AO 120 (Rev. 08/10)

TO:	REPORT ON THE FILING OR DETERMINATION OF AN ACTION REGARDING A PATENT OR TRADEMARK
Mail Stop 8 Director of the U.S. Patent and Trademark Office P.O. Box 1450 Alexandria, VA 22313-1450	

In Compliance with 35 U.S.C. § 290 and/or 15 U.S.C. § 1116 you are hereby advised that a court action has been filed in the U.S. District Court Eastern District of Texas on the following

☐ Trademarks or ☑ Patents. (☐ the patent action involves 35 U.S.C. § 292.):

DOCKET NO. 2:23-CV-539	DATE FILED 11/21/2023	U.S. DISTRICT COURT Eastern District of Texas
PLAINTIFF SK nexilis Co., Ltd.		DEFENDANT Solus Advanced Materials Co., Ltd., Volta Energy Solutions S.A.R.L., Volta Energy Solutions Europe KFT., Volta Energy Solutions Hungary KFT., and Volta Energy Solutions Canada Inc.

	PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1	10,480,090	11/19/2019	SK nexilis Co., Ltd.
2	10,811,689	10/20/2020	SK nexilis Co., Ltd.
3	11,346,014	5/31/2022	SK nexilis Co., Ltd.
4	11,591,706	2/28/2023	SK nexilis Co., Ltd.
5			

In the above—entitled case, the following patent(s)/ trademark(s) have been included:

DATE INCLUDED	INCLUDED BY ☐ Amendment ☐ Answer ☐ Cross Bill ☐ Other Pleading	
PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1		
2		
3		
4		
5		

In the above—entitled case, the following decision has been rendered or judgement issued:

DECISION JUDGEMENT

CLERK	(BY) DEPUTY CLERK	DATE

Copy 1—Upon initiation of action, mail this copy to Director Copy 3—Upon termination of action, mail this copy to Director
Copy 2—Upon filing document adding patent(s), mail this copy to Director Copy 4—Case file copy

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.
15/696,360	10/20/2020	10811689	0313221.00013	7466

24573 7590 09/30/2020

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

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 222 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):

Seung Min KIM, Anyang-si, KOREA, REPUBLIC OF;
LS Mtron Ltd., Anyang-si, 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), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (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)

24573 7590 07/28/2020
K&L Gates LLP-Chicago
P.O. Box 1135
Chicago, IL 60690

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 transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/696,360	09/06/2017	Seung Min KIM	0313221.00013	7466

TITLE OF INVENTION: EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	10/28/2020

EXAMINER	ART UNIT	CLASS-SUBCLASS
ANTHONY, JULIAN	1722	429-245000

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 03-09 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 K&L Gates LLP
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 must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: KCF TECHNOLOGIES CO., LTD.

(B) RESIDENCE: (CITY and STATE OR COUNTRY): ANYANG-SI, 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. Fees submitted: ☒ Issue Fee ☐ Publication Fee (if required) ☐ Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

☒ Electronic Payment via EFS-Web ☐ Enclosed check ☐ Non-electronic payment by credit card (Attach form PTO-2038)

☒ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. 02-1818

5. **Change in Entity Status** (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29

☐ Applicant asserting small entity status. See 37 CFR 1.27

☐ Applicant changing to regular undiscounted fee status.

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.
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.
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 /Matthew S. Dicke/ Date September 15, 2020

Typed or printed name Matthew S. Dicke Registration No. 58,819

Electronic Patent Application Fee Transmittal

Application Number:	15696360
Filing Date:	06-Sep-2017
Title of Invention:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Seung Min KIM
Filer:	Matthew S. Dicke/Meg Boinski
Attorney Docket Number:	0313221.00013

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	1000	1000

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**1000**

Electronic Acknowledgement Receipt	
EFS ID:	40557249
Application Number:	15696360
International Application Number:	
Confirmation Number:	7466
Title of Invention:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Seung Min KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/US Patent Mail
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313221.00013
Receipt Date:	15-SEP-2020
Filing Date:	06-SEP-2017
Time Stamp:	15:03:25
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$1000
RAM confirmation Number	E20209EF03384903
Deposit Account	021818
Authorized User	US Patent Mail
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: 37 CFR 1.21 (Miscellaneous fees and charges) 37 CFR 1.17 (Patent application and reexamination processing fees)	

