍼터링법을 이용하여 부극 활성 물질 입자를 형성한 것을 제외하고, 비교예 2-1과 같은 절차를 거쳤다.

<192> (비교예 10-2)

<193> 실시예 10-2와 동일하게 CVD법을 이용하여 부극 활성 물질 입자를 형성한 것을 제외하고, 비교예 2-1과 같은 절차를 거쳤다.

<194> 이들 실시예 10-1, 10-2 및 비교예 10-1, 10-2의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 10에 나타낸 결과가 얻어졌다. 또한, 표 10에는, 실시예 2-2 및 비교예 2-1의 결과도 더불어 나타낸다.

표 10

부극 활성 물질 입자: 규소

원박의 두께=18 μm, 십점 평균 조도 Rz=3.5 μm,

부극 활성 물질 입자 중의 산소 함유량= 3 원자수%

	부극 활성 물질층		부극 집전체		방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	형성 방법	강도비 I(200)/I(111)	결정자의 단면적 (μm^2)	
실시예 2-2	6	전자 빔 증착법	0.8	50	86
실시예 10-1		스퍼터링법			84
실시예 10-2		CVD법			83
비교예 2-1	6	전자 빔 증착법	0.3	50	69.5
비교예 10-1		스퍼터링법			65
비교예 10-2		CVD법			64

<195>

<196> 표 10에 나타낸 바와 같이, 부극 활성 물질 입자의 형성 방법으로서 스퍼터링법 또는 CVD법을 이용한 실시예 10-1, 10-2에서는, 전자 빔 증착법을 이용한 실시예 2-2와 동등한 방전 용량 유지율이 얻어졌다. 이 경우에는, 부극 활성 물질 입자의 형성 방법을 비교하면, CVD법, 스퍼터링법 및 전자 빔 증착법의 순서로 방전 용량 유지율이 높아지는 경향을 나타내었다. 물론, 강도비 I(200)/I(111)이 0.5 이상 1.5 이하인 실시예 2-2, 10-1, 10-2에서는, 그 범위밖인 비교예 2-1, 10-1, 10-2보다 방전 용량 유지율이 높아졌다. 이로부터, 본 발명의 이차 전지에서는 부극 활성 물질 입자의 형성 방법에 의존하지 않고 사이클 특성이 향상됨과 동시에, 그 부극 활성 물질 입자의 형성 방법으로서 CVD법, 스퍼터링법 및 전자 빔 증착법의 순서로 높은 효과가 얻어지는 것이 확인되었다.

<197> (실시예 11-1)

<198> 이하의 절차에 의해, 라미네이트 필름형 이차 전지 대신에 도 4 및 도 5에 나타낸 각형 이차 전지를 제조한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다.

<199> 우선, 정극 (21) 및 부극 (22)를 제조한 후, 정극 집전체 (21A) 및 부극 집전체 (22A)에 각각 알루미늄제 정극 리드 (24) 및 니켈제 부극 리드 (25)를 용접하였다. 계속해서, 정극 (21), 세퍼레이터 (23) 및 부극 (22)를 이 순서대로 적층하고, 길이 방향에 있어서 권회시킨 후, 편평형으로 성형함으로써 전지 소자 (20)을 제조하였다. 계속해서, 알루미늄제 전지캔 (11)의 내부에 전지 소자 (20)을 수납한 후, 그 전지 소자 (20) 상에 절연판 (12)를 배치하였다. 계속해서, 정극 리드 (24) 및 부극 리드 (25)를 각각 정극 핀 (15) 및 전지캔 (11)에 용접한 후, 전지캔 (11)의 개방 단부에 전지 뚜껑 (13)을 레이저 용접하여 고정시켰다. 마지막으로, 주입 구멍 (19)를 통해 전지캔 (11)의 내부에 전해액을 주입하고, 그 주입 구멍 (19)를 밀봉 부재 (19A)로 막음으로써 각형 전지가 완성되었다.

<200> (실시예 11-2)

<201> 알루미늄제 전지캔 (11) 대신에 철제 전지캔 (11)을 이용한 것을 제외하고, 실시예 11-1과 같은 절차를 거쳤다.

<202> 이들 실시예 11-1, 11-2의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 11에 나타낸 결과가 얻어졌다. 또한, 표 11에는, 실시예 2-2의 결과도 더불어 나타낸다.

표 11

부극 활성 물질 입자: 규소(전자 빔 증착법)
원박의 두께=18㎛, 십점 평균 조도 Rz=3.5㎛,
부극 활성 물질 입자 중의 산소 함유량= 3 원자수%

<203>

	부극 활성 물질층	부극 집전체		전지 구조	방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	강도비 I(200)/I(111)	결정자의 단면적 (μm^2)		
실시예 2-2	6	0.8	50	라미네이트 필름형	86
실시예 11-1				각형(알루미늄)	89
실시예 11-2				각형(철)	92

<204> 표 11에 나타낸 바와 같이, 전지 구조가 각형인 실시예 11-1, 11-2에서는, 라미네이트 필름형인 실시예 2-2보다 방전 용량 유지율이 높아졌다. 즉, 전지캔 (11)의 재질을 비교하면, 알루미늄보다 철에 있어서 방전 용량 유지율이 높아지는 경향을 나타내었다. 이로부터, 본 발명의 이차 전지에서는 전지 구조에 의존하지 않고 사이클 특성이 향상됨과 동시에, 전지 구조가 각형인 경우에는 알루미늄제 전지캔 (11)보다 철제 전지캔 (11)에 있어서 높은 효과가 얻어지는 것이 확인되었다. 또한, 여기서는 구체적인 실시예를 들어 설명하지 않지만, 전지 구조를 비교한 경우에, 필름형 외장 부재를 포함하는 라미네이트 필름형보다 금속제 외장 부재를 포함하는 각형에 있어서 사이클 특성이 향상되었기 때문에, 금속제 외장 부재를 포함하는 원통형에서도 각형과 동일한 결과가 얻어지는 것은 분명하다.

<205> (실시예 12-1)

<206> 용매로서 EC 대신에 불소화 탄산에스테르(탄산모노플루오로에틸렌)인 4-플루오로-1,3-디옥솔란-2-온(FEC)를 이용한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다.

<207> (실시예 12-2)

<208> 용매로서 불소화 탄산에스테르(탄산디플루오로에틸렌)인 4,5-디플루오로-1,3-디옥솔란-2-온(DFEC)를 첨가하여 혼합 용매의 조성을 중량비로 EC:DFEC:DEC=25:5:70으로 한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다.

<209> (실시예 12-3, 12-4)

<210> 전해액에 용매로서 불포화 결합을 갖는 환상 탄산에스테르인 탄산비닐렌(VC: 실시예 12-3) 또는 탄산비닐에틸렌(VEC: 실시예 12-4)을 첨가한 것을 제외하고, 실시예 12-1과 같은 절차를 거쳤다. 이 때, 전해액 중에서의 VC, VEC의 함유량을 10 중량%로 하였다.

<211> (실시예 12-5)

<212> 전해액에 용매로서 술톤인 1,3-프로펜술톤(PRS)을 첨가한 것을 제외하고, 실시예 12-1과 같은 절차를 거쳤다. 이 때, 전해액 중에서의 PRS의 농도를 1 중량%로 하였다.

<213> (실시예 12-6)

<214> 전해액에 전해질염으로서 붕소 및 불소를 갖는 화합물인 사불화붕산리튬($LiBF_4$)을 첨가한 것을 제외하고, 실시예 12-1과 같은 절차를 거쳤다. 이 때, 전해액 중에서의 $LiBF_4$의 농도를 0.1 몰/kg로 하였다.

<215> 이들 실시예 12-1 내지 12-6의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 12에 나타낸 결과가 얻어졌다. 또한, 표 12에는, 실시예 2-2의 결과도 더불어 나타낸다.

<216> 이 때, 실시예 2-2, 12-5의 이차 전지에 대해서는, 사이클 특성뿐만 아니라 팽창 특성도 조사하였다. 이 팽창 특성을 조사할 때는, 이하의 절차에 따라서 이차 전지를 충전시킴으로써 팽창률을 구하였다. 우선, 전지 상태를 안정화시키기 위해서 23 ℃의 분위기 중에서 1 사이클 충방전시킨 후, 2 사이클째 충전 전의 두께를 측정하였다. 계속해서, 동일한 분위기 중에서 다시 충전한 후, 2 사이클째 충전 후의 두께를 측정하였다. 마지막으로, 팽창률(%)=[(충전 후의 두께-충전 전의 두께)/충전 전의 두께]×100을 산출하였다. 이 때, 충전 조건은 사이클 특성을 조사한 경우와 동일하게 하였다.

표 12

부극 활성 물질 입자: 규소(전자 빔 증착법)

원박의 두께=18㎛, 십점 평균 조도 Rz=3.5㎛, 부극 활성 물질 입자 중의 산소 함유량= 3 원자수%

	부극 활성 물질층	부극 집전체		전해액					방전 용량 유지율 (%)	팽창률 (%)
	부극 활성 물질 입자의 층수 (층)	강도비 I(200)/I(111)	결정자의 단면적 (μm^2)	용액 (중량%)				기타		
				EC	FEC	DFEC	DEC			
실시예 2-2	6	0.8	50	50	—	—	50	—	86	3.01
실시예 12-1				—	50	—	50		90	—
실시예 12-2				25	—	5	70		91	—
실시예 12-3				—	50	—	50	VC	92	—
실시예 12-4								VEC	93	—
실시예 12-5								PRS	92	0.30
실시예 12-6								$LiBF_4$	91	—

<217>

<218> 표 12에 나타낸 바와 같이, 용매에 불소화 탄산에스테르(FEC, DFEC)를 첨가하거나, 또는 전해액에 용매로서 불포화 결합을 갖는 환상 탄산에스테르 등(VC, VEC, PRS, $LiBF_4$)을 첨가한 실시예 12-1 내지 12-6에서는, 이들을 첨가하지 않은 실시예 2-2보다 방전 용량 유지율이 높아졌다. 이 경우에는, 용매가 탄산모노플루오로에틸렌인 FEC를 포함하는 실시예 12-1보다 탄산디플루오로에틸렌인 DFEC를 포함하는 실시예 12-2에 있어서 방전 용량 유지율이 높아지는 경향을 나타내었다. 또한, VC 등을 포함하는 실시예 12-3 내지 12-6에서는, 그것을 포함하지 않는 실시예 12-1보다 방전 용량 유지율이 높아지는 경향을 나타내었다. 상세하게는, 용매가 VC 또는 VEC를 포함하는 실시예 12-3, 12-4에서는, PRS 또는 $LiBF_4$를 포함하는 실시예 12-5, 12-6보다 방전 용량 유지율이 높아지며, VC를 포함하는 실시예 12-3보다 VEC를 포함하는 실시예 12-4에 있어서 방전 용량 유지율이 높아졌다. 이로부터, 본 발명의 이차 전지에서는 용매나 전해액의 조성에 의존하지 않고 사이클 특성이 향상됨과 동시에, 그 용매가 불소화 탄산에스테르, 불포화 결합을 갖는 환상 탄산에스테르, 술톤, 또는 붕소 및 불소를 갖는 전해질염을 함유하면 보다 높은 효과가 얻어지는 것이 확인되었다. 특히, 높은 효과를 얻기 위해서는, 불소화 탄산에스테르로서는 탄산모노플루오로에틸렌보다 탄산디플루오로에틸렌이 바람직하고, 불포화 결합을 갖는 환상 탄산에스테르로서는 탄산비닐렌보다 탄산비닐에틸렌이 바람직하다.

<219> 또한, 용매가 PRS를 함유하는 실시예 12-5에서는, 그것을 함유하지 않는 실시예 2-2보다 팽창률이 대폭 저하되었다. 이로부터, 본 발명의 이차 전지에서는 용매가 술톤을 함유함으로써 팽창 특성이 향상되는 것이 확인되었다.

<220> (실시예 13-1)

<221> 부극 활성 물질 입자를 형성한 후에 금속을 형성한 것을 제외하고, 실시예 2-2와 같은 절차를 거쳤다. 이 금속을 형성하는 경우에는, 부극 활성 물질 입자가 형성된 부극 집전체 (54A)의 양면에, 전해 도금법에 의해서 코발트를 퇴적시켜 금속을 형성함으로써, 부극 활성 물질 입자와 함께 금속을 포함하도록 부극 활성 물질층 (54B)를 형성하였다. 이 때, 도금액으로서 닛본 고준도 가가꾸 가부시끼가이샤 제조의 코발트 도금액을 이용하고, 전류 밀도를 2 A/dm^2 내지 5 A/dm^2로 하며, 도금 속도를 10 nm/초로 하였다. 또한, 부극 활성 물질 입자의 단위 면적당 몰수 M1과 금속의 단위 면적당 몰수 M2와의 비(몰비) M2/M1을 1/15로 하였다.

<222> (실시예 13-2 내지 13-7)

<223> 몰비 M2/M1을 1/15 대신에, 1/10(실시예 13-2), 1/5(실시예 13-3), 1/2(실시예 13-4), 1/1(실시예 13-5), 2/1(실시예 13-6) 또는 3/1(실시예 13-7)로 한 것을 제외하고, 실시예 13-1과 같은 절차를 거쳤다.

<224> (실시예 13-8 내지 13-11)

<225> 도금액으로서 코발트 도금액 대신에, 철 도금액(실시예 13-8), 니켈 도금액(실시예 13-9), 아연 도금액(실시예 13-10) 또는 구리 도금액(실시예 13-11)을 이용한 것을 제외하고, 실시예 13-4와 같은 절차를 거쳤다. 이 때, 전류 밀도로서, 철 도금액을 이용하는 경우에는 2 A/dm^2 내지 5 A/dm^2로 하고, 니켈 도금액을 이용하는 경우에는 2 A/dm^2 내지 10 A/dm^2로 하며, 아연 도금액을 이용하는 경우에는 1 A/dm^2 내지 3 A/dm^2로 하고, 구리 도금액을 이용하는 경우에는 2 A/dm^2 내지 8 A/dm^2로 하였다. 상기한 일련의 도금액은 모두 닛본 고준도 가가꾸 가부시끼가이샤 제품이다.

<226> 이들 실시예 13-1 내지 13-11의 이차 전지에 대하여 사이클 특성을 조사한 결과, 표 13 및 도 22에 나타낸 결과가 얻어졌다. 또한, 표 13에는, 실시예 2-2의 결과도 더불어 나타낸다.

<227> 이 때, 실시예 13-1 내지 13-11의 이차 전지에 대해서는, 사이클 특성뿐만 아니라 금속량과 사이클 특성 사이의 상관을 조사하기 위해서, 부극 (54)의 표면에서 금속이 차지하는 원자수의 비율(금속의 점유 비율)도 조사하였다. 이 금속의 점유 비율을 조사할 때는, 부극 (54)의 표면을 EDX로 원소 분석함으로써 그 표면에서의 금속의 존재 비율을 측정하였다.

표 13

부극 활성 물질 입자: 규소(전자 빔 증착법)
원박의 두께=18 μm, 십점 평균 조도 Rz=3.5 μm,
부극 활성 물질 입자 중의 산소 함유량= 3 원자수%

	부극 활성 물질층				부극 집전체		방전 용량 유지율 (%)
	부극 활성 물질 입자의 층수 (층)	금속의 종류	몰비 M2/M1	금속의 점유 비율 (원자수%)	강도비 I(200)/I(111)	결정자의 단면적 (μm^2)	
실시예 2-2	6	—	—	—	0.8	50	86
실시예 13-1		Co	1/15	2			88
실시예 13-2			1/10	4.1			90
실시예 13-3			1/5	6.3			91
실시예 13-4			1/2	8.3			92
실시예 13-5			1/1	10.3			91
실시예 13-6			2/1	18			90
실시예 13-7			3/1	30			89
실시예 13-8		Fe	1/2	11.2			91
실시예 13-9		Ni		9.5			90
실시예 13-10		Zn		8.5			90
실시예 13-11		Cu		8.9			90

<228>

<229> 표 13 및 도 22에 나타낸 바와 같이, 금속을 형성한 실시예 13-1 내지 13-11에서는, 몰비 M2/M1이 1/15 이상 3/1 이하임과 동시에 금속의 점유 비율이 2 원자수% 이상 30 원자수% 이하에 있어서, 금속을 형성하지 않은 실시예 2-2보다 방전 용량 유지율이 높아졌다. 이 경우에는, 금속의 종류가 다른 실시예 13-4, 13-8 내지 13-11을 비교하면, 방전 용량 유지율은 금속으로서 구리, 아연 및 니켈을 이용한 경우보다 철을 이용한 경우에 있어서 높아지고, 코발트를 이용한 경우에 있어서 더 높아졌다. 이로부터, 본 발명의 이차 전지에서는 부극 활성 물질 입자를 형성한 후에 전극 반응 물질과 반응하지 않는 금속 원소를 갖는 금속을 형성함으로써, 사이클 특성이 향상되는 것이 확인되었다. 이 경우에는, 금속으로서 코발트를 이용하면 보다 높은 효과가 얻어지는 것도 확인되었다.

<230> 여기서, 상기한 실시예 2-2, 13-1 내지 13-11을 대표하여 실시예 2-2, 13-4의 이차 전지에 있어서의 부극 (54)의 단면을 관찰한 결과, 이하의 도 23 내지 도 25에 나타낸 결과가 얻어졌다.

<231> 도 23은 사이클 시험 전에서의 부극 (54)의 단면 구조를 나타내는 SEM 사진이고, (A) 및 (B)는 각각 실시예 2-2, 13-4의 관찰 결과를 나타낸다. 또한, 도 24는 사이클 시험 전에서의 실시예 13-4의 부극 (54)의 표면 구조를 나타내는 SEM 사진이다. 도 23에 나타낸 바와 같이 실시예 2-2, 13-4 중 어느 것도 조면화된 부극 집전체 (54A)의 표면에 형성된 부극 활성 물질층 (54B)에서는, 그 표면 상에 부극 활성 물질 입자가 6층 구조가 되도록 성장된 모습이 관찰되었다. 그러나, 실시예 2-2에서는 도 23(A)에 나타낸 바와 같이 부극 활성 물질 입자 사이 및 부극 활성 물질 입자 내에 간극이 생긴 것에 대하여, 실시예 13-4에서는 도 23(B)에 나타낸 바와 같이 상기한 간극에 금속이 들어가 있고, 그 금속을 통해 부극 활성 물질 입자끼리 결착되어 있었다. 특히, 실시예 13-4에서는 부극 활성 물질 입자의 노출면 일부가 금속에 의해 피복되어 있었다. 상기한 간극에 금속이 들어가 있는 모습은 도 24에서도 분명하다. 도 24에서는, 24A로 나타낸 콘트라스트가 짙은 부분이 부극 활성 물질 입자

이고, 24B로 나타낸 콘트라스트가 희미한 부분이 금속이다. 이로부터, 본 발명의 이차 전지에서는 금속에 의해서 부극 활성 물질층 (54B)의 결착성이 향상되는 것이 확인되었다.

<232> 도 25는 도 23(B)에 나타낸 실시예 13-4의 부극 (54)의 단면을 EDX로 원소 분포 분석(소위 원소 분포의 맵핑)한 결과이다. 도 25에서는, (A) 중에 25A로 나타낸 콘트라스트가 희미한 부분이 규소의 분포 범위를 나타내고, (B) 중에 25B로 나타낸 콘트라스트가 희미한 부분이 코발트의 분포 범위를 나타낸다. 도 25에 나타낸 바와 같이, 부극 활성 물질 입자인 규소가 존재하지 않은 범위(도 25(A) 내의 25A로 나타낸 부분에 의해 둘러싸인 부분)는, 금속인 코발트가 존재하는 범위(도 25(B) 내의 25B로 나타낸 부분)와 일치하였고, 그 범위는 인접하는 부극 활성 물질 입자 사이의 간극 및 부극 활성 물질 입자 내의 간극이었다. 특히, 실시예 13-4에서는, 부극 활성 물질 입자의 노출면 상에도 금속이 점재되어 있었다. 이로부터, 본 발명의 이차 전지에서는 부극 활성 물질 입자 사이의 간극 및 부극 활성 물질 입자 내의 간극에 금속이 들어감과 동시에, 부극 활성 물질 입자의 노출면 일부를 금속으로 피복하는 것이 확인되었다.

<233> 이상, 실시 형태 및 실시예를 들어 본 발명을 설명하였지만, 본 발명은 상기한 실시 형태 및 실시예에 있어서 설명한 양태로 한정되지 않고, 다양한 변형이 가능하다. 예를 들면, 본 발명의 집전체 또는 부극의 용도는 반드시 전지로 한정되지 않고, 전지 이외의 다른 전기 화학 디바이스일 수도 있다. 이 외의 용도로서는, 예를 들면 캐패시터 등을 들 수 있다.

<234> 또한, 상기한 실시 형태 및 실시예에서는, 전지의 종류로서, 부극의 용량이 리튬의 흡장 및 방출에 기초하여 표시되는 리튬 이온 이차 전지에 대하여 설명하였지만, 반드시 이것으로 한정되는 것은 아니다. 본 발명의 전지는, 리튬을 흡장 및 방출하는 것이 가능한 부극 재료의 충전 용량을 정극의 충전 용량보다 작게 함으로써, 부극의 용량이 리튬의 흡장 및 방출에 기초하는 용량과 리튬의 석출 및 용해에 기초하는 용량을 포함하며, 이들 용량의 합에 의해 표시되는 이차 전지에 대해서도 동일하게 적용 가능하다.

<235> 또한, 상기한 실시 형태 및 실시예에서는, 전지 구조가 각형, 원통형 및 라미네이트 필름형인 경우, 및 전지 소자가 권회 구조를 갖는 경우를 예로 들어 설명하였지만, 본 발명의 전지는 코인형 또는 버튼형 등의 다른 전지 구조를 갖는 경우나, 전지 소자가 적층 구조 등의 다른 구조를 갖는 경우에 대해서도 동일하게 적용 가능하다. 또한, 본 발명의 전지는 이차 전지로 한정되지 않고, 일차 전지 등의 다른 종류의 전지에 대해서도 동일하게 적용 가능하다.

<236> 또한, 상기한 실시 형태 및 실시예에서는, 전극 반응 물질로서 리튬을 이용하는 경우에 대하여 설명하였지만, 나트륨(Na) 또는 칼륨(K) 등의 다른 1A족 원소나, 마그네슘(Mg) 또는 칼슘(Ca) 등의 2A족 원소나, 알루미늄 등의 다른 경금속을 이용할 수도 있다. 이들 경우에 있어서도, 부극 활성 물질로서 상기한 실시 형태에서 설명한 부극 재료를 이용하는 것이 가능하다.

<237> 또한, 상기한 실시 형태 및 실시예에서는, 본 발명의 집전체에 있어서의 강도비 I(200)/I(111)에 대하여, 실시예의 결과로부터 도출된 수치 범위를 적정 범위로서 설명하였지만, 그 설명은, 강도비가 상기한 범위밖이 될 가능성을 완전히 부정하는 것은 아니다. 즉, 상기한 적정 범위는 어디까지나 본 발명의 효과를 얻는 데에 있어서 특히 바람직한 범위이고, 본 발명의 효과가 얻어지는 것이면 강도비가 상기한 범위에서 다소 벗어날 수도 있다. 이것은 상기한 강도비로 한정되지 않고, 구리 결정자의 단면적이나 집전체의 십점 평균 조도 Rz, 신장률 및 영률이나, 원박의 두께 등에 대해서도 동일하다.

도면의 간단한 설명

<238> 도 1은 본 발명의 한 실시 형태에 따른 집전체를 이용한 부극의 구성을 나타내는 단면도이다.

<239> 도 2는 도 1에 나타낸 부극 집전체의 일부를 확대하여 모식적으로 나타내는 단면도이다.

<240> 도 3은 도 1에 나타낸 부극의 단면 구조를 나타내는 SEM 사진 및 그의 모식도이다.

<241> 도 4는 본 발명의 한 실시 형태에 따른 부극을 구비한 제1 전지의 구성을 나타내는 단면도이다.

<242> 도 5는 도 4에 나타낸 제1 전지의 V-V선에 따른 단면도이다.

<243> 도 6은 본 발명의 한 실시 형태에 따른 부극을 구비한 제2 전지의 구성을 나타내는 단면도이다.

<244> 도 7은 도 6에 나타낸 권회 전극체의 일부를 확대하여 나타내는 단면도이다.

<245> 도 8은 본 발명의 한 실시 형태에 따른 부극을 구비한 제3 전지의 구성을 나타내는 단면도이다.

<246> 도 9는 도 8에 나타낸 권회 전극체의 IX-IX선에 따른 단면도이다.

<247> 도 10은 강도비와 방전 용량 유지율 사이의 상관을 나타내는 도면이다.

<248> 도 11은 부극(실시예 1-2, 1-4)의 XRD 분석 결과이다.

<249> 도 12는 강도비와 방전 용량 유지율 사이의 다른 상관을 나타내는 도면이다.

<250> 도 13은 강도비와 방전 용량 유지율 사이의 또다른 상관을 나타내는 도면이다.

<251> 도 14는 결정자의 단면적과 방전 용량 유지율 사이의 상관을 나타내는 도면이다.

<252> 도 15는 부극 집전체(실시예 2-2, 4-1)의 단면 구조를 나타내는 SEM 사진이다.

<253> 도 16은 십점 평균 조도와 방전 용량 유지율 사이의 상관을 나타내는 도면이다.

<254> 도 17은 원박의 두께와 방전 용량 유지율 사이의 상관을 나타내는 도면이다.

<255> 도 18은 부극 집전체의 신장률과 방전 용량 유지율 사이의 상관을 나타내는 도면이다.

<256> 도 19는 부극 집전체의 영률과 방전 용량 유지율 사이의 상관을 나타내는 도면이다.

<257> 도 20은 산소 함유량과 방전 용량 유지율 사이의 상관을 나타내는 도면이다.

<258> 도 21은 제2 산소 함유 영역의 수와 방전 용량 유지율 사이의 상관을 나타내는 도면이다.

<259> 도 22는 금속의 점유 비율과 방전 용량 유지율 사이의 상관을 나타내는 도면이다.

<260> 도 23은 부극(실시예 2-2, 13-4)의 단면 구조를 나타내는 SEM 사진이다.

<261> 도 24는 부극(실시예 13-4)의 표면 구조를 나타내는 SEM 사진이다.

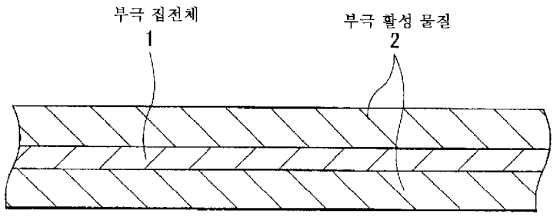
<262> 도 25는 부극(실시예 13-4)의 단면의 EDX 원소 분포 분석 결과이다.

<263> <도면의 주요 부분에 대한 부호의 설명>

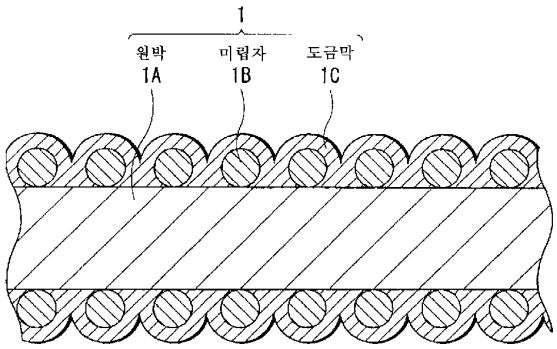
<264> 1, 22A, 42A, 54A… 부극 집전체, 1A… 원박, 1B… 미립자, 1C… 도금막, 2, 22B, 42B, 54B… 부극 활성 물질층, 11, 31… 전지캔, 12, 32, 33… 절연판, 13, 34… 전지 뚜껑, 14… 단자판, 15… 정극 핀, 16… 절연 케이스, 17, 37… 가스켓, 18… 열개 밸브, 19… 주입 구멍, 19A… 밀봉 부재, 20… 전지 소자, 21, 41, 53… 정극, 21A, 41A, 53A… 정극 집전체, 21B, 41B, 53B… 정극 활성 물질층, 22, 42, 54… 부극, 23, 43, 55… 세퍼레이터, 24, 45, 51… 정극 리드, 25, 46, 52… 부극 리드, 35… 안전 밸브 기구, 35A… 디스크 판, 36… 열감 저항 소자, 40, 50… 권회 전극체, 44… 센터핀, 56… 전해질, 57… 보호 테이프, 61… 밀착 필름, 60… 외장 부재, 201… 부극 활성 물질 입자, 202(202A 내지 202C)… 금속.

도면

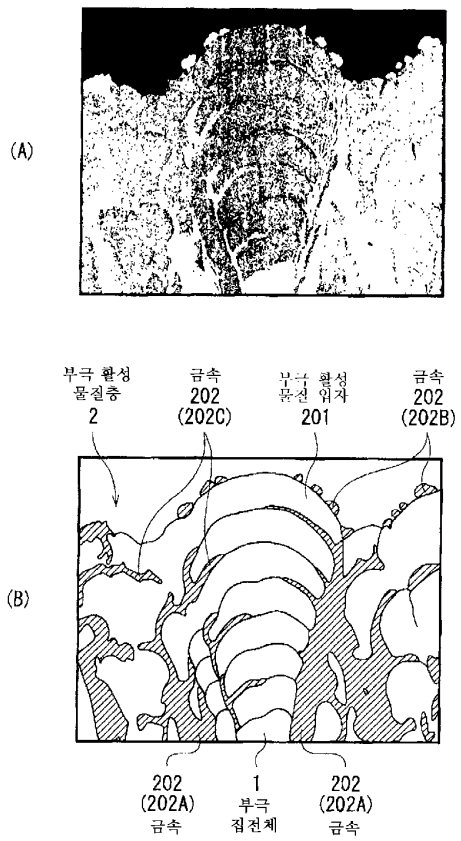
도면1



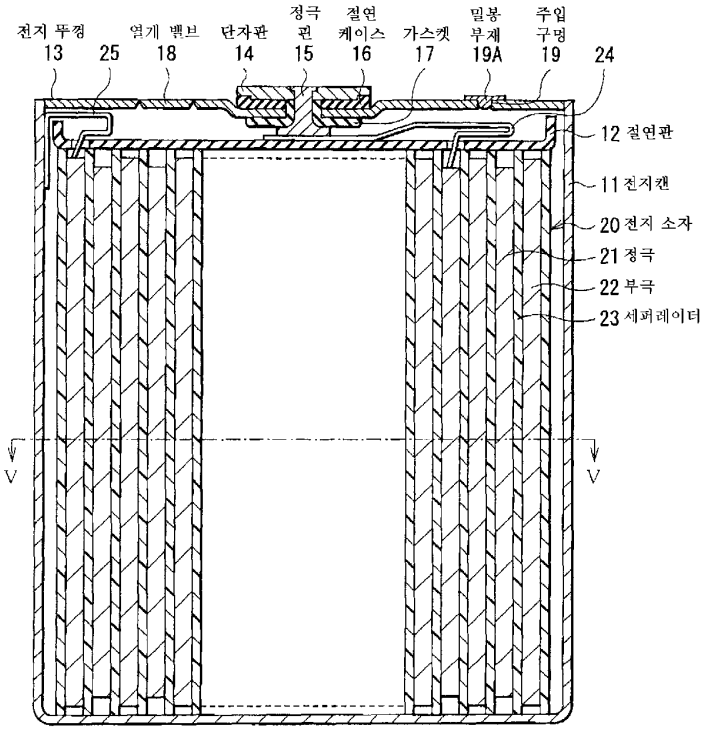
도면3


1
원박
1A
미립자
1B
도금막
1C

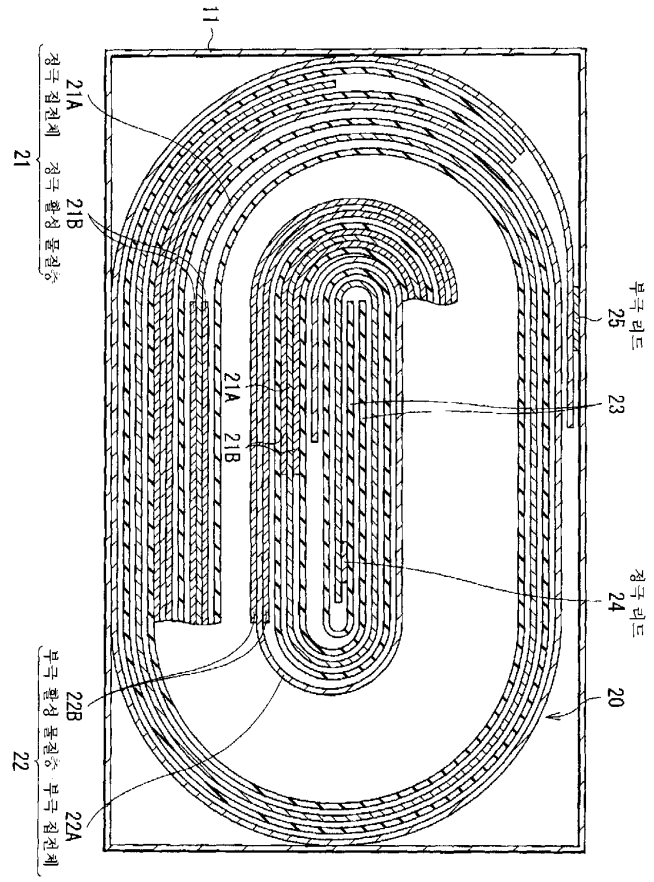
도면3


(A)
(B)
부극 활성
물질층
2
금속
202
(202C)
부극 활성
물질 위자
201
금속
202
(202B)
202
(202A)
금속
1
부극
집전체
202
(202A)
금속

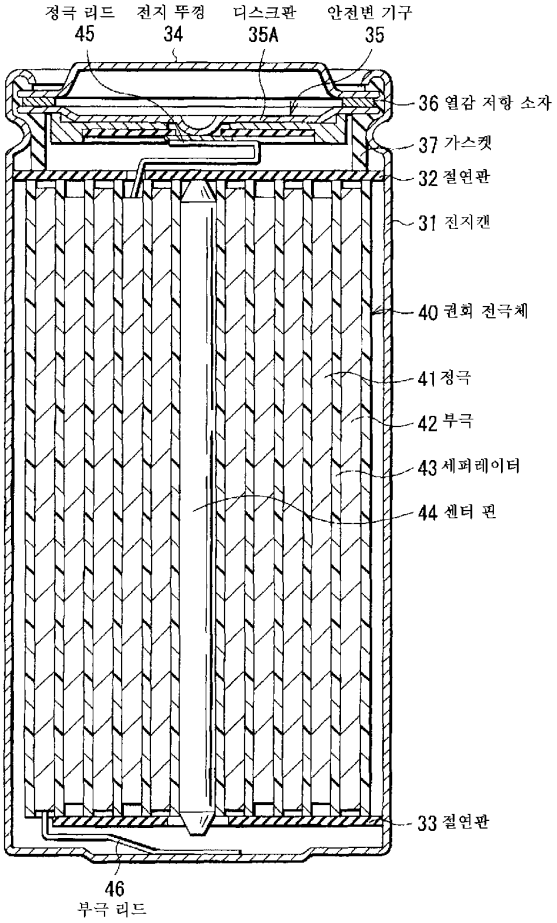
도면4


전지 뚜껑
13
25
열게 밸브
18
단자판
14
정극 핀
15
절연 케이스
16
가스켓
17
밀봉 부재
19A
주입 구멍
19
24
12 절연판
11 전지캔
20 전지 소자
21 정극
22 부극
23 세퍼레이터
V
V

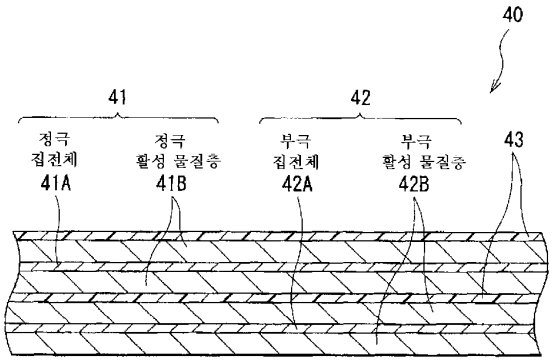
도면5


11
21A
정극 집전체
21
21B
정극 활성 물질층
부극 리드
25
23
21A
21B
정극 리드
24
20
22B
부극 활성 물질층
22
22A
부극 집전체

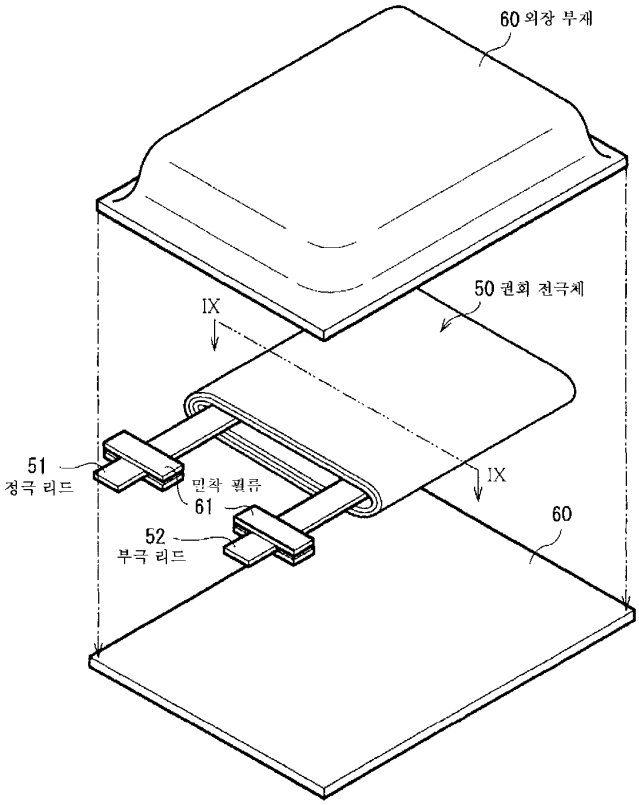
도면6


정극 리드
45
전지 뚜껑
34
디스크판
35A
안전변 기구
35
36 열감 저항 소자
37 가스켓
32 절연판
31 전지캔
40 권회 전극체
41 정극
42 부극
43 세퍼레이터
44 센터 핀
33 절연판
46
부극 리드

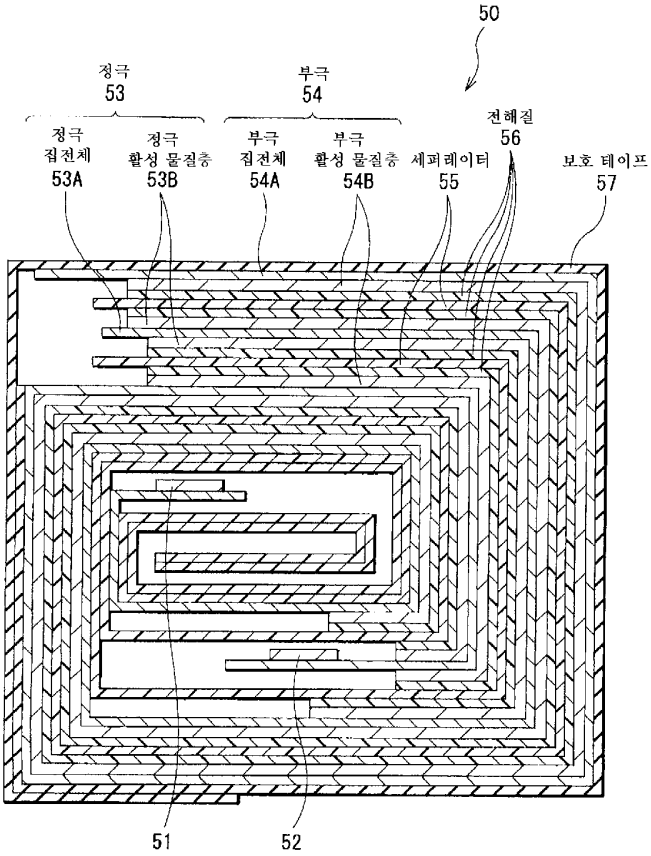
도면7


40
41
42
정극
집전체
41A
정극
활성 물질층
41B
부극
집전체
42A
부극
활성 물질층
42B
43

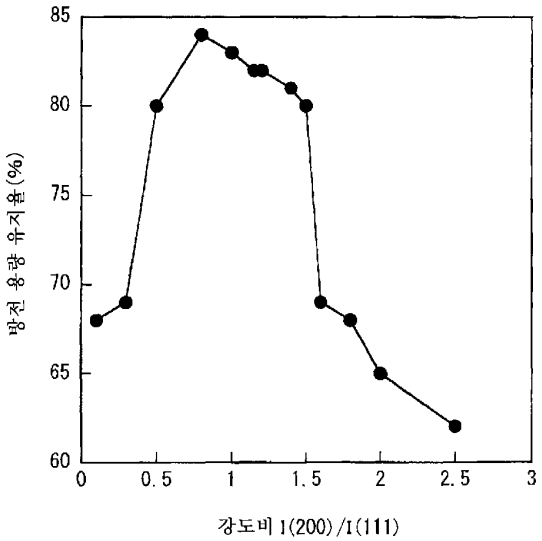
도면8



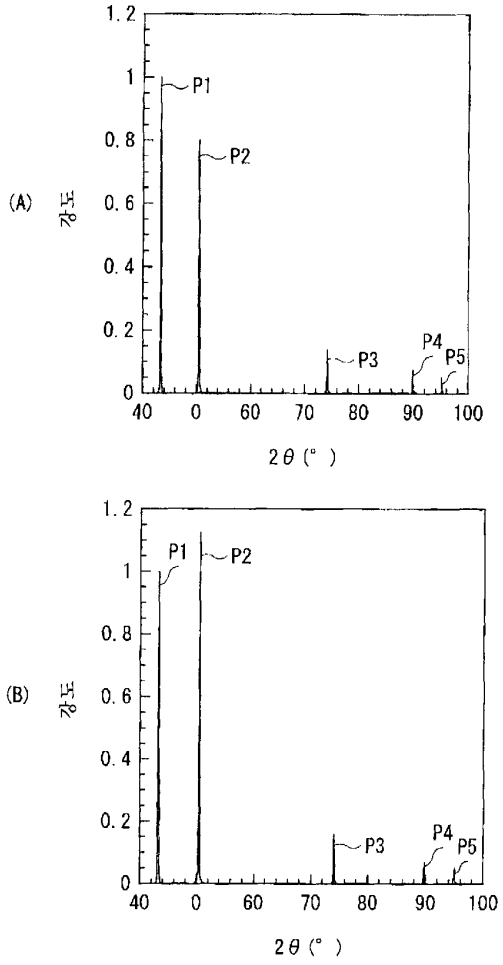
도면9


50
정극
53
부극
54
전해질
56
정극
집전체
53A
정극
활성 물질층
53B
부극
집전체
54A
부극
활성 물질층
54B
세퍼레이터
55
보호 테이프
57
51
52

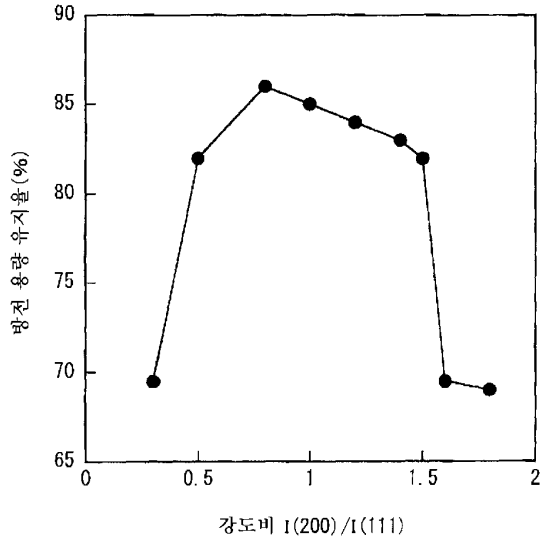
도면10



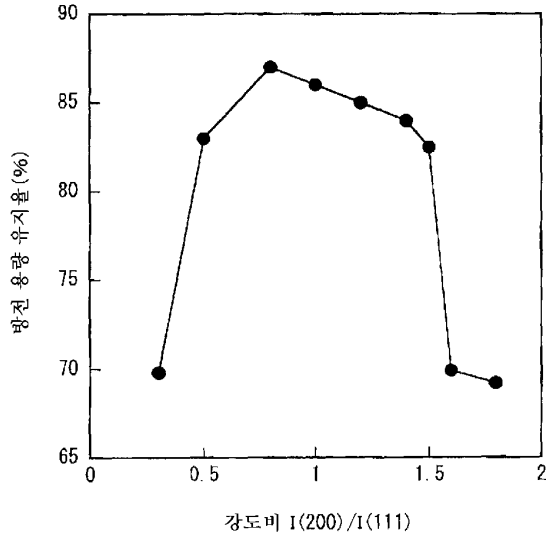
도면11


(A)
강도
1.2
1
0.8
0.6
0.4
0.2
0
P1
P2
P3
P4
P5
40
0
60
70
80
90
100
2θ(°)
(B)
강도
1.2
1
0.8
0.6
0.4
0.2
0
P1
P2
P3
P4
P5
40
0
60
70
80
90
100
2θ(°)

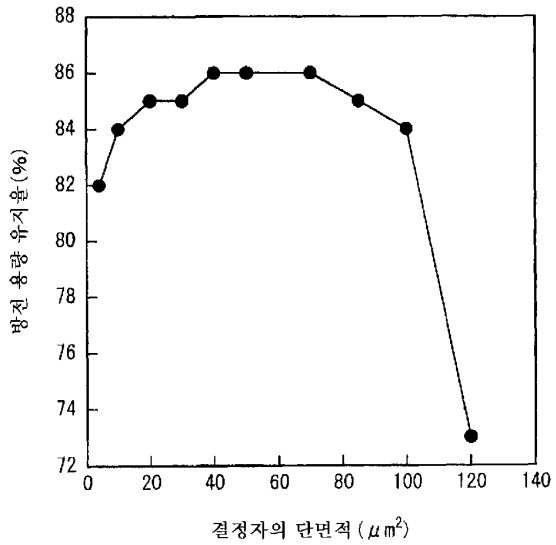
도면12


90
85
80
75
70
65
0
0.5
1
1.5
2
방전 용량 유지율(%)
강도비 I(200)/I(111)

도면13


90
85
80
75
70
65
0
0.5
1
1.5
2
방전 용량 유지율(%)
강도비 I(200)/I(111)

도면14

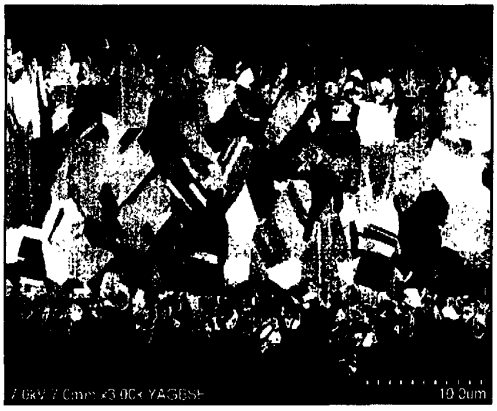

88
86
84
82
80
78
76
74
72
0
20
40
60
80
100
120
140
방전 용량 유지율(%)
결정자의 단면적 (μm^2)

도면16

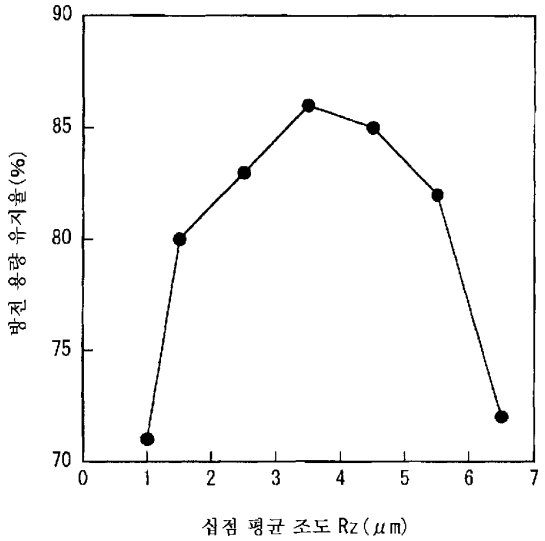
(A)



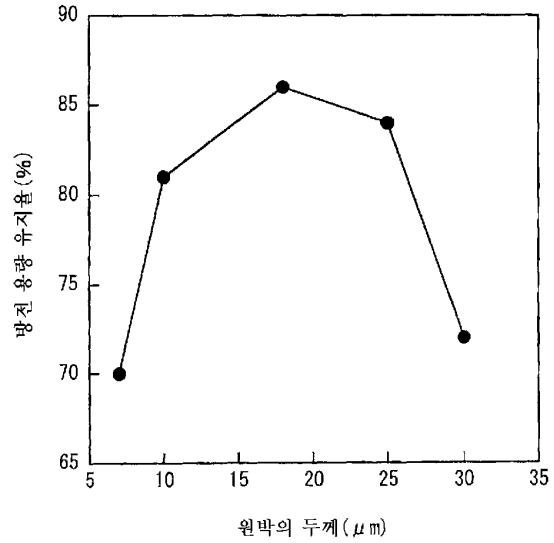
(B)



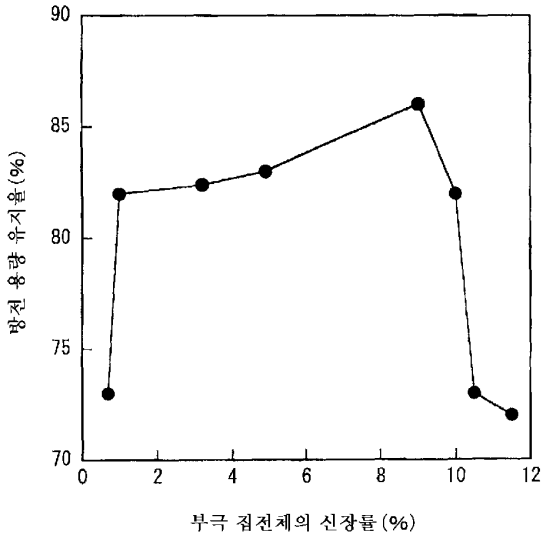
도면16


90
85
80
75
70
0
1
2
3
4
5
6
7
방전 용량 유지율(%)
십점 평균 조도 Rz(㎛)

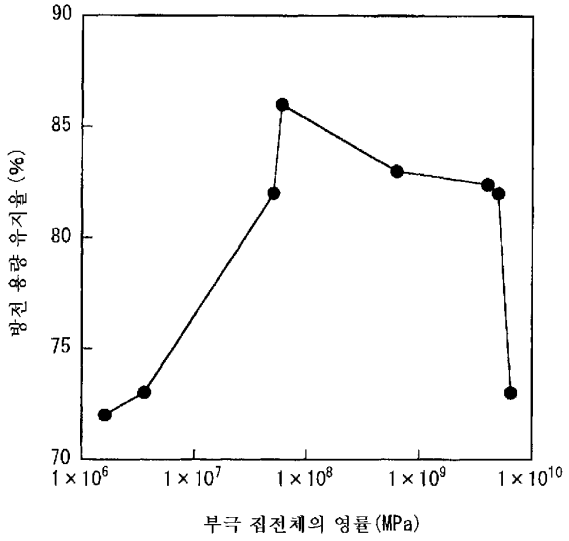
도면17


90
85
80
75
70
65
5
10
15
20
25
30
35
방전 용량 유지율(%)
원박의 두께(㎛)

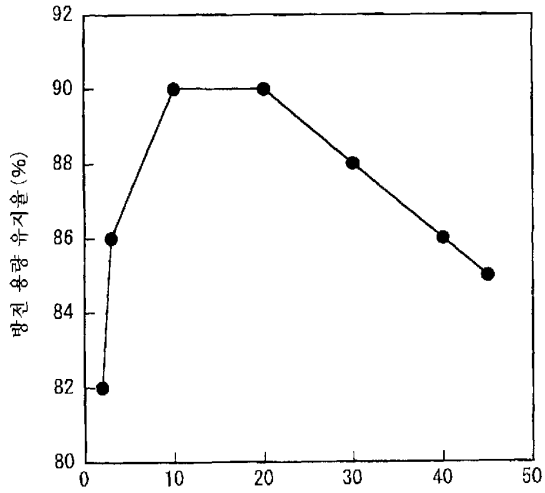
도면18


90
85
80
75
70
0
2
4
6
8
10
12
방전 용량 유지율(%)
부극 집전체의 신장률(%)

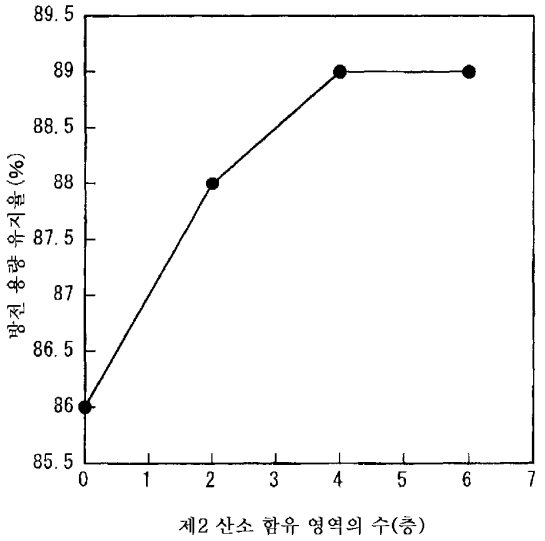
도면19


90
85
80
75
70
1×10⁶
1×10⁷
1×10⁸
1×10⁹
1×10¹⁰
방전 용량 유지율 (%)
부극 집전체의 영률(MPa)

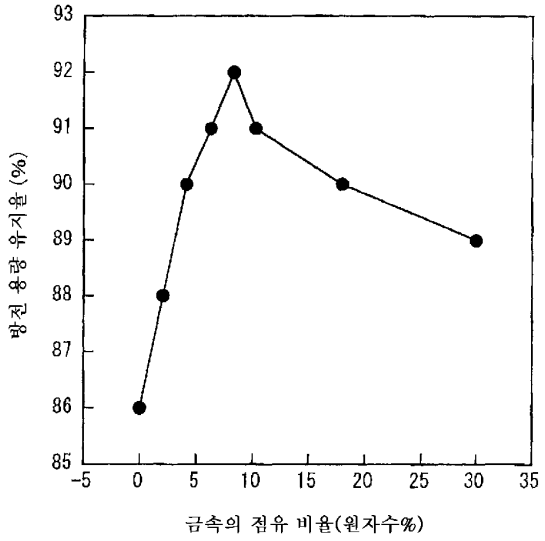
도면20


92
90
88
86
84
82
80
0
10
20
30
40
50
방전 용량 유지율(%)
산소 함유량(원자수%)

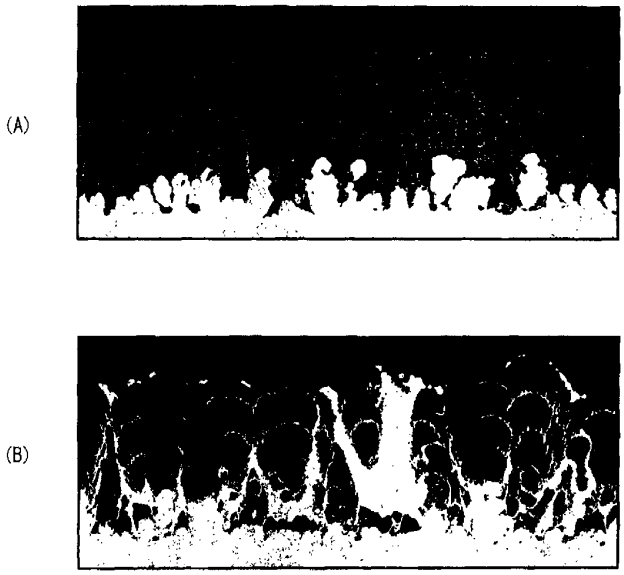
도면21


89.5
89
88.5
88
87.5
87
86.5
86
85.5
0
1
2
3
4
5
6
7
방전 용량 유지율(%)
제2 산소 함유 영역의 수(층)

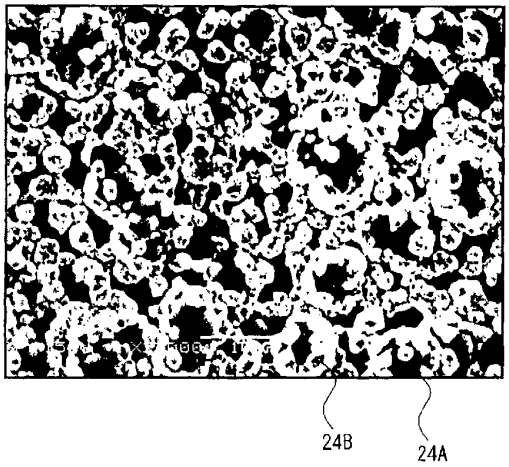
도면22


93
92
91
90
89
88
87
86
85
방전 용량 유지율(%)
-5
0
5
10
15
20
25
30
35
금속의 점유 비율(원자수%)

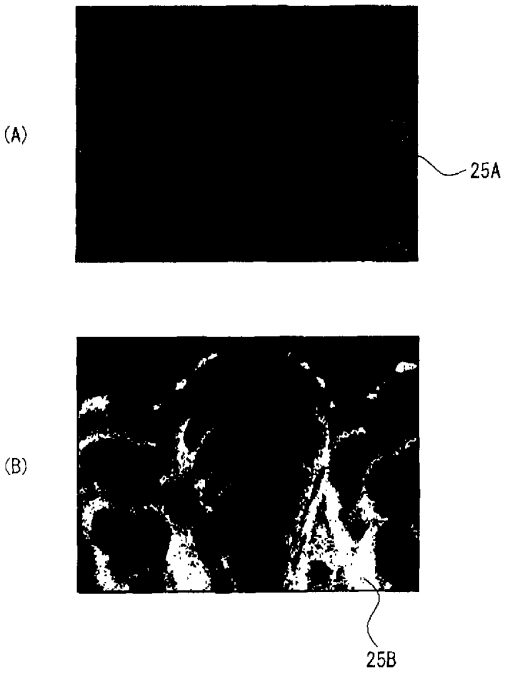
도면23


(A)
(B)

도면24



도면25



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(54) ELECTROLYTE SOLUTION FOR MANUFACTURING ELECTROLYTIC COPPER FOIL AND ELECTROLYTIC COPPER FOIL MANUFACTURING METHOD USING THE SAME

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(52) **U.S. Cl.** **205/76**; 205/291

(57) **ABSTRACT**

The present invention generally relates to an electrolyte solution used to manufacture an electrolytic copper foil for a secondary battery electrode collector and a printed circuit, and based on a 1-liter electrolyte solution, the present invention contains: 0.5 to 40 mg of at least one sulfur compound selected from a disulfur compound, dialky-lamino- T-oxomethyl- thioalkan sulfonic acid, and thioalkan sulfonic acid salt; 1 to 1000 mg of at least more than one kind of an organic compound selected from a group consisting of a poly aklylene glycol-type surfactant and low molecular gelatin; and 0.1 to 80 mg of chlorine ion.

The electrolytic copper foil in accordance with the present invention has a roughness Rz is less than 2.0 μm, if the electrolytic copper foil is in a thin film state, and has the roughness Rz value of the rough surface within a range of 1.0~3.5 μm if the surface of the electrolytic copper foil is treated. Since a roughness value of a polished surface is changed according to polishing of a cathode surface, there is no special restriction.

ELECTROLYTE SOLUTION FOR MANUFACTURING ELECTROLYTIC COPPER FOIL AND ELECTROLYTIC COPPER FOIL MANUFACTURING METHOD USING THE SAME

BACKGROUND OF THE INVENTION

[0001] This application claims the priority of Korean Patent Application No. 2002-70802 filed on 14 Nov. 2002 in the Korean Intellectual Property Office, the disclosure of which is incorporated herein in its entirety by reference.

FIELD OF THE INVENTION

[0002] The present invention generally relates to an electrolyte solution used to manufacture an electrolytic copper foil for a printed circuit and an electrolytic copper foil for an electrode collector of a secondary battery, the electrolytic copper foil using the same, and an electrolytic copper foil manufacturing method thereof.

SUMMARY OF THE INVENTION

[0003] A printed circuit board using the electrolytic copper foil is widely used as a precise control circuit of various electric, electronic communication apparatuses such as radios, TVs, computers, telephone exchanges, wireless transceivers, etc. Recently, as a degree of integration of the printed circuit board increases, circuits of the board get minute and multilayered. Particularly, the electrolytic copper foil is highly demanded in terms of COF (Chip On Flex) and TAB (Tape Automatic Bonding) aspects, and is broadly used as an electrode collector of a secondary battery by improving its physical properties.

[0004] Generally, the electrolytic copper foil is created by electrolytic methods, and is manufactured from a cylinder-shaped cathode (also, called a drum) consisting of titanium, an anode consisting of a lead alloy keeping certain intervals or titanium covered by an iridium oxide, and an electrolytic cell including an electrolyte solution and current power. The electrolyte solution is composed of sulfuric acid and/or a copper sulfate. When DC flows between the cathode and the anode as rotating the cylinder-shaped cathode, copper is electrodeposited on the cathode, thereby consecutively producing the electrolytic copper foil. Thus, a process of restoring a copper ion to metal with the electrolytic methods is called a thin film process.

[0005] Next, when necessary, to improve an adhesive force with an insulating substrate, the copper foil obtained from the thin film process can pass through additional surface treatment processes including a roughness treatment process (also, called a nodule treatment process), a nonproliferation process to prevent the copper ion from being proliferated, an anticorrosive process to prevent oxidation from outside, a chemical adhesive force improving process to complement an adhesive force with the insulating substrate, and so on. If passing through the surface treatment process, the copper foil is made for a low profile printed circuit. And, if only an anticorrosive process of the surface treatment process is performed, the copper foil is made for the secondary battery.

[0006] In case the electrodeposited copper foil is used for the printed circuit, the copper foil is supplied to a PCB (Printed Circuit Board) process manufacturer while being adhered (laminated) to the insulating substrate after the surface treatment process. However, if used for the secondary battery, the copper foil is supplied to a secondary battery manufacturer via the anticorrosive process only.

[0007] For the copper foil appropriate for a minute and highly integrated PCB circuit, the surface of the copper foil contacted with the insulating substrate should have a small roughness. In addition, while coupling the electrolytic copper foil with the insulating substrate, if the copper foil gets stress by thermal expansion or heat-shrink and moreover, the copper foil is laminated in multilayer way, it may have scratches due to friction with a neighboring copper foil. More seriously, the copper foil can be exfoliated from the insulating substrate or have circuit damage, or a PCB may get bent or distorted. To protect the copper foil from these problems, it is necessary to have a proper elongation without suddenly deteriorating mechanical intensity at high temperature. When the electrolytic copper foil is used as the collector for the secondary battery, electrode materials should cover both sides of the copper foil. In this case, if both sides of the electrolytic copper foil have a different roughness, battery characteristics differ from each side. Therefore, it is required to have the same or a similar roughness on both sides of the electrolytic copper foil. Furthermore, to reduce weight and a manufacturing cost of the battery and increase energy density of the battery, the electrolytic copper foil should be manufactured in thin type. Even though the copper foil is thin, it is necessary to have sufficient mechanical intensity and an elongation at high temperature, without being bent in a future treatment process.

[0008] To satisfy the above requirements, the prior art has suggested a method of making an electrolytic copper foil by adding various organic additives to an electrolyte solution. As a representative example, the U.S. Pat. No. 5,431,803 has been suggested to lower a surface roughness, providing a method of manufacturing an electrolytic copper foil that maintains concentration of a chlorine ion less than 1 mg in a 1-liter electrolyte solution. However, the electrolytic copper foil manufactured by a technology suggested in the U.S. Pat. No. 5,431,803 has 61 kgf/mm^2 to 84 kgf/m ^{2} of mechanical intensity at room temperature as well as 17 kgf/mm^2 to 25 kgf/mm^2 at 180° C., and has about 6 μm of the maximum value of the surface roughness: Rmax for a surface treatment. Thus, it is not appropriate for the secondary battery. Also, it is difficult to carry out a consecutive operation as maintaining the concentration of the chlorine ion less than 1 mg in the electrolyte solution.

SUMMARY OF THE INVENTION

[0009] It is therefore an object of the present invention to provide an electrolyte solution for a printed circuit, an electrolytic copper foil produced using the same, and a manufacturing method thereof for controlling a roughness on both sides of the electrolytic copper foil in the same or similar way according to electrolyte solution additives and for preventing sudden intensity changes even at high temperature compared to room temperature by controlling the amount of the electrolyte solution additives.

[0010] It is another object of the present invention to provide an electrolyte solution used to manufacture an electrolytic copper foil, the electrolytic copper foil produced using the same, and an electrolytic copper foil manufactur-

ing method thereof for having a roughness Rz value of a rough surface is less than 2.0 pun in a thin film state and for preventing sudden intensity changes even at high temperature compared to room temperature.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0011] To accomplish the above objects, as an electrolyte solution for manufacturing an electrolytic copper foil, the present invention provides the electrolyte solution, the electrolytic copper foil produced by using the electrolyte solution, and an electrolytic copper foil manufacturing method thereof. In an electrolyte solution containing at least selected one of sulfuric acid and copper sulfate used to manufacture an electrolytic copper foil by electrolysis, the electrolyte solution for manufacturing the electrolytic copper foil, based on the 1-liter electrolyte solution, comprising: 0.5 to 40 mg of at least one sulfur compound selected from a disulfur compound, dialkylamino- T-oxomethyl- thioalkan sulfonic acid, and thioalkan sulfonic acid salt; 1 to 1000 mg of at least more than one kind of an organic compound selected from a group consisting of a poly aklylene glycol-type surfactant and low molecular gelatin; and 0.1 to 80 mg of chlorine ion added.

[0012] A solution comprising i) sulfuric acid and copper salt rather than copper sulfate, or ii) copper sulfate and acid rather than sulfuric acid may be also used as the electrolyte.

[0013] The organic compound comprising low molecular gelatin without polyalkylene gulycol type surfactant may be also used as the organic compound.

[0014] Generally, a process of manufacturing an electrolytic copper foil for a printed circuit is divided into a thin film process and a surface treatment process.

[0015] The thin film process is generally performed by using an electroforming cell. Within an electrolytic cell, a semi-cylinder type anode and a cylinder-type rotating cathode are located at certain intervals, and the electrolyte solution is consecutively supplied between the anode and the cathode. By flowing DC between the anode and the cathode, a copper ion of the electrolyte solution is restored to metal having predetermined thickness from the cathode. Next, a copper foil (undisposed) that does not pass through a future treatment process is exfoliated from the surface of the cathode. A lead alloy is widely used for the anode, but recently, intervals are changed by corrosion of a lead oxide. Therefore, titanium covering an iridium oxide is more used. The cathode is used by plating iron with chromium, however recently, stainless materials are covered with titanium to lengthen the span of life.

[0016] Next, to provide requested characteristics when necessary, an additional treatment process of passing the undisposed copper foil through a processor can be performed. This treatment process includes a roughness treatment process to improve an adhesive force when laminated on an insulating substrate, a nonproliferation process to prevent a copper ion from being proliferated, and an anticorrosive process to prevent oxidation during storage, transportation or a lamination forming process of the copper foil and the insulating substrate. Hereinafter, the above processes will be more fully described. The above processes are performed in the processor having the anode, and a surface treatment copper foil is finally obtained through these processes.

[0017] The electrolyte solution supplied between the anode and the cathode is a copper sulfate solution, and its blending based on 1 liter is as follows:

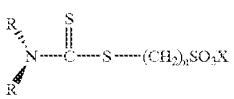
[0018] Copper concentration is between 50 g and 110 g, and desirably, between 60 g and 100 g. Sulfuric acid concentration is between 80 g and 200 g, and desirably, between 90 g and 120 g. Temperature of the electrolyte solution is between 40° C. and 80° C. Current density is between 400A/cm^2 and 10000A/dm^2, and desirably, between 50A/dm^2 and 85A/dm^2. If the copper concentration is less than 50 g, the surface of an electrodeposited copper foil is rough and powder is formed, lowering productivity. However, if more than 110 g, the electrolyte solution is crystallized, deteriorating working efficiency. If the sulfuric acid concentration is less than 80 g, an electrolytic voltage rises, resulting in an increase of production cost. Also, temperature of the electrolyte solution rises, causing deterioration of mechanical intensity of the copper foil. If the sulfuric acid concentration is more than 200 g, the electrolyte solution is highly apt to be corrosive even though the electrolytic voltage lowers, thereby quickly corroding an electrode electrolyzing the copper foil.

[0019] At this time, the electrolyte solution contains a sulfur compound having 0.5 to 40 mg of concentration and at least more than one kind of an organic compound selected from a group consisting of a poly alkylene glycol-type surfactant having 1 to 1000 mg of concentration and low molecular gelatin as additives. In addition, a chlorine ion having a range of 0.1 mg to 80 mg is added.

[0020] More desirably, to increase intensity of the electrolytic copper foil produced by the electrolyte solution, it is possible to use a nitrogen compound. For a thiourea derivative, which is the nitrogen compound, IM(2-imidazolidinimethionie) is used within a range of 0.1 mg to 8 mg. As for the poly alkylene glycol-type surfactant, it is available to use poly ethylene-type, poly propylene-type, and poly butylenes-type surfactants. Particularly, poly ethylene glycol can be representative of the poly ethylene-type surfactant.

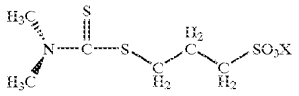
[0021] A disulfur compound and dialkylamino- T-oxomethyl- thioalkan sulfonic acid or thioalkan sulfonic acid salt are included in the sulfur compound. The disulfur compound includes SPS (Bis-(3-sulfopropyl)-disulfide, disodium salt)), and dialkylamino- T-oxomethyl- thioalkan sulfonic acid or salt thereof can contain dithiocarbamic acid or salt thereof, and DPS (N,N-Dimethyldithiocarbamic acid (3-sulfopropyl) ester, sodium salt) is representative. A formula of the dialkylamino- T-oxomethyl- thioalkan sulfonic acid or the salt thereof is shown in a chemical formula 1, and a formula of the DPS as a representative example is shown in a chemical formula 2, then a formula of the SPS is shown in a chemical formula 3.

Chemical formula 1

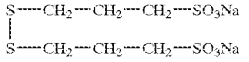


[0022] 'R' in the chemical formula 1 means an alkyl group (carbon atom 1–6), 'n' is 2–3 (ethane, propane), and 'X' means hydrogen atom or alkali metal atom.

Chemical formula 2



Chemical formula 3



[0023] Among the above additives, the roles of the sulfur compound and the surfactant are very important, since these compounds give direct influence on a surface roughness and tensile strength. Compared to a general electrolytic copper foil added with glue or gelatin, the sulfur compound generally has a small size of grains and functions as a grain refiner or a brightener. The added surfactant functions as a carrier or an electrodeposition leveler lowering a surface roughness of a mat surface of the electrolytic copper foil, influencing electroposition. In this case, the surfactant is absorbed into a protruded part of an electrode surface as carrying the sulfur compound, which is a brightener, to a cathode surface, and suppresses growth of the protruded part, thereby interrupting the growth firstly. And the sulfur compound, which is the grain refiner, firstly functions in a minute valley part of an electroposition surface, and enables a copper ion to be restored and grow up in this part first of all, thereby controlling a roughness of the electrodeposition surface.

[0024] The thiourea derivative, the nitrogen compound used in the present invention suppresses crystal growth of copper at room temperature or high temperature by eutectoid-processing nitrogen on an electrodeposition layer, and also restrains strength deterioration. Thus, when the nitrogen compound, the thiourea derivative is added, it is possible to prevent the strength deterioration, which occurs otherwise. So, a defective proportion caused when dealing with the electrolytic copper foil or manufacturing the printed circuit can be reduced. Moreover, the strength can be changed by controlling an amount of the additives, thereby adjusting physical properties of the electrolytic copper foil.

[0025] For the electrolytic copper foil in accordance with the present invention, if it is undisposed, it seems that a roughness of a rough surface (mat surface) has an Rz value having a range of 2.0 μm. RZ has been measured by an IPC TM 650 2.2.17A method. For other copper foil passing through surface treatment, it seems that the roughness of the rough surface (mat surface) has an Rz value having a range of 1.0~3.5 μm. Since a roughness value of a drum surface (bright surface) of the copper foil contacted with the drum surface is produced according to polishing of the drum surface, there is no particular restriction.

[0026] In order to improve an adhesive force with an insulating substrate, if necessary, the above undisposed copper foil can pass through additional surface treatment processes including a roughness treatment process (also, called a nodule treatment process), a nonproliferation process to prevent a copper ion from being proliferated, and an anticorrosive process to prevent oxidation from outside. If passing through the surface treatment process, the copper foil is made for a low profile printed circuit, however, if passing through the anticorrosive process only, the copper foil is for a secondary battery.

[0027] The roughness treatment process consists of two steps or three steps. In a first step, a core of minute powder is made, and the powder is coupled with the copper foil in a second step because the powder does not have an adhesive force with the copper foil. In a third step, a minute protrusion is given to the coupled powder again. The first step is as follows. Based on a 1-liter electrolyte solution, copper concentration is between 10 g and 40 g, and desirably, between 15 g and 25 g. Sulfuric acid concentration is between 40 g and 150 g, and desirably between 60 g and 100 g, and temperature of the electrolyte solution is between 20° C. and 40° C.

[0028] Current density is between 20 A/dm^2 and 100 A/dm^2, and desirably, between 40 A/dm^2 and 80 A/dm^2. The second step is as follows. Copper concentration is between 50 g and 110 g, and desirably, between 55 g and 100 g. Sulfuric acid concentration is between 80 g and 200 g, and desirably, between 90 g and 120 g. Temperature of the electrolyte solution is between 40° C. and 80° C. Current density is between 20 A/dm^2 and 100 A/dm^2, and desirably, between 40 A/dm^2 and 80 A/dm^2. The nonproliferation process is as follows. To prevent the copper ion from being proliferated, a barrier layer is formed with various single metal such as zinc, nickel, iron, cobalt, molybdenum, tungsten, tin, indium, and chrome, or with 2 or 3 kinds of alloys.

[0029] Then, to prevent oxidation during storage, transportation, or a lamination forming process of the copper foil and the insulating substrate, the anticorrosive process is carried out. The anticorrosive process performs chromate passivation with chromic acid, sodium dichromate, potassium dichromate, chromic anhydride, etc. Next, a process for increasing chemical cohesion is executed.

[0030] Also, a chemical adhesive force improving process can be carried out to complement an adhesive force with the insulating substrate. For this, there are usable adhesion accelerators such as a silane coupling agent ($RSiX_3$), silicon peroxygen ($R_{4-n}Si(OOR')_n$), a chromium-based adhesion accelerator ($(RCO_2H_3OHCrOHCrHOH_2)_2OH$), an organic titanium based adhesion accelerator ($(C_4H_9CHC_2H_5CH_2O)_4Ti$), an organic phosphate based adhesion accelerator ($RO_2P(OH)_2$), and others.

[0031] Embodiments

[0032] Hereinafter, the present invention will be described in reference to the embodiments and compared examples. Here, a symbol 'g/L' means a content of a corresponding material based on a 1-liter electrolyte solution.

[0033] For a thin film process, the electrolyte solution having blending like described in Table 1 is prepared. Copper concentration of the electrolyte solution is 80 g/L, sulfuric acid concentration is 90 g/L, and temperature of the electrolyte solution is 45° C. Additives like described in Table 1 have been added. Current density was electrodeposited in 60 A/dm^2, and chlorine ion was maintained in 25 mg/L.

[0034] For embodiment 1, 6 mg/L of DPS(N,N-Dimethyldithiocarbamic acid (3-sulfopropyl) ester, sodium salt) was used as a sulfur compound, and 1 mg/L of PEG (Poly Ethylene Glycol) was used as a poly alkylene glycol-type surfactant.

[0035] For embodiment 2, 1 mg/L of SPS (Bis-(3-sulfopropyl)-disulfide, disodium salt) was used as a sulfur compound, and 30 mg/L of PEG (Poly Ethylene Glycol) was used as a poly alkylene glycol-type surfactant.

[0036] For embodiment 3, 30 mg/L of DPS(N,N-Dimethyldithiocarbamic acid (3-sulfopropyl) ester, sodium salt) was used as a sulfur compound, and 30 mg/L of PEG (Poly Ethylene Glycol) was used as a poly alkylene glycol-type surfactant.

[0037] For embodiment 4, 5 mg/L of SPS (Bis-(3-sulfopropyl)-disulfide, disodium salt) was used as a sulfur compound, and 1 mg/L of PEG (Poly Ethylene Glycol) was used as a poly alkylene glycol-type surfactant.

[0038] For embodiment 5, 3 mg/L of DPS(N,N-Dimethyldithiocarbamic acid (3-sulfopropyl) ester, sodium salt) was used as a sulfur compound, and 800 mg/L of PPG (Poly Propylene Glycol) and 5 mg/L of low molecular gelatin less than molecular weight 6000 were added as a poly ethylene glycol surfactant.

[0039] For embodiment 6, 5 mg/L of SPS (Bis-(3-sulfopropyl)-disulfide, disodium salt) was used as a sulfur compound, 0.5 mg/L of IM (2-imiidazolidinetihione), which was a thiourea derivative, was as a nitrogen compound, and 25 mg/L of PEG (Poly Ethylene Glycol) was used as a poly ethylene glycol-type surfactant.

[0040] For embodiment 7, 3 mg/L of SPS (Bis-(3-sulfopropyl)-disulfide, disodium salt) and 5 mg/L of DPS(N,N-Dimethyldithiocarbamic acid (3-sulfopropyl) ester, sodium salt) were as a sulfur compound, and 30 mg/L of PEG (Poly ethylene glycol) and 30 mg/L of PPG (Poly Propylene Glycol) were used as a poly ethylene glycol-type surfactant.

[0041] By using the electrolyte solution prepared like above, a titanium anode covering an iridium oxide, and a rotating cylinder-type titanium cathode, the undisposed copper foil corresponding to the embodiments 1 to 7 was obtained, respectively, under an electrolytic condition like described in Table 1.

[0042] In case of the sulfur compound, an Rz value tended to exceed 2.0 μm by an increase of a surface roughness of a rough surface in a range of exceeding 40 mg/L. When used less than 0.5 mg/L, the surface roughness did not lower, rather the roughness increased as lowering an elongation. As for the poly ethylene glycol-type surfactant, it was possible to confirm a function of lowering the surface roughness of the rough surface within a range of 1 mg/L to 1000 mg/L. More desirably, a desirable surface roughness could be obtained within a range of 1 mg/L to 300 mg/L. However, in this case, it was required to control using current density in higher or lower way according to its amount. For the sulfur compound and the poly ethylene glycol-type surfactant, if concentration was higher than an upper limit above, the surface got rough and burning phenomenon (electrodeposited into powder) occurred. Thus, they might not be usable for manufacturing a satisfactory electrolytic copper foil.

[0043] So as to control hardness of the manufactured electrolytic copper foil, it was proper to have a range of 0.1 mg/L to 8 mg/L for the nitrogen compound additionally included to form the electrolyte solution. If an amount of an additive was too little, the hardness got slightly improved, and if too much, the hardness got higher but a surface roughness rose, thereby lowering an elongation.

[0044] For each of the undisposed copper foil, a surface roughness Rz was measured according to an IPC TM 650 2.2.17A method, and an elongation and tensile strength of the copper foil have been measured at room temperature (25° C.) and 180° C. according to an IPC TM 650 standard processing method. The results are shown in Table 2.

[0045] Next, a surface treatment process was carried out for the undisposed copper foil in accordance with the embodiments 1 to 7. First, for a nonproliferation process, 110 g/L of sodium cyanide, 60 g/L of sodium hydroxide, 90 g/L of copper cyanide, and 5.3 g/L of zinc cyanide have been electrodeposited with pH 11.0 to 11.5 at 50° C., having 5 A/dm^2 of current density for 10 seconds. For an anticorrosive process, 10 g/L of sodium dichromate has been measured with pH 4.5, having 0.5 A/dm^2 of current density for 2 seconds.

COMPARED EXAMPLES

[0046] The composition of the electrolyte solution and the chlorine ion concentration are the same as the above embodiments. For a compared example 1, 2 mg/L of low molecular gelatin less than 6000 molecular weight has been added as an additive. For a compared example 2, 1 mg/L of TU (thiourea) has been added with 2 mg/L of low molecular gelatin less than 6000 molecular weight. For a compared example 3, 50 mg/L and 30 mg/L of SPS and PEG, respectively, have been added. And for a compared example 4, 3 mg/L and 1500 mg/L of DPS and PPG, respectively, have been added.

[0047] Under the electrolytic condition described in Table 1, the undisposed copper foils corresponding to the compared examples 1 to 4 have been obtained, as well as a surface roughness Rz for the undisposed copper foils, and an elongation and tensile strength were measured at room temperature (25° C.) and 180° C. by an IPC IM 650 2.4.18A method. The results are shown in Table 2. Next, a surface treatment process has been carried out for the undisposed copper foils in accordance with the compared examples 1 to 4.

[0048] Table 2 shows the results of comparing physical properties of the copper foil tentatively manufactured through the embodiments and the compared examples under the condition suggested in Table 1.

[0049] Like displayed in Table 2, according to the embodiments in accordance with the present invention, a roughness (Rz) of a rough surface is controlled less than 2.0 by the sulfur compound. Thus, it is possible to maintain similarly to a roughness (Rz) of a drum surface and change strength by controlling an amount of the thiourea derivative, the nitrogen compound, thereby enabling the electrolytic copper foil to be manufactured for various purposes.

TABLE 1

	Additives								Solution Composition	
	SPS (mg/L)	DPS (mg/L)	IM (mg/L)	PEG (mg/L)	PPG (mg/L)	Low Molecular Gelatin (mg/L)	TU (mg/L)	Cl- (mg/L)	Copper (g/L: Ion)	Sulfur Acid (g/L)
Embodiment 1	----	6	----	1	----	----	----			
Embodiment 2	1	----	----	30	----	----	----			
Embodiment 3	----	30	----	30	----	----	----			
Embodiment 4	5	----	----	1	----	----	----			
Embodiment 5	----	3	----	----	800	5	----			
Embodiment 6	5	----	0.5	25	----	----	----			
Embodiment 7	3	5	----	30	30	----	----			
Compared Example 1	—	—	—	—	—	2	—	25	80	90
Compared Example 2	—	—	—	—	—	2	1			
Compared Example 3	50	—	—	30	—	—	—			
Compared Example 4	—	3	—	—	3500	—	—			

[0050] Current density: 60 A/dm^2, Solution temperature: 45° C.

[0051] DPS: N-Dimethyldithiocarbamic acid (3-sulfopropyl) ester, sodium salt

[0052] SPS: Bis-(3-sulfopropyl)-disulfide, disodium salt

[0053] IM: 2-imidazolidinethione

[0054] PEG: Poly Ethylene Glycol

[0055] PPG: Poly Propylene Glycol

[0056] Low molecular gelatin: gelatin less than 6000 molecular weight

[0057] TU: thiourea

TABLE 2

	Surface Roughness of Rough Surface (Rz;μm)	Surface Roughness of Drum Surface (Rz;μm)	Tensile Strength (Room Temperature) (kgf/mm^2)	Elongation (Room Temperature) (%)	Tensile Strength (180° C.) (kg/mm^2)	Elongation (180° C.) (%)
Embodiment 1	1.52	1.68	33.2	8.9	22.5	7.6
Embodiment 2	1.83	1.76	29.5	9.6	20.9	8.0
Embodiment 3	1.42	1.84	33.4	12.9	22.2	14.4
Embodiment 4	1.88	1.91	30.4	12.9	20.6	10.6
Embodiment 5	1.81	1.79	31.4	4.1	18.4	3.1
Embodiment 6	0.50	1.75	33.2	11.4	23.6	6.0
Embodiment 7	1.14	1.55	32.0	8.8	20.6	4.2
Compared Example 1	3.53	1.81	37.1	5.6	22.8	2.2
Compared Example 2	1.9	1.85	49.0	1.5	22.0	1.9
Compared Example 3	2.23	1.88	34.2	1.9	22.2	3.5
Compared Example 4	2.38	1.79	13.9	0.23	16.9	1.2

[0058] Like shown in the embodiments 1 to 7 suggested in Table 2, the electrolytic copper foil manufactured in the embodiments in accordance with the present invention has a surface roughness Rz value of a rough surface within a range of 2.0 μm in a thin film state. It is also confirmed that tensile strength at room temperature is not rapidly changed even at high temperature (180° C.) as well.

RESULTS OF THE INVENTION

[0059] An electrolytic copper foil in accordance with the present invention has a roughness Rz value of a rough surface (mat surface) with a range of less than 2.0 μm, if undisposed. However, if the copper foil passes through a surface treatment process, it has a roughness Rz value of a rough surface (mat surface) within a range of 1.0-3.5 μm. Therefore, the electrolytic copper foil in accordance with the present invention has a relatively lower roughness on the rough surface, and both sides of the electrolytic copper foil have a similar roughness.

[0060] An electrolytic copper foil manufactured in prior art has a problem of rapidly causing strength deterioration at high temperature (180° C.), though good strength is maintained at room temperature. However, the electrolytic copper foil in accordance with the present invention does not show any sudden strength change even at high temperature. Accordingly, the electrolytic copper foil in accordance with the present invention is appropriate for a minute and highly integrated PCB circuit.

[0061] Furthermore, when used as a collector for a secondary battery, a more reliable battery characteristic can be obtained, since a roughness on both sides of the electrolytic copper foil is similar. The electrolytic copper foil in accordance with the present invention prevents tensile strength from suddenly deteriorating owing to a temperature rise, having excellent elongation characteristics at room temperature and high temperature. Thus, it would not get bent or distorted in a future treatment process nor generate a short circuit. The electrolytic copper foil in accordance with the present invention is proper to be used as the collector for the secondary battery or a printed circuit board.

[0062] It is to be understood that changes and modifications to the embodiments described above will be apparent to those skilled in the art, and are contemplated. It is therefore intended that the foregoing detailed description be regarded as illustrative rather than limiting, and that it be understood that it is the following claims, including all equivalents, that are intended to define the spirit and scope of this invention.

What is claimed is:

1. In an electrolyte solution containing at least selected one of sulfuric acid and copper sulfate used to manufacture an electrolytic copper foil by electrolysis, the electrolyte solution for manufacturing the electrolytic copper foil, based on the 1-liter electrolyte solution, comprising:

0.5 to 40 mg of at least one sulfur compound selected from a disulfur compound, dialkylamino- T-oxomethyl- thioalkan sulfonic acid, and thioalkan sulfonic acid salt;

1 to 1000 mg of at least more than one kind of an organic compound selected from a group consisting of a poly aklylene glycol-type surfactant and low molecular gelatin; and

0.1 to 80 mg of chlorine ion added.

2. The electrolyte solution of claim 1, wherein the dialkylamino- T- oxomethlyl- thioalkan sulfonic acid or the salt thereof is dithiocarbamic acid compound or salt thereof.

3. The electrolyte solution of claim 1, wherein additives of the electrolyte solution further include 0.1 to 8 mg/L of thiourea derivative, a nitrogen compound.

4. The electrolyte solution of claim 1, wherein the disulfur compound is SPS (Bis-(3-sulfopropyl)-disulfide, disodium salt)).

5. The electrolyte solution of claim 1, wherein the organic compound is a poly aklylene glycol-type surfactant.

6. A method of manufacturing an electrolytic copper foil, said method comprising steps of:

A) preparing an electrolyte solution added with 0.5 to 40 mg of at least one sulfur compound selected from a disulfur compound, dialkylamino- T-oxomethyl- thioalkan sulfonic acid, and thioalkan sulfonic acid salt, 1 to 1000 mg of at least more than one kind of an organic compound selected from a group consisting of a poly aklylene glycol-type surfactant and low molecular gelatin, and 0.1 to 80 mg of chlorine ion, based on the 1-liter electrolyte solution;

B) generating the electrolytic copper foil on a cathode by flowing electricity after impregnating an anode and the cathode with the electrolyte solution.

7. The method of claim 6, wherein the dialkylamino-T-oxomethyl-thioalkan sulfonic acid is dithiocarbamic acid compound, and the thioalkan sulfonic acid salt is dithiocarbamic salt.

8. The method of claim 6, wherein 0.1 to 8 mg/L of thiourea derivative, a nitrogen compound is further included in the electrolyte solution.

9. The method of claim 6, wherein the disulfur compound is SPS (Bis-(3-sulfopropyl)-disulfide, disodium salt).

* * * * *

US005326455A

United States Patent [19]

Kubo et al.

[11] Patent Number: 5,326,455

[45] Date of Patent: Jul. 5, 1994

[54] **METHOD OF PRODUCING ELECTROLYTIC COPPER FOIL AND APPARATUS FOR PRODUCING SAME**

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[73] Assignee: **Nikko Gould Foil Co., Ltd.**, Tokyo, Japan

[21] Appl. No.: **965,115**

[22] Filed: **Oct. 22, 1992**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 794,272, Nov. 19, 1991, abandoned.

[30] **Foreign Application Priority Data**

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Dec. 19, 1990 [JP] Japan 2-411765
Dec. 19, 1990 [JP] Japan 2-411766

[51] **Int. Cl.**[5] **C25D 1/04**

[52] **U.S. Cl.** **205/77**; 204/211; 205/84; 205/96

[58] **Field of Search** 205/96, 97, 77, 84; 204/211

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Primary Examiner—John Niebling
Assistant Examiner—William T. Leader
Attorney, Agent, or Firm—Seidel, Gonda, Lavorgna & Monaco

[57] **ABSTRACT**

In a method of producing an electrolytic copper foil by passing an electrolyte between a rotating cathode drum and anode located opposite to the cathode drum, the thickness of the resulting copper foil is made uniform throughout. The anode has a structure including a main portion and an end portion, the end portion being divided widthwise into n foil thickness-uniformizing sub-anodes. Electricity is supplied to the main anode and the sub-anodes at a preset current density D (A/dm^2) to attain a target foil thickness T (g/m^2). Variations of thickness in the direction of the width of the resulting copper foil are measured as the thicknesses Tm (g/m^2) where m=1−n in the direction of the width of the copper foil corresponding to the n sub-anodes, and the quantities of electricity being supplied to the n sub-anodes are individually controlled at current densities Dm (A/dm^2) where m=1−n so that Tm values are made equal to the target foil thickness T (g/m^2). Alternatively, a pattern of thickness deviations of a copper foil produced per revolution of the cathode drum is divided into m sections where m=1−n widthwise and k sections lengthwise, the foil thicknesses Tm−k (g/m^2) where m=1−n of the m ×k sections corresponding to the angle of rotation from a reference point of the cathode drum as determined by an encoder are measured, and the quantities of electricity supplied to the n sub-anodes at current densities Dm−k (A/dm^2) where m=1−n are controlled individually correspondingly to the angle of rotation from the reference point of the cathode drum so that Tm−k becomes equal to the target foil thickness T.

25 Claims, 5 Drawing Sheets

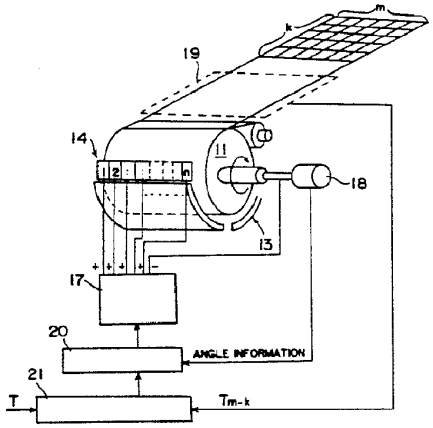
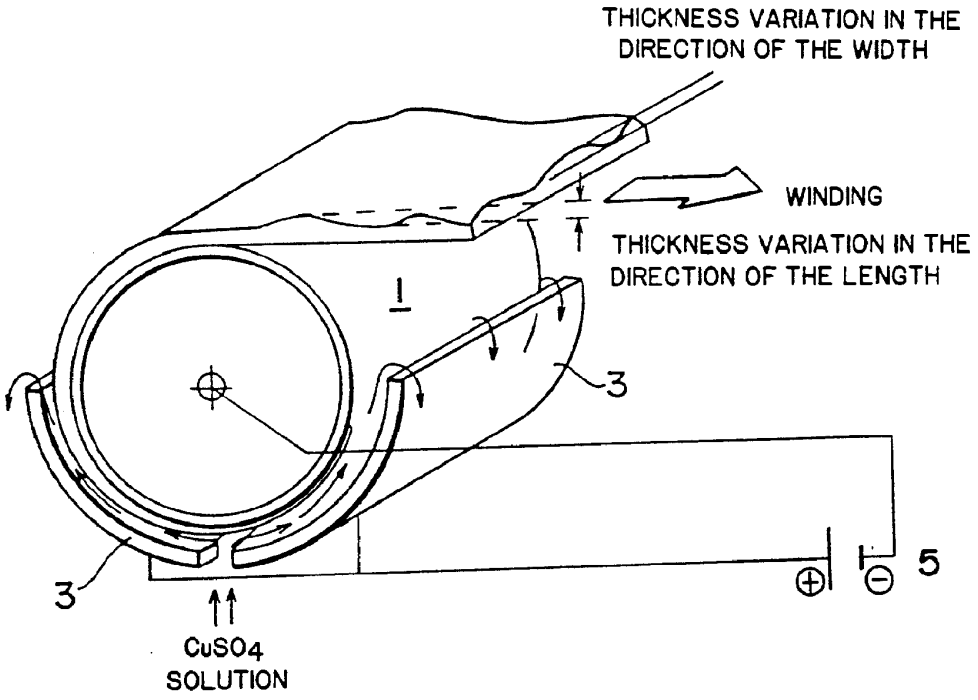


FIG. 1
(PRIOR ART)



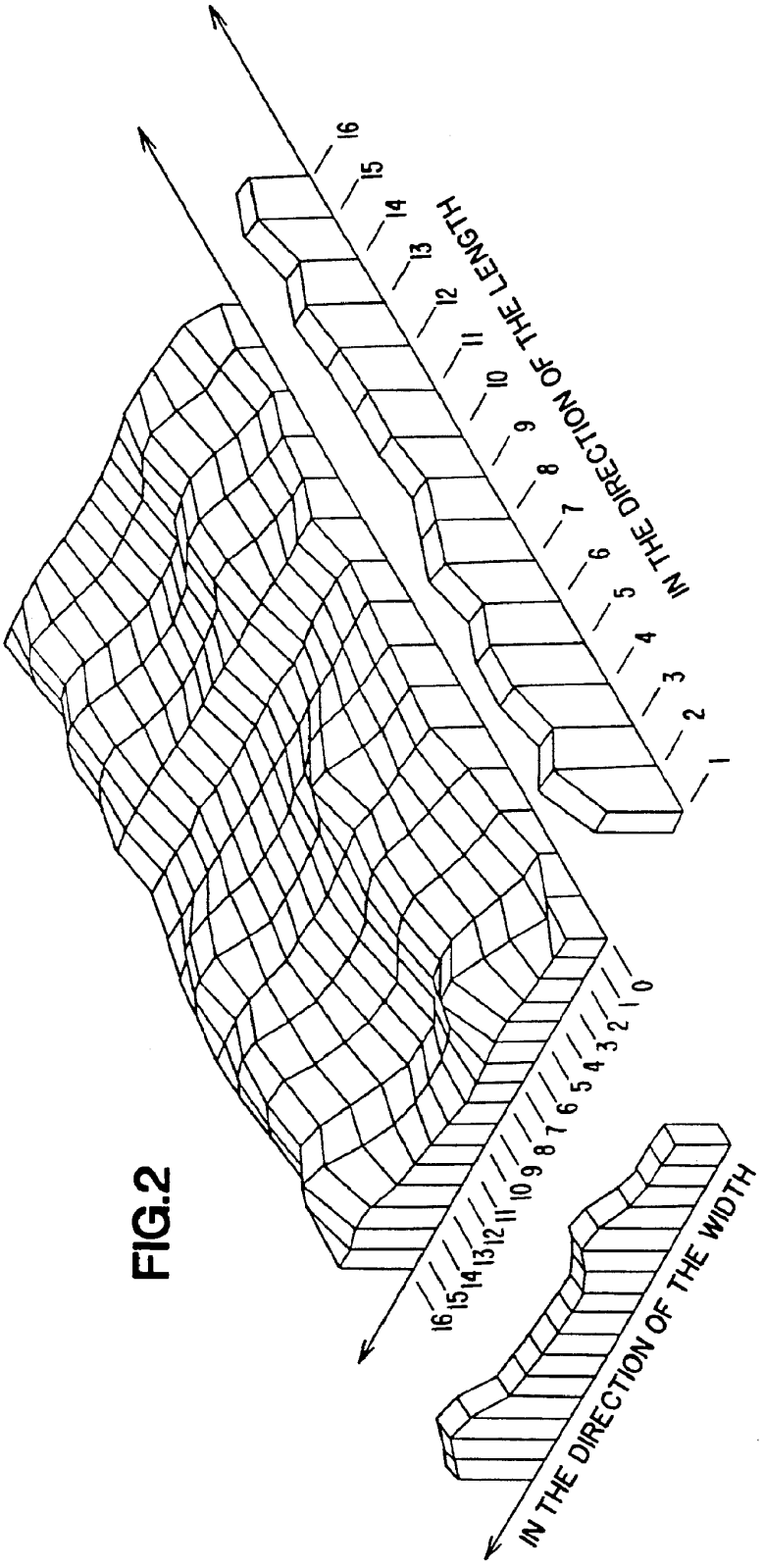

IN THE DIRECTION OF THE LENGTH
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
IN THE DIRECTION OF THE WIDTH

FIG.2

FIG.3

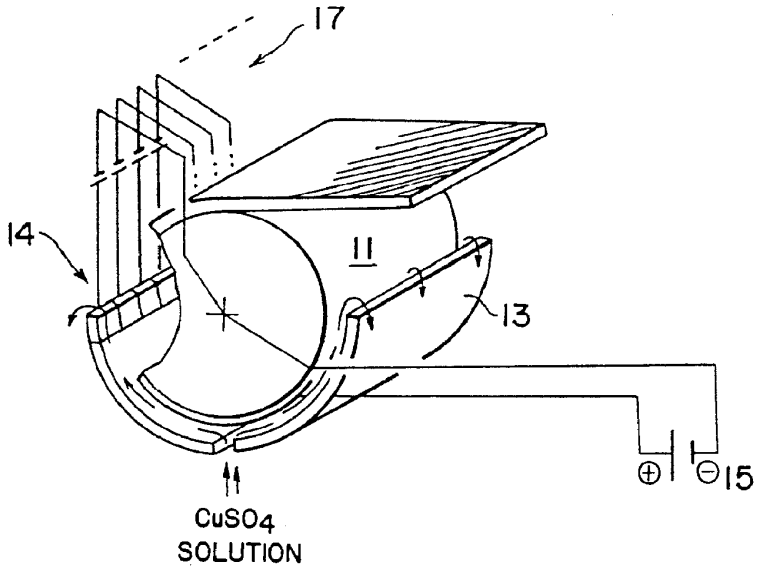


FIG.4

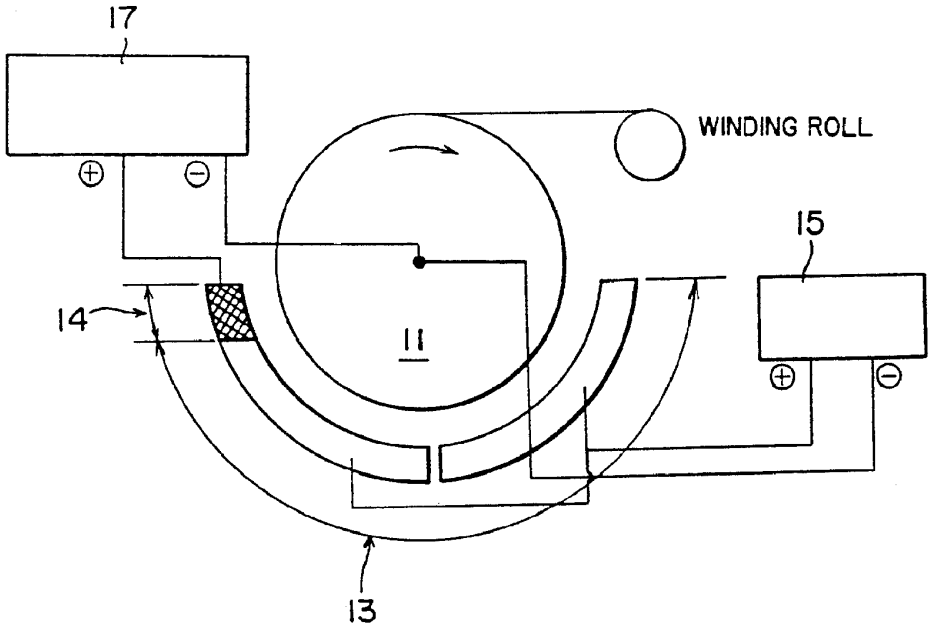


FIG.5

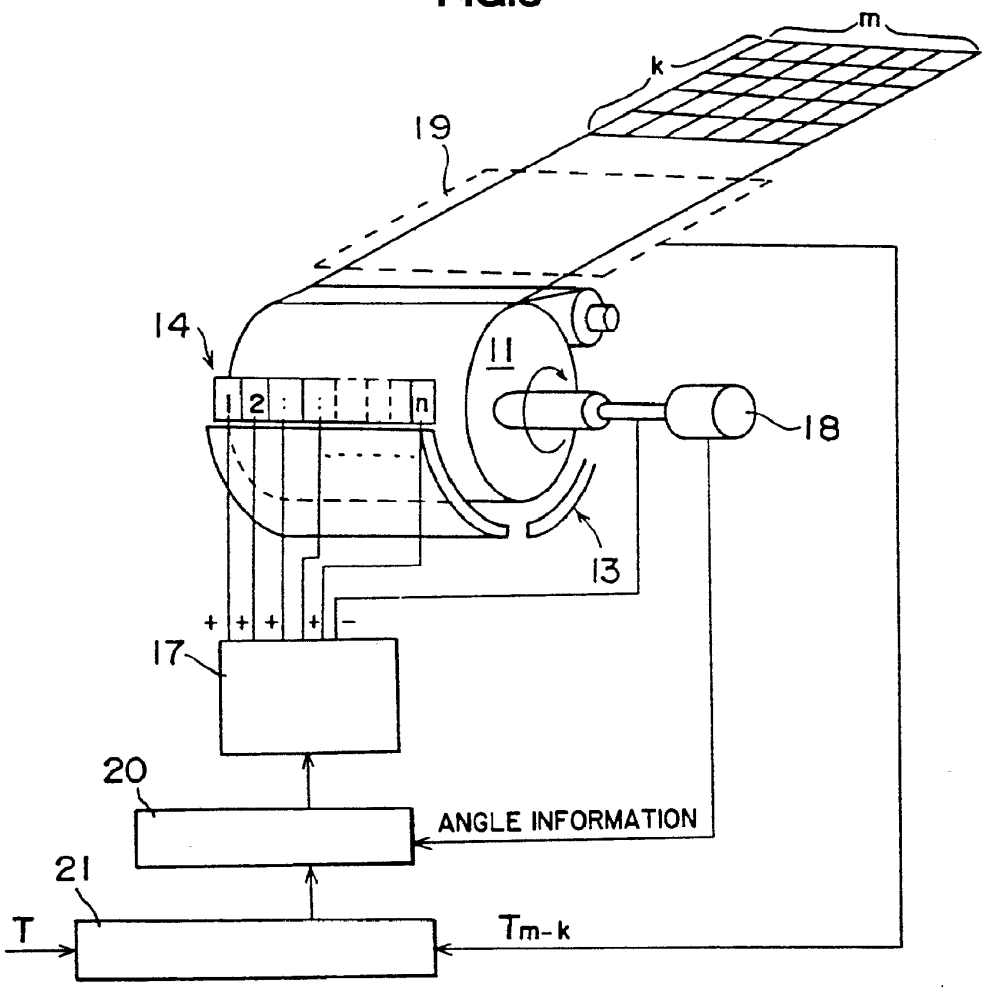


FIG.6

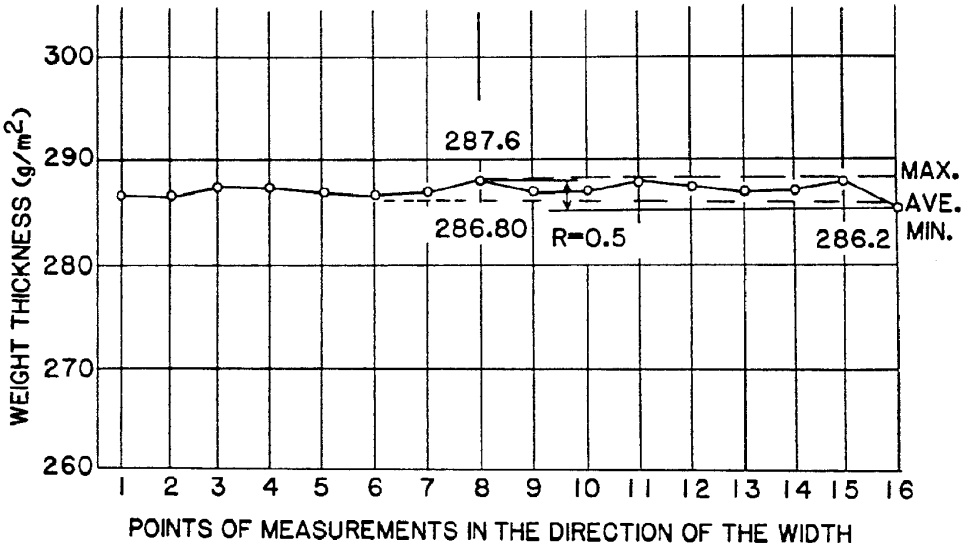
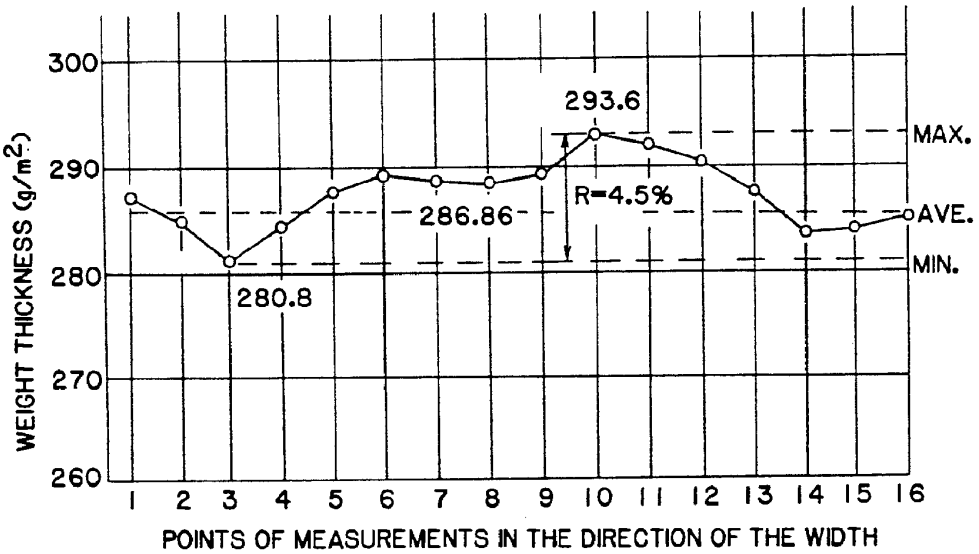

300
290
280
270
260
WEIGHT THICKNESS (g/m²)
287.6
286.80
R=0.5
286.2
MAX.
AVE.
MIN.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
POINTS OF MEASUREMENTS IN THE DIRECTION OF THE WIDTH

FIG.7


300
290
280
270
260
WEIGHT THICKNESS (g/m²)
293.6
286.86
280.8
R=4.5%
MAX.
AVE.
MIN.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
POINTS OF MEASUREMENTS IN THE DIRECTION OF THE WIDTH

METHOD OF PRODUCING ELECTROLYTIC COPPER FOIL AND APPARATUS FOR PRODUCING SAME

CROSS REFERENCE INFORMATION

This is a continuation-in-part application of copending patent application Ser. No. 794,272 filed on Nov. 19, 1991, now abandoned.

FIELD OF THE INVENTION

This invention relates to a method of producing an electrolytic copper foil. More particularly, this invention relates to a method of producing an electrolytic copper foil characterized by the provision of a plurality of foil thickness-uniformizing sub-anodes divided widthwise for uniformizing the thickness of the electrolytic copper foil being made and by the individual control of the quantities of electricity being supplied to the sub-anodes. The invention enables to produce a high-quality electrolytic copper foil having by far the less variation in thickness than heretofore attained and suited, e.g., for use in printed circuits.

BACKGROUND OF THE INVENTION

Electrolytic copper foil is produced by passing a stream of electrolyte between an anode of insoluble metal and a rotatable metallic cathode drum mirror-polished on the surface and supplying a potential between the anode and the cathode drum, thereby causing electrodeposition of copper on the cathode drum surface, and, when the electrodeposit has attained a predetermined thickness, peeling the same from the cathode drum. The copper foil thus obtained, called an untreated foil, is thereafter variously surface-treated to be final products.

FIG. 1 illustrates the relative position of a cathode drum and an anode conventionally used for the manufacture of copper foil. In an electrolytic cell (not shown) containing an electrolyte, the cathode drum 1 is installed to be rotatable (clockwise in this case) as partly submerged in the electrolyte. The anode is disposed as divided into, e.g., two anode sheets 3 to cover generally the submerged lower half of the cathode drum 1 in spaced relation with a given clearance from the drum surface. Inside the electrolytic cell, the electrolyte is supplied at 6 o'clock position (of the hour hand, the same applying hereinafter) between the two anode sheets 3. It flows upward along the space between the cathode drum and the anode and overflows the upper edges of the anode for circulation in the cell. A rectifier 5 maintains a given current between the cathode drum and the anode.

As the cathode drum 1 rotates, the electrodeposit of copper from the electrolyte becomes thicker, until it attains a desired thickness around 9 o'clock position, and the resulting untreated foil of the desired thickness is peeled off by suitable peeler means from the drum and is wound up.

In the apparatus for manufacturing electrolytic copper foil, when the operation has continued for a given time period, the anode, among others, is locally worn with use. Consequently, the space between the cathode drum and the anode sheets becomes uneven and the resulting untreated foil becomes uneven in thickness, depending on the characteristics of the apparatus used, till it becomes unmarketable. That is, by the lack of uniformity of the distance between the anode and the cathode drum and the variation of the flow velocity of the electrolyte being supplied etc., the resulting untreated foil undergoes variation in thickness in the direction of the width.

The resulting foil develops variation in thickness in the direction of the length too, in approximately the same pattern per revolution of the cathode drum, due largely to the eccentricity of the rotating cathode drum with periodic variation of the spacing between the anode and the cathode drum.

FIG. 2 is a schematic representation of an illustrative thickness distribution in a half-width section of a copper foil produced. The remaining half-width section not shown has a generally similar variation in thickness widthwise. Thus, the electrolytic copper foil conventionally produced has inevitable variations in thickness in both width and length directions, to varying degrees depending on the manufacturing conditions encountered.

In fact, much difficulties are involved in uniformizing the thickness of an electrolytic copper foil. For example, ANSI/IPC-CF-150E (May, 1981) "Copper Foil of Printed Wiring Applications", which is a standard developed by the Copper Foil Subcommittee of the Raw Materials Committee of the Institute for Interconnecting and Packaging Electronic Circuits, provides: "The area weight or thickness of the copper foil shall be within $\pm 10\%$ of the values shown in Table 1 for Type E copper (Electrodeposited copper foil) and $\pm 5\%$ for Type W copper (Wrought copper foil)." The provision thus allows for as much as 10% variation in thickness for electrodeposited copper foils in the thickness range from 18 to 498 μm. This shows how difficult it is to control the thickness of electrolytic copper foil so as to uniformize it.

Nevertheless, there has recently been strong demand for electrolytic copper foils of uniform thickness throughout. Copper foils are used chiefly for the fabrication of printed circuit boards, and the tendency toward finer circuits to be formed requires uniform etching of the copper foil and for the purpose a copper foil of uniform thickness is strongly necessitated. For the stabilization of its electric characteristics too, the copper foil must have far less variation in thickness than heretofore.

To make an electrolytic copper foil uniform in thickness throughout the direction of its width, the following steps have hitherto been taken:

(1) Anode milling: With an apparatus for the production of electrolytic copper foil, it has been common that anode after runs for a certain length of time is worn out of use, making the space between itself and the cathode drum uneven. As used herein, the expression "out of use" suggests an abnormal rise of the electrolytic voltage or serious unevenness in thickness of the copper foil produced. In order to avoid this, the anode after service for a given time period is cylindrically reformed on the surface by a special cutting tool.

(2) Partial anode cutting: After anode milling, variation of thickness in the direction of the width of the resulting copper foil is measured. According to the data thus obtained, the anode surface is locally cut off to properly correct the thickness of the copper foil.

Such correcting steps being taken until today restrict the variations of electrolytic copper foil thickness in the direction of its width to the order of about 5% of the target thickness. Little attention has been paid, on the

other hand, to the variations of thickness in the direction of the length.

These correction working is a time-consuming, laborious work, necessitating long downtime at regular intervals. However, the precision is nevertheless unsatisfactory. These counter-measures cannot cope with the variations in thickness widthwise from uncertain causes for which the anode is not to blame. In addition, the effect of such a measure, if achieved, would be short-lived.

OBJECTS OF THE INVENTION

It is an object of the present invention to develop a novel method of producing an electrolytic copper foil whereby the variations of foil thickness in the direction of the width due to the wear of the anode and from indefinite causes can be reduced to by far the lower level than heretofore, without the need of interrupting the operation.

Another object of the invention is to develop such a novel method of producing an electrolytic copper foil which can reduce not only the variations of foil thickness in the direction of the width but also the variations in the direction of the length.

SUMMARY OF THE INVENTION

The inventors conceived the idea of dividing an anode into two parts for separate functions; one for forming the basic thickness of a foil and the other for uniformizing the thickness. For the purposes of the invention, the former is termed main anode and the latter is termed sub-anodes. The main anode is supplied with electricity at a uniform current density throughout the entire width. The sub-anodes are divided into a proper number of pieces in the direction of the width, and the current densities for the individual sub-anodes are controlled on the basis of the production results so as to make the thickness of the resulting foil uniform. As the result, it is concurrently possible to make the foil thickness uniform in the direction of the width and uniform in both directions of the width and length.

The present invention, in its first aspect, provides a method of producing an electrolytic copper foil by passing an electrolyte between a rotating cathode drum and at least one sheet of anode located opposite to the cathode drum, this electrolytically depositing copper on the cathode drum surface, and then peeling off the resulting copper foil from the drum, characterized by:

(a) constructing said anode so as to have a structure such that the end portion thereof on the copper foil-recovering side is divided widthwise into n pieces of foil thickness-uniformizing sub-anodes, and the remainder of the anode serves as a main anode;

(b) supplying electricity to the main anode and the foil thickness-uniformizing sub-anodes at a given current density D (A/dm^2) set to attain a target foil thickness T (g/m^2); and

(c) measuring variations of thickness in the direction of the width of the resulting copper foil as the thicknesses Tm (g/m^2) (where $m=1\sim n$) in the direction of the width of the copper foil corresponding to the n pieces of foil thickness-uniformizing sub-anodes, and individually increasing or decreasing under control the quantities of electricity being supplied to the n pieces of foil thickness-uniformizing sub-anodes at current densities Dm (A/dm^2), preferably by a feedback system, so that the foil thicknesses Tm (g/m^2)(where $m=1\sim n$) are made equal to the target foil thickness T(g/m^2), whereby the foil thickness is made uniform widthwise.

In its second aspect, the invention also provides a method of producing an electrolytic copper foil by passing an electrolyte between a rotating cathode drum and at least one sheet of anode located opposite to the cathode drum, thus electrolytically depositing copper on the cathode drum surface, and then peeling off the resulting copper foil from the drum, characterized by:

(a) constructing said anode so as to have a structure such that the end portion thereof on the copper foil-recovering side is divided widthwise into n pieces of foil thickness-uniformizing sub-anodes, and the remainder of the anode serves as a main anode;

(b) supplying electricity to the main anode and the foil thickness-uniformizing sub-anodes at a given current density D (A/dm^2) set to attain a target foil thickness T (g/m^2); and

(c) dividing a pattern of thickness deviations of a copper foil produced per revolution of the cathode drum into m sections (where $m=1\sim n$) widthwise and k sections lengthwise, thus forming m $\times$k sections, measuring the foil thicknesses Tm−k (g/m^2) (where $m=1\sim n$) of the m $\times$k sections corresponding to the angle of rotation from a reference point of the cathode drum using an encoder which determines the angle of rotation of the cathode drum, and individually increasing or decreasing under control the quantities of electricity supplied to the n pieces of foil thickness-uniformizing sub-anodes at current densities Dm−k (A/dm^2) (where $m=1\sim n$), preferably by a feedback system, correspondingly to the angle of rotation from the reference point of the cathode drum so that the foil thicknesses Tm−k (g/m^2) of the divided sections are as become equal to the target foil thickness T (g/m^2), whereby the foil thickness is made uniform.

In an embodiment of the invention, the main anode forms from 90 to 98% of the target foil thickness T (g/m^2) and the foil thickness-uniformizing sub-anodes from forms 2 to 10% of the target foil thickness. According to this invention, the variations in thickness of the copper foil produced are controlled to a strikingly low level of 1% or less, even on the order of no more than 0.5%, on the basis of the target thickness. It will be appreciated that the uniformity of thickness thus realized is quite remarkable when it is compared with the above-mentioned IPC standard of "within $\pm$10%". This result was beyond one's expectations.

REFERENCES TO THE RELATED TECHNIQUES

U.S. Pat. No. 3,799,847 (Japanese Patent Application Kokai No. 49-27404) discloses a method and apparatus of producing a metal band having a roughened surface with higher adhesive strength than before by providing a plurality of separate anode plates around a cathode drum, said anode plates having increased current densities to form a thoroughly developed roughened surface. The present invention is entirely different from that of this reference in that the object of this reference is to provide a sufficiently developed roughened surface of a metal band to exhibit greater adhesion to a substrate than before and that the anode sheets are spaced from each other longitudinally around the cathode drum so as to change the current densities.

U.S. Pat. No. 4,053,370 (Japanese Patent Application Kokai Nos. 52-36761 and -36762) provides a process wherein a circuit pattern comprising a high density

major layer and a roughened surface layer is formed by a practically single step using a first anode and a second anode, with the roughened surface layer being intended to strengthen the adhesion of the circuit pattern to an insulating base. The first anode is spaced from a cathodic metal strip by a distance in the range of 1 to 10 mm, while the second anode is spaced from the metal strip by a distance in the range of 5 to 25 mm. The first and second anodes are disposed apart from each other around the cathode roll, not widthwise.

U.S. Pat. No. 4,490,218 discloses a process for producing a surface treated metal foil which comprises providing a first current density in a first zone for plating a cathodic surface with a relatively smooth metal deposit and super-imposing a second current density having a magnitude greater than the limiting current density over said first current density in a second zone. The primary anodes and a treatment anode are also herein spaced from each other around a drum as in the aforementioned references.

Japanese Patent Application Kokoku Nos. 49-18902 and 50-2378 also disclose the provision of annular electrolytic cell sections each having an anode around a cathode drum for individually controlling the deposition conditions in the production of a metal foil. The anode in individual cells are not divided widthwise.

Japanese Patent Application Kokai Nos. 63-259098 relates to a method of controlling the plating current in continuous electroplating of a steel strip. The object is to prevent superfluous plating around and beyond the strip edges and overplating at edge portion by the concentration of the current toward to edge portions. Although an anode is divided widthwise, it is for controlling the edge currents of various strips having different widths. The current density of a center portion is kept constant. This reference is entirely different in object from the present invention wherein the thickness of a copper foil is uniformized.

It is apparent that none of the aforementioned references disclose the object and characteristic points of this invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic perspective view of the major parts of a conventional apparatus for producing an electrolytic copper foil;

FIG. **2** is a diagrammatic illustration of variations in thickness of a half-width section of a copper foil in the directions of the width and length;

FIGS. **3** and **4** are perspective and front views, respectively, of the major parts of an apparatus suited for practicing one embodiment of the method of the invention for producing an electrolytic copper foil;

FIG. **5** is a schematic view of an apparatus for practicing another embodiment of the method of the invention for producing an electrolytic copper foil; and

FIGS. **6** and **7** are graphs showing measured thickness distributions in the direction of the width of electrolytic copper foils produced in Example 1 and Comparative Example, respectively.

DESCRIPTION OF THE EMBODIMENTS

FIGS. **3** and **4** show the major parts of an apparatus suited for practicing the method of the invention for producing an electrolytic copper foil. As explained earlier, the electrolytic copper foil is produced by passing a stream of electrolyte through a space between a rotating cathode drum and an anode facing the drum, thus allowing gradual electrodeposition of copper on the cathode drum surface, peeling off the resulting copper foil which has attained a predetermined thickness from the cathode drum, and then winding up the peeled foil on a winding roll.

In accordance with the invention, the end portion of the copper foil-recovering side of the anode is divided widthwise into n pieces of sub-anodes **14** for uniformizing copper foil thickness. The remainder of the anode, i.e., excepting the foil thickness-uniformizing sub-anodes, is in the form of two anode sheets intended to serve as main anodes **13**. The main anodes **13** constitute a region for producing the basic thickness of the copper foil, and the sub-anodes is a region for uniformizing the copper foil thickness. A main rectifier **15** is connected between the cathode drum **11** and the main anodes **13** to supply a controlled quantity of electricity to maintain a constant current density across the entire width of the main anodes. In order that the n pieces of foil thickness-uniformizing sub-anodes **14** can individually control the current densities between themselves and the cathode drum **11**, the corresponding number, or n pieces, of the thickness-uniformizing rectifiers **17** are connected between the individual sub-anodes **14** and the cathode drum **11**.

The larger the number of pieces, n, of the sub-anodes the more precisely the control can be exercised. Greater difficulties will be involved, however, in fabrication and maintenance. Generally, depending on the width of the copper foil to be made and on the conditions of the foil-production equipment used, one end portion of the anode is divided into from 10 to 40, typically around 30 pieces.

Between adjacent sub-anodes is interposed an insulating seal. Too between the sub-anodes and the main anode an insulating seal is interposed. Useful insulating materials for this purpose include sheets of PVC and cold cure rubber (e.g., one marketed under the trade designation "RTV"). Insulation is provided instead by bonding adjacent sub-anodes with an insulating adhesive or by integrally joining the sub-anodes with an insulating film therebetween.

Now the operation for the manufacture of electrolytic copper foil will be explained. In an electrolytic cell (not shown) which contains an electrolyte such as a sulfuric acid solution of copper sulfate, a cathode drum **11** which is a rotatable cylinder, e.g., of stainless steel or titanium, is held in place by support means, as partly submerged in the electrolyte, and made rotatable clockwise in the embodiment shown. There are provided two arcuate insoluble main anodes **13** and n pieces of foil thickness-uniformizing sub-anodes **14** (altogether called "the anode"), surrounding approximately the submerged lower hal f part of the cathode drum **11** and spaced a predetermined distance from the drum surface.

The main anodes **13** preferably consists of two anode sheets each disposed along about a lower quarter of the cathode drum as shown. According to the necessity, it may be replaced by a single anode sheet or by three, four, or more anode sheets.

The space between the cathode drum **11** and the anode **13, 14** is kept constant, usually in the range from 2 to 100 mm. The narrower the space the less the electricity consumption but more difficult will be the control of the foil thickness and quality.

This space between the cathode drum and the anode forms a flow passage for the electrolyte. The electrolyte is supplied at 6 o'clock position between the two anode

sheets **13** by way of a proper pump (not shown) in the cell. It passes as divided streams in opposite directions along the space and overflows the both upper edges of the anode sheets for circulation.

The main rectifier **15** maintains a given current between the cathode drum **11** and the main anodes **13**.

As the cathode drum **11** rotates, electrodeposition of copper from the electrolyte, which starts approximately at 3 o'clock position, progresses until the deposit attains a desired thickness at about 9 o'clock position where the electrodeposition comes to an end. The foil of the desired thickness is peeled off by suitable peeler means at about 12 o'clock position and wound up. In actual operation, however, the copper foil thus peeled off is not uniform in thickness.

Specifically, the anode, especially of the lead type, is locally worn with use. This results in variation in space between the cathode drum and the anode. In addition, the cathode drum can be responsible for some variation in foil thickness, and the electrolyte stream can undergo a certain deflection or irregularity in flow. Altogether, they tend to cause localized variation in thickness in the direction of the width of the resulting foil. Further, the eccentricity of between the anode and the cathode drum can be a primary cause of thickness variations lengthwise of nearly the same pattern on revolutions of the cathode drum **11**.

FIG. **2** schematically shows an illustrative variation in thickness widthwise and lengthwise of a half-width section of a copper foil. In the direction of the width, the remaining half-width section not shown has a generally similar variation in thickness. Usually, the variation in the direction of the width is more pronounced than that in the direction of the length. In the manufacture of electrolytic copper foil it is generally possible in many cases to make the entire copper foil even in thickness by correcting the variation widthwise. However, the mere control in the direction of the width has a limitation in correcting the overall variation, and when this is a problem the removal of variation in the direction of the length must also be taken into account.

By way of example, the case where variation in the direction of the width has resulted from the copper foil manufacture under the above conditions will now be considered. With the embodiment being described, the thickness in the direction of the width of the untreated foil is determined after the peeling and, when a thickness variation beyond a permissible limit has been detected, the electrical currents being supplied to the specific sub-anodes **14** corresponding to the specific portions in the direction of the width are individually controlled toward the removal of the variation. To permit this individual control of the sub-anodes **14**, thickness-uniformizing sub-rectifiers **17** are connected between the individual sub-anodes **14** and the cathode drum **11**.

The thickness values at different points in the direction of the width of the copper foil can be simply determined by suitable sampling, in terms of the weight per unit area. Alternatively, a thickness measuring instrument, such as of the static capacity detection type or X-ray type, may be installed in the winding route to monitor the thickness, cooperatively with the thickness-uniformizing sub-rectifiers **17** via feedback means.

The operation will now be described in detail. Electricities supplied to the main anodes and the foil thickness-uniformizing sub-anodes at a preset current density D (A/dm^2) to attain a target foil thickness T (g/m^2). Variations in the thickness in the direction of the width of the copper foil thus produced are measured as the foil thicknesses Tm (g/m^2) (where $m=1\sim n$) corresponding to the n pieces of foil thickness-uniformizing sub-anodes **14**. The quantities of electricity being supplied to the n pieces of foil thickness-uniformizing sub-anodes are set to current densities Dm (A/dm^2)(where $m=1\sim n$), so that the individual foil thicknesses Tm (g/m^2)(where $m=1\sim n$) are equalized to be the target foil thickness T (g/m^2). The quantities of electricity are preferably controlled through a feedback system for increase or decrease to achieve the uniformity of foil thickness widthwise.

The main anodes are supplied with a given constant quantity of electricity at a current density D (A/dm^2). On the other hand, the n pieces of foil thickness-uniformizing sub-anodes are supplied with electricity at current densities Dm (A/dm^2) (where $m=1\sim n$), with individual control for increase or decrease, so that the foil thicknesses in the width direction Tm (g/m^2) (where $m=1\sim n$) are made equal to the target foil thickness T (g/m^2).

Desirably, the main anodes produce a foil with a thickness equivalent to from 90 to 98% of the target foil thickness T (g/m^2), and the foil thickness-uniformizing sub-anodes make up the remaining 2 to 10% of the target thickness.

In this way, the variation in the thickness widthwise of the resulting copper foil can be controlled within $\pm 1\%$ of the target level.

When the variation in the foil thickness in the direction of the length too is a problem, pattern control is conducted.

In that event, the thicknesses in both length and width directions of the untreated foil are determined after the peeling and, when any thickness deviation from the target level has exceeded a permissible limit, the quantities of electric supply to the specific foil thickness-uniformizing sub-anodes are controlled, on the basis of the combination of thickness patterns in the directions of the length and width, so as to correct the excessive variation.

To be more detail, the thickness patterns per revolution of the cathode drum are determined beforehand, and the quantities of electricity being supplied to the sub-anodes concerned are controlled.

For the purposes of the invention the expression "the thickness pattern per revolution of the cathode drum" is used to mean deviations (e.g., variations) in thickness from the target thickness of the copper foil formed upon one complete turn of the cathode drum measured, e.g., at 900 points chosen by dividing the copper foil area by 30 lengthwise and by 30 widthwise, i.e., $30\times 30=900$. It represents the combination of a thickness pattern in the direction of the length and a thickness pattern in the direction of the width.

The case in which the thickness of a copper foil is measured beforehand at a total of 900 points as chosen above will now be explained.

Any deviation from the target thickness (e.g., variation in thickness) at the 900 points, as noted above, represent those caused by irregularities in the uniformity of the cathode-anode spacing, the flow rate of electrolyte fed, the quantity of electricity supplied, etc. They indirectly represent the relations between a given portion of the cathode drum and the anode during one complete turn of the particular portion round the drum along a given track thereon (the relations given in terms

of changes in the spacing, electrolyte flow rate, quantity of electricity supplied, etc.) and therefore represent the variation in thickness.

It follows that, in order to obtain a copper foil having a predetermined thickness, it is necessary to decide on and control the quantities of electricity to be supplied to the individual sub-anodes in conformity with the thickness deviation pattern from the target thickness of the 900 points. The thickness of the copper foil being produced is monitored and, when a change beyond a permissible limit has taken place, the quantity of electricity being supplied to the corresponding portion of the deviation pattern is controlled. In this way a copper foil having a predetermined thickness in the both directions of the length and width can be obtained.

Referring to FIG. **5**, there is shown a pattern of thickness deviations of a copper foil produced per revolution of the cathode drum **11**, as divided into m sections (where $m=1\sim n$) widthwise and k sections lengthwise, thus forming m $\times$k square sections. Using an encoder **18** which determines the angle of rotation of the cathode drum **11**, the foil thicknesses $Tm-k$ (g/m^2) (where $m=1\sim n$) of the m $\times$k sections corresponding to the angle of rotation from a reference point of the cathode drum are measured in a foil thickness measuring stage **19**. The thickness informations obtained are passed to a calculator **21** for calculating the deviations of the measured $Tm-k$ (g/m^2) from the target foil thickness T (g/m^2) and providing foil thickness variation informations to rectifier controller **20**. The angle informations from the encoder **18** are also sent to the rectifier controller **20**. In order that the foil thicknesses $Tm-k$ (g/m^2) of the divided sections become equal to the target foil thickness T (g/m^2), the quantities of electricity supplied to the n pieces of foil thickness-uniformizing sub-anodes **14** are adjusted to current densities $Dm-k$ (A/dm^2)(where $m=1\sim n$) and controlled individually by the corresponding n units of sub-rectifiers **17** for increase or decrease, preferably by a feedback system, correspondingly to the angle of rotation from the reference point of the cathode drum.

Here again it is desirable that the main anodes produce a foil with a thickness equivalent to form 90 to 98% of the target foil thickness T (g/m^2), and the foil thickness-uniformizing sub-anodes make up the remaining 2 to 10% of the target thickness.

In this manner the variations in thickness of the copper foil produced can be controlled within $\pm 1\%$ of the target level.

With the embodiment being described, the thickness of the electrolytic copper foil being produced can be controlled by individually controlling the quantities of electricity supplied to the sub-anodes on the basis of a combination of the patterns of foil thicknesses in both directions of the length and width.

Although it appears that a single row of sub-anodes usually will do, a plurality or multiplicity of rows may be provided instead where the variation is beyond control with a single row or where more precise control is needed.

Examples of this invention are set forth below. It is to be noted that these examples are not intended to restrict this invention.

EXAMPLE 1 AND COMPARATIVE EXAMPLE

A copper foil 35 μm thick (nominal thickness, 1 ounce/ft^2) was made using a copper sulfate solution and a combination of a cathode drum 2.0 m in diameter and 1.3 m wide and two 1.3 m wide anode sheets arranged arcuately along substantially the lower half of the cathode drum as shown in the drawings. The anode structure according to the invention was as depicted in FIGS. **3** and **4** and comprised 30 sub-anodes. On the basis of the weight values per unit area of the peeled copper foil, the electric currents supplied to the individual sub-anodes were adjusted within the range of 0.1 to 10 A/dm^2. Thus, the method of the invention rendered it possible to reduce the variation in thickness widthwise, from the usual level of about 4.5% down to 0.5% or less as shown in FIGS. **6** and **7**, respectively, where the thicknesses at points 1 to 16 in the half-width sections of the foils made according to this invention and conventionally were measured in terms of weight per unit area (g/m^2).

EXAMPLE 2

A 35 μm-thick copper foil was made using a copper sulfate solution and a combination of a cathode drum 2.0 m in diameter and 1.3 m wide and two 1.3 m wide anode sheets arranged arcuately along substantially the lower half of the cathode drum as shown. The anode structure according to the invention was as depicted in FIGS. **3** and **4** and comprised 30 sub-anodes.

On the basis of thickness patterns in the directions of the length and width per revolution of the cathode drum that had been determined beforehand (at 30 points widthwise $\times$30 points lengthwise =900 points), the electric currents supplied to the individual sub-anodes were calculated with a personal computer and adjusted within the range of 0.1 to 10 A/dm^2. Thus the method of the invention made it possible to reduce the variation in thickness widthwise, from the usual level of about 4.5% down to 0.5% or less. In the direction of the length, the variation was reduced from the usual range of about 2% down to 0.5% or less.

ADVANTAGE OF THE INVENTION

The thickness of copper foil is now successfully made uniform, for the first time in the art, by far the greater degree than heretofore, with thickness variations reduced strikingly from the usual level, to less than about a tenth of the usual level in the direction of the width and to less than about a fourth of the usual level in the direction of the length, by individually controlling, during the operation, the quantities of electricity being supplied into a plurality of foil thickness-uniformizing sub-anodes divided widthwise. The foil product obtained is promising as a copper foil required for future electronic devices or the like.

We claim:

1. A method of producing an electrolytic metallic foil comprising the steps of:

(a) providing electrolyte between a rotating cathode drum and at least one anode structure in the configuration of a sheet, the rotating cathode drum having an outer surface, the anode structure located opposite to the cathode drum outer surface and having a side facing the outer surface of the drum, the anode structure spaced from and along the drum so as to form a gap therebetween and having a width parallel to the rotational axis of the drum and a total length, the anode structure being defined by a main portion serving as a main anode and an end portion, the main portion defined by a first portion of the total length of the anode structure and the end portion defined by a second portion of

the total length of the anode structure, the main portion being undivided widthwise, the end portion being divided widthwise into n foil thickness-uniformizing sub-anodes, the main portion and the sub-anodes being electrically insulated from each other;

(b) electrolytically depositing metal on the cathode drum outer surface by supplying electricity to the main anode at a current density D and supplying electricity to the foil thickness-uniformizing sub-anodes at current densities Dm, the current density D and densities Dm being set to attain a target foil thickness T;

(c) peeling off the resulting metallic deposition as a metallic foil from the cathode drum;

(d) measuring variations of thickness in the direction of the width of the resulting metallic foil as n thicknesses Tm corresponding to the n foil thickness-uniformizing sub-anodes, the foil width being the foil's dimension parallel to the rotational axis of the drum; and

(e) individually increasing or decreasing the quantities of electricity being supplied to the n foil thickness-uniformizing sub-anodes at the current densities Dm in response to the measured thicknesses Tm, so that the n foil thicknesses Tm are made to approach the target foil thickness T.

2. The method of claim **1** wherein the foil thickness formed by steps (a) through (e) is proportional to the total length of the anode structure and electrical potential supplied thereto, the length of the main anode and electrical potential supplied thereto being such that in step (b) the main anode forms essentially from 90 to 98% of the target foil thickness T and the length of the end portion and electrical potential supplied thereto being such that in step (b) its foil thickness-uniformizing sub-anodes form essentially from 2 to 10% of the target foil thickness.

3. The method of claim **2** wherein the variations in thickness of the metallic foil produced using the steps (a) through (e) are 1% or less of the target foil thickness T.

4. The method of claim **1** wherein the variations in thickness of the metallic foil produced using the steps (a) through (e) are 1% or less of the target foil thickness T.

5. The method of claim **1** wherein n = 10 to 40.

6. The method of claim **1** wherein the metallic foil is copper foil.

7. An apparatus for forming a metallic foil from an electrolyte comprising:

(a) a rotating cathode drum having an outer surface;

(b) at least one anode structure in the configuration of a sheet located opposite to the cathode drum outer surface and having a side facing the outer surface of the drum, the anode structure spaced from and along the drum so as to form a gap therebetween and having a width parallel to the rotational axis of the drum and a total length, the anode structure including

(i) a main portion serving as a main anode, the main portion defined by a first portion of the total length of the anode structure and being undivided widthwise; and

(ii) an end portion defined by a second portion of the total length of the anode structure and divided widthwise into n foil thickness-uniformizing sub-anodes, the main portion and the sub-anodes being electrically insulated from each other;

(c) means for applying electrical potentials to the main anode and individual ones of the n foil thickness-uniformizing sub-anodes, the electrical potential applied to the main anode being independent of the electrical potentials applied to the sub-anodes, the electrical potentials being set to attain a target foil thickness T;

(d) means for passing an electrolyte between the rotating cathode drum and the anode structure, thereby electrolytically depositing metal on the cathode drum outer surface;

(e) means for peeling off the metal from the drum, thereby forming a resulting metallic foil;

(f) means for measuring variations of thickness in the direction of the width of the resulting metallic foil as n thicknesses Tm corresponding to the n foil thickness-uniformizing sub-anodes, the foil width being the foil's dimension parallel to the rotational axis of the drum; and

(g) means for individually controlling the electrical potential applied to the individual n foil thickness-uniformizing sub-anodes in response to the measured thicknesses Tm, thereby causing the n foil thicknesses Tm to approach the target foil thickness T.

8. The apparatus in claim **7** wherein the foil thickness formed by the apparatus is proportional to the total length of the anode structure and electrical potential applied thereto, the length of the main anode and electrical potential applied thereto being such that it is adapted to form essentially from 90 to 98% of the target foil thickness T and the length of the end portion and electrical potential applied thereto being such that its foil thickness-uniformizing sub-anodes are adapted to form essentially from 2 to 10% of the target foil thickness.

9. The apparatus in claim **8** wherein elements (a) through (g) are adapted to produce variations in thickness of the metallic foil of 1% or less of the target foil thickness T.

10. The apparatus in claim **7** wherein n = 10 to 40.

11. The apparatus in claim **7** wherein the said apparatus is adapted to produce copper foil.

12. The apparatus in claim **7** wherein elements (a) through (g) are adapted to produce variations in thickness of the metallic foil of 1% or less of the target foil thickness T.

13. A method of producing an electrolytic metallic foil comprising the steps of:

(a) providing electrolyte between a rotating cathode drum and at least one anode structure in the configuration of a sheet, the rotating cathode drum having an outer surface, the anode structure located opposite to the cathode drum outer surface and having a side facing the outer surface of the drum, the anode structure spaced from and along the drum so as to form a gap therebetween and having a width parallel to the rotational axis of the drum and a total length, the anode structure being defined by a main portion serving as a main anode and an end portion, the main portion defined by a first portion of the total length of the anode structure and the end portion defined by a second portion of the total length of the anode structure, the main portion being undivided widthwise, the end portion being divided widthwise into n foil thickness-

uniformizing sub-anodes, the main portion and the sub-anodes being electrically insulated from each other;

(b) electrolytically depositing metal on the cathode drum outer surface by supplying electricity to the main anode at a current density D and supplying electricity to the foil thickness-uniformizing sub-anodes at current densities Dm−k, the current density D and densities Dm−k being set to attain a target foil thickness T;

(c) peeling off the resulting metallic deposition as a metallic foil from the cathode drum;

(d) dividing a pattern of thickness deviations of the metallic foil produced per revolution of the cathode drum into m sections widthwise where m=1−n and k sections lengthwise, thus forming m ×k sections, the widthwise sections corresponding to the foil's dimension parallel to the rotational axis of the drum;

(e) measuring foil thicknesses Tm−k of the m ×k sections corresponding to the angle of rotation from a reference point of the cathode drum; and

(f) individually increasing or decreasing the quantities of electricity being supplied to the n foil thickness-uniformizing sub-anodes at the current densities Dm−k in response to the measured thicknesses Tm−k and the angle of rotation from the reference point of the cathode drum, so that the foil thicknesses Tm−k of the divided sections are made to approach the target foil thickness T.

14. The method of claim **13** wherein the foil thickness formed by steps (a) through (f) is proportional to the total length of the anode structure and electrical potential supplied thereto, the length of the main anode and electrical potential supplied thereto being such that in step (b) the main anode forms essentially from 90 to 98% of the target foil thickness T and the length of the end portion and electrical potential supplied thereto being such that in step (b) its foil thickness-uniformizing sub-anodes form essentially from 2 to 10% of the target foil thickness.

15. The method of claim **14** wherein the variations in thickness of the metallic foil produced using the steps (a) through (f) are 1% or less of the target foil thickness T.

16. The method of claim **13** wherein the variations in thickness of the metallic foil produced using the steps (a) through (f) are 1% or less of the target foil thickness T.

17. The method of claim **13** wherein n=10 to 40.

18. The method of claim **13** wherein the metallic foil is copper foil.

19. An apparatus for forming a metallic foil from an electrolyte comprising:

(a) a rotating cathode drum having an outer surface;

(b) at least one anode structure in the configuration of a sheet located opposite to the cathode drum outer surface and having a side facing the outer surface of the drum, the anode structure spaced from and along the drum so as to form a gap therebetween and having a width parallel to the rotational axis of the drum and a total length, the anode structure including

(i) a main portion serving as a main anode, the main portion defined by a first portion of the total length of the anode structure and being undivided widthwise; and

(ii) an end portion defined by a second portion of the total length of the anode structure and divided widthwise into n foil thickness-uniformizing sub-anodes, the main portion and the sub-anodes being electrically insulated from each other;

(c) means for applying electrical potentials to the main anode and individual ones of the n foil thickness-uniformizing sub-anodes, the electrical potential applied to the main anode being independent of the electrical potentials applied to the sub-anodes, the electrical potentials being set to attain a target foil thickness T;

(d) means for passing an electrolyte between the rotating cathode drum and the anode structure, thereby electrolytically depositing metal on the cathode drum outer surface;

(e) means for peeling off the metal from the drum, thereby forming a resulting metallic foil;

(f) means for dividing a pattern of thickness deviations of the metallic foil produced per revolution of the cathode drum into m sections widthwise where m=1−n and k sections lengthwise, thus forming m ×k sections, the widthwise sections corresponding to the foil's dimension parallel to the rotational axis of the drum;

(g) means for measuring resulting metallic foil thicknesses Tm−k of the m ×k sections corresponding to the angle of rotation from a reference point of the cathode drum;

(h) means for measuring the angle of rotation from the reference point of the cathode drum; and

(i) means for individually controlling the electrical potential applied to the individual n foil thickness-uniformizing sub-anodes in response to the measured thicknesses Tm−k, thereby causing the foil thicknesses Tm−k of the divided sections to approach the target foil thickness T.

20. The apparatus in claim **19** wherein the foil thickness formed by the apparatus is proportional to the total length of the anode structure and electrical potential applied thereto, the length of the main anode and electrical potential applied thereto being such that it is adapted to form essentially from 90 to 98% of the target foil thickness T and the length of the end portion and electrical potential applied thereto being such that its foil thickness-uniformizing sub-anodes are adapted to form essentially from 2 to 10% of the target foil thickness.

21. The apparatus in claim **20** wherein elements (a) through (i) are adapted to produce variations in thickness of the metallic foil of 1% or less of the target foil thickness T.

22. The apparatus in claim **19** wherein n=10 to 40.

23. The apparatus in claim **19** wherein said apparatus is adapted to produce copper foil.

24. The apparatus in claim **19** wherein the means for measuring the angle of rotation comprises an encoder.

25. The apparatus in claim **19** wherein elements (a) through (i) are adapted to produce variations in thickness of the metallic foil of 1% or less of the target foil thickness T.

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(54) **PRODUCTION OF ELECTROLYTIC COPPER FOIL**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for manufacturing electrolytic copper foil by which the electrolytic copper foil which is thin, has large tensile strength and high rigidity and thereby is excellent in handling easiness, both surfaces of which are smooth and have equal surface roughness and which is excellent in extension percentage, can be manufactured by using an electrolytic solution obtained from inexpensive copper scrap.

SOLUTION: Copper scrap is subjected to sintering treatment and then to pickling treatment. Obtained processed copper is dissolved in a sulfuric acid aqueous solution to produce an electrolytic solution. Obtained electrolytic solution is subjected to electrolysis to deposit copper. The sintering treatment is desirably executed by blowing hot air of 500 to 800°C to the copper scrap for 1 to 30 minutes and the pickling treatment is desirably executed by oscillating the sintering-treated copper scrap in the sulfuric acid aqueous solution of 0.1 to 2.0 mol/l.

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最終頁に続く

(54)【発明の名称】　電解銅箔の製造方法

(57)【要約】
【課題】　安価な銅くずから得られる電解液を用いて、薄くて引張強度が大きく、剛性が高いことから取扱性に優れ、両面が平滑で同等の表面粗さを有し、伸び率に優れた電解銅箔を製造することができる電解銅箔の製造方法を提供する。
【解決手段】　銅くずを焼成処理した後、酸洗処理して得られた処理銅を硫酸水溶液に溶解して電解液を作製し、得られた電解液を用いて電気分解により銅析出を行う電解銅箔の製造方法。

【特許請求の範囲】
【請求項１】　銅くずを焼成処理した後、酸洗処理して得られた処理銅を硫酸水溶液に溶解して電解液を作製し、得られた電解液を用いて電気分解により銅析出を行うことを特徴とする電解銅箔の製造方法。
【請求項２】　焼成処理が、銅くずに５００～８００℃の熱風を１～３０分間送風することにより行われる請求項１記載の電解銅箔の製造方法。
【請求項３】　酸洗処理が、焼成処理した銅くずを０．１～２．０ｍｏｌ／ｌの硫酸水溶液中で揺動させることにより行われる請求項１又は２記載の電解銅箔の製造方法。
【請求項４】　銅くずがＪＩＳ　Ｈ　２１０９に規定される１号ナゲット銅である請求項１、２又は３記載の電解銅箔の製造方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、電子部品の回路やリチウム二次電池の負極に好適に用いられる電解銅箔の製造方法に関する。
【０００２】
【従来の技術】電解銅箔の製造工程は、銅原料を電解液に溶解させる溶解工程と銅原料を溶解した電解液を用いて電気分解により銅を析出させる銅析出工程とからなる複合工程であり、析出する銅に見合うだけの銅原料を電解液に溶解させる必要がある。銅原料としては安価であり、表面積の大きな銅くずが使用されている。銅くずとしては、スクラップ銅線を細断したものを用いるのが一般的であるが、その他、溶融押出品を細断したものなども用いられている。これらの銅くずは、押出加工時の伸線油や被覆材料由来の不純物、スクラップ化及び細断時に付着した不純物により汚染されている。
【０００３】近年、高密度電子回路を実現するため、微細回路形成に適した薄い電解銅箔が望まれている。銅原料を硫酸水溶液に溶解させた硫酸銅水溶液にゼラチンなど有機物や塩化物などを添加した電解液を用い、電気分解により薄い電解銅箔を製造する方法が知られているが、この方法により得られた電解銅箔は引張強度が小さく、剛性に乏しいため取扱が難しいという難点があった。また、この製造方法で得られた電解銅箔は銅箔析出面側の表面粗さが比較的大きく、厚さが不均一であるため、薄銅箔ではしわなどの原因となる傾向があった。さらに、表面粗さが大きいことはオーバーエッチングの原因となり、微細回路の形成に支障をきたすという問題があった。
【０００４】
【発明が解決しようとする課題】本発明の目的は、従来から使用されている安価な銅くずから得られる電解液を用いて、薄くて引張強度が大きく、剛性が高いことから取扱性に優れ、両面が平滑で同等の表面粗さを有し、伸び率に優れた電解銅箔を製造することができる電解銅箔の製造方法を提供することにある。
【０００５】
【課題を解決するための手段】本発明者らは、前記目的を達成するために鋭意研究を重ねた結果、電解液に溶解する銅原料として銅くずを用い、銅くずを焼成処理した後、酸洗処理して得られた処理銅くずを用いることにより、薄くて引張強度が大きく、剛性が高いことから取扱性に優れ、両面が平滑で同等の表面粗さを有し、伸び率に優れた電解銅箔を製造することができることを見出し、この知見に基づいて本発明を完成するに至った。
【０００６】すなわち、本発明は、銅くずを焼成処理した後、酸洗処理して得られた処理銅くずを硫酸水溶液に溶解して電解液を作製し、得られた電解液を用いて電気分解により銅析出を行うことを特徴とする電解銅箔の製造方法を提供するものである。
【０００７】本発明により得られた電解銅箔は、薄くて引張強度が大きく、微細回路の形成に適し、伸び率に優れていることから、例えば、内層回路として用いた場合に熱膨張に基づく断線不良を防止することができ、電子回路用銅箔として極めて優れた特性を有している。さらに、両面が平滑で同等の表面粗さを有し、剛性が高いことから二次電池用活物質合剤の両面塗工が容易であり、また、伸び率に優れることから、リチウムイオン二次電池の負極板用銅箔としても極めて有用な銅箔である。
【０００８】
【発明の実施の形態】本発明において用いられる銅くずとしては、好ましくは、異物、異材を混入しない銅分が９９％以上のものが用いられる。より好ましくは、ＪＩＳ　Ｈ　２１０９に規定される１号ナゲット銅が用いられる。これは、安価に入手できる銅くずで、銅線又は銅より線をナゲット加工した（短切線）純良なもので、銅分が９９．９％以上のものである。また、銅覆鋼線など異材及び異物が混入していないものである。また、ＪＩＳ　Ｈ　２１０９に規定される１号銅線くずも使用可能である。本発明においては、この銅くずに焼成処理と酸洗処理を行って得られた処理銅くずを硫酸に溶解して電解液を作製する。
【０００９】焼成処理を行うことにより、銅くずの表面付着物が酸化・燃焼するとともに、酸化された表面が酸で容易に浸食されるため、酸洗効率が向上し、油分などの付着物が容易に除去できるようになる。焼成処理の条件は銅くずの表面に薄い酸化銅層が形成される条件が適切であり、好ましくは銅くずを５００℃～８００℃の酸化雰囲気に、好ましくは１分～３０分間さらすことにより行われる。この操作を繰り返し行ってもよい。具体的には被処理物に５００～８００℃の熱風を１分～３０分送風することにより行われる。焼成処理に用いられる焼成処理装置の形式は問わないが、内部で銅くずを流動させることで酸化が進むため、適切な揺動機構や撹拌機構

を有するものが好ましく用いられる。

【００１０】焼成処理を行った後、焼成処理された銅くずに酸洗処理を行う。酸洗処理において、酸洗液としては０．１～２．０ｍｏｌ／ｌの硫酸水溶液が好ましく用いられる。硫酸水溶液のほか、電気分解に用いる電解液を用いることもできる。その他の無機酸や有機酸の水溶液は、電解液の汚染原因となることから好ましくない。水洗装置も形式を問わないが、銅くずと十分に接触するための機構を有することが好ましい。このような装置は、酸洗液の循環機構を設けて被処理物を揺動させるなどによって実現可能である。酸洗処理は硫酸水溶液中で被処理物を好ましくは１０℃～６０℃の温度で、１分～３０分間揺動させることにより行われる。酸洗処理後に純水を用いて処理銅くずを十分に洗浄し、付着物を除去する。

【００１１】次に、上記で得られた処理銅くずを硫酸水溶液に溶解する。この硫酸水溶液としては、濃度が０．１～５ｍｏｌ／ｌのものが好ましく、０．５～３ｍｏｌ／ｌのものがより好ましい。銅くずの溶解は硫酸水溶液に空気を送り込みながら行うことが好ましい。次いで得られた電解液を用いて電気分解を行い、陰極に銅を析出させる。電気分解の条件は特に限定されず、通常の電解銅箔製造の電解条件で行われる。好ましくは、電流密度５～１５０Ａ／ｄｍ^2、電解時間１～３０分間の条件で行われ、厚さ２μｍ以上の電解銅箔が得られる。薄い、すなわち、２～１０μｍの電解銅箔を得るためには、電流と電解時間適宜制御して行う。更に必要ならば、銅箔面に粗化処理や防錆処理を行うことができる。

【００１２】

【実施例】以下、本発明の実施例及びその比較例によって本発明を更に具体的に説明するが、本発明はこれらの実施例に限定されるものではない。

【００１３】実施例１

ＪＩＳ　Ｈ　２１０９に規定される１号ナゲット銅（平均重量０．２ｇ／個）５００ｇを白金製金網に入れ、下から７００℃の熱風を１分間送風した。ナゲット銅を十分に混合した後、再度７００℃の熱風を１分間送風した。この送風操作を１０回繰り返して行うことで、焼成処理を行った。

【００１４】試薬硫酸から調製した１ｍｏｌ／ｌの硫酸水溶液に焼成処理されたナゲット銅を投入し、硫酸水溶液中で３分間揺動させた。次いでナゲット銅を純水中に移して３分間揺動させた。この二つの操作を三回繰り返した。

【００１５】試薬硫酸から調製した２ｍｏｌ／ｌの硫酸水溶液に酸洗処理したナゲット銅を投入し、空気を送り込みながらナゲット銅を完全に溶解させた。なお、空気は硫酸水溶液、水酸化ナトリウム水溶液とシリカゲルとを通気させた後、０．５μｍフィルタを介してゴミや不純物の混入を防止したものを用いた。

【００１６】次いで硫酸と純水とで硫酸銅２８０ｇ／ｌ、硫酸８０ｇ／ｌに濃度を調節し、電解液とした。

【００１７】陰極として、径５ｃｍのチタン製円筒状電極を用い、表面を２０００番の研磨紙を用いて研磨を行った。表面粗さはＲａで０．２０μｍであった。陽極板には円筒状の鉛板を用い、上記の電解液を用いて液温４０℃、電流密度１０Ａ／ｄｍ^{2}で５分間電気分解を行い、銅箔を析出させた。ただし円筒状電極の回転数は３００ｒｐｍとした。銅箔は両面ともに光沢を有し、重量法により求めた厚さは１２μｍであった。機械特性の測定結果を表１に示す。

【００１８】比較例１

焼成処理を行わないほかは実施例１と同様に銅箔を調製し、機械特性を評価した。結果を表１に示した。

【００１９】比較例２

酸洗処理を行わないほかは実施例１と同様に銅箔を調製し、機械特性を評価した。結果を表１に示した。

【００２０】比較例３

焼成処理と酸洗処理を行わないほかは実施例１と同様に銅箔を調製し、機械特性を評価した。結果を表１に示した。

【００２１】

【表１】

		実施例１	比較例１	比較例２	比較例３
表面粗さ（μｍ、Ｒａ）	電極面側	0.20	0.20	0.20	0.20
	析出面側	0.21	0.55	0.58	0.60
引張強度（Ｎ／ｍｍ^2）	常態	580	350	340	330
	加熱後（180℃／1h）	250	340	330	320
伸び率（％）	常態	4	7	7	6
	加熱後（180℃／1h）	20	8	8	7

表面粗さはＪＩＳ　Ｂ　０６５１に基づいて測定した。引張強度は常態（２３℃）及び１８０℃で１時間加熱後の引張強度をＪＩＳ　Ｃ６５１５に基づいて測定した。伸び率は常態（２３℃）及び１８０℃で１時間加熱後の引張強度をＪＩＳ　Ｃ６５１５に基づいて測定した。

【００２２】

【発明の効果】本発明の製造方法により得られた電解銅箔は、薄くて引張強度が大きく、剛性が高いことから取

扱性に優れ、両面が平滑で同等の表面粗さを有し、伸び率に優れた、微細回路を有する電子回路用銅箔やリチウムイオン二次電池の負極板用銅箔として極めて有用である。

フロントページの続き

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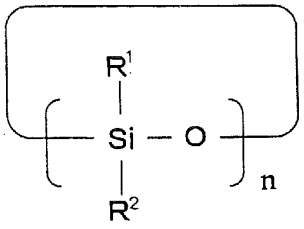
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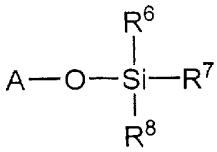
(54)【発明の名称】リチウムイオン二次電池

(57)【要約】　（修正有）
【課題】低い充電深度での充放電の繰り返しに、良好な性能を維持できるリチウムイオン二次電池を提供する。
【解決手段】非水系電解液が、式（１）、式（２）、式（３）で表される化合物、分子内にＳ－Ｆ結合を有する化合物、硝酸塩、亜硝酸塩、モノフルオロリン酸塩、ジフルオロリン酸塩、酢酸塩、プロピオン酸塩を１種以上含有し、かつ負極活物質が異配向性炭素複合物を含有するリチウムイオン二次電池。



(1)

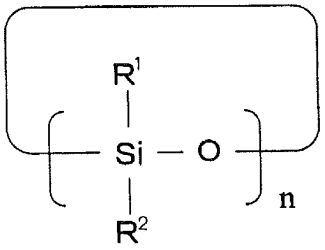
$$SiF_xR^3_pR^4_qR^5_r \qquad (2)$$



(3)

［R^1～R^8は炭素数１～１２の有機基、ｎは３～１０の整数、ｘは１～３の整数、ｐ、ｑ、ｒは０～３の整数。ＡはＨ、Ｃ、Ｎ、Ｏ、Ｆ、Ｓ、Ｓｉ及び／又はＰからなる基。］

【特許請求の範囲】
【請求項１】
リチウム塩を含有する非水系電解液、負極活物質及び正極活物質を少なくとも有するリチウムイオン二次電池であって、該非水系電解液が、一般式（１）で表される環状シロキサン化合物、一般式（２）で表されるフルオロシラン化合物、一般式（３）で表される化合物、分子内にＳ－Ｆ結合を有する化合物、硝酸塩、亜硝酸塩、モノフルオロリン酸塩、ジフルオロリン酸塩、酢酸塩及びプロピオン酸塩からなる群より選ばれた少なくとも１種以上の化合物を、該非水系電解液全体中に１０ｐｐｍ以上含有するものであり、かつ、該負極活物質が、配向性の異なる炭素質物を２種以上含有する異配向性炭素複合物を含有することを特徴とするリチウムイオン二次電池。
【化１】

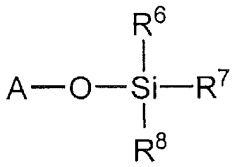


(1)

［一般式（１）中、Ｒ^{1}及びＲ^{2}は互いに同一であっても異なっていてもよい炭素数１～１２の有機基を表し、ｎは３～１０の整数を表す。］
【化２】

$$SiF_xR^3_pR^4_qR^5_r \qquad (2)$$

［一般式（２）中、Ｒ^{3}～Ｒ^{5}は互いに同一であっても異なっていてもよい炭素数１～１２の有機基を表し、ｘは１～３の整数を表し、ｐ、ｑ及びｒはそれぞれ０～３の整数を表し、$1 \leqq p+q+r \leqq 3$である。］
【化３】



(3)

［一般式（３）中、Ｒ^{6}～Ｒ^{8}は互いに同一であっても異なっていてもよい炭素数１～１２の有機基を表し、ＡはＨ、Ｃ、Ｎ、Ｏ、Ｆ、Ｓ、Ｓｉ及び／又はＰから構成される基を表す。］
【請求項２】
異配向性炭素複合物が、配向性の異なる炭素質物が付着及び／又は結合されてなる界面を有し、該界面の炭素質物の配向性が不連続及び／又は連続的に変化するものである請求項１に記載のリチウムイオン二次電池。
【請求項３】
異配向性炭素複合物の円形度が０．１以上である請求項１又は請求項２に記載のリチウムイオン二次電池。
【請求項４】
異配向性炭素複合物のラマンスペクトル法によるラマンＲ値が０．３５以下である請求項１ないし請求項３の何れかの請求項に記載のリチウムイオン二次電池。
【請求項５】
異配向性炭素複合物のタップ密度が０．５５ｇ／ｃｍ^{3}以上である請求項１ないし請求

項４の何れかの請求項に記載のリチウムイオン二次電池。
【請求項６】
異配向性炭素複合物の比表面積が０．１m^2／ｇ以上１００m^2／ｇ以下である請求項１ないし請求項５の何れかの請求項に記載のリチウムイオン二次電池。
【請求項７】
異配向性炭素複合物の体積基準平均粒径が１μｍ以上５０μｍ以下である請求項１ないし請求項６の何れかの請求項に記載のリチウムイオン二次電池。
【請求項８】
配向性の異なる炭素質物の少なくとも１種が、天然黒鉛（Ｄ）に由来する黒鉛系炭素質物（Ｂ）である請求項１ないし請求項７の何れかの請求項に記載のリチウムイオン二次電池。
【請求項９】
天然黒鉛（Ｄ）に由来する黒鉛系炭素質物（Ｂ）の含有量が、異配向性炭素複合物に対して、５質量％以上９９．９質量％以下である請求項８に記載のリチウムイオン二次電池。
【請求項１０】
配向性の異なる炭素質物の少なくとも１種が、以下の（１）ないし（５）からなる群より選ばれた炭素質物（Ｃ）である請求項１ないし請求項９の何れかの請求項に記載のリチウムイオン二次電池。
（１）石炭系コークス、石油系コークス、ファーネスブラック、アセチレンブラック及びピッチ系炭素繊維からなる群より選ばれた炭化物
（２）ピッチ原料、芳香族炭化水素、Ｎ環化合物、Ｓ環化合物、ポリフェニレン、有機合成高分子、天然高分子、熱可塑性樹脂及び熱硬化性樹脂からなる群より選ばれた有機物及び／又はその熱分解物を前駆体とする炭化物
（３）（２）の有機物を低分子有機溶媒に溶解させた溶液の熱分解物を前駆体とする炭化物
（４）有機物を含有する気体の炭化物
（５）（１）ないし（４）の黒鉛化物
【請求項１１】
炭素質物（Ｃ）の含有量が、異配向性炭素複合物に対して、０．１質量％以上である請求項１０に記載のリチウムイオン二次電池。
【請求項１２】
異配向性炭素複合物が、天然黒鉛（Ｄ）に由来する黒鉛系炭素質物（Ｂ）の１種以上と、炭素質物（Ｃ）の１種以上とを含有する請求項１ないし請求項１１の何れかの請求項に記載のリチウムイオン二次電池。
【請求項１３】
異配向複合炭素質物が、４００～３４００℃で１回以上熱処理する工程を経て得られたものである請求項１ないし請求項１２の何れかの請求項に記載のリチウムイオン二次電池。
【請求項１４】
該非水系電解液が、一般式（１）で表される環状シロキサン化合物、一般式（２）で表されるフルオロシラン化合物、一般式（３）で表される化合物、分子内にＳ－Ｆ結合を有する化合物、硝酸塩、亜硝酸塩、モノフルオロリン酸塩、ジフルオロリン酸塩、酢酸塩及びプロピオン酸塩からなる群より選ばれた少なくとも１種以上の化合物を、非水系電解液全体中に０．０１質量％以上、５質量％以下含有するものである請求項１ないし請求項１３の何れかの請求項に記載のリチウムイオン二次電池。
【請求項１５】
二次電池の外装の表面積に対する正極の電極面積の総和が、面積比で２０倍以上である請求項１ないし請求項１４の何れかの請求項に記載のリチウムイオン二次電池。
【請求項１６】

二次電池の直流抵抗成分が、１０ミリオーム（ｍΩ）以下である請求項１ないし請求項１５の何れかの請求項に記載のリチウムイオン二次電池。
【請求項１７】
二次電池の１個の電池外装に収納される電池要素のもつ電気容量が、３アンペアーアワー（Ａｈ）以上である請求項１ないし請求項１６の何れかの請求項に記載のリチウムイオン二次電池。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、リチウムイオン二次電池に関するものであり、更に詳細には、特定の非水系電解液と、特定の負極活物質を有するリチウムイオン二次電池に関するものである。
【背景技術】
【０００２】
情報関連機器、通信機器の分野では、パソコン、ビデオカメラ、携帯電話等の小型化に伴い、これらの機器に用いる電源として、高エネルギー密度であるという点から、リチウムイオン二次電池が実用化され広く普及するに至っている。
【０００３】
近年では、上記の分野に加えて、自動車の分野においても、特に、環境問題、資源問題を背景に開発が急がれている電気自動車用の電源としての利用を中心に、リチウムイオン二次電池が検討されている。
【０００４】
リチウムイオン二次電池のうち、金属リチウムを負極とする二次電池は、高容量化を達成できる電池として古くから盛んに研究が行われている。しかし、これらの電池には、金属リチウムが充放電の繰り返しによりデンドライト状に成長し、最終的に正極に達して電池内部において短絡が生じてしまうという問題があり、この問題は金属リチウムイオン二次電池を実用化する際の最大の技術的な課題となっている。
【０００５】
そこで負極に、例えば、コークス、人造黒鉛、天然黒鉛等のリチウムイオンを吸蔵及び放出することが可能な炭素質材料を用いたリチウムイオン二次電池が提案されている。このようなリチウムイオン二次電池では、リチウムが金属状態で存在しないためデンドライトの形成が抑制され、電池寿命と安全性を向上することができる。特に、人造黒鉛や天然黒鉛等の黒鉛系炭素質材料は、単位体積当たりのエネルギー密度を向上させることができる材料として期待されている。
【０００６】
しかしながら、黒鉛系の種々の電極材料を単独で、あるいはリチウムを吸蔵及び放出することが可能な他の負極材料と混合して負極としたリチウムイオン二次電池に、リチウム一次電池で一般に好んで使用されるプロピレンカーボネートを主溶媒とする非水系電解液を用いると、黒鉛電極表面で溶媒の分解反応が激しく進行し、黒鉛電極へのスムーズなリチウムの吸蔵及び放出が不可能になる。
【０００７】
一方、エチレンカーボネートはこのような分解が少ないことから、リチウムイオン二次電池の非水系電解液の主溶媒として多用されているが、エチレンカーボネートを主溶媒としても、充放電過程において、電極表面で非水系電解液が分解するために充放電効率やサイクル特性の低下を招くといった問題がある。
【０００８】
更に電気自動車用電源としてリチウムイオン二次電池を使用する場合、山道や連続した坂道を登る場合に、充電容量が少ない領域での充放電が繰り返されることが多くなり、電池に対して大きな負担となることが予想される。
【０００９】
これまで、リチウムイオン二次電池の正極や負極の活物質を始めとする様々な電池の構

成要素について、数多くの技術が検討されており、負極活物質に関する技術としても、特願２００４－３５２０７の明細書には、所定範囲内のアスペクト比を有する黒鉛質及びそれとは配向性の異なる黒鉛質が複合化した黒鉛複合体粉末と、人造黒鉛粉末とを含有する黒鉛混合粉末を負極材料として用いることで、高い電極密度において、放電容量が大きく、充放電効率が高く、負荷特性に優れ、かつ、充電時の電極膨張が小さい、高性能のリチウムイオン二次電池を安定して効率的に製造できることが記載されている。しかしながら、この方法を用いても、低い充電深度での長期間充放電の繰り返しに対する特性を改善については十分とは言えなかった。

【００１０】

また、非水系電解液に関する技術としても、特許文献１には、リチウムイオン二次電池において、非水系電解液にモノフルオロリン酸リチウムやジフルオロリン酸リチウムを添加すると、電極界面に良質な被膜が形成されることにより、非水系電解液の分解が抑制されて、保存特性が向上した電池が得られることが記載されている。しかしながら、この方法を用いても、低い充電深度での長期間充放電の繰り返しに対する特性を改善については十分とは言えなかった。

【特許文献１】特開平１１－６７２７０号公報

【発明の開示】

【発明が解決しようとする課題】

【００１１】

本発明は、かかる背景技術に鑑みてなされたものであり、その課題は、低い充電深度での長期間充放電の繰り返しに対して、良好な性能を維持できるリチウムイオン二次電池を提供することにある。

【課題を解決するための手段】

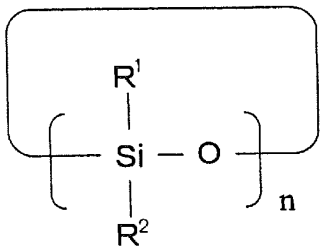
【００１２】

本発明者は、上記課題に鑑み鋭意研究した結果、特定の負極活物質と、特定の化合物を含有する非水系電解液とを組み合わせて用いることによって、低い充電深度での長期間充放電の繰り返しに対する特性が著しく向上することを見出し、本発明を完成した。

【００１３】

すなわち、本発明は、リチウム塩を含有する非水系電解液、負極活物質及び正極活物質を少なくとも有するリチウムイオン二次電池であって、該非水系電解液が、一般式（１）で表される環状シロキサン化合物、一般式（２）で表されるフルオロシラン化合物、一般式（３）で表される化合物、分子内にＳ－Ｆ結合を有する化合物、硝酸塩、亜硝酸塩、モノフルオロリン酸塩、ジフルオロリン酸塩、酢酸塩及びプロピオン酸塩からなる群より選ばれた少なくとも１種以上の化合物を、該非水系電解液全体中に１０ｐｐｍ以上含有するものであり、かつ、該負極活物質が、配向性の異なる炭素質物を２種以上含有する異配向性炭素複合物を含有することを特徴とするリチウムイオン二次電池を提供するものである。

【化４】



(1)

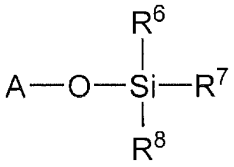
［一般式（１）中、Ｒ^{1}及びＲ^{2}は互いに同一であっても異なっていてもよい炭素数１～１２の有機基を表し、ｎは３～１０の整数を表す。］

【化５】

$$SiF_xR^3_pR^4_qR^5_r \qquad (2)$$

［一般式（２）中、Ｒ^{3}～Ｒ^{5}は互いに同一であっても異なっていてもよい炭素数１～１２の有機基を表し、ｘは１～３の整数を表し、ｐ、ｑ及びｒはそれぞれ０～３の整数を表し、１≦ｐ＋ｑ＋ｒ≦３である。］

【化６】



(3)

［一般式（３）中、Ｒ^{6}～Ｒ^{8}は互いに同一であっても異なっていてもよい炭素数１～１２の有機基を表し、ＡはＨ、Ｃ、Ｎ、Ｏ、Ｆ、Ｓ、Ｓｉ及び／又はＰから構成される基を表す。］

【発明の効果】

【００１４】

本発明によれば、低い充電深度での長期間充放電の繰り返しに対して、良好な性能を維持できるリチウムイオン二次電池の実現が可能である。

【発明を実施するための最良の形態】

【００１５】

以下、本発明の実施の形態について詳細に説明するが、以下に記載する構成要件の説明は、本発明の実施態様の一例（代表例）であり、これらの具体的内容に限定はされず、その要旨の範囲内で種々変形して実施することができる。

【００１６】

＜非水系電解液＞

本発明のリチウムイオン二次電池に用いられる非水系電解液は、リチウム塩及びこれを溶解する非水溶媒を含有する。

【００１７】

［リチウム塩］

リチウム塩としては、リチウムイオン二次電池用非水系電解液の電解質として用いられ得ることが知られているリチウム塩であれば特に制限はないが、例えば次のものが挙げられる。

【００１８】

無機リチウム塩：

ＬｉＰＦ$_{6}$、ＬｉＢＦ$_{4}$、ＬｉＡｓＦ$_{6}$、ＬｉＳｂＦ$_{6}$等の無機フッ化物塩；ＬｉＣｌＯ$_{4}$、ＬｉＢｒＯ$_{4}$、ＬｉＩＯ$_{4}$等の過ハロゲン酸塩；ＬｉＡｌＣｌ$_{4}$等の無機塩化物塩等。

含フッ素有機リチウム塩：

ＬｉＣＦ$_{3}$ＳＯ$_{3}$等のパーフルオロアルカンスルホン酸塩；ＬｉＮ（ＣＦ$_{3}$ＳＯ$_{2}$）$_{2}$、ＬｉＮ（ＣＦ$_{3}$ＣＦ$_{2}$ＳＯ$_{2}$）$_{2}$、ＬｉＮ（ＣＦ$_{3}$ＳＯ$_{2}$）（Ｃ$_{4}$Ｆ$_{9}$ＳＯ$_{2}$）等のパーフルオロアルカンスルホニルイミド塩；ＬｉＣ（ＣＦ$_{3}$ＳＯ$_{2}$）$_{3}$等のパーフルオロアルカンスルホニルメチド塩；Ｌｉ［ＰＦ$_{5}$（ＣＦ$_{2}$ＣＦ$_{2}$ＣＦ$_{3}$）］、Ｌｉ［ＰＦ$_{4}$（ＣＦ$_{2}$ＣＦ$_{2}$ＣＦ$_{3}$）$_{2}$］、Ｌｉ［ＰＦ$_{3}$（ＣＦ$_{2}$ＣＦ$_{2}$ＣＦ$_{3}$）$_{3}$］、Ｌｉ［ＰＦ$_{5}$（ＣＦ$_{2}$ＣＦ$_{2}$ＣＦ$_{2}$ＣＦ$_{3}$）］、Ｌｉ［ＰＦ$_{4}$（ＣＦ$_{2}$ＣＦ$_{2}$ＣＦ$_{2}$ＣＦ$_{3}$）$_{2}$］、Ｌｉ［ＰＦ$_{3}$（ＣＦ$_{2}$ＣＦ$_{2}$ＣＦ$_{2}$ＣＦ$_{3}$）$_{3}$］等のフルオロアルキルフッ化リン酸塩等。

オキサラトボレート塩：

リチウムジフルオロオキサラトボレート、リチウムビス（オキサラト）ボレート等。

【００１９】

これらは、１種を単独で使用しても、２種以上を任意の組み合わせ及び比率で併用しても良い。これらのなかでも、非水溶媒に対する溶解性、二次電池とした場合の充放電特性、出力特性、サイクル特性等を総合的に判断すると、$LiPF_6$、$LiBF_4$等が好ましく、$LiPF_6$が特に好ましい。

【００２０】

非水系電解液中の上記リチウム塩の濃度は、特に制限はないが、通常０．３ｍｏｌ／Ｌ以上、好ましくは０．６ｍｏｌ／Ｌ以上、より好ましくは０．７ｍｏｌ／Ｌ以上である。また、その上限は、通常２ｍｏｌ／Ｌ以下、好ましくは１．８ｍｏｌ／Ｌ以下、より好ましくは１．７ｍｏｌ／Ｌ以下である。濃度が低すぎると、非水系電解液の電気伝導率が不十分の場合があり、一方、濃度が高すぎると、粘度上昇のため電気伝導度が低下する場合があり、リチウムイオン二次電池の性能が低下する場合がある。

【００２１】

非水系電解液中には、リチウム塩として、含フッ素リチウム塩を含有することが好ましく、非水系電解液中の含フッ素リチウム塩の濃度は、特に制限はないが、０．５ｍｏｌ／Ｌ以上が好ましく、特に好ましくは０．７ｍｏｌ／Ｌ以上である。また、その上限は、２ｍｏｌ／Ｌ以下が好ましく、１．７ｍｏｌ／Ｌ以下が特に好ましい。濃度が低すぎると、非水系電解液の電気伝導率が不十分となる場合があり、一方、濃度が高すぎると、粘度上昇のため電気伝導度が低下して、リチウムイオン二次電池の性能が低下する場合がある。

【００２２】

リチウム塩は、１種を単独で使用しても、２種以上を任意の組み合わせ及び比率で併用しても良いが、リチウム塩を２種以上併用する場合の好ましい一例は、$LiPF_6$と$LiBF_4$との併用であり、この場合には、両者の合計に占める$LiBF_4$の割合が、０．０１質量％以上、２０質量％以下であることが特に好ましく、０．１質量％以上、５質量％以下であるのが更に好ましい。また、他の好ましい一例は、無機フッ化物塩とパーフルオロアルカンスルホニルイミド塩との併用であり、この場合には、両者の合計に占める無機フッ化物塩の割合は、７０質量％以上、９９質量％以下であることが特に好ましく、８０質量％以上、９８質量％以下であることがより更に好ましい。この両者の併用は、高温保存による劣化を抑制する効果がある。

【００２３】

［非水溶媒］

非水溶媒としても従来から非水系電解液の溶媒として提案されているものの中から、適宜選択して用いることができる。例えば、次のものが挙げられる。

１）環状カーボネート：

環状カーボネートを構成するアルキレン基の炭素数は２～６が好ましく、特に好ましくは２～４である。具体的には例えば、エチレンカーボネート、プロピレンカーボネート、ブチレンカーボネート等が挙げられる。中でも、エチレンカーボネート、プロピレンカーボネートが好ましい。

２）鎖状カーボネート：

鎖状カーボネートとしては、ジアルキルカーボネートが好ましく、構成するアルキル基の炭素数は、それぞれ、１～５が好ましく、特に好ましくは１～４である。具体的には例えば、ジメチルカーボネート、ジエチルカーボネート、ジ－ｎ－プロピルカーボネート等の対称鎖状カーボネート類；エチルメチルカーボネート、メチル－ｎ－プロピルカーボネート、エチル－ｎ－プロピルカーボネート等の非対称鎖状カーボネート類等のジアルキルカーボネートが挙げられる。中でも、ジメチルカーボネート、ジエチルカーボネート、エチルメチルカーボネートが好ましい。

３）環状エステル：

具体的には例えば、γ－ブチロラクトン、γ－バレロラクトン等が挙げられる。

４）鎖状エステル：

具体的には例えば、酢酸メチル、酢酸エチル、酢酸プロピル、プロピオン酸メチル等が挙げられる。

５）環状エーテル：
具体的には例えば、テトラヒドロフラン、２－メチルテトラヒドロフラン、テトラヒドロピラン等が挙げられる。
６）鎖状エーテル：
具体的には例えば、ジメトキシエタン、ジメトキシメタン等が挙げられる。
７）含硫黄有機溶媒：
具体的には例えば、スルフォラン、ジエチルスルホン等が挙げられる。
【００２４】
これらは単独で用いても、２種類以上を併用してもよいが、２種以上の化合物を併用することが好ましい。例えば、環状カーボネート類や環状エステル類等の高誘電率溶媒と、鎖状カーボネート類や鎖状エステル類等の低粘度溶媒とを併用するのが好ましい。
【００２５】
非水溶媒の好ましい組合せの一つは、環状カーボネート類と鎖状カーボネート類を主体とする組合せである。なかでも、非水溶媒に占める環状カーボネート類と鎖状カーボネート類との合計が、８５容量％以上、好ましくは９０容量％以上、より好ましくは９５容量％以上である。また、環状カーボネート類と鎖状カーボネート類との合計に対する環状カーボネート類の容量が５％以上、好ましくは１０％以上、より好ましくは１５％以上であり、通常５０％以下、好ましくは３５％以下、より好ましくは３０％以下のものである。非水溶媒全体に占めるカーボネート類の合計の上記好ましい容量範囲と、環状及び鎖状カーボネート類に対する環状カーボネート類の好ましい上記容量範囲は、組み合わされていることが特に好ましい。
【００２６】
環状カーボネート類と鎖状カーボネート類の好ましい組み合わせの具体例としては、エチレンカーボネートとジメチルカーボネート、エチレンカーボネートとジエチルカーボネート、エチレンカーボネートとエチルメチルカーボネート、エチレンカーボネートとジメチルカーボネートとジエチルカーボネート、エチレンカーボネートとジメチルカーボネートとエチルメチルカーボネート、エチレンカーボネートとジエチルカーボネートとエチルメチルカーボネート、エチレンカーボネートとジメチルカーボネートとジエチルカーボネートとエチルメチルカーボネート等が挙げられる。これらのエチレンカーボネートと鎖状カーボネート類との組み合わせに、更にプロピレンカーボネートを加えた組み合わせも、好ましい組み合わせとして挙げられる。プロピレンカーボネートを含有する場合には、エチレンカーボネートとプロピレンカーボネートの容量比は、９９：１～４０：６０が好ましく、特に好ましくは９５：５～５０：５０である。
【００２７】
これらの中で、非対称鎖状カーボネート類を含有するものが更に好ましく、特に、エチレンカーボネートとジメチルカーボネートとエチルメチルカーボネート、エチレンカーボネートとジエチルカーボネートとエチルメチルカーボネート、エチレンカーボネートとジメチルカーボネートとジエチルカーボネートとエチルメチルカーボネートといったエチレンカーボネートと対称鎖状カーボネート類と非対称鎖状カーボネート類を含有するものが、サイクル特性と大電流放電特性のバランスが良いので好ましい。中でも、非対称鎖状カーボネート類がエチルメチルカーボネートであるものが好ましく、また、ジアルキルカーボネートを構成するアルキル基の炭素数は１～２が好ましい。
【００２８】
好ましい非水溶媒の他の例は、鎖状エステルを含有するものである。特に、上記、環状カーボネート類と鎖状カーボネート類の混合溶媒に、鎖状エステルを含有するものが、電池の低温特性向上の観点から好ましく、鎖状エステルとしては，酢酸メチル、酢酸エチルが、特に好ましい。非水溶媒に占める鎖状エステルの容量は、通常５％以上、好ましくは８％以上、より好ましくは１５％以上であり、通常５０％以下、好ましくは３５％以下、より好ましくは３０％以下、更に好ましくは２５％以下である。
【００２９】

他の好ましい非水溶媒の例は、エチレンカーボネート、プロピレンカーボネート、γ－ブチロラクトン及びγ－バレロラクトンよりなる群から選ばれた１種の有機溶媒、又は該群から選ばれた２以上の有機溶媒からなる混合溶媒を全体の６０容量％以上を占めるものである。こうした混合溶媒は、引火点が５０℃以上であるものが好ましく、中でも７０℃以上であるものが特に好ましい。この溶媒を用いた非水系電解液は、高温で使用しても溶媒の蒸発や液漏れが少なくなる。中でも、非水溶媒に占めるγ－ブチロラクトンの量が６０容量％以上であるものや、非水溶媒に占めるエチレンカーボネートとγ－ブチロラクトンとの合計が、８０容量％以上、好ましくは９０容量％以上であり、かつエチレンカーボネートとγ－ブチロラクトンとの容量比が５：９５～４５：５５であるもの、又は非水溶媒に占めるエチレンカーボネートとプロピレンカーボネートとの合計が、８０容量％以上、好ましくは９０容量％以上であり、かつエチレンカーボネートとプロピレンカーボネートの容量比が３０：７０～６０：４０であるものを用いると、一般にサイクル特性と大電流放電特性等のバランスがよくなる。

【００３０】

［特定化合物］

本発明の非水系電解液は、一般式（１）で表される環状シロキサン化合物、一般式（２）で表されるフルオロシラン化合物、一般式（３）で表される化合物、分子内にＳ－Ｆ結合を有する化合物、硝酸塩、亜硝酸塩、モノフルオロリン酸塩、ジフルオロリン酸塩、酢酸塩及びプロピオン酸塩からなる群より選ばれた少なくとも１種以上の化合物（以下、これらを「特定化合物」と略記することがある）を、１０ｐｐｍ以上含有することを特徴とする。

【００３１】

かかる特定化合物が含有された非水系電解液と、配向性の異なる炭素質物を２種以上含有する異配向性炭素複合物を含有する負極活物質とを組み合わせることによって、更には、かかる特定化合物が含有された非水系電解液と、結晶性の異なる炭素質物を２種以上含有する異配向性炭素複合物を含有する負極活物質とを組み合わせることによって、低い充電深度での長期間充放電の繰り返しに対する特性を改善する効果がある。

【００３２】

[[一般式（１）で表される環状シロキサン化合物]]

一般式（１）で表される環状シロキサン化合物におけるR^1及びR^2は互いに同一であっても異なっていてもよい炭素数１～１２の有機基であるが、R^1及びR^2としては、メチル基、エチル基、ｎ－プロピル基、イソプロピル基、ブチル基、イソブチル基、ｓｅｃ－ブチル基、ｔ－ブチル基等の鎖状アルキル基；シクロヘキシル基、ノルボルニル基等の環状アルキル基；ビニル基、１－プロペニル基、アリル基、ブテニル基、１，３－ブタジエニル基等のアルケニル基；エチニル基、プロピニル基、ブチニル基等のアルキニル基；トリフルオロメチル基等のハロゲン化アルキル基；３－ピロリジノプロピル基等の飽和複素環基を有するアルキル基；アルキル置換基を有していてもよいフェニル基等のアリール基；フェニルメチル基、フェニルエチル基等のアラルキル基；トリメチルシリル基等のトリアルキルシリル基；トリメチルシロキシ基等のトリアルキルシロキシ基等が挙げられる。

【００３３】

中でも、炭素数が少ないものの方が特性が発現しやすく、炭素数１～６の有機基が好ましい。また、アルケニル基は非水系電解液や電極表面の被膜に作用して入出力特性を向上させ、アリール基は充放電時に電池内で発生するラジカルを捕捉して電池性能全般を向上させる作用を有するので好ましい。従って、R^1及びR^2としては、メチル基、ビニル基又はフェニル基が特に好ましい。

【００３４】

一般式（１）中、ｎは３～１０の整数を表すが、３～６の整数が好ましく、３又は４が特に好ましい。

【００３５】

一般式（１）で表される環状シロキサン化合物の例としては、例えば、ヘキサメチルシクロトリシロキサン、ヘキサエチルシクロトリシロキサン、ヘキサフェニルシクロトリシロキサン、１，３，５－トリメチル－１，３，５－トリビニルシクロトリシロキサン等のシクロトリシロキサン、オクタメチルシクロテトラシロキサン等のシクロテトラシロキサン、デカメチルシクロペンタシロキサン等のシクロペンタシロキサン等が挙げられる。このうち、シクロトリシロキサンが特に好ましい。

【００３６】

[[一般式（２）で表されるフルオロシラン化合物]]

一般式（２）で表されるフルオロシラン化合物におけるR^3～R^5は、互いに同一であっても異なっていてもよい炭素数１～１２の有機基であるが、一般式（１）におけるR^1及びR^2の例として挙げた鎖状アルキル基、環状アルキル基、アルケニル基、アルキニル基、ハロゲン化アルキル基、飽和複素環基を有するアルキル基、アルキル基を有していてもよいフェニル基等のアリール基、アラルキル基、トリアルキルシリル基、トリアルキルシロキシ基に加え、エトキシカルボニルエチル基等のカルボニル基；アセトキシ基、アセトキシメチル基、トリフルオロアセトキシ基等のカルボキシル基；メトキシ基、エトキシ基、プロポキシ基、ブトキシ基、フェノキシ基、アリロキシ基等のオキシ基；アリルアミノ基等のアミノ基；ベンジル基等を挙げることができる。

【００３７】

一般式（２）中、ｘは１～３の整数を表し、ｐ、ｑ及びｒはそれぞれ０～３の整数を表し、$1 \leqq p+q+r \leqq 3$である。また必然的に、ｘ＋ｐ＋ｑ＋ｒ＝４である。

【００３８】

一般式（２）で表されるフルオロシラン化合物の例としては、トリメチルフルオロシラン、トリエチルフルオロシラン、トリプロピルフルオロシラン、フェニルジメチルフルオロシラン、トリフェニルフルオロシラン、ビニルジメチルフルオロシラン、ビニルジエチルフルオロシラン、ビニルジフェニルフルオロシラン、トリメトキシフルオロシラン、トリエトキシフルオロシラン等のモノフルオロシラン類の他、ジメチルジフルオロシラン、ジエチルジフルオロシラン、ジビニルジフルオロシラン、エチルビニルジフルオロシラン等のジフルオロシラン類；メチルトリフルオロシラン、エチルトリフルオロシラン等のトリフルオロシラン類も挙げられる。

【００３９】

一般式（２）で表されるフルオロシラン化合物は、沸点が低いと、揮発してしまうため非水系電解液に所定量含有させるのが難しくなる場合がある。また、非水系電解液に含有させた後も、充放電による電池の発熱や外部環境が高温になる様な条件下で揮発してしまう可能性がある。よって、１気圧で、５０℃以上の沸点を持つものが好ましく、中でも６０℃以上の沸点を持つものが特に好ましい。

【００４０】

また、一般式（１）の化合物と同様に、有機基としては炭素数の少ないものの方が効果が発現しやすく、炭素数１～６のアルケニル基は非水系電解液や電極表面の被膜に作用して入出力特性を向上させ、アリール基は充放電時に電池内で発生するラジカルを捕捉して電池性能全般を向上させる作用を有する。従って、この観点からは有機基としては、メチル基、ビニル基又はフェニル基が好ましく、化合物の例としては、トリメチルフルオロシラン、ビニルジメチルフルオロシラン、フェニルジメチルフルオロシラン、ビニルジフェニルフルオロシラン等が特に好ましい。

【００４１】

[[一般式（３）で表される化合物]]

一般式（３）で表される化合物におけるR^6～R^8は、互いに同一であっても異なっていてもよい炭素数１～１２の有機基であるが、その例としては、一般式（２）のR^3～R^5の例として挙げた鎖状アルキル基、環状アルキル基、アルケニル基、アルキニル基、ハロゲン化アルキル基、飽和複素環基を有するアルキル基、アルキル基を有していてもよいフェニル基等のアリール基、アラルキル基、トリアルキルシリル基、トリアルキルシロキ

シ基、カルボニル基、カルボキシル基、オキシ基、アミノ基、ベンジル基等を同様に挙げることができる。

【００４２】

一般式（３）で表される化合物におけるＡは、II、Ｃ、Ｎ、Ｏ、Ｆ、Ｓ、Ｓｉ及び／又はＰから構成される基であれば特に制限はないが、一般式（３）中の酸素原子に直接結合する元素としては、Ｃ、Ｓ、Ｓｉ又はＰが好ましい。これら原子の存在形態としては、例えば、鎖状アルキル基、環状アルキル基、アルケニル基、アルキニル基、ハロゲン化アルキル基、カルボニル基、スルホニル基、トリアルキルシリル基、ホスホリル基、ホスフィニル基等に含まれるものが好ましい。また、一般式（３）で表される化合物の分子量は、１０００以下が好ましく、中でも８００以下が特に好ましく、５００以下が更に好ましい。

【００４３】

一般式（３）で表される化合物の例としては、ヘキサメチルジシロキサン、１，３－ジエチルテトラメチルジシロキサン、ヘキサエチルジシロキサン、オクタメチルトリシロキサン等のシロキサン化合物類；メトキシトリメチルシラン、エトキシトリメチルシラン等のアルコキシシラン類；ビス（トリメチルシリル）パーオキサイド等の過酸化物類；酢酸トリメチルシリル、酢酸トリエチルシリル、プロピオン酸トリメチルシリル、メタクリル酸トリメチルシリル、トリフルオロ酢酸トリメチルシリル等のカルボン酸エステル類；メタンスルホン酸トリメチルシリル、エタンスルホン酸トリメチルシリル、メタンスルホン酸トリエチルシリル、フルオロメタンスルホン酸トリメチルシリル等のスルホン酸エステル類；ビス（トリメチルシリル）スルフェート等の硫酸エステル類；トリス（トリメチルシロキシ）ボロン等のホウ酸エステル類；トリス（トリメチルシリル）ホスフェート、トリス（トリメチルシリル）ホスファイト等のリン酸若しくは亜リン酸エステル類等が挙げられる。

【００４４】

このうち、シロキサン化合物類、スルホン酸エステル類、硫酸エステル類が好ましく、スルホン酸エステル類が特に好ましい。シロキサン化合物類としては、ヘキサメチルジシロキサンが好ましく、スルホン酸エステル類としては、メタンスルホン酸トリメチルシリルが好ましく、硫酸エステル類としては、ビス（トリメチルシリル）スルフェートが好ましい。

【００４５】

[[分子内にＳ－Ｆ結合を有する化合物]]

分子内にＳ－Ｆ結合を有する化合物としては特に限定はないが、スルホニルフルオライド類、フルオロスルホン酸エステル類が好ましい。例えば、メタンスルホニルフルオライド、エタンスルホニルフルオライド、メタンビス（スルホニルフルオライド）、エタン－１，２－ビス（スルホニルフルオライド）、プロパン－１，３－ビス（スルホニルフルオライド）、ブタン－１，４－ビス（スルホニルフルオライド）、ジフルオロメタンビス（スルホニルフルオライド）、１，１，２，２－テトラフルオロエタン－１，２－ビス（スルホニルフルオライド）、１，１，２，２，３，３－ヘキサフルオロプロパン－１，３－ビス（スルホニルフルオライド）、フルオロスルホン酸メチル、フルオロスルホン酸エチル等が挙げられる。中でも、メタンスルホニルフルオライド、メタンビス（スルホニルフルオライド）又はフルオロスルホン酸メチルが好ましい。

【００４６】

[[硝酸塩、亜硝酸塩、モノフルオロリン酸塩、ジフルオロリン酸塩、酢酸塩、プロピオン酸塩]]

硝酸塩、亜硝酸塩、モノフルオロリン酸塩、ジフルオロリン酸塩、酢酸塩、プロピオン酸塩のカウンターカチオンとしては特に限定はないが、Ｌｉ、Ｎａ、Ｋ、Ｍｇ、Ｃａ、Ｆｅ、Ｃｕ等の金属元素の他、$NR^{9}R^{10}R^{11}R^{12}$（式中、R^{9}～R^{12}は、各々独立に、水素原子又は炭素数１～１２の有機基を表わす。）で表現されるアンモニウム、４級アンモニウムが挙げられる。ここで、R^{9}～R^{12}の炭素数１～１２の有機基としては、ハロゲン原

メチル、硫酸エチレン、スルホラン、ジメチルスルホン、ジエチルスルホン、ジメチルスルホキシド、ジエチルスルホキシド、テトラメチレンスルホキシド、ジフェニルスルフィド、チオアニソール、ジフェニルジスルフィド、ジピリジニウムジスルフィド等の正極保護剤；
等が挙げられる。

【００５１】

過充電防止剤としては、ビフェニル、アルキルビフェニル、ターフェニル、ターフェニルの部分水素化体、シクロヘキシルベンゼン、ｔ－ブチルベンゼン、ｔ－アミルベンゼン、ジフェニルエーテル、ジベンゾフラン等の芳香族化合物が好ましい。これらは２種類以上併用して用いてもよい。２種以上併用する場合は、特に、シクロヘキシルベンゼンやターフェニル（又はその部分水素化体）と、ｔ－ブチルベンゼンやｔ－アミルベンゼンを併用するのが好ましい。

【００５２】

負極被膜形成剤としては、ビニレンカーボネート、ビニルエチレンカーボネート、フルオロエチレンカーボネート、無水コハク酸、無水マレイン酸が好ましい。これらは２種類以上併用して用いてもよい。正極保護剤としては、亜硫酸エチレン、亜硫酸プロピレン、プロパンスルトン、ブタンスルトン、メタンスルホン酸メチル、ブスルファンが好ましい。これらは２種類以上併用して用いてもよい。また、負極皮膜形成剤と正極保護剤との併用や、過充電防止剤と負極皮膜形成剤と正極保護剤との併用が特に好ましい。

【００５３】

非水系電解液中におけるこれら他の化合物の含有割合は特に限定はないが、非水系電解液全体に対し、それぞれ、０．０１質量％以上が好ましく、特に好ましくは０．１質量％以上、更に好ましくは０．２質量％以上であり、上限は、５質量％以下が好ましく、特に好ましくは３質量％以下、更に好ましくは２質量％以下である。これらの化合物を添加することにより、過充電による異常時に電池の破裂・発火を抑制したり、高温保存後の容量維持特性やサイクル特性を向上させたりすることができる。

【００５４】

＜負極＞

以下に本発明のリチウムイオン二次電池に使用される負極について説明する。

[負極活物質]

以下に負極に使用される負極活物質について述べる。

【００５５】

[[異配向性炭素複合物の構成]]

負極活物質としては、電気化学的にリチウムイオンを吸蔵・放出可能なものが用いられる。本発明のリチウムイオン二次電池における負極活物質は、配向性が異なる炭素質を２種以上含有する異配向性炭素複合物を含有する。

【００５６】

ここで、「配向性が異なる」とは、偏光顕微鏡で粉末を観察した際に、光学的異方性組織の異方性単位のパターン、すなわち、異方性単位の大きさ、方向、数等を目視し対比した場合に、それらの大きさ、方向、数等のうち少なくとも何れかが異なることをいう。例えば、炭素質１及び炭素質２のうち、一方が一方向への結晶方向性を有し、他方がランダムな結晶方向性を有する場合や、炭素質１及び炭素質２が共に各々一定の方向への結晶方向性を有し、その方向が異なっている場合等が挙げられる。なお、炭素質１及び炭素質２の一方又は双方が、単一の結晶ではなく、複数の結晶の集合体である場合には、集合体の単位を１領域として、その光学的異方性組織の異方性単位の集合パターンを対比する。

【００５７】

更に、異配向性炭素複合物中の、炭素質１、炭素質２共存の形態は、１つの二次粒子中に含まれていることが好ましい。ここで言う「１つの二次粒子中に含まれている」とは、配向性の異なる炭素質物が物理的に拘束、付着された状態、静電的な拘束、付着によって形状を維持している状態、結合によって拘束された状態等をいう。ここでいう「物理的な

子で置換されていてもよいアルキル基、ハロゲン原子で置換されていてもよいシクロアルキル基、ハロゲン原子で置換されていてもよいアリール基、窒素原子含有複素環基等が挙げられる。R^9～R^{12}としては、それぞれ、水素原子、アルキル基、シクロアルキル基、窒素原子含有複素環基等が好ましい。これらのカウンターカチオン中でも、リチウムイオン二次電池に用いたときの電池特性の点から、リチウム、ナトリウム、カリウム、マグネシウム、カルシウム又は$NR^9R^{10}R^{11}R^{12}$が好ましく、リチウムが特に好ましい。また、中でも、硝酸塩又はジフルオロリン酸塩が、出力向上効果が大きい上、電池のサイクル、高温保存特性の点で好ましく、ジフルオロリン酸リチウムが特に好ましい。また、これらの化合物は非水溶媒中で合成されたものを実質的にそのまま用いてもよく、別途合成して実質的に単離されたものを非水溶媒中又は非水系電解液中に添加してもよい。