37 CFR 1.16 (National application filing, search, and examination fees)

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)	0313221-00013_IssueFee.pdf	1121616 69e218a44fa8cae9974e72573c385cb7b2503061	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30500 a53b562c722b2dd1c1121be261dde014e260739c	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	1152116		

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
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P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

24573 7590 07/28/2020

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

EXAMINER
ANTHONY, JULIAN

ART UNIT	PAPER NUMBER
1722	

DATE MAILED: 07/28/2020

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/696,360	09/06/2017	Seung Min KIM	0313221.00013	7466

TITLE OF INVENTION: EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	10/28/2020

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: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (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)

24573 7590 07/28/2020

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

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 transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/696,360	09/06/2017	Seung Min KIM	0313221.00013	7466

TITLE OF INVENTION: EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	10/28/2020

EXAMINER	ART UNIT	CLASS-SUBCLASS
ANTHONY, JULIAN	1722	429-245000

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 03-09 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 must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). 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. Fees submitted: ❑Issue Fee ❑Publication Fee (if required) ❑Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

❑ Electronic Payment via EFS-Web ❑ Enclosed check ❑ Non-electronic payment by credit card (Attach form PTO-2038)

❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29

❑ Applicant asserting small entity status. See 37 CFR 1.27

❑ Applicant changing to regular undiscounted fee status.

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.
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.
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. _____

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.
15/696,360	09/06/2017	Seung Min KIM	0313221.00013	7466

24573 7590 07/28/2020

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

EXAMINER	
ANTHONY, JULIAN	
ART UNIT	**PAPER NUMBER**
1722	

DATE MAILED: 07/28/2020

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 30 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.** 15/696,360	**Applicant(s)** KIM, Seung Min	
	Examiner JULIAN ANTHONY	**Art Unit** 1722	**AIA (FITF) Status** Yes

-- 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 6-17-20.
   ☐ 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 1-2,4-5 and 7-12 . 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 _____.

/Julian Anthony/ Examiner, AU 1722	/CYNTHIA H KELLY/ Supervisory Patent Examiner, Art Unit 1722

EXAMINER'S AMENDMENT

An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it MUST be submitted no later than the payment of the issue fee.

Authorization for this examiner's amendment was given in an interview with James Jang on July 10, 2020.

The application has been amended as follows:

1. In claim 1,

"a weight deviation of the electrolytic copper foil is 5% or less, and

a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92." in lines 13-15 has been deleted, insert in its place

--a weight deviation of the electrolytic copper foil is 5% or less,

a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92, and

each of the first and second surfaces has a surface roughness (R_z) of 3.5 μm or less.--

2. Claim 6 has been canceled.

3. In claim 8,

"wherein a weight deviation of the electrolytic copper foil is 5% or less, and

wherein a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92." in lines 15-17 has been deleted, insert in its place

--wherein a weight deviation of the electrolytic copper foil is 5% or less,

wherein a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92, and

wherein each of the first and second surfaces has a surface roughness (R_z) of 3.5 μm or less.--

4. In claim 12,

Delete "wherein a weight deviation of the electrolytic copper foil is 5% or less, and

wherein a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92." in lines 21-23 has insert in its place

--wherein a weight deviation of the electrolytic copper foil is 5% or less,

wherein a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92, and

wherein each of the first and second surfaces has a surface roughness (R_z) of 3.5 μm or less.--

5. Claims 13-20 have been canceled.

Allowable Subject Matter

Claims 1, 2, 4, 5 and 7-12 are allowed.

The following is an examiner's statement of reasons for allowance: the prior art of record does not teach or suggest the instant invention regarding an electrolytic copper foil having, for each of its first and second surfaces, a peak count ranging from 3 to 92 and a surface roughness R_z of 3.5 μm or less.

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 JULIAN ANTHONY whose telephone number is (571)272-1289. The examiner can normally be reached on Monday to Friday.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Cynthia Kelly, can be reached on 571-272-1526. 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.