【００４７】

特定化合物、すなわち、一般式（１）で表される環状シロキサン化合物、一般式（２）で表されるフルオロシラン化合物、一般式（３）で表される化合物、分子内にＳ－Ｆ結合を有する化合物、硝酸塩、亜硝酸塩、モノフルオロリン酸塩、ジフルオロリン酸塩、酢酸塩又はプロピオン酸塩は、１種を単独で用いてもよく、２種類以上の化合物を任意の組み合わせ及び比率で併用してもよい。また、特定化合物で、上記それぞれに分類される化合物の中であっても、１種を単独で用いてもよく、２種類以上の化合物を任意の組み合わせ及び比率で併用してもよい。

【００４８】

非水系電解液中のこれら特定化合物の割合は、全非水系電解液に対して、合計で１０ｐｐｍ以上（０．００１質量％以上）が必須であるが、好ましくは０．０１質量％以上、より好ましくは０．０５質量％以上、更に好ましくは０．１質量％以上である。また、上限は、好ましくは５質量％以下、より好ましくは４質量％以下、更に好ましくは３質量％以下である。特定化合物の濃度が低すぎると、長期間使用した後でも、出力特性が維持される効果が得られ難い場合があり、一方、濃度が高すぎると充放電効率の低下を招く場合がある。

【００４９】

また、これら特定化合物は、非水系電解液として実際に二次電池作製に供すると、その電池を解体して再び非水系電解液を取り出しても、その中の含有量が著しく低下している場合が多い。そのため、電池から抜き出した非水系電解液から、少なくとも上記特定化合物が検出できるものは本発明に含まれるとみなされる。

【００５０】

［他の化合物］

本発明のリチウムイオン二次電池における非水系電解液は、電解質であるリチウム塩及び特定化合物を必須成分として含有するが、必要に応じて他の化合物を、本発明の効果を損なわない範囲で、任意の量で含有させることができる。このような他の化合物としては、具体的には、例えば、

（１）ビフェニル、アルキルビフェニル、ターフェニル、ターフェニルの部分水素化体、シクロヘキシルベンゼン、ｔ－ブチルベンゼン、ｔ－アミルベンゼン、ジフェニルエーテル、ジベンゾフラン等の芳香族化合物；２－フルオロビフェニル、ｏ－シクロヘキシルフルオロベンゼン、ｐ－シクロヘキシルフルオロベンゼン等の前記芳香族化合物の部分フッ素化物；２，４－ジフルオロアニソール、２，５－ジフルオロアニソール、２，６－ジフルオロアニソール、３，５－ジフルオロアニソール等の含フッ素アニソール化合物等の過充電防止剤；

（２）ビニレンカーボネート、ビニルエチレンカーボネート、フルオロエチレンカーボネート、トリフルオロプロピレンカーボネート、無水コハク酸、無水グルタル酸、無水マレイン酸、無水シトラコン酸、無水グルタコン酸、無水イタコン酸、シクロヘキサンジカルボン酸無水物等の負極被膜形成剤；

（３）亜硫酸エチレン、亜硫酸プロピレン、亜硫酸ジメチル、プロパンスルトン、ブタンスルトン、メタンスルホン酸メチル、ブスルファン、トルエンスルホン酸メチル、硫酸ジ

拘束、付着」とは、炭素質物の一方が他方に巻き込まれたような状態、引っかかっている状態を示し、「静電的な拘束、付着」とは、炭素質物の一方が他方に、静電的なエネルギーによって付着している状態をいう。この拘束、付着した状態において、前述の配向性が異なる状態となっていれば、元の炭素質物が同等のものであっても構わない。また、「結合によって拘束された状態」とは、水素結合、共有結合、イオン結合等の化学的な結合を意味する。

【００５８】

この中でも、一方の炭素質物の表面の少なくとも一部に、付着及び／又は結合によって、他方の炭素質物が、配向性の異なる界面を有している状態が好ましい。界面を有していることによって、界面を有していない場合に比べて、同一形状の粒子で比較すると、充電時にリチウムがインターカレーションして起こる膨張が、多方面に分散されて、電池劣化を防止できる点で好ましい。

【００５９】

該配向性の異なる部分の形成が、外部から供給された材料及び／又はこれらの変質物との結合によるか、或いは、炭素質物の表面部の材料の変質によるかは問わない。ここで、被覆とは、炭素質物の表面との界面中の少なくとも一部に化学結合を有し、（１）表面全体を覆っている状態、（２）炭素質粒子の局所的に覆っている状態、（３）表面一部を選択的に覆っている状態、（４）化学結合を含む極微小領域に存在している状態を示す。

【００６０】

また、界面近傍では炭素質物の配向性が連続的に変化していても、不連続で変化していても構わない。すなわち、異配向性炭素複合物が、配向性の異なる炭素質物が付着及び／又は結合されてなる界面を有し、該界面の炭素質物の配向性が不連続及び／又は連続的に変化するものであることが好ましい。

【００６１】

また、異配向性炭素質複合物（Ａ）の構成成分としては、結晶性を有していれば特に限定はないが、配向性の異なる炭素質物の１種以上が、天然黒鉛（Ｄ）に由来する黒鉛系炭素質物（Ｂ）（以下、「天然黒鉛系炭素質物（Ｂ）」と略記する）であることが、質量当たりの充電容量が高くなる点で好ましい。

【００６２】

更には、異配向性炭素複合物中に含有される天然黒鉛系炭素質物（Ｂ）の割合は、異配向性炭素複合物に対して、通常５質量％以上、好ましくは２０質量％以上、より好ましくは３０質量％以上、更に好ましくは４０質量％以上、特に好ましくは５０質量％以上の範囲である。上限は、通常９９．９質量％以下、好ましくは９９質量％以下、より好ましくは９５質量％以下、更に好ましくは９０質量％以下の範囲である。この範囲を下回ると、電極の圧延時の荷重が著しく上昇し、電極の剥離等が起こる場合がある。一方この範囲を上回ると、配向性の異なる粒子の複合体としての界面の結着が弱くなる場合がある。

【００６３】

また、異配向性炭素複合物の他の構成成分としては、配向性の異なる炭素質の１種以上が、以下の（１）ないし（５）から選択される炭素質物（Ｃ）であることも、異配向性炭素複合物調製時の界面生成及び界面の結着性向上の観点から好ましい。

（１）石炭系コークス、石油系コークス、ファーネスブラック、アセチレンブラック及びピッチ系炭素繊維からなる群より選ばれた炭化物

（２）ピッチ原料、芳香族炭化水素、Ｎ環化合物、Ｓ環化合物、ポリフェニレン、有機合成高分子、天然高分子、熱可塑性樹脂及び熱硬化性樹脂からなる群より選ばれた有機物及び／又はその熱分解物を前駆体とする炭化物

（３）（２）の有機物を低分子有機溶媒に溶解させた溶液の熱分解物を前駆体とする炭化物

（４）有機物を含有する気体の炭化物

（５）（１）ないし（４）の黒鉛化物

【００６４】

（２）については、炭素化できるものであれば特には限定はないが、ピッチ原料、アセナフチレン、デカシクレン、アントラセン、フェナントレン等の芳香族炭化水素；フェナジン、アクリジン等のＮ環化合物；チオフェン、ビチオフェン等のＳ環化合物；ビフェニル、テルフェニル等のポリフェニレン；ポリ塩化ビニル、ポリビニルアルコール、ポリビニルブチラール、これらのものの不溶化処理品、含窒素性のポリアクニロニトリル、ポリピロール等の有機高分子；含硫黄性のポリチオフェン、ポリスチレン等の有機高分子；セルロース、リグニン、マンナン、ポリガラクトウロン酸、キトサン、サッカロースに代表される多糖類等の天然高分子；ポリフェニレンサルファイド、ポリフェニレンオキシド等の熱可塑性樹脂；フルフリルアルコール樹脂、フェノールーホルムアルデヒド樹脂、イミド樹脂等の熱硬化性樹脂；又はこれらをベンゼン、トルエン、キシレン、キノリン、ｎ－ヘキサン等の低分子有機溶媒に溶解させた溶液等の有機物；炭化可能な気体等が挙げられる。

【００６５】

これらの中で、ピッチ原料は残炭率が高いことから、収率の高い材料を作製することが可能であり好ましい。なお、本明細書において「ピッチ原料」とは、ピッチ及びそれに順ずるものであり、適当な処理を行なうことによって炭素化及び又は黒鉛化することができるものをいう。具体的なピッチ原料の例としては、タールや重質油やピッチ等を用いることができる。タールの具体例としては、コールタール、石油系タール等が挙げられる。重質油の具体例としては、石油系重質油の接触分解油、熱分解油、常圧残油、減圧残油等が挙げられる。また、ピッチの具体例としては、コールタールピッチ、石油系ピッチ、合成ピッチ等が挙げられる。これらの中でもコールタールピッチが芳香族性に高く好ましい。これらのピッチ原料は、何れか１種を単独で用いても良く、２種以上を任意の組み合わせ及び比率で併用しても良い。

【００６６】

（３）については、上記（２）の有機物を、ベンゼン、トルエン、キシレン、キノリン、ｎ－ヘキサン等の低分子有機溶媒に溶解させた溶液の熱分解物を前駆体とする炭化物が、好ましいものとして挙げられる。

【００６７】

（４）については、メタン、エタン、プロパン、ベンゼン、アセチレン、エチレン等の炭化水素化合物、一酸化炭素等が例示される。

【００６８】

異配向性炭素複合物中に含有される炭素質物（Ｃ）の割合が、通常０．１質量％以上、好ましくは１質量％以上、より好ましくは５質量％以上、更に好ましくは１０質量％以上の範囲である。上限は特にはなく、配向性が異なる界面を有していれば問題ない。この範囲を下回ると、異配向性炭素複合物中の界面の結着が弱くなる場合がある。また、この範囲を下回ると、炭素質物（Ｃ）を含有することによる、プレス時の粒子変形抑制の効果が減少し、サイクル特性が低下する場合がある。

【００６９】

本発明のリチウムイオン二次電池に用いられる負極活物質の更に好ましい構成としては、電極圧延時のプレス荷重の観点及び、複合体としての界面の結着性のバランスの点から、異配向性炭素複合物が、１種以上の天然黒鉛系炭素質物（Ｂ）と１種以上の炭素質物（Ｃ）を同時に含有していることが好ましい。

【００７０】

前述の理由と同様の理由で、異配向性炭素複合物中の天然黒鉛系炭素質物（Ｂ）と炭素質物（Ｃ）の質量比率（天然黒鉛系炭素質物（Ｂ）／炭素質物（Ｃ））は、通常２０／８０以上、好ましくは４０／６０以上、更に好ましくは６０／４０以上、より好ましくは７０／３０以上の範囲である。上限としては９９．９／０．１以下、好ましくは９９／１以下、より好ましくは９５／５以下の範囲である。この範囲を上回ると（天然黒鉛系炭素質物（Ｂ）の比率が大きすぎると）、炭素質物（Ｃ）による界面の結着性が低下する可能性がある。一方この範囲を下回ると（天然黒鉛系炭素質物（Ｂ）の比率が小さすぎると）電

極圧延時のプレス荷重が著しく大きくなり、圧延時に剥離する場合がある。

【００７１】

天然黒鉛系炭素質物（Ｂ）及び炭素質物（Ｃ）を含有する異配向性炭素複合物としては、本発明の主旨を超えない範囲であれば、任意の様態と取ることが可能であるが、一例を以下に示す。

（イ）天然黒鉛系炭素質物（Ｂ）の表面全体又は一部が、炭素質物（Ｃ）が付着及び／又は被覆及び／又は結合された形態。

（ロ）天然黒鉛系炭素質物（Ｂ）の表面全体又は一部に、炭素質物（Ｃ）が結着し、２個以上の天然黒鉛系炭素質物（Ｂ）及び／又は炭素質物（Ｃ）が複合化した形態。

（ハ）上記（イ）及び（ロ）が任意の割合で混合した形態。

【００７２】

また、上記の天然黒鉛系炭素質物（Ｂ）が炭素質物（Ｃ）と入れ替わっても良い。また、その異配向性炭素複合物の具体的な複合の様態としては、核となる粒子の表面に、配向性の異なる炭素質が付着及び／又は被覆及び／又は結合された状態、又はこれらの複数が付着及び／又は被覆及び／又は結合された形態、核となる粒子が非平行に造粒したような状態等が挙げられる。ここでいう非平行に造粒した状態とは、一定の結晶性を有する粒子がランダムな方向を向いた状態で、他の炭素質物で固定され、異配向性を示す結合をもった状態となっているものを指す。

【００７３】

[[異配向性炭素複合物の調製]]

異配向性炭素複合物の調製については、「異配向性炭素複合物の製造方法１及び製造方法２」の箇所で後述するが、異配向性炭素複合物の調製に際しては、熱処理を加えることで結晶性の向上を図ることが可能となり、単位重量当たりの容量を増加させることが可能である。熱処理温度としては通常４００℃以上、好ましくは１０００℃以上、より好ましくは２０００℃以上、更に好ましくは２４００℃以上、特に好ましくは２８００℃以上の範囲である。上限としては、通常３４００℃以下、好ましくは３２００℃以下の範囲である。この範囲を下回ると、結晶性が十分向上しておらず、単位重量当たりの容量の増加の効果が得られない可能性がある。一方この範囲を上回ると、炭素の昇華による損失が無視できなくなり、収率の減少が起こる可能性がある。

【００７４】

[[異配向性炭素複合物の性質]]

異配向性炭素複合物についての性質については、次に示す（１）～（５）の何れか１項又は複数項を同時に満たしていることが好ましい。

【００７５】

（１）円形度

異配向性炭素複合物の球形の程度としては、その粒径が３～４０μｍの範囲にある粒子の円形度は通常０．１以上、好ましくは０．５以上、より好ましくは０．８以上、更に好ましくは０．８５以上、最も好ましくは０．９以上である。円形度が大きいと高電流密度充放電特性が向上するため好ましい。円形度は以下の式で定義され、円形度が１のときに理論的真球となる。

円形度

＝（粒子投影形状と同じ面積を持つ相当円の周囲長）／（粒子投影形状の実際の周囲長）

【００７６】

円形度の値としては、例えば、フロー式粒子像分析装置（例えば、シスメックスインダストリアル社製ＦＰＩＡ）を用い、試料約０．２ｇを、界面活性剤であるポリオキシエチレン（２０）ソルビタンモノラウレートの０．２質量％水溶液（約５０ｍＬ）に分散させ、２８ｋＨｚの超音波を出力６０Ｗで１分間照射した後、検出範囲を０．６～４００μｍに指定し、粒径が３～４０μｍの範囲の粒子について測定した値を用いる。

【００７７】

円形度を向上させる方法は、特に限定されないが、球形化処理を施して球形にしたもの

が、電極体にしたときの粒子間空隙の形状が整うので好ましい。球形化処理の例としては、せん断力、圧縮力を与えることによって機械的に球形に近づける方法、複数の微粒子をバインダー若しくは、粒子自身の有する付着力によって造粒する機械的・物理的処理方法等が挙げられる。

【００７８】

（２）ラマンＲ値、ラマン半値幅

アルゴンイオンレーザーラマンスペクトル法を用いて測定した異配向性炭素複合物のラマンＲ値は、通常０．０１以上、好ましくは０．０２以上、より好ましくは０．０４以上、上限としては０．３５以下、好ましくは０．３０以下、より好ましくは０．２５以下の範囲である。ラマンＲ値がこの範囲を下回ると、粒子表面の結晶性が高くなり過ぎて、充放電に伴ってＬｉが層間に入るサイトが少なくなる場合がある。すなわち、充電受入性が低下する場合がある。一方、この範囲を上回ると、粒子表面の結晶性が低下し、非水系電解液との反応性が増し、効率の低下やガス発生の増加を招く場合がある。

【００７９】

また、本発明の炭素材料の１５８０ｃｍ$^{-1}$付近のラマン半値幅は特に制限されないが、通常５ｃｍ$^{-1}$以上、好ましくは１０ｃｍ$^{-1}$以上、また上限として、通常４０ｃｍ$^{-1}$以下、好ましくは３５ｃｍ$^{-1}$以下、より好ましくは３０ｃｍ$^{-1}$以下の範囲である。ラマン半値幅がこの範囲を下回ると、粒子表面の結晶性が高くなり過ぎて、充放電に伴ってＬｉが層間に入るサイトが少なくなる場合がある。すなわち、充電受入性が低下する場合がある。一方、この範囲を上回ると、粒子表面の結晶性が低下し、非水系電解液との反応性が増し、効率の低下やガス発生の増加を招く場合がある。

【００８０】

ラマンスペクトルの測定は、ラマン分光器（例えば、日本分光社製ラマン分光器）を用い、試料を測定セル内へ自然落下させることで試料充填し、測定はセル内のサンプル表面にアルゴンイオンレーザー光を照射しながら、セルをレーザー光と垂直な面内で回転させながら行なう。得られたラマンスペクトルについて、１５８０ｃｍ$^{-1}$付近のピークＰ$_A$の強度Ｉ$_A$と、１３６０ｃｍ$^{-1}$付近のピークＰ$_B$の強度Ｉ$_B$とを測定し、その強度比Ｒ（Ｒ＝Ｉ$_B$／Ｉ$_A$）を算出して、これを炭素材料のラマンＲ値と定義する。また、得られたラマンスペクトルの１５８０ｃｍ$^{-1}$付近のピークＰ$_A$の半値幅を測定し、これを炭素材料のラマン半値幅と定義する。

なお、ここでのラマン測定条件は、次の通りである。

・アルゴンイオンレーザー波長　：５１４．５ｎｍ
・試料上のレーザーパワー　：１５～２５ｍＷ
・分解能　：１０～２０ｃｍ$^{-1}$
・測定範囲　：１１００ｃｍ$^{-1}$～１７３０ｃｍ$^{-1}$
・ラマンＲ値、ラマン半値幅解析：バックグラウンド処理
・スムージング処理　：単純平均、コンボリューション５ポイント

【００８１】

（３）タップ密度

異配向性炭素複合物のタップ密度は、通常０．５５ｇ／ｃｍ^{3}以上であり、好ましくは０．７０／ｃｍ^{3}以上、更に好ましくは０．９ｇ／ｃｍ^{3}以上、特に好ましくは１ｇ／ｃｍ^{3}以上であることが望ましい。また、好ましくは２．０ｇ／ｃｍ^{3}以下、より好ましくは１．８ｇ／ｃｍ^{3}以下、更に好ましくは１．７ｇ／ｃｍ^{3}以下、特に好ましくは１．５ｇ／ｃｍ^{3}以下である。タップ密度がこの範囲を下回ると、負極として用いた場合に充填密度が上がり難く、高容量の電池を得ることができない場合がある。一方、この範囲を上回ると、電極中の粒子間の空隙が少なくなり過ぎ、粒子間の導電性が確保され難くなり、好ましい電池特性が得られにくい場合がある。

【００８２】

本発明においてタップ密度は、目開き３００μｍの篩を通過させて、２０ｃｍ^{3}のタップセルに試料を落下させてセルの上端面まで試料を満たした後、粉体密度測定器（例えば

、セイシン企業社製タップデンサー）を用いて、ストローク長１０ｍｍのタップを１０００回行なって、その時の体積と試料の重量から求めた密度をタップ密度と定義する。

【００８３】

（４）ＢＥＴ比表面積

異配向性炭素複合物のＢＥＴ法を用いて測定した本発明の炭素材料の比表面積は、通常０．１m^2／ｇ以上、好ましくは０．７m^2／ｇ以上、より好ましくは１．０m^2／ｇ以上、更に好ましくは１．２m^2／ｇ以上である。上限は、通常１００m^2／ｇ以下、好ましくは２５m^2／ｇ以下、より好ましくは１５m^2／ｇ以下、更に好ましくは１０m^2／ｇ以下である。比表面積の値がこの範囲を下回ると、負極材料として用いた場合の充電時にリチウムの受け入れ性が悪くなりやすく、リチウムが電極表面で析出しやすくなる場合がある。一方、この範囲を上回ると、負極材料として用いた時に非水系電解液との反応性が増加し、ガス発生が多くなりやすく、好ましい電池が得られにくい場合がある。

【００８４】

ＢＥＴ比表面積は、表面積計（例えば、大倉理研製全自動表面積測定装置）を用い、試料に対して窒素流通下３５０℃で１５分間、予備乾燥を行なった後、大気圧に対する窒素の相対圧の値が０．３となるように正確に調整した窒素ヘリウム混合ガスを用い、ガス流動法による窒素吸着ＢＥＴ１点法によって測定した値で定義する。

【００８５】

（５）体積基準平均粒径

異配向性炭素複合物の体積基準平均粒径は、レーザー回折・散乱法により求めた体積基準の平均粒径（メジアン径）が、通常１μｍ以上、好ましくは３μｍ以上、より好ましくは５μｍ以上、更に好ましくは７μｍ以上である。また、上限は、通常１００μｍ以下、好ましくは５０μｍ以下、より好ましくは４０μｍ以下、更に好ましくは３０μｍ以下、特に好ましくは２５μｍ以下である。上記範囲を下回ると、不可逆容量が増大して、初期の電池容量の損失を招くことになる場合がある。また上記範囲を上回ると、電極極板化時に、不均一な塗面になりやすく、電池製作工程上望ましくない場合がある。

【００８６】

本発明において体積基準平均粒径は、界面活性剤であるポリオキシエチレン（２０）ソルビタンモノラウレートの０．２質量％水溶液（約１ｍＬ）に炭素粉末を分散させて、レーザー回折式粒度分布計（例えば、堀場製作所社製ＬＡ－７００）を用いて測定したメジアン径で定義する。

【００８７】

上記（１）～（５）項以外にも、更に、下記の（６）～（１１）項の１項以上を満たしていることが、電池特性のバランスの観点から好ましい。

【００８８】

（６）Ｘ線パラメータ

異配向性炭素複合物は、学振法によるＸ線回折で求めた格子面（００２面）のｄ値（層間距離）が、０．３３５ｎｍ以上であることが好ましく、通常０．３４０ｎｍ以下、好ましくは０．３３７ｎｍ以下であることが望まれる。この範囲を上回ると、結晶性が低下し、初期不可逆容量が増加する可能性がある。また下限の０．３３５ｎｍは黒鉛の理論値である。また、学振法によるＸ線回折で求めた炭素材料の結晶子サイズ（Ｌｃ）は、通常３０ｎｍ以上、好ましくは５０ｎｍ以上、より好ましくは８０ｎｍ以上の範囲である。この範囲を下回ると、結晶性が低下し、初期不可逆容量が増加する可能性がある。

【００８９】

（７）灰分

異配向性炭素複合物に含まれる灰分は、異配向性炭素複合物の全質量に対して、１質量％以下、中でも０．５質量％以下、特に０．１質量％以下、下限としては１ｐｐｍ以上であることが好ましい。上記の範囲を上回ると充放電時の非水系電解液との反応による電池性能の劣化が無視できなくなる場合がある。この範囲を下回ると、製造に多大な時間とエネルギーと汚染防止のための設備とを必要とし、コストが上昇する場合がある。

【００９０】
（８）細孔分布
異配向性炭素複合物としては、水銀ポロシメトリー（水銀圧入法）により求められる、直径０．０１μｍ以上、１μｍ以下に相当する粒子内の空隙、粒子表面のステップによる凹凸の量が、０．００１ｍＬ／ｇ以上、好ましくは０．００２ｍＬ／ｇ以上、上限として０．６ｍＬ／ｇ以下、好ましくは０．４ｍＬ／ｇ以下、より好ましくは０．３ｍＬ／ｇ以下の範囲である。この範囲を上回ると、極板化時にバインダーを多量に必要となる場合がある。一方この範囲を下回ると、高電流密度充放電特性が低下し、かつ充放電時の電極の膨張収縮の緩和効果が得られない場合がある。
【００９１】
また、全細孔容積が、好ましくは０．１ｍＬ／ｇ以上、より好ましくは０．２５ｍＬ／ｇ以上、上限として１０ｍＬ／ｇ以下、好ましくは５ｍＬ／ｇ以下、より好ましくは２ｍＬ／ｇ以下の範囲である。この範囲を上回ると極板化時にバインダーを多量に必要となる場合がある。下回ると極板化時に増粘剤や結着剤の分散効果が得られない場合がある。
【００９２】
また、平均細孔径が、好ましくは０．０５μｍ以上、より好ましくは０．１μｍ以上、更に好ましくは０．５μｍ以上、上限として５０μｍ以下、好ましくは２０μｍ以下、より好ましくは１０μｍ以下の範囲である。この範囲を上回ると、バインダーを多量に必要となる場合がある。一方この範囲を下回ると高電流密度充放電特性が低下する場合がある。
【００９３】
水銀ポロシメトリー用の装置として、水銀ポロシメータ（オートポア９５２０：マイクロメリテックス社製）を用いた。試料（負極材料）を、０．２ｇ前後の値となるように秤量し、パウダー用セルに封入し、室温、真空下（５０μｍＨｇ以下）にて１０分間脱気して前処理を実施した。引き続き、４ｐｓｉａ（約２８ｋＰａ）に減圧し水銀を導入し、４ｐｓｉａ（約２８ｋＰａ）から４００００ｐｓｉａ（約２８０ＭＰａ）までステップ状に昇圧させた後、２５ｐｓｉａ（約１７０ｋＰａ）まで降圧させた。昇圧時のステップ数は８０点以上とし、各ステップでは１０秒の平衡時間の後、水銀圧入量を測定した。こうして得られた水銀圧入曲線からＷａｓｈｂｕｒｎの式を用い、細孔分布を算出した。なお、水銀の表面張力（γ）は４８５ｄｙｎｅ／ｃｍ、接触角（φ）は１４０°として算出した。平均細孔径には累計細孔体積が５０％となるときの細孔径を用いた。
【００９４】
（９）真密度
異配向性炭素複合物の真密度は、通常２．０ｇ／ｃｍ^{3}以上、好ましくは２．１ｇ／ｃｍ^{3}以上、より好ましくは２．２ｇ／ｃｍ^{3}以上、更に好ましくは２．２２ｇ／ｃｍ^{3}以上であり、上限としては２．２６ｇ／ｃｍ^{3}以下である。上限は黒鉛の理論値である。この範囲を下回ると炭素の結晶性が低すぎて初期不可逆容量が増大する場合がある。本発明においては、真密度は、ブタノールを使用した液相置換法（ピクノメータ法）によって測定したもので定義する。
【００９５】
（１０）配向比（粉）
異配向性炭素複合物の配向比は、通常０．００５以上であり、好ましくは０．０１以上、より好ましくは０．０１５以上、上限は理論上０．６７以下の範囲である。この範囲を下回ると、高密度充放電特性が低下する場合がある。
【００９６】
配向比はＸ線回折により測定する。Ｘ線回折により炭素の（１１０）回折と（００４）回折のピークを、プロファイル関数として非対称ピアソンVIIを用いてフィッティングすることによりピーク分離を行ない、（１１０）回折と（００４）回折のピークの積分強度を各々算出する。得られた積分強度から、（１１０）回折積分強度／（００４）回折積分強度で表わされる比を算出し、活物質配向比と定義する。

【００９７】
ここでのＸ線回折測定条件は次の通りである。なお、「２θ」は回折角を示す。
・ターゲット：Ｃｕ（Ｋα線）グラファイトモノクロメーター
・スリット　：発散スリット＝１度、受光スリット＝０．１ｍｍ、散乱スリット＝１度
・測定範囲及びステップ角度／計測時間：
（１１０）面：７６．５度≦２θ≦７８．５度　０．０１度／３秒
（００４）面：５３．５度≦２θ≦５６．０度　０．０１度／３秒
【００９８】
（１１）アスペクト比（粉）
異配向性炭素複合物のアスペクト比は、理論上１以上であり、上限として１０以下、好ましくは８以下、更に好ましくは５以下である。上限を上回ると、極板化時にスジ引きや、均一な塗布面が得られず、高電流密度充放電特性が低下する場合がある。
【００９９】
なお、アスペクト比は、３次元的に観察した時の炭素材料粒子の最長となる径Ａ、それと直交する最短となる径Ｂとしたとき、Ａ／Ｂであらわされる。炭素粒子の観察は、拡大観察ができる走査型電子顕微鏡で行う。厚さ５０μｍ以下の金属の端面に固定した任意の５０個の黒鉛粒子を選択し、それぞれについて試料が固定されているステージを回転、傾斜させて、Ａ、Ｂを測定し、Ａ／Ｂの平均値を求める。
【０１００】
[[天然黒鉛系炭素質物（Ｂ）の原料]]
異配向性炭素複合物中に含有される天然黒鉛系炭素質物（Ｂ）の原料としては通常、Ｘ線広角回折法による（００２）面の面間隔（ｄ００２）が０．３４０ｎｍ以下を示すような結晶性の高い天然黒鉛を原料とするものが例に挙げられる。具体的には天然黒鉛又はこれらに機械的粉砕品を加えて円形度を向上させたもの及び／又はこれらを１０００℃以上で熱処理品したもの，膨張黒鉛の熱処理品，或いはこれらの黒鉛の高純度精製品から選ばれる粉体が好ましい。
【０１０１】
天然黒鉛系炭素質物（Ｂ）の前駆体となる天然黒鉛（Ｄ）は、その性状によって、鱗片状黒鉛（Flake Graphite)、鱗状黒鉛（Crystalline(Vein) Graphite)、土状黒鉛(Amorphous Graphite)に分類される（「粉粒体プロセス技術集成」（（株）産業技術センター、昭和４９年発行）の黒鉛の項、及び「HANDBOOK OF CARBON,GRAPHITE,DIAMOND AND FULLERENES」（Noyes Publications発行）参照）。黒鉛化度は、鱗状黒鉛が１００％で最も高く、これに次いで鱗片状黒鉛が９９．９％で高いが、土状黒鉛は２８％と低い。天然黒鉛である鱗片状黒鉛は、マダガスカル、中国、ブラジル、ウクライナ、カナダ等に産し、鱗状黒鉛は、主にスリランカに産する。土状黒鉛は、朝鮮半島、中国、メキシコ等を主な産地としている。これらの天然黒鉛の中で、土状黒鉛は一般に粒径が小さいうえ、純度が低い。これに対して、鱗片状黒鉛や鱗状黒鉛は、黒鉛化度や不純物量が低い等の長所があるため、本発明において好ましく使用することができる。
【０１０２】
[[天然黒鉛系炭素質物（Ｂ）の調製]]
天然黒鉛系炭素質物（Ｂ）の調製については、「異配向性炭素複合物の製造方法１及び製造方法２」の箇所で後述する。
【０１０３】
[[天然黒鉛系炭素質物（Ｂ）の性質]]
天然黒鉛系炭素質物（Ｂ）については、次に示す（１）～（１１）の何れか１項又は複数項を同時に満たしていることが望ましい。なお、それぞれの定義、測定方法等は、異配向性炭素複合物の部分に記載した定義、測定方法と同一である。
【０１０４】
（１）Ｘ線パラメータ
天然黒鉛系炭素質は、学振法によるＸ線回折で求めた格子面（００２面）のｄ値（層間

距離）が、０．３３５ｎｍ以上であることが好ましく、通常０．３４０ｎｍ以下、好ましくは０．３３７ｎｍ以下であることが望まれる。この範囲を上回ると、結晶性が低下し、初期不可逆容量の増大が増加する可能性がある。また０．３３５ｎｍは黒鉛の理論値である。また、学振法によるＸ線回折で求めた炭素材料の結晶子サイズ（Ｌｃ）は、通常３０ｎｍ以上、好ましくは５０ｎｍ以上、より好ましくは９０ｎｍ以上の範囲である。この範囲を下回ると、結晶性が低下し、初期不可逆容量の増大が増加する可能性がある。

【０１０５】

（２）灰分

天然黒鉛系炭素質中に含まれる灰分は、天然黒鉛系炭素質の全質量に対して、１質量％以下、中でも０．５質量％以下、特に０．１質量％以下、下限としては１ｐｐｍ以上であることが好ましい。上記の範囲を上回ると充放電時の非水系電解液との反応による電池性能の劣化が無視できなくなる場合がある。この範囲を下回ると、製造に多大な時間とエネルギーと汚染防止のための設備とを必要とし、コストが上昇する場合がある。

【０１０６】

（３）体積基準平均粒径

天然黒鉛系炭素質の体積基準平均粒径は、レーザー回折・散乱法により求めた体積基準の平均粒径（メジアン径）が、通常１μｍ以上、好ましくは３μｍ以上、より好ましくは５μｍ以上、更に好ましくは７μｍ以上である。また、上限は、通常５０μｍ以下、好ましくは４０μｍ以下、より好ましくは３０μｍ以下、更に好ましくは２５μｍ以下である。上記範囲を下回ると、不可逆容量が増大して、初期の電池容量の損失を招くことになる場合がある。また上記範囲を上回ると、電極極板化時に、不均一な塗面になりやすく、電池製作工程上望ましくない場合がある。

【０１０７】

（４）ラマンＲ値、ラマン半値幅

アルゴンイオンレーザーラマンスペクトル法を用いて測定した天然黒鉛系炭素質のラマンＲ値は、通常０．０１以上、好ましくは０．０２以上、より好ましくは０．０４以上、上限としては０．３５以下、好ましくは０．３０以下、より好ましくは０．２５以下の範囲である。ラマンＲ値がこの範囲を下回ると、粒子表面の結晶性が高くなり過ぎて、充放電に伴ってＬｉが層間に入るサイトが少なくなる場合がある。すなわち、充電受入性が低下する場合がある。一方、この範囲を上回ると、粒子表面の結晶性が低下し、非水系電解液との反応性が増し、効率の低下やガス発生の増加を招く場合がある。

【０１０８】

また、本発明の炭素材料の１５８０ｃｍ$^{-1}$付近のラマン半値幅は特に制限されないが、通常５ｃｍ$^{-1}$以上、好ましくは１０ｃｍ$^{-1}$以上、また上限として、通常４０ｃｍ$^{-1}$以下、好ましくは３５ｃｍ$^{-1}$以下、より好ましくは３０ｃｍ$^{-1}$以下の範囲である。ラマン半値幅がこの範囲を下回ると、粒子表面の結晶性が高くなり過ぎて、充放電に伴ってＬｉが層間に入るサイトが少なくなる場合がある。すなわち、充電受入性が低下する場合がある。一方、この範囲を上回ると、粒子表面の結晶性が低下し、非水系電解液との反応性が増し、効率の低下やガス発生の増加を招く場合がある。

【０１０９】

（５）ＢＥＴ比表面積

天然黒鉛系炭素質のＢＥＴ法を用いて測定した比表面積は、通常０．１ｍ^2／ｇ以上、好ましくは０．７ｍ^2／ｇ以上、より好ましくは１．０ｍ^2／ｇ以上、更に好ましくは１．５ｍ^2／ｇ以上である。上限は、通常１００ｍ^2／ｇ以下、好ましくは２５ｍ^2／ｇ以下、より好ましくは１５ｍ^2／ｇ以下、更に好ましくは１０ｍ^2／ｇ以下である。比表面積の値がこの範囲を下回ると、負極材料として用いた場合の充電時にリチウムの受け入れ性が悪くなりやすく、リチウムが電極表面で析出しやすくなる場合がある。一方、この範囲を上回ると、負極材料として用いた時に非水系電解液との反応性が増加し、ガス発生が多くなりやすく、好ましい電池が得られにくい場合がある。

【０１１０】

（６）細孔分布

天然黒鉛系炭素質としては、水銀ポロシメトリー（水銀圧入法）により求められる、直径０．０１μｍ以上、１μｍ以下に相当する粒子内の空隙、粒子表面のステップによる凹凸の量が、０．０１ｍＬ／ｇ以上、好ましくは０．０５ｍＬ／ｇ以上、より好ましくは０．１ｍＬ／ｇ以上、上限として０．６ｍＬ／ｇ以下、好ましくは０．４ｍＬ／ｇ以下、より好ましくは０．３ｍＬ／ｇ以下の範囲である。この範囲を上回ると、極板化時にバインダーを多量に必要となる場合がある。下回ると、高電流密度充放電特性が低下し、かつ充放電時の電極の膨張収縮の緩和効果が得られなにくい場合がある。

【０１１１】

また、全細孔容積が、好ましくは０．１ｍＬ／ｇ以上、より好ましくは０．２５ｍＬ／ｇ以上、上限として１０ｍＬ／ｇ以下、好ましくは５ｍＬ／ｇ以下、より好ましくは２ｍＬ／ｇ以下の範囲である。この範囲を上回ると極板化時にバインダーを多量に必要となる場合がある。下回ると極板化時に増粘剤や結着剤の分散効果が得られない場合がある。

また、平均細孔径が、好ましくは０．０５μｍ以上、より好ましくは０．１μｍ以上、更に好ましくは０．５μｍ以上、上限として５０μｍ以下、好ましくは２０μｍ以下、より好ましくは１０μｍ以下の範囲である。この範囲を上回ると、バインダーを多量に必要となる場合がある。下回ると高電流密度充放電特性が低下する場合がある。

【０１１２】

（７）円形度

天然黒鉛系炭素材料の球形の程度としては、その粒径が３～４０μｍの範囲にある粒子の円形度は０．１以上が好ましく、特に好ましくは０．５以上、より好ましくは０．８以上、更に好ましくは０．８５以上、最も好ましくは０．９以上である。円形度が大きいと高電流密度充放電特性が向上するため好ましい。

【０１１３】

（８）真密度

天然黒鉛系炭素質の真密度は、通常２．０ｇ／ｃｍ^{3}以上、好ましくは２．１ｇ／ｃｍ^{3}以上、より好ましくは２．２ｇ／ｃｍ^{3}以上、更に好ましくは２．２２ｇ／ｃｍ^{3}以上であり、上限としては２．２６ｇ／ｃｍ^{3}以下である。上限は黒鉛の理論値である。この範囲を下回ると炭素の結晶性が低すぎて初期不可逆容量が増大する場合がある。

【０１１４】

（９）タップ密度

天然黒鉛系炭素材料のタップ密度は、通常０．１ｇ／ｃｍ^{3}以上であり、好ましくは０．５ｇ／ｃｍ^{3}以上、更に好ましくは０．７ｇ／ｃｍ^{3}以上、特に好ましくは０．９ｇ／ｃｍ^{3}以上であることが望まれる。また、好ましくは、２．０ｇ／ｃｍ^{3}以下、更に好ましくは、１．８ｇ／ｃｍ^{3}以下、特に好ましくは１．６ｇ／ｃｍ^{3}以下である。タップ密度がこの範囲を下回ると、負極として用いた場合に充填密度が上がり難く、高容量の電池を得ることができない場合がある。一方、この範囲を上回ると、電極中の粒子間の空隙が少なくなり過ぎ、粒子間の導電性が確保され難くなり、好ましい電池特性が得られにくい場合がある。

【０１１５】

（１０）配向比（粉）

天然黒鉛系炭素質の配向比は、通常０．００５以上であり、好ましくは０．０１以上、より好ましくは０．０１５以上、上限は理論上０．６７以下の範囲である。この範囲を下回ると、高密度充放電特性が低下する場合がある。

【０１１６】

（１１）アスペクト比（粉）

天然黒鉛系炭素質のアスペクト比は、理論上１以上であり、上限として１０以下、好ましくは８以下、更に好ましくは５以下である。上限を上回ると、極板化時にスジ引きや、均一な塗布面が得られず、高電流密度充放電特性が低下する場合がある。

【０１１７】

[[炭素質物（Ｃ）の原料]]
本発明の異配向性炭素複合物中に含まれる炭素質物（Ｃ）の原料としては、炭素化できるものであれば特には限定はないが、ピッチ原料、アセナフチレン、デカシクレン、アントラセン、フェナントレン等の芳香族炭化水素；フェナジン、アクリジン等のＮ環化合物；チオフェン、ビチオフェン等のＳ環化合物；ビフェニル、テルフェニル等のポリフェニレン；ポリ塩化ビニル、ポリビニルアルコール、ポリビニルブチラール、これらものの不溶化処理品、含窒素性のポリアクニロニトリル、ポリピロール等の有機高分子；含硫黄性のポリチオフェン、ポリスチレン等の有機高分子；セルロース、リグニン、マンナン、ポリガラクトウロン酸、キトサン、サッカロースに代表される多糖類等の天然高分子；ポリフェニレンサルファイド、ポリフェニレンオキシド等の熱可塑性樹脂；フルフリルアルコール樹脂、フェノールーホルムアルデヒド樹脂、イミド樹脂等の熱硬化性樹脂；又はこれらをベンゼン、トルエン、キシレン、キノリン、ｎーヘキサン等の低分子有機溶媒に溶解させた溶液等の有機物；炭化可能な気体等が挙げられる。

【０１１８】
これらの中で、ピッチ原料は残炭率が高いことから、収率の高い材料を作製することが可能であり好ましい。なお、本明細書において「ピッチ原料」とは、ピッチ及びそれに順ずるものであり、適当な処理を行なうことによって炭素化及び又は黒鉛化することができるものをいう。具体的なピッチ原料の例としては、タールや重質油やピッチ等を用いることができる。タールの具体例としては、コールタール、石油系タール等が挙げられる。重質油の具体例としては、石油系重質油の接触分解油、熱分解油、常圧残油、減圧残油等が挙げられる。また、ピッチの具体例としては、コールタールピッチ、石油系ピッチ、合成ピッチ等が挙げられる。これらの中でもコールタールピッチが芳香族性に高く好ましい。これらのピッチ原料は、何れか１種を単独で用いても良く、２種以上を任意の組み合わせ及び比率で併用しても良い。

【０１１９】
また、上述のピッチ原料であって、キノリン不溶分の含有量は、特に制限されないが、通常３０以下の範囲にあるものを用いる。キノリン不溶分とは、コールタール中に微量に含まれるサブミクロンの炭素粒子や極微小なスラッジ等であり、これが多過ぎると黒鉛化過程での結晶性向上を著しく阻害し、黒鉛化後の放電容量の著しい低下を招く。なお、キノリン不溶分の測定方法としては、例えばＪＩＳ　Ｋ２４２５に規定された方法を用いることができる。

【０１２０】
なお、本発明の効果を妨げない限り、原料として上述のピッチ原料に加え、各種の熱硬化性樹脂、熱可塑性樹脂等を併用してもよい。

【０１２１】
[[炭素質物（Ｃ）の調製]]
炭素質物（Ｃ）の調製については、「異配向性炭素複合物の製造方法１及び製造方法２」の箇所で後述する。

【０１２２】
[[炭素質物（Ｃ）の性質]]
炭素質物（Ｃ）については、次に示す（１）～（４）の何れか１項又は複数項を同時に満たしていることが好ましい。なお、それぞれの定義、測定方法等は、異配向性炭素複合物の部分に記載した定義、測定方法と同一である。

【０１２３】
（１）Ｘ線パラメータ
炭素質物（Ｃ）は、学振法によるＸ線回折で求めた格子面（００２面）のｄ値（層間距離）が、０．３３５ｎｍ以上であることが好ましく、通常０．３４５ｎｍ以下、好ましくは０．３４０ｎｍ以下、より好ましくは０．３３７ｎｍ以下であることが望まれる。また、学振法によるＸ線回折で求めた炭素材料の結晶子サイズ（Ｌｃ）は、通常５ｎｍ以上、好ましくは１０ｎｍ以上、より好ましくは５０ｎｍ以上、更に好ましくは８０ｎｍ以上の

範囲である。この範囲を下回ると、結晶性が低下し、初期不可逆容量の増大が増加する可能性がある。

【０１２４】

（２）灰分

炭素質物（Ｃ）に含まれる灰分は、異配向性炭素複合物の全質量に対して、１質量％以下、中でも０．５質量％以下、特に０．１質量％以下、下限としては１ｐｐｍ以上であることが好ましい。上記の範囲を上回ると充放電時の非水系電解液との反応による電池性能の劣化が無視できなくなる場合がある。この範囲を下回ると、製造に多大な時間とエネルギーと汚染防止のための設備とを必要とし、コストが上昇する場合がある。

【０１２５】

（３）ラマンＲ値、ラマン半値幅

アルゴンイオンレーザーラマンスペクトル法を用いて測定した炭素質物（Ｃ）のラマンＲ値は、通常０．０１以上、好ましくは０．０３以上、より好ましくは０．０５以上、上限としては０．６０以下、好ましくは０．３０以下の範囲である。ラマンＲ値がこの範囲を下回ると、粒子表面の結晶性が高くなり過ぎて、充放電に伴ってＬｉが層間に入るサイトが少なくなる場合がある。すなわち、充電受入性が低下する場合がある。一方、この範囲を上回ると、粒子表面の結晶性が低下し、非水系電解液との反応性が増し、効率の低下やガス発生の増加を招く場合がある。

【０１２６】

また、本発明における炭素質物（Ｃ）の１５８０ｃｍ$^{-1}$付近のラマン半値幅は特に制限されないが、通常５ｃｍ$^{-1}$以上、好ましくは１０ｃｍ$^{-1}$以上、また上限として、通常６０ｃｍ$^{-1}$以下、好ましくは４５ｃｍ$^{-1}$以下、より好ましくは３０ｃｍ$^{-1}$以下の範囲である。ラマン半値幅がこの範囲を下回ると、粒子表面の結晶性が高くなり過ぎて、充放電に伴ってＬｉが層間に入るサイトが少なくなる場合がある。一方、この範囲を上回ると、粒子表面の結晶性が低下し、非水系電解液との反応性が増し、効率の低下やガス発生の増加を招く場合がある。

【０１２７】

（４）真密度

炭素質物（Ｃ）の真密度は、通常２．０ｇ／ｃｍ^{3}以上、好ましくは２．２ｇ／ｃｍ^{3}以上、より好ましくは２．２２ｇ／ｃｍ^{3}以上、上限としては黒鉛の理論上限である２．２６ｇ／ｃｍ^{3}以下である。この範囲を下回ると炭素の結晶性が低すぎて初期不可逆容量が増大する場合がある。

【０１２８】

[異配向性炭素複合物の製造方法]

製造方法としては特に限定はなく、本発明の要旨を超えない範囲であれば、どのような手法を用いてもよいが、好適な例の概略は以下の（１）、（２）の通りである。

（１）炭素質物（Ｃ）の出発原料が何れかの工程で全体又は一部が液状となる状態を形成し、この液状となった状態で天然黒鉛（Ｄ）と混合及び／又は捏合を行う。

（２）この工程で得られた複合物を脱揮発分・焼成及び、黒鉛化を行い、粉砕、分級を行って粒度を調整する。これらの工程の間には粉砕・分級工程を１回以上経ても構わない。

【０１２９】

次に上述の概略の具体例を示す。

[[異配向性炭素複合物の製造方法１]]

本発明における異配向性炭素複合物は、天然黒鉛系炭素質物（Ｂ）と天然黒鉛系炭素質物（Ｂ）とは配向性の異なる炭素質物（Ｃ）が複合化されることが好ましく、例として、前記した天然黒鉛（Ｄ）に、前記した炭素質物（Ｃ）の前駆体であるピッチ原料、又はピッチ原料等を熱処理し粉砕したもの（以下、「熱処理黒鉛結晶前駆体」と略記する）、天然高分子等を、所定の割合で混合し、熱処理Ａを行なった後、更に粉砕し、熱処理Ｂ（焼成、黒鉛化）を行う方法等が挙げられる。また、上記の粉砕は、十分にメジアン径が小さく必要がなければ行わなくても良い。

【０１３０】
[[[熱処理黒鉛結晶前駆体の製造]]]
ピッチ原料に事前に熱処理を施し、熱処理黒鉛結晶前駆体を得る。この事前の熱処理をピッチ熱処理と呼ぶこととする。この熱処理黒鉛結晶前駆体を粉砕後、天然黒鉛（Ｄ）と混合後、熱処理Ａをする際に、その一部又は全部が溶融するが、ここで事前の熱処理（ピッチ熱処理）によって揮発分の含量を調整しておくことにより、その溶融状態を適切に制御することができる。なお、熱処理黒鉛結晶前駆体に含まれる揮発分としては、通常、水素、ベンゼン、ナフタレン、アントラセン、ピレン等が挙げられる。
【０１３１】
ピッチ熱処理の際の温度条件は、特に制限されないが、通常３００℃以上、５５０℃以下の範囲である。熱処理の温度がこの範囲を下回ると、揮発分が多くなるため、大気中で安全に粉砕を行ない難くなる場合がある。一方、上限を上回ると、熱処理Ａ時に熱処理黒鉛結晶前駆体の一部又は全部が溶融せず、天然黒鉛系炭素質物（Ｂ）と熱処理黒鉛結晶前駆体の複合化した粒子（異配向性炭素複合物）が得られ難い場合がある。ピッチ熱処理を行なう際には、窒素ガス等の不活性ガス雰囲気下、又は、ピッチ原料から発生する揮発分雰囲気下で行なう。
【０１３２】
ピッチ熱処理に用いる装置としては特に制限はないが、例えば、シャトル炉、トンネル炉、電気炉、オートクレーブ等の反応槽、コーカー（コークス製造の熱処理槽）等を用いることができる。ピッチ熱処理時には、必要に応じて攪拌を行なってもよい。
【０１３３】
なお、熱処理黒鉛結晶前駆体として、揮発分の含有率が通常５質量％以上のものを用いることが好ましい。揮発分含有率がこの範囲にある黒鉛結晶前駆体を使用することで、熱処理Ａにより天然黒鉛系炭素質物（Ｂ）と炭素質物（Ｃ）が複合化することから、上述に規定する物性を有する異配向性炭素複合物を得ることができる。
【０１３４】
始めに、ピッチ原料に事前に熱処理を施し、黒鉛結晶の前駆体であるバルクメソフェーズ（事前に熱処理した黒鉛結晶前駆体であり、以下、「熱処理黒鉛結晶前駆体」と略記する）の製造方法について説明する。
【０１３５】
（熱処理黒鉛結晶前駆体の揮発分）
ピッチ熱処理によって得られる黒鉛結晶前駆体の揮発分は、特に制限されないが、通常５質量％以上、好ましくは６質量％以上、また、通常２０質量％以下、好ましくは１５質量％以下とする。揮発分が上記範囲を下回ると揮発分が多いため、大気中で安全に粉砕を行ない難くなる場合がある一方で、上限を上回ると熱処理Ａ時に黒鉛結晶前駆体の一部又は全部が溶融せず、天然黒鉛系炭素質物（Ｂ）と熱処理黒鉛結晶前駆体の複合化した粒子（異配向性炭素複合物）を得難い場合がある。なお、揮発分の測定方法としては、例えばＪＩＳ　Ｍ８８１２に規定された方法を用いる。
【０１３６】
（熱処理黒鉛結晶前駆体の軟化点）
ピッチ熱処理によって得られる黒鉛結晶前駆体の軟化点は、特に制限されないが、通常２５０℃以上、好ましくは３００℃以上、更に好ましくは３７０℃以上、また、通常４７０℃以下、好ましくは４５０℃以下、更に好ましくは４３０℃以下の範囲とする。下限を下回ると、熱処理後の黒鉛結晶前駆体の炭素化収率が低く、天然黒鉛系炭素質物（Ｂ）との均一な混合物を得難く、上限を上回ると、熱処理Ａ時に黒鉛結晶前駆体の一部又は全部が溶融せず、天然黒鉛系炭素質物（Ｂ）と熱処理黒鉛結晶前駆体の複合化した粒子（異配向性炭素複合物）を得難い場合がある。
【０１３７】
軟化点としては、錠剤成型器で１ｍｍ厚さに成型した試料について、熱機械分析装置（例えば、ブルカー・エイエックス株式会社製ＴＭＡ４０００）を用いて、窒素流通下、昇

温速度１０℃／分、針先形状１ｍｍφ、加重２０ｇｆの条件で、ペネトレーション法により測定した値を用いる。

【０１３８】

（熱処理黒鉛結晶前駆体の粉砕）

次に、ピッチ熱処理によって得られた熱処理黒鉛結晶前駆体を粉砕する。熱処理により大きな単位で同一方向に並びかけている熱処理黒鉛結晶前駆体の結晶を微細化するため、及び／又は、天然黒鉛（Ｄ）と熱処理黒鉛結晶前駆体との混合、複合化を均一にするためである。

【０１３９】

ピッチ熱処理によって得られる熱処理黒鉛結晶前駆体の粉砕は、特に制限されないが、粉砕後の熱処理黒鉛結晶前駆体の粒度が、通常１μｍ以上、好ましくは５μｍ以上、また、通常１０ｍｍ以下、好ましくは５ｍｍ以下、中でも好ましくは５００μｍ以下、更に好ましくは２００μｍ以下、特に好ましくは５０μｍ以下となるように行なう。前記粒度が１μｍ未満では、粉砕中若しくは粉砕後に熱処理した熱処理黒鉛結晶前駆体の表面が空気と触れることで酸化し、黒鉛化過程での結晶性の向上を阻害し、黒鉛化後の放電容量の低下を招く場合がある。一方、前記粒度が１０ｍｍを超えると、粉砕による微細化効果が薄れ結晶が配向しやすくなり、炭素質物（Ｃ）が配向しやすくなって、異配向性炭素質複合物（Ａ）を用いた電極の活物質配向比が低くなり、電池充電時の電極膨張を抑制し難くなる場合がある。及び／又は、天然黒鉛（Ｄ）と熱処理黒鉛結晶前駆体の粒径差が大きくなる為に、均一な混合がし難くなり、複合化が不均一になりやすくなる場合がある。

【０１４０】

粉砕に用いる装置に特に制限はないが、例えば、粗粉砕機としてはせん断式ミル、ジョークラッシャー、衝撃式クラッシャー、コーンクラッシャー等が挙げられ、中間粉砕機としてはロールクラッシャー、ハンマーミル等が挙げられ、微粉砕機としてはボールミル、振動ミル、ピンミル、撹拌ミル、ジェットミル、ターボミル等が挙げられる。

【０１４１】

[[[天然黒鉛（Ｄ）と熱処理黒鉛結晶前駆体の熱処理]]]

天然黒鉛（Ｄ）と熱処理黒鉛結晶前駆体（炭素質物（Ｃ）の原料）を所定の割合で混合、熱処理Ａ、粉砕、熱処理Ｂ（焼成、黒鉛化）することにより異配向性炭素複合物を作製する。

【０１４２】

（天然黒鉛（Ｄ）と熱処理黒鉛結晶前駆体との混合）

熱処理Ａ前に行なう天然黒鉛（Ｄ）と熱処理黒鉛結晶前駆体との混合割合は、特に制限されないが、混合物に対する天然黒鉛（Ｄ）の割合が、通常２０質量％以上、好ましくは３０質量％以上、更に好ましくは４０質量％以上、また、通常９５質量％以下、好ましくは９０質量％以下となるように行なう。下限を下回ると、異配向性炭素質複合物（Ａ）中の炭素質物（Ｃ）の割合が増える為、電極にした時に充填密度が上がり難く、過大なプレス荷重を必要とし天然黒鉛系炭素質物（Ｂ）を複合化した効果が得られ難い場合がある。上限を上回ると、異配向性炭素質複合物（Ａ）中の天然黒鉛系炭素質物（Ｂ）表面の露出が増し、異配向性炭素質複合物（Ａ）の比表面積が大きくなる可能性があり、粉体物性上好ましくない場合がある。

【０１４３】

天然黒鉛（Ｄ）と、所定粒度に調整した熱処理黒鉛結晶前駆体を混合する際に、用いる装置に特に制限はないが、例えば、Ｖ型混合機、Ｗ型混合機、容器可変型混合機、混練機、ドラムミキサー、せん断ミキサー等が挙げられる。

【０１４４】

（熱処理Ａ）

次に、天然黒鉛（Ｄ）と熱処理黒鉛結晶前駆体の混合物に熱処理Ａを施す。粉砕した熱処理黒鉛結晶前駆体を再溶融又は融着することにより、天然黒鉛（Ｄ）と微細化した熱処理黒鉛結晶前駆体粒子が無配向状態で接触したまま固定化するためである。これにより、

天然黒鉛（Ｄ）と熱処理黒鉛結晶前駆体の混合物は、単なる粒子の混合物ではなく、より均一な複合化した混合物（以下適宜、「黒鉛複合混合物」という）とすることができる。

【０１４５】

熱処理Ａの温度条件は、特に制限されないが、通常３００℃以上、好ましくは４００℃以上、更に好ましくは４５０℃以上、また、通常６５０℃以下、好ましくは６００℃以下である。熱処理Ａの温度が前記範囲を下回ると、熱処理Ａの後の材料中に揮発分が多く残存する為、焼成、若しくは黒鉛化工程時に粉体同志の融着を起こす可能性があり、再粉砕が必要となる場合がある。一方、前記範囲を上回ると、再溶融した成分が粉砕時に針状に割れ、タップ密度の低下を招く場合がある。熱処理Ａは、窒素ガス等の不活性ガス雰囲気下、又は、粉砕により微細化した熱処理黒鉛結晶前駆体から発生する揮発分雰囲気下で行なう。

【０１４６】

熱処理Ａに用いる装置に特に制限はないが、例えば、シャトル炉、トンネル炉、電気炉等を用いることができる。

【０１４７】

（熱処理黒鉛結晶前駆体の粉砕及び熱処理Ａの代替処理）

ところで、上記の粉砕及び熱処理Ａの代替処理として、熱処理黒鉛結晶前駆体の組織を微細化、無配向化することが可能な処理、例えば、熱処理した黒鉛結晶前駆体が溶融若しくは軟化する様な温度領域で機械的エネルギーを付与する処理を行ないながら、天然黒鉛（Ｄ）と混合、熱処理を行なうことも可能である。

【０１４８】

この代替処理としての熱処理は、特に制限されないが、通常２００℃以上、好ましくは２５０℃以上、また、通常４５０℃以下、好ましくは４００℃以下で行なう。温度条件が前記範囲を下回ると代替処理中の黒鉛結晶前駆体の溶融、軟化が不十分であり、天然黒鉛（Ｄ）との複合化がし難くなる場合がある。また、上回ると熱処理が急速に進みやすく、粉砕時に炭素質熱処理黒鉛結晶前駆体等の粒子が針状に割れ、タップ密度の低下を招きやすくなる場合がある。

【０１４９】

この代替処理は、通常、窒素ガス等の不活性雰囲気下、又は空気等の酸化性雰囲気下で行なう。但し、酸化性雰囲気で処理する場合は、黒鉛化後に高結晶性を得ることが難しい場合があるので、酸素による不融化が進み過ぎない様にする必要がある。具体的には、代替処理後の黒鉛結晶前駆体中の酸素量が、通常８質量％以下、好ましくは５質量％以下となるようにする。

【０１５０】

また、代替処理に用いる装置としては特に制限はないが、例えば、ミキサー、ニーダー等を用いることができる。

【０１５１】

（粉砕）

次に、熱処理Ａを行なった黒鉛複合混合物を粉砕する。熱処理Ａにより天然黒鉛（Ｄ）と複合化され組織が微細化、無配向化した状態で溶融又は融着した黒鉛複合混合物の塊を、粉砕により目的の粒子径にするためである。

【０１５２】

粉砕後の黒鉛複合混合物の粒度は、特に制限されないが、通常１μｍ以上、好ましくは３μｍ以上、より好ましくは５μｍ以上、更に好ましくは７μｍ以上、また、通常５０μｍ以下、好ましくは３５μｍ以下、より好ましくは３０μｍ以下とする。粒度が前記範囲を下回ると、異配向性炭素質複合物（Ａ）としてタップ密度が小さくなってしまうため、電極とした場合に活物質の充填密度が上がり難く、高容量の電池を得難い。一方、前記範囲を上回ると、異配向性炭素質複合物（Ａ）として塗布により電極を作製するときに塗工むらが生じやすくなる場合がある。

【０１５３】

粉砕に用いる装置について特に制限はないが、例えば、粗粉砕機としてはジョークラッシャー、衝撃式クラッシャー、コーンクラッシャー等が挙げられ、中間粉砕機としてはロールクラッシャー、ハンマーミル等が挙げられ、微粉砕機としてはボールミル、振動ミル、ピンミル、撹拌ミル、ジェットミル等が挙げられる。

【０１５４】

（熱処理Ｂ：焼成）

熱処理Ｂは、焼成及び黒鉛化のことを言う。以下、焼成から説明する。但し、焼成は、省略することも可能である。粉砕により粉砕された黒鉛複合混合物を焼成する。黒鉛化時の黒鉛複合混合物の融着を抑制するべく、焼成により黒鉛複合混合物の揮発分を除去するためである。

【０１５５】

焼成を行なう際の温度条件は、特に制限されないが、通常６００℃以上、好ましくは１０００℃以上、また上限は、通常２４００℃以下、好ましくは１３００℃以下である。温度条件が前記範囲を下回ると、黒鉛化時に黒鉛複合混合物が粉体の融着を起こしやすくなる場合がある。一方、上記範囲を上回ると、焼成設備に費用が掛かるため、通常上記温度条件の範囲内で行われる。

【０１５６】

焼成は、窒素ガス等の不活性ガス雰囲気下、又は、再粉砕した黒鉛複合混合物から発生するガスによる非酸化性雰囲気下で行なう。また、製造工程の簡略化のため、焼成工程を組み込まずに、直接黒鉛化を行なうことも可能である。

【０１５７】

焼成に用いる装置としては特に制限はないが、例えば、シャトル炉、トンネル炉、電気炉、リードハンマー炉、ロータリーキルン等を用いることができる。

【０１５８】

（熱処理Ｂ：黒鉛化）

次に、焼成を行なった黒鉛複合混合物に黒鉛化を施す。電池評価での放電容量を大きくするために、結晶性を向上させるためである。黒鉛化により、異配向性炭素質複合物（Ａ）を得ることができる。

【０１５９】

黒鉛化を行なう際の温度条件は、特に制限されないが、通常２８００℃以上、好ましくは２９００℃以上、より好ましくは３０００℃以上、また、通常３４００℃以下、好ましくは３２００℃以下である。前記範囲を上回ると、電池の可逆容量が小さくなる場合があり、高容量な電池を作り難い場合がある。また、前記範囲を上回ると、黒鉛の昇華量が多くなりやすくなる場合がある。

【０１６０】

黒鉛化は、アルゴンガス等の不活性ガス雰囲気下、又は、焼成した黒鉛複合混合物から発生するガスによる非酸化性雰囲気下で行なう。黒鉛化に使用する装置としては特に制限はないが、例えば、直接通電炉、アチソン炉、間接通電式として抵抗加熱炉、誘導加熱炉等が挙げられる。

【０１６１】

なお、黒鉛化処理時、若しくはそれ以前の工程、すなわち、熱処理から焼成までの工程で、材料（天然黒鉛（Ｄ）、ピッチ原料又は黒鉛結晶前駆体）の中若しくは表面にＳｉ、Ｂ等の黒鉛化触媒を添加しても構わない。

【０１６２】

（その他の処理）

その他、発明の効果が妨げられない限りにおいて、上記の各処理に加え、分級処理等の各種の処理を行なうことができる。分級処理は、黒鉛化処理後の粒度を目的の粒径にするべく、粗粉や微粉を除去するためのものである。

【０１６３】

分級処理に用いる装置としては特に制限はないが、例えば、乾式篩い分けの場合：回転

式篩い、動揺式篩い、旋動式篩い、振動式篩い、乾式気流式分級の場合：重力式分級機、慣性力式分級機、遠心力式分級機（クラシファイア、サイクロン等）、湿式篩い分け、機械的湿式分級機、水力分級機、沈降分級機、遠心式湿式分級機等を用いることができる。

【０１６４】

分級処理は、熱処理Ａ後の粉砕のすぐ後に続けて行なうこともできるし、その他のタイミング、例えば、粉砕後の焼成の後、あるいは黒鉛化の後に行なってもよい。更には、分級処理自体を省略することも可能である。但し、異配向性炭素質複合物（Ａ）のＢＥＴ比表面積を低下させる点、及び、生産性の点からは、熱処理Ａ後の粉砕のすぐ後に続けて分級処理を行なうことが好ましい。

【０１６５】

（異配向性炭素質複合物（Ａ）の製造後の処理）

上述の手順で製造した異配向性炭素質複合物（Ａ）に対して、更に、負極材料のＢＥＴ比表面積の制御、電極プレス性の向上、放電容量の向上、安価化等の目的で、別に製造した人造黒鉛粉末又は天然黒鉛粉末を加えて混合しても良い。

【０１６６】

［異配向性炭素複合物の製造方法２］

異配向性炭素複合物の製造は、次のような方法によっても可能である。本発明における異配向性炭素複合物は、天然黒鉛系炭素質物（Ｂ）と天然黒鉛系炭素質物（Ｂ）とは配向性の異なる炭素質物（Ｃ）が複合化されることが好ましく、例として、前記した天然黒鉛（Ｄ）に、前記した炭素質物（Ｃ）の前駆体であるピッチ原料を「捏合（混合）」「成型」「焼成」「黒鉛化」「粉砕」の工程を経て製造されること等が挙げられる。但しこれらの工程で「成型」「焼成」「粉砕」は省略及び／又は他工程と同時に実施することも可能である。具体的には、以下に挙げる製造方法等によって得ることができる。

【０１６７】

[[捏合（混合）]]

天然黒鉛（Ｄ）、ピッチ原料及び所望により添加された黒鉛化触媒等の原料の、混合を行う。このとき、均一な混合のために、加熱することが好ましい。これにより、天然黒鉛（Ｄ）及び捏合温度では溶融しない原料に液状のピッチ原料が添着された状態となる。この場合、捏合機に全原料を仕込んで捏合と昇温を同時に行っても良いし、捏合機にピッチ原料以外の成分を仕込んで撹拌状態で加熱し、捏合温度まで温度が上がった後に常温又は加硫溶融状態のピッチ原料を仕込んでも良い。

【０１６８】

加熱温度は、通常ピッチ原料の軟化点以上、好ましくは軟化点より１０℃以上高い温度、より好ましくは軟化点より２０℃以上高い温度範囲で行われる。また上限としては通常３００℃以下、好ましくは２５０℃以下の範囲である。この範囲を下回るとピッチ原料の粘度が高くなり、混合が困難となる可能性がある。一方この範囲を上回ると揮発と重縮合によって混合系の粘度が高くなりすぎる場合もある。

【０１６９】

混合機は撹拌翼をもつ機種が好ましく、撹拌翼はＺ型、マチスケータ型といった汎用的なものを用いることができる。混合機に投入する原料の量は、通常混合機容積の１０体積％以上、好ましくは１５体積％以上で、５０体積％以下、好ましくは３０体積％以下である。混合時間は５分以上必要であり、最長でも揮発分の揮散による大きな粘性の変化を来たす時間までで、通常は３０～１２０分である。混合機は混合に先立ち捏合温度まで予熱しておくことが好ましい。

【０１７０】

[[成形]]

得られた混合物は、そのまま揮発成分の除去と炭化を目的とする脱揮発成分・焼成工程に供してもよいが、ハンドリングしやすいように、成形してから脱揮発成分・焼成工程に供することが好ましい。

【０１７１】

成形方法は形状を保持することが可能であれば特に制限はなく、押し出し成形、金型成形、静水圧成形等を採用することができる。このうち、成形体内で粒子が配向しやすい押し出し成形や、粒子の配向はランダムに保たれるが生産性の点から、静水圧成形より、比較的操作が容易であり、また、混合でランダムな配向となった構造を破壊せずに成形体を得ることができる金型成形が好ましい。

【０１７２】

成形温度は、室温（冷間）、加熱下（熱間、ピッチ原料の軟化点以上の温度）のどちらでもよい。冷間で成形する場合は、成形性の向上と成形体の均一性を得るために、捏合後冷却された混合物を予め最大寸法が１ｍｍ以下に粗砕することが望ましい。成形体の形状、大きさは特に制限は無いが、熱間成形では、成形体が大きすぎると成形に先立つ均一な予熱を行うのに時間がかかるので、通常最大寸法で１５０ｃｍ程度以下の大きさとすることが好ましい。

【０１７３】

成形圧力は、圧力が高すぎると成形体の細孔を通しての揮発成分除去が困難となり、かつ真円ではない天然黒鉛（Ｄ）が配向し、後工程における粉砕が難しくなるので、成形圧力の上限は、通常３０００ｋｇｆ／ｃｍ^2（２９４ＭＰａ）以下、好ましくは５００ｋｇｆ／ｃｍ^2（４９ＭＰａ）以下、更に好ましくは１０ｋｇｆ／ｃｍ^2（０．９８ＭＰａ）以下である。下限の圧力は特に制限はないが、脱揮発成分・焼成工程で成形体の形状を保持できる程度に設定することが好ましい。

【０１７４】

[[脱揮発成分・焼成]]

得られた成形体は、天然黒鉛（Ｄ）及びピッチ原料の揮発成分を除去して、黒鉛化時の充填物の汚染、充填物の成形体への固着を防ぐために、脱揮発成分・焼成を行う。脱揮発成分・焼成は、通常６００℃以上、好ましくは６５０℃以上で、通常１３００℃以下、好ましくは１１００℃以下の温度で、通常０．１時間～１０時間行う。加熱は、酸化を防止するために、通常、窒素、アルゴン等不活性ガスの流通下又はブリーズ、パッキングコークス等の粒状炭素材料を間隙に充填した非酸化性雰囲気で行う。

【０１７５】

脱揮発成分・焼成に用いる設備は、電気炉やガス炉、電極材用リードハンマー炉等、非酸化性雰囲気で焼成可能であれば特に限定されない。加熱時の昇温速度は揮発分の除去のために低速であることが望ましく、通常、低沸分の揮発が始まる２００℃付近から水素の発生のみとなる７００℃近傍までを、３～１００℃／ｈｒで昇温する。

【０１７６】

[[黒鉛化]]

脱揮発成分・焼成により得られた炭化物成形体は、次いで、高温で加熱して黒鉛化する。黒鉛化の条件については製造方法１記載と同様である。

【０１７７】

黒鉛化時の雰囲気は、酸化を防止するため、窒素、アルゴン等の不活性ガスの流通下又はブリーズ、パッキングコークス等の粒状炭素材料を間隙に充填した非酸化性雰囲気下で行う。黒鉛化に用いる設備は、電気炉やガス炉、電極材用アチソン炉等、上記の目的に添うものであれば特に限定されず、昇温速度、冷却速度、熱処理時間等は使用する設備の許容範囲で任意に設定することができる。

【０１７８】

[[粉砕]]

このようにして得られた黒鉛化処理物は、通常はこのままでは塊状であり負極活物質としては使用が困難であることから、粉砕及び／又は大径粒状物・小径粒状物除去を行う。黒鉛化処理物の粉砕方法は特に制限はないが、粉砕手段としては、機械的に摩砕する手段、例えば、ボールミル、ハンマーミル、ＣＦミル、アトマイザーミル、パルベライザー等、風力を利用した粉砕手段、例えば、ジェットミル等が例示される。粗粉砕、中粉砕については、ジョークラッシャー、ハンマーミル、ローラーミル等の衝撃力による粉砕方式を

用いてもよい。ここで、粉砕のタイミングは、黒鉛化前であっても黒鉛化後であってもよい。

【０１７９】

［副材混合］

本発明のリチウムイオン二次電池における負極活物質には、上記異配向性炭素複合物以外に、それとは炭素質の物性が異なる炭素質物（炭素質材料）を１種以上含有させることにより、更に、電池性能の向上を図ることが可能である。ここで述べた「炭素質の物性」とは、Ｘ線回折パラメータ、メジアン径、アスペクト比、ＢＥＴ比表面積、配向比、ラマンＲ値、タップ密度、真密度、細孔分布、円形度、灰分量のうちの一つ以上の特性を示す。また、好ましい実施の形態としては、体積基準粒度分布がメジアン径を中心としたときに左右対称とならないことや、ラマンＲ値異なる炭素材料を２種以上含有していること、Ｘ線パラメータが異なること等が挙げられる。その効果の一例としては、天然黒鉛、人造黒鉛等の黒鉛（グラファイト）、アセチレンブラック等のカーボンブラック、ニードルコークス等の無定形炭素等の炭素材料を副材として含有されることにより電気抵抗を低減させること等が挙げられる。これらは、１種を単独で用いても、２種以上を任意の組み合わせ及び比率で併用しても良い。副材として添加する場合には０．１質量％以上、好ましくは０．５質量％以上、より好ましくは０．６質量％以上であり、上限としては８０質量％以下、好ましくは５０質量％以下、より好ましくは４０質量％以下、更に好ましくは３０質量％以下の範囲である。この範囲を下回ると、導電性向上の効果が得にくい場合がある。上回ると、初期不可逆容量の増大を招く場合がある。

【０１８０】

［電極作製］

負極の製造は、常法によればよい。例えば、負極活物質に、バインダー、溶媒、必要に応じて、増粘剤、導電材、充填材等を加えてスラリーとし、これを集電体に塗布、乾燥した後にプレスすることによって形成することができる。電池の非水系電解液注液工程直前の段階での片面あたりの負極活物質層の厚さは通常１５μｍ以上、好ましくは２０μｍ以上、より好ましくは３０μｍ以上であり、上限は１５０μｍ以下、好ましくは１２０μｍ以下、より好ましくは１００μｍ以下である。この範囲を上回ると、非水系電解液が集電体界面付近まで浸透しにくいため、高電流密度充放電特性が低下する場合がある。またこの範囲を下回ると、負極活物質に対する集電体の体積比が増加し、電池の容量が減少する場合がある。また、負極活物質をロール成形してシート電極としたり、圧縮成形によりペレット電極としても良い。

【０１８１】

［［集電体］］

負極活物質を保持させる集電体としては、公知のものを任意に用いることができる。負極の集電体としては、銅、ニッケル、ステンレス鋼、ニッケルメッキ鋼等の金属材料が挙げられ、中でも加工し易さとコストの点から特に銅が好ましい。集電体の形状は、集電体が金属材料の場合は、例えば金属箔、金属円柱、金属コイル、金属板、金属薄膜、エキスパンドメタル、パンチメタル、発泡メタル等が挙げられる。中でも好ましくは金属薄膜、より好ましくは銅箔であり、更に好ましくは圧延法による圧延銅箔と、電解法による電解銅箔があり、どちらも集電体として用いることができる。銅箔の厚さが２５μｍよりも薄い場合、純銅よりも強度の高い銅合金（リン青銅、チタン銅、コルソン合金、Ｃｕ－Ｃｒ－Ｚｒ合金等）を用いることができる。

【０１８２】

圧延法により作製した銅箔からなる集電体は、銅結晶が圧延方向に並んでいるため、負極を密に丸めても、鋭角に丸めても割れにくく、小型の円筒状電池に好適に用いることができる。電解銅箔は、例えば、銅イオンが溶解された非水系電解液中に金属製のドラムを浸漬し、これを回転させながら電流を流すことにより、ドラムの表面に銅を析出させ、これを剥離して得られるものである。上記の圧延銅箔の表面に、電解法により銅を析出させていても良い。銅箔の片面又は両面には、粗面化処理や表面処理（例えば、厚さが数ｎｍ

～１μｍ程度までのクロメート処理、Ｔｉ等の下地処理等）がなされていても良い。

【０１８３】

また、集電体基板には、更に次のような物性が望まれる。

（１）平均表面粗さ（Ｒａ）

ＪＩＳＢ０６０１－１９９４に記載の方法で規定される集電体基板の活物質薄膜形成面の平均表面粗さ（Ｒａ）は、特に制限されないが、通常０．０１μｍ以上、好ましくは０．０３μｍ以上、通常１．５μｍ以下、好ましくは１．３μｍ以下、特に好ましくは１．０μｍ以下である。集電体基板の平均表面粗さ（Ｒａ）を上記した下限と上限の間の範囲内とすることにより、良好な充放電サイクル特性が期待できる。上記下限値以上とすることにより、活物質薄膜との界面の面積が大きくなり、活物質薄膜との密着性が向上する。平均表面粗さ（Ｒａ）の上限値は特に制限されるものではないが、平均表面粗さ（Ｒａ）が１．５μｍを超えるものは電池として実用的な厚みの箔としては一般に入手しにくいため、１．５μｍ以下のものが好ましい。

【０１８４】

（２）引張強度

集電体基板の引張強度は、特に制限されないが、通常５０Ｎ／ｍｍ^{2}以上、好ましくは１００Ｎ／ｍｍ^{2}以上、更に好ましくは１５０Ｎ／ｍｍ^{2}以上である。引張強度とは、試験片が破断に至るまでに要した最大引張力を、試験片の断面積で割ったものである。本発明における引張強度は、伸び率と同様な装置及び方法で測定される。引張強度が高い集電体基板であれば、充電・放電に伴う活物質薄膜の膨張・収縮による集電体基板の亀裂を抑制することができ、良好なサイクル特性を得ることができる。

【０１８５】

（３）０．２％耐力

集電体基板の０．２％耐力は、特に制限されないが、通常３０Ｎ／ｍｍ^{2}以上、好ましくは１００Ｎ／ｍｍ^{2}以上、特に好ましくは１５０Ｎ／ｍｍ^{2}以上である。０．２％耐力とは、０．２％の塑性（永久）歪みを与えるに必要な負荷の大きさであり、この大きさの負荷を加えた後に除荷しても０．２％変形している事を意味している。本発明における０．２％耐力は、伸び率と同様な装置及び方法で測定される。０．２％耐力が高い集電体基板であれば、充電・放電に伴う活物質薄膜の膨張・収縮による集電体基板の塑性変形を抑制することができ、良好なサイクル特性を得ることができる。金属薄膜の厚さは任意であるが、通常１μｍ以上、好ましくは３μｍ以上、より好ましくは５μｍ以上である。また、上限は、通常１ｍｍ以下、好ましくは１００μｍ以下、より好ましくは３０μｍ以下である。１μｍより薄くなると強度が低下するため塗布が困難となり工程上好ましくない場合がある。１００μｍより厚くなると捲回等で所望の電極の形に変形させることがあり、工程上困難となる場合がある。また、金属薄膜は、メッシュ状でもよい。

【０１８６】

[[集電体と活物質層の厚さの比]]

集電体と活物質層の厚さの比は特には限定されないが、（非水系電解液注液直前の片面の活物質層の厚さ）／（集電体の厚さ）の値が１５０以下、好ましくは２０以下、より好ましくは１０以下であり、下限は０．１以上、好ましくは０．４以上、より好ましくは１以上の範囲である。この範囲を上回ると、高電流密度充放電時に集電体がジュール熱による発熱を生じる場合がある。この範囲を下回ると、負極活物質に対する集電体の体積比が増加し、電池の容量が減少する場合がある。

【０１８７】

[[電極密度]]

負極活物質の電極化した際の電極構造は特には限定されないが、集電体上に存在している活物質の密度は、好ましくは１ｇ／ｃｍ^{3}以上、より好ましくは１．２ｇ／ｃｍ^{3}以上、更に好ましくは１．３ｇ／ｃｍ^{3}以上であり、上限として２ｇ／ｃｍ^{3}以下、好ましくは１．９ｇ／ｃｍ^{3}以下、より好ましくは１．８ｇ／ｃｍ^{3}以下、更に好ましくは１．７ｇ／ｃｍ^{3}以下の範囲である。この範囲を上回ると活物質粒子が破壊され、初期不可逆容量の増

加や、集電体／活物質界面付近への非水系電解液の浸透性が低下し、高電流密度充放電特性の低下を招く場合がある。また下回ると活物質間の導電性が低下し、電池抵抗が増大し、単位容積当たりの容量低下を招く場合がある。

【０１８８】

[[バインダー]]

活物質を結着するバインダーとしては、非水系電解液や電極製造時に用いる溶媒に対して安定な材料であれば、特に制限されない。具体的には、ポリエチレン、ポリプロピレン、ポリエチレンテレフタレート、ポリメチルメタクリレート、ポリイミド、芳香族ポリアミド、セルロース、ニトロセルロース等の樹脂系高分子；ＳＢＲ（スチレン－ブタジエンゴム）、イソプレンゴム、ブタジエンゴム、フッ素ゴム、ＮＢＲ（アクリロニトリル－ブタジエンゴム）、エチレン－プロピレンゴム等のゴム状高分子；スチレン・ブタジエン・スチレンブロック共重合体及びその水素添加物；ＥＰＤＭ（エチレン・プロピレン・ジエン三元共重合体）、スチレン・エチレン・ブタジエン・スチレン共重合体、スチレン・イソプレン・スチレンブロック共重合体及びその水素添加物等の熱可塑性エラストマー状高分子；シンジオタクチック－１，２－ポリブタジエン、ポリ酢酸ビニル、エチレン・酢酸ビニル共重合体、プロピレン・α－オレフィン共重合体等の軟質樹脂状高分子；ポリフッ化ビニリデン、ポリテトラフルオロエチレン、フッ素化ポリフッ化ビニリデン、ポリテトラフルオロエチレン・エチレン共重合体等のフッ素系高分子；アルカリ金属イオン（特にリチウムイオン）のイオン伝導性を有する高分子組成物等が挙げられる。これらは、１種を単独で用いても、２種以上を任意の組み合わせ及び比率で併用しても良い。

【０１８９】

スラリーを形成するための溶媒としては、活物質、バインダー、必要に応じて使用される増粘剤及び導電材を、溶解又は分散することが可能な溶媒であれば、その種類に特に制限はなく、水系溶媒と有機系溶媒のどちらを用いても良い。水系溶媒の例としては水、アルコールと水との混合溶媒等が挙げられ、有機系溶媒の例としてはＮ－メチルピロリドン（ＮＭＰ）、ジメチルホルムアミド、ジメチルアセトアミド、メチルエチルケトン、シクロヘキサノン、酢酸メチル、アクリル酸メチル、ジエチルトリアミン、Ｎ，Ｎ－ジメチルアミノプロピルアミン、テトラヒドロフラン（ＴＨＦ）、トルエン、アセトン、ジエチルエーテル、ジメチルアセトアミド、ヘキサメリルホスファルアミド、ジメチルスルフォキシド、ベンゼン、キシレン、キノリン、ピリジン、メチルナフタレン、ヘキサン等が挙げられる。特に水系溶媒を用いる場合、上述の増粘剤に併せて分散剤等を加え、ＳＢＲ等のラテックスを用いてスラリー化する。なお、これらは、１種を単独で用いても、２種以上を任意の組み合わせ及び比率で併用しても良い。

【０１９０】

活物質に対するバインダーの割合は、０．１質量％以上、好ましくは０．５質量％以上、より好ましくは０．６質量％以上であり、上限としては２０質量％以下、好ましくは１５質量％以下、より好ましくは１０質量％以下、更に好ましくは８質量％以下の範囲である。この範囲を上回るとバインダー量が電池容量に寄与しないバインダー割合が増加して、電池容量が低下する場合がある。また下回ると、負極電極の強度低下を招き、電池作製工程上好ましくない場合がある。特に、ＳＢＲに代表されるゴム状高分子を主要成分に含有する場合には、活物質に対するバインダーの割合は、０．１質量％以上、好ましくは０．５質量％以上、より好ましくは０．６質量％以上であり、上限としては５質量％以下、好ましくは３質量％以下、より好ましくは２質量％以下の範囲である。また、ポリフッ化ビニリデンに代表されるフッ素系高分子を主要成分に含有する場合には活物質に対する割合は、１質量％以上、好ましくは２質量％以上、より好ましくは３質量％以上であり、上限としては１５質量％以下、好ましくは１０質量％以下、より好ましくは８質量％以下の範囲である。

【０１９１】

増粘剤は、通常、スラリーの粘度を調製するために使用される。増粘剤としては、特に制限はないが、具体的には、カルボキシメチルセルロース、メチルセルロース、ヒドロキ

シメチルセルロース、エチルセルロース、ポリビニルアルコール、酸化スターチ、リン酸化スターチ、カゼイン及びこれらの塩等が挙げられる。これらは、１種を単独で用いても、２種以上を任意の組み合わせ及び比率で併用しても良い。更に増粘剤を添加する場合には、活物質に対する増粘剤の割合は、０．１質量％以上、好ましくは０．５質量％以上、より好ましくは０．６質量％以上であり、上限としては５質量％以下、好ましくは３質量％以下、より好ましくは２質量％以下の範囲である。この範囲を下回ると、著しく塗布性が低下する場合がある。上回ると、負極活物質層に占める活物質の割合が低下し、電池の容量が低下したり、負極活物質間の抵抗が増大したりする場合がある。

【０１９２】

[[極板配向比]]

極板配向比は、０．００１以上、好ましくは０．００５以上、より好ましくは０．０１以上、上限は理論値である０．６７以下である。この範囲を下回ると、高密度充放電特性が低下する場合がある。

【０１９３】

極板配向比の測定は以下のとおりである。目的密度にプレス後の負極電極について、Ｘ線回折により電極の活物質配向比を測定する。具体的手法は特に制限されないが、標準的な方法としては、Ｘ線回折により炭素の（１１０）回折と（００４）回折のピークを、プロファイル関数として非対称ピアソンVIIを用いてフィッティングすることによりピーク分離を行ない、（１１０）回折と（００４）回折のピークの積分強度を各々算出する。得られた積分強度から、（１１０）回折積分強度／（００４）回折積分強度で表わされる比を算出する。該測定で算出される電極の活物質配向比を極板配向比と定義する。

【０１９４】

ここでのＸ線回折測定条件は次の通りである。なお、「２θ」は回折角を示す。

・ターゲット：　Ｃｕ（Ｋα線）グラファイトモノクロメーター

・スリット　：　発散スリット＝１度、受光スリット＝０．１ｍｍ、散乱スリット＝１度

・測定範囲、及び、ステップ角度／計測時間：

（１１０）面　：　７６．５度≦２θ≦７８．５度　　０．０１度／３秒

（００４）面　：　５３．５度≦２θ≦５６．０度　　０．０１度／３秒

・試料調製　：　硝子板に０．１ｍｍ厚さの両面テープで電極を固定

【０１９５】

[[インピーダンス]]

放電状態から公称容量の６０％まで充電した時の負極の抵抗が１００Ω以下が好ましく、特に好ましくは５０Ω以下、より好ましくは２０Ω以下、及び／又は二重層容量が1×10^{-6}Ｆ以上が好ましく、特に好ましくは1×10^{-5}Ｆ以上、より好ましくは1×10^{-4}Ｆ以上である。この範囲であると出力特性が良く好ましい。

【０１９６】

負極の抵抗及び二重層容量は、次の手順で測定する。測定するリチウムイオン二次電池は、公称容量を５時間で充電できる電流値にて充電した後に、２０分間充放電をしない状態を維持し、次に公称容量を１時間で放電できる電流値で放電したときの容量が公称容量の８０％以上あるものを用いる。前述の放電状態のリチウムイオン二次電池について公称容量を５時間で充電できる電流値にて公称容量の６０％まで充電し、直ちにリチウムイオン二次電池をアルゴンガス雰囲気下のグローブボックス内に移す。ここで該リチウムイオン二次電池を負極が放電又はショートしない状態ですばやく解体して取り出し、両面塗布電極であれば、片面の電極活物質を他面の電極活物質を傷つけずに剥離し、負極電極を１２．５ｍｍφに２枚打ち抜き、セパレータを介して活物質面がずれないよう対向させる。電池に使用されていた非水系電解液６０μＬをセパレータと両負極間に滴下して密着し、外気と触れない状態を保持して、両負極の集電体に導電をとり、交流インピーダンス法を実施する。測定は温度２５℃で、10^{-2}～10^{5}Ｈｚの周波数帯で複素インピーダンス測定を行ない、求められたコール・コール・プロットの負極抵抗成分の円弧を半円で近似して表面抵抗（Ｒ）と、二重層容量（Ｃｄｌ）を求める。

【０１９７】
＜正極＞
以下に本発明のリチウムイオン二次電池に使用される正極について説明する。
［正極活物質］
以下に正極に使用される正極活物質について述べる。
【０１９８】
［［組成］］
正極活物質としては、電気化学的にリチウムイオンを吸蔵・放出可能なものであれば特に制限はない。リチウムと少なくとも１種の遷移金属を含有する物質が好ましく、例えば、リチウム遷移金属複合酸化物、リチウム含有遷移金属リン酸化合物が挙げられる。
【０１９９】
リチウム遷移金属複合酸化物の遷移金属としてはＶ、Ｔｉ、Ｃｒ、Ｍｎ、Ｆｅ、Ｃｏ、Ｎｉ、Ｃｕ等が好ましく、具体例としては、$LiCoO_2$等のリチウム・コバルト複合酸化物、$LiNiO_2$等のリチウム・ニッケル複合酸化物、$LiMnO_2$、$LiMn_2O_4$、Li_2MnO_3等のリチウム・マンガン複合酸化物、これらのリチウム遷移金属複合酸化物の主体となる遷移金属原子の一部をＡｌ、Ｔｉ、Ｖ、Ｃｒ、Ｍｎ、Ｆｅ、Ｃｏ、Ｌｉ、Ｎｉ、Ｃｕ、Ｚｎ、Ｍｇ、Ｇａ、Ｚｒ、Ｓｉ等の他の金属で置換したもの等が挙げられる。置換されたものの具体例としては、例えば、$LiNi_{0.5}Mn_{0.5}O_2$、$LiNi_{0.85}Co_{0.10}Al_{0.05}O_2$、$LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$、$LiMn_{1.8}Al_{0.2}O_4$、$LiMn_{1.5}Ni_{0.5}O_4$等が挙げられる。
【０２００】
リチウム含有遷移金属リン酸化合物の遷移金属としては、Ｖ、Ｔｉ、Ｃｒ、Ｍｎ、Ｆｅ、Ｃｏ、Ｎｉ、Ｃｕ等が好ましく、具体例としては、例えば、$LiFePO_4$、$Li_3Fe_2(PO_4)_3$、$LiFeP_2O_7$等のリン酸鉄類、$LiCoPO_4$等のリン酸コバルト類、これらのリチウム遷移金属リン酸化合物の主体となる遷移金属原子の一部をＡｌ、Ｔｉ、Ｖ、Ｃｒ、Ｍｎ、Ｆｅ、Ｃｏ、Ｌｉ、Ｎｉ、Ｃｕ、Ｚｎ、Ｍｇ、Ｇａ、Ｚｒ、Ｎｂ、Ｓｉ等の他の金属で置換したもの等が挙げられる。
【０２０１】
［［表面被覆］］
また、これら正極活物質の表面に、正極活物質を構成する物質とは異なる組成の物質が付着したものを用いることもできる。表面付着物質としては酸化アルミニウム、酸化ケイ素、酸化チタン、酸化ジルコニウム、酸化マグネシウム、酸化カルシウム、酸化ホウ素、酸化アンチモン、酸化ビスマス等の酸化物、硫酸リチウム、硫酸ナトリウム、硫酸カリウム、硫酸マグネシウム、硫酸カルシウム、硫酸アルミニウム等の硫酸塩、炭酸リチウム、炭酸カルシウム、炭酸マグネシウム等の炭酸塩、炭素等が挙げられる。
【０２０２】
これら表面付着物質は、例えば、溶媒に溶解又は懸濁させて正極活物質に含浸添加、乾燥する方法、表面付着物質前駆体を溶媒に溶解又は懸濁させて正極活物質に含浸添加後、加熱等により反応させる方法、正極活物質前駆体に添加して同時に焼成する方法等により正極活物質表面に付着させることができる。尚、炭素を付着させる場合には、炭素質を、例えば、活性炭などの形で後から機械的に付着させる方法を用いることもできる。
【０２０３】
表面付着物質の量としては、正極活物質に対して質量で、下限として好ましくは０．１ｐｐｍ以上、より好ましくは１ｐｐｍ以上、更に好ましくは１０ｐｐｍ以上、上限として好ましくは２０質量％以下、より好ましくは１０質量％以下、更に好ましくは５質量％以下で用いられる。表面付着物質により、正極活物質表面での非水系電解液の酸化反応を抑制することができ、電池寿命を向上させることができるが、その付着量が少なすぎる場合その効果は十分に発現せず、多すぎる場合には、リチウムイオンの出入りを阻害するため抵抗が増加する場合がある。
【０２０４】

[[形状]]

本発明における正極活物質粒子の形状は、従来用いられるような、塊状、多面体状、球状、楕円球状、板状、針状、柱状等が用いられるが、中でも一次粒子が凝集して、二次粒子を形成して成り、その二次粒子の形状が球状ないし楕円球状であるものが好ましい。通常、電気化学素子はその充放電に伴い、電極中の活物質が膨張収縮をするため、そのストレスによる活物質の破壊や導電パス切れ等の劣化がおきやすい。そのため一次粒子のみの単一粒子活物質であるよりも、一次粒子が凝集して、二次粒子を形成したものである方が膨張収縮のストレスを緩和して、劣化を防ぐため好ましい。また、板状等軸配向性の粒子であるよりも球状ないし楕円球状の粒子の方が、電極の成形時の配向が少ないため、充放電時の電極の膨張収縮も少なく、また電極を作成する際の導電材との混合においても、均一に混合されやすいため好ましい。

【０２０５】

[[タップ密度]]

正極活物質のタップ密度は、通常１．３ｇ／ｃｍ^{3}以上、好ましくは１．５ｇ／ｃｍ^{3}以上、更に好ましくは１．６ｇ／ｃｍ^{3}以上、最も好ましくは１．７ｇ／ｃｍ^{3}以上である。正極活物質のタップ密度が上記下限を下回ると正極活物質層形成時に、必要な分散媒量が増加すると共に、導電材や結着剤の必要量が増加し、正極活物質層への正極活物質の充填率が制約され、電池容量が制約される場合がある。タップ密度の高い金属複合酸化物粉体を用いることにより、高密度の正極活物質層を形成することができる。タップ密度は一般に大きいほど好ましく特に上限はないが、大きすぎると、正極活物質層内における非水系電解液を媒体としたリチウムイオンの拡散が律速となり、負荷特性が低下しやすくなる場合があるため、通常２．５ｇ／ｃｍ^{3}以下、好ましくは２．４ｇ／ｃｍ^{3}以下である。なお、タップ密度は、前記した方法と同様な方法で測定され定義される。

【０２０６】

[[メジアン径ｄ$_{50}$]]

粒子のメジアン径ｄ$_{50}$（一次粒子が凝集して二次粒子を形成している場合には二次粒子径）は通常０．１μｍ以上、好ましくは０．５μｍ以上、より好ましくは１μｍ以上、最も好ましくは３μｍ以上で、上限は、通常２０μｍ以下、好ましくは１８μｍ以下、より好ましくは１６μｍ以下、最も好ましくは１５μｍ以下である。上記下限を下回ると、高タップ密度品が得られなくなる場合があり、上限を超えると粒子内のリチウムの拡散に時間がかかるため、電池性能の低下をきたしたり、電池の正極作成すなわち活物質と導電材やバインダー等を溶媒でスラリー化し、薄膜状に塗布する際に、スジを引く等の問題を生ずる場合がある。ここで、異なるメジアン径ｄ$_{50}$をもつ正極活物質を２種類以上混合することで、正極作成時の充填性を更に向上させることもできる。

【０２０７】

なお、本発明におけるメジアン径ｄ$_{50}$は、公知のレーザー回折／散乱式粒度分布測定装置によって測定される。粒度分布計としてＨＯＲＩＢＡ社製ＬＡ－９２０を用いる場合、測定の際に用いる分散媒として、０．１質量％ヘキサメタリン酸ナトリウム水溶液を用い、５分間の超音波分散後に測定屈折率１．２４を設定して測定される。

【０２０８】

[[平均一次粒子径]]

一次粒子が凝集して二次粒子を形成している場合には、正極活物質の平均一次粒子径としては、通常０．０１μｍ以上、好ましくは０．０５μｍ以上、更に好ましくは０．０８μｍ以上、最も好ましくは０．１μｍ以上で、上限は、通常３μｍ以下、好ましくは２μｍ以下、更に好ましくは１μｍ以下、最も好ましくは０．６μｍ以下である。上記上限を超えると球状の二次粒子を形成し難く、粉体充填性に悪影響を及ぼしたり、比表面積が大きく低下するために、出力特性等の電池性能が低下する可能性が高くなる場合がある。逆に、上記下限を下回ると、通常、結晶が未発達であるために充放電の可逆性が劣る場合がある。

【０２０９】

なお、一次粒子径は、走査電子顕微鏡（ＳＥＭ）を用いた観察により測定される。具体的には、１００００倍の倍率の写真で、水平方向の直線に対する一次粒子の左右の境界線による切片の最長の値を、任意の５０個の一次粒子について求め、平均値をとることにより求められる。

【０２１０】

[[ＢＥＴ比表面積]]

本発明の二次電池に供する正極活物質のＢＥＴ比表面積は、０．２m^2／ｇ以上、好ましくは０．３m^2／ｇ以上、更に好ましくは０．４m^2／ｇ以上で、上限は４m^2／ｇ以下、好ましくは２．５m^2／ｇ以下、更に好ましくは１．５m^2／ｇ以下である。ＢＥＴ比表面積がこの範囲よりも小さいと電池性能が低下しやすく、大きいとタップ密度が上がりにくくなり、正極活物質形成時の塗布性に問題が発生しやすい場合がある。

【０２１１】

ＢＥＴ比表面積は、表面積計（例えば、大倉理研製全自動表面積測定装置）を用い、試料に対して窒素流通下１５０℃で３０分間、予備乾燥を行なった後、大気圧に対する窒素の相対圧の値が０．３となるように正確に調整した窒素ヘリウム混合ガスを用い、ガス流動法による窒素吸着ＢＥＴ１点法によって測定した値で定義される。

【０２１２】

[[製造法]]

正極活物質の製造法としては、無機化合物の製造法として一般的な方法が用いられる。特に球状ないし楕円球状の活物質を作成するには種々の方法が考えられるが、例えば、遷移金属硝酸塩、遷移金属硫酸塩等の遷移金属原料物質と、必要に応じ他の元素の原料物質を水等の溶媒中に溶解ないし粉砕分散して、撹拌をしながらｐＨを調節して球状の前駆体を作成回収し、これを必要に応じて乾燥した後、ＬｉＯＨ、Li_2CO_3、$LiNO_3$等のＬｉ源を加えて高温で焼成して活物質を得る方法、遷移金属硝酸塩、遷移金属硫酸塩、遷移金属水酸化物、遷移金属酸化物等の遷移金属原料物質と、必要に応じ他の元素の原料物質を水等の溶媒中に溶解ないし粉砕分散して、それをスプレードライヤー等で乾燥成型して球状ないし楕円球状の前駆体とし、これにＬｉＯＨ、Li_2CO_3、$LiNO_3$等のＬｉ源を加えて高温で焼成して活物質を得る方法、また、遷移金属硝酸塩、遷移金属硫酸塩、遷移金属水酸化物、遷移金属酸化物等の遷移金属原料物質と、ＬｉＯＨ、Li_2CO_3、$LiNO_3$等のＬｉ源と、必要に応じ他の元素の原料物質とを水等の溶媒中に溶解ないし粉砕分散して、それをスプレードライヤー等で乾燥成型して球状ないし楕円球状の前駆体とし、これを高温で焼成して活物質を得る方法等が挙げられる。

【０２１３】

［正極の構成］

以下に、本発明に使用される正極の構成について述べる。

[[電極構造と作製法]]

本発明のリチウムイオン二次電池用正極は、正極活物質と結着剤とを含有する正極活物質層を、集電体上に形成して作製される。正極活物質を用いる正極の製造は、常法により行うことができる。すなわち、正極活物質と結着剤、並びに必要に応じて導電材及び増粘剤等を乾式で混合してシート状にしたものを正極集電体に圧着するか、又はこれらの材料を液体媒体に溶解又は分散させてスラリーとして、これを正極集電体に塗布し、乾燥することにより、正極活物質層を集電体上に形成させることにより正極を得ることができる。

【０２１４】

正極活物質はその２種類以上を事前に混合して用いてもよいし、正極作成時に同時に加えることによって混合されてもよい。

【０２１５】

[[正極活物質]]

本発明のリチウムイオン二次電池の正極に用いられる正極活物質の、正極活物質層中の含有量は、好ましくは８０質量％以上、より好ましくは８２質量％以上、特に好ましくは８４質量％以上である。また上限は、好ましくは９５質量％以下、より好ましくは９３質

量％以下である。正極活物質層中の正極活物質の含有量が低いと電気容量が不十分となる場合がある。逆に含有量が高すぎると正極の強度が不足する場合がある。

【０２１６】

[[導電材]]

導電材としては、公知の導電材を任意に用いることができる。具体例としては、銅、ニッケル等の金属材料；天然黒鉛、人造黒鉛等の黒鉛（グラファイト）；アセチレンブラック等のカーボンブラック；ニードルコークス等の無定形炭素等の炭素材料等が挙げられる。なお、これらは、１種を単独で用いてもよく、２種以上を任意の組み合わせ及び比率で併用してもよい。

【０２１７】

導電材は、正極活物質層中に、通常０．０１質量％以上、好ましくは０．１質量％以上、より好ましくは１質量％以上であり、また上限は、通常５０質量％以下、好ましくは３０質量％以下、より好ましくは１５質量％以下含有するように用いられる。含有量がこの範囲よりも低いと導電性が不十分となる場合がある。逆に、含有量がこの範囲よりも高いと電池容量が低下する場合がある。

【０２１８】

[[結着剤]]

正極活物質層の製造に用いる結着剤としては、特に限定されず、塗布法の場合は、電極製造時に用いる液体媒体に対して溶解又は分散される材料であれば良いが、具体例としては、ポリエチレン、ポリプロピレン、ポリエチレンテレフタレート、ポリメチルメタクリレート、芳香族ポリアミド、セルロース、ニトロセルロース等の樹脂系高分子；ＳＢＲ（スチレン－ブタジエンゴム）、ＮＢＲ（アクリロニトリル－ブタジエンゴム）、フッ素ゴム、イソプレンゴム、ブタジエンゴム、エチレン－プロピレンゴム等のゴム状高分子；スチレン・ブタジエン・スチレンブロック共重合体又はその水素添加物、ＥＰＤＭ（エチレン・プロピレン・ジエン三元共重合体）、スチレン・エチレン・ブタジエン・エチレン共重合体、スチレン・イソプレン・スチレンブロック共重合体又はその水素添加物等の熱可塑性エラストマー状高分子；シンジオタクチック－１，２－ポリブタジエン、ポリ酢酸ビニル、エチレン・酢酸ビニル共重合体、プロピレン・α－オレフィン共重合体等の軟質樹脂状高分子；ポリフッ化ビニリデン（ＰＶｄＦ）、ポリテトラフルオロエチレン、フッ素化ポリフッ化ビニリデン、ポリテトラフルオロエチレン・エチレン共重合体等のフッ素系高分子；アルカリ金属イオン（特にリチウムイオン）のイオン伝導性を有する高分子組成物等が挙げられる。なお、これらの物質は、１種を単独で用いても良く、２種以上を任意の組み合わせ及び比率で併用しても良い。

【０２１９】

正極活物質層中の結着剤の割合は、通常０．１質量％以上、好ましくは１質量％以上、更に好ましくは３質量％以上であり、上限は通常８０質量％以下、好ましくは６０質量％以下、更に好ましくは４０質量％以下、最も好ましくは１０質量％以下である。結着剤の割合が低すぎると、正極活物質を十分保持できずに正極の機械的強度が不足し、サイクル特性等の電池性能を悪化させてしまう場合がある。一方で、高すぎると、電池容量や導電性の低下につながる場合がある。

【０２２０】

[[液体媒体]]

スラリーを形成するための液体媒体としては、正極活物質、導電材、結着剤、並びに必要に応じて使用される増粘剤を溶解又は分散することが可能な溶媒であれば、その種類に特に制限はなく、水系溶媒と有機系溶媒のどちらを用いても良い。

【０２２１】

水系媒体としては、例えば、水、アルコールと水との混合媒等が挙げられる。有機系媒体としては、例えば、ヘキサン等の脂肪族炭化水素類；ベンゼン、トルエン、キシレン、メチルナフタレン等の芳香族炭化水素類；キノリン、ピリジン等の複素環化合物；アセトン、メチルエチルケトン、シクロヘキサノン等のケトン類；酢酸メチル、アクリル酸メチ

ル等のエステル類；ジエチレントリアミン、Ｎ，Ｎ－ジメチルアミノプロピルアミン等のアミン類；ジエチルエーテル、プロピレンオキシド、テトラヒドロフラン（ＴＨＦ）等のエーテル類；Ｎ－メチルピロリドン（ＮＭＰ）、ジメチルホルムアミド、ジメチルアセトアミド等のアミド類；ヘキサメチルホスファルアミド、ジメチルスルフォキシド等の非プロトン性極性溶媒等を挙げることができる。

【０２２２】

[[増粘剤]]

特に水系媒体を用いる場合、増粘剤と、スチレンブタジエンゴム（ＳＢＲ）等のラテックスを用いてスラリー化するのが好ましい。増粘剤は、通常、スラリーの粘度を調製するために使用される。増粘剤としては、特に制限はないが、具体的には、カルボキシメチルセルロース、メチルセルロース、ヒドロキシメチルセルロース、エチルセルロース、ポリビニルアルコール、酸化スターチ、リン酸化スターチ、カゼイン及びこれらの塩等が挙げられる。これらは、１種を単独で用いても、２種以上を任意の組み合わせ及び比率で併用しても良い。更に増粘剤を添加する場合には、活物質に対する増粘剤の割合は、０．１質量％以上、好ましくは０．５質量％以上、より好ましくは０．６質量％以上であり、また、上限としては５質量％以下、好ましくは３質量％以下、より好ましくは２質量％以下の範囲である。この範囲を下回ると、著しく塗布性が低下する場合がある。上回ると、正極活物質層に占める活物質の割合が低下し、電池の容量が低下したり、正極活物質間の抵抗が増大したりする場合がある。

【０２２３】

[[圧密化]]

塗布、乾燥によって得られた正極活物質層は、正極活物質の充填密度を上げるために、ハンドプレス、ローラープレス等により圧密化することが好ましい。正極活物質層の密度は、下限として好ましくは１．５ｇ／ｃｍ^{3}以上、より好ましくは２ｇ／ｃｍ^3、更に好ましくは２．２ｇ／ｃｍ^{3}以上であり、上限としては、好ましくは３．５ｇ／ｃｍ^{3}以下、より好ましくは３ｇ／ｃｍ^{3}以下、更に好ましくは２．８ｇ／ｃｍ^{3}以下の範囲である。この範囲を上回ると集電体／活物質界面付近への非水系電解液の浸透性が低下し、特に高電流密度での充放電特性が低下する場合がある。また下回ると活物質間の導電性が低下し、電池抵抗が増大する場合がある。

【０２２４】

[[集電体]]

正極集電体の材質としては特に制限は無く、公知のものを任意に用いることができる。具体例としては、アルミニウム、ステンレス鋼、ニッケルメッキ、チタン、タンタル等の金属材料；カーボンクロス、カーボンペーパー等の炭素材料が挙げられる。中でも金属材料、特にアルミニウムが好ましい。

【０２２５】

集電体の形状としては、金属材料の場合、金属箔、金属円柱、金属コイル、金属板、金属薄膜、エキスパンドメタル、パンチメタル、発泡メタル等が挙げられ、炭素材料の場合、炭素板、炭素薄膜、炭素円柱等が挙げられる。これらのうち、金属薄膜が好ましい。なお、薄膜は適宜メッシュ状に形成してもよい。薄膜の厚さは任意であるが、通常１μｍ以上、好ましくは３μｍ以上、より好ましくは５μｍ以上、また上限は、通常１ｍｍ以下、好ましくは１００μｍ以下、より好ましくは５０μｍ以下である。薄膜がこの範囲よりも薄いと集電体として必要な強度が不足する場合がある。逆に、薄膜がこの範囲よりも厚いと取り扱い性が損なわれる場合がある。

【０２２６】

集電体と正極活物質層の厚さの比は特には限定されないが、（非水系電解液注液直前の片面の活物質層の厚さ）／（集電体の厚さ）が２０以下であることが好ましく、より好ましくは１５以下、最も好ましくは１０以下であり、下限は、０．５以上が好ましく、より好ましくは０．８以上、最も好ましくは１以上の範囲である。この範囲を上回ると、高電流密度充放電時に集電体がジュール熱による発熱を生じる場合がある。この範囲を下回る

と、正極活物質に対する集電体の体積比が増加し、電池の容量が減少する場合がある。

【０２２７】

[[電極面積]]

本発明の非水系電解液を用いる場合、高出力かつ高温時の安定性を高める観点から、正極活物質層の面積は、電池外装ケースの外表面積に対して大きくすることが好ましい。具体的には、二次電池の外装の表面積に対する前記正極の電極面積の総和が面積比で２０倍以上とすることが好ましく、更に４０倍以上とすることがより好ましい。外装ケースの外表面積とは、有底角型形状の場合には、端子の突起部分を除いた発電要素が充填されたケース部分の縦と横と厚さの寸法から計算で求める総面積をいう。有底円筒形状の場合には、端子の突起部分を除いた発電要素が充填されたケース部分を円筒として近似する幾何表面積である。正極の電極面積の総和とは、負極活物質を含む合材層に対向する正極合材層の幾何表面積であり、集電体箔を介して両面に正極合材層を形成してなる構造では、それぞれの面を別々に算出する面積の総和をいう。

【０２２８】

[[放電容量]]

本発明の二次電池用非水系電解液を用いる場合、二次電池の１個の電池外装に収納される電池要素のもつ電気容量（電池を満充電状態から放電状態まで放電したときの電気容量）が、３アンペアーアワー（Ａｈ）以上であると、低温放電特性の向上効果が大きくなるため好ましい。そのため、正極板は、放電容量が満充電で、３アンペアアワー（Ａｈ）以上２０Ａｈ以下になるように設計することが好ましく、更に４Ａｈ以上１０Ａｈ以下がより好ましい。３Ａｈ未満では、大電流の取り出し時に電極反応抵抗による電圧低下が大きくなり電力効率が悪くなる場合がある。２０Ａｈ以上では、電極反応抵抗が小さくなり電力効率は良くなるが、パルス充放電時の電池内部発熱による温度分布が大きく、充放電繰り返しの耐久性が劣り、また、過充電や内部短絡等の異常時の急激な発熱に対して放熱効率も悪くなり、内圧が上昇してガス放出弁が作動する現象（弁作動）、電池内容物が外に激しく噴出する現象（破裂）に至る確率が上がる場合がある。

【０２２９】

[[正極板の厚さ]]

正極板の厚さは特に限定されるものではないが、高容量かつ高出力の観点から、芯材の金属箔厚さを差し引いた合材層の厚さは、集電体の片面に対して下限として、好ましくは１０μｍ以上、より好ましくは２０μｍ以上で、上限としては、好ましくは２００μｍ以下、より好ましくは１００μｍ以下である。

【０２３０】

＜リチウムイオン二次電池＞

以下に、本発明のリチウムイオン二次電池について詳細に記す。

【０２３１】

[電池形状]

電池形状は特に限定されるものではないが、有底筒型形状、有底角型形状、薄型形状、シート形状、ペーパー形状が挙げられる。システムや機器に組み込まれる際に、容積効率を高めて収納性を上げるために、電池周辺に配置される周辺システムへの収まりを考慮した馬蹄形、櫛型形状等の異型のものであってもよい。電池内部の熱を効率よく外部に放出する観点から、比較的平らで大面積の面を少なくとも一つを有する角型形状が好ましい。

【０２３２】

有底筒型形状の電池では、充填される発電素子に対する外表面積が小さくなるので、充電や放電時に内部抵抗による発生するジュール発熱を効率よく外部に逃げる設計にすることが好ましい。また、熱伝導性の高い物質の充填比率を高め、内部での温度分布が小さくなるように設計することが好ましい。

【０２３３】

有底角型形状では、一番大きい面の面積Ｓ（端子部を除く外形寸法の幅と高さとの積、単位ｃｍ^2）の２倍と電池外形の厚さＴ（単位ｃｍ）との比率２Ｓ／Ｔの値が１００以上

であることが好ましく、２００以上であることが更に好適である。最大面を大きくすることにより高出力かつ大容量の電池であってもサイクル性や高温保存等の特性を向上させるとともに、異常発熱時の放熱効率を上げることができ、「弁作動」や「破裂」という危険な状態になることを抑制することができる。

【０２３４】

［電池構成］

本発明のリチウムイオン二次電池は、リチウムイオンを吸蔵放出可能な正極及び負極、非水系電解液、正極と負極の間に配設されるセパレータ、集電端子、及び外装ケース等によって少なくとも構成される。要すれば、電池の内部及び／又は電池の外部に保護素子を装着してもよい。

【０２３５】

[[セパレータ]]

本発明で用いられるセパレータは、両極間を電子的に絶縁する所定の機械的強度を有し、イオン透過度が大きく、かつ、正極と接する側における酸化性と負極側における還元性への耐性を兼ね備えるものであれば特に限定されるものではない。このような要求特性を有するセパレータの材質として、樹脂、無機物、ガラス繊維等が用いられる。前記樹脂としては、オレフィン系ポリマー、フッ素系ポリマー、セルロース系ポリマー、ポリイミド、ナイロン等が用いられる。具体的には、電解液に対して安定で、保液性の優れた材料の中から選ぶのが好ましく、ポリエチレン、ポリプロピレン等のポリオレフィンを原料とする多孔性シート又は不織布等を用いるのが好ましい。

【０２３６】

前記無機物としては、アルミナや二酸化珪素等の酸化物類、窒化アルミニウムや窒化珪素等の窒化物類、硫酸バリウムや硫酸カルシウム等の硫酸塩類が用いられ、粒子形状若しくは繊維形状のものが用いられる。形態としては、不織布、織布、微多孔性フィルム等の薄膜形状のものが用いられる。薄膜形状では、孔径が０．０１～１μｍ、厚さが５～５０μｍのものが好適に用いられる。前記の独立した薄膜形状以外に、樹脂製の結着剤を用いて前記無機物の粒子を含有する複合多孔層を正極及び／又は負極の表層に形成させてなるセパレータを用いることができる。例えば、正極の両面に９０％粒径が１μｍ未満のアルミナ粒子をフッ素樹脂を結着剤として多孔層を形成させることが挙げられる。

【０２３７】

[[電極群]]

電極群は、前述の正極板と負極板とを前述のセパレータを介してなる積層構造のもの、及び前述の正極板と負極板とを前述のセパレータを介して渦巻き状に捲回した構造のものの何れでもよい。

【０２３８】

電極群の体積が電池内容積に占める割合（以下、電極群占有率と称する）は、４０％～９０％にすることが好ましく、５０％～８０％にすることが更に好ましい。前記の電極群占有率が４０％未満では、電池容量が小さくなり、また、９０％以上では空隙スペースが少なく、電池が高温になることによって部材が膨張したり電解質の液成分の蒸気圧が高くなったりして内部圧力が上昇し、電池としての充放電繰り返し性能や高温保存等の諸特性を低下させたり、更には、内部圧力を外に逃がすガス放出弁が作動する場合がある。

【０２３９】

[[集電構造]]

集電構造は特に限定されるものではないが、本発明の非水系電解液による低温放電特性の向上をより効果的に実現するには、配線部分や接合部分の抵抗を低減する構造にする必要がある。こうした内部抵抗が小さい場合、本発明の非水系電解液を使用した効果は特に良好に発揮される。

【０２４０】

電極群が前述の積層構造のものでは、各電極層の金属芯部分を束ねて端子に溶接して形成される構造が好適に用いられる。一枚の電極面積が大きくなる場合には、内部抵抗が大

きくなるので、電極内に複数の端子を設けて抵抗を低減することも好適に用いられる。電極群が前述の捲回構造のものでは、正極及び負極にそれぞれ複数のリード構造を設け、端子に束ねることにより、内部抵抗を低くすることができる。

【０２４１】

前述の構造を最適化することにより、内部抵抗をできるだけ小さくすることができる。大電流で用いられる電池では、１０ｋＨｚ交流法で測定されるインピーダンス（以下、「直流抵抗成分」と略記する）を１０ミリオーム（ｍΩ）以下にすることが好ましく、直流抵抗成分を５ミリオーム（ｍΩ）以下にすることがより好ましい。直流抵抗成分を０．１ミリオーム（ｍΩ）未満にすると高出力特性が向上するが、用いられる集電構造材の占める比率が増え、電池容量が減少する場合がある。

【０２４２】

本発明の非水系電解液は、電極活物質に対するリチウムの脱挿入に係わる反応抵抗の低減に効果があり、それが良好な低温放電特性を実現できる要因になっていると考えられる。しかし、通常の直流抵抗が大きな電池では、直流抵抗に阻害されて反応抵抗低減の効果を低温放電特性に１００％反映できないことがわかった。直流抵抗成分の小さな電池を用いることでこれを改善し、本発明の非水系電解液の効果を充分に発揮できるようになる。

【０２４３】

また、非水系電解液の効果を引き出し、高い低温放電特性をもつ電池を作製するという観点からは、この要件と前述した二次電池の１個の電池外装に収納される電池要素のもつ電気容量（電池を満充電状態から放電状態まで放電したときの電気容量）が、３アンペアーアワー（Ａｈ）以上である、という要件を同時に満たすことが特に好ましい。

【０２４４】

[[外装ケース]]

外装ケースの材質は用いられる非水系電解質に対して安定な物質であれば特に限定されるものではない。具体的には、ニッケルめっき鋼板、ステンレス、アルミニウム又はアルミニウム合金、マグネシウム合金等の金属類、又は、樹脂とアルミ箔との積層フィルム（ラミネートフィルム）が用いられる。軽量化の観点から、アルミニウム又はアルミニウム合金の金属、ラミネートフィルムが好適に用いられる。

【０２４５】

前記金属類を用いる外装ケースでは、レーザー溶接、抵抗溶接、超音波溶接により金属同士を溶着して封止密閉構造とするもの、若しくは、樹脂製ガスケットを介して前記金属類を用いてかしめ構造とするものが挙げられる。

【０２４６】

前記ラミネートフィルムを用いる外装ケースでは、樹脂層同士を熱融着することにより封止密閉構造とするもの等が挙げられる。シール性を上げるために、前記樹脂層の間にラミネートフィルムに用いられる樹脂と異なる樹脂を介在させてもよい。特に、集電端子を介して樹脂層を熱融着して密閉構造とする場合には、金属と樹脂との接合になるので、介在する樹脂として極性基を有する樹脂や極性基を導入した変成樹脂が好適に用いられる。

【０２４７】

[[保護素子]]

前述の保護素子として、異常発熱や過大電流が流れた時に抵抗が増大するＰＴＣ（Positive Temperature Coefficient）、温度ヒューズ、サーミスター、異常発熱時に電池内部圧力や内部温度の急激な上昇により回路に流れる電流を遮断する弁（電流遮断弁）等が挙げられる。前記保護素子は高電流の通常使用で作動しない条件のものを選択することが好ましく、高出力の観点から、保護素子がなくても異常発熱や熱暴走に至らない設計にすることがより好ましい。

【０２４８】

＜作用・原理＞

特定物質を含有する非水系電解液と異配向性炭素複合物を含有する負極活物質とを組み合わせると、より大型にした際にも、低充電深度での長期間の使用に対しても、良好な容

量維持率を発現できるリチウムイオン二次電池を提供できる作用・原理は明らかではないが、また、その作用原理によって本発明は限定されるものではないが、電池作成後の初回の充電時に配向性の異なる面が混在することによって特定化合物との複雑な反応を生み出し、これによって生じたＳＥＩ（Solid Electrolyte Interface 固体電解質界面）被膜が通常のＳＥＩ被膜に対して、低充電深度の状態でも安定な層となり、低充電深度での過酷な使用においても被膜の溶解や増大を招かず、高い容量維持率を発現できると推察している。

【実施例】

【０２４９】

以下、実施例及び比較例を挙げて本発明を更に具体的に説明するが、本発明は、その要旨を超えない限り、これらの実施例に限定されるものではない。

【０２５０】

［負極材料の作製１］

キノリン不溶分が０．０５質量％以下のコールタールピッチを、反応炉にて４６０℃で１０時間熱処理し、軟化点３８５℃の、溶融性のある塊状の熱処理黒鉛結晶前駆体を得た。得られた塊状の熱処理黒鉛結晶前駆体を、中間粉砕機（セイシン企業社製オリエントミル）を用いて粉砕し、更に微粉砕機（マツボー社製ターボミル）を用いて微粉砕して、メジアン径１７μｍの微細化した黒鉛結晶前駆体粉末（Ｅ）を得た。

【０２５１】

上記の微細化した黒鉛結晶前駆体粉末（Ｅ）に、メジアン径１７μｍ、アスペクト比１．４、タップ密度１．０ｇ／ｃｍ^3、ＢＥＴ比表面積６．５ｍ^2／ｇ、円形度０．９２の天然黒鉛を、微細化黒鉛結晶前駆体粉末及び天然黒鉛の全重量に対して５０質量％混合し、混合粉末を得た。

【０２５２】

この熱処理黒鉛結晶前駆体の混合粉末を金属製の容器に詰め、箱形の電気炉で窒素ガス流通下、５４０℃で２時間、熱処理Ａを行なった。熱処理Ａ中に、微細化した黒鉛結晶前駆体粉末は溶融し、天然黒鉛と均一に複合化した熱処理黒鉛結晶前駆体の混合物の塊となった。

【０２５３】

この固化した熱処理黒鉛結晶前駆体混合物の塊を粗砕機（吉田製作所製ロールジョークラッシャー）で粉砕、更に微粉砕機（マツボー社製ターボミル）を用いて微粉砕し、メジアン径１８．５μｍの粉末を得た。

【０２５４】

得られた粉末を容器に入れ、電気炉にて窒素雰囲気下、１０００℃で１時間焼成した。焼成後に得られた粉体（熱処理Ｂ前前駆体混合物（Ｆ））は粉末のままの形態であり、溶融、融着は殆ど見られなかった。

【０２５５】

更に、焼成した粉末を黒鉛坩堝に移し替え、直接通電炉を用いて不活性雰囲気下で３０００℃にて５時間かけて黒鉛化し、粗大粒子の混入を防ぐため、ＡＳＴＭ４００メッシュの篩いを５回繰り返し、異配向性炭素複合物（Ｇ）を得た。

【０２５６】

［負極材料の作製２］

［負極材料の作製１］で用いた天然黒鉛と黒鉛化可能なバインダーとして軟化点８８℃のバインダーピッチとを、１００：３０の重量比で混合し、予め１２８℃に加熱されたマチスケータ型撹拌翼を持つニーダーに投入して２０分間混合した。

【０２５７】

十分に捏合された混合物を、予め１０８℃に予熱されたモールドプレス機の金型に充填し、５分間放置し混合物の温度が安定したところでプランジャーを押し、２ｋｇｆ／ｃｍ^2（０．２０ＭＰａ）の圧力を加えて成形した。１分間この圧力を保持した後、駆動を止め、圧力低下が収まった後、天然黒鉛と黒鉛結晶前駆体粉末の複合した成形体を取り出し

た。

【０２５８】

得られた成形体を耐熱容器である金属製サガーに収納し、間隙に黒鉛質ブリーズを充填した。電気炉で室温から１０００℃まで４８時間かけて昇温し、１０００℃で３時間保持し、脱揮発成分・焼成を行った。次に、成形体を黒鉛ルツボに収納し、間隙に黒鉛質ブリーズを充填し、直接通電炉を用いて不活性雰囲気下で３０００℃にて４時間加熱して黒鉛化を行った。

【０２５９】

得られた黒鉛質の成形体をジョークラッシャーで粗砕した後、粉砕羽根回転数を４０００回転／分に設定したターボミルにて微粉砕した。更に、分級処理としては粗大粒子の混入を防ぐため、ＡＳＴＭ４００メッシュの篩いを５回繰り返し、異配向性炭素複合物（Ｈ）を得た。

【０２６０】

［負極材料の作製３］

［負極材料の作製２］の直接通電炉を用いた熱処理を２２００℃で行った以外は同様の方法にて異配向性炭素複合物（Ｉ）を得た。

【０２６１】

［負極材料の作製４］

［負極材料の作製２］の天然黒鉛をメジアン径１０μｍ、アスペクト比２．３、タップ密度０．６４ｇ／ｃｍ^3、ＢＥＴ比表面積９．５ｍ^2／ｇ、円形度０．８３のコークスとした以外は、同様にして異配向性炭素複合物（Ｊ）を得た。

【０２６２】

［負極材料の作製５］

［負極材料の作製４］で用いたコークスと黒鉛化触媒の炭化珪素と黒鉛化可能なバインダーとして軟化点８８℃のバインダーピッチとを、１００：１０：３０の質量比で混合した以外は、［負極材料の作製２］と同様にして、異配向性炭素複合物（Ｋ）を得た。

【０２６３】

［負極材料の作製６］

［負極材料の作製２］の天然黒鉛をメジアン径１９．８μｍ、アスペクト比３．２、タップ密度０．４７ｇ／ｃｍ^3、ＢＥＴ比表面積５．９ｍ^2／ｇ、円形度０．８１のリン片状天然黒鉛とした以外は、同様にして異配向性炭素複合物（Ｌ）を得た。

【０２６４】

［負極材料の作製７］

［負極材料の作製２］の天然黒鉛をメジアン径３５μｍ、アスペクト比１．４、タップ密度１．０２ｇ／ｃｍ^3、ＢＥＴ比表面積３．９ｍ^2／ｇ、円形度０．９０の天然黒鉛とした以外は、同様にして異配向性炭素複合物（Ｍ）を得た。

【０２６５】

［負極材料の作製８］

［負極材料の作製２］の粉砕羽根回転数を１５００回転／分に設定した以外は同様にして異配向性炭素複合物（Ｎ）を得た。

【０２６６】

［負極材料の作製９］

［負極材料の作製２］の天然黒鉛をメジアン径６μｍ、アスペクト比１．５、タップ密度０．１５ｇ／ｃｍ^{3}の天然黒鉛とした以外は、同様にして異配向性炭素複合物（Ｏ）を得た。

【０２６７】

［負極材料の作製１０］

［負極材料の作製１］で得られた黒鉛結晶前駆体粉末（Ｅ）を金属製の容器に詰め、箱形の電気炉で窒素ガス流通下、５４０℃で２時間、熱処理Ａを行なった。熱処理Ａ中に、黒鉛結晶前駆体粉末（Ｅ）は溶融し、塊状となった。

【０２６８】
この固化した熱処理黒鉛結晶前駆体塊を粗砕機（吉田製作所製ロールジョークラッシャー）で粉砕、更に微粉砕機（マツボー社製ターボミル）を用いて微粉砕し、メジアン径１８．５μｍの粉末を得た。
【０２６９】
得られた粉末を容器に入れ、電気炉にて窒素雰囲気下、１０００℃で１時間焼成した。焼成後に得られた粉体は粉末のままの形態であり、溶融、融着は殆ど見られなかった。
更に、焼成した粉末を黒鉛坩堝に移し替え、直接通電炉を用いて不活性雰囲気下で３０００℃にて５時間かけて黒鉛化し、粗大粒子の混入を防ぐため、ＡＳＴＭ４００メッシュの篩いを５回繰り返し、炭素質物（Ｐ）を得た。
【０２７０】
［負極材料の作製１１］
［負極材料の作製１］で用いた天然黒鉛を金属製の容器に詰め、箱形の電気炉で窒素ガス流通下、５４０℃で２時間、熱処理Ａを行なった。熱処理Ａ後においても、天然黒鉛に溶融・融着は見られなかった。得られた粉末を容器に入れ、電気炉にて窒素雰囲気下、１０００℃で１時間焼成した。焼成後に得られた粉体は粉末のままの形態であり、溶融、融着は見られなかった。
【０２７１】
更に、焼成した粉末を黒鉛坩堝に移し替え、直接通電炉を用いて不活性雰囲気下で３０００℃にて５時間かけて黒鉛化し、粗大粒子の混入を防ぐため、ＡＳＴＭ４００メッシュの篩いを５回繰り返し、炭素質物（Ｑ）を得た。
【０２７２】
［負極材料の作製１２］
炭素質物（Ｐ）と炭素質物（Ｑ）を５０質量％ずつとなるよう混まぜ、均一となるよう混合し、炭素質物混合物（Ｒ）を得た。
【０２７３】
〔電池の作製〕
《正極の作製１》
正極活物質としてのコバルト酸リチウム（$LiCoO_2$）９０質量％と、導電材としてのアセチレンブラック５質量％と、結着剤としてのポリフッ化ビニリデン（ＰＶｄＦ）５質量％とを、Ｎ－メチルピロリドン溶媒中で混合して、スラリー化した。得られたスラリーを厚さ１５μｍのアルミ箔の両面に塗布して乾燥し、プレス機で厚さ８０μｍに圧延したものを、活物質層のサイズとして幅１００ｍｍ、長さ１００ｍｍ及び幅３０ｍｍの未塗工部を有する形状に切り出し、正極とした。このときの正極の活物質の密度は２．３５ｇ／cm^3であった。
【０２７４】
《負極の作製１》
負極活物質を９８重量部に、増粘剤、バインダーとしてそれぞれ、カルボキシメチルセルロースナトリウムの水性ディスパージョン（カルボキシメチルセルロースナトリウムの濃度１質量％）１００重量部、及び、スチレン－ブタジエンゴムの水性ディスパージョン（スチレン－ブタジエンゴムの濃度５０質量％）２重量部を加え、ディスパーザーで混合してスラリー化した。得られたスラリーを厚さ１０μｍの圧延銅箔の両面に塗布して乾燥し、プレス機で厚さ７５μｍに圧延したものを、活物質層のサイズとして幅１０４ｍｍ、長さ１０４ｍｍ及び幅３０ｍｍの未塗工部を有する形状に切り出し、負極とした。このときの負極の活物質の密度は１．３５ｇ／cm^3であった。
【０２７５】
《非水系電解液の作製１》
乾燥アルゴン雰囲気下、エチレンカーボネート（ＥＣ）、ジメチルカーボネート（ＤＭＣ）及びエチルメチルカーボネート（ＥＭＣ）の混合物（体積比３：３：４）に、１ｍｏｌ／Ｌの濃度で、充分に乾燥したヘキサフルオロリン酸リチウム（$LiPF_6$）を溶解さ

せた。更に、ジフルオロリン酸リチウム塩（$LiPO_2F_2$）を０．３質量％となるように含有させた。

【０２７６】

《非水系電解液の作製２》

乾燥アルゴン雰囲気下、エチレンカーボネート（ＥＣ）、ジメチルカーボネート（ＤＭＣ）及びエチルメチルカーボネート（ＥＭＣ）の混合物（体積比３：３：４）に、１ｍｏｌ／Ｌの濃度で、充分に乾燥したヘキサフルオロリン酸リチウム（$LiPF_6$）を溶解させた。更に、メタンスルホン酸トリメチルシリルを０．３質量％となるように含有させた。

【０２７７】

《非水系電解液の作製３》

乾燥アルゴン雰囲気下、エチレンカーボネート（ＥＣ）、ジメチルカーボネート（ＤＭＣ）及びエチルメチルカーボネート（ＥＭＣ）の混合物（体積比３：３：４）に、１ｍｏｌ／Ｌの濃度で、充分に乾燥したヘキサフルオロリン酸リチウム（$LiPF_6$）を溶解させた。更に、ヘキサメチルシクロトリシロキサンを０．３質量％となるように含有させた。

【０２７８】

《非水系電解液の作製４》

乾燥アルゴン雰囲気下、エチレンカーボネート（ＥＣ）、ジメチルカーボネート（ＤＭＣ）及びエチルメチルカーボネート（ＥＭＣ）の混合物（体積比３：３：４）に、１ｍｏｌ／Ｌの濃度で、充分に乾燥したヘキサフルオロリン酸リチウム（$LiPF_6$）を溶解させた。

【０２７９】

《電池の作製１》

正極３２枚と負極３３枚は交互となるように配置し、各電極の間に多孔性ポリエチレンシートのセパレータ（厚さ２５μｍ）が挟まれるよう積層した。この際、正極活物質面が負極活物質面内から外れないよう対面させた。この正極と負極それぞれについての未塗工部同士を溶接して集電タブを作製し、電極群としたものを電池缶（外寸：１２０×１１０×１０ｍｍ）に封入した。その後、電極群を装填した電池缶に非水系電解液を２０ｍＬ注入して、電極に充分浸透させ、密閉し角型電池を作製した。この電池の定格放電容量は約６アンペアーアワー（Ａｈ）であり、１０ｋＨｚ交流法で測定される直流抵抗は約５ミリオーム（ｍΩ）である。

【０２８０】

実施例１

《負極の作製１》項の負極活物質を異配向性炭素複合物（Ｇ）として作製した負極と、《正極の作製１》項で作製した正極と《非水系電解液の作製１》項で作製した非水系電解液を用いて、《電池の作製１》項の手法で電池を作製した。この電池について、下記の《電池の評価》の項で述べる方法及び上記した測定方法で、測定を実施した。

【０２８１】

実施例２

実施例１の《負極の作製１》項の負極活物質に異配向性炭素複合物（Ｈ）を用いた以外は同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。

【０２８２】

実施例３

実施例１の《負極の作製１》項の負極活物質に異配向性炭素複合物（Ｉ）を用いた以外は同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。

【０２８３】

実施例４

実施例１の《負極の作製１》項の負極活物質に異配向性炭素複合物（Ｊ）を用いた以外は同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。

【０２８４】
実施例５
実施例１の《負極の作製１》項の負極活物質に異配向性炭素複合物（Ｋ）を用いた以外は同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。
【０２８５】
実施例６
実施例１の《負極の作製１》項の負極活物質に異配向性炭素複合物（Ｌ）を用いた以外は同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。
【０２８６】
実施例７
実施例１の《負極の作製１》項の負極活物質に異配向性炭素複合物（Ｍ）を用いた以外は同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。
【０２８７】
実施例８
実施例１の《負極の作製１》項の負極活物質に異配向性炭素複合物（Ｎ）を用いた以外は同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。
【０２８８】
実施例９
実施例１の《負極の作製１》項の負極活物質に異配向性炭素複合物（Ｏ）を用いた以外は同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。
【０２８９】
実施例１０～１８
実施例１～９の非水系電解液を、《非水系電解液の作製２》の項で作製した非水系電解液に代えた以外は同様にして電池を作製し、同様の方法にて電池評価を実施した。
【０２９０】
実施例１９～２７
実施例１～９の非水系電解液を、《非水系電解液の作製３》の項で作製した非水系電解液に代えた以外は同様にして電池を作製し、同様の方法にて電池評価を実施した。
【０２９１】
比較例１
実施例１の《負極の作製１》項の負極活物質に炭素質物（Ｐ）を用いた以外は同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。
【０２９２】
比較例２
比較例１の非水系電解液を、《非水系電解液の作製４》の項で作製した非水系電解液に代えた以外は、同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。
【０２９３】
比較例３
実施例１の《負極の作製１》項の負極活物質に炭素質物（Ｑ）を用いた以外は同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。
【０２９４】
比較例４
比較例３の非水系電解液を、《非水系電解液の作製４》の項で作製した非水系電解液に代えた以外は、同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。
【０２９５】
比較例５
実施例１の《負極の作製１》項の負極活物質に炭素質物混合物（Ｒ）を用いた以外は同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。
【０２９６】
比較例６

比較例５の非水系電解液を、《非水系電解液の作製４》の項で作製した非水系電解液に代えた以外は、同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。

【０２９７】

比較例７

実施例１の非水系電解液を、《非水系電解液の作製４》の項で作製した非水系電解液に代えた以外は、同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。

【０２９８】

比較例８

実施例２の非水系電解液を、《非水系電解液の作製４》の項で作製した非水系電解液に代えた以外は、同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。

【０２９９】

比較例９

実施例４の非水系電解液を、《非水系電解液の作製４》の項で作製した非水系電解液に代えた以外は、同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。

【０３００】

比較例１０

実施例５の非水系電解液を、《非水系電解液の作製４》の項で作製した非水系電解液に代えた以外は、同様にして電池を作製し、《電池の評価》項記載の電池評価を実施した。

【０３０１】

比較例１１～１３

比較例１、３、５の非水系電解液を、《非水系電解液の作製２》の項で作製した非水系電解液に代えた以外は同様にして電池を作製し、同様の方法にて電池評価を実施した。

【０３０２】

比較例１４～１６

比較例１、３、５の非水系電解液を、《非水系電解液の作製３》の項で作製した非水系電解液に代えた以外は同様にして電池を作製し、同様の方法にて電池評価を実施した。

【０３０３】

《電池の評価》

（容量測定）

充放電サイクルを経ていない電池に対して、２５℃で電圧範囲４．２Ｖ～３．０Ｖ、電流値０．２Ｃ（１時間率の放電容量による定格容量を１時間で放電する電流値を１Ｃとする、以下同様）にて５サイクル初期充放電を行った。この時の５サイクル目０．２Ｃ放電容量を初期容量とした。次に下記に示す出力測定を実施した。

【０３０４】

（低充電深度サイクル試験）

リチウムイオン二次電池の実使用上限温度と目される６０℃の高温環境下にてサイクル試験を行った。容量測定で測定した初期容量の２０％となる容量まで、充電上限電圧４．２Ｖまで２Ｃの定電流定電圧法で充電した後、放電終止電圧３．０Ｖまで２Ｃの定電流で放電する充放電サイクルを１サイクルとし、このサイクルを５００サイクルまで繰り返した。

【０３０５】

サイクル試験終了後の電池に対し、２５℃環境下で３サイクルの充放電を行い、その３サイクル目の０．２Ｃ放電容量を低充電深度サイクル後容量とした。サイクルに先だって測定した初期容量とサイクル試験終了後に測定した低充電深度サイクル後容量から下記計算式によってサイクル維持率を求めた。

サイクル維持率（％）＝１００×低充電深度サイクル後容量／初期容量

【０３０６】

実施例及び比較例に用いた負極活物質一覧を表１に、電池評価の結果を表２及び表３に示す。表２及び表３の結果から分かるように、ジフルオロリン酸リチウム塩、メタンスルホン酸トリメチルシリル又はヘキサメチルシクロトリシロキサンを含有すること、及び負

極活物質として異配向性炭素複合物を組み合わせることで、飛躍的に低充電深度のサイクル試験後における容量の維持率（サイクル維持率）が向上していることが分かった。

【０３０７】

【表１】

負極活物質	粒径 μm	円形度 -	比表面積 m^2/g	ラマンR値 -	ラマン半値幅 cm^{-1}	タップ密度 g/cm^3	d002 nm	Lc nm	灰分 質量%	微小細孔分布 mL/g	全細孔分布 mL/g	真密度 g/cm^3	アスペクト比 -
異配向性炭素複合物(G)	17.5	0.92	2.3	0.06	20.1	1.20	0.3357	>100	0.02	0.042	0.448	2.26	1.3
異配向性炭素複合物(H)	18.0	0.93	2.8	0.12	22.1	1.17	0.3358	>100	0.02	0.022	0.467	2.26	1.2
異配向性炭素複合物(I)	18.5	0.91	3.0	0.17	24.5	1.10	0.3610	>100	0.05	0.030	0.489	2.24	1.4
異配向性炭素複合物(J)	21.4	0.88	2.3	0.12	21.4	0.75	0.3359	>100	0.03	0.067	0.569	2.25	1.5
異配向性炭素複合物(K)	20.7	0.89	3.0	0.08	21.9	0.73	0.3357	>100	0.05	0.079	0.656	2.26	1.5
異配向性炭素複合物(L)	21.4	0.82	2.5	0.13	23.5	0.63	0.3357	>100	0.03	0.033	0.556	2.26	2.5
異配向性炭素複合物(M)	35.2	0.91	1.4	0.05	21.1	1.11	0.3356	>100	0.04	0.018	0.405	2.26	1.3
異配向性炭素複合物(N)	22.0	0.92	0.9	0.06	22.1	1.25	0.3356	>100	0.05	0.020	0.455	2.26	1.2
異配向性炭素複合物(O)	16.5	0.90	3.8	0.09	24.3	0.50	0.3359	>100	0.03	0.102	0.764	2.25	1.7
炭素質物(P)	18.9	0.86	1.5	0.11	27.8	1.06	0.3357	>100	0.04	0.024	0.459	2.25	2.3
炭素質物(Q)	17.7	0.93	5.4	0.03	20.5	1.00	0.3354	>100	0.03	0.112	0.701	2.26	1.3
炭素質物混合物(R)	18.8	0.90	3.4	0.06	23.8	1.02	0.3355	>100	0.03	0.090	0.590	2.26	1.8

【０３０８】

【表２】

NO.	負極活物質	特定化合物	初期容量 mAh	低充電深度サイクル後容量 mAh	サイクル維持率 %
実施例 1	異配向性炭素複合物(G)	ジフルオロリン酸リチウム塩	6045	5592	92.5
実施例 2	異配向性炭素複合物(H)	ジフルオロリン酸リチウム塩	6032	5640	93.5
実施例 3	異配向性炭素複合物(I)	ジフルオロリン酸リチウム塩	5780	5162	89.3
実施例 4	異配向性炭素複合物(J)	ジフルオロリン酸リチウム塩	6013	5478	91.1
実施例 5	異配向性炭素複合物(K)	ジフルオロリン酸リチウム塩	6003	5427	90.4
実施例 6	異配向性炭素複合物(L)	ジフルオロリン酸リチウム塩	6009	5426	90.3
実施例 7	異配向性炭素複合物(M)	ジフルオロリン酸リチウム塩	6001	5383	89.7
実施例 8	異配向性炭素複合物(N)	ジフルオロリン酸リチウム塩	5914	5246	88.7
実施例 9	異配向性炭素複合物(O)	ジフルオロリン酸リチウム塩	5959	5375	90.2
実施例 10	異配向性炭素複合物(G)	メタンスルホン酸トリメチルシリル	6037	5410	89.6
実施例 11	異配向性炭素複合物(H)	メタンスルホン酸トリメチルシリル	6035	5441	90.2
実施例 12	異配向性炭素複合物(I)	メタンスルホン酸トリメチルシリル	5806	5058	87.1
実施例 13	異配向性炭素複合物(J)	メタンスルホン酸トリメチルシリル	6019	5346	88.8
実施例 14	異配向性炭素複合物(K)	メタンスルホン酸トリメチルシリル	5997	5241	87.4
実施例 15	異配向性炭素複合物(L)	メタンスルホン酸トリメチルシリル	6011	5300	88.2
実施例 16	異配向性炭素複合物(M)	メタンスルホン酸トリメチルシリル	6006	5233	87.1
実施例 17	異配向性炭素複合物(N)	メタンスルホン酸トリメチルシリル	5921	5104	86.2
実施例 18	異配向性炭素複合物(O)	メタンスルホン酸トリメチルシリル	5968	5101	85.5
実施例 19	異配向性炭素複合物(G)	ヘキサメチルシクロトリシロキサン	6039	5767	95.5
実施例 20	異配向性炭素複合物(H)	ヘキサメチルシクロトリシロキサン	6023	5580	92.6
実施例 21	異配向性炭素複合物(I)	ヘキサメチルシクロトリシロキサン	5793	5208	89.9
実施例 22	異配向性炭素複合物(J)	ヘキサメチルシクロトリシロキサン	6009	5364	89.3
実施例 23	異配向性炭素複合物(K)	ヘキサメチルシクロトリシロキサン	6003	5349	89.1
実施例 24	異配向性炭素複合物(L)	ヘキサメチルシクロトリシロキサン	6010	5306	88.3
実施例 25	異配向性炭素複合物(M)	ヘキサメチルシクロトリシロキサン	5996	5413	90.3
実施例 26	異配向性炭素複合物(N)	ヘキサメチルシクロトリシロキサン	5917	5275	89.1
実施例 27	異配向性炭素複合物(O)	ヘキサメチルシクロトリシロキサン	5961	5500	92.3

【０３０９】

【表３】

NO.	負極活物質	特定化合物	初期容量 mAh	低充電深度サイクル後容量 mAh	サイクル維持率 %
比較例 1	炭素質物(P)	ジフルオロリン酸リチウム塩	5890	4671	79.3
比較例 2	炭素質物(P)	—	5873	4552	77.5
比較例 3	炭素質物(Q)	ジフルオロリン酸リチウム塩	6058	4919	81.2
比較例 4	炭素質物(Q)	—	6067	4866	80.2
比較例 5	炭素質物混合物(R)	ジフルオロリン酸リチウム塩	5890	4836	82.1
比較例 6	炭素質物混合物(R)	—	5887	4739	80.5
比較例 7	異配向性炭素複合物(G)	—	6031	4915	81.5
比較例 8	異配向性炭素複合物(H)	—	6045	4975	82.3
比較例 9	異配向性炭素複合物(J)	—	5790	4713	81.4
比較例10	異配向性炭素複合物(K)	—	5813	4604	79.2
比較例11	炭素質物(P)	メタンスルホン酸トリメチルシリル	5903	4728	80.1
比較例12	炭素質物(Q)	メタンスルホン酸トリメチルシリル	6038	4921	81.5
比較例13	炭素質物混合物(R)	メタンスルホン酸トリメチルシリル	5900	4832	81.9
比較例14	炭素質物(P)	ヘキサメチルシクロトリシロキサン	5940	4764	80.2
比較例15	炭素質物(Q)	ヘキサメチルシクロトリシロキサン	6002	4874	81.2
比較例16	炭素質物混合物(R)	ヘキサメチルシクロトリシロキサン	5970	4782	80.1

【産業上の利用可能性】

【０３１０】

本発明のリチウムイオン二次電池の用途は特に限定されず、公知の各種の用途に用いることが可能である。具体例としては、ノートパソコン、ペン入力パソコン、モバイルパソコン、電子ブックプレーヤー、携帯電話、携帯ファックス、携帯コピー、携帯プリンター、ヘッドフォンステレオ、ビデオムービー、液晶テレビ、ハンディークリーナー、ポータブルＣＤ、ミニディスク、トランシーバー、電子手帳、電卓、メモリーカード、携帯テープレコーダー、ラジオ、バックアップ電源、モーター、自動車、バイク、原動機付自転車、自転車、照明器具、玩具、ゲーム機器、時計、電動工具、ストロボ、カメラ等を挙げることができる。特に、本発明のリチウムイオン二次電池は、低い充電深度での長期間充放電の繰り返しに対して良好な性能を維持できることから、広く好適に利用できるものである。

フロントページの続き

Ｆターム(参考) 5H029 AJ05 AK01 AK03 AL06 AL07 AM02 AM03 AM04 AM05 AM07
BJ02 BJ04 CJ02 DJ02 DJ12 EJ01 EJ12 HJ01 HJ02 HJ05
HJ07 HJ08 HJ14 HJ19 HJ20
5H050 AA07 BA17 CA01 CA07 CA08 CA09 CB07 CB08 EA10 EA23
EA24 EA28 FA12 FA17 FA19 GA02 HA00 HA01 HA05 HA07
HA08 HA14

【要約の続き】
【選択図】なし

酸銅水溶液（以下、「第２の硫酸－硫酸銅水溶液」ともいう。）を用いて電解する方法（以下、「第２の製造方法」ともいう。）であり、第３の方法が、未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満である銅箔の製造方法であって、電解液として、活性炭処理して得られる、Cl^-イオン濃度が１０ｍｇ／ｌ～５０ｍｇ／ｌ、タンパク質濃度が０．２ｍｇ／ｌ以下の硫酸－硫酸銅水溶液（以下、「第３の硫酸－硫酸銅水溶液」ともいう。）を用いて電解する方法（以下、「第３の製造方法」ともいう。）である。

【００４６】

（第１の製造方法）

第１の製造方法について説明する。該方法において電解液として用いられる第１の硫酸－硫酸銅水溶液は、イオンとして実質的にCu^{2+}及びSO_4^{2-}のみを含む水溶液である。ここで、本発明で用いられる第１の硫酸－硫酸銅水溶液がCl^-イオンを実質的に含まないとは、第１の硫酸－硫酸銅水溶液中のCl^-イオン濃度が、０．５ｍｇ／ｌ以下、好ましくは０．３ｍｇ／ｌ以下、さらに好ましくは０．１ｍｇ／ｌ以下であることを意味する。該Cl^-イオン濃度が０．５ｍｇ／ｌを超えると、電解して得られる第１の銅箔がボイド発生の抑制効果を十分に発現し難くなるため好ましくない。

【００４７】

第１の硫酸－硫酸銅水溶液は、上記Cu^{2+}、SO_4^{2-}又はCl^-イオン以外の添加剤を含んでいてもよい。該添加剤としては、例えば、タンパク質等の有機物が挙げられる。また、タンパク質としては、例えば、ゼラチン、にかわ等が挙げられる。添加剤がタンパク質である場合、第１の硫酸－硫酸銅水溶液はタンパク質を、通常５ｍｇ／ｌ以下、好ましくは３ｍｇ／ｌ以下の範囲内で含むことができる。なお、タンパク質の含有量が５ｍｇ／ｌを超えると、純銅めっき層が硬くて脆くなり易いため好ましくない。

【００４８】

本発明で用いられる第１の硫酸－硫酸銅水溶液は、Cu^{2+}イオン濃度が、通常４０ｇ／ｌ～１２０ｇ／ｌ、好ましくは６０ｇ／ｌ～１００ｇ／ｌである。Cu^{2+}イオン濃度が４０ｇ／ｌ未満であると、電解してもヤケめっきになり易く緻密な銅層を形成し難いため好ましくない。また、Cu^{2+}イオン濃度が１２０ｇ／ｌを超えると、硫酸銅の結晶が析出し易くなるため好ましくない。

【００４９】

また、本発明で用いられる第１の硫酸－硫酸銅水溶液は、フリーSO_4^{2-}イオン濃度が、通常１００ｇ／ｌ～２００ｇ／ｌ、好ましくは１２０ｇ／ｌ～１８０ｇ／ｌである。ここでフリーSO_4^{2-}濃度とは、第１の硫酸－硫酸銅水溶液中のCu^{2+}濃度を$CuSO_4$に換算して得られるSO_4^{2-}濃度を、第１の硫酸－硫酸銅水溶液中に含まれる全SO_4^{2-}濃度から減じた残余のSO_4^{2-}濃度を示す。フリーSO_4^{2-}イオン濃度が１００ｇ／ｌ未満であると溶液抵抗が高くなるため好ましくない。また、フリーSO_4^{2-}イオン濃度が２００ｇ／ｌを超えると、第１の銅箔に析出異常が生じ易いため好ましくない。

【００５０】

本発明で用いられる第１の硫酸－硫酸銅水溶液は、例えば、純水に硫酸を添加した後、硫酸銅を溶解したり、銅くず等の銅原料を希硫酸又は第１の硫酸－硫酸銅水溶液で溶解したりすることにより得られる。

【００５１】

第１の製造方法は、上記第１の硫酸－硫酸銅水溶液を電解液として用いて電解して、第１の銅箔を形成する。

【００５２】

上記第１の硫酸－硫酸銅水溶液を用いて電解する際、上記第１の硫酸－硫酸銅水溶液の液温を、通常４０℃～６０℃、好ましくは４５℃～５５℃とする。液温が４０℃未満であると第１の銅箔の粗面の表面粗度が高くなり易いため好ましくなく、また、液温が６０℃を超えると塩化ビニル製配管等の設備の老朽化が加速され易いため好ましくない。

【００５３】

箔の粗面の粗度R_{zJIS}が未処理電解銅箔の厚さにほぼ比例して増減する。このため、該未処理電解銅箔の厚さが１８μｍより大きい場合、例えば３５μｍである場合には、粗面の粗度R_{zJIS}が上記のように３．５μｍ以下にならないこともある。しかし、このような場合でも、未処理電解銅箔の電解条件のうち電解時間以外の電解条件、例えば電解液組成及び電流密度が同様である場合は、電解銅箔の厚さの差異に関わらず未処理電解銅箔自体の組成及び結晶構造はほぼ同様であるため、本発明においては未処理の低粗度電解銅箔と判断する。

【００３８】

第１の銅箔は、該未処理銅箔中のＣｌ含有量が、３０ｐｐｍ未満、好ましくは２０ｐｐｍ未満、さらに好ましくは１０ｐｐｍ未満である。Ｃｌ含有量が該範囲内にあると、スズめっき後のフュージング処理でボイドが発生し難いため好ましい。

【００３９】

第１の銅箔は、Ｃｕ以外の金属成分やＣｌ以外の元素、例えばＣ、Ｎ等を、これら元素の含有量の合計量の重量基準で、通常２００ｐｐｍ以下、好ましくは１００ｐｐｍ以下、さらに好ましくは５０ｐｐｍ以下含有していてもよい。

【００４０】

第１の銅箔は、必要により、銅箔表面のいずれか又は両方に防錆処理を行ってもよい。該防錆処理を行うと、銅箔を製造してからＴＡＢテープのポリイミド等の可撓性絶縁フィルムに接着するまでの間の防錆性がよくなるため好ましい。ただし、該防錆処理は、ＴＡＢテープの製造の際の表面へのスズめっきの障害にならない組成、厚さのものであることが必要である。

【００４１】

防錆処理としては、無機防錆処理又は有機防錆処理のいずれか又は両方が挙げられる。無機防錆処理としては、例えば、亜鉛、ニッケル及びスズ等の金属元素の少なくとも１種を用いた金属防錆処理やクロメート処理等が挙げられる。

【００４２】

なお、金属防錆処理が亜鉛、ニッケル及びスズ等の金属元素を２種以上組み合わせたものである場合、金属防錆処理により形成される金属防錆処理層は、各金属元素からなる防錆処理層が複数形成された複層構造を有するものであってもよいし、防錆処理形成時又は複層構造の防錆処理層形成後の熱処理等により合金化して単層構造を有するものであってもよい。また、無機防錆処理は、金属防錆処理後にクロメート処理を行うと、防錆処理層の防錆性がより高くなるため好ましい。

【００４３】

有機防錆処理層を形成する有機防錆処理としては、例えば、シランカップリング剤、ベンゾトリアゾール等が挙げられる。無機防錆処理と有機防錆処理とを組み合わせて行う場合には、無機防錆処理層の形成後に有機防錆処理層を形成することが好ましい。上記無機処理及び有機処理の処理方法としては、公知の方法を用いることができる。

【００４４】

第１の銅箔は、未処理銅箔中のＣｌ含有量が特定量未満であるため、銅箔の両表面において、例えば未処理銅箔が電解銅箔であれば、該銅箔の光沢面及び粗面の両表面において、スズめっき層をフュージング処理してもボイドが発生し難い。第１の銅箔は、例えば、下記の本発明に係る第１の銅箔の製造方法により製造することができる。

【００４５】

［本発明に係る第１の銅箔の製造方法］

本発明に係る第１の銅箔の製造方法は、第１の方法が、未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満である銅箔の製造方法であって、電解液としてＣｌ$^-$イオン濃度が０．５ｍｇ／ｌ以下の硫酸－硫酸銅水溶液（以下、「第１の硫酸－硫酸銅水溶液」ともいう。）を用いて電解する方法（以下、「第１の製造方法」ともいう。）であり、第２の方法が、未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満である銅箔の製造方法であって、電解液としてＣｌ$^-$イオン濃度が２．０ｍｇ／ｌ以下、タンパク質濃度が０．５ｍｇ／ｌ以下の硫酸－硫

【００３０】
また、本発明（１０）に係る銅箔の製造方法によれば、本発明（９）に係る銅箔の製造方法に比べて、より効率よく本発明（８）に係る銅箔を製造することができる。
【００３１】
本発明（１１）に係るＴＡＢテープは、本発明（１）に係る銅箔を用いて形成することにより、該銅箔から形成された回路の表面にスズめっき層を形成後、フュージング処理してもボイドが発生し難い。
【００３２】
本発明（１２）に係るＴＡＢテープは、本発明（８）に係る銅箔を用いて形成することにより、本発明（１１）に係るＴＡＢテープの奏する効果に加え、特に相対強度比Ｉ（２００）／Ｉ（１１１）が特定範囲内にある銅箔表面が回路の表面となる構成のＴＡＢテープにおいてよりボイドが発生し難くなる。
【発明を実施するための最良の形態】
【００３３】
［本発明に係る銅箔］
本発明に係る銅箔は、未処理銅箔中のＣｌ含有量が特定範囲内にある銅箔（以下、「第１の銅箔」ともいう）、及び未処理銅箔中のＣｌ含有量が特定範囲内にあって、該未処理銅箔の両表面のうち少なくともスズめっき層の形成される表面の上記相対強度比Ｉ（２００）／Ｉ（１１１）が特定範囲内にある銅箔（以下、「第２の銅箔」ともいう）を含む。以下、これらを分けて説明する。
【００３４】
（第１の銅箔）
まず、第１の銅箔について説明する。第１の銅箔は、未処理銅箔中のＣｌ含有量が特定範囲内にある。ここで未処理銅箔とは、コブ処理、ヤケめっき等の粗化処理を行う前の状態にある全ての銅箔を含む意味で用いる。すなわち、本発明において、未処理銅箔は、粗化処理前に研磨処理等の処理が行われたもの等も含む概念であり、例えば、未処理銅箔が電解銅箔であれば、電解製造後且つ粗化処理前に機械研磨や化学研磨等の研磨処理を行うことにより粗面の粗度を低下させたものも、本発明における未処理銅箔に該当する。第１の銅箔における未処理銅箔としては、未処理電解銅箔でも未処理圧延銅箔でもよく、特に限定されない。
【００３５】
第１の銅箔において、未処理銅箔の物性は、銅箔中のＣｌ含有量が後述のように特定範囲内にあるものであればよく、常態及び熱間における抗張力、常態及び熱間における伸び、硬さ、結晶粒の大きさ並びに銅の結晶の配向性等に、特に限定されるものではない。すなわち、第１の銅箔は、例えば、ＩＰＣ規格ＩＰＣ－ＭＦ－１５０のグレード１～グレード３に記載のいずれの電解銅箔であってもよいし、グレード５又はグレード６に記載のいずれの圧延銅箔であってもよい。
【００３６】
また、未処理銅箔は、表面粗度について特に限定されるものではなく、粗度の高い銅箔から低粗度銅箔までのいずれであってもよい。なお、第１の銅箔において低粗度銅箔とは、圧延銅箔にあっては全ての圧延銅箔、電解銅箔にあっては、電解製造直後の厚さ１８μｍの銅箔、すなわち電解製造後に表面粗度を変化させる研磨処理等を何ら行わない厚さ１８μｍの銅箔において粗面の粗度R_{zJIS}が３．５μｍ以下になる組成及び結晶構造を有する未処理電解銅箔、並びに、電解製造後に表面粗度を変化させる研磨処理等を行った銅箔であって銅箔の厚さにかかわらず粗面の粗度R_{zJIS}が３．５μｍ以下になっている未処理電解銅箔のいずれも含む意味で用いる。本明細書において粗度R_{zJIS}とは、ＪＩＳ　Ｂ０６０１－２００１に規定される十点平均粗さを意味する。
【００３７】
なお、未処理電解銅箔が、電解製造直後の厚さ１８μｍの銅箔において粗面の粗度R_{zJIS}が３．５μｍ以下になる組成及び結晶構造を有するものである場合、該未処理電解銅

られた回折線のうち（２００）面の回折線の相対ピーク強度をＩ（２００）、（１１１）面の回折線の相対ピーク強度をＩ（１１１）としたときに前記Ｉ（２００）を前記Ｉ（１１１）で除して算出される相対強度比Ｉ（２００）／Ｉ（１１１）が０．２０以下であることを特徴とする銅箔を提供するものである。

【００１９】

また、本発明（９）は、未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満で、該未処理銅箔の両表面のうち少なくともスズめっき層の形成される表面が、該表面をＸ線回折分析して得られた回折線のうち（２００）面の回折線の相対ピーク強度をＩ（２００）、（１１１）面の回折線の相対ピーク強度をＩ（１１１）としたときに前記Ｉ（２００）を前記Ｉ（１１１）で除して算出される相対強度比Ｉ（２００）／Ｉ（１１１）が０．２０以下である銅箔の製造方法であって、電解液としてＣｌ$^-$イオン濃度が１．０ｍｇ／ｌ～２．０ｍｇ／ｌ、タンパク質濃度が０．２ｍｇ／ｌ以下の硫酸－硫酸銅水溶液を用いて電解することを特徴とする銅箔の製造方法を提供するものである。

【００２０】

また、本発明（１０）は、本発明（９）において、前記硫酸－硫酸銅水溶液は、Cu^{2+}イオン濃度が４０ｇ／ｌ～１２０ｇ／ｌ、フリーSO_4^{2-}イオン濃度が１００ｇ／ｌ～２００ｇ／ｌであることを特徴とする銅箔の製造方法を提供するものである。

【００２１】

また、本発明（１１）は、本発明（１）に記載の銅箔を用いて形成したことを特徴とするＴＡＢテープを提供するものである。

【００２２】

また、本発明（１２）は、本発明（８）に記載の銅箔を用いて形成したことを特徴とするＴＡＢテープを提供するものである。

【発明の効果】

【００２３】

本発明（１）に係る銅箔は、Ｃｌ含有量の低い未処理銅箔を用いることにより、該銅箔の表面にスズめっき層を形成後、フュージング処理してもボイドが発生し難いから、ＴＡＢテープ製造用銅箔として好適である。

【００２４】

本発明（２）、本発明（４）又は本発明（６）に係る銅箔の製造方法によれば、本発明（１）に係る銅箔を効率よく製造することができる。

【００２５】

また、本発明（３）に係る銅箔の製造方法によれば、本発明（２）に係る銅箔の製造方法に比べて、より効率よく本発明（１）に係る銅箔を製造することができる。

【００２６】

また、本発明（５）に係る銅箔の製造方法によれば、本発明（４）に係る銅箔の製造方法に比べて、より効率よく本発明（１）に係る銅箔を製造することができる。

【００２７】

また、本発明（７）に係る銅箔の製造方法によれば、本発明（６）に係る銅箔の製造方法に比べて、より効率よく本発明（１）に係る銅箔を製造することができる。

【００２８】

本発明（８）に係る銅箔は、Ｃｌ含有量が低く、且つ、両表面のうち少なくともスズめっき層の形成される表面が、該表面をＸ線回折分析して得られた回折線の相対強度比Ｉ（２００）／Ｉ（１１１）が特定範囲内にある未処理銅箔を用いるから、本発明（１）に係る銅箔の奏する効果に加え、特に相対強度比Ｉ（２００）／Ｉ（１１１）が特定範囲内にある銅箔表面においてボイドが発生し難くなり、該表面にスズめっき層を形成する構成のＴＡＢテープ製造用銅箔として好適である。

【００２９】

本発明（９）に係る銅箔の製造方法によれば、本発明（８）に係る銅箔を効率よく製造することができる。

【発明が解決しようとする課題】
【０００８】
しかしながら、特許文献１記載の方法では、銅表面にニッケル、コバルト及びモリブデンからなる合金層を形成するため、これら異種金属からなる合金層が回路形成時における銅箔のエッチング性を悪化させるという問題があった。
【０００９】
従って、本発明の目的は、スズめっき層をフュージング処理してもボイドが発生し難く、且つエッチング性が良い銅箔を提供することにある。また、本発明の他の目的は、スズめっき層をフュージング処理してもボイドが発生し難いＴＡＢテープを提供することにある。
【課題を解決するための手段】
【００１０】
かかる実情において、本発明者は鋭意検討を行った結果、所定の物性を有する銅箔を用いると、該銅箔の表面又は両表面のうち少なくともスズめっき層の形成される表面に形成されるスズめっき層をフュージング処理してもボイドが発生し難くなることを見出し、本発明を完成するに至った。また、本発明者は、該銅箔を用いて作製したＴＡＢテープは、該銅箔から形成された銅回路上に形成されるスズめっき層をフュージング処理してもボイドが発生し難くなることを見出し、本発明を完成するに至った。
【００１１】
すなわち、本発明（１）は、未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満であることを特徴とする銅箔を提供するものである。
【００１２】
また、本発明（２）は、未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満である銅箔の製造方法であって、電解液としてCl^-イオン濃度が０．５ｍｇ／ｌ以下の硫酸－硫酸銅水溶液を用いて電解することを特徴とする銅箔の製造方法を提供するものである。
【００１３】
また、本発明（３）は、本発明（２）において、前記硫酸－硫酸銅水溶液は、Cu^{2+}イオン濃度が４０ｇ／ｌ～１２０ｇ／ｌ、フリーSO_4^{2-}イオン濃度が１００ｇ／ｌ～２００ｇ／ｌであることを特徴とする銅箔の製造方法を提供するものである。
【００１４】
また、本発明（４）は、未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満である銅箔の製造方法であって、電解液としてCl^-イオン濃度が２．０ｍｇ／ｌ以下、タンパク質濃度が０．５ｍｇ／ｌ以下の硫酸－硫酸銅水溶液を用いて電解することを特徴とする銅箔の製造方法を提供するものである。
【００１５】
また、本発明（５）は、本発明（４）において、前記硫酸－硫酸銅水溶液は、Cu^{2+}イオン濃度が４０ｇ／ｌ～１２０ｇ／ｌ、フリーSO_4^{2-}イオン濃度が１００ｇ／ｌ～２００ｇ／ｌであることを特徴とする銅箔の製造方法を提供するものである。
【００１６】
また、本発明（６）は、未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満である銅箔の製造方法であって、電解液として、活性炭処理して得られる、Cl^-イオン濃度が１０ｍｇ／ｌ～５０ｍｇ／ｌ、タンパク質濃度が０．２ｍｇ／ｌ以下の硫酸－硫酸銅水溶液を用いて電解することを特徴とする銅箔の製造方法を提供するものである。
【００１７】
また、本発明（７）は、本発明（６）において、前記硫酸－硫酸銅水溶液は、Cu^{2+}イオン濃度が４０ｇ／ｌ～１２０ｇ／ｌ、フリーSO_4^{2-}イオン濃度が１００ｇ／ｌ～２００ｇ／ｌであることを特徴とする銅箔の製造方法を提供するものである。
【００１８】
また、本発明（８）は、未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満で、該未処理銅箔の両表面のうち少なくともスズめっき層の形成される表面が、該表面をＸ線回折分析して得

請求項８に記載の銅箔を用いて形成したことを特徴とするＴＡＢテープ。

【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、銅箔及びその製造方法、並びにＴＡＢテープ及びその製造方法に関し、詳しくはＴＡＢテープ製造用銅箔及びその製造方法、並びにＴＡＢテープ及びその製造方法に関するものである。
【背景技術】
【０００２】
ＴＡＢ（Ｔａｐｅ　Ａｕｔｏｍａｔｅｄ　Ｂｏｎｄｉｎｇ）方式は、ＩＣやＬＳＩ等の半導体素子の実装の自動化及び高速化を図る技術である。ＴＡＢ方式は、具体的には、長尺状等のポリイミド等の可撓性絶縁フィルムに接着した銅箔をエッチングして該フィルム上にインナーリード及びアウターリードを含む銅リードを形成したＴＡＢテープを用い、基板のパッドと上記アウターリードのパッド、上記インナーリードのパッドと半導体素子のパッドとを、一括接続することにより、基板と半導体素子とを接続するものである。なお、本発明においてＴＡＢ方式とは、可撓性絶縁フィルムにデバイスホールを形成する通常のＴＡＢ方式に加え、可撓性絶縁フィルムにデバイスホールを形成しない以外は通常のＴＡＢ方式と同様であるＣＯＦ(Ｃｈｉｐ　Ｏｎ　Ｆｉｌｍ)方式をも含む概念を意味する。従って、本発明においてＴＡＢテープは、ＣＯＦ方式で用いられるＣＯＦテープをも含む概念で用いる。
【０００３】
上記ＴＡＢテープにおいて、上記インナーリードのパッドと半導体素子のパッドとの接続や上記アウターリードのパッドと基板のパッドとの接続は、はんだボール等のはんだ材料を介在させることにより行う。このため、インナーリードやアウターリードのパッドは、はんだ材料との濡れ性に優れたものであることが好ましく、通常は、インナーリードやアウターリードのパッドの表面にはんだとの濡れ性のよいスズめっきが施されている。なお、スズめっきは、インナーリードやアウターリードを形成する銅の表面酸化を抑制する効果も有するものである。
【０００４】
しかし、銅リードに形成したスズめっき皮膜は、特に処理をしないと、時間経過と共に皮膜表面からひげ状の針状結晶からなるスズウィスカーが発生して回路の短絡の原因になる。このため、通常は、スズめっき皮膜に熱処理（フュージング処理）を行ってスズウィスカーの発生しないスズめっき皮膜を形成している。
【０００５】
ところが、このようにフュージング処理を行うと、銅層とスズめっき層との界面にカーケンドール効果により形成されると思われるボイドが発生し易い。しかも、該ボイドは、原因は不明であるが種々ある低粗度箔のうち一部の種類のものに発生し易いことが判っていた。このため、このような種類の低粗度箔は、従来のような回路幅が大きいＴＡＢテープ用の銅箔としては十分な信頼性があり問題なく用いることができたものの、近年のようにファインピッチ化の要請により回路幅が小さくなったＴＡＢテープ用の銅箔としてはフュージング処理に対する回路の信頼性が十分でないため、使用し難くなってきている。
【０００６】
これに対し、特許文献１（特開２００２－１６１１１号公報）には、銅箔の少なくとも光沢面側にニッケル、コバルト及びモリブデンからなる合金層を有するＴＡＢテープに用いる銅箔が開示されている。該銅箔を用いれば、信頼性の高いＳｎホイスカ及びカーケンドールボイドの抑制効果を有するＴＡＢテープが得られる。
【０００７】
【特許文献１】特開２００２－１６１１１号公報（第２頁第１欄）
【発明の開示】

【特許請求の範囲】
【請求項１】
未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満であることを特徴とする銅箔。
【請求項２】
未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満である銅箔の製造方法であって、電解液としてＣｌ$^-$イオン濃度が０．５ｍｇ／ｌ以下の硫酸－硫酸銅水溶液を用いて電解することを特徴とする銅箔の製造方法。
【請求項３】
前記硫酸－硫酸銅水溶液は、Ｃｕ$^{2+}$イオン濃度が４０ｇ／ｌ～１２０ｇ／ｌ、フリーＳＯ$_4^{2-}$イオン濃度が１００ｇ／ｌ～２００ｇ／ｌであることを特徴とする請求項２に記載の銅箔の製造方法。
【請求項４】
未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満である銅箔の製造方法であって、電解液としてＣｌ$^-$イオン濃度が２．０ｍｇ／ｌ以下、タンパク質濃度が０．５ｍｇ／ｌ以下の硫酸－硫酸銅水溶液を用いて電解することを特徴とする銅箔の製造方法。
【請求項５】
前記硫酸－硫酸銅水溶液は、Ｃｕ$^{2+}$イオン濃度が４０ｇ／ｌ～１２０ｇ／ｌ、フリーＳＯ$_4^{2-}$イオン濃度が１００ｇ／ｌ～２００ｇ／ｌであることを特徴とする請求項４に記載の銅箔の製造方法。
【請求項６】
未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満である銅箔の製造方法であって、電解液として、活性炭処理して得られる、Ｃｌ$^-$イオン濃度が１０ｍｇ／ｌ～５０ｍｇ／ｌ、タンパク質濃度が０．２ｍｇ／ｌ以下の硫酸－硫酸銅水溶液を用いて電解することを特徴とする銅箔の製造方法。
【請求項７】
前記硫酸－硫酸銅水溶液は、Ｃｕ$^{2+}$イオン濃度が４０ｇ／ｌ～１２０ｇ／ｌ、フリーＳＯ$_4^{2-}$イオン濃度が１００ｇ／ｌ～２００ｇ／ｌであることを特徴とする請求項６に記載の銅箔の製造方法。
【請求項８】
未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満で、該未処理銅箔の両表面のうち少なくともスズめっき層の形成される表面が、該表面をＸ線回折分析して得られた回折線のうち（２００）面の回折線の相対ピーク強度をＩ（２００）、（１１１）面の回折線の相対ピーク強度をＩ（１１１）としたときに前記Ｉ（２００）を前記Ｉ（１１１）で除して算出される相対強度比Ｉ（２００）／Ｉ（１１１）が０．２０以下であることを特徴とする銅箔。
【請求項９】
未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満で、該未処理銅箔の両表面のうち少なくともスズめっき層の形成される表面が、該表面をＸ線回折分析して得られた回折線のうち（２００）面の回折線の相対ピーク強度をＩ（２００）、（１１１）面の回折線の相対ピーク強度をＩ（１１１）としたときに前記Ｉ（２００）を前記Ｉ（１１１）で除して算出される相対強度比Ｉ（２００）／Ｉ（１１１）が０．２０以下である銅箔の製造方法であって、電解液としてＣｌ$^-$イオン濃度が１．０ｍｇ／ｌ～２．０ｍｇ／ｌ、タンパク質濃度が０．２ｍｇ／ｌ以下の硫酸－硫酸銅水溶液を用いて電解することを特徴とする銅箔の製造方法。
【請求項１０】
前記硫酸－硫酸銅水溶液は、Ｃｕ$^{2+}$イオン濃度が４０ｇ／ｌ～１２０ｇ／ｌ、フリーＳＯ$_4^{2-}$イオン濃度が１００ｇ／ｌ～２００ｇ／ｌであることを特徴とする請求項９に記載の銅箔の製造方法。
【請求項１１】
請求項１に記載の銅箔を用いて形成したことを特徴とするＴＡＢテープ。
【請求項１２】

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(54)【発明の名称】銅箔及びその製造方法、並びにＴＡＢテープ

(57)【要約】
【課題】
スズめっき層をフュージング処理してもボイドが発生し難く、且つエッチング性が良い銅箔を提供すること。
【解決手段】
未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満である銅箔。電解液としてＣｌ$^-$イオン濃度が２．０ｍｇ／ｌ以下、タンパク質濃度が０．５ｍｇ／ｌ以下の硫酸－硫酸銅水溶液を用いて電解する銅箔の製造方法。未処理銅箔中のＣｌ含有量が３０ｐｐｍ未満で、該未処理銅箔の両表面のうち少なくともスズめっき層の形成される表面が、該表面をＸ線回折分析して得られた回折線のうち（２００）面の回折線の相対ピーク強度をＩ（２００）、（１１１）面の回折線の相対ピーク強度をＩ（１１１）としたときに前記Ｉ（２００）を前記Ｉ（１１１）で除して算出される相対強度比Ｉ（２００）／Ｉ（１１１）が０．２０以下である銅箔。
【選択図】　なし

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(71)Applicant : **MITSUI MINING & SMELTING CO LTD**

(72)Inventor : **SUGIOKA AKIKO**

(54) **COPPER FOIL, MANUFACTURING METHOD THEREFOR, AND TAB TAPE**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a copper foil which hardly causes voids even after having been subjected to fusing treatment with a tin-plated layer coated thereon, and is properly etched.

SOLUTION: The copper foil includes less than 30 ppm Cl in an untreated state. The method for manufacturing the copper foil includes electrolysis by using an electrolytic solution that is an aqueous solution of sulfuric acid and copper sulfate, in which Cl- ion concentration is controlled to 2.0 mg/l or less and protein concentration is controlled to 0.5 mg/l or less. The copper foil has a composition containing less than 30 ppm Cl in the untreated state; and has such crystal grains on at least the surface to be tin-plated out of both surfaces of the untreated copper foil, as to have a relative intensity ratio I (200)/I (111) of 0.20 or less, which is a value determined by dividing the I (200) by the I (111), when the I (200) indicates a relative peak intensity of a diffraction line on a face (200) among the diffraction lines obtained through X-ray diffraction analysis on the surface, and the I (111) indicates the relative peak intensity of the diffraction line on a face (111).

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	C22F	1/00	613	

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Fターム(参考)　4E351 BB01　DD04　DD54　GG20

(54)【発明の名称】高い伸びを有する圧延銅箔

(57)【要約】
【課題】本発明の目的は、箔を再結晶焼鈍した際に高い伸びが得られ、さらに減肉のためのエッチング処理を施したときに平滑な表面が得られる圧延銅箔を提供することである。
【解決手段】再結晶焼鈍を施すことにより、X線回折で求めた圧延面の（２００）面の強度（Ｉ）が、微粉末銅のX線回折で求めた（２００）面の強度（I_0）に対し、
$I_{(200)} / I_{0(200)} < 1.0$
である集合組織が発現することを特徴とする圧延銅箔

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	C22F	1/00	630K	
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	C22F	1/00	683	
	C22F	1/00	685Z	
	C22F	1/00	686B	

表１に実施例の評価結果を示す。Ｎｏ．１～９は発明例であり、Ｎｏ．１０～２２は成分または圧延上がりの板面方位が請求の範囲から外れる比較例である。比較例のうち、Ｎｏ．１０は無酸素銅であり、Ｎｏ．２１および２２は、Ｓｎを添加する代わりにＡｇを添加したもので、Ｎｏ．２１のＡｇ濃度は０．０２０ｍａｓｓ％、Ｎｏ．２２のＡｇ濃度は０．１４６ｍａｓｓ％である。

発明例のＮｏ１～８は、再結晶焼鈍後における板面方位が、請求項１を満たしており、いずれも２０％以上の高い伸びが得られ、また、再結晶後の結晶粒が微細なためエッチング面の粗さが小さい。

【００３０】

一方、比較例のＮｏ．１０はＳｎを添加していないため、Ｎｏ．１１はＳｎ濃度が０．０１ｍａｓｓ％に満たないため、最終圧延後の結晶方位が規定を外れ、再結晶後に立方体集合組織が著しく発達している。このため伸びが２０％より低く、また再結晶後の結晶粒が粗大なためエッチング面の粗さが大きい。Ｓｎの代わりにＡｇを添加したＮｏ．２１および２２、また、Ｓｎを添加しても、最終圧延後の結晶方位が規定を満たしていないＮｏ．１３～２０についても、同様の結果になっている。

【００３１】

Ｎｏ．１２はＳｎ濃度が０．２ｍａｓｓ％を超えたため、伸びが高くエッチング面の粗さも小さいが、導電率が８０％を下回り、高導電性が求められるコイルなどの用途には不適当である。

なお、圧延上がりの板面方位には、上述した圧延条件のほか、圧延機自体の特性（構造、剛性等）も影響を及ぼす。また、厚み、幅、機械的特性、表面粗さ等の材料要因も影響を及ぼす。したがって、圧延上がりの板面方位は、圧延条件によって、一義的に決定されるものではないが、参考までに、厚みとＳｎ濃度が同等である発明例Ｎｏ．４と比較例Ｎｏ．１６について、圧延条件を対比すると、次の通りであった。

・圧延ロールの直径（ｍｍ）…　Ｎｏ．４：５０、Ｎｏ．１６：５０。
・１パスあたりの加工度（％）…　Ｎｏ．４：４３．７、Ｎｏ．１６：６８．３。
・圧延張力（ＭＰａ）…　Ｎｏ．４：１００、Ｎｏ．１６：１５０。
・圧延油の温度（℃）…　Ｎｏ．４：３０、Ｎｏ．１６：２５。

【００３２】

【発明の効果】

本発明の銅箔は、再結晶焼鈍が施した際に、高い伸びを発現する。このため極細線のコイル、フレキシブルプリント回路基板、過酷な曲げ加工を必要とする微小部品等の用途として好適である。また、減肉のためのエッチング処理を施したときに平滑な表面が得られるので、ファインピッチ加工のために減肉エッチング処理を施されるフレキシブルプリント回路基板等に対しては、特に好適である。

【００２６】
（３）導電率
再結晶焼鈍後の試料について、定電圧直流電位差計を用いて比抵抗を測定し、導電率（ＩＡＣＳ％）を求めた。測定試験片は引張試験片と同じものを用いた。
【００２７】
（４）エッチング試験
温度５０℃、濃度１００ｇ／Ｌの過硫酸ナトリウム水溶液を試料表面に、２ｋｇ／ｃｍ２の圧力で噴射し、厚みが半分になるように深さ方向にエッチングした。その後、ＪＩＳＢ０６０１（１９９９年）に従い、接触粗さ計を用いて表面の最大高さ（Ｒｙ）を求めた。基準長さを０．８ｍｍとし、圧延方向と平行な方向に測定した。Ｒｙの測定は場所を変えて５回行い、５回の測定値の最大値を求めた。
【００２８】
【表１】

	No.	厚み (μm)	Sn濃度 (mass%)	各結晶方位の積分強度比 (I/I_0)						再結晶後の結晶粒径 (μm)	伸び (%)	導電率 (IACS%)	エッチング面のRy (μm)
				圧延上がり				再結晶後					
				(111)	(200)	(220)	(311)	(200)					
本発明例	1	17	0.025	0.03	0.85	2.61	0.26	0.93		5.1	23.2	96.5	1.3
	2	17	0.081	0.03	0.67	2.94	0.35	0.81		3.5	25.5	92.0	1.4
	3	17	0.103	0.03	0.46	3.28	0.38	0.74		3.2	26.1	91.4	1.3
	4	17	0.124	0.04	0.33	3.65	0.40	0.66		3.5	26.8	88.3	1.1
	5	17	0.154	0.05	0.30	4.19	0.47	0.47		2.4	27.2	88.0	0.8
	6	17	0.190	0.05	0.28	5.05	0.49	0.31		3.0	28.3	86.1	1.0
	7	12	0.078	0.04	0.33	3.65	0.40	0.44		3.2	24.6	94.2	1.2
	8	9	0.082	0.04	0.28	4.03	0.46	0.65		2.8	21.5	91.1	0.8
	9	7	0.122	0.05	0.24	3.02	0.33	0.27		2.1	20.1	88.6	0.7
比較例	10	17	<0.001	0.010	10.34	0.84	0.11	35.40		45.3	9.4	100.8	4.2
	11	17	0.008	0.02	6.66	2.21	0.14	13.60		18.6	13.2	99.1	3.9
	12	17	0.220	0.03	0.45	2.72	0.33	0.55		3.2	26.6	79.2	1.4
	13	17	0.103	0.002	0.93	4.95	0.36	2.13		8.4	17.6	91.6	2.6
	14	17	0.105	0.23	0.18	2.79	0.54	1.46		8.8	16.2	89.5	2.5
	15	17	0.156	0.07	1.45	2.32	0.36	3.46		9.4	13.7	88.2	2.8
	16	17	0.123	0.09	0.08	5.39	0.58	1.88		10.2	15.8	89.5	3.2
	17	17	0.134	0.012	0.18	2.05	0.43	2.04		10.5	13.2	88.3	3.4
	18	17	0.113	0.14	0.91	7.66	0.55	1.97		8.1	15.3	91.6	2.9
	19	17	0.122	0.06	0.75	3.64	0.09	2.66		9.6	15.1	88.2	3.0
	20	17	0.108	0.04	0.64	2.78	0.79	1.23		7.3	14.6	90.6	2.2
	21	17	<0.001	0.007	9.65	1.83	0.35	45.30		42.4	11.7	99.7	4.6
	22	17	<0.001	0.02	3.39	2.29	0.49	10.40		13.6	16.8	96.0	3.3

【００２９】

８５％以上とし、最後の冷間圧延直前の焼鈍で得られる結晶粒径を２０μｍ以下にすることが好ましい。なお、冷間圧延加工度（Ｒ）は、圧延前の厚さをt_0、圧延後の厚さをｔとし、

$R=(t_0-t)/t_0\times100$（％）

で定義される。

【００２１】

【実施例】

以下、本発明の様態を実施例により説明する

カーボン脱酸によりＯ濃度を５ｍａｓｓ　ｐｐｍ以下に下げた溶銅に所定量のＳｎを添加し、表１に示す成分の厚さ２００　ｍｍ、幅６００　ｍｍの銅インゴットを製造した。インゴットを熱間圧延した後、焼鈍と冷間圧延を繰り返し、最後に加工度９０％の冷間圧延で所定の厚みの箔に仕上げた。最終圧延前の再結晶焼鈍は，結晶粒径が約１５μｍになる条件で行った。なお、焼鈍後の結晶粒径は、圧延方向に直角な断面において切断法で測定した。

【００２２】

最終圧延上がりの結晶方位を変化させるために、圧延ロールの直径、１パスあたりの圧延加工度、圧延張力および圧延油の温度を種々変化させた。これら圧延条件と圧延後の板面方位には次のような傾向が認められた。

・圧延ロールの直径を大きくすると、（３１１）面の強度が低くなる。

・１パスあたりの圧延加工度を大きくすると、（２００）面の強度が低くなる。

・圧延油温度を低くすると（１１１）面の強度が高くなる。

・圧延張力を高くすると（２２０）面の強度が高くなる。

最終圧延上がりの銅箔につき、まず、焼鈍時間を３０分としたときの半軟化温度を求めた。そして、この半軟化温度より５０℃高い温度で３０分間の焼鈍を施し、銅箔を再結晶させた。ここで、半軟化温度とは、引張り強さが焼鈍前の値と完全軟化後（本実施例では５００℃で３０分間焼鈍したときの値を採用）の値の中間の値になるときの焼鈍温度である。

【００２３】

以上の銅箔試料について、次の評価を行った。

（１）圧延上がりの板面方位

圧延上がりの銅箔の表面について、Ｘ線回折により（１１１）、（２００）、（２２０）および（３１１）面の強度の積分値（Ｉ）求めた。この値をあらかじめ測定しておいた微粉末銅のそれぞれの面強度の積分値（I_0）で割り、I/I_0の値を計算した。なお、ピーク強度の積分値の測定では、Ｃｏ管球を用い、２θ（θは回折角度）は以下の範囲で行なった。

（１１１）：４８～５３°

（２００）：５７～６２°

（２２０）：８６～９１°

（２００）：１０８～１１３°

同様に、再結晶焼鈍後の試料について、（２００）面の積分強度比I/I_0を求めた。

【００２４】

（２）再結晶後の結晶粒径

再結晶焼鈍後の試料について、圧延面を鏡面研磨後に化学腐食し、切断法（ＪＩＳ　Ｈ０５０１（１９９９年））に準じ、所定長さの線分により完全に切られる結晶粒数を数える方法により結晶粒径を求めた。

【００２５】

（３）伸び

再結晶焼鈍後の試料について、引張試験により伸びを求めた。

引張試験片は幅１２．７ｍｍ、長さ１５０ｍｍの短冊片を用い、引張速度を５０ｍｍ／ｍｉｎに固定し、破断後の伸びを実測した。伸び測定の標点距離は５０ｍｍとした。

以下に本発明を構成する各要素の限定理由について説明する。

（１）再結晶焼鈍後の結晶方位

再結晶焼鈍を施した銅箔の結晶方位が、

$I_{(200)}/I_{0(200)}<1.0$

の関係にあれば、高い伸びが得られ、減肉エッチング面が平滑化する。ここで、$I_{(hkl)}$および$I_{0(hkl)}$は、それぞれ銅箔の圧延面および微粉末銅（ランダム方位試料）について、Ｘ線ディフラクトメータを使用して測定した（ｈｋｌ）面のＸ線強度の積分値である。

【００１５】

（２）銅箔の素材

ＣｕにＳｎを添加すると、積層欠陥エネルギーが低下して、（２００）立方体集合組織の発達が抑制される。しかし、Ｓｎ濃度が０．０１ｍａｓｓ％未満では、圧延上がりの結晶方位を後述するように調整しても、再結晶焼鈍後に上記結晶方位を得ることができない。また、Ｓｎが０．２　ｍａｓｓ％を超えると導電率が８０％を下回り、高導電性が求められる用途に向かなくなる。

【００１６】

一方、Ｓｎを添加するベースとなるＣｕには、酸素濃度が０．００５ｍａｓｓ％以下である無酸素銅と酸素濃度が０．０２～０．０５ｍａｓｓ％のタフピッチ銅の二種類がある。本発明では無酸素銅にＳｎを添加する。タフピッチ銅にＳｎを添加すると、Ｓｎと酸素が化合物を生成するため、銅箔を引張った際にこの粒子を起点にして破断が起こり、高い伸びは期待できない。なお、　ＪＩＳ－Ｈ３１００（１９９９年）により、無酸素銅Ｃ１０２０の組成は、Ｃｕが９９．６ｍａｓｓ％以上と定義されている。

【００１７】

（３）最終圧延上がりの結晶方位

再結晶焼鈍後に上記結晶方位を得るためには、最終圧延上がり（再結晶焼鈍前）において、銅合金の主要４面（（２２０）、（１１１）、（２００）、（３１１））の配向を、

$0.01<I_{(111)}/I_{0(111)}<0.1$

$0.15<I_{(200)}/I_{0(200)}<1.0$

$2.5<I_{(220)}/I_{0(220)}<5.5$

$0.2<I_{(311)}/I_{0(311)}<0.6$

に調整する必要がある。この範囲に調整しないと、０．０１　ｍａｓｓｔ％以上のＳｎを添加しても、再結晶焼鈍後に所望の結晶方位を得ることができない。

【００１８】

（４）箔の厚み

最終圧延によって得られる箔の厚みを２０μｍ以下としたが、より望ましくは５～１８μｍである。箔の厚みが５μｍ未満の場合、各種部品に加工される際にしわがよったり、破れやすくなるなどハンドリングに困難が生じる。また、２０μｍを超えると、小型化が求められるコイル用素材や２層ＣＣＬ用には採用しにくくなる。

【００１９】

（５）伸び

２０％以上の伸びが安定して得られれば、従来の銅箔に対して明らかに伸びが向上したと判断でき、部品の設計の変更、新たな用途への銅箔の適用などが可能となる。なお、本発明に関わるＳｎ含有銅箔の再結晶焼鈍の温度は、概ね３５０～４５０℃の範囲が適正である。この温度より低い条件では未再結晶領域が存在し、また、これより高い条件では結晶粒が粗大化し、いずれの場合にも所望の伸びを得ることができなくなる。

【００２０】

（６）製造プロセス

上記の最終焼鈍上がりの結晶方位を得るための製造プロセスは特に限定されない。ただし、圧延上がりの強度を高めるためには、インゴットを熱間圧延した後、冷間圧延と焼鈍とを繰り返し最後に冷間圧延で箔に仕上げるプロセスにおいて、最後の冷間圧延の加工度を

【００１０】
そこで本発明者らは、再結晶焼鈍を施した圧延銅箔について、結晶方位と伸びとの関係に着目し、そのデータを蓄積し解析した。その結果、圧延面への（２００）面の集合度を所定のレベルに抑制した銅箔は、従来の銅箔に対し、再結晶焼鈍後の伸びがより優れていることを見出した。いいかえれば、極薄銅箔において、伸びを改善する方策を見出したのである。
【００１１】
金属結晶のヤング率は結晶方位に依存して変化するため、金属材料の弾性的変形挙動は結晶方位によって変化する。また、金属結晶は固有のすべり面とすべり方向を持つことから、金属材料の塑性的変形挙動も結晶方位によって変化する。立方体方位の発達度が材料の伸びに影響を及ぼすメカニズムの詳細は明らかでないが、金属材料の変形挙動が結晶方位に依存することと関係していると思われた。
さらに，本発明者らは（２００）面の集合度を充分に抑制するためには、Ｓｎを添加するだけでは不十分であり、再結晶焼鈍前（最終圧延上がり）の結晶方位をも制御する必要があることを知見した。
【００１２】
なお、本発明者らは、特願２００２－５０７００において、銅張積層板用にＳｎを添加した銅箔を提案しているが、この発明は銅箔が圧延上がりの組織状態で用いられる場合に、銅箔の成分、組織などを最適化したものである。これに対し、本発明は、圧延銅箔が再結晶焼鈍を経て使用される場合に、再結晶後の伸びを高めることを主目的に、成分と組織を最適化するものである。
一方、立方体方位に配向する再結晶粒の成長速度は極めて大きいため、再結晶焼鈍時に立方体集合組織が発達する銅箔では、再結晶粒が粗大化する。したがって、立方体集合組織の発達を抑制すると結晶粒が微細化する。この結晶粒微細化により、減肉エッチングを施した際に、エッチング面が平滑になるという効果も得られた。エッチング面の凹凸は、隣接する結晶粒の方位差に起因して結晶粒単位で発生するものであり、結晶粒が微細になることにより凹凸のピッチが小さくなり、表面が平滑化するのである。
【００１３】
減肉エッチング面の平滑化について、本発明者らは特願２００１－３９５７７４にて、立方体集合組織を極度に発達させることを提案している。これは、隣接する結晶粒の方位差を無くすことを意図したものである。本発明によるエッチング面平滑化は、これとは異なる機構を利用したものである。
すなわち、本発明は、
（１）再結晶焼鈍を施すことにより、Ｘ線回折で求めた圧延面の（２００）面の強度（Ｉ）が、微粉末銅のＸ線回折で求めた（２００）面の強度（I_0）に対し、
$I_{(200)}/I_{0(200)}<1.0$
である集合組織が発現することを特徴とする圧延銅箔、
（２）Ｓｎを０．０１～０．２ｍａｓｓ％含有し、ＳｎとＣｕの合計が９９．９％以上であり、さらに、Ｘ線回折で求めた圧延面の（１１１）、（２００）、（２２０）、（３１１）面の強度（Ｉ）が、微粉末銅のＸ線回折で求めたそれぞれの面の強度（I_0）に対し、
$0.01<I_{(111)}/I_{0(111)}<0.1$
$0.15<I_{(200)}/I_{0(200)}<1.0$
$2.5<I_{(220)}/I_{0(220)}<5.5$
$0.2<I_{(311)}/I_{0(311)}<0.6$
であることを特徴とする圧延銅箔、
（３）厚みが２０μｍ以下であり、再結晶焼鈍したあとに、２０％以上の伸びが得られることを特徴とする請求項１、２に記載の圧延銅箔、である。
【０００１４】
【発明の実施の形態】

し、厚さが１０μｍ以下の圧延銅箔を工業的に安定して製造することは困難であり、また、銅張積層板の製造プロセスにおける銅箔の取り扱いも難しくなる。そこで、例えば銅回路の厚みが６μｍのフレキシブル基板は、まず１２μｍの銅箔を用いて銅張積層板を製造し、エッチングにより銅箔の厚みを６μｍに減肉するというプロセスにより製造されることが多い。このエッチング処理（以下、減肉エッチング）に対し、銅箔表面が均一にエッチングされることが要求される。その理由はエッチングが不均一に進むとエッチング後の表面に凹凸が生じるため、回路のエッチング（以下、回路エッチング）に先立ちレジストを銅箔表面に塗布する際に、銅箔とレジスト膜との間に気泡が発生し、エッチング後の回路形状が劣化するためである。

【０００５】

銅箔の伸びの向上については、ＦＰＣ以外の用途でも求められている。例えば、電線被覆材用として、銅箔を合成樹脂材料と重ねて張り合わせた積層材が用いられている。銅箔の伸びは厚みが薄くなるに従い減少する。軟化点以上の温度で焼鈍し伸びを高めた銅箔を用いても、ごく薄い銅箔を電線被覆材用として電線に巻きつける場合には、銅箔に亀裂が入り破断するという問題があった。

従来、上記用途の銅箔の素材は、主としてタフピッチ銅（酸素含有量１００～５００ｍａｓｓ　ｐｐｍ）または無酸素銅（酸素含有量１０ｍａｓｓ　ｐｐｍ以下）であり、このインゴットを熱間圧延し、その後冷間圧延および中間焼鈍を繰り返し、最終圧延で厚み９～３５μｍの箔に加工する。この圧延上がりの銅箔を焼鈍したときにより高い伸びが得られるように、銅箔の製造工程において、中間焼鈍の条件を種々変化させたり、最終焼鈍後の圧延加工度を調整することが試みられたが、銅箔の厚みが１０μｍ以下になると１０％を超える伸びを得ることは困難であった。

【０００６】

これに対して、タフピッチ銅にＡｇを０．０５～０．３５質量％添加し、伸びを高めた銅箔が提唱されている（例えば、特許文献１参照。）。しかし、この方法により得られた銅箔においても、厚さ８μｍの銅箔を焼鈍したときの伸びは１０％を超えていない。

純銅を再結晶焼鈍すると立方体集合組織（（１００）面、［００１］方位）が発達する。銅箔の製造プロセスにおいて最終圧延での加工度を高くすること、および最終圧延直前の焼鈍での結晶粒径を小さくすることで、再結晶焼鈍後に立方体集合組織がより発達する。タフピッチ銅にＡｇを微量添加した銅箔においても、同様の製造プロセスにより立方体集合組織が発達する傾向が認められる。立方体集合組織の発達度が高くなるにしたがって、箔の引張強さと伸びが同時に低下する。また、再結晶焼鈍後の結晶粒の形態に着目すると、立方体集合組織が発達した銅箔では、丸みを帯びて圧延方向に長く伸びた粗大な再結晶粒となる。

【０００７】

【特許文献１】

特開平１１－１４０５６４号公報

【０００８】

【発明が解決しようとする課題】

本発明の目的は、箔を再結晶焼鈍した際に高い伸びが得られ、さらに減肉のためのエッチング処理を施したときに平滑な表面が得られる圧延銅箔を提供することである。

【０００９】

【課題を解決するための手段】

本発明者らは、無酸素銅に微量の元素を添加したインゴットを素材とし、熱間圧延後に冷間圧延と中間焼鈍を行い、最後に冷間圧延で箔に仕上げる工程で、厚さ１８μｍ以下の銅箔を製造した。このプロセスにおいて、添加元素の種類と量、圧延条件等を種々に変化させ、これら条件が再結晶焼鈍後の伸びに及ぼす影響を検討した。その結果、無酸素銅にＳｎを添加した銅箔では、箔を再結晶焼鈍したときに高い伸びが得られることを知見した。高い伸びが得られた銅箔では、純銅の再結晶集合組織である立方体方位の発達度が著しく低かった。

【特許請求の範囲】
【請求項１】
再結晶焼鈍を施すことにより、圧延面のＸ線回折で求めた（２００）面の強度（Ｉ）が、微粉末銅のＸ線回折で求めた（２００）面の強度（I_0）に対し、
$I_{(200)}/I_{0(200)}<1.0$
である集合組織が発現することを特徴とする圧延銅箔
【請求項２】
Ｓｎを０．０１～０．２ｍａｓｓ％含有し、ＳｎとＣｕの合計が９９．９％以上であり、さらに、Ｘ線回折で求めた圧延面の（１１１）、（２００）、（２２０）、（３１１）面の強度（Ｉ）が、微粉末銅のＸ線回折で求めたそれぞれの面の強度（I_0）に対し、
$0.01<I_{(111)}/I_{0(111)}<0.1$
$0.15<I_{(200)}/I_{0(200)}<1.0$
$2.5<I_{(220)}/I_{0(220)}<5.5$
$0.2<I_{(311)}/I_{0(311)}<0.6$
であることを特徴とする圧延銅箔。
【請求項３】
厚みが２０μｍ以下であり、再結晶焼鈍したあとに、２０％以上の伸びが得られることを特徴とする請求項１、２に記載の圧延銅箔。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】
本発明は高い伸びを有する圧延銅箔およびその製造方法に関するものであり、フレキシブルプリント回路基板（Ｆｌｅｘｉｂｌｅ　Ｐｒｉｎｔｅｄ　Ｃｉｒｃｕｉｔ、以下ＦＰＣと表記する）および多層フレキシブルプリント回路基板等の可撓性配線部材、小型モーター用箔巻きコイル、トランス用箔巻きコイル、電線被覆材などのコイル材等に好適な高い伸びを有する圧延銅箔を提供するものである。
【０００２】
【従来の技術】
電子機器の電子回路にはＦＰＣが多用される。ＦＰＣは可撓性を持つことを特徴とし、可動部の配線に用いられる他に、電子機器内で折り曲げた状態で収納することが可能であるために、省スペース配線材料としても用いられている。ＦＰＣは、ポリイミド等の樹脂フィルムに銅箔を貼り付けた銅張積層板に、エッチング加工で銅の配線パターンを形成したものである。
【０００３】
近年、電子機器の薄型化およびコンパクト化が進み、より厳しい折り曲げ変形がＦＰＣに加えられるようになった。ＦＰＣには三層銅張積層板と二層銅張積層板の二種類がある。三層材では接着剤を使用して銅箔と樹脂フィルムとを接着するのに対し、二層材では接着剤を介さずポリイミドフィルムと銅箔が一体化される。このため，二層材は三層板よりも薄く、薄いことにより折り曲げ性に優れる。したがって、特に可撓性が要求されるＦＰＣには二層材が用いられる傾向にある。
二層材の製造方法としては、ポリイミド樹脂の前駆体であるポリアミック酸を含むワニスを銅箔上に塗布して加熱硬化させる“キャスティング法”、銅箔をポリイミドフィルムに直接に積層する“ラミネート法”等がある。この製造プロセスでの熱履歴により銅箔は再結晶し軟化する。二層材の折曲げ性をさらに改善するために、銅張積層の構成材料である銅箔に対しても、再結晶後の伸びを高め、折り曲げ性を改善することが求められている。
【０００４】
また、ＦＰＣにおける銅配線の幅と配線間隔はますます小さくなっている。このような銅配線のファインピッチ化を進めるためには、銅箔を薄くすることが不可欠である。すなわち、従来、フレキシブル基板に用いられていた銅箔の厚みは１８μｍまたは１２μｍが主流であったが、最近は９μｍあるいはこれより薄い銅箔が要求されるようになった。しか

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HATANO TAKATSUGU

(54) ROLLED COPPER FOIL HAVING HIGH ELONGATION

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a rolled copper foil which has high elongation when the foil is recrystallization-annealed, and further has a flat surface when etched in order to reduce the foil thickness.
SOLUTION: The rolled copper foil, when recrystallization-annealed, develops a texture in which the intensity (I) of a rolled face (200) determined by X-ray diffraction has such a relation with the intensity (I0) of the face (200) on the fine powder of copper determined by the X-ray diffraction, as to satisfy I(200)/I0(200)<1.0.