/Julian Anthony/
Examiner, Art Unit 1722

/CYNTHIA H KELLY/
Supervisory Patent Examiner, Art Unit 1722

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/696,360	KIM, Seung Min
	Examiner	**Art Unit**
	JULIAN ANTHONY	1722

CPC						
Symbol					**Type**	**Version**
H01M	/	4	/	661	F	2013-01-01
C25D	/	1	/	20	I	2013-01-01
C25D	/	1	/	04	I	2013-01-01
C25D	/	3	/	38	I	2013-01-01
C25D	/	7	/	00	I	2013-01-01
H01M	/	4	/	0452	I	2013-01-01
H01M	/	4	/	0471	I	2013-01-01
H01M	/	4	/	133	I	2013-01-01
H01M	/	4	/	1395	I	2013-01-01
H01M	/	4	/	667	I	2013-01-01
H01M	/	10	/	0525	I	2013-01-01
H01M	/	10	/	052	A	2013-01-01
C25D	/	3	/	58	A	2013-01-01

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

/Julian Anthony/	16 July 2020	**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	11	
/CYNTHIA H KELLY/ Supervisory Patent Examiner, Art Unit 1722	20 July 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office — Part of Paper No.: 20200708

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/696,360	KIM, Seung Min
	Examiner	Art Unit
	JULIAN ANTHONY	1722

INTERNATIONAL CLASSIFICATION				
CLAIMED				
H01M	/	4	/	66
H01M	/	4	/	68
H01M	/	4	/	13
H01M	/	4	/	58
H01M	/	4	/	00
H01M	/	4	/	13

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	SUBCLASS
429	245

CROSS REFERENCES(S)						
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)					
429	218.1	221	231.6	231.95		

/Julian Anthony/ (Assistant Examiner)	16 July 2020 (Date)	Total Claims Allowed: 11	
/CYNTHIA H KELLY/ Supervisory Patent Examiner, Art Unit 1722 (Primary Examiner)	20 July 2020 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure 1

U.S. Patent and Trademark Office — Part of Paper No.: 20200708

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/696,360	KIM, Seung Min
	Examiner	**Art Unit**
	JULIAN ANTHONY	1722

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

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original

/Julian Anthony/	16 July 2020	**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	11	
/CYNTHIA H KELLY/ Supervisory Patent Examiner, Art Unit 1722	20 July 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office — Part of Paper No.: 20200708

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/696,360	KIM, Seung Min
	Examiner	Art Unit
	JULIAN ANTHONY	1722

CPC - Searched*		
Symbol	Date	Examiner

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
EAST class/keyword search	07/08/2020	JA
Consulted A. Usyatinsky	07/08/2020	JA
Inventor search	07/16/2020	JA

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner
429/H01M	see search history	07/16/2020	JA

UNITED STATES PATENT AND TRADEMARK OFFICE

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www.uspto.gov

BIB DATA SHEET

CONFIRMATION NO. 7466

SERIAL NUMBER	FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
15/696,360	09/06/2017 **RULE**	429	1722	0313221.00013

APPLICANTS
LS Mtron Ltd., Anyang-si, KOREA, REPUBLIC OF;

INVENTORS
Seung Min KIM, Anyang-si, KOREA, REPUBLIC OF;

** **CONTINUING DATA** *************************

** **FOREIGN APPLICATIONS** *************************
REPUBLIC OF KOREA 10-2016-0131979 10/12/2016

** **IF REQUIRED, FOREIGN FILING LICENSE GRANTED** **
09/14/2017

		STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
Foreign Priority claimed ☑ Yes ☐ No 35 USC 119(a-d) conditions met ☑ Yes ☐ No Verified and Acknowledged /JULIAN ANTHONY/ Examiner's Signature	☐ Met after Allowance Initials	KOREA, REPUBLIC OF	1	20	4

ADDRESS

K&L Gates LLP-Chicago
P.O. Box 1135
Chicago, IL 60690
UNITED STATES

TITLE

EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

FILING FEE RECEIVED		
2020	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

BIB (Rev. 05/07).