US005834140A

United States Patent [19]

Wolski et al.

[11] Patent Number: 5,834,140

[45] Date of Patent: Nov. 10, 1998

[54] **ELECTRODEPOSITED COPPER FOIL FOR FINE PATTERN AND METHOD FOR PRODUCING THE SAME**

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[21] Appl. No.: **715,104**

[22] Filed: **Sep. 18, 1996**

[30] **Foreign Application Priority Data**

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Apr. 26, 1996 [JP] Japan 8-106743

[51] **Int. Cl.**[6] **C25D 1/04**

[52] **U.S. Cl.** **429/220**; 205/57; 205/77; 205/296; 428/606; 428/607; 428/612; 428/675; 428/687; 428/935; 429/122; 429/245

[58] **Field of Search** 205/50, 76, 77, 205/57, 296; 428/606, 607, 612, 675, 687, 935; 429/122, 220, 245

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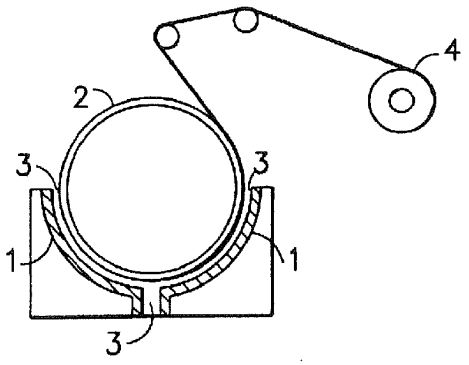
41 26 502 2/1993 Germany .

Primary Examiner—Kathryn L. Gorgos
Assistant Examiner—William T. Leader
Attorney, Agent, or Firm—Frishauf. Holtz, Goodman, Langer & Chick, P.C.

[57] **ABSTRACT**

The present invention is an electrodeposited copper foil characterised in that roughening treatment is performed on a matte side of an untreated copper foil wherein the surface roughness R_z of the matte side of the untreated copper foil is the same as or less than the surface roughness R_z of the shiny side of this untreated copper foil. The electrodeposited copper foil is made by electrodepositing copper onto a drum from an electrolyte which contains 0.05 to 5 ppm 3-mercapto 1-propanesulfonate; at least one organic compound selected from 0.1 to 15 ppm of a polysaccharide which is a carbohydrate such as starches, celluloses and vegetable rubbers, and 0.3 to 35 ppm of a low molecular weight glue having a weight average molecular weight of 10,000 or less; and 10 to 60 ppm of a chloride ion. The copper foil may be used in making a printed circuit board or as a component of a secondary battery cell.

15 Claims, 1 Drawing Sheet



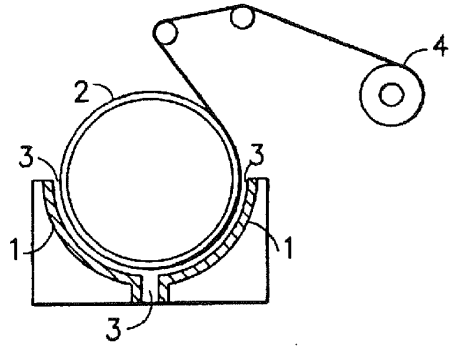


FIG. 1

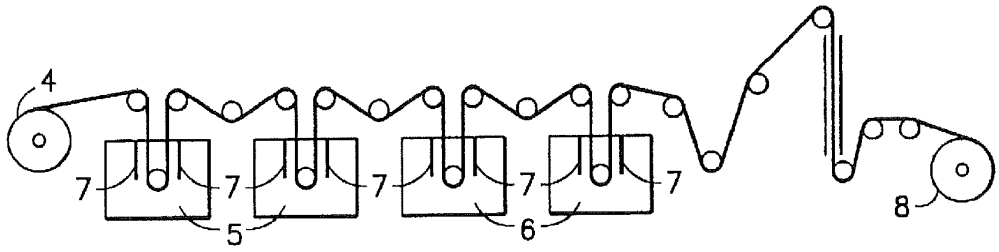


FIG. 2

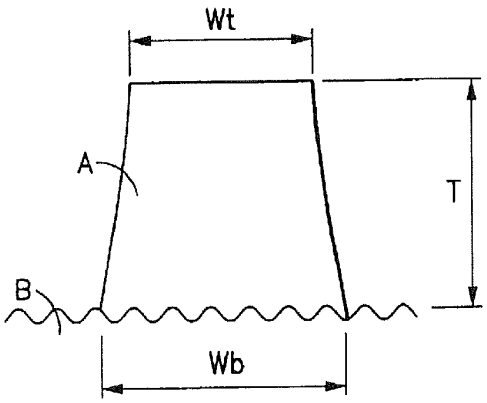


FIG. 3

ELECTRODEPOSITED COPPER FOIL FOR FINE PATTERN AND METHOD FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an electrodeposited copper foil which is capable of making a fine pattern and capable of obtaining a high etching factor, a method for producing the same, and a copper-clad laminated board and a printed-wiring board (printed circuit) using the same.

Also, the untreated copper foil according to the present invention has flatter surfaces on both surfaces as compared with the conventional ones so that it can be used as an electrode material for a secondary battery, a flat cable, a shielding material for covering cables and others, but use of the electrodeposited copper foil of the present invention is not limited thereto.

2. Prior Art

An electrodeposited copper foil for a printed circuit has been produced industrially by filling a gap between an insoluble electrode such as a lead electrode or a titanium electrode covered with a platinum group metal and a rotating cathode drum which is made of stainless steel or titanium and opposed to the insoluble electrode, with an electrolyte of a copper sulfate aqueous solution, passing electricity to these electrodes to electrodeposit copper on the rotating cathode drum and peeling off the electrodeposited copper continuously.

In general, when an aqueous solution containing only a copper ion and a sulfuric acid ion is used as an electrolyte, pinhole or microporosity is generated on the copper foil due to dust or oils inevitably existing in the equipments and causes serious problems in practical use. Also, the mountain-valley shape of a surface (a matte side) of the copper foil which contacts with the electrolyte is deformed so that sufficient strength cannot be obtained when the copper foil is adhered to an insulating substrate material in a later stage. When roughness of the matte side is large, there are caused problems that insulation resistance between layers and circuit conductivity of a multilayer printed-wiring board (printed circuit) are lowered, or at pattern etching after adhering the copper foil to a substrate material, transfer of copper to the substrate or undercutting of a circuit portion occurs, whereby various characteristics as a circuit substrate are damaged.

In order to prevent the pinhole or the like, a chloride ion is added to the electrolyte, or the electrolyte is passed through a filter containing activated carbon to remove dust and oils. In order to prevent microporosity and adjust the mountain-valley shape of the matte side, glue has heretofore been added to the electrolyte, and it has been also proposed to add various organic materials and inorganic materials as additives other than glue. Technology of producing an electrodeposited copper foil for a printed-wiring board is based on plating technology as can be understood from the point that electrodes are provided in a solution containing a metal salt and electricity is passed to the electrodes to electrodeposit a metal on a cathode. As an additive for producing the electrodeposited copper foil for a printed-wiring board, an additive for copper plating can be diverted in many cases. Glue, thiourea and molasses have heretofore been known as a brightener for copper plating, and when the above additives are added to the electrolyte, it can be expected to exhibit a so-called brightening effect, i.e., an effect of making roughness of the matte side smaller with

respect to the electrodeposited copper foil for a printed-wiring board. In U.S. Pat. No. 5,171,417, there has been disclosed a method of producing an electrodeposited copper foil, in which activated sulfur such as thiourea is used as an additive. However, the electrodeposited copper foil for a printed-wiring board is produced with current density which is higher than that of common plating in order to improve productivity, etc.; in recent years, characteristics required for the electrodeposited copper foil for a printed-wiring board have been heightened significantly; and in particular, there has been demanded strongly a copper foil in which roughness of the matte side is suppressed without impairing mechanical characteristics such as elongation, whereby satisfactory characteristics cannot be obtained under the present circumstances even when the above additives for plating are used as such as additives for the electrodeposited copper foil for a printed-wiring board.

On the other hand, in recent years, developments in electronic circuit technology including a semiconductor and an integrated circuit are remarkable. As a matter of course, further technological innovation has been demanded even in a printed-wiring board which is a forming portion or a mounting portion thereof. These demands are to develop a highly multilayered and finely patterned printed circuit board.

Characteristics required for the electrodeposited copper foil for a printed-wiring board in order to satisfy these demands are good insulation property between layers and patterns, low profiling of a matte side (lowering in roughness) in order to prevent undercutting at etching, improved high temperature elongation characteristic in order to prevent crack due to thermal stress and also high tensile strength for dimensional stability of the printed-wiring board. A demand for further low profiling for fine patterning has been particularly strong.

Low profiling of the matte side can be accomplished by, for example, adding a large amount of glue or thiourea to the electrolyte as described above, but accompanied with increase in its amount added, both of ordinary temperature elongation and high temperature elongation are lowered abruptly. On the other hand, a copper foil obtained from an electrolyte to which no additive is added has extremely high values of ordinary temperature elongation and high temperature elongation, but the shape of the matte side is deformed, roughness is enlarged, high tensile strength cannot be maintained, and further it is impossible to produce an electrodeposited copper foil in which these characteristics are stable. When electrolysis current density is suppressed to a lower value, as compared with an electrodeposited foil prepared with high current density, roughness of the matte side is lowered and elongation and tensile strength are improved, but lowering in productivity is not preferred from an economical view.

As described above, it is not easy to realize further low profiling, good room temperature elongation, good high temperature elongation and high tensile strength which have been demanded for a recent electrodeposited copper foil for a printed-wiring board.

As the reason why fine pattern cannot be produced by the conventional electrodeposited copper foil, there may be mentioned that a surface roughness of the foil is rough.

An electrodeposited copper foil can be generally produced by firstly using an electroforming cell as shown in FIG. 1 to produce a copper foil which is called to as an untreated copper foil and then using a treater as shown in FIG. 2, the produced copper foil is subjected to bond

enhancing treatment and stain proofing treatment to prepare a surface treated copper foil.

In the electroforming cell, an electrolyte **3** is passed through an apparatus comprising a drum-shaped cathode **2** (the surface of which is made of SUS (stainless steel) or titanium) which is rotating and an anode **1** (a lead electrode or a titanium electrode covered by a noble metal oxide) provided to a concentric circle shape to said cathode **2**, and an electric current is passed through both electrodes to deposit copper on the surface of said cathode with a desired thickness and then the copper foil is peeled off from the surface of said cathode. The thus prepared foil is called to as an untreated copper foil.

Thereafter, in order to provide characteristics necessary for a copper-clad laminated board, the untreated copper foil **4** is passed through the treater as shown in FIG. **2** to carry out an electrochemical or chemical surface treatment continuously. Among these treatments, there is a process of depositing copper modules on the surface of the foil for enhancing bonding strength of the foil when it is laminated to an insulating resin substrate. This process is called to as a bond enhancing treatment. The copper foil subjected to the above treatments is called a treated copper foil **8** and can be used for a copper-clad laminated board.

Mechanical characteristics of the electrodeposited copper foil can be determined by the characteristics of the untreated copper foil **4**, and an etching characteristic of a copper foil, i.e. an etching rate and uniform dissolution property are also determined in a large part by the characteristics of the untreated foil.

A main factor which affects an etching characteristic among the characteristics of a copper foil is a surface roughness of the foil. An effect of a roughness of the surface which is subjected to the bond enhancing treatment and to be laminated to an insulating resin substrate is remarkable. Factors which affect the roughness of the copper foil can be roughly divided into two. One of which is a surface roughness of the untreated copper foil and the other is a manner of copper nodules to be deposited to the surface subjected to the bond enhancing treatment of the foil. When the surface roughness of the untreated copper foil which is a raw foil is rough, the roughness of the copper foil after the bond enhancing treatment becomes rough. Also, generally speaking, when a deposited amount of copper nodules to the foil is a large, the roughness of the copper foil after the bond enhancing treatment becomes rough. The deposited amount of copper nodules at the bond enhancing treatment can be controlled by the amount of the electric current to be flown at the time of the treatment while the surface roughness of the untreated copper foil is almost determined by the electrolysis conditions when copper is deposited on the drum-shaped cathode as mentioned above, particularly by an additive to be added to an electrolyte.

In general, in the untreated copper foil, the so-called shiny side which is a surface at the side contacting with the drum has a relatively smooth surface, but at the reverse surface called a matte side, unevenness is relatively remarkable. In order to smooth the matte side, some attempts have been made until now. For example, there is a method for producing an electrodeposited copper foil prepared by using an active sulfur such as thiourea, etc., as an additive as disclosed in the above-mentioned U.S. Pat. No. 5,171,417. However, in this case, while the roughened surface can be smoothened as compared with the case where a conventional additive such as glue is used, it is still rough as compared with the shiny side and the effect is not yet complete.

Also, since the shiny side is relatively smooth so that, as disclosed in Japanese Provisional Patent Publication No. 270331/1994, an attempt has been made that copper nodules are deposited to the shiny side whereby laminating it with a resin substrate. However, in this case, there is a disadvantage that it must adhere a dry film or a resist to the usual matte side whereby adhesive force to the copper foil lowers due to unevenness of the surface and the film or the resist easily peels off from the foil.

SUMMARY OF THE INVENTION

The present invention has been made in order to cancel the problems of the prior art techniques, and an object thereof is to provide a copper foil which has a high etching factor without lowering peeling resistance and acomplishes fine pattern without remaining copper particles at the root of the circuit pattern, and also has a large high temperature elongation and high tensile strength.

Here, the measure of the fine pattern can be generally shown by the etching factor (=2T/(Wb−Wt)) shown in FIG. **3**. If the value is larger, the shape of the section of a circuit becomes more sharp.

The present invention is an electrodeposited copper foil which comprises a copper foil having a shiny side and a matte side and said matte side which has a surface roughness R_z measured by JIS B 0601-1994 of substantially the same as that of the shiny side or less being subjected to a surface roughening treatment. Surface roughness R_z means R_z as specified by the definition of JIS B 0601-1994 "Indication of definition of surface roughness" 5.1, i.e. 10-point mean roughness (R_z).

This untreated copper foil can be obtained by electrolysis using an electrolyte to which has been added a chemical compound having a mercapto group and apart from this at least one type of organic compound and chloride ions.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a sectional view showing the structure of an electroforming cell wherein the reference numeral **1** is an anode of an electroforming cell, **2** is a cathode of an electroforming cell, **3** is an electrolyte of an electroforming cell and **4** is an untreated copper foil.

FIG. **2** is a sectional view showing the structure of a treater wherein the reference numeral **4** is the same as in FIG. **1**, **5** is an electrolyte of a treater, **6** is an electrolyte of a treater, **7** is an anode of a treater, and **8** is a surface-treated copper foil.

FIG. **3** is a schematic view showing a calculating method of an etching factor wherein A is a cross-section of copper foil, B is an insulating board, Wt is a top width of copper foil cross-section, Wb is a bottom width of copper foil cross-section and T is a thickness of a copper foil.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

An electrodeposited copper foil of the present invention comprises an untreated copper foil having a shiny side and a matte side, and a surface roughness R_z of the matte side is the same as a surface roughness R_z of the shiny side or less and the matte side is subjected to a surface bond enhancing treatment. Here, the surface roughness R_z means a ten-point mean roughness (R_z) defined at the paragraph 5.1 of "Definition and Designation of Surface Roughness" according to "JIS B 0601-1994".

In the present invention, an additive which is a base of a combination is 3-mercapto 1-propanesulfonate as a com-

pound having a mercapto group. 3-Mercapto 1-propanesulfonate is a compound representatively shown by $HS(CH_2)_3SO_3R$ or the like, wherein R represents an alkali metal atom such as lithium, sodium, potassium, etc. Among these, sodium is particularly preferred as an alkali metal atom. This compound does not have a strong effect of making copper crystal fine when it is used alone. However, by using the compound in combination with other organic compound, copper crystal can be made fine and a plating surface having less unevenness can be obtained. Detailed action and mechanism thereof have not yet been clarified, but it is estimated that a molecule of the compound is reacted with a copper ion in a copper sulfate electrolyte to be converted into a complex, or the compound acts on a plating interface to elevate overvoltage, whereby copper crystal can be made fine and a plating surface having less unevenness can be formed.

One organic compound other than the compound having a mercapto group to be used in combination is a high molecular weight polysaccharide. The high molecular weight polysaccharide is a carbohydrate such as a starch, a cellulose and a vegetable rubber and generally becomes colloid in water. As a polysaccharide produced industrially and inexpensively, there may be mentioned edible starch, starch for industrial use and dextrin as a starch; water-soluble cellulose ether as disclosed in Japanese Provisional Patent Publication No. 182890/1990, i.e., sodium carboxymethyl cellulose and carboxymethylhydroxyethyl cellulose ether as a cellulose; and gum arabic and tragacanth gum as a vegetable rubber.

By using the above organic compound in combination with 3-mercapto 1-propanesulfonate, copper crystal can be made fine and a plating surface having less unevenness can be obtained. In addition to the action of making copper crystal fine, the organic compound has an action of preventing a produced copper foil from being fragile. The organic compound alleviates inner stress accumulated in the copper foil so that the organic compound not only prevents breaking and curling of the copper foil occurring when the copper foil is wound from a cathode drum, but also improves elongations at room temperature and high temperature.

The other organic compound to be used in combination of the present invention is a low molecular weight glue. The low molecular weight glue is a glue or gelatin a molecular weight of which is made small by decomposing a generally produced glue or gelatin with an enzyme, an acid or an alkali. The low molecular weight glue is commercially available as, for example, "PBF" (trade name) produced by Nippi Gelatin Co. in Japan and "PCRA" (trade name) produced by Peter-Cooper Co. in U.S.A. These commercially available products have weight average molecular weights (Mw) of 10,000 or less and are characterized in that jelly strength is extremely low due to the low molecular weights.

Common glue and gelatin have effects of preventing microporosity and controlling roughness of a matte side to improve a shape thereof, but they have a problem of lowering elongation characteristics. However, it has been found that by using a glue having a molecular weight which is smaller than those of commercially available common glue and gelatin, it is possible to obtain effects of preventing microporosity and controlling roughness of a matte side to improve a shape thereof without greatly impairing elongation and other characteristics.

When the high molecular weight polysaccharide and the low molecular weight glue are simultaneously added to 3-mercapto 1-propanesulfonate, elongation at high temperature is further improved and also it is possible to prevent microporosity and obtain a fine and uniform uneven surface as compared with the case of adding the high molecular weight polysaccharide or the low molecular weight glue alone.

An amount of 3-mercapto 1-propanesulfonate to be added to the electrolyte is preferably in the range of 0.05 to 5 ppm by weight, an amount of the high molecular weight polysaccharide of 0.1 to 15 ppm by weight, and an amount of the low molecular weight glue of 0.3 to 35 ppm by weight, respectively.

Further, in addition to the above organic additive, a chloride ion is added to the electrolyte. When no chloride ion exists in the electrolyte, the desired copper foil having a matte side which is low-profiled cannot be obtained. Its amount to be added may be several ppm by which the effects exhibit, but in order to produce a low-profiled copper foil in a broad current density range stably, it is preferred to keep the amount in a range of 10 to 60 ppm. Even when the amount exceeds 60 ppm, low profiling can be effected. However, the effect of low profiling is not increased significantly accompanied with increase in the amount, and when the amount is excessive, dendritic electrodeposition occurs or limiting current density is lowered. As the method of adding the chloride ion, hydrochloric acid or sodium chloride is dissolved in water and the aqueous solution is added to the electrolyte.

As described above, by adding 3-mercapto 1-propanesulfonate in combination of the high molecular weight polysaccharide and/or the low molecular weight glue and a minute amount of the chloride ion to the electrolyte, various characteristics required for a low-profiled copper foil for fine patterning can be realized at a high level.

Further, the surface roughness R_z at the matte side of the untreated copper foil of the present invention is the same or smaller than the surface roughness R_z at the shiny side of said untreated copper foil so that the surface treated copper foil after subjecting to bond enhancing treatment onto the matte side becomes more low-profiled one as compared with the conventional foil whereby it becomes a foil having a large etching factor.

EXAMPLES

In the following, the present invention is described in more detail by referring to Examples, but the present invention is not limited by these Examples.

Examples 1 to 4

(1) Foil preparation

Electrolytes having compositions shown in Table 1 (copper sulfate-sulfuric acid solutions before additives were added) were cleaned by passing them through activated carbon filters. Then, to the electrolytes were added sodium 3-mercapto 1-propanesulfonate, hydroxyethyl cellulose as a high molecular weight polysaccharide, a low molecular weight glue (molecular weight: 3,000) and a chloride ion so as to have concentrations shown in Table 1, respectively, whereby electrolytes for foil preparation were prepared. All of the concentrations of the chloride ion were adjusted to 30 ppm, but the present invention is not limited by this concentration. By using the electrolytes thus prepared and using a noble metal oxide-coated titanium electrode as an anode and a rotating drum made of titanium as a cathode, untreated

copper foils each having a thickness of 18 μm were prepared by electroforming preparation under electrolysis conditions shown in Table 1.

(2) Evaluation of matte side roughness and mechanical characteristics

With respect to the untreated copper foils of the respective Examples obtained in (1), surface roughnesses R_z and R_a were measured by using a surface roughness meter (SE-3C model produced by Kosaka Kenkyujo, Japan). Here, the surface roughnesses R_z and R_a are R_z and R_a defined in "Definitions and Designation of Surface Roughness" of JIS B 0601-1994. That is, R_z is a ten-point mean roughness expressed in micrometer (μm) which is the value of difference between the mean value of altitudes of peaks from the highest to the 5th, measured in the direction of vertical magnification from a straight line that is parallel to the mean line and that does not intersect the profile, and the mean value of altitudes of valleys from the deepest to the 5th, within a sampled portion, of which length corresponds to the reference length, from the profile, and R_a is a center-line mean roughness expressed in micrometer (μm) which is the value, when the roughness curve has been expressed by $y=f(x)$, obtained from the following formula, extracting a part of measuring length l in the direction of its center-line from the roughness curve, and taking the centerline of this extracted part as X-axis and the direction of vertical magnification as Y-axis.

$$R_a = \frac{1}{l}\int_0^l |f(x)|dx$$

Incidentally, a reference length: l is 2.5 mm when the matte side is measured and 0.8 mm when the shiny side is measured. Also, elongation after holding the copper foils for 5 minutes in the longitudinal direction at room temperature and a temperature of 180° C. and also tensile strength at the respective temperatures were measured by using a tensile tester (1122 model produced by Instron Co., England), respectively. The results are shown in Table 2.

Comparative Examples 1 and 2

With respective to copper foils prepared in the same manner as in Examples except for carrying out electrolysis by using electrolytes having compositions shown in Table 1 under electrolysis conditions shown in Table 1, matte side roughness and mechanical characteristics were evaluated. The results are shown in Table 2.

TABLE 1

Examples or Comparative examples	Electrolyte compositions and electrolysis conditions: Additives MPS (ppm)	HEC (ppm)	Glue (ppm)	Thio-urea (ppm)	Cl^- (ppm)	Electrolysis conditions: Current density (A/dm^2)	Temperature (°C.)
Example 1	1.5	10.0	—	—	30	50	58
Example 2	0.5	—	3.0	—			
Example 3	0.5	3.0	6.0	—			
Example 4	1.0	5.0	5.0	—			
Comparative example 1	—	—	1.5	0.4			
Comparative example 2	—	—	4.0	—			

Electrolyte is copper sulfate/sulfuric acid solution and the concentrations are 90 g/l of copper and 110 g/l of sulfuric acid.

MPS: Sodium 3-mercapto 1-propanesulfonate

HEC: Hydroxyethyl cellulose

Glue: The low molecular weight glue (molecular weight Mw: 3,000) was used in Examples 2 to 4 and common glue (molecular weight Mw: 60,000) was used in Comparative examples 1 and 2.

TABLE 2

	Surface roughness and mechanical characteristics of untreated copper foil							
	Matte side roughness (μm)		Shiny side roughness (μm)		Room temperature (25° C.)		High temperature (180° C.)	
	R_z	R_a	R_z	R_a	Tensile strength (kgf/mm²)	Elongation (%)	Tensile strength (kgf/mm²)	Elongation (%)
Example 1	1.3	0.30	2.0	0.40	37.2	18.1	18.6	26.7
Example 2	2.1	0.32	2.1	0.35	33.6	11.7	19.5	19.7
Example 3	1.1	0.20	1.8	0.35	35.3	19.8	19.0	24.6
Example 4	0.6	0.14	1.4	0.23	33.8	14.4	18.7	25.8
Comparative example 1	3.3	0.40	2.0	0.37	36.8	9.0	20.3	8.0
Comparative example 2	4.8	0.70	2.1	0.32	33.7	9.5	20.5	2.0

In Example 1 in which sodium 3- mercapto 1-propanesulfonate and hydroxyethyl cellulose were added and in Example 2 in which sodium 3-mercapto 1-propanesulfonate and the low molecular weight glue were added, matte side roughnesses (surface roughnesses at matte sides) are sufficiently small, and high temperature elongation characteristics are excellent.

In Examples 3 and 4 in which hydroxyethyl cellulose and the low molecular weight glue were added to sodium 3-mercapto 1-propanesulfonate, matte side roughnesses become smaller as compared with those of Examples 1 and 2.

To the contrary, in Comparative example 1 in which thiourea and glue were added, whereas the roughness of the matte side becomes small as compared with the conventional untreated copper foil, it is rougher than the untreated copper foil of the present invention and only an untreated copper foil having a matte side with a larger roughness than that of the shiny side is obtained. Also, in the case of the untreated copper foil, high temperature elongation is small.

In Comparative example 2, characteristics of an electrodeposited copper foil prepared by using common glue are shown for reference as Prior art copper foil example.

Next, bond enhancing treatment was carried out onto the matte sides of the untreated copper foils shown in Examples 1 to 4 and Comparative examples 1 and 2, respectively. Also, the same bond enhancing treatment was carried out onto the shiny side of the untreated copper foil shown in Comparative example 2. Bath composition and conditions for the treatment are as mentioned below. After the bond enhancing treatment, stain proofing was further carried out to the foil to prepare a treated copper foil. The surface roughness of the copper foil was measured by using a surface roughness meter (SE-3C model produced by Kosaka Kenkyujo, Japan). The results are shown in Table 3. In Table 3, Examples 1 to 4 and Comparative examples 1 and 2 each correspond to copper foils in which untreated copper foils of Examples 1 to 4 and Comparative examples 1 and 2 in Table 2 are subjected to bond enhancing treatment onto their matte sides, respectively, and Comparative example 3 in Table 3 is a foil in which the untreated copper foil of Comparative example 2 in Table 2 is subjected to bond enhancing treatment onto its shiny side.

1. Copper plating conditions of First layer

Bath composition	
Metal copper	20 g/l
Sulfuric acid	100 g/l
Bath temperature	25 °C.
Current density	30 A/dm²
Plating time	10 seconds

2. Copper plating conditions of Second layer

Bath composition	
Metal copper	60 g/l
Sulfuric acid	100 g/l
Bath temperature	60 °C.
Current density	15 A/dm²
Plating time	10 seconds

The resulting copper foils are each laminated to one surface of a glass epoxy resin FR-4 (trade name) substrate to prepare copper-clad laminated boards, respectively. Further, evaluation of etching property was carried out by the following "evaluation method".

Evaluation Method

Evaluation of the etching property was carried out by the following method. That is, after washing the surface of each copper-clad laminated board, a liquid resist was uniformly coated with a thickness of 5 μm on said surface and dried. Next, a circuit pattern for testing was placed on the resist and ultraviolet ray was irradiated with 200 mJ/cm² by using an exposure machine. The test pattern comprises ten parallel lines with a line width of 100 μm, a space width of 100 μm and a length of 5 cm. Immediately after irradiation, development, washing and drying were carried out.

Thus, to the respective copper-clad laminated boards in which a circuit was formed by the resist, etching was carried out by using an etching evaluation device. The etching evaluation device is to inject an etching solution to the vertically standing copper-clad laminated board sample from a right angle direction with a single nozzle. As the etching solution, a solution in which ferric chloride and hydrochloric acid were mixed ($FeCl_3$: 2 mole/l, HCl: 0.5

mole/l) was used. Etching was carried out at a solution temperature of 50° C., an injection pressure of 0.16 MPa, a solution flow amount of 1 l/min and a distance of the sample and the nozzle of 15 cm. An injection time was made 55 seconds. Immediately after injection, washing was carried out and the resist was removed by using acetone to obtain a printed circuit pattern.

To the resulting respective printed circuit patterns, an etching factor at a bottom width of 70 μm was measured. At the same time, peeling strength (peeling resistance) was also measured. The results are shown in Table 3.

TABLE 3

	Surface roughness and etching property after bond enhancing treatment			
Examples or Comparative examples	Roughness of bond enhancing treated surface (μm) R_z	R_a	Etching factor	Peeling strength* (kgf/cm)
Example 1	1.8	0.3	3.9	1.14
Example 2	2.2	0.5	3.8	1.17
Example 3	1.6	0.3	3.9	1.16
Example 4	1.1	0.3	4.1	1.13
Comparative example 1	3.7	0.5	3.2	1.06
Comparative example 2	7.3	1.1	2.3	1.64
Comparative example 3	4.6	0.7	3.5	1.13

*measured by using FR-4 substrate.

When a etching factor value is large, etching characteristics can be judged to be good. As can be seen from Table 3, the etching factors of Examples 1 to 4 are markedly larger than those of Comparative examples 1 to 3.

In Comparative examples 1 and 2, roughnesses of the matte sides of the untreated copper foils are large as compared with those of Examples 1 to 4 so that roughnesses after bond enhancing treatment are large whereby etching factors are not good. Incidentally, the roughness of the matte side of the untreated copper foil of Example 2 and that of the shiny side of the untreated copper foil of Comparative example 3 are substantially the same. However, although these foils are treated under the same conditions, the surface roughness after bond enhancing treatment of Example 2 is smaller than that of Comparative example 3 which is a conventional example. The reason of the above can be considered that, since the shiny side is a surface directly contacted with a titanium drum, a flaw in the drum is transferred as such and when the bond enhancing treatment is carried out thereon, roughened copper grains become likely rough and large and finally the surface roughness after the bond enhancing treatment becomes large. On the other hand, the matte side of the copper foil according to the present invention is extremely dense due to mirror surface-state electrodeposition, and when a bond enhancing treatment is carried out thereon, roughened copper grains become finer and the surface roughness after the bond enhancing treatment becomes finally smaller. This is more remarkable in Examples 1, 3 and 4 where each of the surface roughness of a matte side of the untreated copper foil is further small, whereby their roughnesses of the surfaces subjected to bond enhancing treatment become extremely small and etching factors thereof are large. The reason why the peeling strengths of Examples 1 to 4 are substantially the same as that of Comparative example 3 irrespective of having extremely small roughness of the treated surface can be considered that roughened copper grains become finer by the bond enhancing treatment so that the surface area becomes large whereby peeling strength becomes large in spite of small roughness.

Although the value of the etching factor of Comparative example 3 shows a value closer to that of Examples 1 to 4, it is inferior to Examples 1 to 4 in terms of the traces left behind at the time of etching because the roughness of the roughening treatment is larger in Comparative example 3 than it is in the case of Examples 1 to 4.

As described above, according to the present invention, low profiling of an electrodeposited copper foil can be realized easily, and also an electrodeposited copper foil having excellent elongations at room temperature and high temperature and also high tensile strength can be obtained. The electrodeposited copper foil thus obtained can be used suitably as an inner or outer layer copper foil for a high density printed-wiring board and further as an electrodeposited copper foil for a flexible substrate because of improvement in flexibility.

Further, as compared with a conventional untreated copper foil, both surfaces of the untreated copper foil obtained by the present invention are flat, whereby the foil obtained by the present invention can be used as an electrode for a secondary battery, a flat cable, a material for electric cable-covering and shielding material or the like.

We claim:

1. An electroplated copper foil formed by electrodeposition of copper onto a drum and which comprises a copper foil having a shiny side formed in contact with the drum and a matte side wherein, without surface treatment, said matte side has a surface roughness Rz measured by JIS B 0601-1994 substantially the same as or less than that of the shiny side formed as a result of the electrodeposition of the copper foil using an electrolyte containing 0.05 to 5 ppm by weight 3-mercapto 1-propanesulfonate; at least one organic compound selected from the group consisting of 0.1 to 15 ppm by weight of a polysaccharide which is a carbohydrate selected from the group consisting of starches, celluloses and vegetable rubbers, and 0.3 to 35 ppm by weight of a low molecular weight glue having a weight average molecular weight of 10,000 or less; and 10 to 60 ppm of a chloride ion.

2. The foil according to claim 1, wherein the 3-mercapto 1-propanesulfonate is sodium 3-mercapto 1-propanesulfonate.

3. The foil according to claim 1, wherein the organic compound is the polysaccharide.

4. The foil according to claim 1, wherein the organic compound is the low molecular weight glue having the weight average molecular weight of 10,000 or less.

5. The foil according to claim 1, wherein the organic compound is a mixture of the polysaccharide and the low molecular weight glue having a weight average molecular weight of 10,000 or less.

6. The foil according to claim 1, wherein the foil is subjected to a surface bond enhancing treatment.

7. The foil according to claim 6, wherein the surface bond enhancing treatment is carried out by electrodeposition.

8. A copper-clad laminated board comprising an electrodeposited copper foil according to claim 1.

9. A printed circuit board comprising an electrodeposited copper foil according to claim 1.

10. A secondary battery cell including a component comprising an electrodeposited copper foil according to claim 1.

11. An improved method for electrolytically producing a copper foil formed by electrodeposition of copper onto a

drum, the copper foil having a shiny side formed in contact with the drum and a matte side, the improvement wherein the method produces a copper foil wherein, without treatment, the matte side has a surface roughness Rz measured by JIS B 0601-1994 substantially the same as or less than that of the shiny side, said method comprising carrying out electrolysis with an electrolyte comprising 0.05 to 5 ppm by weight 3-mercapto 1-propanesulfonate; at least one organic compound selected from the group consisting of 0.1 to 15 ppm by weight of a polysaccharide which is a carbohydrate selected from the group consisting of starches, celluloses and vegetable rubbers, and 0.3 to 35 ppm by weight of a low molecular weight glue having a weight average molecular weight of 10,000 or less; and 10 to 60 ppm of a chloride ion.

12. The method according to claim 11, wherein the 3-mercapto 1-propanesulfonate is sodium 3-mercapto 1-propanesulfonate.

13. The method according to claim 11, wherein the organic compound is the polysaccharide.

14. The method according to claim 11, wherein the organic compound is the low molecular weight glue having the weight average molecular weight of 10,000 or less.

15. The method according to claim 11, wherein the organic compound is a mixture of the polysaccharide and the low molecular weight glue having a weight average molecular weight of 10,000 or less.

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(54)【発明の名称】電解銅箔

(57)【特許請求の範囲】
【請求項１】
メルカプト基を持つ化合物、塩化物イオン、並びに分子量１００００以下の低分子量膠及び高分子多糖類を添加した電解液を用いて電解製箔された電解銅箔であって、該電解銅箔は、析出面の表面粗度Ｒｚが２．１μｍ以下であり、かつ、光沢面の表面粗度Ｒｚと同じかそれより小さいことを特徴とする電解銅箔。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、ファインパターン化が可能な電解銅箔、すなわち高いエッチングファクターが得られる電解銅箔に関するものである。
【背景技術】
【０００２】
プリント回路用電解銅箔は、工業的には硫酸銅水溶液の電解液を、鉛や白金族を被覆したチタン電極などの不溶性電極と、これに対向して設けられたステンレスやチタン製の陰極回転ドラムの隙間に満たしてこれら電極に通電し、陰極回転ドラムの上に銅を析出させ、これを連続的に巻取る電解製箔装置により製造されている。
【０００３】
一般に銅イオンと硫酸イオンだけを含む水溶液を電解液として用いると、設備上混入が避けられないゴミや油類によって銅箔にピンホールやマイクロポロシティーが発生して実

用上重大な欠陥となったり、該銅箔の電解液と接する側の面（粗面）が持つ山谷の形状が崩れてしまい、後にこの銅箔を絶縁基板材料と接合する際に十分な強度が得られなかったり、該粗面の粗さが大きい場合には多層プリント配線板の層間絶縁抵抗や回路導電率が低下したり、基板材料に接合後のパターンエッチング時に基板への残銅現象あるいは回路部のアンダーカット現象を引き起し、回路基板として種々の性能を劣化させてしまうという問題を生じる。

【０００４】

このピンホール等の防止のため電解液に塩化物イオンを添加したり、電解液を活性炭等を含むフィルターに通してゴミや油類を除去している。またマイクロポロシティー防止及び粗面の山谷形状を整えるために、古くから膠を電解液に添加する事が行われており、膠以外にも種々の有機物や無機物を添加剤として用いることが提案されてきた。プリント配線板用電解銅箔の製造技術は銅塩を含む溶液に電極を設け、これに通電して、カソードに銅を析出させるという点から分かるように、めっき技術を基礎としており、プリント配線板用電解銅箔製造用の添加剤としては銅めっき用添加剤を転用できる場合が多い。

【０００５】

膠、チオ尿素、糖蜜などは古くから銅めっき用の光沢剤として知られており、このことから電解液にこれら添加剤を添加した場合にはいわゆる光沢作用、プリント配線板用電解銅箔に関しては粗面の粗さを小さくする効果の発現が期待でき、特許文献１（米国特許５，１７１，４１７号明細書）には、チオ尿素などの活性イオウを添加剤として用いた電解銅箔の製造方法が開示されている。しかしながら、プリント配線板用電解銅箔は、生産性の向上などを目的として、通常のめっきより高い電流密度で生産されている点や、近年プリント配線板用電解銅箔に要求される性能が著しく高度になったこと、特に伸びなどの機械的性能を損なうことなく、粗面の粗さを低く抑えた銅箔に対する要求が強くなったことなどから、これらめっき用の添加剤をそのままプリント配線板用電解銅箔の添加剤として使用しても満足できる特性が得られないのが現状である。

【０００６】

一方、近年、半導体、集積回路をはじめとした電子回路技術の発達はめざましく、当然のことながら、その部品の形成部あるいは搭載部であるプリント配線板においてもなお一層の技術革新が求められている。プリント配線板の高多層化、ファインパターン化の要求等がそれである。

【０００７】

これらの要求を満足させるためにプリント配線板用電解銅箔に求められる性能は、層間及びパターン間の絶縁性、エッチング時のアンダーカット防止のための粗面（析出面。以下、同様）のロープロファイル化（粗さの低下）及び熱応力によるクラック防止のための高温伸び特性の向上、さらにはプリント配線板の寸法安定性のための高い引張り強さが求められている。特にファインパターン化のための更なるロープロファイル化の要求が強い。

【０００８】

粗面のロープロファイル化は、例えば前述の様に膠やチオ尿素を多量に電解液に添加すれば達成されるが、反面、その添加量の増加に伴って常温伸び率、高温伸び率とも急激に低下してしまう。一方、添加剤を添加しない電解液から得られる銅箔は、常温伸び率、高温伸び率ともに非常に高いものになるが、粗面の形状が乱れ、粗さが大きくなったり、高い引張り強さを維持出来なくなり、さらにはこれら性能が安定したものを製造すると言った点では無理がある。電解電流密度を低く抑えた場合、高電流密度での電解箔に比べ、粗面の粗さは低くなり、伸び率や引張り強さも向上するが、生産性の低下は経済上好ましくない。

【０００９】

このように、近年のプリント配線板用電解銅箔に要求される、更なるロープロファイル化、良好な常温伸び率、高温伸び率及び高い引張り強さを実現することは容易ではない。

電解銅箔は、通常、前述した電解製箔装置により製箔された未処理銅箔に、表面処理装

置により密着性向上のための粗化処理、防錆処理を施して製造される。
このようにして製造される電解銅箔の機械的性能は未処理銅箔４の性能によって決定され、銅箔のエッチング特性、すなわちエッチング速度と均一溶解性も、この未処理銅箔の性能によって多くが決定される。

【００１０】

銅箔の性能でエッチング性に大きな影響のある要因は表面の粗さである。粗化処理を施して絶縁樹脂基板と接着する面の粗さの影響が大きい。銅箔の粗さに影響する要因には大きく分けて２つある。ひとつは未処理銅箔の表面粗さであり、もうひとつは粗化処理の粒状の銅の付き方である。元箔である未処理銅箔の表面粗さが粗いと粗化処理後の銅箔の粗さも粗くなる。また、一般的に粒状の銅の付着量が多いと粗化処理後の銅箔の粗さは粗くなる。粗化処理時の粒状の銅の付着量は処理時に流す電流により調節が可能であるが、未処理銅箔の表面粗さは、前述のドラム状のカソードに銅を析出させる時の電解条件、特に電解液に加える添加剤によって決まるところが大きい。

【００１１】

一般的には、未処理箔は光沢面と呼ぶドラムに接触していた側の面は比較的平滑であるが、逆の面である析出面は粗面となる。析出面を平滑化するために、過去幾つかの試みがなされている。例えば前述の特許文献１に開示された、チオ尿素などの活性イオウを添加剤として用いた電解銅箔の製造方法がそれである。しかし、この場合は従来の膠等の添加剤を用いた場合に比較して析出面は平滑化されるが、光沢面に比較すると未だ粗く、効果は完全ではない。

【００１２】

また、光沢面は比較的平滑であることから、特許文献２（特開平６－２７０３３１号公報）に開示されているように、光沢面側に粒状の銅を付着させ樹脂基板と接着させる試みもなされている。しかしこの場合は、回路のエッチング時に、通常の粗面側にドライフィルムやレジストを貼るが、表面の凹凸のためにこれらドライフィルムやレジストと銅箔との接着力が低くなり、剥離しやすくなるという欠点がある。

【００１３】

【特許文献１】　米国特許５，１７１，４１７号公報
【特許文献２】　特開平６－２７０３３１号公報

【発明の開示】

【発明が解決しようとする課題】

【００１４】

本発明はこのような従来技術の問題点を解消すべくなされたものであり、引き剥し強さを低下させることなく、高いエッチングファクターを持ち、配線パターンの根元に銅粒子が残ることなく、ファインパターンを達成できる銅箔であると共に大きな高温伸び率及び高い引張り強さを有する銅箔を提供するものである。

ここで、ファインパターン化の尺度は、エッチングしたときの形状から、一般的にエッチングファクターＦとして

Ｆ＝２Ｔ／（Ｗｂ－Ｗｔ）

Ｔは銅箔の厚さ、Ｗｂは基板との接着面の幅、Ｗｔは銅箔表面の幅

によって表すことができ、この値が大きいほど回路断面はシャープな形状となる。

【課題を解決するための手段】

【００１５】

本発明は、電解銅箔であって、未処理銅箔の析出面の表面粗度Ｒｚが２．１μｍ以下であり、かつ、光沢面の表面粗度Ｒｚと同じか、それより小さいことを特徴とする。
ここで、表面粗度Ｒｚとは、ＪＩＳ　Ｂ０６０１－１９９４「表面粗さの定義と表示」の５．１十点平均粗さ（Ｒｚ）の定義に規定されたＲｚをいう。

前記の未処理銅箔は、メルカプト基を持つ化合物並びにそれ以外の少なくとも１種以上の有機化合物及び塩化物イオンを添加した電解液を用いた電解製箔装置にて製造することができる。

【発明の効果】
【００１６】
本発明によれば、電解銅箔のロープロファイル化を容易に実現でき、しかも常温及び高温における伸び率が優れ、かつ高い引張り強さを有する電解銅箔を得ることができる。
【発明を実施するための最良の形態】
【００１７】
本発明は、未処理銅箔の析出面の表面粗度Ｒｚが２．１μｍ以下であり、かつ、光沢面の表面粗度Ｒｚと同じか、それより小さいことを特徴とする電解銅箔である。このような電解銅箔の製造につき、先ず説明する。
本発明電解銅箔を製造する電解浴に添加する添加剤のベースとなるのは、３－メルカプト１－プロパンスルホン酸塩である。３－メルカプト１－プロパンスルホン酸塩は、ＨＳ（CH_2）$_3$ SO_3 Ｎａ等で代表して示される化合物である。この化合物は、単独では銅の結晶を微細化する効果はそれほどないが、他の有機化合物と組み合わせて用いることにより、銅の結晶を微細化し、凹凸の少ないめっき表面を得ることができる。その詳しい作用機構は不明であるが、当該分子が硫酸銅電解液中の銅イオンと反応し、錯体となる事により、あるいはめっき界面に作用して過電圧を上昇させる事によって、銅の結晶を微細化し、凸凹の少ないめっき面の形成を可能ならしめるのではないかと推定される。
【００１８】
上記３－メルカプト１－プロパンスルホン酸塩と組み合わせる有機化合物の一つ目は、高分子多糖類である。高分子多糖類とは、デンプン、セルロース、植物ゴムなどの炭水化物であり、一般に水中でコロイドとなる。工業的に安価に製造されているものとして、デンプンでは食用デンプン、工業用デンプン、デキストリン、セルロースとしては特開平２－１８２８９０号公報に開示されているような水溶性セルロースエーテル、すなわち、カルボキシメチルセルロースナトリウム、カルボキシメチルヒドロキシエチルセルロースエーテルなどがある。植物ゴムとしてはアラビアゴムやトラカンドゴムがある。
これらの有機化合物は、３－メルカプト１－プロパンスルホン酸塩と組み合わせることにより、銅の結晶を微細化し、凹凸のないめっき面を得ることができるが、結晶の微細化に加えて、これらの有機化合物には、製造された銅箔の脆化を防止する働きがある。これらの有機化合物は銅箔に蓄積される内部応力を緩和するため、陰極ドラムから巻き取られる際の破れや銅箔が丸まってしまう現象を防止するばかりでなく、常温及び高温の伸び率も改善する。
【００１９】
本発明未処理銅箔を製造する電解液の組み合わせにかかるもう一つの有機化合物は、分子量１００００以下の低分子量膠である。低分子量膠とは一般に製造されている膠、ゼラチンを酵素や酸若しくはアルカリで分解し、その分子量を小さくしたものである。例えばニッピゼラチン社製の“ＰＢＦ”や米国Ｐｅｔｅｒ－Ｃｏｏｐｅｒ社製の“ＰＣＲＡ”として市販されている。これらの分子量は１万以下で、低分子量のためゼリー強度が著しく低いのが特徴である。
【００２０】
通常の膠やゼラチンは、マイクロポロシティーの防止や粗面の粗さを抑え、形状を整える効果があるが、伸び特性を低下させるという弊害がある。しかしながら通常の膠やゼラチンとして市販されているものよりも分子量の小さい膠を使用すれば、伸び特性などを大きく犠牲にせず、マイクロポロシティーの防止や粗面の粗さを抑え形状を整える効果がある。なお、３－メルカプト１－プロパンスルホン酸塩に高分子多糖類と低分子量膠を同時に加えると、それぞれを単独で加えるよりも、高温の伸び率が改善されるとともに、マイクロポロシティーの防止や細かで均一な凸凹面を得ることが可能である。
【００２１】
更に、上記の有機添加剤に加え塩化物イオンを電解液に添加する。電解液中に塩化物イオンがまったく存在しないと、所望される粗面がロープロファイル化された銅箔を得ることができないからである。その添加量としては、数ｐｐｍで効果が出てくるが、広い電流

密度範囲で安定してロープロファイル銅箔を製造するためには、１０～６０ｐｐｍの範囲に保つことが好ましい。６０ｐｐｍを越える添加量でもロープロファイル化されるが、添加量を増加したほどにはその効果に著しい増進が認められず、逆に添加量が過剰になると、樹枝状の電析が起こったり限界電流密度が低下するので好ましくない。

【００２２】

以上述べた通り、電解液に３－メルカプト１－プロパンスルホン酸塩と高分子多糖類及び／又は低分子量膠と微量の塩化物イオンを併用添加することにより、ファインパターン化のためのロープロファイル銅箔に求められる種々の特性を高いレベルで実現させることが可能となった。さらには、本発明による未処理銅箔の析出面の表面粗度Ｒｚは該未処理銅箔の光沢面の表面粗度Ｒｚと同程度か、それより小さい箔となるため、析出面上に粗化処理を施した後の表面処理銅箔は従来のものに比較して更にロープロファイルとなり、大きなエッチングファクターを持った銅箔となる。

【００２３】

以下に本発明を実施例に基づいて更に詳しく説明するが、本発明はこれらに限定されるものではない。

【００２４】

〔実施例１～４〕

（１）製箔

添加剤を添加する前の下記配合の硫酸銅－硫酸溶液

Ｃｕ　　９０ｇ／ｌ

H_2SO_4　　１１０ｇ／ｌ

を、活性炭フィルターに通して清浄処理した。次いで、この電解液に表１に示す配合割合で３－メルカプト１－プロパンスルホン酸ナトリウムと、高分子多糖類としてヒドロキシエチルセルロース及び低分子量膠（分子量３，０００）と、塩化物イオンをそれぞれ添加して製箔用電解液を調製した。このようにして調製した電解液を用い、アノードには貴金属酸化物被覆チタン電極、陰極にはチタン製回転ドラムを用いて表１に示す電解条件の下に、１８μｍ厚みの未処理銅箔を電解製箔によって製造した。

【００２５】

（２）粗面粗さ及び機械的特性の評価

上記（１）で得られた実施例１～４の未処理銅箔の表面粗さＲｚ、Ｒａを表面粗さ計（小坂研究所製ＳＥ－３Ｃ型）で測定した（ここで、表面粗さＲｚ、Ｒａとは、ＪＩＳ　Ｂ０６０１－１９９４「表面粗さの定義と表示」に規定されたＲｚ、Ｒａである。なお、基準長さ：ｌは、粗面測定時２．５ｍｍ、光沢面測定時０．８ｍである）。そして幅方向の常温で、及び１８０℃の温度における５分間保持後での伸び率、並びに各々の温度での引張り強さを引張り試験機（インストロン社製１１２２型）を用いて、それぞれ測定した。結果を表２に示す。

【００２６】

〔比較例１～２〕

表１に示す比較例１，２の組成の電解液及び電解条件の下に電解した以外、実施例と同様に製箔して得られた未処理銅箔の表面粗さ及び機械的特性を評価した。結果を表２に併記して示す。

【００２７】

[表１]

実施例又は比較例	添加剤					電解条件	
	MPS (PPM)	HEC (PPM)	膠 (PPM)	チオ尿素 (PPM)	Cl^- (PPM)	電流密度 (A/dm^2)	液温 (℃)
実施例１	１．５	１０．０	—	—	３０	５０	５８
実施例２	０．５	—	３．０	—			
実施例３	０．８	３．０	６．０	—			
実施例４	１．０	５．０	５．０	—			
比較例１	—	—	１．５	０．４			
比較例２	—	—	４．０	—			

ＭＰＳ；３－メルカプト１－プロパンスルホン酸ナトリウム
ＨＥＣ：ヒドロキシエチルセルロース

【００２８】

[表２]

実施例又は比較例	粗面粗さ（μm）		光沢面粗さ（μm）		常温		高温（１８０℃）	
	Ｒｚ	Ｒａ	Ｒｚ	Ｒａ	引張強さ kgf/mm^2	伸び %	引張強さ kgf/mm^2	伸び %
実施例１	１．３	０．３０	２．０	０．４０	３７．２	１８．１	１８．６	２６．７
実施例２	２．１	０．３２	２．１	０．３５	３３．６	１１．７	１９．５	１９．７
実施例３	１．１	０．２０	１．８	０．３５	３５．３	１９．８	１９．０	２４．６
実施例４	０．６	０．１４	１．４	０．３２	３３．８	１４．４	１８．７	２５．８
比較例１	３．３	０．４０	２．０	０．３７	３６．８	９．０	２０．３	８．０
比較例２	４．８	０．７０	２．１	０．３２	３３．７	９．５	２０．５	２．０

【００２９】

３－メルカプト１－プロパンスルホン酸ナトリウム及びヒドロキシエチルセルロースを添加した実施例１、３－メルカプト１－プロパンスルホン酸ナトリウム及び低分子量膠を添加した実施例２では、析出面の粗面粗さは充分に小さく、高温伸び特性が優れている。３－メルカプト１－プロパンスルホン酸ナトリウムにヒドロキシエチルセルロースと低分子量膠を添加した実施例３及び実施例４では、実施例２及び３に比較して更に析出面の粗さが小さくなっている。

【００３０】

これに対して、チオ尿素と通常膠を加えた比較例１では、従来の未処理銅箔に比較すると析出面の粗さは小さくなっているが本発明の未処理銅箔に比較すると粗く、光沢面に比較して大きな粗度の粗面を持つ未処理銅箔しか得ることができない。しかも、この未処理銅箔の場合、高温伸びが小さい。なお、比較例２には、従来の銅箔の例として通常膠を用いて製箔した未処理銅の性能を参考までに示した。

【００３１】

次いで、実施例１～４及び比較例１～２に示した未処理銅箔の析出面に粗化処理を行った。また比較例２に示した未処理箔には更に光沢面に同様な粗化処理を行った。粗化のための浴組成と条件は下記の通りである。粗化処理後、更に防錆処理を施して表面処理銅箔を製造した。この銅箔の表面粗さを表面粗さ計（小坂研究所製ＳＥ－３Ｃ型）で測定した。結果を表３に示した。なお、表３において、実施例１～４及び比較例１～２は、それぞれ表２の実施例１～４及び比較例１～２の未処理銅箔の粗面に粗化処理を行ったものであり、比較例３は表２の比較例２の未処理銅箔の光沢面に粗化処理を行ったものである。

【００３２】

１．第１層目の銅めっき条件

浴組成　金属銅　２０ｇ／ｌ
　　硫酸　１００ｇ／ｌ

浴温度　２５℃
電流密度　３０Ａ／ｄｍ^2
処理時間　１０秒

【００３３】
２．第２層目の銅めっき条件
浴組成　金属銅　６０ｇ／ｌ
硫酸　１００ｇ／ｌ
浴温度　６０℃
電流密度　１５Ａ／ｄｍ^2
処理時間　１０秒

【００３４】
得られた銅箔をガラスエポキシ樹脂ＦＲ－４基板の片面に熱融着して銅張積層板を作成した。更に、下記の「評価法」によりエッチング性の評価を行った。

【００３５】
評価法
エッチング特性の評価は次に示す方法で行った。
各銅張積層板表面を洗浄後、該表面に液レジストを５μｍの厚みで均一に塗布して乾燥した。次にレジストに試験用回路パターンを重ね、露光機を用いて２００ｍＪ／ｃｍ^{2}で紫外線照射した。テストパターンは線幅１００μｍ、線間１００μｍ、長さ５ｃｍの平行直線を１０本並べたものである。照射後直ちに現像し、水洗、乾燥した。

【００３６】
このように、レジストによる回路が形成された各銅張積層板のそれぞれに対し、エッチング評価装置によりエッチング性を評価した。エッチング評価装置は単ノズルで、垂直に立てた試料の銅張積層板に対して直角方向からエッチング液を噴射するものである。エッチング液には塩化第二鉄と塩酸を混合した液（$FeCl_3$：２ｍｏｌ／ｌ、ＨＣｌ：０．５ｍｏｌ／ｌ）を使用し、液温５０℃、噴射圧０．１６Ｍｐａ、液流量１ｌ／ｍｉｎ、試料とノズルの距離１５ｃｍにて行った。噴射時間は５５秒とした。噴射後直ちに水洗し、アセトンにてレジストを剥離してプリント回路パターンを得た。

【００３７】
得られた各々のプリント回路パターンに対し、ボトム幅７０μｍの時のエッチングファクターＦを測定した。また同時に引き剥し強さも測定した。その結果を表３に示す。エッチングファクターＦ値が大きいほどエッチング特性が良好と判断できる。実施例１～４は比較例１～３よりもエッチングファクターが格段に大きい。

【００３８】
比較例１～２は、実施例１～４に比し未処理銅箔の粗面の粗度が大きいため、粗化処理後の粗度も大きくエッチングファクターＦは良くない。これに対し実施例２の未処理銅箔の粗面と、比較例３の未処理銅箔の光沢面の粗度はほぼ等しい。しかし、同条件で処理したにもかかわらず粗化処理後の表面粗度は実施例２の方が小さく、従来例２の方が大きい。これは、光沢面の場合は、チタンドラムに接していた面であるため、ドラムの傷がそのまま転写されており、そのうえに粗化処理がなされると粗化の銅粒が粗大化しやすく最終的に粗化処理後の表面粗度は大きくなってしまう。一方、本発明による銅箔の粗面は鏡面状態の電析で非常に緻密であるため、その上に粗化処理がなされると粗化の銅粒が微細化し、最終的に粗化処理後の表面粗度は小さくなるものと思われる。これは未処理銅箔の粗面の表面粗度が更に小さい実施例１、実施例３及び実施例４の場合更に顕著になり、粗化処理面の粗さは非常に小さくなり、エッチングファクターＦも大きくなっている。粗化処理面の粗さが非常に小さいにもかかわらず比較例３と同程度の引き剥し強さとなるのは、粗化処理において粗化の銅粒が微細化する結果、表面積が大きくなり、粗さが小さいにもかかわらず引き剥し強さが大きくなると考えられる。なお、比較例３は、粗化処理面の粗さが実施例１～４のそれに比較して大きくなるため、エッチングファクターＦの値では比較例１～２のそれより実施例１～４のそれに近い値を示すが、エッチング時の足残りの点

で実施例１～４に比べて劣る。

【００３９】

［表３］

実施例又は比較例	粗化処理面粗さ（μｍ）		エッチングファクターＦ	引き剥がし強さ（ｋｇｆ／ｃｍ）
	Ｒｚ	Ｒａ		Ｒａ
実施例１	１．８	０．３	３．９	１．１４
実施例２	２．２	０．５	３．８	１．１７
実施例３	１．６	０．３	３．９	１．１６
実施例４	１．１	０．３	４．１	１．１３
比較例１	３．７	０．５	３．２	１．０６
比較例２	７．３	１．１	２．３	１．６４
比較例３	４．６	０．７	３．５	１．１３

【００４０】

上述の通り、本発明によれば、電解銅箔のロープロファイル化を容易に実現でき、しかも常温及び高温における伸び率が優れ、かつ高い引張り強さを有する電解銅箔を得ることができる。このようにして得られる電解銅箔は、高密度プリント配線板用の内外層銅箔に、更には耐折性の向上からフレキシブル基板用電解銅箔にも適用することができる。

また、従来の未処理銅箔に比し両面がフラットなため、本発明により得られる未処理銅箔は、二次電池用電極やフラットケーブル、電線被覆シールド材等にも使用することが可能である。

【産業上の利用可能性】

【００４１】

本発明は、電解銅箔を使用した銅張積層板並びにプリント配線板に適用可能である。

また、本発明の未処理銅箔は、従来に比べ両面がフラットなため、二次電池用電極やフラットケーブル、電線被覆シールド材等に適用可能である。

しかし、本発明による電解銅箔はこれらの用途に限られるものではない。

フロントページの続き

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(54) ELECTRODEPOSITED COPPER FOIL AND ELECTRODEPOSITED COPPER FOIL FOR SECONDARY BATTERY COLLECTOR

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(57) ABSTRACT

An electrodeposited copper foil having an extremely smooth surface roughness at the deposition surface, having an extremely fine crystal structure, and yet not having too high an ordinary temperature tensile strength, superior in elongation, maintaining a stable strength without softening by heat even after heat treatment, and having a high elongation rate even in a high temperature atmosphere. The electrodeposited copper foil has a surface roughness Rz at a deposition surface at ordinary temperature smaller than 2.5 μm in terms of 10-point average roughness Rz, has a minimum distance between peaks of a base foil peak of at least 5 μm, has an ordinary temperature tensile strength of not more than 40 kg/mm^2, and has a drop in ordinary temperature tensile strength after heat treatment at 130° C. for 15 hours of less than 15%. Also, copper foil for a secondary battery collector using that foil.

ELECTRODEPOSITED COPPER FOIL AND ELECTRODEPOSITED COPPER FOIL FOR SECONDARY BATTERY COLLECTOR

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to an electrodeposited copper foil having an extremely smooth surface roughness at the deposition surface, having an extremely fine crystal structure, and yet not having too high an ordinary temperature tensile strength, superior in elongation, maintaining a stable strength without softening by heat even after heat treatment, and having a high elongation rate even in a high temperature atmosphere and an electrodeposited copper foil for a collector of a secondary battery comprised of this foil.

[0003] Further, the present invention relates to an electrodeposited copper foil for a collector of a secondary battery which increases the charge/discharge cycle life and is resistant to damage even with overcharging.

[0004] 2. Description of the Related Art

[0005] In recent years, along with the reduction in size of mobile phones, video cameras, and other electronic devices, secondary batteries with high energy densities have become required. In particular, Li-ion batteries have superior properties such as high energy densities, superior charge/discharge cycle life, and light weight, so have come into wide use. The cathode collector of a Li-ion battery is generally made using copper foil. The collector is formed by coating the surface of the foil with carbon powder or other cathode active materials processed to a paste, drying this, then press flattening this by rolling etc. This is then rolled up together with a separator and aluminum foil coated with an anode active material to form the Li-ion battery.

[0006] As the copper foil used for the cathode collector, there are rolled copper foil obtained by rolling the copper and electrodeposited copper foil obtained by passing a current through a solution comprised mainly of copper sulfate to cause copper to deposit on a titanium or SUS rotating cathode and continuously peeling this off.

[0007] Up to now, the copper foil used for the cathode collector electrodes of Li-ion batteries has mainly been rolled copper foil. However, the rolled copper foil of a thickness of about 10 μm used for this is expensive. Further, it recrystallizes. Therefore, the tensile strength becomes extremely low. Accordingly, the handling ability in the step of coating and drying the carbon powder or other cathode active materials, then bonding the two by rolling becomes poor, wrinkles are easily caused, and sometimes the foil breaks. Further, the width of the copper foil produced by rolling is ordinarily about 60 cm. Therefore, there was also the defect of a poor efficiency at the time of production.

[0008] As opposed to this, electrodeposited copper foil has a larger tensile strength than rolled copper foil, which drops sharply in tensile strength upon recrystallization, so is superior in handling ability. Further, production of copper foil of a width of more than 100 cm is possible and productivity can be improved, so the foil is cheaper compared with rolled copper foil. Recently, there have been increased attempts to employ electrodeposited copper foil instead of rolled copper foil.

[0009] However, the deposition surface of a conventional electrodeposited copper foil features a columnar crystal structure. The surface roughness of the deposition surface of the electrodeposited copper foil is high, so it is learned that there are little contact portions with the carbon powder or other cathode active materials, the contact resistance is large, and the charge/discharge cycle life is short. Accordingly, an electrodeposited copper foil has been developed with a finer crystal structure and with a reduced surface roughness of the deposition surface on a par of that of a rolled copper foil. This has been put into use for Li-ion batteries.

[0010] As electrodeposited copper foils having fine crystal structures and surface roughnesses, there are the electrodeposited copper foils disclosed in Japanese Unexamined Patent Publication (Kokai) No. 7-188969, Japanese Unexamined Patent Publication (Kokai) No. 8-53789, and Japanese Unexamined Patent Publication (Kokai) No. 2000-182623. The electrodeposited copper foils disclosed there are reduced in the surface roughness of the deposition surfaces by controlling the various additives, electrolyte compositions, electrolyte temperatures, electrolyte flow rates, current densities, etc.

[0011] Two of the important properties in a secondary battery are the charge/discharge cycle life and the overcharge factor. Further improvement of these properties is sought. Regarding the charge/discharge cycle life, the stress etc. caused by expansion and contraction upon repeated charging and discharging causes the contact between the collector (copper foil) and active material to become poorer, part of the active material to become low electrically conductive and unable to be used for charging and discharging, and the capacity to deteriorate. Regarding the overcharge factor, it is required that splits or tears do not occur due to deterioration over time of the collector (copper foil) at the time of overcharging.

[0012] The electrodeposited copper foils having the finer crystal structures and lower surface roughnesses described in Japanese Unexamined Patent Publication (Kokai) No. 7-188969, Japanese Unexamined Patent Publication (Kokai) No. 8-53789, and Japanese Unexamined Patent Publication (Kokai) No. 2000-182623 are superior to the rolled copper foils of the past, but cannot be said to sufficiently meet the requirements of the market in terms of the charge/discharge cycle life and overcharge factor.

[0013] That is, the following conditions should be considered for electrodeposited copper foil for use as cathode collectors for Li-ion batteries:

[0014] 1. Surface smoothness: The surfaces of the electrodeposited copper foils disclosed in the above three publications have 10-point average roughnesses Rz smaller thau 2.5 μm, but if observing the surfaces by an electron microscope, fine crystal grainshaving an average particle size of several tenths of a micron are uniformly exposed and collect at the deposition surfaces, so the smoothness is not sufficient. Further, if these form base foil peak, the distance between peaks becomes several tenths of a micron the same as the grains. At such an uneven surface of an electrodeposited copper foil, the contact with the carbon powder or other cathode active materials is poor, therefore the capacity deteriorates and the charge/discharge cycle life drops. Note that the 10-point average roughness Rz is the value measured by a surface roughness meter based on JIS-B-0601.

[0015] 2. Ordinary temperature tensile strength: The electrodeposited copper foils disclosed in the above three publications all have ordinary tensile strengths of over 50 kg/mm^2 and therefore are extremely hard. In general, in a copper foil comprised of fine crystals with an average particle size of the crystal structure of several tenths of a micron and having an 10-point average roughness Rz of not more than 2.5 μm, the ordinary temperature tensile strength becomes extremely high and a hard foil results. Since the copper foil is hard, the copper foil does not sufficiently deform along with the active material surface in the rolling or other press flattening step performed after coating the active material, contact with the active material becomes poor, and deterioration of the capacity and a drop in the charge/discharge cycle life are caused. Note that in general the fact that the tensile strength and hardness are in a proportional relationship is known.

[0016] 3. Elongation rate at ordinary temperature: The elongation rates of the electrodeposited copper foils disclosed in the above three publications are all below 11%. Since the elongation rates are low in this way; stress is applied to the copper foils in the rolling or other press flattening step performed after coating the active material, the copper foils split, the capacities deteriorate, and the charge/discharge cycle lives drop.

[0017] 4. Nonrecrystallization: The electrodeposited copper foil described in Japanese Unexamined Patent Publication (Kokai) No. 2000-182623 recrystallizes at around 130° C. Therefore, in the same way as rolled copper foil, the tensile strength sharply drops due to softening under heat and stretching wrinkles or tears occur at the time of coating the active material and heating for drying. Further, splits arise along the interface of the recrystallized structure and cause a drop in capacity and a drop in the charge/discharge cycle life.

[0018] 5. Elongation rate in 180° C. high temperature atmosphere: The electrodeposited foil described in Example 2 of Japanese Unexamined Patent Publication (Kokai) No. 8-53789 has an elongation rate in a 180° C. high temperature atmosphere of 9.5% at a thickness of 35 μm. This is lower than an ordinary electrodeposited copper foil and further lower than the elongation rate at ordinary temperature. Therefore, in a test of the overcharge factor, the expansion stress due to the heat buildup at the time of overcharging cannot be withstood and defects such as splits occur in the copper foil. On the other hand, the electrodeposited copper foils described in Japanese Unexamined Patent Publication (Kokai) No. 7-188969 and Japanese Unexamined Patent Publication (Kokai) No. 2000-182623, which do not split in overcharge factor tests, have elongation rates in a high temperature atmosphere higher than the elongation rates at ordinary temperature.

SUMMARY OF THE INVENTION

[0019] An object of the present invention is to provide an electrodeposited copper foil with a low surface roughness and an electrodeposited copper foil suitable for the collector of a cathode of a secondary battery.

[0020] According to a first aspect of the present invention, there is provided an electrodeposited copper foil having a surface roughness at a deposition surface at ordinary temperature smaller than 2.5 μm in terms of 10-point average roughness Rz, having a minimum distance between peaks of a base foil peak of at least 5 μm, having an ordinary temperature tensile strength of not more than 40 kg/mm^2, and having a drop in ordinary temperature tensile strength after heat treatment at 130° C. for 15 hours of less than 15%.

[0021] Preferably, the electrodeposited copper foil does not soften under heat after the heat treatment.

[0022] More preferably, the elongation rate at ordinary temperature is at least 14% at a thickness of 35 μm and the elongation rate increases along with a rise in temperature in an atmosphere from ordinary temperature to 200° C.

[0023] According to a second aspect of the invention, there is provided an electrodeposited copper foil for a secondary battery collector using such a foil.

[0024] Preferably, the secondary battery is a Li-ion battery.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0025] The present inventors engaged in intensive studies to reduce the defects etc. of the electrodeposited copper foils disclosed in the above publications so as to obtain an electrodeposited copper foil with a low surface roughness and as a result discovered that the important properties of the copper foil affecting the charge/discharge cycle life and the overcharge factor are the surface smoothness, which cannot be expressed by the 10-point average roughness Rz, ordinary temperature tensile strength, elongation rate, nonrecrystallization, and elongation rate in a high temperature atmosphere and thereby succeeded in obtaining a copper foil with the highest effects in secondary battery characteristics.

[0026] The electrodeposited copper foil of the present invention has surface roughness at its deposition surface smaller than 2.5 μm in terms of 10-point average roughness Rz. Regardless of this, there is no exposure of fine crystal grains of an average particle sizes of several tenths of a micron at the deposition surface as with other electrodeposited copper foil with low surface roughnesses and the distance between peaks of the base foil peak is at least 5 μm, so the surface is extremely smooth. Therefore, contact between the active material and collector is good, the electroconductivity becomes greater, and the charge/discharge cycle life is superior.

[0027] Even if the 10-point average roughness Rz is low, if crystal grains of an average particle size of 0.1 μm or more are exposed at the surface and the collector surface becomes rough, the contact points between the carbon powder active materials and collector will become smaller and the contact resistance will become greater. If repeatedly charging and discharging a secondary battery prepared using this copper foil, the stress accompanying expansion and contraction etc. will cause the distance between the collector and the active material to gradually increase and result in part of the active material becoming electroconductive unusable for charging and discharging and in the end deterioration of the capacity.

[0028] Therefore, it is necessary not only that the surface roughness of the electrodeposited copper foil be less than 2.5 μm in terms of 10-point average roughness Rz, but also that no fine crystal grains of an average particle size of several tenths of a micron be exposed at the deposition surface and

that the distance between peaks of the rough surface be at least 5 μm. If the distance between peaks of the base foil peak is smaller than 5 μm, as explained above, the number of contact points with the cathode active material becomes smaller and a sufficient contact resistance can no longer be obtained.

[0029] Further, the electrodeposited copper foil according to the present invention has an ordinary temperature tensile strength of not more than 40 kg/mm^2 while has an extremely fine crystal structure, so the copper foil itself is soft.

[0030] In general, an electrode comprised of a flat collector formed on its surface with an electrode-forming substance layer is prepared by coating an electrode-forming substance containing an active material and binder on the surface of the collector, then pressing this by rolling etc. This pressing step has the action of compressing the electrode to a predetermined density and the action of bringing the active material particles closer to have suitable conductivity. The electrode after the pressing step has a small distance between active material particles and good contact between the active material and collector and a larger electroconductivity. Further, to obtain sufficient battery characteristics, it is important to make the distance between active material particles and between the active material and collector smaller and to have the collector deform in shape accordance with the shape of the active material surface. If the charge collector deforms in accordance with the active material surface, the contact between the active material and collector becomes better, the electroconductivity becomes further greater, and the charge/discharge cycle life is improved.

[0031] Therefore, the ordinary temperature tensile strength must not be more than 40 kg/mm^2. If the ordinary temperature tensile strength is more than 40 kg/mm^2, the softness of the copper foil itself is insufficient and the deformation of the copper foil along the active material surface in the processing for rolling or other press flattening performed after coating the active material does not sufficiently occur, so the contact with the active material becomes poor, the capacity deteriorates, and the charge/discharge cycle life drops and these are not preferable.

[0032] The electrodeposited copper foil according to the present invention preferably has an elongation rate at ordinary temperature of at least 14% at a thickness of 35 μm.

[0033] Further, the electrodeposited copper foil according to the present invention features a drop in the ordinary temperature tensile strength at the state St after heat treatment at 130° C. for 15 hours of less than 15% and does not recrystallize, so is superior in the charge/discharge cycle life and productivity.

[0034] Next, the present invention will be explained in more detail below with reference to examples and comparative examples, but of course the invention is not limited to these.

EXAMPLE 1

[0035] 7 ppm of low molecular weight gelatin having an average molecular weight of 3000, 3 ppm of hydroxyethyl cellulose, and 1 ppm of sodium 3-mercapto 1-propanesulfonate were added to a cupper sulfate electrolyte with sulfuric acid containing 280 g/liter of copper sulfate pentahydrate, 100 g/liter of sulfuric acid, and 35 ppm of chlorine ions. A foil was produced using this under conditions of an electrolyte temperature of 55° C., a flow rate of 0.3 m/min, and a current density of 50 A/dm^2. At this time, the electrolyte was passed through an activated carbon tower before entering the electrolysis tank and was brought to a boil after leaving the electrolysis tank after the end of the electrolysis, then was adjusted to the desired copper concentration, free sulfuric acid concentration, and chlorine ion concentration and provided again for electrolysis in a continuous cycle. Due to this, electrodeposited copper foils having a thickness of 35 μm for measurement of foil properties and having a thickness of 12 μm for use for a secondary battery electrode were produced.

[0036] The electrodeposited copper foil of the thickness of 35 μm obtained was used to test the characteristics of the foil for the items shown in Table 1. The results are shown in Table 1. The 10-point average roughness Rz was measured by an SE-3C type surface roughness meter made by Kosaka laboratory Co. based on JIS-B-0601. Further, the minimum distance between peaks Ds of the base foil peak was measured from a photograph taken at a magnification of X2000 by an electron microscope. The tensile strength and elongation rate at ordinary temperature, at 180° C. and 200° C. high temperature atmospheres, and after being returned to ordinary temperature after heat treatment at 150° C. for 15 hours were measured based on IPC-TM-650. In Table 1, the state when returned to ordinary temperature after heat treatment at 150° C. for 15 hours is indicated as "State St" Note that when the ordinary temperature tensile strength and elongation rate were measured right after production of the foil, strain from the time of electrolysis remained, so these appeared high in trend. Therefore, these properties were measured after leaving the foils standing at ordinary temperature for three days.

[0037] Further, the electrodeposited copper foil of the thickness of 12 μm was immersed in a 1 g/liter concentration CrO_3 aqueous solution for 5 seconds and chromating and then rinsed and dried. Note that here chromating was applied, but benzotriazole series treatment or silane coupling treatment may also be performed of course.

[0038] The thus obtained 12 μm thick electrodeposited copper foil was used to fabricate the chathode of a secondary battery in the following way. As the cathode active material, 90 wt % of a coke material powder obtained by sintering petroleum pitch, pulverizing the obtained coarse grain pitch coke to an average particle size of 20 μm, then sintering this in an inert gas at 1000° C. to remove impurities was mixed with 10 wt % of polyvinylidene fluoride as a binder to prepare a cathode composition. Next, this cathode composition was dispersed in a solvent of N-methyl 2-pyrrolidone to make a slurry which was coated and dried on the two surfaces of the electrodeposited copper foil which was then pressed by a roller press to a strip shape to obtain the cathode. This strip-shaped cathode had thicknesses of the cathode composition after forming of a same 90 μm on its two surfaces, a width of 55.6 mm, and a length of 551.5 mm. Next, the anode was prepared using $LiCoO_2$ as an anode active material, mixing 91 wt % of this, 6 wt % of graphite as a conductive agent, and 3 wt % of polyvinylidene fluoride as a binder to prepare an anode composition, then dispersing this in N-methyl 2-pyrrolidone to make a slurry.

[0039] Next, this slurry was uniformly coated and dried on the two surfaces of an anode collector comprised of 20 μm thick strip-shaped aluminum which was then pressed by a roller press to obtain a strip-shaped anode of 160 μm thickness. This strip-shaped anode had thicknesses of the anode composition after forming of 70 μm on its two surfaces, a width of 53.6 mm, and a length of 523.5 mm. The thus prepared strip-shaped anode and strip-shaped catahode were laminated with a separator having a thickness of 25 μm and a width of 58.1 mm comprised of microporous polypropylene film to form a multilayer electrode member. This multilayer electrode member was rolled up along the longitudinal direction with the cathode at the inside in a spiral manner into several layers. The endmost part of the outermost layer separator was secured by tape to obtain a spiral-shaped electrode member.

[0040] The thus formed hollow tube of this spiral-shaped electrode member had an inside diameter of 35 mm and an outside diameter of 17 mm. The thus prepared spiral-shaped electrode member was inserted into a steel battery case plated with nickel in a state with insulator plates above and below it, leads were attached, then 5.0 g of a nonaqueous electrolyte obtained by dissolving $LiPF_6$ at a ratio of 1 mole/liter into an equal volume mixed solvent of propylene carbonate and diethyl carbonate was injected and the assembly sealed to obtain a cylindrical Li-ion battery. This Li-ion battery was investigated as to its capacity retention rate R_B after 100 cycles and for the presence of breakage of the copper foil by disassembling the battery after overcharging by DC 2A for 40 minutes. The number of tears in the copper foil after this overcharging was expressed by N_B. The results are shown in Table 1.

EXAMPLE 2

[0041] 10 ppm of hydroxyethyl cellulose and 1 ppm of sodium 3-mercapto 1-propanesulfonate were added to a cupper sulfate electrolyte with sulfuric acid containing 280 g/liter of copper sulfate pentahydrate, 100 g/liter of sulfuric acid, and 50 ppm of chlorine ions. A foil was produced using this under conditions of an electrolyte temperature of 55° C., a flow rate of 0.5 m/min, and a current density of 50 A/dm^2. At this time, the electrolyte was passed through an activated carbon tower before entering the electrolysis tank and was brought to a boil after leaving the electrolysis tank after the end of the electrolysis, then was adjusted to the desired concentration and provided again for electrolysis in a continuous cycle. Due to this, electrodeposited copper foils having a thickness of 35 μm and 12 μm were produced and tested for characteristics in the same way as in Example 1. The results are shown in Table 1. The electrodeposited copper foil of the thickness of 12 μm was used to fabricate a Li-ion battery in the same way as in Example 1. In the same way as in Example 1, this was investigated as to its capacity retention rate R_B, after 100 cycles and for the presence of breakage of the copper foil by disassembling the battery after overcharging by DC 2A for 40 minutes. The results are shown in Table 1.

EXAMPLE 3

[0042] 10 ppm of low molecular weight gelatin having an average molecular weight of 3000, 3 ppm of hydroethyl cellulose, and 1 ppm of sodium 3-mercapto 1-propanesulfonate were added to a cupper sulfate electrolyte with sulfuric acid containing 280 q/liter of copper sulfate pentahydrate, 100 g/liter of sulfuric acid, and 50 ppm of chlorine ions. A foil was produced using this under conditions of an electrolyte temperature of 55° C., a flow rate of 0.3 m/min, and a current density of 50 A/dm^2. At this time, the electrolyte was passed through an activated carbon tower before entering the electrolysis tank and was brought to a boil after leaving the electrolysis tank after the end of the electrolysis, then was adjusted to the desired concentration and provided again for electrolysis in a continuous cycle. Further, the deposition surface of this electrodeposited copper foil was plated to give a copper gloss by adding 10 cc/liter of a makeup agent of Copperacid **210** made by Schering Co., 0.5 cc/liter of a gloss agent (A), and replenishing amounts of a gloss agent (B) to an electrolyte of 200 g/liter of copper sulfate pentahydrate, 60 g/liter of sulfuric acid, and 40 ppm of chlorine ions of a liquid temperature of 55° C. Due to this, electrodeposited copper foils having a thickness of 35 μm and 12 μm were produced and tested for characteristics in the same way as in Example 1. The results are shown in Table 1. The electrodeposited copper foil of the thickness of 12 μm was used to fabricate a Li-ion battery in the same way as in Example 1. In the same way as in Example 1. this was investigated as to its capacity retention rate R_B after 100 cycles and for the presence of breakage of the copper foil by disassembling the battery after overcharging by DC 2A for 40 minutes. The results are shown in Table 1.

Comparative Example 1

[0043] Electrodeposited copper foils having thicknesses of 35 μm and 12 μm were produced under the conditions of Example 1-A described in Japanese Unexamined Patent Publication (Kokai) No. 7-188969 and tested for properties in the same way as in Example 1. The results are shown in Table 1. Further, the 12 μm thickness copper foil was used to produce a Li-ion battery in the same way as in Example 1. In the same way as in Example 1, the capacity retention rate R_B after 100 cycles and the presence of breakage to the copper foil after disassembling the battery after overcharging by a direct current of 2A for 40 minutes were investigated. The results are shown in Table 1.

Comparative Example 2

[0044] Electrodeposited copper foils having thicknesses of 35 μm and 12 μm were produced under the conditions of Example 2 described in Japanese Unexamined Patent Publication (Kokai) No. 8-53789 and tested for properties in the same way as in Example 1. The results are shown in Table 1. Further, the 12 μm thickness copper foil was used to produce a Li-ion battery in the same way as in Example 1. In the same way as in Example 1, the capacity retention rate R_B after 100 cycles and the presence of breakage to the copper foil after disassembling the battery after overcharging by a direct current of 2A for 40 minutes were investigated. The results are shown in Table 1.

Comparative Example 3

[0045] Electrodeposited copper foils having thicknesses of 35 μm and 12 μm were produced under the conditions of Example 1 described in Japanese Unexamined Patent Publication (Kokai) No. 2000-182623 and tested for properties in the same way as in Example 1. The results are shown in Table 1. Further, the 12 μm thickness copper foil was used

to produce a Li-ion battery in the same way as in Example 1. In the same way as in Example 1, the capacity retention rate R_B after 100 cycles and the presence of breakage to the copper foil after disassembling the battery after overcharging by a direct current of 2A for 40 minutes were investigated. The results are shown in Table 1.

TABLE 1

		Minimum	Ordinary temperature				State St Tensile		Reduction		
	Roughness Rz (μm)	distance between peaks Ds (μm)	Tensile strength (A) (kg/mm^2)	Elongation rate (%)	180° C. elongation rate (%)	200° C. elongation rate (%)	strength (B) (kg/mm^2)	Elongation rate (%)	rate (1-B/A (%)	Retention rate R_B (%)	No. of tears N_B
Ex. 1	1.3	5.2	32	18	24	26	31	19	3.1	95	0
Ex. 2	2.1	5.0	38	14	18	21	37	15	2.6	91	0
Ex. 3	1.2	5.4	36	17	22	25	35	18	2.8	95	0
Comp. Ex. 1	2.0	0.8	67	8	23	24	65	8	3.0	71	0
Comp. Ex. 2	2.4	1.2	51	11	9	6	50	11	2.0	62	21
Comp. Ex. 3	1.6	0.5	56	7	26	23	23	26	59.0	78	0

[0046] In Examples 1 to 3, the electrodeposited copper foils of the present invention had 10-point average roughnesses Rz of not more than 2.5 μm and yet had minimum distances between peaks Ds of the base foil peak of at least 5 μm and had fine crystal structures at ordinary temperature yet had ordinary temperature tensile strengths of not more than 40 kg/mm^2 and ordinary temperature elongation rates of at least 14% at 35 μm thicknesses. Further, the drops in ordinary temperature tensile strengths at the state St after heat treatment at 130° C. for 15 hours were within 15%. The foils did not soften under heat and tended to rise in elongation rates along with the rise of temperature from ordinary temperature to a high temperature atmosphere of 200° C. The elongation rates in 180° C. atmosphere were at least 18% at 35 μm thicknesses. Due to these characteristics and explained as follows, the charge/discharge cycle life and overcharge factor were satisfied.

[0047] That is, the electrodeposited copper foil of the present invention did not have fine crystal grains of an average particle size of several tenths of a micron exposed at the deposition surface and therefore was extremely smooth, so exhibited good contact with the active material. Further, while the crystal structure was extremely fine, the ordinary temperature tensile strength was not too high, so the collector sufficiently deformed along with the active material and good contact between the active material and collector could be maintained. On top of this, the elongation rate at ordinary temperature was high, so it was possible to prevent splits in the copper foil in the rolling or other press flattening step performed after coating the active material. Further, the foil did not recrystallize, so it was superior in charge/discharge cycle life and had an elongation rate which was high in a high temperature atmosphere and increased along with the rise in temperature. Therefore, by employing this electrodeposited copper foil, it was possible to provide an electrodeposited copper foil for a secondary battery collector superior in overcharge factor.

[0048] Conventionally, rolled copper foil, which had been used as a copper foil for a secondary battery collector and a part of electrodeposited copper foil recrystallize at one hundred and several ten ° C. Therefore, when using as a collector, the tensile strength of them drop over time and expansion and contraction of active material accompanying charge/discharge causes split and breakage of collector copper foil, the capacities deteriorate, the charge/discharge cycle lives drop, and especially splits arise easily along the interface of the recrystallized structure.

[0049] Further, since tensile strength becomes extremely small after recrystallize. Accordingly, the handling ability in the step of coating and drying the cathode active material substance, wrinkles are easily caused, and sometimes the foil breaks. Therefore, it is needed for a copper foil for a secondary battery collector not to recrystallize. The electrodeposited copper foil of the present invention does not split and tear because it dose not recrystallize, has a long charge/discharge cycle life, and has a good handling ability. To satisfy the above conditions, the drops in ordinary temperature tensile strengths of the electrodeposited copper foil at the state St after heat treatment at 130° C. for 15 hours is decided to be within 15%.

[0050] If the above described elongation rate is low, stress is applied to the copper foils in the rolling or other press flattening step performed after coating the active material, the copper foils split, the capacities deteriorate, and the charge/discharge cycle lives drop. Therefore, it is preferable that the elongation rate at ordinary temperature of the electrodeposited copper foil is at least 14%.

[0051] Further, the electrodeposited copper foil of the present invention has an elongation rate increases in temperature in an atmosphere from ordinary temperature to 200° C. And the elongation rate in a 180° C. atmosphere is at least 18% at 35 μm thickness. Therefore, the copper foil of the present invention exhibits the properties of superior overcharge factor of the secondary battery.

[0052] On the other hand, comparative Example 1 showed a smooth foil having a 10-point average roughness Rz of 2.0

μm and a fine crystal structure, but having a minimum distance between peaks of the base foil peak of 0.8 μm. Therefore, there were few contact points with the carbon powder active materials and the contact resistance became large. The stress accompanying expansion and contraction during the charge/discharge cycle caused the distance between the collector and the active material to gradually increase and resulted in part of the active material becoming electroconductive unusable for charging and discharging and therefore deterioration of the capacity. Further, compared with the electrodeposited copper foils of Examples 1 to 3, the ordinary temperature tensile strength was high and the foil extremely hard and the ordinary temperature elongation rate also low. Therefore, the copper foil did not sufficiently deform along with the active material surface in the rolling or other press flattening step, contact with the active material was poor, splits occurred in part of the copper foil, the capacity deteriorated, and the charge/discharge cycle life dropped.

[0053] Comparative Example 2 is similar to Comparative Example 1, but has a further lower elongation rate in a high temperature atmosphere and a rate lower than the value at ordinary temperature as well. Therefore, in a test of the overcharge factor, the expansion stress due to the heat buildup at the time of overcharging cannot be withstood and tears occurred in the copper foil.

[0054] Comparative Example 3 is similar to Comparative Example 1, but when heat treated at 130° C. for 15 hours had an ordinary temperature tensile strength dropping down to 23 kg/mm^2 and recrystallized. Therefore, due to the expansion and contraction of the active material accompanying the charging and discharging, splits and tears occurred in the collector copper foil, the capacity dropped, and the charge/discharge cycle life fell.

[0055] Summarizing the effects of the invention, the electrodeposited copper foil of the present invention is extremely smooth with a low surface roughness at the deposition surface and has an extremely fine crystal structure, yet does not have too high an ordinary temperature tensile strength, is superior in elongation rate, maintains a stable strength without softening under heat even after heat treatment, is superior in elongation rate even in a high temperature atmosphere, and is therefore suitable for copper foil for a collector of a secondary battery. It exhibits the properties of a long charge/discharge cycle life of the secondary battery and superior overcharge factor as well and therefore has a superior industrial effect.

[0056] While the invention has been described with reference to specific embodiments chosen for purpose of illustration, it should be apparent that numerous modifications could be made thereto by those skilled in the art without departing from the basic concept and scope of the invention.

What is claimed is:

1. An electrodeposited copper foil having a surface roughness at a deposition surface at ordinary temperature smaller than 2.5 μm in terms of 10-point average roughness Rz, having a minimum distance between peaks of a base foil peak of at least 5 μm, having an ordinary temperature tensile strength of not more than 40 kg/mm^2, and having a drop in ordinary temperature tensile strength after heat treatment at 130° C. for 15 hours of less than 15%.

2. An electrodeposited copper foil as set forth in claim 1, which does not soften under heat after said heat treatment.

3. An electrodeposited copper foil as set forth in claim 2, wherein the elongation rate at ordinary temperature is at least 14% at a thickness of 35 μm and wherein the elongation rate increases along with a rise in temperature in an atmosphere from ordinary temperature to 200° C.

4. An electrodeposited copper foil for a secondary battery collector using a foil as set forth in any one of claims 1 to 3.

5. An electrodeposited copper foil for a secondary battery collector as set forth in claim 4, wherein said secondary battery is a Li-ion battery.

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(54)【発明の名称】電解銅箔および二次電池集電体用電解銅箔

(57)【特許請求の範囲】
【請求項１】
電解銅箔析出面の表面粗さが、常温での結晶組織が１０点平均粗さＲｚにして、２．５μｍより小さい微細結晶でありながら、素地山の最小ピーク間距離が５μｍ以上であり、常温抗張力が４０ｋｇ／ｍｍ^{2}以下であり、且つ１３０℃、１５時間熱処理後の常温抗張力の低下が１５％以内であり、熱軟化しないことを特徴とする二次電池集電体用電解銅箔。
【請求項２】
常温の伸び率が３５μｍ厚さにおいて１４％以上であり、常温から２００℃までの高温雰囲気中での伸び率が増大傾向を示すことを特徴とする請求項１記載の二次電池集電体用電解銅箔。
【請求項３】
前記の二次電池がリチウムイオン二次電池である請求項１又は２に記載の二次電池集電体用電解銅箔。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は電解銅箔析出面の表面粗さが非常に平滑であり、且つ結晶組織が非常に微細でありながら、常温抗張力が高すぎず、伸び率に優れ、熱処理後でも熱軟化せずに安定した強度を維持し、高温雰囲気中でも伸び率が高い電解銅箔と、この電解銅箔からなる二次電

池の集電体用電解銅箔に関するものである。

更に、充放電サイクルを長寿命化し、過充電時でも破断し難い二次電池の集電体用電解銅箔に関するものである。

【背景技術】

【０００２】

近年、携帯電話、ビデオカメラ等の電子機器の小型化に伴い、エネルギー密度の高い二次電池が要求されている。とりわけリチウムイオン二次電池はエネルギー密度が高く、充放電サイクル特性に優れ、且つ軽量という優れた特性を有するため、広く使われるようになってきている。リチウムイオン二次電池の負極集電体としては、一般に銅箔が使用されており、その表面にペースト状に加工された炭素粉等の負極活物質を塗布、乾燥した後、ロール圧延等でプレス平坦化して作製される。更にセパレート材と正極活物質を塗布したアルミ箔と共に巻き回されてリチウムイオン二次電池が製造されている。

【０００３】

負極集電体に使用する銅箔には圧延加工を施して箔状とした圧延銅箔と硫酸銅を主成分とする溶液を電解して、チタン或いはＳＵＳ製の回転する陰極上に銅を析出させ、これを連続的に引き剥がして製造する電解銅箔がある。

【０００４】

これまで、リチウムイオン二次電池の負極集電体電極用銅箔には、圧延銅箔を使用する場合が多かった。しかし、リチウムイオン二次電池の負極集電体電極用電極に使用される厚みが１０μｍ 前後の圧延銅箔は高価であり、しかも再結晶しているために、引張り強さが極端に小さくなるため炭素等の負極活物質を塗布、乾燥後ロール圧延等で圧着する製造工程でのハンドリング性が悪く、シワが発生しやすく、ときには、破断するケースがあった。また、圧延で製造される銅箔の幅は通常６０cm程度であり、製造時の能率が悪いといった欠点もあった。

【０００５】

これに対して、電解銅箔は、再結晶した極端に引張り強さが落ちた圧延銅箔に比べて引張り強さが大きいためハンドリング性に優れ、更に通常１００cm以上の幅の銅箔を製造することが可能であり、生産性を向上できることから、圧延銅箔に比較して安価であり最近は、圧延銅箔に代えて電解銅箔を採用しようとする試みが多くなってきている。

【０００６】

しかし、従来の電解銅箔の析出面は柱状の結晶組織であり、電解銅箔析出面の表面粗さが粗いため、炭素粉等の負極活物質との接触部分が少なく、接触抵抗が大きく、充放電サイクル寿命が短いことがわかったため、結晶組織を微細化し、電解銅箔析出面の表面粗さを圧延銅箔のように小さくした電解銅箔が開発され、リチウムイオン二次電池用として採用されてきている。

【０００７】

結晶組織を微細化し、電解銅箔析出面の表面粗さを小さくした電解銅箔としては、特許文献１、特許文献２、特許文献３に開示されている。これらに開示された電解銅箔の特性は各種添加剤、電解液組成、電解液温度、電解液流速、電流密度等を制御することによって電解銅箔析出面の表面粗さを小さくしている。

【特許文献１】特開平７－１８８９６９

【特許文献２】特開平８－５３７８９

【特許文献３】特開２０００－１８２６２３公報

【発明の開示】

【発明が解決しようとする課題】

【０００８】

ところで二次電池における重要な特性の一つに充放電サイクル寿命と過充電特性があり、更なる特性向上が求められている。充放電サイクル寿命とは充放電を繰り返すと膨張収縮によるストレスなどによって集電体（銅箔）と活物質との接触が悪くなり、一部の活物質が充放電に利用できない電気伝導度になって容量の劣化を引き起こすものである。過充

電特性とは、過充電が行われた際、集電体（銅箔）の経時的劣化による亀裂や破断が発生しないことを要求するものである。

【０００９】

結晶組織を微細化し、表面粗さを小さくした前記特許文献１、特許文献２、特許文献３の各公報に記載の電解銅箔は、これまでの圧延銅箔より優れてはいるが、充放電サイクル寿命、過充電特性の面で市場の要求に対して十分とはいえない状況にある。

【００１０】

即ち、リチウムイオン二次電池用負極電極集電体として使用される電解銅箔の条件を検討すると、

１．表面の平滑性について：前記３つの公報で開示されている電解銅箔の表面は、十点平均粗さＲｚは２．５μｍよりも小さいものの、電子顕微鏡でその表面を観察すると平均粒径は０．数μｍの微細な結晶粒子が電解銅箔析出面に均一に露出、密集しており、平滑性が十分ではない。そして、平均粒径０．数μｍの結晶粒子が表面に露出、密集しているので、それを素地山とすると、そのピーク間距離は粒径と同じ０．数μｍである。このように、凹凸のある電解銅箔の表面では、炭素粉等の負極活物質との接触が悪く、容量の劣化、充放電サイクル寿命の低下を招く。なお、十点平均粗さＲｚはＪＩＳ－Ｂ－０６０１に基づいて、表面粗さ計で測定した値である。

【００１１】

２．常温抗張力について：前記３つの公報で開示されている電解銅箔は全て５０ｋｇ／ｍｍ^{2}以上であり非常に硬い。一般に結晶組織の平均粒径が０．数μｍの微細結晶で、十点平均粗さＲｚが２．５μｍ以下の銅箔の場合、常温抗張力は非常に高く硬い箔になる。銅箔が硬いため、活物質塗布後に実施されるロール圧延等のプレス平坦化工程で活物質表面に合うような銅箔の変形が十分に起こらず、活物質との接触が悪く、容量の劣化、充放電サイクル寿命の低下を招く結果となる。なお、一般に、抗張力と硬さは比例関係にあることは周知である。

【００１２】

３．常温での伸び率について：前記３つの公報で開示されている電解銅箔の伸び率は全て１１％以下である。このように伸び率が低いため、活物質塗布後に実施されるロール圧延等のプレス平坦化工程で銅箔にストレスがかかり、銅箔に亀裂が入り、容量の劣化、充放電サイクルの低下を招く。

【００１３】

４．非再結晶性について：特許文献３に記載の電解銅箔は１３０℃くらいで再結晶する箔である。このため、圧延銅箔と同様に熱軟化により抗張力が極端に低下し、活物質塗布、加熱乾燥時の伸びシワや箔切れが発生する。また再結晶組織界面に沿って亀裂が入り、容量の低下、充放電サイクル寿命の低下を招く。

【００１４】

５．１８０℃高温雰囲気中の伸び率について：特許文献２の実施例２に記載の電解銅箔は１８０℃高温雰囲気中の伸び率が３５μｍ厚で９．５％であり、通常の電解銅箔よりも低く、更に常温での伸び率よりも低下する傾向にある。このため、過充電特性テストにおいて、過充電時の発熱による膨張ストレスに耐えられず、銅箔に亀裂が発生する欠陥がある。一方、過充電特性テストで銅箔に亀裂が入らなかった、特許文献１および特許文献３に記載の電解銅箔は高温雰囲気中での伸び率の方が常温での伸び率より高くなる傾向にある。

【００１５】

そこで本発明者らは表面粗さの小さい電解銅箔を提供することを目的として前記各公報で開示された電解銅箔の欠陥等を改良すべく鋭意検討を重ねた結果、充放電サイクル寿命および過充電特性に影響する銅箔の特性として十点平均粗さＲｚでは表せない表面の平滑性、常温抗張力、伸び率、非再結晶性、高温雰囲気中の伸び率が重要であることを見出し、二次電池特性において最も効果の高い銅箔を得ることに成功した。

【課題を解決するための手段】

【００１６】
本発明請求項１に係る二次電池集電体用電解銅箔は、電解銅箔析出面の表面粗さが、常温での結晶組織が１０点平均粗さＲｚにして、２．５μｍより小さい微細結晶でありながら、素地山の最小ピーク間距離が５μｍ以上であり、常温抗張力が４０ｋｇ／ｍｍ^{2}以下であり、且つ１３０℃、１５時間熱処理後の常温抗張力の低下が１５％以内であり、熱軟化しないことを特徴とするものである。
【００１７】
本発明請求項２に係る二次電池集電体用電解銅箔は、前記二次電池集電体用電解銅箔であって、その常温の伸び率が３５μｍ厚さにおいて１４％以上であり、常温から２００℃までの高温雰囲気中での伸び率が増大傾向を示すことを特徴とするものである。
【００１９】
本発明請求項３に係る二次電池集電体用電解銅箔は、前記の二次電池がリチウムイオン二次電池であることを特徴とするものである。
【００２０】
本発明電解銅箔は、電解銅箔析出面に平均粒径０．数μｍの微細な結晶粒子が露出しておらず、非常に平滑であるため、活物質との接触が良好になり、且つ結晶組織が非常に微細でありながら常温抗張力が高すぎないため、活物質に沿って集電体が十分に変形し、活物質と集電体との接触を良好に保つことができ、常温での伸び率が高いため、活物質塗布後に実施されるロール圧延等のプレス平坦化工程での銅箔の亀裂を防ぐことができ、更に、再結晶しないため、充放電サイクル寿命特性に優れると共に、高温雰囲気中での伸び率が高く、温度上昇と共に増大する。そのため、かかる電解銅箔を採用することにより過充電特性に優れた二次電池集電体用電解銅箔を提供することができる。
【００２１】
本発明に係る電解銅箔はその析出面の表面粗さが１０点平均粗さＲｚにして、２．５μｍより小さいながら、他の表面粗さが小さい電解銅箔のように析出面に平均粒径０．数μｍの微細な結晶粒子が露出しておらず、素地山のピーク間距離が５μｍ以上あり、非常に平滑であることから、活物質と集電体との接触性が良く、電気伝導度が大きくなって、充放電サイクル寿命に優れたものになる。
【００２２】
十点平均粗さＲｚが小さくても、平均粒径０．１μｍ以上の結晶粒子が表面に露出して、集電体表面に凹凸がある場合には、炭素粉である活物質と集電体の接触点が少なくなり接触抵抗が大きくなる。これに充放電を繰り返すと、膨張収縮に伴うストレス等により集電体と活物質との距離が徐々に大きくなり、一部の活物質が充放電に利用できない電気伝導度になって容量の劣化が起きる。
【００２３】
従って、電解銅箔析出面の表面粗さが１０点平均粗さＲｚにして２．５μｍより小さいだけでなく、析出面に平均粒径０．数μｍの微細な結晶粒子が露出しておらず、素地山のピーク間距離が５μｍ以上であることを要する。素地山のピーク間距離が５μｍよりも小さいと、前述したように負極活物質との接触点が少なくなり、充分な接触抵抗を得ることができないためである。
【００２４】
また、本発明に係る電解銅箔は、結晶組織が非常に微細でありながら常温抗張力が４０ｋｇ／ｍｍ^{2}以下であるため、銅箔自体が軟らかい。
【００２５】
一般的に、平面状集電体の表面に電極構成物質層が形成されてなる電極は、活物質とバインダーとを含有する電極構成物質層が集電体の表面に塗布され、その後ロール圧延等でプレスされて作製される。このプレス工程は、電極を所定の密度に圧縮する作用と、適切な導電性を有するように活物質粒子間を接近させる作用とを有する。プレス工程を経た電極は活物質粒子間、および活物質と集電体との接触性が良くなり、電気伝導度が大きくなる。更に、十分な電池特性を得るには、活物質粒子間、および活物質と集電体の距離を小

さくすると共に、集電体の形状が活物質表面の形状に合わせて変形することが重要である。活物質表面に沿って集電体が変形した場合には、活物質と集電体との接触性が更に良くなり、電気伝導度が更に大きくなり、充放電サイクル特性が向上する。

【００２６】

このためには、常温抗張力が４０ｋｇ／ｍｍ^{2}以下であることが必要で、常温抗張力が４０ｋｇ／ｍｍ^{2}を越えると銅箔自体の軟らかさが不足し、活物質塗布後に実施されるロール圧延等のプレス平坦化処理で活物質表面に沿った銅箔の変形が十分に起こらないため、活物質との接触が悪くなり、容量の劣化、充放電サイクル寿命が低下するため好ましくない。

【００２７】

また本発明に係る電解銅箔は、常温の伸び率が３５μｍ厚さにおいて１４％以上であることが望ましい。

【００２８】

また本発明に係る電解銅箔は１３０℃、１５時間熱処理後の常温抗張力の低下が１５％以内であり、再結晶しないため、充放電サイクル特性と生産性に優れることを特徴とする。

【００２９】

従来、二次電池の集電体用銅箔に使用されてきた圧延銅箔や、一部の電解銅箔は１００数十℃で再結晶するため、集電体にした場合、抗張力が経時的に低下し、充放電に伴う活物質の膨張収縮によって、集電体用銅箔に亀裂や破断が発生し、容量の低下、充放電サイクル寿命の低下を招き、特に再結晶組織界面に沿って亀裂が入りやすい。

【００３０】

また、再結晶後は抗張力が極端に小さくなるため負極活物質を塗布、乾燥後圧着する製造工程でのハンドリング性が悪く、シワが発生しやすく、ときには、破断するケースがあり、二次電池の集電体用銅箔は再結晶しないことが要求されていた。本発明電解銅箔は再結晶しないために亀裂や破断が発生せず、充放電サイクル寿命が長期にわたり、ハンドリング性も優れている。電解銅箔の１３０℃、１５時間熱処理後の常温抗張力の低下を１５％以内と規定したのはこれらの条件を満足するためである。

【００３１】

この伸び率が低いと、活物質塗布後に実施されるロール圧延等のプレス平坦化工程でストレスがかかり、銅箔に亀裂が入り、容量の劣化、充放電サイクルの低下を招く。従って、電解銅箔の常温伸び率は１４％以上であることが望ましい。

【００３２】

また、本発明に係る電解銅箔は、常温から２００℃までの高温雰囲気中での伸び率が増大傾向にあり、且つ１８０℃雰囲気中の伸び率が３５μｍ厚さにおいて１８％以上とすることにより、二次電池において過充電特性に優れたものとなり好ましい。

【発明の効果】

【００３３】

本発明の電解銅箔は電解銅箔析出面の表面粗さが非常に平滑であり、且つ結晶組織が非常に微細でありながら、常温抗張力が高すぎず、伸び率に優れ、熱処理後でも熱軟化せずに安定した強度を維持し、高温雰囲気中でも伸び率に優れ、二次電池の集電体用銅箔として好適であり、二次電池の充放電サイクルを長寿命化し、過充電特性に優れた特性を発揮するものであり、工業的に優れた効果を有するものである。

【発明を実施するための最良の形態】

【００３４】

以下に本発明の一実施形態と比較例を示す。なお、本発明はこれらの実施形態に限定されるものではない。

【００３５】

〔実施例１〕

硫酸銅五水和物２８０ｇ／ｌ、硫酸１００ｇ／ｌ、塩素イオン３５ｐｐｍを含む硫酸酸

性硫酸銅電解液に平均分子量３０００の低分子量ゼラチン７ｐｐｍ、ヒドロキシエチルセルロース３ｐｐｍ、３－メルカプト－１－プロパンスルホン酸ナトリウム１ｐｐｍを添加し、電解液温度５５℃、流速０．３ｍ/分、電流密度５０A/dm^{2}の条件で、電解銅箔を製箔した。この時電解液は、電解槽に入る前に活性炭処理塔を通り、電解が終了して電解槽から出た電解液を沸騰させる処理をした後、銅濃度、遊離の硫酸濃度、塩素イオン濃度を希望する濃度に調整して再度電解に供するサイクルとした。これによって箔特性測定用の厚さ３５μｍの電解銅箔と、二次電池電極用の厚さ１２μの電解銅箔を製箔した。

【００３６】

得られた厚さ３５μｍの電解銅箔を用いて箔の特性試験を表１の項目について実施した。その結果を表１に示す。表面粗さＲｚはＪＩＳ－Ｂ－０６０１に基づき、（株）小坂研究所製SE－３C型表面粗さ計で測定した。また、素地山のピーク間距離は電子顕微鏡で倍率２０００倍にて撮影した写真から測定した。常温および１８０℃と２００℃高温雰囲気中および、１５０℃で１５時間熱処理後の抗張力、伸び率はＩＰＣ－TM－６５０に基づいて測定した。なお、常温の抗張力、伸び率は、製箔直後に測定すると、電解時の歪が残っているので高く出る傾向があるため、常温で３日放置後に測定した。

また、１２μｍ厚の電解銅箔の方を１ｇ／ｌ濃度のCrO_3水溶液に５秒間浸漬して、クロメート処理を施し、水洗乾燥させた。なお、ここではクロメート処理を行ったが、ベンゾトリアゾール系処理、或いはシランカップリング剤処理を行ってもよいことは勿論である。

【００３７】

このようにして得られた１２μｍ厚の電解銅箔を用いて二次電池の負極を次のようにして作製した。負極活物質としては石油ピッチを焼成した粗粒状のピッチコークスを平均粒径２０μｍの粉末とし、不活性ガス中で１０００℃にて焼成して不純物を除去して得たコークス材料粉末９０重量部と、結着剤としてポリフッ化ビニリデンを１０重量部の割合で混合して負極合剤を調整した。次いで、この負極合剤を溶剤であるN－メチル２－ピロリドンに分散させてスラリーにし、電解銅箔の両面に塗布し、乾燥後ローラープレス機で圧縮成形し、帯状にして負極を得た。この帯状負極は成形後の負極合剤の膜厚が両面ともに９０μｍで同一であり、その幅は５５．６ｍｍ、長さは５５１．５ｍｍに形成した。次に正極は、$LiCoO_2$を正極活物質とし、それを９１重量％、導電材としてグラファイトを６重量％、結着剤としてポリフッ化ビニリデンを３重量％の割合で混合して正極合剤を作製し、これをN－メチル－２－ピロリドンに分散してスラリー状とした。

【００３８】

次にこのスラリーを厚み２０μｍの帯状のアルミニウムからなる正極集電体の両面に均一に塗布し、乾燥後ローラープレス機で圧縮成形して厚さ１６０μｍの帯状正極を得た。この帯状正極は成形後の正極合剤の膜厚が表面ともに７０μｍであり、その幅は５３．６ｍｍ、長さは５２３．５ｍｍに形成した。このようにして作製した帯状正極と帯状負極と厚さが２５μｍ、幅が５８．１ｍｍの微多孔性ポリプロピレンフィルムよりなるセパレータとを積層して積層電極体とした。この積層電極体は、その長さ方向に沿って負極を内側にして渦巻き型に多数回巻き回し、最外周セパレータの最終端部をテープで固定して渦巻き式電極体とした。

【００３９】

この渦巻き式電極体の中空部分は、その内径を３．５ｍｍ、外形を１７ｍｍに形成した。上述のように作製した渦巻き式電極体を、その上下に絶縁板を設置した状態で、ニッケルメッキが施された鉄製の電池缶に収納し、各リードを導出した後、プロピレンカーボネイトとジエチルカーボネイトとの等容量混合溶媒中に$LiPF_6$を１モル／１の割合で溶解した非水電解液５．０ｇを注入し、封をして円筒形リチウムイオン二次電池を作製した。このリチウムイオン二次電池について、１００サイクル後の容量維持率と、直流２Ａで４０分間過充電後の電池を解体し、銅箔の破れの有無を調べた。その結果を表１に示す。

【００４０】

〔実施例２〕

硫酸銅五水和物２８０ｇ／ｌ、硫酸１００ｇ／ｌ、塩素イオン５０ｐｐｍを含む硫酸酸性硫酸銅電解液にヒドロキシエチルセルロース１０ｐｐｍ、３－メルカプト－１－プロパンスルホン酸ナトリウム１ｐｐｍを添加し、電解液温度５５℃、流速０．５ｍ/分、電流密度５０Ａ／ｄｍ^{2}の条件で電解銅箔を製箔した。電解液は、電解槽に入る前に活性炭処理塔を通り、電解が終了して電解槽から出た電解液を沸騰させる処理をした後、希望する濃度に調整してまた電解に供するサイクルとした。これによって、厚さ３５μｍと１２μｍの電解銅箔を製箔し、実施例１と同じ特性試験を実施した。その結果を表１に示す。またこの厚さ１２μｍの銅箔を用いて実施例１と同様にリチウムイオン二次電池を製造し、実施例１と同様に１００サイクル後の容量維持率と、直流２Ａで４０分間過充電後の電池を解体し、銅箔の破れの有無を調べた。その結果を表１に示す。

【００４１】

〔実施例３〕

硫酸銅五水和物２８０ｇ／ｌ、硫酸１００ｇ／ｌ、塩素イオン５０ｐｐｍを含む硫酸酸性硫酸銅電解液に、平均分子量３０００の低分子量ゼラチン１０ｐｐｍ、ヒドロキシエチルセルロース３ｐｐｍ、３－メルカプト－１－プロパンスルホン酸ナトリウム１ｐｐｍを添加し、電解液温度５５℃、流速０．３ｍ／分、電流密度５０Ａ／ｄｍ^{2}の条件で電解銅箔を製箔した。この時電解液は、電解槽に入る前に活性炭処理塔を通り、電解が終了して電解槽から出た電解液を沸騰させる処理をした後、希望する濃度に調整してまた電解に供するサイクルとした。更にこの電解銅箔の電解析出面に、硫酸銅五水和物２００ｇ／ｌ、硫酸６０ｇ／ｌ、塩素イオン４０ｐｐｍ、液温５５℃の電解液に、日本シェーリング（株）製カパラシド２１０のメイキャップ剤１０ｃｃ／ｌ、光沢剤(A)０．５ｃｃ／ｌ、光沢剤(B)を随時補充し添加して、銅光沢めっきを施した。これによって、厚さ３５μｍと１２μｍの電解銅箔を製箔し、実施例１と同じ特性試験を実施した。その結果を表１に示す。またこの厚さ１２μｍの銅箔を用いて実施例１と同様にリチウムイオン二次電池を製造し、実施例１と同様に１００サイクル後の容量維持率と、直流２Ａで４０分間過充電後の電池を解体し、銅箔の破れの有無を調べた。その結果を表１に示す。

【００４２】

〔比較例１〕

特許文献１に記載の実施例１－Ａの条件で厚さ３５μｍと１２μｍの電解銅箔を製箔し、実施例１と同じ特性試験を実施した。その結果を表１に示す。またこの厚さ１２μｍの銅箔を用いて実施例１と同様にリチウムイオン二次電池を製造し、実施例１と同様に１００サイクル後の容量維持率と、直流２Ａで４０分間過充電後の電池を解体し、銅箔の破れの有無を調べた。その結果を表１に示す。

【００４３】

〔比較例２〕

特許文献２に記載の実施例２の条件で厚さ３５μｍと１２μｍの電解銅箔を製箔し、実施例１と同じ特性試験を実施した。その結果を表１に示す。またこの厚さ１２μｍの銅箔を用いて実施例１と同様にリチウムイオン二次電池を製造し、実施例１と同様に１００サイクル後の容量維持率と、直流２Ａで４０分間過充電後の電池を解体し、銅箔の破れの有無を調べた。その結果を表１に示す。

【００４４】

〔比較例３〕

特許文献３に記載の実施例１の条件で厚さ３５μｍと１２μｍの電解銅箔を製箔し、実施例１と同じ特性試験を実施した。その結果を表１に示す。またこの厚さ１２μｍの銅箔を用いて実施例１と同様にリチウムイオン二次電池を製造し、実施例１と同様に１００サイクル後の容量維持率と、直流２Ａで４０分間過充電後の電池を解体し、銅箔の破れの有無を調べた。その結果を表１に示す。

【００４５】

【表１】

	十点平均粗さ（微細結晶）Rz (μm)	素地山の最小ピーク間距離 (μm)	常温 抗張力(A) (kg/mm2)	常温 伸び率 (%)	180℃分間 気中伸び率 (%)	200℃分間 気中伸び率 (%)	130℃×15時間熱処理後常温 抗張力(B) (kg/mm2)	常温伸び率 (%)	常温抗張力の低下 (1−B／A) (%)	100サイクル後の容量維持率 (%)	過充電後の破孔数 (個)
実施例1	1.3	5.2	32	18	24	26	31	19	3.1	95	0
実施例2	2.1	5.0	38	14	18	21	37	15	2.6	91	0
実施例3	1.2	5.4	36	17	22	25	35	18	2.8	95	0
比較例1	2.0	0.8	67	8	23	24	65	8	3.0	71	0
比較例2	2.4	1.2	51	11	9	6	50	11	2.0	62	21
比較例3	1.6	0.5	56	7	26	23	23	26	59.0	78	0

【００４６】

実施例１から３において、本発明の電解銅箔は１０点平均粗さＲｚが２．５μｍ以下でありながら、素地山の最小ピーク間距離が５μｍ以上であり、常温での結晶組織が微細結晶でありながら、常温抗張力が４０ｋｇ／ｍｍ^{2}以下であり、常温の伸び率が３５μｍ厚

さにおいて１４％以上ある。更に１３０℃、１５時間熱処理後の常温抗張力の低下が１５％以内であり、熱軟化せず、常温から２００℃までの高温雰囲気中での伸び率が増大傾向にあり、且つ１８０℃雰囲気中の伸び率が、３５μｍ厚さにおいて１８％以上である。これらの特性によって、充放電サイクル寿命と過充電特性が満足するものとなっている。

【００４７】

一方、比較例１は１０点平均粗さＲｚは２．０μｍで平滑であり、微細結晶だが、素地山の最小ピーク間距離が０．８μｍであるため、炭素粉である活物質との接触点が少なく接触抵抗が大きくなり、充放電サイクル時の膨張収縮に伴うストレス等により集電体と活物質との距離が徐々に大きくなり、一部の活物質が充放電に利用できない電気伝導度になって容量の劣化が起きた。また、常温抗張力が高く、非常に硬い箔であり、常温伸び率も低いため、活物質塗布後に実施されるロール圧延等のプレス平坦化工程で活物質表面に沿った銅箔の変形が十分に起こらず、活物質との接触が悪く、銅箔に一部、亀裂が発生し、容量の劣化、充放電サイクル寿命の低下を招いていた。

【００４８】

比較例２は比較例１と同様であるが、更に高温雰囲気中の伸び率が低く、常温の値よりも低下する傾向にある。このため、過充電特性テストにおいて、過充電時の発熱による膨張ストレスに耐えられず、銅箔に破れが発生した。

【００４９】

比較例３は比較例１と同様であるが、１３０℃×１５時間熱処理すると常温抗張力が２３ｋｇ／ｍｍ^{2}まで低下し、再結晶した。このため充放電に伴う活物質の膨張収縮によって、集電体用銅箔に亀裂や破断が発生し、容量の低下、充放電サイクル寿命の低下を招いていた。

【産業上の利用可能性】

【００５０】

本発明電解銅箔は二次電池の集電体用箔としての用途の他に、配線用基板等の用途にも適用可能である。

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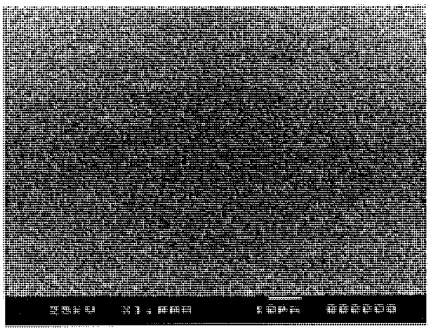
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(54)【発明の名称】低粗面電解銅箔及びその製造方法

(57)【要約】
【課題】プリント配線板用途やリチウム二次電池用負極集電体用途に実用できる低粗面を持つと共に前記疲労屈曲性にも優れた低粗面電解銅箔、具体的には、粗面粗さＲｚが２．０　μｍ以下で該粗面に凹凸のうねりがなく均一に低粗度化された粗面を持ち、且つ、１８０　℃における伸び率が１０．０％以上である低粗面電解銅箔を提供する。
【解決手段】硫酸－硫酸銅水溶液を電解液とし、白金属元素又はその酸化物元素で被覆したチタン板からなる不溶性陽極と該陽極に対向する陰極にチタン製ドラムを用い、当該両極間に直流電流を通じる電解銅箔の製造方法において、前記電解液にオキシエチレン系界面活性剤、ポリエチレンイミン又はその誘導体、活性有機イオウ化合物のスルフォン酸塩及び塩素イオンを存在させることによって粗面粗さＲｚが２．０　μｍ以下で該粗面に凹凸のうねりがなく均一に低粗度化された粗面を持ち、且つ、１８０　℃における伸び率が１０．０％以上である低粗面電解銅箔を得る。
【選択図】　図１



【特許請求の範囲】
【請求項１】
電解銅箔の粗面粗さＲｚが２．０　μｍ以下で該粗面に凹凸のうねりがなく均一に低粗度化された粗面を持ち、且つ、１８０　℃における伸び率が１０．０％以上であることを特徴とする低粗面電解銅箔。
【請求項２】
ＪＩＳＺ８７４１に基づきＧｓ（８５°）にて測定した粗面の鏡面光沢度が１００　以上である請求項１記載の低粗面電解銅箔。
【請求項３】
硫酸－硫酸銅水溶液を電解液とし、白金属元素又はその酸化物元素で被覆したチタン板からなる不溶性陽極と該陽極に対向する陰極にチタン製ドラムを用い、当該両極間に直流電流を通じる電解銅箔の製造方法において、前記電解液にオキシエチレン系界面活性剤、ポリエチレンイミン又はその誘導体、活性有機イオウ化合物のスルフォン酸塩及び塩素イオンを存在させることによって粗面粗さＲｚが２．０　μｍ以下で該粗面に凹凸のうねりがなく均一に低粗度化された粗面を持ち、且つ、１８０　℃における伸び率が１０．０％以上である低粗面電解銅箔を得ることを特徴とする低粗面電解銅箔の製造方法。
【請求項４】
低粗面電解銅箔におけるＪＩＳＺ８７４１に基づきＧｓ（８５°）にて測定した粗面の鏡面光沢度が１００　以上である請求項３記載の低粗面電解銅箔の製造方法。
【請求項５】
電解液中におけるオキシエチレン系界面活性剤の濃度が１０～２００　ｍｇ／Ｌである請求項３又は４記載の低粗面電解銅箔の製造方法。
【請求項６】
電解液中におけるポリエチレンイミン又はその誘導体の濃度が０．５　～３０．０ｍｇ／Ｌである請求項３又は４記載の低粗面電解銅箔の製造方法。
【請求項７】
電解液中における活性有機イオウ化合物のスルフォン酸塩の濃度が５．５　～４５０　μｍｏｌ／Ｌ　である請求項３又は４記載の低粗面電解銅箔の製造方法。
【請求項８】
電解液中における塩素イオンの濃度が２０～１２０ｍｇ／Ｌ　である請求項３又は４記載の低粗面電解銅箔の製造方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】
本発明は、低粗面電解銅箔及びその製造方法に関するものである。
【０００２】
【従来の技術】
周知のとおり、電解銅箔は、硫酸－硫酸銅水溶液を電解液とし、白金属元素又はその酸化物元素で被覆したチタン板からなる不溶性陽極と該陽極に対向する陰極にチタン製ドラムを用い、当該両極間に直流電流を通ずることによってチタン製ドラム表面に電解銅を析出させ、このときチタン製ドラムは一定速度で回転しており、析出した電解銅をドラム表面から引き剥がして連続的に巻き取るという方法によって製造されている。
【０００３】
なお、本発明においては、電解銅箔のドラム表面に接していた側の面を「光沢面」と指称し、逆の面を「粗面」と指称する。
【０００４】
前記の様にして電解銅箔は製造されているが、この電解銅箔は当業者間において「未処理銅箔」と呼ばれており、通常はこの未処理銅箔のままで使用されることはなく、印刷回路用電解銅箔の場合には、樹脂との接着性を向上させることを目的にした粗化処理工程や耐熱性、耐薬品性及び防錆力を付与することを目的にした各種表面処理工程を経て製品とさ

れている。
【０００５】
古くは、未処理電解銅箔の製造工程において電解液に１０～１００ｍｇ／Ｌ　の塩素イオンと０．１　～４．０ｍｇ／Ｌ　のにかわ又はゼラチンとを存在させることによって粗面側の山谷形状を先鋭化させる（粗くする）手段が採られているが、近年に到っては、電解銅箔の用途であるプリント配線板やリチウム二次電池用負極集電体には粗面側の粗度ができるだけ低く、光沢面と粗面との粗度差が小さく（光沢面は陰極ドラム表面の平滑な形状を写し取るので、光沢面と粗面との間には必然的に粗度差が生じる。）、しかも薄い電解銅箔が求められてきている。
【０００６】
これは、プリント配線板の場合には、ファインライン化やファインパターン化に伴う回路精度向上の観点からの要求からであり、また、リチウムイオン二次電池用負極集電体の場合には、光沢面と粗面との粗度差、換言すれば、表面積の差に基づく電池反応の差を考慮する必要が少なくなるという理由からである。
【０００７】
しかし、光沢面と粗面との粗度差を小さくし、しかも実用可能な機械的諸特性を満足させることは困難である。
【０００８】
従来、電解銅箔の製造方法において、電解液に各種水溶性高分子物質、各種界面活性剤、各種有機イオウ系化合物、塩素イオンなどを適宜選定して添加することによって光沢面と粗面との粗度差を小さくできることが知られており、例えば後出特許文献１には、電解液に低分子量水溶性セルロースエーテル、低分子量水溶性ポリアルキレングリコールエーテル、低分子量水溶性ポリエチレンイミン及び水溶性スルフォン化有機硫黄化合物を添加する場合には粗面側に約３．８　μｍ以下の高さの微細突端を持つ電解銅箔（未処理電解銅箔）が得られることが開示されており、例えば後出特許文献２には、電解液にセルロースエーテル、低分子量膠、メルカプト基を持つ化合物及び塩化物イオンを添加する場合には、粗面側の粗度が低くて光沢面と粗面との粗度差が小さく、しかも高い高温時伸び率を示す電解銅箔（未処理電解銅箔）が得られることが開示されている。
【０００９】
【特許文献１】
特表２００２－５０６４８４号公報
【特許文献２】
特許第３３１３２７７号公報
【００１０】
本発明者等は、硫酸－硫酸銅水溶液からなる電解液に特許文献１，２に記載されている各種水溶性高分子物質、各種有機イオウ系化合物、塩素イオンなどを適宜組み合せて添加し、電解銅箔を得る実験を数多く行ったところ、得られた電解銅箔の粗面側の粗度は低くできたが、当該粗面には緩やかな凹凸のうねり（後出図７参照）が生じていた。
【００１１】
電解銅箔（未処理銅箔）の粗面に生じている緩やかな凹凸のうねりは、前記粗化処理工程において銅結晶粒子の異常折出を誘起する要因となり、製品の粗面粗さ（Ｒｚ）を上昇させることになる。
【００１２】
また、フレキシブルプリント配線板用途では絶縁フイルムと接着させる工程で銅箔は熱履歴を受けるが、この熱履歴によって銅結晶粒子が小さい場合には該銅結晶粒子が粒成長して粗大化する。
【００１３】
【発明が解決しようとする課題】
そこで、本発明は、プリント配線板用途やリチウム二次電池用負極集電体用途に実用できる粗面に凹凸のうねりがなく均一に低粗度化された粗面を持つ低粗面電解銅箔、具体的に

は、粗面粗さＲｚが２．０　μｍ以下で該粗面に凹凸のうねりがなく均一に低粗度化された粗面を持ち、且つ、１８０　℃における伸び率が１０．０％以上である低粗面電解銅箔を提供することを技術的課題とする。

【００１４】

本発明者等は、前記課題を達成すべく鋭意検討を重ねた結果、硫酸－硫酸銅水溶液からなる電解液にポリオキシエチレン系界面活性剤、ポリエチレンイミンまたはその誘導体、活性有機イオウ化合物のスルフォン酸塩及び塩素イオンの４つの添加剤を存在させる場合には、粗面粗さＲｚが２．０　μｍ以下で該粗面に凹凸のうねりが実質的になく均一に低粗度化された粗面を持ち、且つ、１８０　℃における伸び率が１０．０％以上である低粗面電解銅箔が得られるという刮目すべき知見を得、当該課題を達成したのである。

【００１５】

【課題を解決するための手段】

すなわち、本発明は、電解銅箔の粗面粗さＲｚが２．０　μｍ以下で該粗面に凹凸のうねりがなく均一に低粗度化された粗面を持ち、且つ、１８０　℃における伸び率が１０．０％以上であることを特徴とする低粗面電解銅箔である。

【００１６】

また、本発明は、前記低粗面電解銅箔において、ＪＩＳＺ８７４１に基づきＧｓ（８５°）にて測定した粗面の鏡面光沢度が１００　以上のものである。

【００１７】

また、本発明は、硫酸－硫酸銅水溶液を電解液とし、白金属元素又はその酸化物元素で被覆したチタン板からなる不溶性陽極と該陽極に対向する陰極にチタン製ドラムを用い、当該両極間に直流電流を通じる電解銅箔の製造方法において、前記電解液にオキシエチレン系界面活性剤、ポリエチレンイミン又はその誘導体、活性有機イオウ化合物のスルフォン酸塩及び塩素イオンを存在させることによって粗面粗さＲｚが２．０　μｍ以下で該粗面に凹凸のうねりがなく均一に低粗度化された粗面を持ち、且つ、１８０　℃における伸び率が１０．０％以上である低粗面電解銅箔を得ることを特徴とする低粗面電解銅箔の製造方法である。

【００１８】

また、本発明は、前記低粗面電解銅箔の製造方法において、ＪＩＳＺ８７４１に基づきＧｓ（８５°）にて測定した粗面の鏡面光沢度が１００　以上である低粗面電解銅箔を得ることができるものである。

【００１９】

また、本発明は、電解液中におけるオキシエチレン系界面活性剤の濃度が１０～２００ｍｇ／Ｌである前記低粗面電解銅箔の製造方法である。

【００２０】

また、本発明は、電解液中におけるポリエチレンイミン又はその誘導体の濃度が０．５～３０．０ｍｇ／Ｌである前記低粗面電解銅箔の製造方法である。

【００２１】

また、本発明は、電解液中における活性有機イオウ化合物のスルフォン酸塩の濃度が５．５　～４５０　μｍｏｌ／Ｌ　である前記低粗面電解銅箔の製造方法である。

【００２２】

また、本発明は、電解液中における塩素イオンの濃度が２０～１２０ｍｇ／Ｌ　である前記低粗面電解銅箔の製造方法である。

【００２３】

本発明の構成を詳しく説明すれば、次のとおりである。

【００２４】

本発明において硫酸－硫酸銅水溶液からなる電解液中に添加する添加剤は、オキシエチレン系界面活性剤、ポリエチレンイミンまたはその誘導体、活性有機イオウのスルフォン酸塩及び塩素イオンの４つの添加剤であるが、これら添加剤が一定の濃度領域であって、しかも水溶性高分子群については一定の分子量域でのみ、目的とする低粗面電解銅箔を得る

ことが出来る。

【００２５】

先ず、本発明に用いるオキシエチレン系界面活性剤としては、ポリエチレングリコールであって平均分子量が２０００～３５０００　のものポリオキシエチレン・ポリオキシプロピレン共重合体であってオキシプロピレン部分の平均分子量が２０００～４０００で全分子量中のオキシエチレンの重量比が８０ｗｔ％以上のもの、ポリオキシエチレンラウリルエーテル、ポリオキシエチレンノニルフェニルエーテル、ビスフェノールＡ－エチレンオキサイド付加物などが挙げられる。なお、全分子量中のオキシエチレンの重量比が８０ｗｔ％以下のものは、硫酸－硫酸銅水溶液からなる電解液に溶解しない。

【００２６】

ポリエチレングリコールの平均分子量が２０００以下の場合には電解銅箔の表面に異常電着が起こる。

【００２７】

本発明においては、前記化合物の内の１種類又は２種類以上を組み合わせて、その単独もしくは合計の電解液中における濃度が１０～２００ｍｇ／Ｌ　となるように電解液に添加する。この濃度範囲の下限値は重要であり、ポリエチレンイミン及びその誘導体、活性有機イオウのスルフォン酸塩及び塩素イオンの三者が後述する各好適濃度範囲に調整されていても目的とする低粗面電解銅箔が得られない閾値を示している。これに対して上限値は下限域が示すような目的とする低粗面電解銅箔が得られるか、得られないかを分ける閾値では無く、工業的な操業条件下では経済的な観点からその濃度を高い値に保つことは何ら積極的価値を持たない。従って、ここで規定した上限値は得られる電解銅箔の特性を規定する為のものではなく、実際には上限域を超える領域でも目的とする低粗面電解銅箔を得ることは出来るが現実的ではない。

【００２８】

また、平均分子量の下限値も重要であり、平均分子量２０００に満たない場合には目的とする低粗面電解銅箔が得られない。一方、上限値は濃度範囲の上限値と同称のことが言え、例えば、平均分子量３５０００　を超えるポリエチレングリコールを用いても低粗面電解銅箔が得られる可能性が十分推察できる。

【００２９】

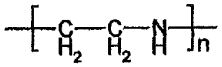
次に、オキシエチレン系界面活性剤、活性有機イオウ化合物及び塩素イオンを電解液中に添加することによって得られる電解銅箔の粗面には緩やかな凹凸のうねりが生じるが、ポリエチレンイミンを添加することによってこの様なうねりの発生を抑制することが出来る。

【００３０】

本発明に用いるポリエチレンイミンは、重量平均分子量が６００　以上のものが望ましく、１００００　以上のものがより望ましい。重量平均分子量が６００　以上のものであれば、化１に示す直線型、化２に示す分岐型のいずれを用いてもよく、両者の混合物を用いることもできる。

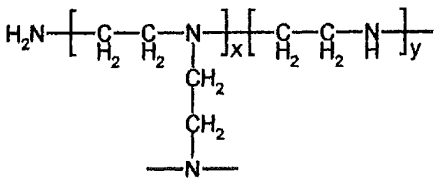
【００３１】

【化１】



【００３２】

【化２】

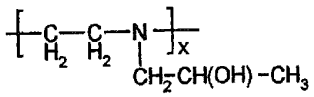


【００３３】
なお、市販品としては、例えば「エポミン：商品名・品番：Ｐ－１０００・日本触媒製・重量平均分子量：７００００　」が挙げられる。

【００３４】
ポリエチレンイミン誘導体としては、プロピレンオキサイド付加物であってその重量平均分子量が１０００以上のものが望ましく、プロピレンオキサイドが付加されるポリエチレンイミンの分子量は６００　以上であることが望ましい。

【００３５】
また、化３に示すようにポリエチレンイミンの第１級及び第２級アミン水素への置換基ができることが望ましい。

【００３６】
【化３】



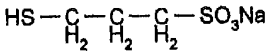
【００３７】
なお、市販品としては、例えば「エポミン：商品名・品番：ＰＰ－０６１・日本触媒製・重量平均分子量：１２００」が挙げられる。

【００３８】
ポリエチレンイミンの重量平均分子量が６００　未満の場合及び前記ポリエチレンイミン誘導体の重量平均分子量が１０００未満の場合には、その濃度によらず得られる電解銅箔の粗面には緩やかな凹凸のうねりが生じて光沢化（均一な低粗度化）しない。なお、粗面に緩やかな凹凸のうねりが生じておらず均一に低粗度化されている場合にはその外観は光沢を有しているが、粗面に緩やかな凹凸のうねりが生じ均一に低粗度化されていない場合にはその外観は半光沢乃至くすんだものとなる。

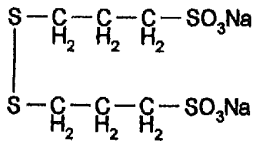
【００３９】
ポリエチレンイミン及びその誘導体の濃度領域と分子量の関係の一般的傾向として、分子量が高くなるに従い、粗面が半光沢から光沢へと変化し始める濃度閾値が上昇し、メッキ膜を形成せず粉状の銅析出となる「ヤケメッキ」領域へと変化し始める濃度もより高濃度側へと移行する。また、光沢領域内であってもポリエチレンイミンの濃度を上昇させて行くと高温時の伸び率の低下が生じるようになる。このようなポリエチレンイミン及びその誘導体の分子量とその濃度が与える影響を考慮した上で分子量と濃度の各範囲を定める必要があり、ポリエチレンイミン及びその誘導体の分子量は６００　～７００００　であることが望ましく、その電解液中における濃度は０．５　～３０．０ｍｇ／Ｌの範囲、好ましくは１．０　～１０．０ｍｇ／Ｌの範囲であることが望ましい。

【００４０】
ポリエチレンイミン及びその誘導体の電解液中における濃度が０．５ｍｇ／Ｌ　未満の場合には粗面はくすんだ外観を呈し、３０ｍｇ／Ｌを超えるとヤケメッキ領域へと移行し、もはや電解銅箔が得られることはない。

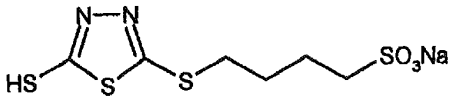
【００４１】
次に、本発明に用いる活性有機イオウ化合物は、水難溶性のアルキルチオールを可溶化した化合物であることが必須であるが、可溶化する為に水酸基またはカルボキシル基を付加した場合には目的とする低粗面電解銅箔を得ることは出来ない。従って、必ずスルフォン酸塩の形で可溶化する必要がある。本発明に好適な活性有機イオウ化合物のスルフォン酸塩の代表的な化合物は化４、化５、化６、化７に示すものである。
【００４２】
【化４】



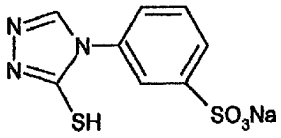
【００４３】
【化５】



【００４４】
【化６】



【００４５】
【化７】



【００４６】
これら化合物の添加量を質量濃度として表現することは適当では無い。これら化合物はその構造内に存在するチオール基によってその効果が決定されることに注目すれば、化４で示した３－メルカプト－１－　プロパンスルフォン酸の２分子会合形である化５の化合物は２つのチオール基が生成することになり、１分子でも３－メルカプト－１－　プロパンスルフォン酸ナトリウムの２倍の効果を示すことになるから、分子内に存在するチオール基のモル数によって規定できることになる。
【００４７】

そこで、チオール基の存在量をモル濃度で表現すれば、本発明における活性有機イオウ化合物の好ましい電解液への添加量（モル濃度）　は５．５　～４５０　μｍｏｌ／Ｌ　の範囲、好ましくは５５～１８０　μｍｏｌ／Ｌ　の範囲であることが望ましい。電解液中における濃度が５．５　μｍｏｌ／Ｌ　に満たない場合には、粗面に緩やかな凹凸のうねりが生じ均一に低粗度化せずにくすんだ外観を呈し光沢が生じない。しかも１８０　℃における伸び率も低い。添加量が４５０　μｍｏｌ／Ｌ　を越えても粗面状態や１８０　℃伸び率に影響はないが、電解液中の活性有機イオウ化合物の濃度を高く保つことは、不溶性陽極を使って電解銅箔を得る場合には、高いアノード電位の為に高価な有機イオウ系化合物を無駄に分解消耗することになるので現実的ではない。

【００４８】

次に、本発明においては、塩素イオンの存在が非常に重要であり、オキシエチレン系界面活性剤、ポリエチレンイミン又はその誘導体及び活性有機イオウ化合物のスルフォン酸塩の三者が前述した各好適濃度範囲に調整されていても目的とする低粗面電解銅箔を得ることは出来ない。塩素イオンが共存する時にのみ本発明の目的が達せられるのである。

【００４９】

また、塩素イオン濃度と活性有機イオウ化合物濃度との関係も重要であり、粗面が光沢外観（粗面に緩やかな凹凸のうねりが生じておらず均一に低粗度している状態）を呈する濃度領域は両者によってほぼ決定づけられ、この光沢範囲は塩素イオン濃度が上昇するに従い縮小する傾向にあり、活性有機イオウ化合物の濃度を低下させて操業する為にも塩素イオンの濃度を低く抑えることが望ましい。従って、電解液中における塩素イオン濃度は２０～１２０ｍｇ／Ｌ　の範囲、好ましくは３０～１００ｍｇ／Ｌ　の範囲であることが望ましい。塩素イオンの濃度が２０ｍｇ／Ｌに満たない場合には粗面が粗面粗さ２．０　μｍ以下にまで低粗度化しない。塩素イオンが１２０ｍｇ／Ｌ　をこえるとメッキ面にざらつきが生じる。

【００５０】

塩素イオンの供給源は、水溶液中で解離して塩素イオンを放出する無機塩類であれば良く、その代表例としてはＮａＣｌやＨＣｌ　などがあげられる。

【００５１】

本発明においては、前記オキシエチレン系界面活性剤、前記ポリエチレンイミン又はその誘導体、前記活性有機イオン化合物のスルフォン酸塩及び塩素イオンの４つの添加剤を、それぞれ前述の各好適濃度範囲に調整してなる硫酸－硫酸銅水溶液を電解液として用い、陽極には白金属酸化物被覆チタン板を陰極にはチタン製ドラムを使って、電解液温３５～５０℃及び電解電流密度３０～５０Ａ／ｄｍ^2　の条件で電解することによって、目的とする低粗面電解銅箔を得ることが出来る。

【００５２】

【発明の実施の形態】

硫酸（H_2SO_4）：１００ｇ／Ｌ、硫酸銅五水和物（$CuSO_4 \cdot 5H_2O$）：２８０ｇ／Ｌの硫酸－硫酸銅水溶液からなる電解液を調整した（以下、この電解液を「基本電解液」という）。

【００５３】

添加剤としてポリエチレングリコール（平均分子量２００００　・三洋化成製）、ポリエチレンイミン（エポミン：商品名・品番：Ｐ－１０００・日本触媒製・重量平均分子量：７００００　）、３－メルカプト－１－　プロパンスルフォン酸ナトリウム及び塩酸を基本電解液に添加してポリエチレングリコール：３０ｍｇ／Ｌ、ポリエチレンイミン：０．５ｍｇ／Ｌ　、３－メルカプト－１－　プロパンスルフォン酸ナトリウム：２２０　μｍｏｌ／Ｌ　及び塩素イオン：３５ｍｇ／Ｌに調整した。

【００５４】

この添加剤を含む電解液を陽極である白金属酸化物被覆チタン板と陰極であるチタン製ドラムとの間に流入させ、電解電流密度：４５Ａ／ｄｍ^2　、電解液温：４０℃、で電析して厚さ１８μｍの低粗面電解銅箔を得た。なお、目視観察により、この低粗面電解銅箔の

粗面が光沢を有していることが確認できた。

【００５５】

ここに得た低粗面電解銅箔（未処理電解銅箔）の室温（約２５℃）及び１８０　℃での抗張力（ＭＰａ　）と伸び率（％）をＩＰＣ－ＴＭ－６５０に基づき、インテスコ社製の２００１型引張力試験機を用いて測定すると共に、粗面の表面粗さ（Ｒｚ）をＪＩＳＢ０６０１に基づき、小坂研究所製のサーフコーダーＳＥ１７００αを用いて測定した。また、当該低粗面電解銅箔の粗面における凹凸のうねり度合いを表す指標として、粗面の鏡面光沢度をＪＩＳＺ８７４１に基づき、ミノルタ株式会社製の光沢計（商品名：マルチグロス２６８　型）を用い、Ｇｓ（８５°）にて低粗面電解銅箔の幅方向と長さ（流れ）方向の二方向について測定した。各測定結果を表２に示す。

【００５６】

なお、前記鏡面光沢度Ｇｓ（８５°）は、粗面に凹凸のうねりが実質的に生じていない場合には１００　以上の数値を示し、粗面に緩やかな凹凸のうねりが生じている場合には１００　未満の数値を示す（後出表２及び図１～７参照）。すなわち、前記鏡面光沢度Ｇｓ（８５°）の値を粗面における凹凸のうねり度合いの指標とすることができ、該値が小さくなるほど凹凸のうねり度合いは大きく、該値が大きくなるほど凹凸のうねり度合いは小さい。

【００５７】

図１は、ここに得た低粗面電解銅箔（未処理電解銅箔）の粗面を撮影した電子顕微鏡写真（倍率×１０００）であり、同図により、粗面には凹凸のうねりが実質的になく均一に低粗度化している粗面状態が確認できる。

【００５８】

【実施例】

【００５９】

実施例１～７，比較例１～９．

【００６０】

添加剤の種類と電解液中における濃度及び電解電流密度と電解液温を表１に示すとおりに変更した外は、前記発明の実施の形態と同じ条件で厚さ１８μｍの電解銅箔を得た。得られた各電解銅箔（未処理電解銅箔）の室温（約２５℃）及び１８０　℃での抗張力（ＭＰａ　）と伸び率（％）並びに表面粗さ（Ｒｚ）・（μｍ）、及び粗面における幅方向と長さ（流れ）方向の前記鏡面光沢度Ｇｓ（８５°）を前記発明の実施の形態と同じ測定法によって測定した結果を表２に示す。

【００６１】

【表１】

	添加剤濃度条件				電解条件	
	ポリエチレングリコール (M.W.20,000) (mg/L)	ポリエチレンイミン (mg/L)	3-メルカプト-1-プロパンスルホン酸ナトリウム(μmol/L)	塩素イオン濃度(mg/L)	電流密度 (A/dm²)	液温 (℃)
発明の実施の形態	30	0.5(1)	220	35	45	40
実施例1	30	10.0(1)	220	35	45	40
実施例2	100	30.0(2)	140	35	50	45
実施例3	70(6)	1.0(1)	140	35	50	40
実施例4	200	1.0(2)	330	70	30	35
実施例5	10	6.0(2)	220	100	45	40
実施例6	25	10.0(2)	220	110	45	50
実施例7	20	20.0(2)	6.0	20	50	50
比較例1	70(3)	0.1(1)	140	35	45	40
比較例2	100	0.1(1)	140	35	45	40
比較例3	10	1.0(4)	170	35	45	40
比較例4	50	35.0(5)	170	35	45	40
比較例5	50	35.0(1)	140	35	45	40
比較例6	50	0.3(1)	140	35	45	40
比較例7	25	0.2(1)	3.0	35	45	40
比較例8	25	0.2(1)	140	150	45	40
比較例9	25	0.2(1)	140	2	45	40

(1) 平均分子量 70000
(2) ポリエチレンイミン誘導体（エポミン：商品名・品番：ＰＰ－０６１・日本触媒製・重量平均分子量：1200）
(3) 平均分子量 1000
(4) 平均分子量 300
(5) 平均分子量 600

【００６２】
【表２】

	室温		180℃		表面粗さ (Rz)		粗面の鏡面光沢度 Gs(85°)	
	抗張力 (MPa)	伸び率 (%)	抗張力 (MPa)	伸び率 (%)	粗面 (μm)	光沢面 (μm)	幅方向	長さ方向 (流れ方向)
発明の実施の形態	350	16.0	230	14.0	1.8	2.2	121	128
実施例1	390	12.0	250	10.0	1.7	2.2	120	125
実施例2	500	15.0	280	12.0	1.7	2.1	122	125
実施例3	350	10.0	220	20.0	2.0	2.1	130	128
実施例4	340	18.0	180	15.0	1.2	2.2	125	126
実施例5	350	12.0	210	14.0	1.5	2.1	120	118
実施例6	360	11.0	210	10.0	1.5	2.2	131	135
実施例7	360	15.0	205	20.0	0.9	2.2	132	136
比較例1	350	5.0	200	6.0	2.5	2.2	78	73
比較例2	350	6.0	200	3.0	4.5	2.2	60	62
比較例3	360	20.0	250	24.0	3.0	2.2	74	74
比較例4	480	5.5	365	3.0	3.0	2.2	38	41
比較例5	430	4.5	305	2.8	1.8	2.1	40	42
比較例6	335	10.0	230	14.0	2.8	2.1	63	63
比較例7	350	10.0	220	3.0	4.0	2.1	21	18
比較例8	360	7.0	230	7.0	3.0	2.2	20	22
比較例9	350	6.0	210	5.0	3.2	2.2	26	25

【００６３】
図２～６は、各比較例で得た各電解銅箔（未処理電解銅箔）の粗面を撮影した電子顕微鏡写真（倍率×１０００）であり、図２は比較例１（ポリエチレングリコールの平均分子量が低くポリエチレンイミンの濃度が低い場合）の粗面状態を、図３は比較例３（ポリエチレンイミンの重量平均分子量が低い場合）の粗面状態を、図４は比較例４（ポリエチレングリコールの平均分子量が低くポリエチレンイミンの濃度が高い場合）の粗面状態を、図５は比較例６（ポリエチレンイミンの濃度が低い場合）の粗面状態を、図６は比較例７（３－メルカプト－１－　プロパンスルフォン酸ナトリウムの濃度が低い場合）の粗面状態を、それぞれ示している。
【００６４】
図７は、ポリエチレンイミンを添加しなかった外は、前記発明の実施の形態と同じ条件で得た厚さ１８μｍの電解銅箔（未処理電解銅箔）の粗面を撮影した電子顕微鏡写真（倍率×１０００）であり、粗面に緩やかな凹凸のうねりが生じている状態が確認できる。なお、図７と前記発明の実施の形態における図１とを対比すれば、ポリエチレンイミンの添加によって粗面に緩やかな凹凸のうねりが生じず表面粗さが顕著に低下することが確認できる。
【００６５】
また、表１及び表２から、前記発明の実施の形態並びに実施例１～７の各電解液において

は、ポリエチレンイミンの濃度が増すに従って室温での抗張力が増加するが粗面粗さ（Ｒｚ）はほぼ一定の値を維持していることが確認できる。

【００６６】

なお、本発明者らは、数多くの実験によって基本電解液中に、ポリエチレングリコールが存在しない場合には粗面が光沢外観を呈さず、ポリエチレンイミンが存在しない場合には粗面が粗くてくすんだ外観を呈し、１８０　℃での伸び率が低く、３－メルカプト－１－プロパンスルフォン酸ナトリウムが存在しない場合には粗面が非常に粗く、１８０　℃での伸び率が低く、塩素イオンが存在しない場合には電着面（メッキ面）が割れ、１８０　℃の伸び率が低いことを確認している。

【００６７】

また、水溶性高分子の濃度や平均分子量を前記所定範囲内で増加させた場合には、これに伴って前記鏡面光沢度Ｇｓ（８５°）が増す傾向にあることを確認している。なお、前記鏡面光沢度Ｇｓ（８５°）が１００　以上の低粗面電解銅箔を得るには、基本電解液中にポリエチレングリコール、３－メルカプト－１－　プロパンスルフォン酸ナトリウム、ポリエチレンイミン及び塩素イオンを存在させることが好適であるが、これらの内いずれか一つの物質でも欠落したり、濃度又は平均分子量が前記所定範囲外になった場合には前記鏡面光沢度（８５°）が１００　未満になる。

【００６８】

【発明の効果】

本発明によれば、プリント配線板用途や二次電池用負極集電体用途に最適の粗面粗さＲｚが２．０　μｍ以下で該粗面に凹凸のうねりが実質的になく前記鏡面光沢度Ｇｓ（８５°）が１００　以上の均一に低粗度化された粗面を持ち、且つ、１８０　℃における伸び率が１０．０％以上であり、光沢面と粗面との間の粗度差が可及的に小さい低粗面電解銅箔（未処理電解銅箔）を提供することができる。

【００６９】

従って、本発明の作業利用性は非常に高いといえる。

【図面の簡単な説明】

【図１】発明の実施の形態で得た電解銅箔（未処理電解銅箔）の粗面を撮影した電子顕微鏡写真（倍率×１０００）である。

【図２】比較例１で得た電解銅箔（未処理電解銅箔）の粗面を撮影した電子顕微鏡写真（倍率×１０００）である。

【図３】比較例３で得た電解銅箔（未処理電解銅箔）の粗面を撮影した電子顕微鏡写真（倍率×１０００）である。

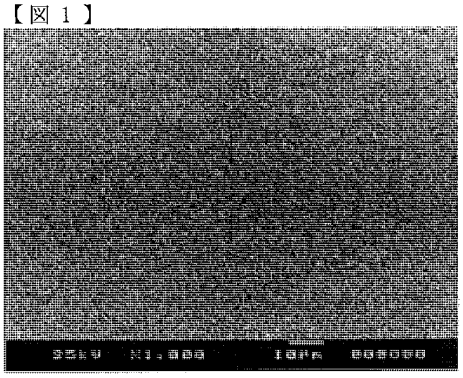
【図４】比較例４で得た電解銅箔（未処理電解銅箔）の粗面を撮影した電子顕微鏡写真（倍率×１０００）である。

【図５】比較例６で得た電解銅箔（未処理電解銅箔）の粗面を撮影した電子顕微鏡写真（倍率×１０００）である。

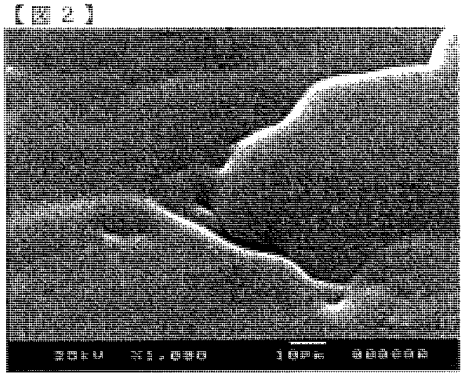
【図６】比較例７で得た電解銅箔（未処理電解銅箔）の粗面を撮影した電子顕微鏡写真（倍率×１０００）である。

【図７】ポリエチレンイミンを添加しない電解液を用いて得た電解銅箔（未処理電解銅箔）の粗面を撮影した電子顕微鏡写真（倍率×１０００）である。

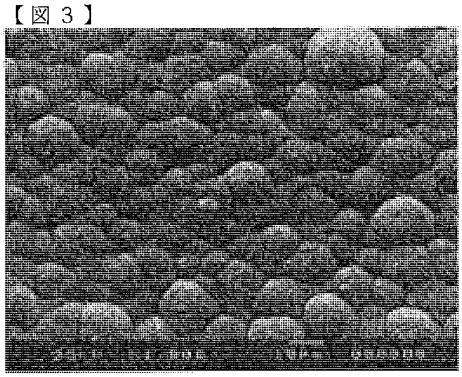
【図１】



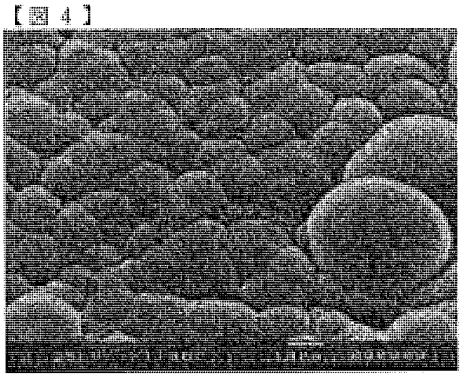
【図２】



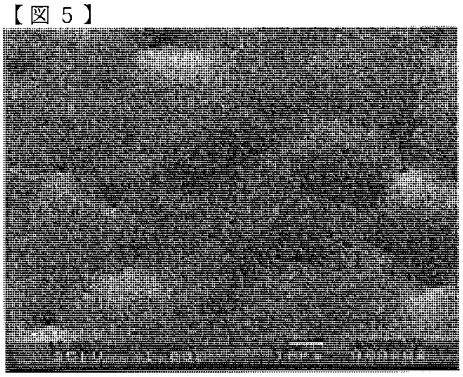
【図３】



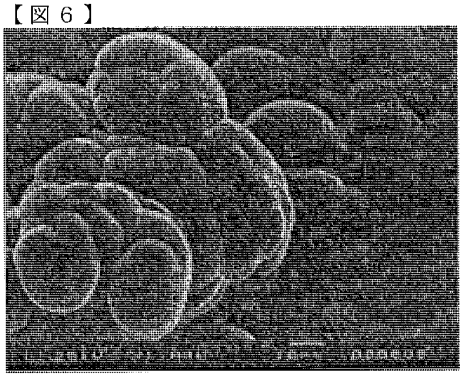
【図４】



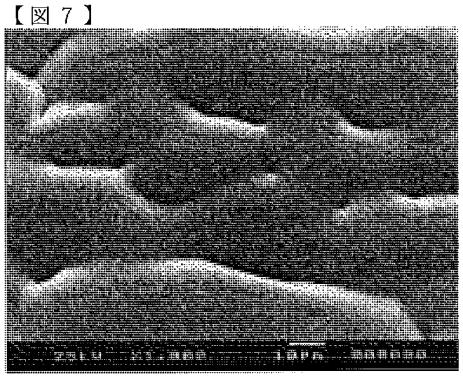
【図５】



【図６】



【図７】



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(54) **COPPER ELECTROLYTE COMPRISING AMINE COMPOUND HAVING SPECIFIC SKELETON AND ORGANIC SULFUR COMPOUND AND ELECTROLYTIC COPPER FOIL PREPARED USING THE SAME**

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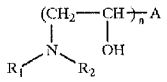
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(57) **ABSTRACT**

The invention has an object to obtain a low-profile electrolytic copper foil made by electrolytic copper foil manufacturing using a cathode drum such that the surface roughness on the rough surface side (the opposite side to the lustrous surface) is low. And in particular, the invention has an object to obtain an electrolytic copper foil that can be finely patterned and has excellent elongation and tensile strength at normal and high temperatures. This object is attained by using a copper electrolytic solution containing, as additives, an organosulfur compound, and an amine compound having a specific skeleton represented by undermentioned general formula (1) obtained by additively reacting an amine compound and a componnd having one or more epoxy groups in a molecule thereof to an addition reaction.

(1)



(In general formula (1), R_1 and R_2 are each selected from a group consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups, A represents an epoxy compound residue, and n represents an integer greater than or equal to 1.)

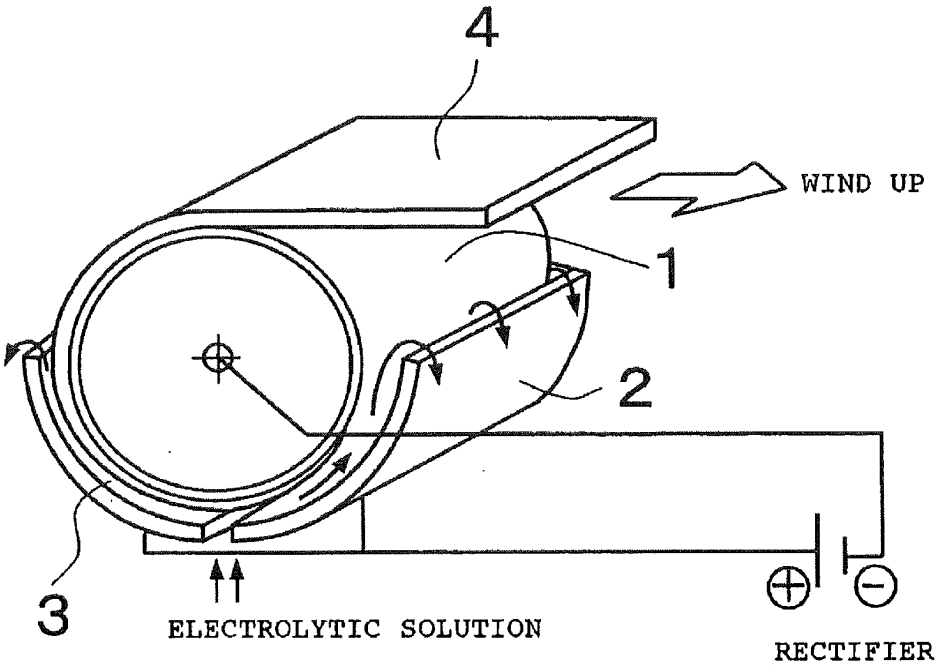
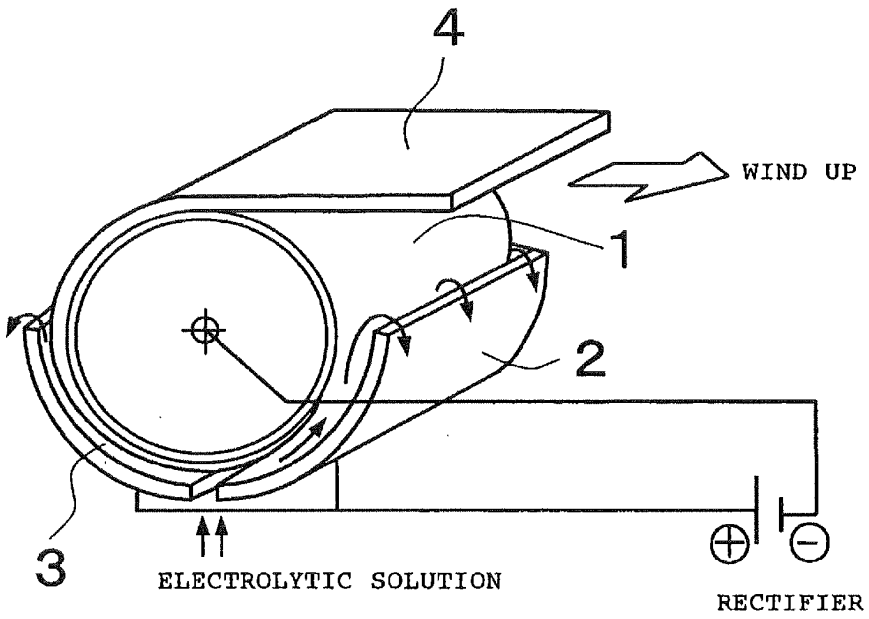


FIG. 1



TRANSMITTANCE
20.00
40.00
60.00
80.00
100.00
4000
3600
3200
2800
2400
2000
1600
1200
800
WAVENUMBERS(cm-1)
3351
2865
2773
1461
1324
1265
1180
1122
939
854

FIG. 2

FIG. 3

0.0564
5.4471
1.1303
2.0000
0.0965
PPM
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

FIG. 4

COPPER ELECTROLYTE COMPRISING AMINE COMPOUND HAVING SPECIFIC SKELETON AND ORGANIC SULFUR COMPOUND AND ELECTROLYTIC COPPER FOIL PREPARED USING THE SAME

TECHNICAL FIELD

[0001] The present invention relates to a copper electrolytic solution used in the manufacture of an electrolytic copper foil, and in particular to a copper electrolytic solution used in the manufacture of an electrolytic copper foil that can be finely patterned and has excellent elongation and tensile strength at normal temperature and high temperature.

BACKGROUND ART

[0002] In general, to manufacture an electrolytic copper foil, a rotating metal cathode drum having a polished surface, and an insoluble metal anode that goes around the periphery of approximately the lower half of the cathode drum are used, and a copper electrolytic solution is made to flow between the cathode drum and the anode. A potential is also applied between the cathode drum and the anode, whereby copper is electrodeposited onto the cathode drum. Once the electrodeposited copper has reached a prescribed thickness, the electrodeposited copper is peeled off from the cathode drum, whereby copper foil is manufactured continuously.

[0003] Copper foil obtained in this way is generally referred to as raw foil; this raw foil is subsequently subjected to various surface treatment and is then used in printed wiring boards or the like.

[0004] A conventional copper foil manufacturing apparatus is shown schematically in FIG. 1. In this electrolytic copper foil apparatus, a cathode drum is installed in an electrolysis bath housing an electrolytic solution. The cathode drum **1** rotates in a state partially submerged (i.e. with approximately the lower half submerged) in the electrolytic solution.

[0005] An insoluble anode **2** is provided so as to go around the lower half of the outer periphery of the cathode drum **1**. There is a constant gap **3** between the cathode drum **1** and the anode **2**, and the electrolytic solution flows through this gap. In the apparatus of **FIG. 1**, two anode plates are used.

[0006] In **FIG. 1**, the constitution is such that the electrolytic solution is fed in from below, passes through the gap **3** between the cathode drum **1** and the anode **2**, and flows over upper edges of the anode **2**, thus circulating. A prescribed voltage is maintained between the cathode drum I and the anode **2** using a rectifier.

[0007] As the cathode drum **1** rotates, the copper electrodeposited from the electrolytic solution glows thicker, and once the copper has become at least a certain thickness, the raw foil **4** is peeled off, and is wound up continuously. The thickness of the raw foil manufactured in this way is adjusted through the distance between the cathode drum 1 and the anode **2**, the flow rate of the electrolytic solution fed in, and the amount of electricity fed in.

[0008] With copper foil manufactured using such an electrolytic copper foil manufacturing apparatus, the surface contacting the cathode drum becomes a specular surface, but the surface on the other side becomes a rough surface having irregularities. With ordinary electrolysis, the irregularities on the rough surface are severe, and hence there is a problem that undercutting is prone to occurring during etching, and thus fine patterning is difficult.

[0009] However, recently, as the density on printed wiring boards has been increased, the circuit width has been reduced and the number of layers has been increased, and accompanying this copper foil that can be finely patterned has come to be required. To carry out fine patterning, copper foil having crystal grains of a uniform size and having a uniform etching rate and a uniform solubility, i.e. copper foil having excellent etching properties, is required.

[0010] Moreover, regarding properties required of copper foil for printed wiring boards, not only elongation at normal temperature, but also elongation at high temperature are required to prevent cracking due to thermal stress. Furthermore, high tensile strength for dimensional stability of printed wiring boards are required. However, copper foil for which irregularities on the rough surface are severe as above causes a problem of not being suited to fine patterning at all as described above. Studies have thus been proceeded into making the rough surface have a low profile.

[0011] It is known that, in general, a low profile can be achieved by adding a large amount of animal glue or thiourea to the electrolytic solution. However, such additives have a problem of causing the elongation percentage to drop dramatically at normal temperature and high temperature, thus causing a great deterioration in the properties as a copper foil for printed wiring boards.

DISCLOSURE OF THE INVENTION

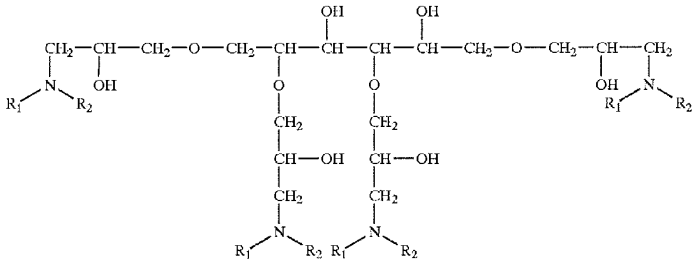
[0012] It is an object of the present invention to obtain a low-profile electrolytic copper foil by electrolytic copper foil manufacturing using a cathode drum such that the surface roughness on the rough surface side (the opposite side to the lustrous surface) is low. And in particular, it is an object to obtain an electrolytic copper foil that can be finely patterned and has excellent elongation and tensile strength at normal temperature and high temperature.

[0013] The present inventors found that by adding optimum additives enabling a low profiled foil to an electrolytic solution, therefore, it is possible to obtain an electrolytic copper foil that can be finely patterned and has excellent elongation and tensile strength at normal temperature and high temperature.

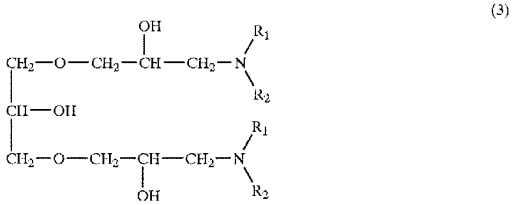
[0014] Based on this finding, the present inventors discovered that, by electrolysis using a copper electrolytic solution containing an amine compound having a specific skeleton and an organosulfur compound, it is possible to obtain an electrolytic copper foil that can be finely patterned and has excellent elongation and tensile strength at normal temperature and high temperature, in the case of an electrolytic copper foil manufacturing method in which a copper electrolytic solution is made to flow between a cathode drum and an anode, copper is electrodeposited onto the cathode drum, and the electrodeposited copper is peeled off from the cathode drum to continuously manufacture copper foil; the present invention was thus achieved.

[0015] Specifically, the present invention is constituted as follows.

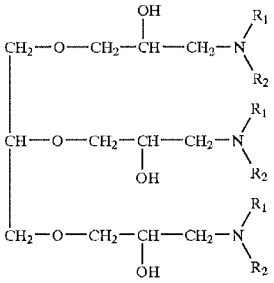
[0016] (1) A copper electrolytic solution containing, as additives, an organosulfur compound, and an amine compound having a specific skeleton represented by undermentioned general formula (1) obtained by additively reacting an amine compound and a compound having one or more epoxy groups in a molecule thereof.



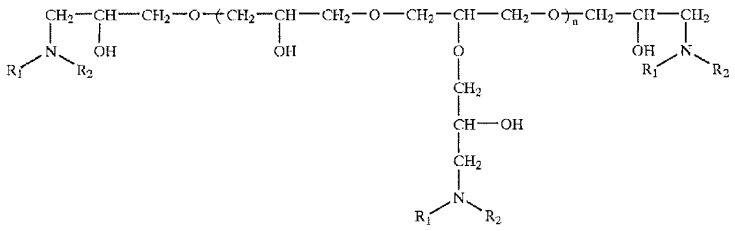
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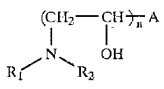
(3)



(4)



(5)



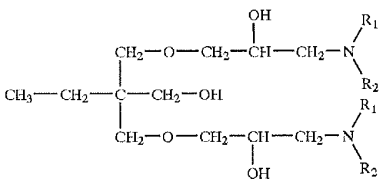
(1)

[0017] (In general formula (1), R_1 and R_2 are each selected from a group consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups, A represents an epoxy compound residue, and n represents an integer greater than or equal to 1.)

[0018] (2) A copper electrolytic solution according to (1) above, wherein the epoxy compound residue A of said amine compound having a specific skeleton has a linear ether linkage.

[0019] (3) A copper electrolytic solution according to (1) or (2) above, wherein said amine compound having a specific skeleton includes any of undermentioned general formulae (2) to (9).

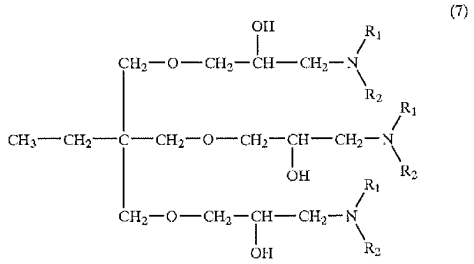
[0020] (n: an integer from 1 to 5)



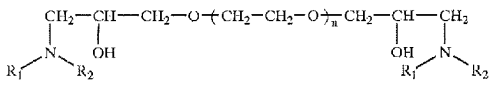
(6)

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(7)

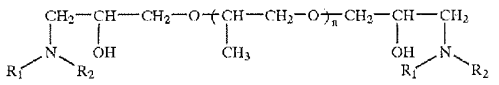


(8)



(n: an integer from 1 to 22)

(9)



[0021] (n: an integer from 1 to 3)

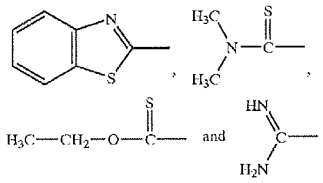
[0022] (In general formulae (2) to (9), R_1 and R_2 are each selected from a group consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups.)

[0023] (4) A copper electrolytic solution according to (1) above, wherein said organosulfur compound is a compound represented by undermentioned general formula (10) or (11).

$$X—R^1—(S)_n—R^2—YO_3Z^1 \quad (10)$$

$$R^4—S—R^3—SO_3Z^2 \quad (11)$$

[0024] (In general formulae (10) and (11), R^1, R^2 and R^3 are each an alkylene group having 1 to 8 carbon atoms, R^4 is selected from a group consisting of hydrogen,



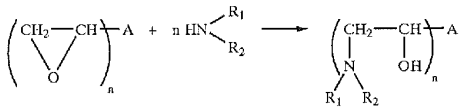
[0025] , X is selected from a group consisting of hydrogen, a sulfonic acid group, a phosphonic acid group, and sulfonic acid or phosphonic acid alkali metal salt groups or ammonium salt groups, Y is sulfur or phosphorus, Z^1 and Z^2 are each hydrogen, sodium or potassium, and n is 2 or 3.)

[0026] (5) An electrolytic copper foil produced using the copper electrolytic solution according to any of (1) through (4) above.

[0027] (6) A copper-clad laminate using the electrolytic copper foil according to (5) above.

[0028] In the present invention, it is important for the electrolytic solution to contain an organosulfur compound, and the amine compound having the specific skeleton represented by above-mentioned general formula (1) that is obtained through an addition reaction between an amine compound and a compound having one or more epoxy groups in a molecule thereof. If only one of these were to be added, then it would not be possible to attain the object of the present invention.

[0029] The amine compound (1) having the specific skeleton is synthesized through the addition reaction represented by the undermentioned reaction formula. Specifically, the amine compound having the specific skeleton can be produced by mixing together an amine compound and a compound having one or more epoxy groups in a molecule thereof, and reacting for approximately 30 minutes to 6 hours at 50 to 150° C.

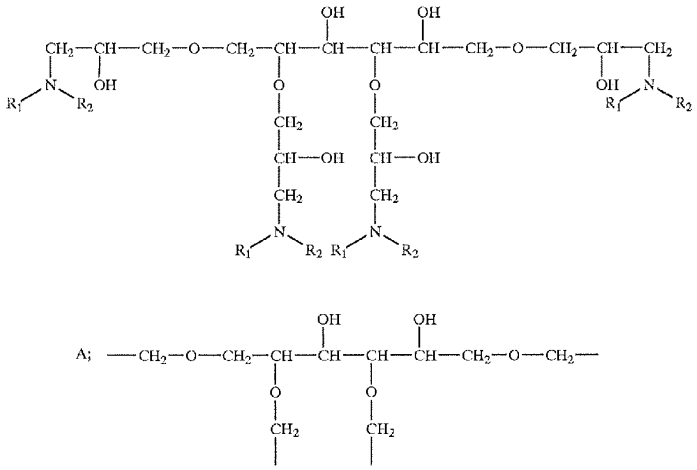


[0030] (In the above formula, R_1 and R_2 are each selected from the set consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups, A represents an epoxy residue, and n represents an integer greater than or equal to 1.)

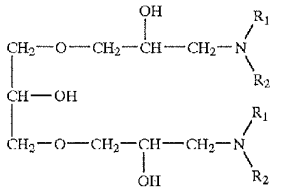
[0031] Specific examples of R_1 and R_2 in the structure of the amine compound having the specific skeleton are a hydroxyethyl group and a hydroxyisopropyl group ('hydroxyalkyl groups' above), a 2-ethoxyethyl group and a 2-propoxyethyl group ('ether groups' above), a phenyl group and a naphthyl group ('aromatic groups' above), a tolyl group, a xylyl group, a cumenyl group and a 1-phenylethyl group ('aromatic-substituted alkyl groups' above), an allyl group, a 1-propenyl group, an isopropenyl group, a 1-butenyl group, a 2-butenyl group and a 2-methylallyl group ('unsaturated hydrocarbon groups' above), and a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group and an octyl group ('alkyl groups' above). From the viewpoint of water-solubility, substituents having too large a number of carbon atoms are not desirable, with it being preferable for the number of carbon atoms per one substituent to be not more than 8.

[0032] It is preferable for the amine compound having the specific skeleton to be a compound having a linear ether linkage in the epoxy compound residue A. Compounds having the structural formulae of undermentioned general formulae (2) to (9) are preferable as such compounds in which the epoxy compound residue A has a linear ether linkage, with the epoxy compound residue A in each of general formulae (2) to (9) being as shown below.

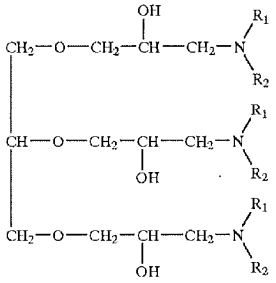
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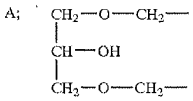


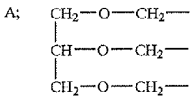
(3)



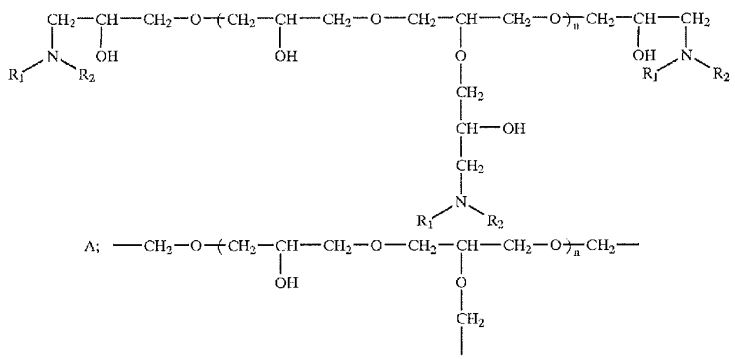
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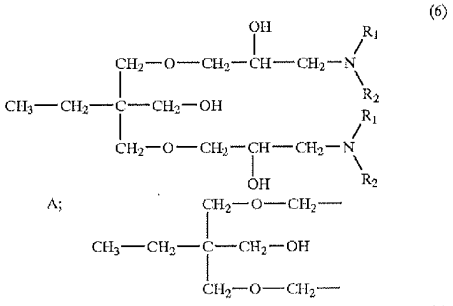




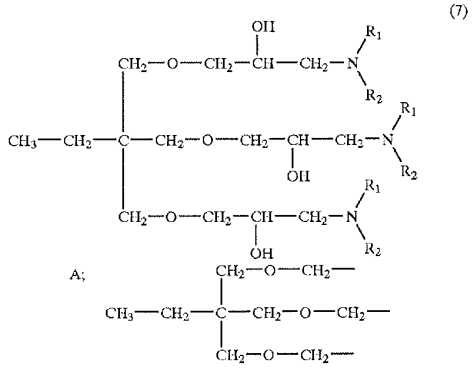
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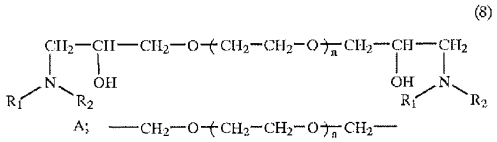
[0033] (n: an integer from 1 to 5)



(6)

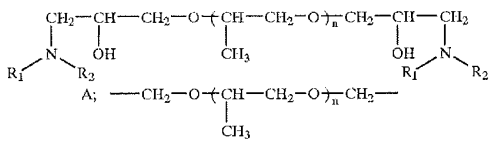


(7)



(8)

[0034] (n: an integer from 1 to 22)



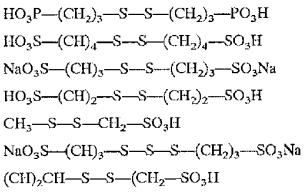
(9)

[0035] (n: an integer from 1 to 3)

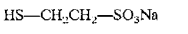
[0036] (In general formulae (2) to (9), R_1 and R_2 are each selected from a group consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups.)

[0037] Moreover, the organosulfur compound is preferably a compound having a structural formula of above-mentioned general formula (10) or (11).

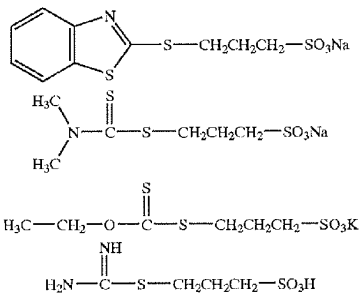
[0038] Examples of organosulfur compounds represented by above-mentioned general formula (10) are as follows, with it being preferable to use these.



[0039] Moreover, examples of organosulfur compounds represented by above-mentioned general formula (11) are as follows, with it being preferable to use these.



[0040]



[0041] The weight ratio of the amine compound to the organosulfur compound in the copper electrolytic solution is preferably in a range of 1:5 to 5:1, more preferably 1:2 to 2:1. The concentration of the amine compound in the copper electrolytic solution is preferably in a range of 1 to 50 ppm.

[0042] In addition to the amine compound having the specific skeleton and the organosulfur compound described above, publicly known additives, for example polyether compounds such as polyethylene glycol and polypropylene glycol, and, polyethyleneimine, phenazine dyes, animal glue and cellulose may be added into the copper electrolytic solution.

[0043] Moreover, a copper-clad laminate obtained by laminating on the electrolytic copper foil of the present invention has excellent elongation and tensile strength at normal temperature and high temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

[0044] **FIG. 1** is a drawing showing an example of an electrolytic copper foil manufacturing apparatus.

[0045] **FIG. 2** is the FT-IR spectrum of a dimethylamine compound obtained in an example of synthesis of the amine compound having the specific skeleton.

[0046] **FIG. 3** is the H-NMR spectrum of the dimethylamine compound obtained in the example of synthesis of the amine compound having the specific skeleton.

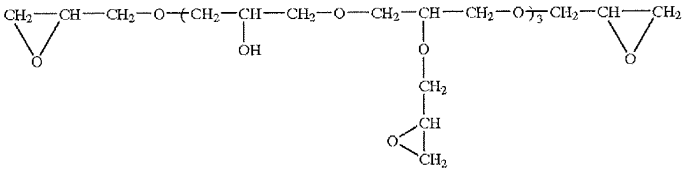
[0047] **FIG. 4** is the ^{13}C-NMR spectrum of the dimethylamine compound obtained in the example of synthesis of the amine compound having the specific skeleton.

BEST MODE FOR CARRYING OUT THE INVENTION

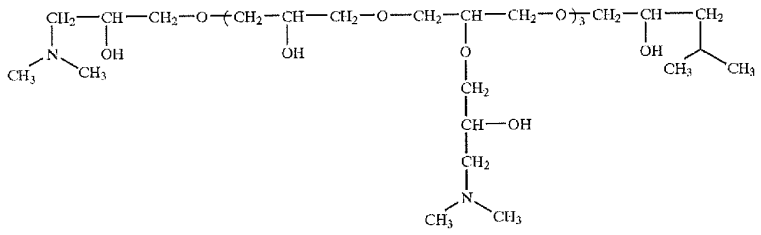
[0048] Following is a more detailed description of the present invention, showing examples.

Example of Synthesis of the Amine Compound Having the Specific Skeleton

[0049] 10.0 g of the epoxy compound represented by the undermentioned chemical formula (Denacol EX-521 made by Nagase Kasei Kogyo K.K.) (0.0544 mol of epoxy groups) and 10.7 g (0.0544 mol) of dibenzylamine were put into a 3-mouth flask, and using a condenser tube with dry ice-methanol as a coolant, reaction was carried out at 60° C. for 3 hours, thus obtaining an epoxy resin modified with dibenzylamine.



[0050] Similarly, epoxy resins modified with each of bis(2-ethoxyethyl)amine, diethanolamine, diphenylamine, diallylamine and dimethylamine were obtained. The FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra of the epoxy resin modified with dimethylamine are shown in FIGS. **2** to **4**. The compound obtained was the dimethylamine compound represented by the undermentioned chemical formula.



tion was as follows, with the amounts added of the additives being as shown in Table 1.

Cu:	90 g/l
H_2SO_4:	80 g/l
Cl:	60 ppm
Temperature:	55 to 57° C.
Additive A:	Disodium bis(3-sulfopropyl)disulfide (CPS, made by Raschig Inc.)
Additive B:	Sodium 3-mercapto-1-propanesulfonate (MPS, made by Raschig Inc.)
Additive C:	The amine compound having the specific skeleton obtained in the example of synthesis described above
C1:	Dibenzylamine-modified substance
C2:	Bis(2-ethoxyethyl)amine-modified substance
C3:	Diethanolamine-modified substance
C4:	Diphenylamine-modified substance
C5:	Diallylamine-modified substance
C6:	Dimethylamine-modified substance

[0052] The surface roughness Rz (μm) of each electrolytic copper foil obtained was measured in accordance with JIS B

EXAMPLES 1 TO 12 AND COMPARATIVE EXAMPLES 1 TO 9

[0051] 35 μm electrolytic copper foil was manufactured using an electrolytic copper foil manufacturing apparatus as shown in **FIG. 1**. The composition of the electrolytic solu-

0601, and the normal-temperature elongation (%), the normal-temperature tensile strength (kgf/mm^2), the high-temperature elongation (%) and the high-temperature tensile strength (kgf/mm^2) were measured in accordance with IPC-TM650. The results are shown in Table 1.

TABLE 1

	Additive A	Additive B	Additive C (ppm)						Rz	Elongation*1	Tensile strength*1	Elongation*2	Tensile strength*2
	(ppm)	(ppm)	C1	C2	C3	C4	C5	C6	(μm)	(%)	(kgf/mm^2)	(%)	(kgf/mm^2)
Example 1	50	0	50	0	0	0	0	0	1.02	8.10	32.2	13.9	21.7
Example 2	50	0	0	50	0	0	0	0	1.00	6.62	30.5	16.2	21.0
Example 3	50	0	0	0	50	0	0	0	0.90	8.71	31.0	18.2	20.6
Example 4	50	0	0	0	0	50	0	0	1.13	8.90	37.9	12.6	20.7
Example 5	50	0	0	0	0	0	50	0	1.15	7.12	34.2	12.1	20.1
Example 6	50	00	0	0	0	0	0	50	0.97	6.75	31.5	16.9	21.1
Example 7	0	50	50	0	0	0	0	0	1.10	8.23	32.9	14.2	20.8
Example 8	0	50	0	50	0	0	0	0	1.02	6.69	31.2	17.0	22.3
Example 9	0	50	0	0	50	0	0	0	0.92	8.90	33.0	17.3	22.2
Example 10	0	50	0	0	0	50	0	0	1.16	8.70	36.6	12.3	21.0
Example 11	0	50	0	0	0	0	50	0	1.20	7.23	34.9	12.4	20.3
Example 12	0	50	0	0	0	0	0	50	0.98	6.83	31.9	16.5	21.4
Comparative Example 1	0	0	0	0	0	0	0	0	5.8	8.90	37.9	12.6	20.7
Comparative Example 2	100	0	0	0	0	0	0	0	5.3	0.2	10.3	1.0	15.3
Comparative Example 3	0	100	0	0	0	0	0	0	6.1	0.2	11.2	1.2	14.9
Comparative Example 4	0	0	100	0	0	0	0	0	5.3	0.3	10.9	1.1	16.0
Comparative Example 5	0	0	0	100	0	0	0	0	5.8	0.1	11.1	1.0	15.8
Comparative Example 6	0	0	0	0	100	0	0	0	5.3	0.2	12.3	1.3	15.3
Comparative Example 7	0	0	0	0	0	100	0	0	5.8	0.2	13.0	1.2	14.9
Comparative Example 8	0	0	0	0	0	0	100	0	5.2	0.2	12.2	1.1	15.9
Comparative Example 9	0	0	0	0	0	0	0	100	4.9	0.2	10.3	2.7	12.8

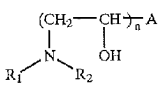
*1 at normal temperature
*2 at high temperature

[0053] As shown in Table 1 above, for Examples 1 to 12 in which the additives of the present invention (the amine compound having the specific skeleton and the organosulfur compound) were added, each Rz was in a range of 0.90 to 1.20 μm, each normal-temperature elongation was in a range of 6.62 to 8.90%, each normal-temperature tensile strength was in a range of 30.5 to 37.9 kgf/mm^2, each high-temperature elongation was in a range of 12.1 to 18.2%, and each high-temperature tensile strength was in a range of 20.1 to 22.3 kgf/mm^2. In this way, even though a remarkably low profile was achieved, the normal-temperature elongation, the normal-temperature tensile strength, the high-temperature elongation and the high-temperature tensile strength all exhibited values similar to or better than those of Comparative Example 1 in which no additives were added. In contrast, for Comparative Example 1 in which no additives were added and Comparative Examples 2 to 9 in which only one of the additives was added, a low profile was not achieved. Moreover, in the cases in which only one of the additives was added, the normal-temperature elongation, the normal-temperature tensile strength, the high-temperature elongation and the high-temperature tensile strength actually became worse.

[0054] Industrial Applicability

[0055] As described above, the copper electrolytic solution of the present invention to which the amine compound having the specific skeleton and the organosulfur compound have been added is extremely effective in making the rough surface of an electrolytic copper foil obtained have a low profile; moreover excellent properties are observed in that extension properties can be maintained effectively not only at normal temperature but also at high temperature, and furthermore high tensile strength can similarly be obtained. Moreover, it is understood that addition of both the amine compound having the specific skeleton and the organosulfur compound is important, since only then can the above properties be obtained.

1. A copper electrolytic solution containing, as additives, an organosulfur compound, and an amine compound having a specific skeleton represented by undermentioned general formula (1) obtained by additively reacting an amine compound and a compound having one or more epoxy groups in a molecule thereof.



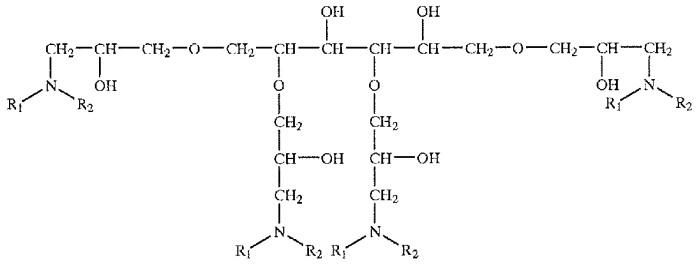
(1)

(In general formula (1), R_1 and R_2 are each selected from a group consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups, A represents an epoxy compound residue, and n represents an iuteger greater than or equal to 1.)

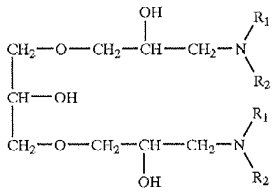
2. A copper electrolytic solution according to claim 1, wherein the epoxy compound residue A of said amine compound having a specific skeleton has a linear ether linkage.

3. A copper electrolytic solution according to claim 1 or 2, wherein said amine compound having a specific skeleton includes any of undermentioned general formulae (2) to (9).

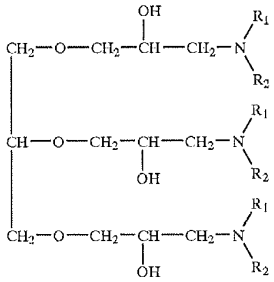
(2)



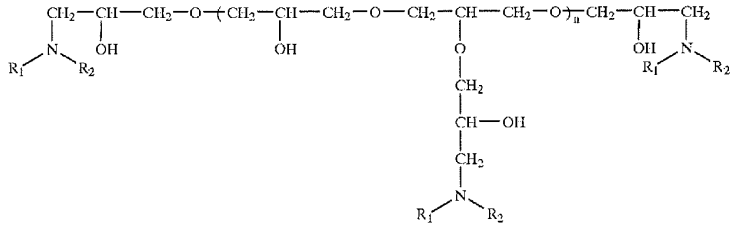
(3)



(4)



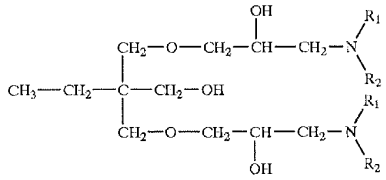
(5)



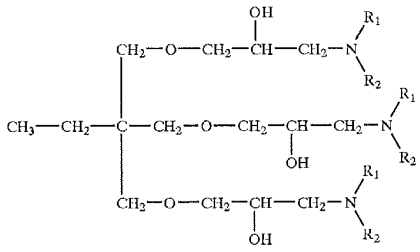
(n: an integer from 1 to 5)

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(6)

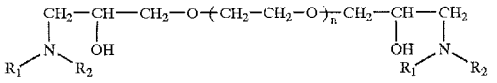


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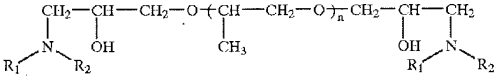
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(8)



(n: an integer from 1 to 22)

(9)



(n: an integer from 1 to 3)

(In general formulae (2) to (9), R_1 and R_2 are each selected from a group consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups.)

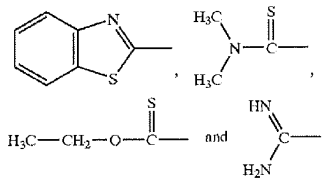
4. A copper electrolytic solution according to claim 1, wherein said organosulfur compound is a compound represented by undermentioned general formula (10) or (11).



(10)

(11)

(In general formulae (10) and (11), R^1, R^2 and R^3 are each an alkylene group having 1 to 8 carbon atoms, R^4 is selected from a group consisting of hydrogen,



, X is selected from a group consisting of hydrogen, a sulfonic acid group, a phosphonic acid group, and sulfonic acid or phosphonic acid alkali metal salt groups or ammonium salt groups, Y is sulfur or phosphorus, Z^1 and Z^2 are each hydrogen, sodium or potassium, and n is 2 or 3.)

5. An electrolytic copper foil produced using the copper electrolytic solution according to any of claims 1 through 4.

6. A copper-clad laminate using the electrolytic copper foil according to claim 5.

* * * * *

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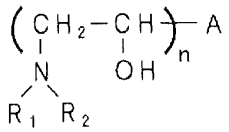
審査請求 有　請求項の数 6　ＯＬ　（全 17 頁）

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(54)【発明の名称】特定骨格を有するアミン化合物及び有機硫黄化合物を添加剤として含む銅電解液並びにそれにより製造される電解銅箔

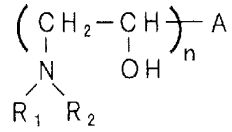
(57)【要約】
【課題】陰極ドラムを用いた電解銅箔製造における粗面側（光沢面の反対側）の表面粗さの小さいローブロファイル電解銅箔を得ること、特にファインパターン化が可能であり、さらに常温及び高温における伸びと抗張力に優れた電解銅箔を得ることを課題とする。
【解決手段】１分子中に１個以上のエポキシ基を有する化合物とアミン化合物とを付加反応させることにより得られる下記一般式（１）で記載される特定骨格を有するアミン化合物と有機硫黄化合物を添加剤として含む銅電解液。
【化１】



（１）

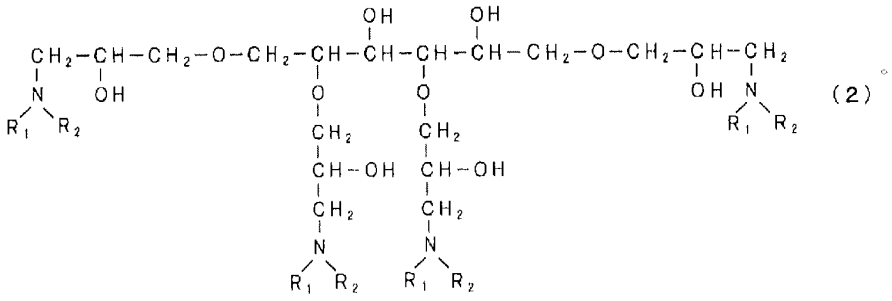
（一般式（１）中、R_1及びR_2はヒドロキシアルキル基、エーテル基、芳香族基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものであり、Ａはエポキシ化合物残基を、ｎは１以上の整数を表す。）
【選択図】　なし

【特許請求の範囲】
【請求項１】
１分子中に１個以上のエポキシ基を有する化合物とアミン化合物とを付加反応させることにより得られる下記一般式（１）で記載される特定骨格を有するアミン化合物と有機硫黄化合物を添加剤として含む銅電解液。
【化１】



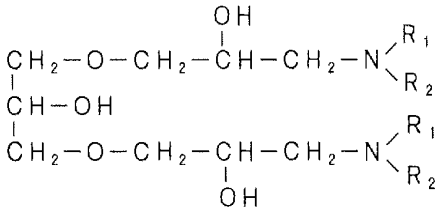
（１）

（一般式（１）中、R_1及びR_2はヒドロキシアルキル基、エーテル基、芳香族基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものであり、Ａはエポキシ化合物残基を、ｎは１以上の整数を表す。）
【請求項２】
前記特定骨格を有するアミン化合物のエポキシ化合物残基Ａが、線状エーテル結合を有することを特徴とする請求項１記載の銅電解液。
【請求項３】
前記特定骨格を有するアミン化合物が下記一般式（２）～（９）のいずれかを含有することを特徴とする請求項１又は２記載の銅電解液。
【化２】



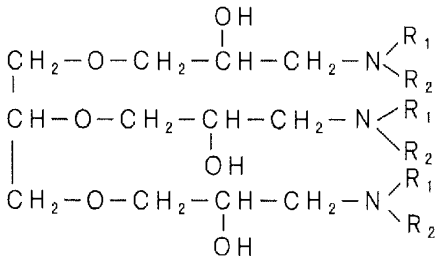
（２）

【化３】



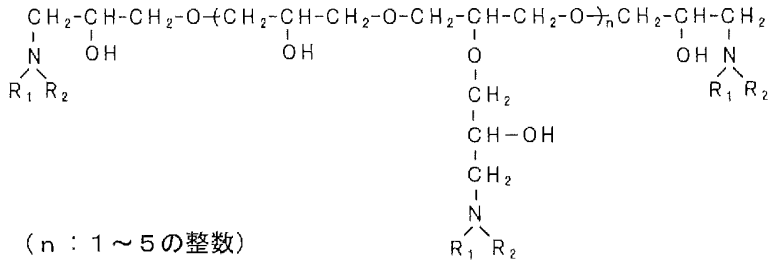
（３）

【化４】



(4)

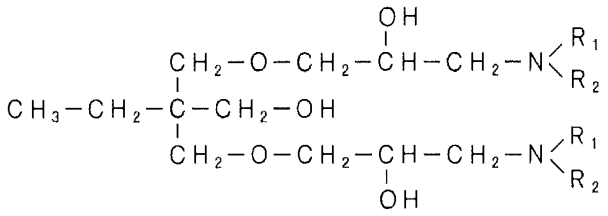
【化５】



(5)

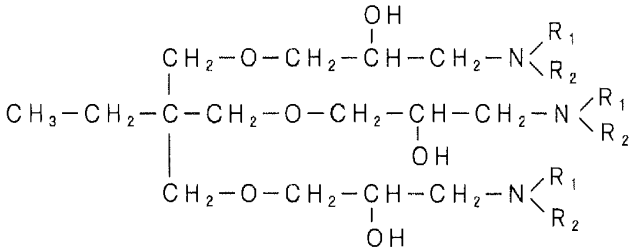
(ｎ：１～５の整数)

【化６】



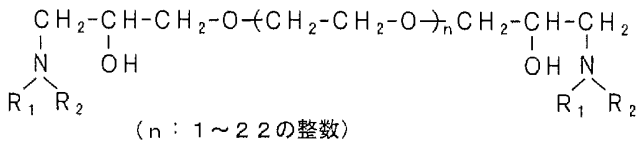
(6)

【化７】



(7)

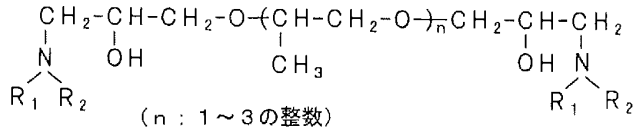
【化８】



(8)

(ｎ：１～２２の整数)

【化９】



（９）

（一般式（２）～（９）中、R_1及びR_2はヒドロキシアルキル基、エーテル基、芳香族基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものである。）

【請求項４】

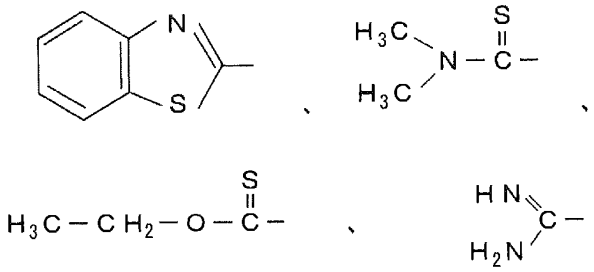
前記有機硫黄化合物が下記一般式（１０）又は（１１）で表される化合物であることを特徴とする請求項１記載の銅電解液。

$X-R^1-(S)_n-R^2-YO_3Z^1$ （１０）

$R^4-S-R^3-SO_3Z^2$ （１１）

（一般式（１０）及び（１１）中、R^1、R^2、及びR^3は炭素数１～８のアルキレン基であり、R^4は、水素、

【化１０】



からなる一群から選ばれるものであり、Ｘは水素、スルホン酸基、ホスホン酸基、スルホン酸又はホスホン酸のアルカリ金属塩基又はアンモニウム塩基からなる一群から選ばれるものであり、Ｙは硫黄又は燐のいずれかであり、Z^1及びZ^2は水素、ナトリウム、カリウムのいずれかであり、ｎは２又は３である。）

【請求項５】

請求項１～４のいずれかに記載の銅電解液を用いて製造される電解銅箔。

【請求項６】

請求項５記載の電解銅箔を用いてなる銅張積層板。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】

本発明は、電解銅箔の製造に用いる銅電解液、特にファインパターン化が可能であり、常温及び高温における伸びと抗張力に優れた電解銅箔の製造に用いる銅電解液に関する。

【０００２】

【従来の技術】

一般に、電解銅箔を製造するには、表面を研磨した回転する金属製陰極ドラムと、該陰極ドラムのほぼ下半分の位置に配置した該陰極ドラムの周囲を囲む不溶性金属アノード（陽極）を使用し、前記陰極ドラムとアノードとの間に銅電解液を流動させるとともに、これらの間に電位を与えて陰極ドラム上に銅を電着させ、所定厚みになったところで該陰極ドラムから電着した銅を引き剥がして連続的に銅箔を製造する。

このようにして得た銅箔は一般的に生箔と言われているが、その後いくつかの表面処理を施してプリント配線板等に使用されている。

【０００３】

従来の銅箔製造装置の概要を図１に示す。この電解銅箔装置は、電解液を収容する電解槽の中に、陰極ドラムが設置されている。この陰極ドラム１は電解液中に部分的（ほぼ下半分）に浸漬された状態で回転するようになっている。

この陰極ドラム１の外周下半分を取り囲むように、不溶性アノード（陽極）２が設けられている。この陰極ドラム１とアノード２の間は一定の間隙３があり、この間を電解液が流動するようになっている。図１の装置には２枚のアノード板が配置されている。

【０００４】

この図１では、下方から電解液が供給され、この電解液は陰極ドラム１とアノード２の間隙３を通り、アノード２の上縁から溢流し、さらにこの電解液は循環するように構成されている。陰極ドラム１とアノード２の間には整流器を介して、両者の間に所定の電圧が維持できるようになっている。

陰極ドラム１が回転するにつれ、電解液から電着した銅は厚みを増大し、ある厚み以上になったところで、この生箔４を剥離し、連続的に巻き取っていく。このようにして製造された生箔は、陰極ドラム１とアノード２の間の距離、供給される電解液の流速あるいは供給する電気量により厚みを調整する。

【０００５】

このような電解銅箔製造装置によって製造される銅箔は、陰極ドラムと接触する面は鏡面となるが、反対側の面は凸凹のある粗面となる。通常の電解では、この粗面の凸凹が激しく、エッチング時にアンダーカットが発生し易く、ファインパターン化が困難であるという問題を有している。

【０００６】

一方、最近ではプリント配線板の高密度化に伴い、回路幅の狭小化、多層化に伴いファインパターン化が可能である銅箔が要求されるようになってきた。このファインパターン化のためには、エッチング速度と均一溶解性を持つ銅箔、すなわちエッチング特性に優れた銅箔が必要である。

【０００７】

他方、プリント配線板用銅箔に求められる性能は、常温における伸びだけでなく、熱応力によるクラック防止のための高温伸び特性、さらにはプリント配線板の寸法安定性のために高い引張り強さが求められている。ところが、上記のような粗面の凸凹が激しい銅箔は、上記のようにファインパターン化には全く適合しないという問題を有している。このようなことから粗面のローブロファイル化が検討されている。

【０００８】

一般に、このローブロファイル化のためには、膠やチオ尿素を電解液に多量添加することによって達成できることが知られている。

しかし、このような添加剤は、常温及び高温における伸び率が急激に低下し、プリント配線板用銅箔としての性能を大きく低下させてしまうという問題を有している。

【０００９】

【発明が解決しようとする課題】

本発明は、陰極ドラムを用いた電解銅箔製造における粗面側（光沢面の反対側）の表面粗さの小さいローブロファイル電解銅箔を得ること、特にファインパターン化が可能であり、さらに常温及び高温における伸びと抗張力に優れた電解銅箔を得ることを課題とする。

【００１０】

【課題を解決するための手段】

本発明者らは、ローブロファイル化が可能である最適な添加剤を電解液に添加することにより、ファインパターン化が可能であり、常温及び高温における伸びと抗張力に優れた電解銅箔を得ることができるとの知見を得た。

【００１１】

本発明者らはこの知見に基づいて、陰極ドラムとアノードとの間に銅電解液を流して陰極ドラム上に銅を電着させ、電着した銅箔を該陰極ドラムから剥離して連続的に銅箔を製造する電解銅箔製造方法において、特定骨格を有するアミン化合物と有機硫黄化合物を含有する銅電解液を用いて電解することにより、ファインパターン化が可能であり、常温及び高温における伸びと抗張力に優れた電解銅箔を得ることができることを見いだし本発明に至った。

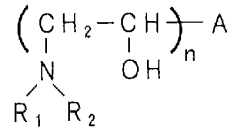
【００１２】

すなわち、本発明は以下の構成よりなる。

（１）１分子中に１個以上のエポキシ基を有する化合物とアミン化合物とを付加反応させることにより得られる、下記一般式（１）で記載される特定骨格を有するアミン化合物と有機硫黄化合物を添加剤として含む銅電解液。

【００１３】

【化１１】



（１）

（一般式（１）中、R_1及びR_2はヒドロキシアルキル基、エーテル基、芳香族基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものであり、Ａはエポキシ化合物残基を、ｎは１以上の整数を表す。）

【００１４】

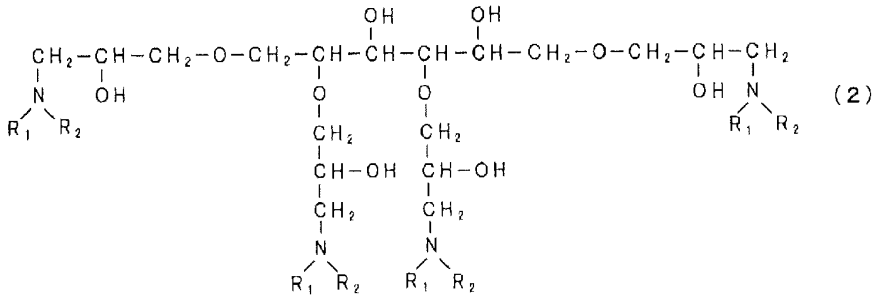
（２）前記特定骨格を有するアミン化合物のエポキシ化合物残基Ａが、線状エーテル結合を有することを特徴とする（１）記載の銅電解液。

【００１５】

（３）前記特定骨格を有するアミン化合物が下記一般式（２）～（９）いずれかを含有することを特徴とする前記（１）又は（２）記載の銅電解液。

【００１６】

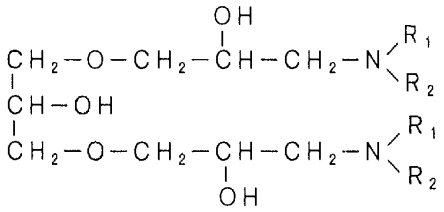
【化１２】



（２）

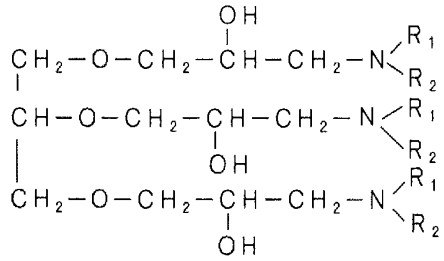
【００１７】

【化１３】



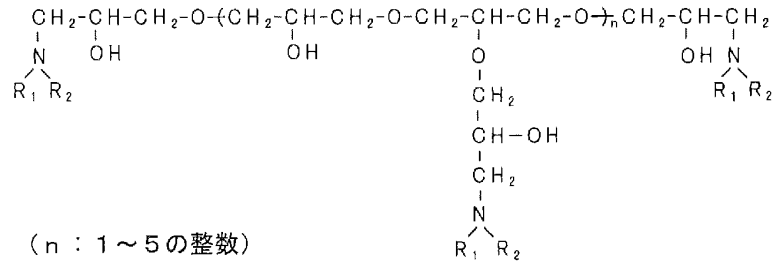
(3)

【００１８】
【化１４】



(4)

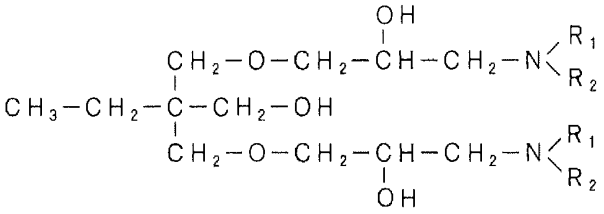
【００１９】
【化１５】



(n：１～５の整数)

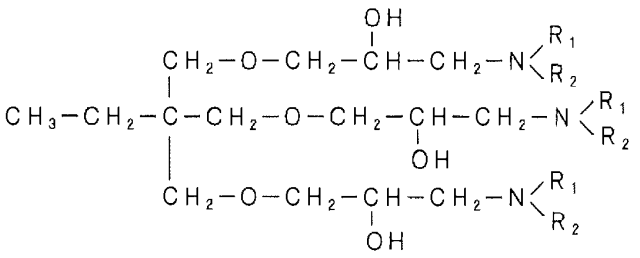
(5)

【００２０】
【化１６】



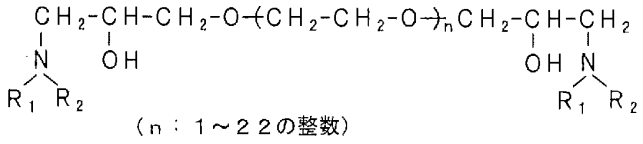
(6)

【００２１】
【化１７】



(7)

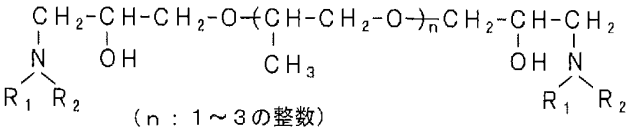
【００２２】
【化１８】



(8)

（ｎ：１～２２の整数）

【００２３】
【化１９】



(9)

（ｎ：１～３の整数）

（一般式（２）～（９）中、R_1及びR_2はヒドロキシアルキル基、エーテル基、芳香族基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものである。）

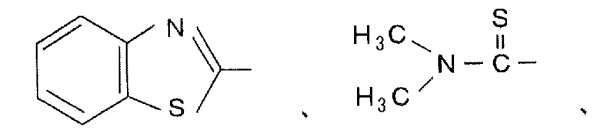
【００２４】
（４）前記有機硫黄化合物が下記一般式（１０）又は（１１）で表される化合物であることを特徴とする前記（１）記載の銅電解液。

$X-R^1-(S)_n-R^2-YO_3Z^1$ （１０）

$R^4-S-R^3-SO_3Z^2$ （１１）

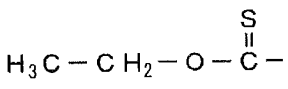
（一般式（１０）及び（１１）中、R^1、R^2、及びR^3は炭素数１～８のアルキレン基であり、R^4は、水素、

【化２０】

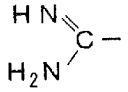


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からなる一群から選ばれるものであり、Ｘは水素、スルホン酸基、ホスホン酸基、スルホ

ン酸又はホスホン酸のアルカリ金属塩基又はアンモニウム塩基からなる一群から選ばれるものであり、Ｙは硫黄又は燐のいずれかであり、Z^1 及び Z^2 は水素、ナトリウム、カリウムのいずれかであり、ｎは２又は３である。）

【００２５】

（５）前記（１）～（４）のいずれかに記載の銅電解液を用いて製造される電解銅箔。

（６）前記（５）記載の電解銅箔を用いてなる銅張積層板。

【００２６】

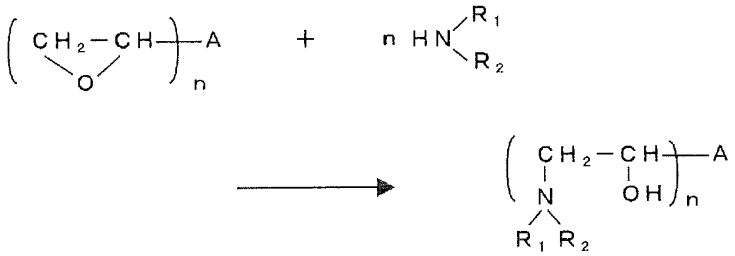
本発明においては、電解液中に、１分子中に１個以上のエポキシ基を有する化合物とアミン化合物とを付加反応させることにより得られる上記一般式（１）で表される特定骨格を有するアミン化合物と、有機硫黄化合物を含むことが重要である。どちらか一方のみの添加では、本発明の目的は達成できない。

【００２７】

特定骨格を有するアミン化合物（１）は、下記反応式で表される付加反応により合成される。すなわち、１分子中に１個以上のエポキシ基を有する化合物とアミン化合物を混合し、５０～１５０℃で３０分～６時間程度反応させることにより製造することができる。

【００２８】

【化２１】



（上記式中、R_1 及び R_2 はヒドロキシアルキル基、エーテル基、芳香族基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものであり、Ａはエポキシ残基を、ｎは１以上の整数を表す。）

【００２９】

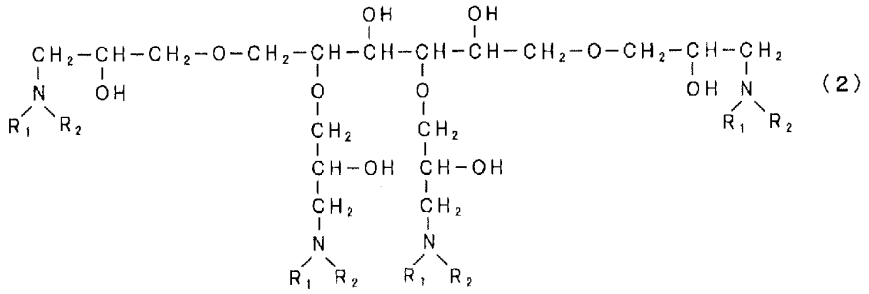
特定骨格を有するアミン化合物構造中の R_1 及び R_2 の具体的な例としては、ヒドロキシエチル基、ヒドロキシイソプロピル基（以上ヒドロキシアルキル基）、２－エトキシエチル基、２－プロポキシエチル基（以上エーテル基）、フェニル基、ナフチル基（以上芳香族基）、トリル基、キシリル基、クメニル基、１－フェニルエチル基（以上芳香族置換アルキル基）、アリル基、１－プロペニル基、イソプロペニル基、１－ブテニル基、２－ブテニル基、２－メチルアリル基（以上不飽和炭化水素基）、メチル基、エチル基、プロピル基、ブチル基、ペンチル基、ヘキシル基、ヘプチル基、オクチル基（以上アルキル基）を挙げることができるが、水溶性の観点からは炭素数のあまり大きい置換基は好ましくなく、置換基１つあたりの炭素数としては８以下が好ましい。

【００３０】

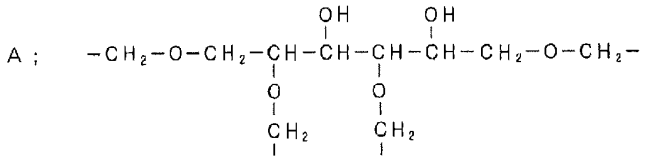
特定骨格を有するアミン化合物としては、エポキシ化合物残基Ａに線状エーテル結合を有する化合物が好ましい。エポキシ化合物残基Ａが線状エーテル結合を有する化合物としては、下記一般式（２）～（９）の構造式を持つ化合物が好ましく、一般式（２）～（９）におけるエポキシ化合物残基Ａは以下のとおりである。

【００３１】

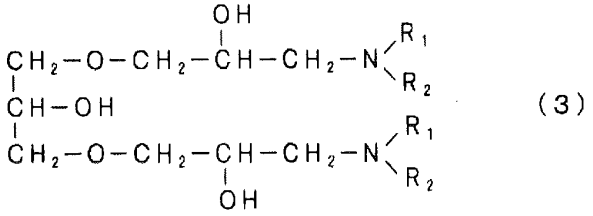
【化２２】



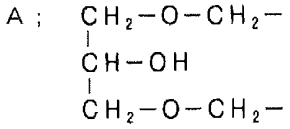
(2)



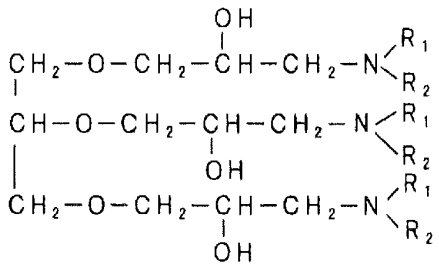
【００３２】
【化２３】



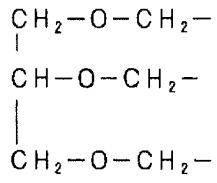
(3)



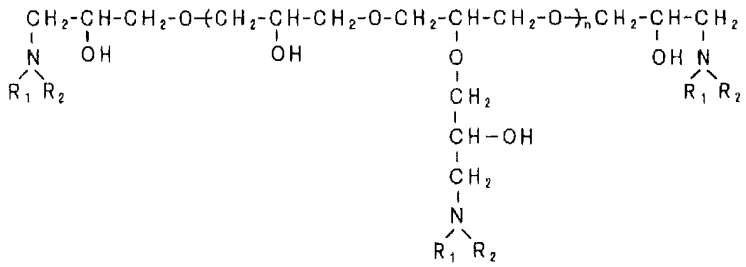
【００３３】
【化２４】



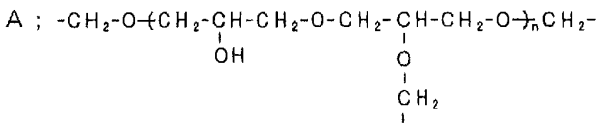
(4)

A； 

【００３４】
【化２５】

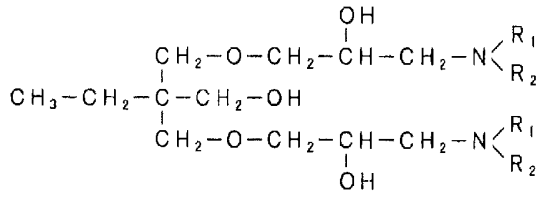


(5)

A； 

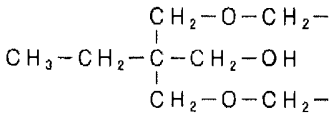
（ｎ：１～５の整数）

【００３５】
【化２６】

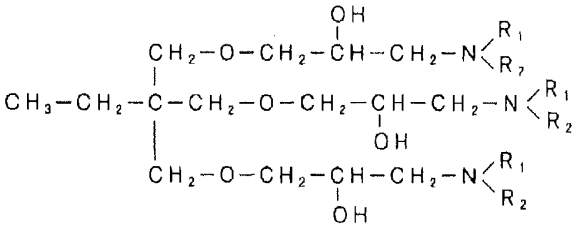


(6)

A；

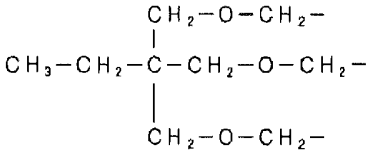


【００３６】
【化２７】

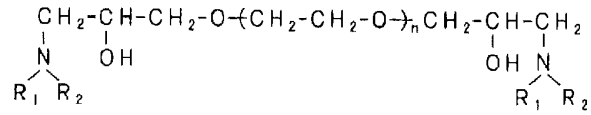


(7)

A；



【００３７】
【化２８】

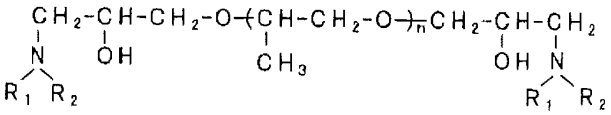


(8)

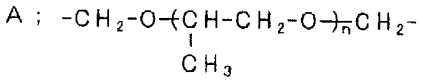
A； $-CH_2-O-(CH_2-CH_2-O-)_nCH_2-$

（n：１～２２の整数）

【００３８】
【化２９】



(9)



（ｎ：１～３の整数）

（一般式（２）～（９）中、R_1及びR_2はヒドロキシアルキル基、エーテル基、芳香族基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものである。）

【００３９】

また、有機硫黄化合物は上記一般式（１０）又は（１１）の構造式を持つ化合物であることが好ましい。

上記一般式（１０）で表される有機硫黄化合物としては、例えば以下のものが挙げられ、好ましく用いられる。

$HO_3P-(CH_2)_3-S-S-(CH_2)_3-PO_3H$

$HO_3S-(CH_2)_4-S-S-(CH_2)_4-SO_3H$

$NaO_3S-(CH_2)_3-S-S-(CH_2)_3-SO_3Na$

$HO_3S-(CH_2)_2-S-S-(CH_2)_2-SO_3H$

$CH_3-S-S-CH_2-SO_3H$

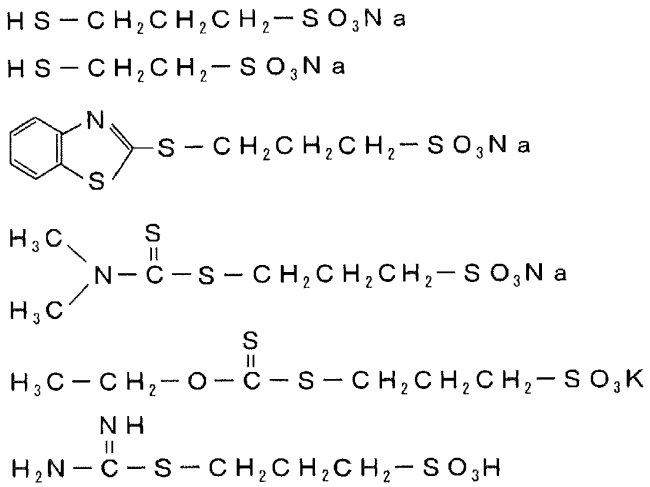
$NaO_3S-(CH_2)_3-S-S-S-(CH_2)_3-SO_3Na$

$(CH_3)_2CH-S-S-(CH_2)_2-SO_3H$

【００４０】

また、上記一般式（１１）で表される有機硫黄化合物としては、例えば以下のものが挙げられ、好ましく用いられる。

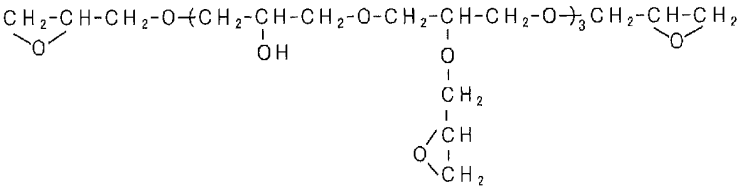
【化３０】



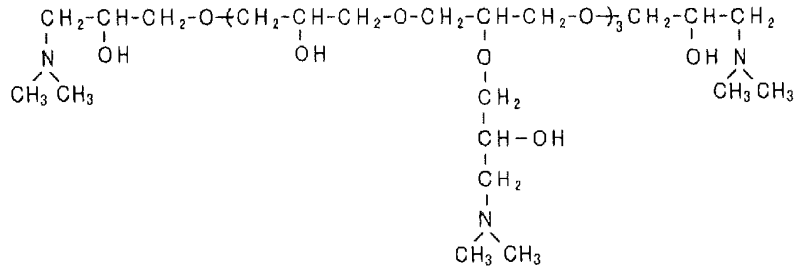
【００４１】

銅電解液中のアミン化合物と有機硫黄化合物の比は重量比で１：５～５：１が好ましく、さらに好ましくは１：２～２：１である。アミン化合物の銅電解液中の濃度は１～５０ｐ

ｐｍが好ましい。
銅電解液中には、上記特定骨格を有するアミン化合物及び有機硫黄化合物の他に、ポリエチレングリコール、ポリプロピレングリコール等のポリエーテル化合物、ポリエチレンイミン、フェナジン染料、膠、セルロース等の公知の添加剤を添加してもよい。
【００４２】
また、本発明の電解銅箔を積層して得られる銅張積層板は、常温及び高温における伸びと抗張力に優れた銅張積層板となる。
【００４３】
【発明の実施の形態】
以下に実施例を示し、本発明をさらに詳細に説明する。
特定骨格を有するアミン化合物の合成例
下記化学式で表されるエポキシ化合物（ナガセ化成工業（株）製デナコールＥＸ－５２１）１０．０ｇ（エポキシ基０．０５４４ｍｏｌ）とジベンジルアミン１０．７ｇ（０．０５４４ｍｏｌ）を三口フラスコに投入し、ドライアイス－メタノールを冷却媒体とする冷却管を使用して、６０℃で３時間反応を行い、ジベンジルアミンで変性したエポキシ樹脂を得た。
【００４４】
【化３１】



【００４５】
同様にしてビス（２－エトキシエチル）アミン、ジエタノールアミン、ジフェニルアミン、ジアリルアミン、ジメチルアミンでそれぞれ変性したエポキシ樹脂を得た。ジメチルアミンで変成したエポキシ樹脂のＦＴ－ＩＲ、^{1}Ｈ－ＮＭＲ、^{13}Ｃ－ＮＭＲスペクトルを図２～４に示す。得られた化合物は下記化学式で表されるジメチルアミン化合物であった。
【００４６】
【化３２】



【００４７】
実施例１～１２及び比較例１～９
図１に示すような電解銅箔製造装置を使用して３５μｍの電解銅箔を製造した。電解液組成は次の通りであり、添加剤の添加量は表１記載の通りである。
Ｃｕ：　９０ｇ／Ｌ
H_2SO_4：８０ｇ／Ｌ

Ｃｌ：　６０ｐｐｍ
液温：　５５～５７℃
添加剤Ａ：ビス（３－スルフォプロピル）ジスルファイド２ナトリウム（ＲＡＳＣＨＩＧ社製　ＣＰＳ）
添加剤Ｂ：３－メルカプト－１－プロパンスルフォン酸ナトリウム塩（ＲＡＳＣＨＩＧ社製　ＭＰＳ）
添加剤Ｃ：上記合成例で得られた特定骨格を有するアミン化合物
Ｃ１：ジベンジルアミン変性物
Ｃ２：ビス（２－エトキシエチル）アミン変性物
Ｃ３：ジエタノールアミン変性物
Ｃ４：ジフェニルアミン変性物
Ｃ５：ジアリルアミン変性物
Ｃ６：ジメチルアミン変性物
得られた電解銅箔の表面粗さＲｚ（μｍ）をＪＩＳ　Ｂ　０６０１に準じて、常温伸び（％）、常温抗張力（ｋｇｆ／ｍｍ^2）、高温伸び（％）、高温抗張力（ｋｇｆ／ｍｍ^2）をＩＰＣ－ＴＭ６５０に準じて測定した。結果を表１に示す。

【００４８】

【表１】

表１

	添加剤A (ppm)	添加剤B (ppm)	添加剤C (ppm) C1	C2	C3	C4	C5	C6	Rz (μm)	常温伸び (%)	常温抗張力 (kgf/mm²)	高温伸び (%)	高温抗張力 (kgf/mm²)
実施例１	50	0	50	0	0	0	0	0	1.02	8.10	32.2	13.9	21.7
実施例２	50	0	0	50	0	0	0	0	1.00	6.62	30.5	16.2	21.0
実施例３	50	0	0	0	50	0	0	0	0.90	8.71	31.0	18.2	20.6
実施例４	50	0	0	0	0	50	0	0	1.13	8.90	37.9	12.6	20.7
実施例５	50	0	0	0	0	0	50	0	1.15	7.12	34.2	12.1	20.1
実施例６	50	0	0	0	0	0	0	50	0.97	6.75	31.5	16.9	21.1
実施例７	0	50	50	0	0	0	0	0	1.10	8.23	32.9	14.2	20.8
実施例８	0	50	0	50	0	0	0	0	1.02	6.69	31.2	17.0	22.3
実施例９	0	50	0	0	50	0	0	0	0.92	8.90	33.0	17.3	22.2
実施例10	0	50	0	0	0	50	0	0	1.16	8.70	36.6	12.3	21.0
実施例11	0	50	0	0	0	0	50	0	1.20	7.23	34.9	12.4	20.3
実施例12	0	50	0	0	0	0	0	50	0.98	6.83	31.9	16.5	21.4
比較例１	0	0	0	0	0	0	0	0	5.8	8.90	37.9	12.6	20.7
比較例２	100	0	0	0	0	0	0	0	5.3	0.2	10.3	1.0	15.3
比較例３	0	100	0	0	0	0	0	0	6.1	0.2	11.2	1.2	14.9
比較例４	0	0	100	0	0	0	0	0	5.3	0.3	10.9	1.1	16.0
比較例５	0	0	0	100	0	0	0	0	5.8	0.1	11.1	1.0	15.8
比較例６	0	0	0	0	100	0	0	0	5.3	0.2	12.3	1.3	15.3
比較例７	0	0	0	0	0	100	0	0	5.8	0.2	13.0	1.2	14.9
比較例８	0	0	0	0	0	0	100	0	5.2	0.2	12.2	1.1	15.9
比較例９	0	0	0	0	0	0	0	100	4.9	0.2	10.3	2.7	12.8

【００４９】

上記表１に示す通り、本発明の添加剤（特定骨格を有するアミン化合物および有機硫黄化

合物）を添加した実施例１～１２については表面粗さＲｚが０．９０～１．２０μｍの範囲にあり、常温伸び６．６２～８．９０％、常温抗張力３０．５～３７．９ｋｇｆ／ｍｍ^2、高温伸び１２．１～１８．２％、高温抗張力２０．１～２２．３ｋｇｆ／ｍｍ^{2}となった。このように著しいロープロファイル化が達成できているにも関わらず、常温伸び、常温抗張力、高温伸び、高温抗張力がいずれも添加剤を添加しない比較例１と同様又はそれ以上の優れた特性を示している。これらに対し、無添加の比較例１及び一方のみを添加した比較例２～９ではロープロファイル化は達成できていない。また、一方のみを添加した場合には、常温伸び、常温抗張力、高温伸び、高温抗張力がかえって悪い結果となった。

【００５０】

【発明の効果】

以上から、本発明の特定骨格を有するアミン化合物及び有機硫黄化合物を添加した銅電解液は、得られる電解銅箔の粗面のロープロファイル化に極めて有効であり、また常温における伸びだけでなく高温伸び特性を有効に維持でき、さらには高い引張り強さも同様に得られるという優れた特性が確認できる。また、上記共添加は重要であり、これによって初めて、上記の特性を得ることができることがわかる。

【図面の簡単な説明】

【図１】電解銅箔製造装置の一例を示す図である。

【図２】特定骨格を有するアミン化合物の合成例で得られたジメチルアミン化合物のＦＴ－ＩＲスペストルである。

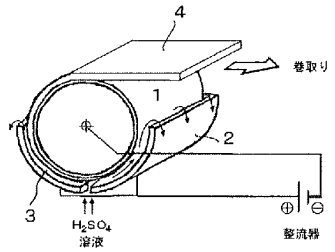
【図３】特定骨格を有するアミン化合物の合成例で得られたジメチルアミン化合物の^{1}Ｈ－ＮＭＲスペクトルである。

【図４】特定骨格を有するアミン化合物の合成例で得られたジメチルアミン化合物の^{13}Ｃ－ＮＭＲスペクトルである。

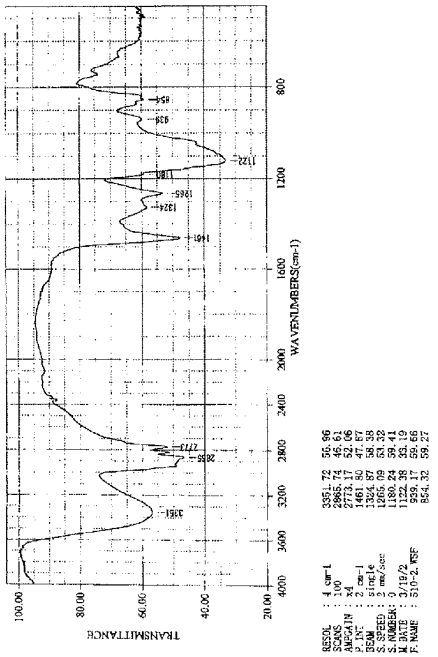
【符号の説明】

１　陰極ドラム
２　アノード
３　間隙
４　生箔

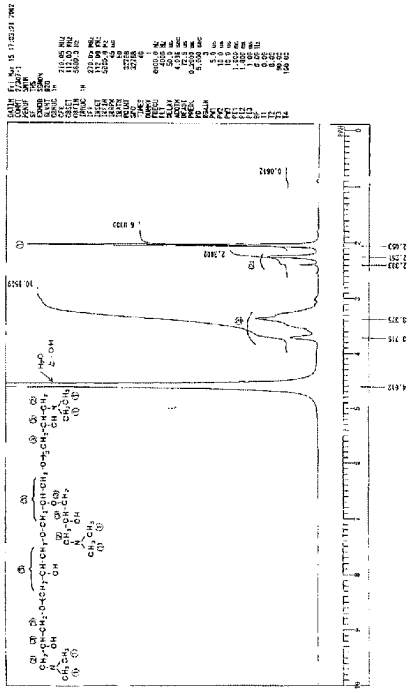
【図１】


4
巻取り
1
2
3
H_2SO_4
溶液
整流器

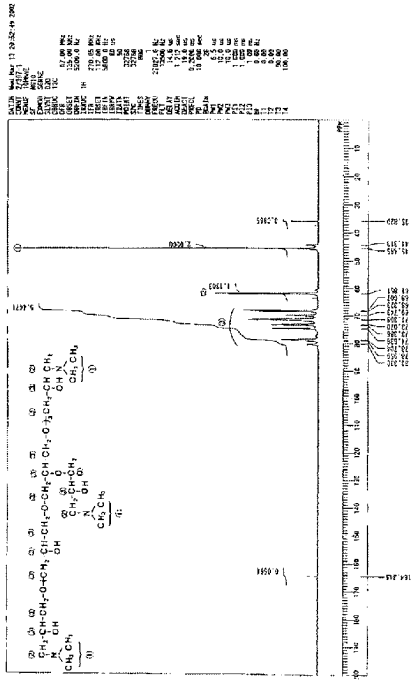
【図２】


TRANSMITTANCE
WAVENUMBERS(cm-1)
100.00
80.00
60.00
40.00
20.00
4000
3600
3200
2800
2400
2000
1600
1200
800
3381
2773
2626
1941
1924
1865
1180
1122
856
838

【図３】



【図４】



D18

Partial English translations of the reference No. JP 3,742,144 B

[0031]

First, an anode current collector 4 of an electrolytic copper foil was manufactured by the following method. Under the conditions of a copper sulfate solution of the following composition 1 as an electrolyte solution, precious metal oxide coated titanium as an anode, current density of 50A/dm2, and solution temperature of 50°C, electrolysis was performed, to obtain a 12 μm thick electrolytic copper foil. The surface roughness of the electrolytic copper foil was measured by the following method, and its result is shown in Table 1.

[0032]

(Composition 1)

Copper sulfate ($CuSO_4 \cdot 5H_2O$)350g/l

Sulfuric acid (H_2SO_4)110g/l

thio element 0.4ppm

Arabischgom 0.8ppm

Low molecular weight linking (Molecular weight 5000) 0.4ppm

Cl^- 30ppm

It is certified that the above is the same as the original.

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最終頁に続く

(54)【発明の名称】非水電解液二次電池及び非水電解液二次電池用の平面状集電体

(57)【特許請求の範囲】

【請求項１】

平面状集電体の表面に電極構成物質層が形成されてなる正極及び負極を備える非水電解液二次電池において、

負極の平面状集電体は、銅を電解析出して形成される電解銅箔からなり、

上記電解銅箔は、マット面の表面粗さが１０点平均粗さにして３．０μｍより小さく、このマット面と反対側の光沢面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さいことを特徴とする非水電解液二次電池。

【請求項２】

非水電解液二次電池の負極を構成する平面状集電体であって、

当該平面状集電体は、銅を電解析出して形成される電解銅箔からなり、

上記電解銅箔は、マット面の表面粗さが１０点平均粗さにして３．０μｍより小さく、このマット面と反対側の光沢面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さいことを特徴とする平面状集電体。

【請求項３】

上記電解銅箔の少なくとも一方の面が、防錆被膜によって被覆されていることを特徴とする請求項１記載の非水電解液二次電池。

【請求項４】

上記電解銅箔の少なくとも一方の面が、シランカップリング剤によって被覆されていることを特徴とする請求項１記載の非水電解液二次電池。

【発明の詳細な説明】
【０００１】
【発明の属する技術分野】
本発明は、平面状集電体の表面に電極構成物質層が形成されてなる電極を備える非水電解液二次電池に関し、特に平面状集電体の改良に関するものである。
【０００２】
【従来の技術】
近年の電子技術のめざましい進歩により、電子機器の小型化、軽量化、高性能化が進み、これら電子機器には、エネルギー密度の高い二次電池が要求されている。従来、これら電子機器に使用される二次電池としてニッケル・カドミウム電池や鉛電池などが挙げられるが、これら電池では、エネルギー密度が高い電池を得るという点で不十分であった。
【０００３】
このような状況下で、正極としてリチウムコバルト複合酸化物などのリチウム複合酸化物を使用し、負極として炭素材料などのようなリチウムイオンをドープ及び脱ドープ可能な物質を使用した非水電解液二次電池、いわゆるリチウムイオン二次電池の研究・開発が行われている。このリチウムイオン二次電池は、高エネルギー密度を有し、自己放電も少なく、サイクル特性に優れ、かつ軽量という優れた特性を有する。
【０００４】
ところで、上記リチウムイオン二次電池の集電体としては、一般に金属箔が使用されている。特に、銅からなる金属箔は、リチウム金属と合金を形成しない、電気伝導性が良い、低コストといった特徴を有するため、負極集電体として多用されている。この銅箔には、一般に、銅板を機械的にローラ圧延した、いわゆる厚み１０～３０μｍの圧延銅箔が使用されている。しかしながら、圧延銅箔は、圧延装置のサイズの規制から、幅の広いものを得るのが難しい。
【０００５】
一方、銅の電解析出によって形成される、いわゆる電解銅箔は、圧延銅箔に比べ比較的幅の広いものも容易に得られる。また、この電解銅箔をリチウムイオン二次電池の負極集電体に使用した場合には、生産性が飛躍的に向上し、電池生産のコストを大幅に下げることができる。
【０００６】
【発明が解決しようとする課題】
しかしながら、市販の電解銅箔を負極集電体に使用したリチウムイオン二次電池においては、電池特性、特に充放電でのサイクル特性が悪く、使用することができなかった。
【０００７】
そこで、本発明者らが鋭意検討を重ねた結果、上述した問題は、電解金属箔の一方の主面に大きな凹凸が形成されて、電解金属箔の両主面の表面粗さの差が大きすぎるために生じていることがわかった。
【０００８】
これまで電解金属箔は、一般にその用途が主にプリント基板、フレキシブル基板であり、プラスチックとの密着性を良くするために（アンカー効果をねらうために）、その主面に大きな凹凸を形成していた。そのため、この電解金属箔を非水電解液二次電池の集電体に用いた場合には、活物質表面に沿った変形が十分に起こらないため、活物質と集電体の接触が悪く、容量の劣化やサイクル特性の低下が生じていた。
【０００９】
本発明は、上述のような問題点を解決するために提案されたものであり、活物質表面に沿って集電体が十分に変形し、活物質と集電体の接触性を良好に保って、充放電サイクルに優れた安価な非水電解液二次電池及び非水電解液二次電池用の平面状集電体を提供することを目的とする。
【００１０】
【課題を解決するための手段】

本発明に係る非水電解液二次電池は、平面状集電体の表面に電極構成物質層が形成されてなる正極及び負極を備える非水電解液二次電池において、負極の平面状集電体が、銅を電解析出して形成される電解銅箔からなり、上記電解銅箔が、マット面の表面粗さが１０点平均粗さにして３．０μｍより小さく、このマット面と反対側の光沢面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さいことを特徴とする。

【００１１】

また、本発明は、非水電解液二次電池の負極を構成する平面状集電体であって、当該平面状集電体が、銅を電解析出して形成される電解銅箔からなり、上記電解銅箔が、マット面の表面粗さが１０点平均粗さにして３．０μｍより小さく、このマット面と反対側の光沢面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さいことを特徴とする。

【００１２】

本発明に係る非水電解液二次電池においては、上記平面状集電体の負極に、銅の電解析出から形成される電解銅箔を用いたことから、製造上の大きさの制約がなく、電池生産のコストを下げることができる。

また、本発明に係る非水電解液二次電池においては、集電体である電解銅箔のマット面の表面粗さが１０点平均粗さにして３．０μｍより小さく、このマット面と反対側の光沢面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さいことから、集電体と活物質との接触性が良く、電気伝導度が大きくなって、充放電サイクルに優れたものとなる。

【００１３】

一般に、平面状集電体の表面に電極構成物質層が形成されてなる電極は、活物質とバインダーとを含有する電極構成物質層が集電体の表面に塗布され、その後ロール圧延等でプレスされて作製される。このプレス工程は、電極を所定の密度に圧縮する作用と、適切な導電性を有するように活物質粒子間を接近させる作用とを有する。プレス工程を経た電極は、活物質粒子間、及び活物質と集電体との接触性が良くなり、電気伝導度が大きくなる。

【００１４】

さらに、十分な電池特性を得るには、活物質粒子間、及び活物質と集電体の距離を小さくすると共に、集電体の形状が活物質表面の形状に沿って変形することが重要である。活物質表面に沿って集電体が変形した場合には、活物質と集電体との接触性がさらに良くなり、電気伝導度がさらに大きくなり、望ましい電池特性が得られる。

【００１５】

しかし、活物質表面に沿って集電体が変形しない場合には、活物質と集電体の接触部分が少なくなり、電気伝導度が小さい。また、集電体表面の凹凸が大きい場合には、活物質と集電体の接触点も少ない。このような接触抵抗が大きい電極は、充放電を繰り返すと、活物質の充放電に伴う膨張収縮によるストレスや、接着剤であるバインダーの電解液への溶解などによって、集電体と活物質との距離が段々と大きくなり、一部の活物質が充放電に利用できない電気伝導度になって容量の劣化が起きる。

【００１６】

したがって、この電解銅箔のマット面の表面粗さが１０点平均粗さにして３．０μｍより大きい場合、或いは光沢面との表面粗さとの差が１０点平均粗さにして２．５μｍより大きい場合には、活物質が負極集電体に塗布されてプレスされる際に、集電体が活物質の表面に沿った変形が十分起こらず、また、表面の凹凸が大きいために活物質との接触点が少なく、充放電に伴って容量の劣化が起きて十分な電池特性が得られない。

【００１７】

【発明の実施の形態】

本発明に係る非水電解液二次電池は、平面状集電体の表面に電極構成物質層が形成されてなる電極を備えて構成され、上記平面状集電体の少なくとも負極が銅の電解析出から形成される電解銅箔からなる。そして、この電解銅箔は、一方の主面であるマット面の表面粗さが１０点平均粗さにして３．０μｍより小さく、このマット面とは反対側の他方の主

面である光沢面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さく形成される。

【００１８】

なお、一般に、電解銅箔は、銅を主成分とする溶液を電解液とし、回転ドラムを電極として、ドラム表面に形成される。この時、形成された電解銅箔は、ドラム側の主面を光沢面と称し、電解液側のもう一方の主面をマット面と称す。

【００１９】

上記電解銅箔は、表面の凹凸が小さく、マット面と光沢面との表面粗さの差が小さいため、プレス工程時に活物質表面に沿った変形が十分に起こり、活物質との接触性が良好に保たれる。

【００２０】

なお、上述する表面粗さは、ＪＩＳ規格Ｂ０６０１において、１０点平均線粗さ（R_Z）についての定義がなされている。１０点平均粗さ（R_Z）は、図１に示すように、断面曲線から基準長さＬだけだけ抜き取った部分の平均線から縦倍率の方向に測定した、最も高い山頂から５番目までの山頂の標高（Y_p）の絶対値の平均値（$|Y_{p1}+Y_{p2}+Y_{p3}+Y_{p4}+Y_{p5}|/5$）と、最も低い谷底から５番目までの谷底の標高（$Y_v$）の絶対値の平均値（$|Y_{v1}+Y_{v2}+Y_{v3}+Y_{v4}+Y_{v5}|/5$）との和を求めたものである。

【００２１】

本発明は、電池を構成する物質について特に限定するものではないが、正極が少なくともリチウムを含む金属酸化物からなり、負極がリチウムをドープ及び脱ドープ可能な負極とからなるようないわゆるリチウムイオン二次電池において好適である。

【００２２】

また、本発明に係るリチウムイオン二次電池に用いられる負極集電体には、電解銅箔が用いられる。電解銅箔は、リチウム金属と合金を形成することがなく、電気伝導性が良く、低コストで生産できるなどの種々の利点を有している。

【００２３】

上記電解銅箔の少なくとも一方の面には、銅箔の酸化を抑制するために、防錆被膜が被覆されていてもよい。また、上記電解銅箔の少なくとも一方の面には、銅箔表面と活物質との吸着性を向上させるために、シランカップリング剤からなる膜が被覆されていてもよい。

【００２４】

なお、上記リチウムイオン二次電池において、正極活物質としては、Li_xMO_2（但し、Ｍは、１種類以上の遷移金属を表す。ｘは、リチウムの組成比である。）を含んだ活物質が使用可能である。かかる活物質としては、Li_xCoO_2、Li_xNiO_2、$Li_xMn_2O_4$、Li_xMnO_3、$Li_xNi_yCo_{(1-y)}O_2$などの複合酸化物が挙げられる。

【００２５】

上記複合酸化物は、例えば、リチウム、コバルト、ニッケルの炭酸塩を出発原料とし、これら炭酸塩を組成に応じて混合し、酸素存在雰囲気下６００℃～１０００℃の温度範囲で焼成することにより得られる。また、出発原料は、炭酸塩に限定されず、水酸化物、酸化物からも同様に合成可能である。

【００２６】

一方、負極活物質としては、リチウムをドープ及び脱ドープ可能なものであれば良く、熱分解炭素類、コークス類（ピッチコークス、ニードルコークス、石油コークスなど）、グラファイト類、ガラス状炭素類、有機高分子化合物焼成体（フェノール樹脂、フラン樹脂などを適当な温度で焼成し炭素化したもの）、炭素繊維、活性炭などの炭素質材料、あるいは、金属リチウム、リチウム合金（例えば、リチウムーアルミ合金）の他、ポリアセチレン、ポリピロールなどのポリマーも使用可能である。

【００２７】

電解液には、リチウム塩を電解質とし、これを有機溶媒に溶解させた電解液が用いられる。ここで有機溶媒としては、特に限定されるものではないが、例えば、プロピレンカーボ

ネート、エチレンカーボネート、１，２－ジメトキシエタン、γ－ブチロラクトン、テトラヒドロフラン、２－メチルテトラヒドロフラン、１，３－ジオキソラン、スルホラン、アセトニトリル、ジエチルカーボネート、ジプロピルカーボネートなどの単独もしくは２種類以上の混合溶媒の使用が可能である。

【００２８】

電解質には、$LiClO_4$、$LiAsF_6$、$LiPF_6$、$LiBF_4$、$LiB(C_6H_5)_4$、LiCl、LiBr、CH_3SO_3Li、CF_3SO_3Liなどの使用が可能である。

【００２９】

【実施例】

以下、本発明を適用した非水電解液二次電池について、好適な実施例を図面を参照しながら説明する。なお、本発明は、本実施例に限定されるものではないことは言うまでもない。

【００３０】

実施例１

本実施例で作製したリチウムイオン二次電池は、図２に示すように、正極集電体１に正極活物質２を塗布してなる正極３と、負極集電体４に負極活物質５を塗布してなる負極６とから構成される。そして、この非水電解液二次電池は、正極３、セパレータ７、負極６、セパレータ７をこの順に積層して積層電極体とし、この積層電極体を多数回巻回されてなる渦巻式電極体の上下に絶縁体８、９を配置した状態で電池缶１０に収納してなるものである。

【００３１】

先ず始めに、電解銅箔からなる負極集電体４は、次のようにして作製した。組成１で示される硫酸銅溶液を電解液として、貴金属酸化物被覆チタンを陽極に、チタン製回転ドラムを陰極として、電流密度５０Ａ／ｄｍ２、液温５０℃の条件で電解することによって、厚み１２μｍの電解銅箔を得た。この電解銅箔の表面粗さについては、後述する測定法により測定し、表１に示した。

【００３２】

（組成１）

硫酸銅（$CuSO_4 \cdot 5H_2O$）	３５０ｇ／ｌ
硫酸（H_2SO_4）	１１０ｇ／ｌ
チオ尿素	０．４ｐｐｍ
アラビアゴム	０．８ｐｐｍ
低分子量膠（分子量５０００）	０．４ｐｐｍ
Cl^-	３０ｐｐｍ

次いで、この電解銅箔をCrO_3；１ｇ／ｌ水溶液に５秒間浸漬して、クロメート処理を施し、水洗後乾燥させた。なお、ここでは、クロメート処理を行ったが、ベンゾトリアゾール系処理、或いはシランカップリング剤処理、又はクロメート処理後にシランカップリング剤処理を行ってもよいことは勿論である。

【００３３】

そして、負極６は次のようにして作製した。負極活物質５としては、出発原料として石油ピッチを用い、これを焼成して粗粒状のピッチコークスを得た。この粗粒状ピッチコークスを粉砕して平均粒径２０μｍの粉末とし、この粉末を不活性ガス中、１０００℃にて焼成して不純物を除去し、コークス材料粉末を得た。

【００３４】

このようにして得られたコークス材料粉末を９０重量部、結着材としてポリフッ化ビニリデンを１０重量部の割合で混合して負極合剤を調整した。次いで、この負極合剤を溶剤であるＮ－メチルピロリドンに分散させてスラリーにした。そして、このスラリーを上述した厚さ１２μｍの帯状の電解銅箔である負極集電体４の両面に塗布し、乾燥後ローラプレス機で圧縮形成して、帯状負極６を得た。この帯状負極６は、成形後の負極合剤の膜厚が両面共に９０μｍで同一であり、その幅が５５．６ｍｍ、長さが５５１．５ｍｍに形成

される。

【００３５】

次に、正極３は、次にようにして作製した。正極活物質（$LiCoO_2$）２は、炭酸リチウム０．５モルと炭酸コバルト１モルと混合し、空気中で９００℃、５時間焼成して$LiCoO_2$を得た。

【００３６】

このようにして得られた正極活物質（$LiCoO_2$）２を９１重量％、導電剤としてグラファイトを６重量％、結着剤としてポリフッ化ビニリデンを３重量％の割合で混合して正極合材を作製し、これをＮ－メチル－２ピロリドンに分散してスラリー状とした。次に、このスラリーを厚み２０μｍの帯状のアルミニウムからなる正極集電体の両面に均一に塗布し、乾燥後ローラープレス機で圧縮成形して厚み１６０μｍの帯状正極３を得た。この帯状正極３は、成形後の正極合剤の膜厚が表面共に７０μｍであり、その幅が５３．６ｍｍ、長さが５２３．５ｍｍに形成される。

【００３７】

このようにして作製された帯状正極３と、帯状負極６と、厚さが２５μｍ、幅が５８．１ｍｍの微多孔性ポリプロピレンフィルムよりなるセパレータ７とを、上述したように積層し、これを積層電極体とした。この積層電極体は、その長さ方向に沿って負極６を内側にして渦巻型に多数回巻回され、最外周セパレータの最終端部をテープで固定されて、渦巻式電極体となる。この渦巻式電極体の中空部分は、その内径が、３．５ｍｍ、外形が１７ｍｍに形成される。

【００３８】

上述のように作製された渦巻式電極体を、その上下両面に絶縁板８、９が設置された状態で、ニッケルメッキが施された鉄製の電池缶１０に収納した。そして、正極３及び負極６の集電を行うために、アルミニウム製の正極リード１３を正極集電体１から導出して電池蓋１１に接続し、ニッケル製の負極リード１４を負極集電体４から導出して電池缶１０に接続した。

【００３９】

そして、この渦巻式電極体が収納された電池缶１０に、プロピレンカーボネイトとジエチルカーボネイトとの等容量混合溶媒中に$LiPF_6$を１モル／１の割合で溶解した非水電解液５．０ｇを注入した。次いで、アスファルトで表面を塗布された絶縁封口ガスケット１２を介して電池缶１０をかしめることにより、電池蓋１１を固定し、電池缶１０内の気密性を保持させた。

【００４０】

以上のようにして、直径１８ｍｍ、高さ６５ｍｍの円筒形非水電解液二次電池（実施例１）を作製した。

【００４１】

実施例２

先ず始めに、電解銅箔からなる負極集電体４は次のようにして作製した。組成２で示される硫酸銅溶液を電解液として、貴金属酸化物被覆チタンを陽極に、チタン製回転ドラムを陰極として、電流密度５０Ａ／ｄｍ２、液温５０℃の条件で電解することによって、厚み１２μｍの電解銅箔を作成し、この電解箔にクロメート処理を行った。なお、この電解銅箔の表面粗さについては、後述する測定方法により測定し、表１に示した。

【００４２】

（組成２）

硫酸銅（$CuSO_4 \cdot 5H_2O$）	３５０ｇ／ｌ
硫酸（H_2SO_4）	１１０ｇ／ｌ
１－メルカプト３－プロパンスルホン酸ナトリウム	１ｐｐｍ
ヒドロキシエチルセルロース	４ｐｐｍ
低分子量膠（分子量３０００）	４ｐｐｍ
Cl^-	３０ｐｐｍ

上述した電解金属箔を使用した以外は、実施例１と同様にして円筒形非水電解液二次電池（実施例２）を作製した。

【００４３】

実施例３

先ず始めに、電解銅箔からなる負極集電体４は次のようにして作製した。組成３で示される硫酸銅溶液を電解液として、貴金属酸化物被覆チタンを陽極に、チタン製回転ドラムを陰極として、電流密度５０Ａ／ｄｍ^2、液温５８℃の条件で電解することによって、厚み９μｍの電解銅箔を得た。

【００４４】

（組成３）

硫酸銅（ＣｕＳＯ４・５Ｈ２Ｏ）	３５０ｇ／ｌ
硫酸（Ｈ２ＳＯ４）	１１０ｇ／ｌ
膠（分子量６００００）	２ｐｐｍ
Ｃｌ－	３０ｐｐｍ

この電解銅箔の表面粗さは、後述する測定方法により測定した結果、光沢面がＲＺ＝２．００μｍ、マット面がＲＺ＝３．５２μｍであった。

【００４５】

次いで、この電解銅箔に、組成４で示される電解液からなる銅電解浴を用いて、電流密度６Ａ／ｄｍ２、液温５８℃でマット面に光沢銅メッキを施し、この電解銅箔の表面粗さを後述する測定方法により測定し、表１に示した。なお、本発明では、マット面に光沢銅メッキを施した面もマット面と表現する。そして、この銅メッキが施された電解銅箔に同様にクロメート処理を施した。

【００４６】

（組成４）

硫酸銅（$CuSO_4 \cdot 5H_2O$）	２４０ｇ／ｌ
硫酸（H_2SO_4）	６０ｇ／ｌ
膠	２ｐｐｍ
日本シェーリング（株）製カバシラド２１０	
メイキャップ剤	１０ｃｃ／ｌ
光沢剤（Ａ）	０．５ｃｃ／ｌ
光沢剤（Ｂ）	補充にのみ使用
Cl^-	３０ｐｐｍ

光沢剤の補充は、電流量１０００Ａｈに対して光沢剤（Ａ）及び光沢剤（Ｂ）を各々３００ｃｃ添加した。

【００４７】

上述した電解銅箔を使用した以外は、実施例１と同様にして円筒形非水電解液二次電池（実施例３）を作製した。

【００４８】

比較例１

先ず始めに、電解銅箔からなる負極集電体４は次のようにして作製した。組成５で示される硫酸銅溶液を電解液として、貴金属酸化物被覆チタンを陽極に、チタン製回転ドラムを陰極として、電流密度５０Ａ／ｄｍ２、液温５８℃の条件で電解することによって、厚み１２μｍの電解銅箔を作成し、この電解銅箔の表面粗さを後述する測定方法により測定し、表１に示した。そして、この電解銅箔にクロメート処理を行った。

【００４９】

（組成５）

硫酸銅（$CuSO_4 \cdot 5H_2O$）	３５０ｇ／ｌ
硫酸（H_2SO_4）	１１０ｇ／ｌ
膠	２ｐｐｍ
Cl^-	３０ｐｐｍ

上述した電解銅箔を使用した以外は、実施例１と同様にして円筒形非水電解液二次電池（比較例１）を作製した。

【００５０】

そして、実施例１～実施例３及び比較例１で得られた電解銅箔において、その表面粗さ（１０点平均粗さR_z）を表面粗さ計（株式会社小坂研究所製ＳＥ－３Ｃ型）で調べた。この結果を表１に示す。なお、光沢面の表面粗さを測定する際には、基準長さＬを０．８ｍｍとし、マット面の表面粗さを測定する際には、基準長さＬを２．５ｍｍとした。

【００５１】

【表１】

		表面粗さ(μm)
実施例１	光沢面	1.58
	マット面	2.10
実施例２	光沢面	1.60
	マット面	1.32
実施例３	光沢面	2.00
	マット面	0.70
比較例１	光沢面	1.93
	マット面	3.7

【００５２】

また、それぞれの電解銅箔を負極集電体に用いた実施例１～実施例３及び比較例１の円筒形非水電解液二次電池について、１００サイクル後の容量維持率を調べた。その結果を図３、図４及び表２に示す。

【００５３】

さらに、それぞれの電解銅箔を負極集電体に用いた実施例１～実施例３及び比較例１の円筒形非水電解液二次電池について、１００サイクル前後のインピーダンスの変化を調べた。その結果を図５、図６及び表２に示す。

【００５４】

【表２】

	100サイクル後の容量維持率(%)	インピーダンス(mΩ) 100サイクル前/後
実施例１	85	108/190
実施例２	90	105/183
実施例３	70	112/220
比較例１	60	119/242

【００５５】

図３、図５及び表２に示すように、マット面の表面粗さが３μｍ以上になると容量維持率が大幅に低下し、インピーダンスの変化が大きくなるため、マット面の表面粗さは、３μｍ未満が好ましい。また、図４及び図６に示すように、マット面と光沢面との表面粗さの

差が大きくなるほど容量維持率が低くなり、インピーダンスが大きくなっている。このことから、マット面と光沢面との表面粗さの差は、２．５μｍ未満であることが好ましい。

【００５６】

また、電解銅箔のマット面の粗さは、実施例１及び実施例２のように、最初の電解条件によって規制してもよいし、実施例３のように、銅メッキを後から施して規制してもよい。

【００５７】

以上のことから、上述した非水電解液二次電池においては、圧延銅箔に比べ製造上大きさの制約がなく、生産性が高い電解銅箔を負極集電体に用いていることから、生産性が向上し、電池生産コストを大幅に下げることができる。

【００５８】

さらに、上述した非水電解液二次電池においては、集電体である電解銅箔の一方の面であるマット面の表面粗さが３．０μｍより小さく、光沢面とマット面との表面粗さとの差が２．５μｍより小さいことから、集電体と活物質との接触性が良く、電気伝導度が大きくなって、充放電サイクルに優れたものとなる。

【００５９】

【発明の効果】

以上の説明からも明らかなように、本発明に係る非水電解液二次電池は、集電体に銅を電解析出して形成される電解銅箔を用いてなることから、電池の生産性を向上させ、電池生産のコストを下げることができる。

【００６０】

また、この電解銅箔は、一方の面であるマット面の表面粗さが１０点平均粗さにして３．０μｍより小さく、このマット面と反対側の光沢面との表面粗さとの差が１０点平均粗さにして２．５μｍより小さく形成される。このことから、本発明に係る非水電解液二次電池においては、集電体と活物質との接触性が良く、電気伝導度が大きくなって、充放電サイクルに優れたものとなる。

【図面の簡単な説明】

【図１】１０点平均粗さ（R_z）の定義を説明するための断面図である。

【図２】本発明を適用した円筒形非水電解液二次電池の概略断面図である。

【図３】上記円筒形非水電解液二次電池において、電解銅箔のマット面の表面粗さと容量維持率との関係を示す特性図である。

【図４】上記円筒形非水電解液二次電池において、電解銅箔のマット面と光沢面との表面粗さの差と、容量維持率との関係を示す特性図である。

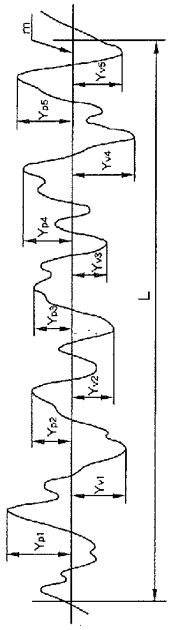
【図５】上記円筒形非水電解液二次電池において、電解銅箔のマット面の表面粗さと１００サイクル後のインピーダンスとの関係を示す特性図である。

【図６】上記円筒形非水電解液二次電池において、電解銅箔のマット面と光沢面との表面粗さの差と、１００サイクル後のインピーダンスとの関係を示す特性図である。

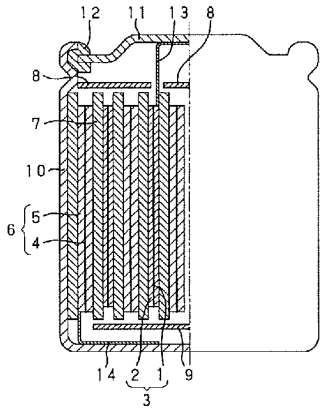
【符号の説明】

１　正極集電体、２　正極活物質、３　正極、４　負極集電体、５　負極活物質、６　負極、７　セパレータ、８　絶縁体、９　絶縁体、１０　電池缶、１１　電池蓋、１２　絶縁封口ガスケット、１３　正極リード、１４　負極リード、

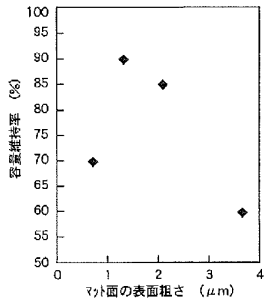
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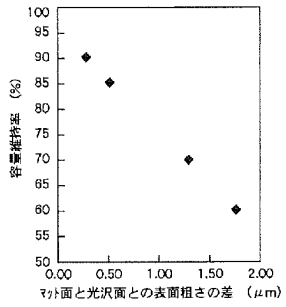
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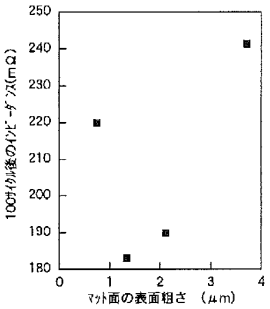
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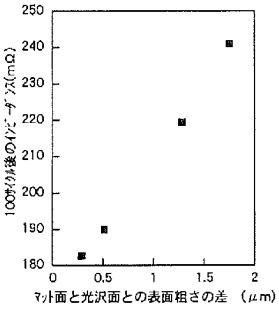
【図４】



【図５】



【図６】



フロントページの続き

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審査官 青木 千歌子

(56)参考文献 特開平０６－２６０１６８（ＪＰ，Ａ）

(58)調査した分野(Int.Cl., ＤＢ名)
H01M 4/64-4/84

Docket No.
001333-0037

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: **KIM, Dae-Young** Group Art Unit: **1784**

Application No.: **13/722,585** Examiner: **Lam, Cathy F.F.**

Filed: **December 20, 2012**

For: **COPPER FOIL FOR CURERNT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS**

Date: **August 21, 2014**

INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In compliance with the duty of disclosure under 37 C.F.R. § 1.56 and in accordance with the practice under 37 C.F.R. §§ 1.97 and 1.98, the Examiner's attention is directed to the documents listed on the enclosed Information Disclosure Statement by Applicant form (PTO/SB/08A and/or B, PTO-1449, or equivalent).

The following checked sections apply to this Information Disclosure Statement:

☒ In accordance with 37 C.F.R. § 1.98(a)(2)(ii) as revised at 69 Fed. Reg. 56481 (September 21, 2004), copies of the cited U.S. patent application publication(s) and/or U.S. patent(s) have not been submitted.

☐ The cited reference(s) were called to Applicant'(s) attention in a counterpart foreign patent application. A copy of the official communication in that counterpart foreign patent application citing the reference(s) is submitted herewith, and the Examiner is respectfully directed thereto for a concise explanation of the relevance of the cited art.

☒ At least some of the cited references are not (or the cited reference is not) in English, and so English abstracts of those references (that reference) are provided, if available.

☐ At least some of the cited references are not (or the cited reference is not) in English, and so machine English translations of those references (that reference) are provided, where available.

☐ This Information Disclosure Statement is being filed (1) within three months of the filing date of a national application other than a continued prosecution application under Sec. 1.53(d), (2) within three months of the date of entry of the national stage as set forth in Sec. 1.491 in an international application, (3) before the mailing of a first Office action on the merits, or (4) before the mailing of a first Office action after the filing of a Request for Continued Examination under 37 C.F.R. § 1.114. Accordingly, neither a fee nor Statement under 37 C.F.R. § 1.97(e) is due.

☒ This Information Disclosure Statement is being filed before the mailing date of any of a final action under 37 C.F.R. § 1.113, a Notice of Allowance under 37 C.F.R. § 1.311, or an action that otherwise closes prosecution in the application, and so is accompanied by one of:

(1) A Statement under 37 C.F.R. § 1.97(e), which follows; **or**

(2) The fee set forth in 37 C.F.R. § 1.17(p), authorization for which follows.

☐ This Information Disclosure Statement is being filed either (1) on or after the mailing date of a final action under 37 C.F.R. § 1.113, or (2) on or before payment of the issue fee, and is accompanied by:

(1) A Statement under 37 C.F.R. § 1.97(e), which follows; **and**

(2) The fee set forth in 37 C.F.R. § 1.17(p), authorization for which follows.

☒ Fee Under 37 C.F.R. § 1.17(p)

The Commissioner is authorized to charge the fee under 37 C.F.R. § 1.17(p) ($180) to Deposit Account No. 19-4709.

☐ Statement Under 37 C.F.R. § 1.97(e)

Each item of information contained in this Information Disclosure Statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the Information Disclosure Statement; or

No item of information contained in the Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in Sec. 1.56(c) more than three months prior to the filing of the Information Disclosure Statement.

☐ Additional Comments

Applicant(s) have the following additional comments:

It is respectfully requested that the above information be considered by the Examiner and that an initialed copy of the accompanying Information Disclosure Statement by Applicant form (PTO/SB/08A and/or B, PTO-1449, or equivalent) be returned to the undersigned indicating that such information has been considered.

Other than any fees mentioned above, no fees are believed to be due in connection with this Information Disclosure Statement. Nevertheless, the Commissioner is authorized to charge any fees which are deemed to be now or hereafter due in connection with this paper to Deposit Account No. 19-4709.

Favorable consideration and prompt allowance of this application is respectfully requested. In the event that there are any questions, or should additional information be required, please contact Applicant'(s) attorney at the number listed below.

Respectfully submitted,

/Brian M. Rothery/

Brian M. Rothery
Reg. No. **35,340**
Attorney for Applicant(s)
Stroock & Stroock & Lavan, LLP
180 Maiden Lane
New York, New York 10038
(212) 806-5400

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
13/722,585	12/20/2012	Dae-Young KIM	001333-0037

CONFIRMATION NO. 8652

26610
STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

POA ACCEPTANCE LETTER

OC000000070194627

Date Mailed: 08/15/2014

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 08/11/2014.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

/hteffera/

Office of Data Management, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

Application Number	Application/Control No.	Applicant(s)/Patent under Reexamination	
	13/722,585	KIM ET AL.	

Document Code - DISQ	Internal Document – DO NOT MAIL

TERMINAL DISCLAIMER	☒ APPROVED	☐ DISAPPROVED
Date Filed : 8/11/14	**This patent is subject to a Terminal Disclaimer**	

Approved/Disapproved by:

Felicia D. Roberts

8,349,518

U.S. Patent and Trademark Office

Doc Code: PA..
Document Description: Power of Attorney

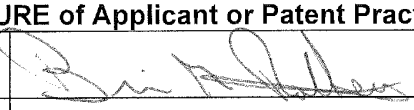
PTO/AIA/82A (07-13)
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NOTE: This form is to be submitted with the Power of Attorney by Applicant form (PTO/AIA/82B) to identify the application to which the Power of Attorney is directed, in accordance with 37 CFR 1.5, unless the application number and filing date are identified in the Power of Attorney by Applicant form. If neither form PTO/AIA/82A nor form PTO/AIA82B identifies the application to which the Power of Attorney is directed, the Power of Attorney will not be recognized in the application.

Application Number	13/722,585
Filing Date	December 20, 2012
First Named Inventor	Kim, Dae-Young et al.
Title	Copper Foil For Current Collector of Lithium secondary battery With Improved Wrinkle Characteristics
Art Unit	1784
Examiner Name	Lam, Cathy F.F.
Attorney Docket Number	001333/0037

SIGNATURE of Applicant or Patent Practitioner

Signature		Date (Optional)	2014-08-11
Name	Brian M. Rothery	Registration Number	35,340
Title (if Applicant is a juristic entity)			
Applicant Name (if Applicant is a juristic entity)			

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. If more than one applicant, use multiple forms.

☑ *Total of 1 forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82B (07-13)
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POWER OF ATTORNEY BY APPLICANT

I hereby revoke all previous powers of attorney given in the application identified in either the attached transmittal letter or the boxes below.

Application Number	Filing Date
13/722,585	December 20, 2012

(Note: The boxes above may be left blank if information is provided on form PTO/AIA/82A.)

☑ I hereby appoint the Patent Practitioner(s) associated with the following Customer Number as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above: 26610

OR

☐ I hereby appoint Practitioner(s) named in the attached list (form PTO/AIA/82C) as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the patent application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above. (Note: Complete form PTO/AIA/82C.)

Please recognize or change the correspondence address for the application identified in the attached transmittal letter or the boxes above to:

☑ The address associated with the above-mentioned Customer Number

OR

☐ The address associated with Customer Number:

OR

Firm or Individual Name					
Address					
City		State		Zip	
Country					
Telephone		Email			

I am the Applicant (if the Applicant is a juristic entity, list the Applicant name in the box):

LS MTRON LTD.

☐ Inventor or Joint Inventor (title not required below)

☐ Legal Representative of a Deceased or Legally Incapacitated Inventor (title not required below)

☑ Assignee or Person to Whom the Inventor is Under an Obligation to Assign (provide signer's title if applicant is a juristic entity)

☐ Person Who Otherwise Shows Sufficient Proprietary Interest (e.g., a petition under 37 CFR 1.46(b)(2) was granted in the application or is concurrently being filed with this document) (provide signer's title if applicant is a juristic entity)

SIGNATURE of Applicant for Patent

The undersigned (whose title is supplied below) is authorized to act on behalf of the applicant (e.g., where the applicant is a juristic entity).

Signature		Date (Optional)	August 7, 2014
Name	KIM, YOUNG HWAN		
Title	Intellectual Property Team Leader, LS MTRON LTD.		

NOTE: Signature - This form must be signed by the applicant in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. If more than one applicant, use multiple forms.

☑ Total of 1 forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Electronic Acknowledgement Receipt

EFS ID:	19825555
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	26610
Filer:	Brian M. Rothery/ERICA GODLEWSKI
Filer Authorized By:	Brian M. Rothery
Attorney Docket Number:	001333-0037
Receipt Date:	11-AUG-2014
Filing Date:	20-DEC-2012
Time Stamp:	11:28:17
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Power of Attorney	POA.pdf	287040 c396d5b04724ca1bcd12a896fb899efd55fe963e	no	2
Warnings:					
Information:					

Total Files Size (in bytes):	287040

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/AIA/26 (04-14)
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TERMINAL DISCLAIMER TO OBVIATE A DOUBLE PATENTING REJECTION OVER A "PRIOR" PATENT	Docket Number (Optional) 001333/0037

In re Application of: Dae-Young KIM

Application No.: 13/722,585

Filed: December 20, 2012

For: COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

The applicant, LS MTRON LTD., owner of 100 percent interest in the instant application hereby disclaims, except as provided below, the terminal part of the statutory term of any patent granted on the instant application which would extend beyond the expiration date of the full statutory term of **prior patent** No. 8,349,518 as the term of said **prior patent** is presently shortened by any terminal disclaimer. The applicant hereby agrees that any patent so granted on the instant application shall be enforceable only for and during such period that it and the **prior patent** are commonly owned. This agreement runs with any patent granted on the instant application and is binding upon the grantee, its successors or assigns.

In making the above disclaimer, the applicant does not disclaim the terminal part of the term of any patent granted on the instant application that would extend to the expiration date of the full statutory term of the **prior patent**, "as the term of said **prior patent** is presently shortened by any terminal disclaimer," in the event that said **prior patent** later:

expires for failure to pay a maintenance fee;
is held unenforceable;
is found invalid by a court of competent jurisdiction;
is statutorily disclaimed in whole or terminally disclaimed under 37 CFR 1.321;
has all claims canceled by a reexamination certificate;
is reissued; or
is in any manner terminated prior to the expiration of its full statutory term as presently shortened by any terminal disclaimer.

Check either box 1 or 2 below, if appropriate.

1. ☐ The undersigned is the applicant. If the applicant is an assignee, the undersigned is authorized to act on behalf of the assignee.

I hereby acknowledge that any willful false statements made are punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

2. ☑ The undersigned is an attorney or agent of record. Reg. No. 35,340

/Brian M. Rothery/ — Signature
August 11, 2014 — Date

Brian M. Rothery — Typed or printed name

Title
Telephone Number

☑ Terminal disclaimer fee under 37 CFR 1.20(d) included.

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

This collection of information is required by 37 CFR 1.321. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Privacy Act Statement

The **Privacy Act of 1974** (**P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PTO/AIA/96 (08-12)
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STATEMENT UNDER 37 CFR 3.73(c)

Applicant/Patent Owner: Dae-Young KIM

Application No./Patent No.: 13/722,585 Filed/Issue Date: December 20, 2012

Titled: COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

LS MTRON LTD., a corporation

(Name of Assignee) (Type of Assignee, e.g., corporation, partnership, university, government agency, etc.)

states that, for the patent application/patent identified above, it is (choose **one** of options 1, 2, 3 or 4 below):

1. ☑ The assignee of the entire right, title, and interest.

2. ☐ An assignee of less than the entire right, title, and interest (check applicable box):

   ☐ The extent (by percentage) of its ownership interest is _____%. Additional Statement(s) by the owners holding the balance of the interest must be submitted to account for 100% of the ownership interest.

   ☐ There are unspecified percentages of ownership. The other parties, including inventors, who together own the entire right, title and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

3. ☐ The assignee of an undivided interest in the entirety (a complete assignment from one of the joint inventors was made). The other parties, including inventors, who together own the entire right, title, and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

4. ☐ The recipient, via a court proceeding or the like (*e.g.*, bankruptcy, probate), of an undivided interest in the entirety (a complete transfer of ownership interest was made). The certified document(s) showing the transfer is attached.

The interest identified in option 1, 2 or 3 above (not option 4) is evidenced by either (choose **one** of options A or B below):

A. ☑ An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in the United States Patent and Trademark Office at Reel 0030038, Frame 0382, or for which a copy thereof is attached.

B. ☐ A chain of title from the inventor(s), of the patent application/patent identified above, to the current assignee as follows:

   1. From: _____ To: _____

      The document was recorded in the United States Patent and Trademark Office at

      Reel _____, Frame _____, or for which a copy thereof is attached.

   2. From: _____ To: _____

      The document was recorded in the United States Patent and Trademark Office at

      Reel _____, Frame _____, or for which a copy thereof is attached.

This collection of information is required by37 CFR3.73(b). The information is required toobtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentialityis governed by35 U.S.C. 122and 37 CFR1.11 and1.14. Thiscollection is estimated to take 12 minutes to complete, including gathering, preparing, and submittingthe completed application form to the USPTO.Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent tothe Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS.**SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PTO/AIA/96 (08-12)
Approved for use through 01/31/2013. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

STATEMENT UNDER 37 CFR 3.73(c)

3. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

4. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

5. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

6. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

☐ Additional documents in the chain of title are listed on a supplemental sheet(s).

☐ As required by 37 CFR 3.73(c)(1)(i), the documentary evidence of the chain of title from the original owner to the assignee was, or concurrently is being, submitted for recordation pursuant to 37 CFR 3.11.

[NOTE: A separate copy (i.e., a true copy of the original assignment document(s)) must be submitted to Assignment Division in accordance with 37 CFR Part 3, to record the assignment in the records of the USPTO. See MPEP 302.08]

The undersigned (whose title is supplied below) is authorized to act on behalf of the assignee.

/Brian M. Rothery/	August 11, 2014
Signature	Date
Brian M. Rothery	35,340
Printed or Typed Name	Title or Registration Number

[Page 2 of 2]

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that yoube given certain informationin connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, pleasebe advised that: (1) the general authority forthe collection of thisinformation is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and(3) the principal purpose forwhich the information isused by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent applicationor patent. If you do not furnish the requested information,the U.S. Patent and Trademark Office may not be able to process and/or examineyour submission,which may result in termination of proceedings or abandonment of the applicationor expiration of the patent.

The informationprovided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the informationin order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an InternationalApplication filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, arecord may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from thissystem of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt

EFS ID:	19829582
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	26610
Filer:	Brian M. Rothery/ERICA GODLEWSKI
Filer Authorized By:	Brian M. Rothery
Attorney Docket Number:	001333-0037
Receipt Date:	11-AUG-2014
Filing Date:	20-DEC-2012
Time Stamp:	14:52:37
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Terminal Disclaimer Filed	TermDisclaimer.pdf	160126 a9b93bf91e5ec37259247017790da8e4ec56c191	no	2

Warnings:	
Information:	

2	Assignee showing of ownership per 37 CFR 3.73.	STatement373C.pdf	118130 1135a8a4d4cf595734c82dc2325efef1dc73cab4	no	3

Warnings:	
Information:	
Total Files Size (in bytes):	278256

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Application Number	Application/Control No.	Applicant(s)/Patent under Reexamination	
	13/722,585	KIM ET AL.	

Document Code - DISQ	Internal Document – DO NOT MAIL

TERMINAL DISCLAIMER	☐ APPROVED	☒ DISAPPROVED
Date Filed : 13 JUN 2013	This patent is subject to a Terminal Disclaimer	

Approved/Disapproved by:

The person who signed the terminal disclaimer (only for applications mailed on or after September 16, 2012);

is not the applicant, patentee or an attorney or agent of record, 37 CFR 1.321(a) and (b), (See FP 14.26.08.).

JAB

U.S. Patent and Trademark Office

Docket No.
001333/0037

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventors: **Kim, Dae-Young et al.** Group Art Unit: **1784**

Application No.: **13/722,585** Examiner: **Lam, Cathy F.F.**

Filed **December 20, 2012** Confirmation No.: **8652**

For: **Copper Foil For Current Collector of Lithium secondary battery With Improved Wrinkle Characteristics**

RESPONSE TO NON-FINAL REJECTION

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In reply to the Office Action of the United States Patent & Trademark Office, dated March 14, 2014 (the "Office Action"), Applicant submits the following remarks beginning on page 2 of this paper.

REMARKS

Claims 1-6 are pending in this application and are rejected under the doctrine of non-statutory double patenting as being unpatentable over claim 1 of U.S. Patent No. 8,349,518.

No amendments are made by this response. Reconsideration and withdrawal of the rejections in the Office Action in view of the following remarks is respectfully requested.

Rejection under non-statutory double patenting

Claims 1-6 are rejected under the doctrine of non-statutory double patenting as being unpatentable over claim 1 of U.S. Patent No. 8,349,518.

Without conceding to the arguments raised by the Examiner, to facilitate a quick allowance of this application, a terminal disclaimer and related fees are submitted herewith.

In view of the above, Applicant respectfully requests the withdrawal of the rejections of claims 1-6 and that the claims be allowed.

CONCLUSION

In view of the foregoing remarks, Applicant respectfully requests reconsideration of the application and prompt allowance of the pending claims.

Other than the fee for the terminal disclaimer, no additional fees are believed to be due in connection with the filing of this paper. Nevertheless, should any fee(s) be deemed now or hereafter due, the Commissioner is authorized to charge all such fees to Deposit Account No. 19-4709.

In the event that there are any questions, or should additional information be required, please contact Applicant's attorney at the number listed below.

Respectfully submitted,

Date: June 13, 2014

Brian M. Rothery
Registration No. 35,340
Attorneys for Applicant
Stroock & Stroock & Lavan LLP
180 Maiden Lane
New York, New York 10038
(212) 806-5400

PTO/AIA/26 (04-14)
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TERMINAL DISCLAIMER TO OBVIATE A DOUBLE PATENTING REJECTION OVER A "PRIOR" PATENT	Docket Number (Optional) 001333/0037

In re Application of: Dae-Young KIM

Application No.: 13/722,585

Filed: December 20, 2012

For: COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

The applicant, LS MTRON LTD., owner of 100 percent interest in the instant application hereby disclaims, except as provided below, the terminal part of the statutory term of any patent granted on the instant application which would extend beyond the expiration date of the full statutory term of **prior patent** No. 8,349,518 as the term of said **prior patent** is presently shortened by any terminal disclaimer. The applicant hereby agrees that any patent so granted on the instant application shall be enforceable only for and during such period that it and the **prior patent** are commonly owned. This agreement runs with any patent granted on the instant application and is binding upon the grantee, its successors or assigns.

In making the above disclaimer, the applicant does not disclaim the terminal part of the term of any patent granted on the instant application that would extend to the expiration date of the full statutory term of the **prior patent**, "as the term of said **prior patent** is presently shortened by any terminal disclaimer," in the event that said **prior patent** later:

expires for failure to pay a maintenance fee;
is held unenforceable;
is found invalid by a court of competent jurisdiction;
is statutorily disclaimed in whole or terminally disclaimed under 37 CFR 1.321;
has all claims canceled by a reexamination certificate;
is reissued; or
is in any manner terminated prior to the expiration of its full statutory term as presently shortened by any terminal disclaimer.

Check either box 1 or 2 below, if appropriate.

1. ☐ The undersigned is the applicant. If the applicant is an assignee, the undersigned is authorized to act on behalf of the assignee.

I hereby acknowledge that any willful false statements made are punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

2. ☑ The undersigned is an attorney or agent of record. Reg. No. 35,340



Signature — June 13, 2014 (Date)

Brian M. Rothery
Typed or printed name

Title — Telephone Number

☑ Terminal disclaimer fee under 37 CFR 1.20(d) included.

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

This collection of information is required by 37 CFR 1.321. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PTO/AIA/96 (08-12)
Approved for use through 01/31/2013. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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STATEMENT UNDER 37 CFR 3.73(c)

Applicant/Patent Owner: Dae-Young KIM

Application No./Patent No.: 13/722,585 Filed/Issue Date: December 20, 2012

Titled: COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

LS MTRON LTD., a corporation

(Name of Assignee) (Type of Assignee, e.g., corporation, partnership, university, government agency, etc.)

states that, for the patent application/patent identified above, it is (choose **one** of options 1, 2, 3 or 4 below):

1. ☑ The assignee of the entire right, title, and interest.

2. ☐ An assignee of less than the entire right, title, and interest (check applicable box):

   ☐ The extent (by percentage) of its ownership interest is _____%. Additional Statement(s) by the owners holding the balance of the interest must be submitted to account for 100% of the ownership interest.

   ☐ There are unspecified percentages of ownership. The other parties, including inventors, who together own the entire right, title and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

3. ☐ The assignee of an undivided interest in the entirety (a complete assignment from one of the joint inventors was made). The other parties, including inventors, who together own the entire right, title, and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

4. ☐ The recipient, via a court proceeding or the like (*e.g.*, bankruptcy, probate), of an undivided interest in the entirety (a complete transfer of ownership interest was made). The certified document(s) showing the transfer is attached.

The interest identified in option 1, 2 or 3 above (not option 4) is evidenced by either (choose **one** of options A or B below):

A. ☑ An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in the United States Patent and Trademark Office at Reel 0030038, Frame 0382, or for which a copy thereof is attached.

B. ☐ A chain of title from the inventor(s), of the patent application/patent identified above, to the current assignee as follows:

   1. From: _____ To: _____

      The document was recorded in the United States Patent and Trademark Office at

      Reel _____, Frame _____, or for which a copy thereof is attached.

   2. From: _____ To: _____

      The document was recorded in the United States Patent and Trademark Office at

      Reel _____, Frame _____, or for which a copy thereof is attached.

This collection of information is required by 37 CFR 3.73(b). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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STATEMENT UNDER 37 CFR 3.73(c)

3. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

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4. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

5. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

6. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

☐ Additional documents in the chain of title are listed on a supplemental sheet(s).

☐ As required by 37 CFR 3.73(c)(1)(i), the documentary evidence of the chain of title from the original owner to the assignee was, or concurrently is being, submitted for recordation pursuant to 37 CFR 3.11.

[NOTE: A separate copy (i.e., a true copy of the original assignment document(s)) must be submitted to Assignment Division in accordance with 37 CFR Part 3, to record the assignment in the records of the USPTO. See MPEP 302.08]

The undersigned (whose title is supplied below) is authorized to act on behalf of the assignee.

Signature	June 13, 2014 Date
Brian M. Rothery Printed or Typed Name	35,340 Title or Registration Number

Electronic Patent Application Fee Transmittal	
Application Number:	13722585
Filing Date:	20-Dec-2012
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Filer:	Brian M. Rothery/Erica Brauer
Attorney Docket Number:	001333-0037
Filed as Large Entity	

Utility under 35 USC 111(a) Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
Statutory or Terminal Disclaimer	1814	1	160	160
		Total in USD ($)		**160**

Electronic Acknowledgement Receipt	
EFS ID:	19303956
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	26610
Filer:	Brian M. Rothery/Erica Brauer
Filer Authorized By:	Brian M. Rothery
Attorney Docket Number:	001333-0037
Receipt Date:	13-JUN-2014
Filing Date:	20-DEC-2012
Time Stamp:	16:55:40
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	$160
RAM confirmation Number	3685
Deposit Account	194709
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: Charge any Additional Fees required under 37 C.F.R. Section 1.16 (National application filing, search, and examination fees) Charge any Additional Fees required under 37 C.F.R. Section 1.17 (Patent application and reexamination processing fees)	

Charge any Additional Fees required under 37 C.F.R. Section 1.19 (Document supply fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.20 (Post Issuance fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		Response0613.pdf	404892 cd7232fda12c94df2bbb92d116fae17eba7e5e8b	yes	6

Multipart Description/PDF files in .zip description		
Document Description	**Start**	**End**
Amendment/Req. Reconsideration-After Non-Final Reject	1	3
Terminal Disclaimer Filed	4	4
Assignee showing of ownership per 37 CFR 3.73.	5	6

Warnings:

Information:

2	Fee Worksheet (SB06)	fee-info.pdf	30292 94103b94a24550d8f46a5a46072f7956684c12ba	no	2

Warnings:

Information:

Total Files Size (in bytes):	435184

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

<u>New International Application Filed with the USPTO as a Receiving Office</u>
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	001333-0037	8652

26610 7590 03/14/2014
STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

EXAMINER	
LAM, CATHY FONG FONG	
ART UNIT	**PAPER NUMBER**
1784	

MAIL DATE	DELIVERY MODE
03/14/2014	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No. 13/722,585	Applicant(s) KIM ET AL.	
	Examiner CATHY LAM	Art Unit 1784	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *Jan 21, 2014*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5)☒ Claim(s) *1-6* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-6* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☒ All b)☐ Some** c)☐ None of the:

1.☒ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☐ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

DETAILED ACTION

1. The present application is being examined under the pre-AIA first to invent provisions.

2. In view of the remarks filed on Jan 21, 2014, the Double Patenting rejection has been withdrawn. The pending claims however continue to be unpatentable as following:

Double Patenting

3. Claims 1-6 are rejected on the ground of nonstatutory double patenting as being unpatentable over claim 1 of U.S. Patent No. 8,349,518. Although the claims at issue are not identical, they are not patentably distinct from each other because the claim in 8,349518 fully compasses the present claims.

4. The nonstatutory double patenting rejection is based on a judicially created doctrine grounded in public policy (a policy reflected in the statute) so as to prevent the unjustified or improper timewise extension of the "right to exclude" granted by a patent and to prevent possible harassment by multiple assignees. A nonstatutory double patenting rejection is appropriate where the claims at issue are not identical, but at least one examined application claim is not patentably distinct from the reference claim(s) because the examined application claim is either anticipated by, or would have been obvious over, the reference claim(s). See, e.g., *In re Berg*, 140 F.3d 1428, 46 USPQ2d 1226 (Fed. Cir. 1998); *In re Goodman*, 11 F.3d 1046, 29 USPQ2d 2010 (Fed. Cir. 1993); *In re Longi*, 759 F.2d 887, 225 USPQ 645 (Fed. Cir. 1985); *In re Van Ornum*, 686 F.2d 937, 214 USPQ 761 (CCPA 1982); *In re Vogel*, 422 F.2d 438, 164 USPQ 619 (CCPA 1970); and *In re Thorington*, 418 F.2d 528, 163 USPQ 644 (CCPA 1969).

A timely filed terminal disclaimer in compliance with 37 CFR 1.321(c) or 1.321(d) may be used to overcome an actual or provisional rejection based on a nonstatutory double patenting ground provided the reference application or patent either is shown to be commonly owned with this application, or claims an invention made as a result of activities undertaken within the scope of a joint research agreement. A terminal disclaimer must be signed in compliance with 37 CFR 1.321(b).

The USPTO internet Web site contains terminal disclaimer forms which may be used. Please visit http://www.uspto.gov/forms/. The filing date of the application will determine what form should be used. A web-based eTerminal Disclaimer may be filled out completely online using web-screens. An eTerminal Disclaimer that meets all requirements is auto-processed and approved immediately upon submission. For more information about eTerminal Disclaimers, refer to http://www.uspto.gov/patents/process/file/efs/guidance/eTD-info-I.jsp.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CATHY LAM whose telephone number is (571)272-1538. The examiner can normally be reached on 9am-6pm.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Humera Sheikh can be reached on (571) 272-0604. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CATHY LAM/
Primary Examiner, Art Unit 1784

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	Art Unit
	CATHY LAM	1784

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	08/14/2013								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								

Docket No.
001333/0037

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventors: **Kim, Dae-Young et al.** Group Art Unit: **1784**

Application No.: **13/722,585** Examiner: **Lam, Cathy F.F.**

Filed **December 20, 2012** Confirmation No.: **8652**

For: **Copper Foil For Current Collector of Lithium secondary battery With Improved Wrinkle Characteristics**

RESPONSE TO NON-FINAL REJECTION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In reply to the Office Action of the United States Patent & Trademark Office, dated August 19, 2013 (the "Office Action"), Applicant submits the following remarks beginning on page 2 of this paper.

A request of two-month extension of time is filed concurrently herewith, with the requisite extension fee.

REMARKS

Claims 1-6 are pending in this application and rejected under 35 U.S.C. 101 for statutory double patenting.

No amendments are made by this response. Reconsideration and withdrawal of the rejections in the Office Action in view of the following remarks is respectfully requested.

Summary of Examiner Interview

Applicant would like to thank Examiner Cathy Lam for the courtesy extended in the telephonic Examiner Interview conducted on January 13, 2014. During the interview, Applicant's representative, the undersigned attorney, explained that none of the invention claimed in any of currently pending claims 1-6 is the same invention as claimed in the sole issued claim 1 of the parent patent, U.S. 8,349,518. Examiner Lam considered such explanation persuasive, and acknowledged that rejections under statutory double patenting were not appropriate. However, no agreement was reached on the patentability of the claims. Examiner Lam indicated that upon the Applicant filing a written response to the Office Action, she will withdraw the double patenting rejections and perform further search. Further, Examiner Lam agreed to issue the next Office Action as a **non-final** Office Action.

Rejections under 35 U.S.C. 101

Claims 1-6 are rejected under 35 U.S.C. 101 as claiming the same invention as that of claim 1 of the parent patent, U.S. Patent No. 8,349,518. Applicant respectfully disagree.

As provided in MPEP 804, "same invention" under 35 U.S.C. 101 means an invention drawn to *identical subject matter* (citing *Miller v. Eagle Mfg. Co.*, 151 U.S. 186 (1894); remaining citations omitted), and that a reliable test for double patenting under 35 U.S.C. 101 is whether a claim in the application could be literally infringed without literally infringing a corresponding claim in the patent (citing *In re Vogel*, 422 F.2d 438, 164 USPQ 619 (CCPA 1970). Applicant notes that none of the claims 1-6 in the instant application include all the limitations of claim 1 of the parent patent. On the other hand, claim 1 of the parent patent includes limitations that are not present in each of claims 1-6 of the instant application. Therefore, none of the claims 1-6 can be considered as claiming the *identical subject matter* as the subject matter claimed in claim 1 of the parent patent.

In view of the above and the discussions with the Examiner in the telephone Examiner Interview of January 13, 2014, Applicant respectfully requests the withdrawal of the rejections under 35 U.S.C. 101.

CONCLUSION

In view of the foregoing remarks, Applicant respectfully requests reconsideration of the application and prompt allowance of the pending claims.

Other than the fee for the extension of time, no additional fees are believed to be due in connection with the filing of this paper. Nevertheless, should any fee(s) be deemed now or hereafter due, the Commissioner is authorized to charge all such fees to Deposit Account No. 19-4709.

In the event that there are any questions, or should additional information be required, please contact Applicant's attorney at the number listed below.

Respectfully submitted,

Date: January 21, 2014

/Yong Chen/
Yong Chen
Registration No.: 67,315
For: Brian M. Rothery
Registration No. 35,340
Attorneys for Applicant
Stroock & Stroock & Lavan LLP
180 Maiden Lane
New York, New York 10038
(212) 806-5400

Electronic Patent Application Fee Transmittal

Application Number:	13722585
Filing Date:	20-Dec-2012
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Filer:	Brian M. Rothery/Miguel Villarin
Attorney Docket Number:	001333-0037

Filed as Large Entity

Utility under 35 USC 111(a) Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Extension - 2 months with $0 paid	1252	1	600	600

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
			Total in USD ($)	**600**

Electronic Acknowledgement Receipt	
EFS ID:	17965068
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	26610
Filer:	Brian M. Rothery/Miguel Villarin
Filer Authorized By:	Brian M. Rothery
Attorney Docket Number:	001333-0037
Receipt Date:	21-JAN-2014
Filing Date:	20-DEC-2012
Time Stamp:	13:01:28
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	$600
RAM confirmation Number	15860
Deposit Account	194709
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: Charge any Additional Fees required under 37 C.F.R. Section 1.16 (National application filing, search, and examination fees) Charge any Additional Fees required under 37 C.F.R. Section 1.17 (Patent application and reexamination processing fees)	

Charge any Additional Fees required under 37 C.F.R. Section 1.19 (Document supply fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.20 (Post Issuance fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		ResponsetoNonFinalRejection.pdf	108490 be5aba962094def9fc0514c2872310187cf58d31	yes	4
	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	
	Amendment/Req. Reconsideration-After Non-Final Reject		1	1	
	Applicant Arguments/Remarks Made in an Amendment		2	4	
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30637 4c1d2da34d279e4e5465d0752d4b1a5f5d87305a	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	139127		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

<u>New International Application Filed with the USPTO as a Receiving Office</u>
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 13/722,585	Filing Date 12/20/2012	☐ To be Mailed

ENTITY: ☒ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT	01/21/2014	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 6	Minus	** 20	= 0	X $80 =	0
	Independent (37 CFR 1.16(h))	* 1	Minus	***3	= 0	X $420 =	0
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	0

AMENDMENT		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

LIE
/DEANNA RORIE/

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	001333-0037	8652

26610 7590 01/15/2014
STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

EXAMINER	
LAM, CATHY FONG FONG	
ART UNIT	**PAPER NUMBER**
1784	
MAIL DATE	**DELIVERY MODE**
01/15/2014	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Applicant-Initiated Interview Summary	**Application No.** 13/722,585	**Applicant(s)** KIM ET AL.	
	Examiner CATHY LAM	**Art Unit** 1784	

All participants (applicant, applicant's representative, PTO personnel):

(1) *CATHY LAM*. (3)_____.

(2) *Atty:Yong Chen* . (4)_____.

Date of Interview: *13 January 2014*.

Type: ☒ Telephonic ☐ Video Conference
☐ Personal [copy given to: ☐ applicant ☒ applicant's representative]

Exhibit shown or demonstration conducted: ☐ Yes ☒ No.
If Yes, brief description: _____.

Issues Discussed ☐101 ☐112 ☐102 ☐103 ☒Others
(For each of the checked box(es) above, please describe below the issue and detailed description of the discussion)

Claim(s) discussed: _____.

Identification of prior art discussed: _____.

Substance of Interview
(For each issue discussed, provide a detailed description and indicate if agreement was reached. Some topics may include: identification or clarification of a reference or a portion thereof, claim interpretation, proposed amendments, arguments of any applied references etc...)

Applicant's rep points out that the pending claims should not have been rejected under 35 USC 101 straight double patenting rejection. Examiner agrees and will withdrawn the double patenting rejection upon filing an amendment/request for reconsideration..

Applicant recordation instructions: The formal written reply to the last Office action must include the substance of the interview. (See MPEP section 713.04). If a reply to the last Office action has already been filed, applicant is given a non-extendable period of the longer of one month or thirty days from this interview date, or the mailing date of this interview summary form, whichever is later, to file a statement of the substance of the interview

Examiner recordation instructions: Examiners must summarize the substance of any interview of record. A complete and proper recordation of the substance of an interview should include the items listed in MPEP 713.04 for complete and proper recordation including the identification of the general thrust of each argument or issue discussed, a general indication of any other pertinent matters discussed regarding patentability and the general results or outcome of the interview, to include an indication as to whether or not agreement was reached on the issues raised.

☐ Attachment

/CATHY LAM/ Primary Examiner, Art Unit 1784	

Summary of Record of Interview Requirements

Manual of Patent Examining Procedure (MPEP), Section 713.04, Substance of Interview Must be Made of Record
A complete written statement as to the substance of any face-to-face, video conference, or telephone interview with regard to an application must be made of record in the application whether or not an agreement with the examiner was reached at the interview.

Title 37 Code of Federal Regulations (CFR) § 1.133 Interviews
Paragraph (b)

In every instance where reconsideration is requested in view of an interview with an examiner, a complete written statement of the reasons presented at the interview as warranting favorable action must be filed by the applicant. An interview does not remove the necessity for reply to Office action as specified in §§ 1.111, 1.135. (35 U.S.C. 132)

37 CFR §1.2 Business to be transacted in writing.
All business with the Patent or Trademark Office should be transacted in writing. The personal attendance of applicants or their attorneys or agents at the Patent and Trademark Office is unnecessary. The action of the Patent and Trademark Office will be based exclusively on the written record in the Office. No attention will be paid to any alleged oral promise, stipulation, or understanding in relation to which there is disagreement or doubt.

The action of the Patent and Trademark Office cannot be based exclusively on the written record in the Office if that record is itself incomplete through the failure to record the substance of interviews.

It is the responsibility of the applicant or the attorney or agent to make the substance of an interview of record in the application file, unless the examiner indicates he or she will do so. It is the examiner's responsibility to see that such a record is made and to correct material inaccuracies which bear directly on the question of patentability.

Examiners must complete an Interview Summary Form for each interview held where a matter of substance has been discussed during the interview by checking the appropriate boxes and filling in the blanks. Discussions regarding only procedural matters, directed solely to restriction requirements for which interview recordation is otherwise provided for in Section 812.01 of the Manual of Patent Examining Procedure, or pointing out typographical errors or unreadable script in Office actions or the like, are excluded from the interview recordation procedures below. Where the substance of an interview is completely recorded in an Examiners Amendment, no separate Interview Summary Record is required.

The Interview Summary Form shall be given an appropriate Paper No., placed in the right hand portion of the file, and listed on the "Contents" section of the file wrapper. In a personal interview, a duplicate of the Form is given to the applicant (or attorney or agent) at the conclusion of the interview. In the case of a telephone or video-conference interview, the copy is mailed to the applicant's correspondence address either with or prior to the next official communication. If additional correspondence from the examiner is not likely before an allowance or if other circumstances dictate, the Form should be mailed promptly after the interview rather than with the next official communication.

The Form provides for recordation of the following information:
- Application Number (Series Code and Serial Number)
- Name of applicant
- Name of examiner
- Date of interview
- Type of interview (telephonic, video-conference, or personal)
- Name of participant(s) (applicant, attorney or agent, examiner, other PTO personnel, etc.)
- An indication whether or not an exhibit was shown or a demonstration conducted
- An identification of the specific prior art discussed
- An indication whether an agreement was reached and if so, a description of the general nature of the agreement (may be by attachment of a copy of amendments or claims agreed as being allowable). Note: Agreement as to allowability is tentative and does not restrict further action by the examiner to the contrary.
- The signature of the examiner who conducted the interview (if Form is not an attachment to a signed Office action)

It is desirable that the examiner orally remind the applicant of his or her obligation to record the substance of the interview of each case. It should be noted, however, that the Interview Summary Form will not normally be considered a complete and proper recordation of the interview unless it includes, or is supplemented by the applicant or the examiner to include, all of the applicable items required below concerning the substance of the interview.

A complete and proper recordation of the substance of any interview should include at least the following applicable items:
1) A brief description of the nature of any exhibit shown or any demonstration conducted,
2) an identification of the claims discussed,
3) an identification of the specific prior art discussed,
4) an identification of the principal proposed amendments of a substantive nature discussed, unless these are already described on the Interview Summary Form completed by the Examiner,
5) a brief identification of the general thrust of the principal arguments presented to the examiner,
   (The identification of arguments need not be lengthy or elaborate. A verbatim or highly detailed description of the arguments is not required. The identification of the arguments is sufficient if the general nature or thrust of the principal arguments made to the examiner can be understood in the context of the application file. Of course, the applicant may desire to emphasize and fully describe those arguments which he or she feels were or might be persuasive to the examiner.)
6) a general indication of any other pertinent matters discussed, and
7) if appropriate, the general results or outcome of the interview unless already described in the Interview Summary Form completed by the examiner.

Examiners are expected to carefully review the applicant's record of the substance of an interview. If the record is not complete and accurate, the examiner will give the applicant an extendable one month time period to correct the record.

Examiner to Check for Accuracy

If the claims are allowable for other reasons of record, the examiner should send a letter setting forth the examiner's version of the statement attributed to him or her. If the record is complete and accurate, the examiner should place the indication, "Interview Record OK" on the paper recording the substance of the interview along with the date and the examiner's initials.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/722,585	12/20/2012	Dae-Young KIM	001333-0037	8652

26610 7590 08/19/2013
STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

EXAMINER	
LAM, CATHY FONG FONG	
ART UNIT	**PAPER NUMBER**
1784	
MAIL DATE	**DELIVERY MODE**
08/19/2013	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No. 13/722,585	Applicant(s) KIM ET AL.	
	Examiner CATHY LAM	Art Unit 1784	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *3* MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☐ Responsive to communication(s) filed on _____.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

5)☒ Claim(s) *1-6* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-6* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☒ The drawing(s) filed on *20 December 2012* is/are: a)☒ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☒ All b)☐ Some * c)☐ None of the:

1.☒ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date *12-20-2012*.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

DETAILED ACTION

It is acknowledged by the examiner that the present application is a continuation of Application number 13/029,656, now U.S. Patent number 8,349,518.

Double Patenting

1. A rejection based on double patenting of the "same invention" type finds its support in the language of 35 U.S.C. 101 which states that "whoever invents or discovers any new and useful process... may obtain a patent therefor..." (Emphasis added). Thus, the term "same invention," in this context, means an invention drawn to identical subject matter. See *Miller v. Eagle Mfg. Co.*, 151 U.S. 186 (1894); *In re Vogel*, 422 F.2d 438, 164 USPQ 619 (CCPA 1970); and *In re Ockert*, 245 F.2d 467, 114 USPQ 330 (CCPA 1957).

A statutory type (35 U.S.C. 101) double patenting rejection can be overcome by canceling or amending the claims that are directed to the same invention so they are no longer coextensive in scope. The filing of a terminal disclaimer cannot overcome a double patenting rejection based upon 35 U.S.C. 101.

2. Claims 1-6 are rejected under 35 U.S.C. 101 as claiming the same invention as that of claim 1 of prior U.S. Patent No. 8,349,518. This is a statutory double patenting rejection.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CATHY LAM whose telephone number is (571)272-1538. The examiner can normally be reached on 9am-6pm.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Jennifer McNeil can be reached on (571) 272-1540. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Cathy Lam/
Primary Examiner, Art Unit 1784

PTO/SB/08a (01-10)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	
	Filing Date	
	First Named Inventor	Dae-Young KIM
	Art Unit	
	Examiner Name	Unassigned
	Attorney Docket Number	001333-0037

U.S.PATENTS						Remove
Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
/C.L./	1	7927663		2011-04-19	Ruppi, Sakari	
	2	6333098		2001-12-25	Olsson et al.	
	3	5501911		1996-03-26	Ebe et al.	
	4	4777078		1988-10-11	Miyabayashi, Takeshi	
	5	7060618		2006-06-13	Inoue et al.	
	6	7282255		2007-10-16	Hiranaka et al.	
	7	7279408		2007-10-09	Inoue et al.	
	8	7883783		2011-02-08	Nagatani, Seiji	

Receipt date: 12/20/2012	Application Number	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT	Filing Date	
(Not for submission under 37 CFR 1.99)	First Named Inventor	Dae-Young KIM
	Art Unit	
	Examiner Name	Unassigned
	Attorney Docket Number	001333-0037

/C.L./	9	6451441		2002-09-17	Nishimoto et al.	

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U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
/C.L./	1	2010161088	JP		2010-07-15			☒

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
/C.L./	1	JCPDS (Joint Committee for Powder Diffraction Studies) card for standard powder specimens (04-0836) of copper (Cu) used in the subject invention.	☐
	2	Caglar et al. Journal of Optoelectronics and Advanced Materials, 8(4), 1410-1413 (2006)	☐
	3	Singh et al. Digest Journal Nanomaterials and Biostructures, 6(2) 403-412 (2011)	☐

Receipt date: 12/20/2012	Application Number	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99**)	Filing Date	
	First Named Inventor	Dae-Young KIM
	Art Unit	
	Examiner Name	Unassigned
	Attorney Docket Number	001333-0037

If you wish to add additional non-patent literature document citation information please click the Add button Add			
EXAMINER SIGNATURE			
Examiner Signature	/Cathy Lam/	Date Considered	08/14/2013

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

Receipt date: 12/20/2012	Application Number	
	Filing Date	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT	First Named Inventor	Dae-Young KIM
	Art Unit	
(Not for submission under 37 CFR 1.99)	Examiner Name	Unassigned
	Attorney Docket Number	001333-0037

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature		Date (YYYY-MM-DD)	2012-12-20
Name/Print	Brian M. Rothery	Registration Number	35,340

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Receipt date: 12/20/2012

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

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5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13722585	KIM ET AL.
	Examiner	Art Unit
	CATHY LAM	1784

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	08/14/2013								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
13/722,585	12/20/2012	Dae-Young KIM	001333-0037

CONFIRMATION NO. 8652

26610
STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

PUBLICATION NOTICE

OC000000060905478

Title:COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

Publication No.US-2013-0108887-A1
Publication Date:05/02/2013

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Office of Public Records. The Office of Public Records can be reached by telephone at (703) 308-9726 or (800) 972-6382, by facsimile at (703) 305-8759, by mail addressed to the United States Patent and Trademark Office, Office of Public Records, Alexandria, VA 22313-1450 or via the Internet.

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Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

Doc Code: Oath
Document Description: Oath or declaration filed

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)

☐ Declaration Submitted With Initial Filing OR ■ Declaration Submitted After Initial Filing (surcharge (37 CFR 1.16(f)) required)

Attorney Docket Number	001333-0037
First Named Inventor	Dae-Young KIM
COMPLETE IF KNOWN	
Application Number	13/722,585
Filing Date	December 20, 2012
Art Unit	1784
Examiner Name	Unassigned

COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

(Title of the Invention)

As a below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application,

OR

■ United States Application Number or PCT International application number 13/722,585 filed on December 20, 2012.

The above-identified application was made or authorized to be made by me.

I believe I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

Authorization To Permit Access To Application by Participating Office

☑ If checked, the undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the World Intellectual Property Office (WIPO), and any other intellectual property offices in which a foreign application claiming priority to the above-identified patent application is filed access to the above-identified patent application. See 37 CFR 1.14(c) and (h). This box should not be checked if the applicant does not wish the EPO, JPO, KIPO, WIPO, or other intellectual property office in which a foreign application claiming priority to the above-identified patent application is filed to have access to the above-identified patent application.

In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the above-identified patent application with respect to: 1) the above-identified patent application-as-filed; 2) any foreign application to which the above-identified patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the above-identified patent application; and 3) any U.S. application-as-filed from which benefit is sought in the above-identified patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date of filing the Authorization to Permit Access to Application by Participating Offices.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 21 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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DECLARATION — Utility or Design Patent Application

Direct all correspondence to: ■ The address associated with Customer Number: 26610	OR ☐ Correspondence address below
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Address	
City	State / Zip
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LEGAL NAME OF SOLE OR FIRST INVENTOR:

(*E.g.*, Given Name (first and middle (if any)) and Family Name or Surname)

Dae-Young KIM

Inventor's Signature	Date (Optional)

Residence: City	State	Country
Gyeonggi-do		KR

Mailing Address

415-1101, Halla 2 Cha Apt., Ogeum-dong, Gunpo-si

City	State	Zip	Country
Gyeonggi-do		435-760	KR

☐ Additional inventors are being named on the _____ supplemental sheet(s) PTO/AIA/10 attached hereto

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SUPPLEMENTAL SHEET FOR DECLARATION | **ADDITIONAL INVENTOR(S)**
Supplemental Sheet (for PTO/AIA/08,09) Page 3 of 3

Legal Name of Additional Joint Inventor, if any:

(*E.g.*, Given Name (first and middle (if any)) and Family Name or Surname)

Byoung-Kwang LEE

Inventor's Signature  Date (Optional)

Residence: City: Gyeonggi-do | State | Country: KR

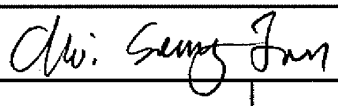
Mailing Address: 201-102 Sinil Apt., Songjeong-dong, Icheon-sin

City: Gyeonggi-do | State | Zip: 467-741 | Country: KR

Legal Name of Additional Joint Inventor, if any:

(*E.g.*, Given Name (first and middle (if any)) and Family Name or Surname)

Seung-Jun CHOI

Inventor's Signature  Date (Optional)

Residence: City: Gyeonggi-do | State | Country: KR

Mailing Address: 106-404 Byucksan Blooming Pureunsup Apt., Hwaseo-dong, Paldal-gu, Suwon-si

City: Gyeonggi-do | State | Zip: 442-150 | Country: KR

Legal Name of Additional Joint Inventor, if any:

(*E.g.*, Given Name (first and middle (if any)) and Family Name or Surname)

Inventor's Signature | Date (Optional)

Residence: City | State | Country

Mailing Address

City | State | Zip | Country

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 21 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Electronic Patent Application Fee Transmittal

Application Number:	13722585
Filing Date:	20-Dec-2012
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Filer:	Brian M. Rothery/Diana Guido
Attorney Docket Number:	001333-0037

Filed as Large Entity

Utility under 35 USC 111(a) Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Late Filing Fee for Oath or Declaration	1051	1	140	140
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
			Total in USD ($)	**140**

Electronic Acknowledgement Receipt	
EFS ID:	15620459
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	26610
Filer:	Brian M. Rothery/Diana Guido
Filer Authorized By:	Brian M. Rothery
Attorney Docket Number:	001333-0037
Receipt Date:	26-APR-2013
Filing Date:	20-DEC-2012
Time Stamp:	11:12:59
Application Type:	Utility under 35 USC 111(a)

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Warnings:					
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<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

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If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	LS MTRON LTD.	Confirmation No.:	8652
Application No.:	13/722,585	Art Unit:	1784
Filed:	December 20, 2012	Examiner:	Unassigned
Attorney Docket No:	001333-0037		
For:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS		

SUBMISSION OF DECLARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

Applicant respectfully submits herewith an executed Declaration signed by the inventors.

In addition, applicant respectfully submits herewith the $140.00 surcharge fee under 37 C.F.R. §1.16(f). The Commissioner is authorized to charge this and any other fee which may now or hereafter be due in this application to Deposit Account No. 19-4709.

In the event that there are any questions, or should additional information be required, please contact Applicant's attorney at the number listed below.

Respectfully submitted,

/Brian M. Rothery/

Date: April 26, 2013

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日本国特許庁
JAPAN PATENT OFFICE

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出願年月日 Date of Application:	２０１０年　７月１５日
出願番号 Application Number:	特願２０１０－１６１０８８
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出願人 Applicant(s):	エル　エス　エムトロン　リミテッド

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深野弘行

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　【物件名】　要約書　1
　【物件名】　図面　1

【書類名】明細書
【発明の名称】リチウム二次電池の集電体用銅箔
【技術分野】
【０００１】
本発明は、リチウム二次電池の集電体として用いられる銅箔に関するものであって、より詳しくは、銅箔表面にしわ（ｗｒｉｎｋｌｅ）が発生することを防止することができる構造を有したリチウム二次電池の集電体用銅箔に関する。
【背景技術】
【０００２】
リチウム二次電池は、他の二次電池に比べて相対的にエネルギー密度が高く、作動電圧が高いだけでなく優れた保存及び寿命特性を示すなど多くの長所があって、ＰＣ、カムコーダー、携帯電話機、携帯用ＣＤプレーヤー、ＰＤＡなど各種の携帯用電子機器に広く用いられている。
【０００３】
一般に、リチウム二次電池は、セパレータを挟んで配置されたカソード及びアノードと、電解質とを備える。前記カソード及びアノードは、それぞれカソード活物質及びアノード活物質と、前記カソード活物質及びアノード活物質にそれぞれ接触するカソード集電体及びアノード集電体とを備えた構造を有する。
【０００４】
リチウム二次電池において、アノード集電体の素材としては主に銅箔が用いられ、通常この銅箔にはカーボン（ｃａｒｂｏｎ）系スラリーの活物質がコートされる。ここで、銅箔は、電気めっき法で電解銅箔を製造する製箔工程と、原箔に剥離強度（ｐｅｅｌ　ｓｔｒｅｎｇｔｈ）などを付与するための後処理工程とを通じて製造される。電気めっきによって電解銅箔の一面には製箔機のドラム（ｄｒｕｍ）の表面形状に沿った、いわゆる光沢面（ｓｈｉｎｙ　ｓｉｄｅ）が形成され、他面には山（ｍｏｕｎｔａｉｎ）構造によって相対的に粗度が高いマット面（ｍａｔｔｅ　ｓｉｄｅ）が形成される。また、電解銅箔は、後処理工程において、耐食性及び耐変色性を確保するために、保護性コーティングをさらに行う。
【０００５】
リチウム二次電池は集電体として用いられる銅箔の表面状態によって電池特性が大きく変わるので、歩留まりの向上のためにはしわ特性（ｗｒｉｎｋｌｅ　ｃｈａｒａｃｔｅｒｉｓｔｉｃｓ）のような表面特性を改善することが非常に重要である。
【０００６】
図１に示すように、銅箔の表面にしわが存在する場合、表面形状の不均一によって活物質が均一にコートされず、ゆえに充・放電するとき短絡が発生するか、銅箔から活物質が剥離される現象が発生する。
【先行技術文献】
【特許文献】
【０００７】
【特許文献１】特開２０００－２００６１０号公報
【発明の概要】
【発明が解決しようとする課題】
【０００８】
本発明は前記のような問題点を解決するために創案されたものであって、銅箔表面にしわを低減することができる結晶構造を有したリチウム二次電池の集電体用銅箔を提供することにその目的がある。
【０００９】
本発明の他の目的は、銅箔表面にしわをより有効に低減するために、表面粗度（ｓｕｒｆａｃｅ　ｒｏｕｇｈｎｅｓｓ）、重量偏差、引張強度、延伸率、厚さなどの因子が最適化されたリチウム二次電池の集電体用銅箔を提供することにある。

【課題を解決するための手段】
【００１０】
前記のような目的を達成するために、本発明によるリチウム二次電池の集電体用銅箔は、結晶構造において、（１１１）面、（２００）面、（２２０）面の集合組織係数（ｔｅｘｔｕｒｅ　ｃｏｅｆｆｉｃｉｅｎｔ）の全体合計の中で（１１１）面と（２００）面との集合組織係数の合計が占める比率が６０～８５％であり、前記（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計に対する（１１１）面の集合組織係数の比率が１８～３８％、（２００）面の集合組織係数の比率が２８～６２％、（２２０）面の集合組織係数の比率が１５～４０％であることを特徴とする。
【００１１】
前記銅箔の表面粗度（R_z－ＪＩＳ）は、２μｍ以下であることが望ましい。
【００１２】
前記銅箔の重量偏差特性は、３％以下であることが望ましい。
【００１３】
前記銅箔の引張強度は、３０～４０ｋｇｆ／ｍｍ^{2}であることが望ましい。
【００１４】
前記銅箔の延伸率は、３～２０％であることが望ましい。
【００１５】
前記銅箔の厚さは、１～３５μｍであることが望ましい。
【発明の効果】
【００１６】
本発明によるリチウム二次電池の集電体用銅箔は、表面にしわが実質的に発生しないので、活物質をコートするとき均一なコーティング面を形成することができ、短絡の発生を防止することができる。
【図面の簡単な説明】
【００１７】
本明細書に添付される下記の図面は本発明の望ましい実施例を例示するものであって、発明の詳細な説明とともに本発明の技術思想をさらに理解させる役割を果たすものであるため、本発明はそのような図面に記載された事項にのみ限定されて解釈されてはいけない。
【図１】従来技術によるリチウム二次電池の集電体用銅箔にしわが発生した状態を示す写真である。
【図２】本発明によるリチウム二次電池の集電体用銅箔の集合組織係数の算出のために、Ｘ線回折法（ＸＲＤ）を行った結果を示すグラフである。
【発明を実施するための形態】
【００１８】
以下、添付した図面を参照しながら本発明の望ましい実施例を詳しく説明する。これに先立って、本明細書及び請求範囲に使われた用語や単語は通常的や辞書的な意味に限定して解釈されてはいけず、発明者は自らの発明を最善の方法で説明するために用語の概念を適切に定義することができるという原則に則して、本発明の技術的思想に符合する意味と概念とに解釈されなければならない。従って、本明細書に記載された実施例は本発明の最も望ましい一実施例に過ぎず、本発明の技術的思想の全てを代弁するものではないため、本出願時点においてこれらに代替できる多様な均等物と変形例があり得ることを理解しなければならない。
【００１９】
本発明によるリチウム二次電池の集電体用銅箔は、結晶構造、表面粗度、重量偏差、引張強度、延伸率などの因子が最適化されてしわが発生しない表面特性を提供する。
【００２０】
望ましくは、本発明によるリチウム二次電池の集電体用銅箔は、硫酸銅、硫酸及び塩素から構成された硫酸銅めっき液を基本にし、微量の有機添加剤を添加して製造される。こ

こで、添加剤としては、めっき表面に光沢を付与し微細なめっき層を得るための光沢剤（ｂｒｉｇｈｔｅｎｅｒ）としてスルフィド（ｓｕｌｆｉｄｅ）を含有したスルホネート（ｓｕｌｐｈｏｎａｔｅ）系列の添加剤と、低粗度の銅箔を得るために添加するレベラー（ｌｅｖｅｌｅｒ）として分子量１，０００～１００，０００程度の低分子量を有するゼラチン（ｇｅｌａｔｉｎ）と、安定した低粗度を具現するためのサプレッサー（ｓｕｐｐｒｅｓｓｏｒ）としてセルロース（ｃｅｌｌｕｌｏｓｅ）系列の添加剤とが用いられる。工程条件としては、３０～８０ＡＳＤ（Ａ／ｄｍ^{2}の電流密度及び３０～６０℃の温度において製箔機のドラム表面に銅を電着して原箔を製造し、防錆処理のために銅箔表面をクロメート（ｃｈｒｏｍａｔｅ）処理する工程を経て製造される。

【００２１】

銅箔の結晶構造は、（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計の中で（１１１）面と（２００）面との集合組織係数の合計が占める比率が６０～８５％を満たす。また、（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計に対する（１１１）面の集合組織係数の比率は１８～３８％、（２００）面の集合組織係数の比率は２８～６２％、（２２０）面の集合組織係数の比率は１５～４０％を満たす。

【００２２】

前記集合組織係数の数値範囲を外れる場合、銅箔の幅方向にしわが多数発生することになり、このため活物質をコートするとき銅箔表面に対する活物質の密着性が低下する問題がある。ここで、集合組織係数（ＴＣ）は、Ｘ線回折法（ＸＲＤ）を適用して図２に示すように各結晶面の回折強度ピーク（ｐｅａｋ）値を得た後、基準ピーク値と比較して以下の数学式１に従う範囲内で換算することで定められる。数学式１において、Ｉ（ｈｋｌ）は、（ｈｋｌ）面に対する測定回折強度を示し、Ｉ$_0$（ｈｋｌ）は、ＡＳＴＭ（Ａｍｅｒｉｃａｎ　Ｓｏｃｉｅｔｙ　ｏｆ　Ｔｅｓｔｉｎｇ　Ｍａｔｅｒｉａｌｓ）標準の粉末状回折データの標準回折強度を示す。

【００２３】

【数１】

$$TC(hkl) \geq \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{n}\sum\frac{I(hkl)}{I_0(hkl)}}$$

【００２４】

銅箔の表面粗度（Ｒ$_z$）は、日本工業標準規格（ＪＩＳ）を基準にして２μｍ以下を満たす。表面粗度（Ｒ$_z$）が２μｍを超える場合、表面が不均一であるのでリチウム二次電池を充・放電するとき短絡が発生する恐れがあり、アノード活物質のコーティング状態が不均一になる問題が発生する。

【００２５】

銅箔の重量偏差特性は、３％以下を満たす。重量偏差特性が３％を超える場合、銅箔表面に物性偏差が発生してしわ数が増加し、集電体の物性が不均一になる問題が発生する。ここで、重量偏差は、銅箔を５ｃｍ×５ｃｍのサイズに切り出して試片を作った後その重量を測定して単位面積当たりの銅箔の重量値を換算し、銅箔の幅方向に沿って前記試片を切り出す過程を繰り返して行って各試片に対する銅箔重量値を測定した後標準偏差を計算することで算出する。このとき、銅箔は、クロメート表面処理を通じて防錆処理された電解銅箔を用いることが望ましい。

【００２６】

その他に、銅箔の引張強度は３０～４０ｋｇｆ／ｍｍ^2、延伸率は３～２０％、厚さは

１～３５μｍを満たす。このような範囲を外れた場合、銅箔の物性偏差が発生してしわ数が増加し、集電体の物性が不均一になる問題が発生する。

【００２７】

下記表１は、本発明の実施例１ないし７と比較例１ないし９によるリチウム二次電池の集電体用銅箔に対してしわ特性を測定した結果を示す。表１において、引張強度はＵＴＭ（Ｕｎｉｖｅｒｓａｌ　Ｔｅｓｔｉｎｇ　Ｍａｃｈｉｎｅ）を利用して測定し、このときゲージ長（ｇａｕｇｅ　ｌｅｎｇｔｈ）は５ｃｍに設定した。

【００２８】

【表１】

区分	銅箔	銅箔厚さ［μm］	(111)+(200)比率[%]	(111)比率［%］	(200)比率［%］	(220)比率［%］	引張強度［kg/㎟］	重量偏差［%］	リンクル発生数［ea］
実施例１	電解銅箔	8	76	26	50	24	32.2	0.4	0
実施例２	電解銅箔	8	62	31	31	38	33.7	0.7	0
実施例３	電解銅箔	8	83	32	51	17	34.5	0.8	0
実施例４	電解銅箔	8	70	20	50	30	32.6	1.6	0
実施例５	電解銅箔	8	72	35	36	29	32.1	0.4	0
実施例６	電解銅箔	8	81	22	59	19	37.2	2.6	0
実施例７	電解銅箔	8	66	36	30	34	33.1	1.2	0
比較例１	電解銅箔	8	64	16	48	36	36.8	0.5	2
比較例２	電解銅箔	8	73	41	32	27	33.2	0.9	3
比較例３	電解銅箔	8	62	37	25	38	31.4	0.5	3
比較例４	電解銅箔	8	83	19	64	17	37.1	0.9	4
比較例５	電解銅箔	8	87	34	53	13	33.1	0.7	2
比較例６	電解銅箔	8	57	26	31	43	32.4	0.8	3
比較例７	電解銅箔	8	80	30	49	21	27.4	0.6	2
比較例８	電解銅箔	8	75	23	51	26	41.5	0.9	2
比較例９	電解銅箔	8	76	25	50	25	31.8	3.4	5

【００２９】

表１を参照すれば、本発明の実施例１ないし７による銅箔は、前述した集合組織係数の比率、引張強度、重量偏差、銅箔厚さの条件をすべて満たすことで、しわが発生しない結果を示すことが確認できる。その反面、比較例１ないし９による銅箔は、しわが多数発生して、リチウム二次電池の集電体として用いるには不適な特性を示すことが確認できる。

【００３０】

本発明によるリチウム二次電池の集電体用銅箔は、集合組織係数の比率の条件のみを満たしてもしわ特性が従来に比べて改善できるが、比較例１ないし９に示すように引張強度や重量偏差などの他の条件が該当の数値範囲を外れた場合には、改善した特性に悪影響を及ぼして最終的にしわ特性の低下をもたらすので、前述した集合組織係数の比率、引張強度、重量偏差、銅箔厚さなどの条件をすべて満たすことが最も望ましい。

【００３１】

以上のように、本発明は、たとえ限定された実施例と図面とによって説明されたが、本発明はこれによって限定されず、本発明が属する技術分野において通常の知識を持つ者により本発明の技術思想と特許請求範囲の均等範囲内で多様な修正及び変形が可能なのは言うまでもない。

【産業上の利用可能性】

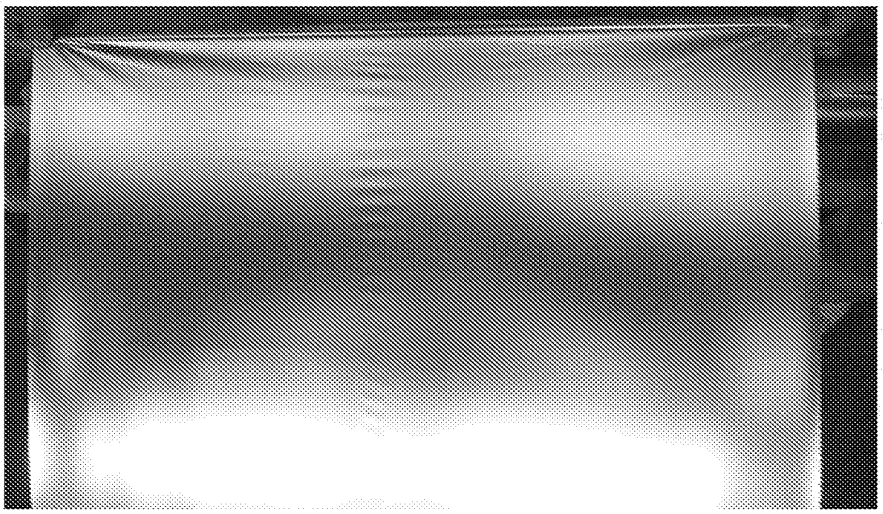
【００３２】

本発明によるリチウム二次電池の集電体用銅箔は、カーボン系スラリーのようなアノード活物質と接触するとき密着力が十分確保されて剥離強度に優れているので、電池容量を安定して維持することができるリチウム二次電池を具現することができる。

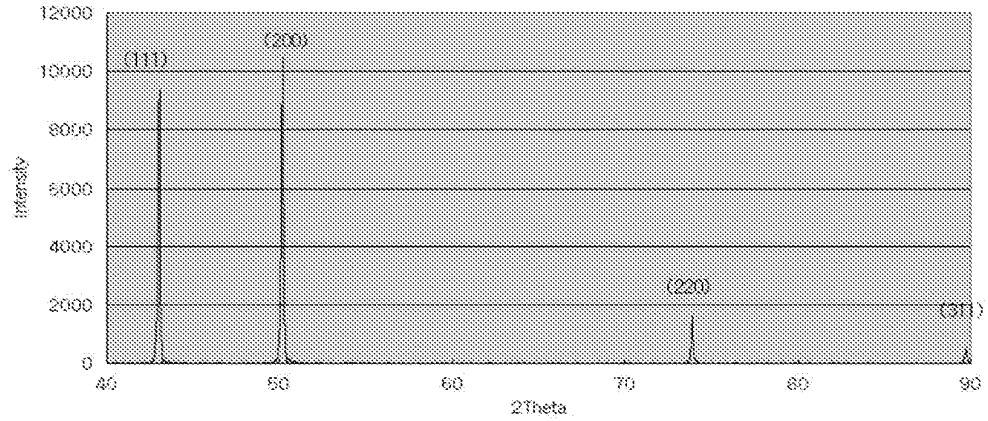
【書類名】特許請求の範囲
【請求項１】
リチウム二次電池の集電体として用いられる銅箔であって、
結晶構造において、（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計の中で（１１１）面と（２００）面との集合組織係数の合計が占める比率が６０～８５％であり、前記（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計に対する（１１１）面の集合組織係数の比率が１８～３８％、（２００）面の集合組織係数の比率が２８～６２％、（２２０）面の集合組織係数の比率が１５～４０％であることを特徴とするリチウム二次電池の集電体用銅箔。
【請求項２】
表面粗度（Ｒｚ－ＪＩＳ）が２μｍ以下であることを特徴とする請求項１に記載のリチウム二次電池の集電体用銅箔。
【請求項３】
重量偏差特性が３％以下であることを特徴とする請求項１または請求項２に記載のリチウム二次電池の集電体用銅箔。
【請求項４】
引張強度が３０～４０ｋｇｆ／ｍｍ^{2}であることを特徴とする請求項１ないし請求項３のうち何れかに記載のリチウム二次電池の集電体用銅箔。
【請求項５】
延伸率が３～２０％であることを特徴とする請求項１ないし請求項４のうち何れかに記載のリチウム二次電池の集電体用銅箔。
【請求項６】
銅箔厚さが１～３５μｍであることを特徴とする請求項１ないし請求項５のうち何れかに記載のリチウム二次電池の集電体用銅箔。
【請求項７】
リチウム二次電池の集電体として用いられる銅箔であって、
結晶構造において、（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計の中で（１１１）面と（２００）面との集合組織係数の合計が占める比率が６０～８５％であり、前記（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計に対する（１１１）面の集合組織係数の比率が１８～３８％、（２００）面の集合組織係数の比率が２８～６２％、（２２０）面の集合組織係数の比率が１５～４０％であり、
表面粗度（Ｒｚ－ＪＩＳ）が２μｍ以下であり、
重量偏差特性が３％以下であり、
引張強度が３０～４０ｋｇｆ／ｍｍ^{2}であり、
延伸率が３～２０％であり、
銅箔の厚さが１～３５μｍであることを特徴とするリチウム二次電池の集電体用銅箔。

【書類名】要約書
【要約】
【課題】銅箔表面にしわを低減することができる結晶構造を有したリチウム二次電池の集電体用銅箔を提供する。
【解決手段】本発明によるリチウム二次電池の集電体用銅箔は、結晶構造において、（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計の中で（１１１）面と（２００）面との集合組織係数の合計が占める比率が６０～８５％であり、前記（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計に対する（１１１）面の集合組織係数の比率が１８～３８％、（２００）面の集合組織係数の比率が２８～６２％、（２２０）面の集合組織係数の比率が１５～４０％であり、表面粗度（Ｒｚ－ＪＩＳ）が２μｍ以下であり、重量偏差特性が３％以下であり、引張強度が３０～４０ｋｇｆ／ｍｍ^{2}であり、延伸率が３～２０％であり、銅箔の厚さが１～３５μｍであることを特徴とする。
【選択図】図２

【書類名】図面
【図１】



【図２】


12000
10000
8000
6000
4000
2000
0
Intensity
(111)
(200)
(220)
(311)
40
50
60
70
80
90
2Theta

【書類名】　手続補正書
【整理番号】　17458
【提出日】　平成24年11月14日
【あて先】　特許庁長官　深野　弘行　殿
　特許庁審査官　岸　智之　殿
【事件の表示】
　【出願番号】　特願2010-161088
【補正をする者】
　【識別番号】　509023012
　【氏名又は名称】　エル　エス　エムトロン　リミテッド
【代理人】
　【識別番号】　100080621
　【弁理士】
　【氏名又は名称】　矢野　寿一郎
【発送番号】　311430
【手続補正1】
　【補正対象書類名】　特許請求の範囲
　【補正対象項目名】　全文
　【補正方法】　変更
　【補正の内容】
　　【書類名】特許請求の範囲
　　【請求項１】
　重量偏差特性が３％以下であり、引張強度が３０～４０ｋｇｆ／ｍｍ^{2}であるリチウム二次電池の集電体として用いられる銅箔であって、
　結晶構造において、（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計の中で（１１１）面と（２００）面との集合組織係数の合計が占める比率が６０～８５％であり、前記（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計に対する（１１１）面の集合組織係数の比率が１８～３８％、（２００）面の集合組織係数の比率が２８～６２％、（２２０）面の集合組織係数の比率が１５～４０％であることを特徴とするリチウム二次電池の集電体用銅箔。
　　【請求項２】
　表面粗度（Ｒ$_z$－ＪＩＳ）が２μｍ以下であることを特徴とする請求項１に記載のリチウム二次電池の集電体用銅箔。
　　【請求項３】
　延伸率が３～２０％であることを特徴とする請求項２に記載のリチウム二次電池の集電体用銅箔。
　　【請求項４】
　銅箔厚さが１～３５μｍであることを特徴とする請求項３に記載のリチウム二次電池の集電体用銅箔。
　　【請求項５】
　リチウム二次電池の集電体として用いられる銅箔であって、
　結晶構造において、（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計の中で（１１１）面と（２００）面との集合組織係数の合計が占める比率が６０～８５％であり、前記（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計に対する（１１１）面の集合組織係数の比率が１８～３８％、（２００）面の集合組織係数の比率が２８～６２％、（２２０）面の集合組織係数の比率が１５～４０％であり、
　表面粗度（Ｒｚ－ＪＩＳ）が２μｍ以下であり、
　重量偏差特性が３％以下であり、
　引張強度が３０～４０ｋｇｆ／ｍｍ^{2}であり、
　延伸率が３～２０％であり、

銅箔の厚さが１～３５μｍであることを特徴とするリチウム二次電池の集電体用銅箔。

出願人履歴

５０９０２３０１２

20090122

新規登録

大韓民国，　ギョンギード，　アニャン－シティー，　ドン－アン－グ，　ホゲードン，　１０２６－６

エル　エス　エムトロン　リミテッド

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
13/722,585	12/20/2012	Dae-Young KIM	001333-0037

CONFIRMATION NO. 8652

26610
STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038

NOTICE

OC000000058783196

Date Mailed: 01/23/2013

INFORMATIONAL NOTICE TO APPLICANT

Applicant is notified that the above-identified application contains the deficiencies noted below. No period for reply is set forth in this notice for correction of these deficiencies. However, if a deficiency relates to the inventor's oath or declaration, the applicant must file an oath or declaration in compliance with 37 CFR 1.63, or a substitute statement in compliance with 37 CFR 1.64, executed by or with respect to each actual inventor no later than the expiration of the time period set in the "Notice of Allowability" to avoid abandonment. See 37 CFR 1.53(f).

The item(s) indicated below are also required and should be submitted with any reply to this notice to avoid further processing delays.

A new inventor's oath or declaration that identifies this application (e.g., by Application Number and filing date) is required. The inventor's oath or declaration does not comply with 37 CFR 1.63 in that it:

- does not state that the above-identified application was made or authorized to be made by the person executing the oath or declaration.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 13/722,585

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	390
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	620
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	250
TOTAL CLAIMS (37 CFR 1.16(i))	6 minus 20 =	*			OR	x 62 =	0.00
INDEPENDENT CLAIMS (37 CFR 1.16(h))	1 minus 3 =	*				x 250 =	0.00
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	1260

APPLICATION AS AMENDED - PART II

AMENDMENT A

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
Application Size Fee (37 CFR 1.16(s))									
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

AMENDMENT B

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		RATE($)	ADDITIONAL FEE($)
Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
Application Size Fee (37 CFR 1.16(s))									
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
13/722,585	12/20/2012	1784	1260	001333-0037	6	1

CONFIRMATION NO. 8652

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FILING RECEIPT



Date Mailed: 01/23/2013

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

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Byoung-Kwang Lee, Gyeonggi-do, KOREA, REPUBLIC OF;
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Assignment For Published Patent Application

LS Mtron Ltd., Gyeonggi-do, KOREA, REPUBLIC OF

Power of Attorney: None

Domestic Priority data as claimed by applicant

This application is a CON of 13/029,656 02/17/2011 PAT 8349518

Foreign Applications (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.)
JAPAN 2010-161088 07/15/2010

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If Required, Foreign Filing License Granted: 01/18/2013

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 13/722,585**

Projected Publication Date: 05/02/2013

Non-Publication Request: No

Early Publication Request: No
Title

COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

Preliminary Class

428

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
13/722,585	12/20/2012	Dae-Young KIM	001333-0037

CONFIRMATION NO. 8652

IMPROPER CPOA LETTER

26610
STROOCK & STROOCK & LAVAN LLP
180 MAIDEN LANE
NEW YORK, NY 10038



Date Mailed: 01/23/2013

NOTICE REGARDING POWER OF ATTORNEY

This is in response to the power of attorney filed 12/20/2012. The power of attorney in this application is not accepted for the reason(s) listed below:

- The power of attorney from the inventors has not been accepted because the power of attorney must be signed by the applicant for patent. See 37 CFR 1.32(b)(4).

/dnguyen/

Office of Data Management, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

PTO/AIA/15 (07-12)
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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.	001333-0037
First Inventor	Dae-Young KIM
Title	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WI
Express Mail Label No.	

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

1. [✓] **Fee Transmittal Form.** (PTO/SB/17 or equivalent)
2. [ ] **Applicant claims small entity status.** See 37 CFR 1.27.
3. [✓] **Specification.** [*Total Pages* 15] Both the claims and abstract must start on a new page *(For information on the preferred arrangement, see MPEP § 608.01(a))*
4. [✓] **Drawing(s).** *(35 U.S.C. 113)* [*Total Sheets* 1]
5. **Inventor's Oath or Declaration.** [*Total Sheets* 4] *(including substitute statements under 37 CFR 1.64 and assignments serving as an oath or declaration under 37 CFR 1.63(e))*
   a. [ ] Newly executed (original or copy)
   b. [✓] A copy from a prior application (37 CFR 1.63(d))
6. [✓] **Application Data Sheet.** **See Note below.* See 37 CFR 1.76 (PTO/AIA/14 or equivalent)
7. [ ] **CD-ROM or CD-R.** in duplicate, large table or Computer Program *(Appendix)*
   [ ] Landscape Table on CD
8. **Nucleotide and/or Amino Acid Sequence Submission.** *(if applicable, items a. – c. are required)*
   a. [ ] Computer Readable Form (CRF)
   b. [ ] Specification Sequence Listing on:
      i. [ ] CD-ROM or CD-R (2 copies); or
      ii. [ ] Paper
   c. [ ] Statements verifying identity of above copies

ADDRESS TO: **Commissioner for Patents, P.O. Box 1450, Alexandria VA 22313-1450**

ACCOMPANYING APPLICATION PARTS

9. [ ] **Assignment Papers.** (cover sheet & document(s)) Name of Assignee
10. [ ] **37 CFR 3.73(c) Statement.** [ ] **Power of Attorney.** *(when there is an assignee)*
11. [ ] **English Translation Document.** *(if applicable)*
12. [X] **Information Disclosure Statement.** (PTO/SB/08 or PTO-1449) [X] Copies of citations attached
13. [ ] **Preliminary Amendment.**
14. [ ] **Return Receipt Postcard.** *(MPEP § 503) (Should be specifically itemized)*
15. [ ] **Certified Copy of Priority Document(s).** *(if foreign priority is claimed)*
16. [ ] **Nonpublication Request.** Under 35 U.S.C. 122(b)(2)(B)(i). Applicant must attach form PTO/SB/35 or equivalent.
17. [ ] **Other:**

***Note:** (1) Benefit claims under 37 CFR 1.78 and foreign priority claims under 1.55 **must** be included in an Application Data Sheet (ADS).
(2) For applications filed under 35 U.S.C. 111, the application must contain an ADS specifying the applicant if the applicant is an assignee, person to whom the inventor is under an obligation to assign, or person who otherwise shows sufficient proprietary interest in the matter. See 37 CFR 1.46(b).

18. CORRESPONDENCE ADDRESS

[ ] The address associated with Customer Number: _____ ***OR*** [ ] Correspondence address below

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Address					
City		State		Zip Code	
Country		Telephone		Email	

Signature	Brian M. Rothery	Date	December 20, 2012
Name (Print/Type)	Brian M. Rothery	Registration No. (Attorney/Agent)	35,340

This collection of information is required by 37 CFR 1.53(b). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**
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Electronic Patent Application Fee Transmittal	
Application Number:	
Filing Date:	
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Filer:	Brian M. Rothery/Diana Guido
Attorney Docket Number:	001333/0037
Filed as Large Entity	

Utility under 35 USC 111(a) Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Utility application filing	1011	1	390	390
Utility Search Fee	1111	1	620	620
Utility Examination Fee	1311	1	250	250
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**1260**

Electronic Acknowledgement Receipt	
EFS ID:	14533391
Application Number:	13722585
International Application Number:	
Confirmation Number:	8652
Title of Invention:	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS
First Named Inventor/Applicant Name:	Dae-Young KIM
Customer Number:	26610
Filer:	Brian M. Rothery/Diana Guido
Filer Authorized By:	Brian M. Rothery
Attorney Docket Number:	001333/0037
Receipt Date:	20-DEC-2012
Filing Date:	
Time Stamp:	17:35:42
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	$1260
RAM confirmation Number	6429
Deposit Account	194709
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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Oath or Declaration filed	001333-0037DECPOA.pdf	309170 e2446313c15c6aa308698ed6379a62b2d7ef4ea4	no	4
Warnings:					
Information:					
2	Drawings-only black and white line drawings	001333-0037Drawings.pdf	218899 54b8babe203aaeb2002ac7ceafb0cd9adde7505a	no	1
Warnings:					
Information:					
3	Transmittal Letter	001333-0037IDSTransmittal.pdf	200171 e4b8dbed8ddfa711492c3be764a20fd66d6c8f09	no	3
Warnings:					
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4	Foreign Reference	001333-0037JP2010-161088.pdf	1010028 593533b9e266ce391f90ed8ef7947249dd484bd5	no	12
Warnings:					
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5	Non Patent Literature	001333-0037NPLDocument1.pdf	39005 891a547d40deaaf10ba15c085f4c57acb039fa15	no	1
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8	Information Disclosure Statement (IDS) Form (SB08)	001333-0037SB08.pdf	612462 9750784636cdaf1a76eb3ec3d181cbcb4a7d8369	no	5

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9		001333-0037Specification.pdf	429211 b1160cfd5e401f271c4d39eb3371526fce684893	yes	17
	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	
	Specification		1	13	
	Claims		14	16	
	Abstract		17	17	
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10	Application Data Sheet	001333-0037ADS.pdf	749244 02eabcd9e5f2aaa7e5553dc341f9a398b033313b	no	7
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11	Transmittal of New Application	001333-0037ApplicationTransmittal.pdf	250554 962a55b4f8b81d0a5f61569ace2786a16d02ea16	no	1
Warnings:					
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12	Fee Worksheet (SB06)	fee-info.pdf	33337 6319bf9b30e0a30d7c1d5ea23a99282541b9f1df	no	2
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National Stage of an International Application under 35 U.S.C. 371
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PTO/SB/08a (01-10)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	
Filing Date	
First Named Inventor	Dae-Young KIM
Art Unit	
Examiner Name	Unassigned
Attorney Docket Number	001333-0037

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	7927663		2011-04-19	Ruppi, Sakari	
	2	6333098		2001-12-25	Olsson et al.	
	3	5501911		1996-03-26	Ebe et al.	
	4	4777078		1988-10-11	Miyabayashi, Takeshi	
	5	7060618		2006-06-13	Inoue et al.	
	6	7282255		2007-10-16	Hiranaka et al.	
	7	7279408		2007-10-09	Inoue et al.	
	8	7883783		2011-02-08	Nagatani, Seiji	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Dae-Young KIM
	Art Unit	
	Examiner Name	Unassigned
	Attorney Docket Number	001333-0037

	9	6451441		2002-09-17	Nishimoto et al.	

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	1	2010161088	JP		2010-07-15			☒

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NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	JCPDS (Joint Committee for Powder Diffraction Studies) card for standard powder specimens (04-0836) of copper (Cu) used in the subject invention.	☐
	2	Caglar et al. Journal of Optoelectronics and Advanced Materials, 8(4), 1410-1413 (2006)	☐
	3	Singh et al. Digest Journal Nanomaterials and Biostructures, 6(2) 403-412 (2011)	☐

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	
	Filing Date	
	First Named Inventor	Dae-Young KIM
	Art Unit	
	Examiner Name	Unassigned
	Attorney Docket Number	001333-0037

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Examiner Signature		Date Considered	
*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.			

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	
	Filing Date	
	First Named Inventor	Dae-Young KIM
	Art Unit	
	Examiner Name	Unassigned
	Attorney Docket Number	001333-0037

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature		Date (YYYY-MM-DD)	2012-12-20
Name/Print	Brian M. Rothery	Registration Number	35,340

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3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

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5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

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7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS

BACKGROUND OF THE INVENTION

Cross-Reference to Related Application

This application is a continuation of U.S. Serial No. 13/029,656, filed February 17, 2011, now U.S. Patent No. 8,349,518 and claims priority under 35 USC 119(a) to Japanese Patent Application No. 2010-0161088 filed in Japan on July 15, 2010, the entire contents of which are incorporated herein by reference.

Field of the Invention

The present invention relates to a copper foil used as a current collector of a lithium secondary battery, and more particularly to a copper foil for a current collector of a lithium secondary battery, which has a structure capable of preventing the generation of wrinkles on a surface of the copper foil.

Description of the Related Art

A lithium secondary battery has many advantages such as high energy density, high operation voltage, excellent preservation and excellent life cycle in comparison to other

kinds of secondary batteries, so the lithium secondary battery is widely used for various portable electronic devices such as personal computers, camcorders, cellular phones, portable CD players and PDA.

A lithium secondary battery generally includes a cathode and an anode, which are arranged with a separator being interposed between them, and an electrolyte. The cathode and the anode respectively include cathode active material and anode active material, and a cathode current collector and an anode current collector respectively contacted with the cathode active material and the anode active material.

In the lithium secondary battery, a copper foil is mostly used as material of the anode current collector, and the copper foil is generally coated with active material such as carbon-based slurry. Here, the copper foil is made by making an electrodeposited copper foil by means of electroplating and then conducting a post-processing to give peel strength to the original foil. A so-called shiny side is formed on one surface of the electrodeposited copper foil by means of electroplating in accordance with a surface shape of a drum of a foil making machine, and a matte side having a relatively high surface roughness due to a mountain structure is formed on the other side of the electrodeposited copper foil. Also, the

electrodeposited copper foil is additionally coated with a protective layer at a post-processing so as to ensure corrosion resistance and color fastness.

Battery characteristics of a lithium secondary battery are greatly changed in accordance with a surface state of a copper foil used as a current collector, so it is very important to improve surface characteristics such as wrinkle characteristics in order to improve a yield.

In case a wrinkle exists on a surface of a copper foil as shown in Fig. 1, active material is not uniformly coated due to the irregularity of the surface shape, which may cause a short-circuit or separate the active material from the copper foil during a charging or discharging process.

SUMMARY OF THE INVENTION

The present invention is designed to solve the problems of the prior art, and therefore it is an object of the present invention to provide a copper foil for a current collector of a lithium secondary battery with a crystal structure capable of decreasing the generation of wrinkles at a surface of the copper foil.

Another object of the present invention is to provide a copper foil for a current collector of a lithium secondary

battery, wherein factors such as surface roughness, weight deviation, tensile strength, elongation, and thickness are optimized so as to effectively decrease the generation of wrinkles at a surface of the copper foil.

In one aspect of the present invention, there is provided a copper foil for a current collector of a lithium secondary battery, wherein, in a crystalline structure, a ratio of the sum of texture coefficients of a (111) surface and a (200) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and a (220) surface is 60 to 85%, a ratio of the texture coefficient of the (111) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 18 to 38%, a ratio of the texture coefficient of the (200) surface thereto is 28 to 62%, and a ratio of the texture coefficient of the (220) surface thereto is 15 to 40%.

Preferably, the copper foil has a surface roughness (R_z-JIS) of 2 μm or less.

Preferably, the copper foil has a weight deviation of 3% or less.

Preferably, the copper foil has a tensile strength of 30 to 40 kgf/mm^2.

Preferably, the copper foil has an elongation of 3 to 20%.

Preferably, the copper foil has a thickness of 1 to 35 μm.

The copper foil for a current collector of a lithium secondary battery according to the present invention does substantially not cause the generation of a wrinkle at a surface of the copper foil, so it is possible to form a uniform coating surface and prevent a short circuit when being coated with active material.

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects and aspects of the present invention will become apparent from the following description of embodiments with reference to the accompanying drawing in which:

Fig. 1 is a photograph showing that a wrinkle is generated at a conventional copper foil for a current collector of a lithium secondary battery; and

Fig. 2 is a graph showing a result of X-ray diffraction (XRD) to calculate a texture coefficient of a copper foil for a current collector of a lithium secondary battery according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Hereinafter, preferred embodiments of the present invention will be described in detail with reference to the

accompanying drawings. Prior to the description, it should be understood that the terms used in the specification and the appended claims should not be construed as limited to general and dictionary meanings, but interpreted based on the meanings and concepts corresponding to technical aspects of the present invention on the basis of the principle that the inventor is allowed to define terms appropriately for the best explanation. Therefore, the description proposed herein is just a preferable example for the purpose of illustrations only, not intended to limit the scope of the invention, so it should be understood that other equivalents and modifications could be made thereto without departing from the spirit and scope of the invention.

A copper foil for a current collector of a lithium secondary battery according to the present invention gives surface characteristics in which factors such as crystal structure, surface roughness, weight deviation, tensile strength and elongation are optimized not to generate a wrinkle.

Preferably, the copper foil for a current collector of a lithium secondary battery according to the present invention is made by adding a small amount of organic additives to a copper sulfate solution containing copper sulfate, sulfuric acid and chlorine. Here, the additive may be a sulfonate-based additive containing sulfide as a brightener to polish a plating surface

and obtain a fine plating layer, gelatin having a low molecular weight of 1,000 to 100,000 as a leveler added to obtain a low roughness copper foil, or a cellulose-based additive serving as a suppressor to realize a stable low roughness. As the process condition, copper is electrodeposited on a drum surface of a foil making machine with a current density of 30 to 80 ASD (A/dm^2) at a temperature of 30 to 60°C, and the surface of the copper foil is chromated to prevent corrosion.

A crystalline structure of the copper foil should satisfies a condition that a ratio of the sum of texture coefficients of the (111) surface and the (200) surface, to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface, is 60 to 85%. Also, a ratio of the texture coefficient of the (111) surface to the total sum of the texture coefficients of the (111) surface, the (200) surface and the (220) surface should be 18 to 38%, a ratio of the texture coefficient of the (200) surface thereto should be 28 to 62%, and a ratio of the texture coefficient of the (220) surface thereto should be 15 to 40%. Such a crystalline structure may be obtained by controlling additives or plating conditions during an electroplating process for making a copper foil. In detail, the plating solution for obtaining the crystalline structure basically includes a copper

sulfate plating solution having copper sulfate, sulfuric acid and chlorine, to which at least two kinds of organic additives selected from the following group are added in the range of 1 to 50 ppm, respectively. The organic additive includes a gelatin-based compound with a molecular weight of 1,000 to 100,000 or a cellulose-based compound in addition to a mercapto compound. As the plating conditions to obtain the crystalline structure, copper is electrodeposited onto a drum surface of a foil making machine with a current density of 30 to 80 ASD at a temperature of 30 to 60℃ to make an original foil, and a nodule is formed thereat as necessary. After that, the surface of the copper foil is finally chromated to prevent corrosion.

If the texture coefficients are not within the above ranges, many wrinkles are created in a width direction of the copper foil, and accordingly the adhesion of active material to the surface of the copper foil may be deteriorated when the active material is coated. Here, the texture coefficient (TC) is determined by applying the X-ray diffraction (XRD) to obtain a diffraction intensity peak of each crystal surface as shown in Fig. 2 and then comparing the diffraction intensity peak with a criterion peak to convert it within the range defined by the following equation 1. In the equation 1, I(hkl) represents a measured diffraction intensity with respect to the (hkl)

surface, and $I_0(hkl)$ represents a standard diffraction intensity of an ASTM (American Society of Testing Materials) standard powder-shaped diffraction data.

Equation 1

$$TC(hkl) \geq \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{n}\Sigma\frac{I(hkl)}{I_0(hkl)}}$$

Surface roughness (R_z) of the copper foil should be 2 μm or less, based on JIS (Japanese Industrial Standards). In case the surface roughness (R_z) exceeds 2 μm, the surface is irregular, so a short circuit may occur during a charging or discharging process. In addition, the coating state of the anode active material becomes irregular.

The weight deviation of the copper foil should be 3% or less. If the weight deviation exceeds 3%, property deviations occur at the surface of the copper foil, which may increase the number of wrinkles and make properties of the current collector irregular. Here, the weight deviation is obtained by cutting a copper foil by an area of 5 cm × 5 cm to make a test piece, measuring weight of the test piece and converting the weight into a weight of the copper foil per a unit area, cutting the

test piece along a width direction of the copper foil, repeating the above processes to measure weights of copper foils of every test piece, and then calculating a standard deviation. At this time, the copper foil is preferably an electrodeposited copper foil that is surface-chromated for the prevention of corrosion.

In addition, the copper foil should satisfy the following conditions: a tensile strength of 30 to 40 kgf/mm^2, an elongation of 3 to 20%, and a thickness of 1 to 35 μm. Out of the above ranges, the properties of the copper foil are deviated to increase the number of wrinkles, and the properties of the current collector become irregular.

The following table 1 shows measurement results of wrinkle characteristics of the copper foils for a current collector of a lithium secondary battery according to examples 1 to 7 of the present invention and comparative examples 1 to 9. In the table 1, the tensile strength was measured by using a UTM (Universal Testing Machine), and at this time the gauge length was set to 5 cm.

Table 1

	Examples							Comparative examples								
	1	2	3	4	5	6	7	1	2	3	4	5	6	7	8	9
Copper foil	Electrodeposited copper foil															
Thickness of copper foil [μm]	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
(111)+(200) ratio [%]	76	62	83	70	72	81	66	64	73	62	83	87	57	80	75	76
(111) ratio [%]	26	31	32	20	35	22	36	16	41	37	19	34	26	30	23	25
(200) ratio [%]	50	31	51	50	36	59	30	48	32	25	64	53	31	49	51	50
(220) ratio [%]	24	38	17	30	29	19	34	36	27	38	17	13	43	21	26	25
Tensile strength [kg/mm^2]	32.2	33.7	34.5	32.6	32.1	37.2	33.1	36.8	33.2	31.4	37.1	33.1	32.4	27.4	41.5	31.8
Weight deviation [%]	0.4	0.7	0.8	1.6	0.4	2.6	1.2	0.5	0.9	0.5	0.9	0.7	0.8	0.6	0.9	3.4
Number of wrinkles [ea]	0	0	0	0	0	0	0	2	3	3	4	2	3	2	2	5

Seeing the table 1, it would be understood that the copper foils according to the examples 1 to 7 of the present invention satisfy all conditions of the texture coefficient ratio, the tensile strength, the weight deviation and the copper foil thickness, so no wrinkle occurs. Meanwhile, it would be also found that the copper foils according to the comparative

examples 1 to 9 have inappropriate characteristics as a current collector of a lithium secondary battery since a lot of winkles occur.

The copper foil for a current collector of a lithium secondary battery according to the present invention may have an improved wrinkle characteristic in comparison to conventional cases even if it satisfies only the condition of texture coefficient ratio. However, if other conditions such as tensile strength and weight deviation are out of the above numerical ranges, bad influences are given to the improved characteristics, thereby deteriorating the wrinkle characteristic. Thus, it is most preferable to satisfy all conditions of the texture coefficient ratio, the tensile strength, the weight deviation and the copper foil thickness.

The present invention has been described in detail. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

APPLICABILITY TO THE INDUSTRY

The copper foil for a current collector of a lithium secondary battery according to the present invention has excellent peel strength since a sufficient adhesive force is ensured when the copper foil is contacted with anode active material such as carbon-based slurry, so it is possible to realize a lithium secondary battery that may stably keep a battery capacity.

CLAIMS

What is claimed is:

1. A copper foil for a current collector of a lithium secondary battery,

wherein, in a crystalline structure, a ratio of a sum of texture coefficients of a (111) surface and a (200) surface to a total sum of texture coefficients of the (111) surface, the (200) surface and a (220) surface is 60 to 85%, a ratio of a texture coefficient of the (111) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 18 to 38%, a ratio of the texture coefficient of the (200) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 28 to 62%, and a ratio of the texture coefficient of the (220) surface to the total sum of texture coefficients of the (111) surface, the (200) surface and the (220) surface is 15 to 40%, and

wherein the texture coefficient satisfies the following equation:

$$TC(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{n}\sum\frac{I(hkl)}{I_0(hkl)}}$$

where I(hkl) represents a measured diffraction intensity with respect to a (hkl) surface, and I_0(hkl) represents a standard diffraction intensity of ASTM (American Society of Testing Materials) standard powder-shaped diffraction data.

2. The copper foil for a current collector of a lithium secondary battery according to claim 1, wherein the copper foil has a surface roughness (R_z-JIS) of 2 μm or less.

3. The copper foil for a current collector of a lithium secondary battery according to claim 1, wherein the copper foil has a weight deviation of 3% or less.

4. The copper foil for a current collector of a lithium secondary battery according to claim 1, wherein the copper foil has a tensile strength of 30 to 40 kgf/mm^2.

5. The copper foil for a current collector of a lithium secondary battery according to claim 1, wherein the copper foil has an elongation of 3 to 20%.

6. The copper foil for a current collector of a lithium secondary battery according to claim 1, wherein the copper foil has a thickness of 1 to 35 μm.

ABSTRACT

A copper foil for a current collector of a lithium secondary battery has a crystalline structure, in which a ratio of the sum of texture coefficients of a (111) surface and a (200) surface to the total sum of texture coefficients of the (111), (200) and (220) surfaces is 60 to 85%, a ratio of the texture coefficient of the (111) surface to the total sum of texture coefficients of the (111), (200) and (220) is 18 to 38%, a ratio of the texture coefficient of the (200) surface thereto is 28 to 62%, and a ratio of the texture coefficient of the (220) surface thereto is 15 to 40%. The copper foil has surface roughness (R_z-JIS) of 2 μm or less, weight deviation of 3% or less, tensile strength of 30 to 40 kgf/mm^2, elongation of 3 to 20%, and thickness of 1 to 35 μm.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	001333-0037
	Application Number	
Title of Invention	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
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Secrecy Order 37 CFR 5.2

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

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	Application Number	
Title of Invention	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS	

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Application Information:

Title of the Invention	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS		
Attorney Docket Number	001333-0037	**Small Entity Status Claimed**	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Suggested Class (if any)		**Sub Class (if any)**	
Suggested Technology Center (if any)			
Total Number of Drawing Sheets (if any)	1	**Suggested Figure for Publication (if any)**	

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Prior Application Status			Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
	Continuation of	13029656	2011-02-17

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Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Priority Claimed
2010-161088	KR	2010-07-15	◉ Yes ○ No

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☒ Authorization to Permit Access to the Instant Application by the Participating Offices

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	001333-0037
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Title of Invention	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS	

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In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the instant patent application with respect to: 1) the instant patent application-as-filed; 2) any foreign application to which the instant patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the instant patent application; and 3) any U.S. application-as-filed from which benefit is sought in the instant patent application.

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If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

◉ Assignee	○ Legal Representative under 35 U.S.C. 117	○ Joint Inventor
○ Person to whom the inventor is obligated to assign.	○ Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor :	
If the Applicant is an Organization check here. ☒	
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Email Address	

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Signature				Date (YYYY-MM-DD)	2012-12-20
First Name	Brian	Last Name	Rothery	Registration Number	35340

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Title of Invention	COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS		

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Declaration and Power of Attorney for Patent Application

특허 출원 관련 서언 및 위임권

Korean Language Declaration

아래 지명된 발명자로서, 본인은 하기 사항을 선언합니다.

As a below named inventor, I hereby declare that :

본인의 거주지, 우송 주소 및 국적은 본인의 성명 아래에 기재된 것과 동일합니다.

My residence, post office address and citizenship are as stated next to my name.

본인은 하기 명시된 발명에 대한 특허를 청구하는 주제의 최초 원래 단독 발명자이거나 (아래에 한 이름만이 기재된 경우) 또는 최초 원래 공동 발명자임을 (아래 에 여러 이름이 기재된 경우) 확인합니다.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below)of the subject matter which is claimed and for which a patent is sought on the invention entitled

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the specification of which is attached hereto unless the following box is checked:

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☐ was filed on as United States Application Number or PCT International Application Number and was amended on _____ (if applicable).

☐ 미합중국 출원번호 또는 PCT 국제 출원번호는 _____ 로 _____ 일에 출원되었고 _____ 일에 개정되었음 (해당 경우).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

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본인은 연방 규정 코드인 제37장의 제 1.56항에 의거하여 특허 자격에 관한 자료 정보를 공개할 의무를 인정합니다.

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본인은 외국인 특허 출원(들)이나 발명자의 증명서 관련 경우에는 미합중국코드인 제 35장의 제 17.9(a)-(d)항이나 제356(b)항에 의거하여 또는 미합중국 이외에 적어도 한 국가를 지정하는 PCT국제출원의 경우에는 제 365(a)항에 의거하여 하기 명시된 특허 출원의 외국 우선권을 주장하며, 외국인 특허출원, 발명자 증명서 또는 우선권이 주장되는 출원일 이전에 제출된 PCT 국제 출원도 또한 아래의 해당란을 체크 함으로서 확인하였습니다.

I hereby claim foreign priority under Title 35, United Sates Code, § 119(a)-(d) or § 365(a) of any foreign application(s) for patent or inventor's certificate, of § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority NOT Claimed
우선권 주장 않음

(Number) (번호)	(Country) (국가)	(Day/Month/Year Filed) (출원일자 일/월/년)	
2010-161088	Japan	15/07/2010	☐
(Number) (번호)	(Country) (국가)	(Day/Month/Year Filed) (출원일자 일/월/년)	

본인은 미합중국 코드인 제35장 제119항(e)에 명시된 바와같이 하기 미합중국 가출원에 관련된 특권을 요구합니다.

I hereby claim the benefit under Title 35, United States Code, 119(e) of any United States provisional application(s) listed below.

(Application No.) (출원 번호)	(Filing Date) (출원일자)
(Application No.) (출원 번호)	(Filing Date) (출원일자)

본인은 미합중국 코드인 제35장의 미국인 출원(들) 관련 제120항에 명시된 바와 같이 또는 미합중국을 지정하는 PCT 국제 출원 관련 제365(C) 항에 명시된 바와 같이 하기 출원의 특권을 요구합니다. 이출원서에 있는 각 특허 청구의 내용이 미합중국 코드인 제35장 제112항의 첫번째 절에서 명시된 바와 같이 종전의 미국 또는 PCT국제출원에 발표되지 않았으면 본인은 연방 규정 코드인 제37장 제1.56항에 명시된 바와 같이 종전 출원일자와 이 출원서의 국내 또는 PCT국제 출원일자 사이에 특허 자격에 대한 자료 정보를 공개할 의무를 인정합니다.

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s), of §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application

(Application No.) (출원 번호)	(Filing Date) (출원일자)	(Status)(patented, pending, abandoned) (현황)(특허획득,출원중,포기)
(Application No.) (출원 번호)	(Filing Date) (출원일자)	(Status)(patented, pending, abandoned) (현황)(특허획득,출원중,포기)

본인이 아는 한도 내에서 여기에 제공된 모든 내용이 사실이고, 제공된 정보나 소신이 모두 사실임을 확인하며, 더 나아가 미합중국 코드 제18장의 제 1001절에 명시된 바와 같이 고의의 허위 진술 및 이와 유사한 행위는 벌금이나 투옥으로 처벌 받거나 벌금과 감옥형을 모두 받을 수 있고 이러한 고의의 허위 진술은 특허 출원이나 후에 발급된 특허의 유효성을 위태롭게 함을 인지하면서 여기에 진술 함을 선언합니다.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application of any patent issued thereon.

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대리권: 지명된 발명자로서 본인은 이 특허를 출원하고 이와 관련하여 특허 및 상표청이 요구하는 실무를 처리하기 위하여 하기 변호사(들) 또는 대리인(들)을 임명합니다. (성명 및 등록번호 기입)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)

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단독 또는 첫번째 발명자의 성명	Full name of sole or first inventor KIM, Dae-Young
발명자의 서명 일자	First Inventor's signature Date Feb. 10, 2011
거주지	415-1101, Halla 2 Cha Apt., Ogeum-dong, Gunpo-si, Gyeonggi-do 435-760, Republic of Korea
국적	Citizenship Republic of Korea
우송 주소	Post Office Address: Same as residence
만약 있으면 두번째 공동 발명자의 이름	Full name of second joint inventor, if any LEE, Byoung-Kwang
두번째 발명자의 서명 일자	Second inventor's signature Date Feb. 10, 2011
거주지	Residence 201-102, Sinil Apt., Songjeong-dong, Icheon-si, Gyeonggi-do 467-741, Republic of Korea
국적	Citizenship Republic of Korea
우송 주소	Post Office Address: Same as residence
만약 있으면 세번째 공동 발명자의 이름	Full name of third joint inventor, if any CHOI, Seung-Jun
세번째 발명자의 서명 일자	Third inventor's signature Date Date Feb. 10, 2011
거주지	Residence 106-404, Byucksan Blooming Pureunsup Apt., Hwaseo-dong, Paldal-gu, Suwon-si, Gyeonggi-do 442-150,

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국적	Citizenship Republic of Korea
우송 주소	Post Office Address: Same as residence

FIG. 1

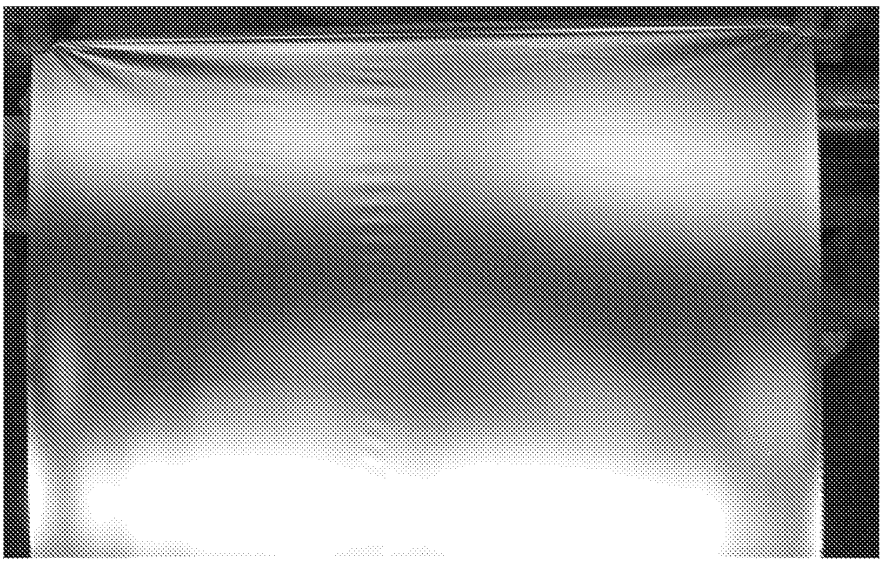
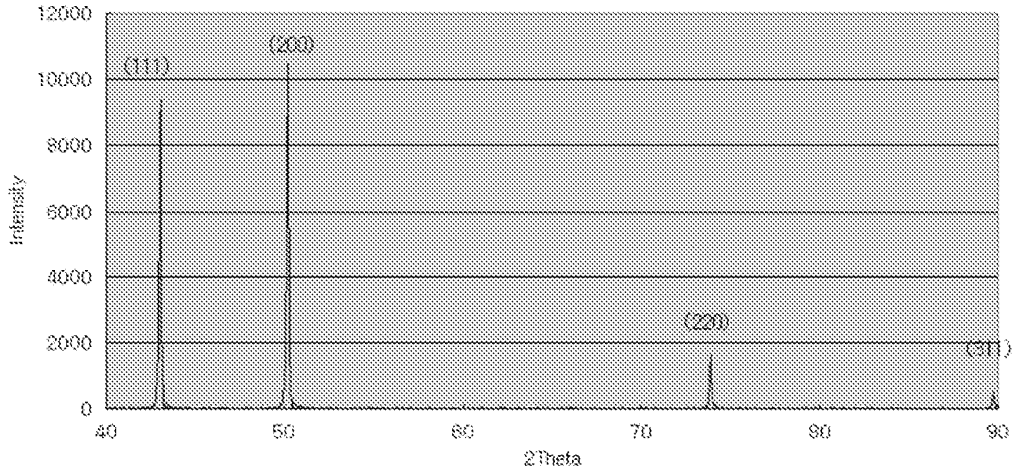


FIG. 2


12000
10000
8000
6000
4000
2000
0
Intensity
(111)
(200)
(220)
(311)
40
50
60
70
80
90
2Theta

Docket No.
001333-0037

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: **Ha-Young LEE** Group Art Unit: **Unassigned**

Application No.: **Unassigned** Examiner: **Unassigned**

Filed: **Herewith**

For: **COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY WITH IMPROVED WRINKLE CHARACTERISTICS**

Date: **December 20, 2012**

INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In compliance with the duty of disclosure under 37 C.F.R. § 1.56 and in accordance with the practice under 37 C.F.R. §§ 1.97 and 1.98, the Examiner's attention is directed to the documents listed on the enclosed Information Disclosure Statement by Applicant form (PTO/SB/08A and/or B, PTO-1449, or equivalent).

The following checked sections apply to this Information Disclosure Statement:

☒ In accordance with 37 C.F.R. § 1.98(a)(2)(ii) as revised at 69 Fed. Reg. 56481 (September 21, 2004), copies of the cited U.S. patent application publication(s) and/or U.S. patent(s) have not been submitted.

☐ The cited reference(s) were called to Applicant'(s) attention in a counterpart foreign patent application. A copy of the official communication in that counterpart foreign patent application citing the reference(s) is submitted herewith, and the Examiner is respectfully directed thereto for a concise explanation of the relevance of the cited art.

☒ At least some of the cited references are not (or the cited reference is not) in English, and so English abstracts of those references (that reference) are provided, if available.

☐ At least some of the cited references are not (or the cited reference is not) in English, and so machine English translations of those references (that reference) are provided, where available.

☒ This Information Disclosure Statement is being filed (1) within three months of the filing date of a national application other than a continued prosecution application under Sec. 1.53(d), (2) within three months of the date of entry of the national stage as set forth in Sec. 1.491 in an international application, (3) before the mailing of a first Office action on the merits, or (4) before the mailing of a first Office action after the filing of a Request for Continued Examination under 37 C.F.R. § 1.114. Accordingly, neither a fee nor Statement under 37 C.F.R. § 1.97(e) is due.

☐ This Information Disclosure Statement is being filed before the mailing date of any of a final action under 37 C.F.R. § 1.113, a Notice of Allowance under 37 C.F.R. § 1.311, or an action that otherwise closes prosecution in the application, and so is accompanied by one of:

(1) A Statement under 37 C.F.R. § 1.97(e), which follows; **or**

(2) The fee set forth in 37 C.F.R. § 1.17(p), authorization for which follows.

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(2) The fee set forth in 37 C.F.R. § 1.17(p), authorization for which follows.

☐ Fee Under 37 C.F.R. § 1.17(p)

The Commissioner is authorized to charge the fee under 37 C.F.R. § 1.17(p) ($180) to Deposit Account No. 19-4709.

☐ Statement Under 37 C.F.R. § 1.97(e)

Each item of information contained in this Information Disclosure Statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the Information Disclosure Statement; or

No item of information contained in the Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in Sec. 1.56(c) more than three months prior to the filing of the Information Disclosure Statement.

☐ Additional Comments

Applicant(s) have the following additional comments:

It is respectfully requested that the above information be considered by the Examiner and that an initialed copy of the accompanying Information Disclosure Statement by Applicant form (PTO/SB/08A and/or B, PTO-1449, or equivalent) be returned to the undersigned indicating that such information has been considered.

Other than any fees mentioned above, no fees are believed to be due in connection with this Information Disclosure Statement. Nevertheless, the Commissioner is authorized to charge any fees which are deemed to be now or hereafter due in connection with this paper to Deposit Account No. 19-4709.

Favorable consideration and prompt allowance of this application is respectfully requested. In the event that there are any questions, or should additional information be required, please contact Applicant'(s) attorney at the number listed below.

Respectfully submitted,



Brian M. Rothery
Reg. No. **35,340**
Attorney for Applicant(s)
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180 Maiden Lane
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No documents available for this priority number.

Espacenet

Bibliographic data: JP2010161088 (A) — 2010-07-22

ELECTRICAL CONNECTOR EQUIPPED WITH ELECTRIC SHIELD WITH LATCH AND INSTALLATION ARM

Inventor(s): CASEY DANIEL T; PETERS JR GEORGE I ± (CASEY DANIEL T, ; PETERS JR GEORGE I)

Applicant(s): FCI AMERICAS TECHNOLOGY INC ± (FCI AMERICAS TECHNOLOGY INC)

Classification: - international: ***H01R12/16; H01R12/20; H01R13/627; H01R13/639; H01R13/648; H01R13/652; H01R13/658; H01R24/00; H01R24/08; H05K1/00; H05K9/00;*** *H01R107/00*
- cooperative: **H01R13/6275**; **H01R13/65802**; **H01R23/7052**; **H01R23/7068**; H01R23/7021

Application number: JP20100101007 20100426

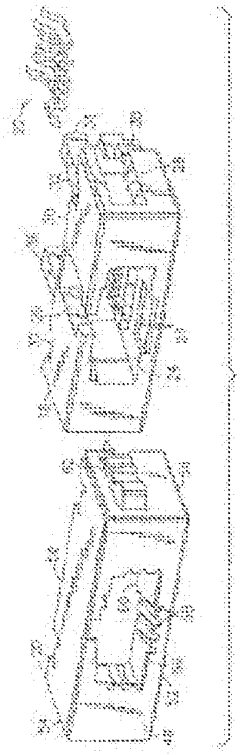
Priority number (s): US19990410004 19990930

Also published as: JP4883655 (B2) EP1089385 (A2) EP1089385 (A3) US2001049209 (A1) US6537084 (B2) more

Abstract of JP2010161088 (A)

PROBLEM TO BE SOLVED: To provide an electrical connector equipped with an electric shield with a latch and an installation arm. SOLUTION: The electrical connector includes: a housing that is suitable for storing one portion of a printing circuit substrate; an electrical contact that is connected to the housing; and an electromagnetic interference (EMI) shield that is connected to the housing. The shield has transmission holes for passing a pair of the electrical connectors to a storing region of the housing. In addition, the shield has a spring finger section extending inside the transmission hole and a first arm extending from a rear end section of the shield. The arm is suitable for retaining the shield to the housing and for relatively retaining a printing circuit substrate to the housing. ; COPYRIGHT: (C)2010,JPO&INPIT

Last updated: 19.12.2012 Worldwide
Database 5.6.4; 92p



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This is to certify that the annexed is a true copy of the following application as filed with this Office.

出 願 年 月 日 Date of Application:	２０１０年　７月１５日
出 願 番 号 Application Number:	特願２０１０－１６１０８８
パリ条約による外国への出願に用いる優先権の主張の基礎となる出願の国コードと出願番号 The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is	ＪＰ２０１０－１６１０８８
出 願 人 Applicant(s):	エル　エス　エムトロン　リミテッド

２０１２年　２月１７日

特許庁長官
Commissioner,
Japan Patent Office　岩井良行

【書類名】　特許願
【整理番号】　17458
【提出日】　平成22年 7月15日
【あて先】　特許庁長官殿
【国際特許分類】　H01M 10/00
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　【氏名】　キム，デ－ヨン
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　【氏名】　チェ，スン－ジュン
【特許出願人】
　【識別番号】　509023012
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　【電話番号】　06-6944-0651
【手数料の表示】
　【予納台帳番号】　001890
　【納付金額】　15,000円
【提出物件の目録】
　【物件名】　明細書　1
　【物件名】　特許請求の範囲　1
　【物件名】　要約書　1
　【物件名】　図面　1

【書類名】明細書
【発明の名称】リチウム二次電池の集電体用銅箔
【技術分野】
【０００１】
本発明は、リチウム二次電池の集電体として用いられる銅箔に関するものであって、より詳しくは、銅箔表面にしわ（ｗｒｉｎｋｌｅ）が発生することを防止することができる構造を有したリチウム二次電池の集電体用銅箔に関する。
【背景技術】
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【０００３】
一般に、リチウム二次電池は、セパレータを挟んで配置されたカソード及びアノードと、電解質とを備える。前記カソード及びアノードは、それぞれカソード活物質及びアノード活物質と、前記カソード活物質及びアノード活物質にそれぞれ接触するカソード集電体及びアノード集電体とを備えた構造を有する。
【０００４】
リチウム二次電池において、アノード集電体の素材としては主に銅箔が用いられ、通常この銅箔にはカーボン（ｃａｒｂｏｎ）系スラリーの活物質がコートされる。ここで、銅箔は、電気めっき法で電解銅箔を製造する製箔工程と、原箔に剥離強度（ｐｅｅｌ　ｓｔｒｅｎｇｔｈ）などを付与するための後処理工程とを通じて製造される。電気めっきによって電解銅箔の一面には製箔機のドラム（ｄｒｕｍ）の表面形状に沿った、いわゆる光沢面（ｓｈｉｎｙ　ｓｉｄｅ）が形成され、他面には山（ｍｏｕｎｔａｉｎ）構造によって相対的に粗度が高いマット面（ｍａｔｔｅ　ｓｉｄｅ）が形成される。また、電解銅箔は、後処理工程において、耐食性及び耐変色性を確保するために、保護性コーティングをさらに行う。
【０００５】
リチウム二次電池は集電体として用いられる銅箔の表面状態によって電池特性が大きく変わるので、歩留まりの向上のためにはしわ特性（ｗｒｉｎｋｌｅ　ｃｈａｒａｃｔｅｒｉｓｔｉｃｓ）のような表面特性を改善することが非常に重要である。
【０００６】
図１に示すように、銅箔の表面にしわが存在する場合、表面形状の不均一によって活物質が均一にコートされず、ゆえに充・放電するとき短絡が発生するか、銅箔から活物質が剥離される現象が発生する。
【先行技術文献】
【特許文献】
【０００７】
【特許文献１】特開２０００－２００６１０号公報
【発明の概要】
【発明が解決しようとする課題】
【０００８】
本発明は前記のような問題点を解決するために創案されたものであって、銅箔表面にしわを低減することができる結晶構造を有したリチウム二次電池の集電体用銅箔を提供することにその目的がある。
【０００９】
本発明の他の目的は、銅箔表面にしわをより有効に低減するために、表面粗度（ｓｕｒｆａｃｅ　ｒｏｕｇｈｎｅｓｓ）、重量偏差、引張強度、延伸率、厚さなどの因子が最適化されたリチウム二次電池の集電体用銅箔を提供することにある。

【課題を解決するための手段】
【００１０】
前記のような目的を達成するために、本発明によるリチウム二次電池の集電体用銅箔は、結晶構造において、（１１１）面、（２００）面、（２２０）面の集合組織係数（ｔｅｘｔｕｒｅ　ｃｏｅｆｆｉｃｉｅｎｔ）の全体合計の中で（１１１）面と（２００）面との集合組織係数の合計が占める比率が６０～８５％であり、前記（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計に対する（１１１）面の集合組織係数の比率が１８～３８％、（２００）面の集合組織係数の比率が２８～６２％、（２２０）面の集合組織係数の比率が１５～４０％であることを特徴とする。
【００１１】
前記銅箔の表面粗度（R_z－ＪＩＳ）は、２μｍ以下であることが望ましい。
【００１２】
前記銅箔の重量偏差特性は、３％以下であることが望ましい。
【００１３】
前記銅箔の引張強度は、３０～４０ｋｇｆ／ｍｍ^{2}であることが望ましい。
【００１４】
前記銅箔の延伸率は、３～２０％であることが望ましい。
【００１５】
前記銅箔の厚さは、１～３５μｍであることが望ましい。
【発明の効果】
【００１６】
本発明によるリチウム二次電池の集電体用銅箔は、表面にしわが実質的に発生しないので、活物質をコートするとき均一なコーティング面を形成することができ、短絡の発生を防止することができる。
【図面の簡単な説明】
【００１７】
本明細書に添付される下記の図面は本発明の望ましい実施例を例示するものであって、発明の詳細な説明とともに本発明の技術思想をさらに理解させる役割を果たすものであるため、本発明はそのような図面に記載された事項にのみ限定されて解釈されてはいけない。
【図１】従来技術によるリチウム二次電池の集電体用銅箔にしわが発生した状態を示す写真である。
【図２】本発明によるリチウム二次電池の集電体用銅箔の集合組織係数の算出のために、Ｘ線回折法（ＸＲＤ）を行った結果を示すグラフである。
【発明を実施するための形態】
【００１８】
以下、添付した図面を参照しながら本発明の望ましい実施例を詳しく説明する。これに先立って、本明細書及び請求範囲に使われた用語や単語は通常的や辞書的な意味に限定して解釈されてはいけず、発明者は自らの発明を最善の方法で説明するために用語の概念を適切に定義することができるという原則に則して、本発明の技術的思想に符合する意味と概念とに解釈されなければならない。従って、本明細書に記載された実施例は本発明の最も望ましい一実施例に過ぎず、本発明の技術的思想の全てを代弁するものではないため、本出願時点においてこれらに代替できる多様な均等物と変形例があり得ることを理解しなければならない。
【００１９】
本発明によるリチウム二次電池の集電体用銅箔は、結晶構造、表面粗度、重量偏差、引張強度、延伸率などの因子が最適化されてしわが発生しない表面特性を提供する。
【００２０】
望ましくは、本発明によるリチウム二次電池の集電体用銅箔は、硫酸銅、硫酸及び塩素から構成された硫酸銅めっき液を基本にし、微量の有機添加剤を添加して製造される。こ

こで、添加剤としては、めっき表面に光沢を付与し微細なめっき層を得るための光沢剤（ｂｒｉｇｈｔｅｎｅｒ）としてスルフィド（ｓｕｌｆｉｄｅ）を含有したスルホネート（ｓｕｌｐｈｏｎａｔｅ）系列の添加剤と、低粗度の銅箔を得るために添加するレベラー（ｌｅｖｅｌｅｒ）として分子量１，０００～１００，０００程度の低分子量を有するゼラチン（ｇｅｌａｔｉｎ）と、安定した低粗度を具現するためのサプレッサー（ｓｕｐｐｒｅｓｓｏｒ）としてセルロース（ｃｅｌｌｕｌｏｓｅ）系列の添加剤とが用いられる。工程条件としては、３０～８０ＡＳＤ（Ａ／ｄｍ^{2}の電流密度及び３０～６０℃の温度において製箔機のドラム表面に銅を電着して原箔を製造し、防錆処理のために銅箔表面をクロメート（ｃｈｒｏｍａｔｅ）処理する工程を経て製造される。

【００２１】

銅箔の結晶構造は、（１１１）面、（２００）面、（２２０）面の集合組職係数の全体合計の中で（１１１）面と（２００）面との集合組職係数の合計が占める比率が６０～８５％を満たす。また、（１１１）面、（２００）面、（２２０）面の集合組職係数の全体合計に対する（１１１）面の集合組職係数の比率は１８～３８％、（２００）面の集合組職係数の比率は２８～６２％、（２２０）面の集合組職係数の比率は１５～４０％を満たす。

【００２２】

前記集合組職係数の数値範囲を外れる場合、銅箔の幅方向にしわが多数発生することになり、このため活物質をコートするとき銅箔表面に対する活物質の密着性が低下する問題がある。ここで、集合組職係数（ＴＣ）は、Ｘ線回折法（ＸＲＤ）を適用して図２に示すように各結晶面の回折強度ピーク（ｐｅａｋ）値を得た後、基準ピーク値と比較して以下の数学式１に従う範囲内で換算することで定められる。数学式１において、Ｉ（ｈｋｌ）は、（ｈｋｌ）面に対する測定回折強度を示し、I_o（ｈｋｌ）は、ＡＳＴＭ（Ａｍｅｒｉｃａｎ　Ｓｏｃｉｅｔｙ　ｏｆ　Ｔｅｓｔｉｎｇ　Ｍａｔｅｒｉａｌｓ）標準の粉末状回折データの標準回折強度を示す。

【００２３】

【数１】

$$TC(hkl) \geq \frac{\frac{I(hkl)}{I_o(hkl)}}{\frac{1}{n}\sum\frac{I(hkl)}{I_o(hkl)}}$$

【００２４】

銅箔の表面粗度（R_z）は、日本工業標準規格（ＪＩＳ）を基準にして２μｍ以下を満たす。表面粗度（R_z）が２μｍを超える場合、表面が不均一であるのでリチウム二次電池を充・放電するとき短絡が発生する恐れがあり、アノード活物質のコーティング状態が不均一になる問題が発生する。

【００２５】

銅箔の重量偏差特性は、３％以下を満たす。重量偏差特性が３％を超える場合、銅箔表面に物性偏差が発生してしわ数が増加し、集電体の物性が不均一になる問題が発生する。ここで、重量偏差は、銅箔を５ｃｍ×５ｃｍのサイズに切り出して試片を作った後その重量を測定して単位面積当たりの銅箔の重量値を換算し、銅箔の幅方向に沿って前記試片を切り出す過程を繰り返して行って各試片に対する銅箔重量値を測定した後標準偏差を計算することで算出する。このとき、銅箔は、クロメート表面処理を通じて防錆処理された電解銅箔を用いることが望ましい。

【００２６】

その他に、銅箔の引張強度は３０～４０ｋｇｆ／ｍｍ^2、延伸率は３～２０％、厚さは

１～３５μｍを満たす。このような範囲を外れた場合、銅箔の物性偏差が発生してしわ数が増加し、集電体の物性が不均一になる問題が発生する。

【００２７】

下記表１は、本発明の実施例１ないし７と比較例１ないし９によるリチウム二次電池の集電体用銅箔に対してしわ特性を測定した結果を示す。表１において、引張強度はＵＴＭ（Ｕｎｉｖｅｒｓａｌ　Ｔｅｓｔｉｎｇ　Ｍａｃｈｉｎｅ）を利用して測定し、このときゲージ長（ｇａｕｇｅ　ｌｅｎｇｔｈ）は５ｃｍに設定した。

【００２８】

【表１】

区分	銅箔	銅箔厚さ［μm］	(111)+(200)比率［%］	(111)比率［%］	(200)比率［%］	(220)比率［%］	引張強度［kg/㎟］	重量偏差［%］	リンクル発生数［ea］
実施例１	電解銅箔	8	76	26	50	24	32.2	0.4	0
実施例２	電解銅箔	8	62	31	31	38	33.7	0.7	0
実施例３	電解銅箔	8	83	32	51	17	34.5	0.8	0
実施例４	電解銅箔	8	70	20	50	30	32.6	1.6	0
実施例５	電解銅箔	8	72	35	36	29	32.1	0.4	0
実施例６	電解銅箔	8	81	22	59	19	37.2	2.6	0
実施例７	電解銅箔	8	66	36	30	34	33.1	1.2	0
比較例１	電解銅箔	8	64	16	48	36	36.8	0.5	2
比較例２	電解銅箔	8	73	41	32	27	33.2	0.9	3
比較例３	電解銅箔	8	62	37	25	38	31.4	0.5	3
比較例４	電解銅箔	8	83	19	64	17	37.1	0.9	4
比較例５	電解銅箔	8	87	34	53	13	33.1	0.7	2
比較例６	電解銅箔	8	57	26	31	43	32.4	0.8	3
比較例７	電解銅箔	8	80	30	49	21	27.4	0.6	2
比較例８	電解銅箔	8	75	23	51	26	41.5	0.9	2
比較例９	電解銅箔	8	76	25	50	25	31.8	3.4	5

【００２９】

表１を参照すれば、本発明の実施例１ないし７による銅箔は、前述した集合組織係数の比率、引張強度、重量偏差、銅箔厚さの条件をすべて満たすことで、しわが発生しない結果を示すことが確認できる。その反面、比較例１ないし９による銅箔は、しわが多数発生して、リチウム二次電池の集電体として用いるには不適な特性を示すことが確認できる。

【００３０】

本発明によるリチウム二次電池の集電体用銅箔は、集合組織係数の比率の条件のみを満たしてもしわ特性が従来に比べて改善できるが、比較例１ないし９に示すように引張強度や重量偏差などの他の条件が該当の数値範囲を外れた場合には、改善した特性に悪影響を及ぼして最終的にしわ特性の低下をもたらすので、前述した集合組織係数の比率、引張強度、重量偏差、銅箔厚さなどの条件をすべて満たすことが最も望ましい。

【００３１】

以上のように、本発明は、たとえ限定された実施例と図面とによって説明されたが、本発明はこれによって限定されず、本発明が属する技術分野において通常の知識を持つ者により本発明の技術思想と特許請求範囲の均等範囲内で多様な修正及び変形が可能なのは言うまでもない。

【産業上の利用可能性】

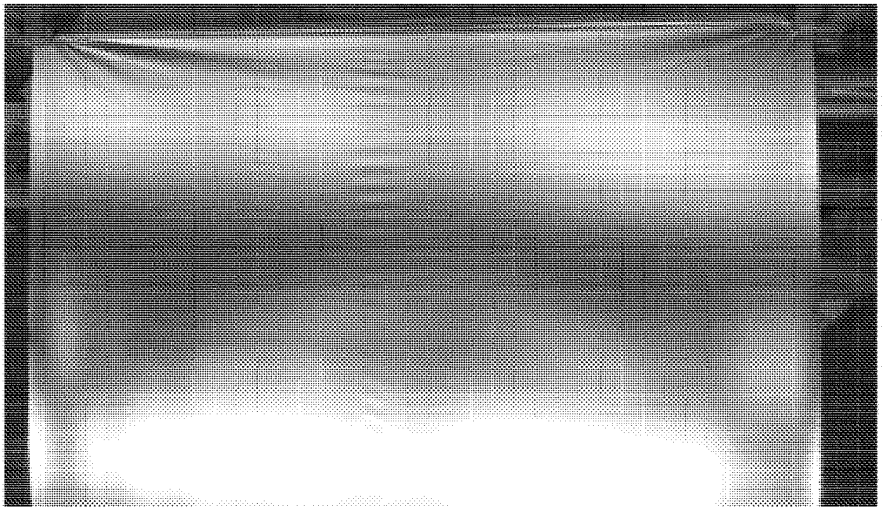
【００３２】

本発明によるリチウム二次電池の集電体用銅箔は、カーボン系スラリーのようなアノード活物質と接触するとき密着力が十分確保されて剥離強度に優れているので、電池容量を安定して維持することができるリチウム二次電池を具現することができる。

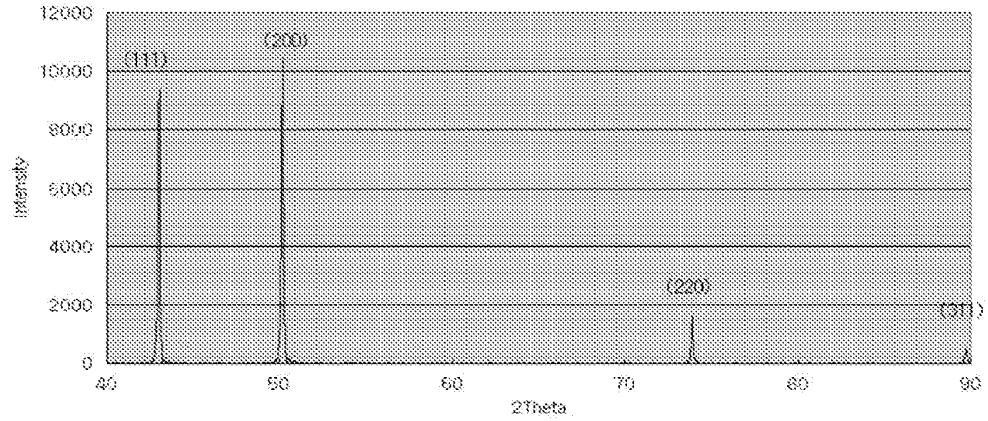
【書類名】特許請求の範囲
【請求項１】
リチウム二次電池の集電体として用いられる銅箔であって、
結晶構造において、（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計の中で（１１１）面と（２００）面との集合組織係数の合計が占める比率が６０～８５％であり、前記（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計に対する（１１１）面の集合組織係数の比率が１８～３８％、（２００）面の集合組織係数の比率が２８～６２％、（２２０）面の集合組織係数の比率が１５～４０％であることを特徴とするリチウム二次電池の集電体用銅箔。
【請求項２】
表面粗度（Ｒｚ－ＪＩＳ）が２μｍ以下であることを特徴とする請求項１に記載のリチウム二次電池の集電体用銅箔。
【請求項３】
重量偏差特性が３％以下であることを特徴とする請求項１または請求項２に記載のリチウム二次電池の集電体用銅箔。
【請求項４】
引張強度が３０～４０ｋｇｆ／ｍｍ^{2}であることを特徴とする請求項１ないし請求項３のうち何れかに記載のリチウム二次電池の集電体用銅箔。
【請求項５】
延伸率が３～２０％であることを特徴とする請求項１ないし請求項４のうち何れかに記載のリチウム二次電池の集電体用銅箔。
【請求項６】
銅箔厚さが１～３５μｍであることを特徴とする請求項１ないし請求項５のうち何れかに記載のリチウム二次電池の集電体用銅箔。
【請求項７】
リチウム二次電池の集電体として用いられる銅箔であって、
結晶構造において、（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計の中で（１１１）面と（２００）面との集合組織係数の合計が占める比率が６０～８５％であり、前記（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計に対する（１１１）面の集合組織係数の比率が１８～３８％、（２００）面の集合組織係数の比率が２８～６２％、（２２０）面の集合組織係数の比率が１５～４０％であり、
表面粗度（Ｒｚ－ＪＩＳ）が２μｍ以下であり、
重量偏差特性が３％以下であり、
引張強度が３０～４０ｋｇｆ／ｍｍ^{2}であり、
延伸率が３～２０％であり、
銅箔の厚さが１～３５μｍであることを特徴とするリチウム二次電池の集電体用銅箔。

【書類名】要約書
【要約】
【課題】銅箔表面にしわを低減することができる結晶構造を有したリチウム二次電池の集電体用銅箔を提供する。
【解決手段】本発明によるリチウム二次電池の集電体用銅箔は、結晶構造において、（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計の中で（１１１）面と（２００）面との集合組織係数の合計が占める比率が６０～８５％であり、前記（１１１）面、（２００）面、（２２０）面の集合組織係数の全体合計に対する（１１１）面の集合組織係数の比率が１８～３８％、（２００）面の集合組織係数の比率が２８～６２％、（２２０）面の集合組織係数の比率が１５～４０％であり、表面粗度（Ｒｚ－ＪＩＳ）が２μｍ以下であり、重量偏差特性が３％以下であり、引張強度が３０～４０ｋｇｆ／ｍｍ２であり、延伸率が３～２０％であり、銅箔の厚さが１～３５μｍであることを特徴とする。
【選択図】図２

【書類名】図面
【図１】



【図２】


12000
10000
8000
6000
4000
2000
0
Intensity
(111)
(200)
(220)
(311)
40
50
60
70
80
90
2Theta

出願人履歴

５０９０２３０１２

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