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor:	Seung Min KIM
Appl. No.:	15/696,360
Conf. No.:	7466
Filed:	September 6, 2017
Title:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1722
Examiner:	ANTHONY, Julian
Docket No.:	0313221.00013

OK TO ENTER: /J.A/

RESPONSE AFTER FINAL OFFICE ACTION

VIA ELECTRONIC FILING

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

Dear Commissioner:

The present Response is in reply to the Final Office Action mailed March 20, 2019 issued in connection with the above-identified application. Applicant also submits herewith a request for consideration of this Response under the After Final Consideration Pilot 2.0 program. In response to the Final Office Action, Applicant submits the following:

Listing of the Claims begins on page 2 of this paper; and

Remarks begin on page 7 of this paper.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor:	Seung Min KIM
Appl. No.:	15/696,360
Conf. No.:	7466
Filed:	September 6, 2017
Title:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1722
Examiner:	ANTHONY, Julian
Docket No.:	0313221.00013

RESPONSE AFTER FINAL OFFICE ACTION

VIA ELECTRONIC FILING

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

Dear Commissioner:

The present Response is in reply to the Final Office Action mailed March 20, 2019 issued in connection with the above-identified application. Applicant also submits herewith a request for consideration of this Response under the After Final Consideration Pilot 2.0 program. In response to the Final Office Action, Applicant submits the following:

Listing of the Claims begins on page 2 of this paper; and

Remarks begin on page 7 of this paper.

The following Listing of the Claims replaces all prior Listing(s) of the Claims in the Subject Application.

Listing of Claims:

1. (Previously Presented) An electrolytic copper foil, which includes a first surface and a second surface opposite the first surface, the electrolytic copper foil comprising:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

wherein:

a coefficient of thermal expansion of the electrolytic copper foil, which is measured using a thermomechanical analyzer (TMA) while heating the electrolytic copper foil from 30°C to 190°C at a speed of 5°C/min, ranges from 16 to 22 μm/(m•°C),

a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190 °C for 1 hour, ranges from 21 to 36 kgf/mm^2,

a weight deviation of the electrolytic copper foil is 5% or less, and

a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92.

2. (Original) The electrolytic copper foil of claim 1, having an elongation of 3% or more at room temperature.

3. (Cancelled)

4. (Original) The electrolytic copper foil of claim 1, wherein each of the first and second protective layers includes at least one of chromium (Cr), a silane compound, and a nitrogen compound.

5. (Original) The electrolytic copper foil of claim 1, having a thickness of 4 to 30 μm.

6. (Previously Presented) The electrolytic copper foil of claim 1, wherein each of the first and second surfaces has a surface roughness (R_z) of 3.5 μm or less.

7. (Original) The electrolytic copper foil of claim 1, having a coefficient of thermal expansion of 17.3 to 22 μm/(m•°C).

8. (Previously Presented) A secondary battery electrode comprising:

an electrolytic copper foil including a first surface and a second surface opposite the first surface; and

a first active material layer on the first surface of the electrolytic copper foil,

wherein the electrolytic copper foil comprises:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

wherein a coefficient of thermal expansion of the electrolytic foil, which is measured using a TMA while heating the electrolytic copper foil from 30 °C to 190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m•°C),

wherein a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190°C for 1 hour, ranges from 21 to 36 kgf/mm^2,

wherein a weight deviation of the electrolytic copper foil is 5% or less, and

wherein a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92.

9. (Previously Presented) The secondary battery electrode of claim 8, wherein the first active material layer includes at least one active material selected from the group consisting of carbon, a metal (Me) such as Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni, or Fe, an alloy containing the metal (Me), an oxide of the metal (MeO_x), and a composite of the metal (Me) and carbon.

10. (Original) The secondary battery electrode of claim 8, wherein the first active material layer comprises Si.

11. (Original) The secondary battery electrode of claim 8, further comprising a second active material layer on the second protective layer.

12. (Previously Presented) A secondary battery comprising:

a cathode;

an anode including a secondary battery electrode;

an electrolyte configured to provide an environment in which lithium ions may move between the cathode and the anode; and

a separator configured to electrically insulate the cathode from the anode,

wherein the secondary battery electrode comprises:

an electrolytic copper foil including a first surface and a second surface opposite the first surface; and

a first active material layer on the first surface of the electrolytic copper foil,

wherein the electrolytic copper foil comprises:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

wherein a coefficient of thermal expansion of the electrolytic foil, which is measured using a TMA while heating the electrolytic copper foil from 30 °C to 190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m•°C),

wherein a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190°C for 1 hour, ranges from 21 to 36 kgf/mm^2,

wherein a weight deviation of the electrolytic copper foil is 5% or less, and

wherein a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92.

13. (Withdrawn) A method of manufacturing a secondary battery electrolytic copper foil, the method comprising:

preparing an electrolytic solution containing 70 to 90 g/L of copper ions and 80 to 130 g/L of sulfuric acid;

forming a copper layer by performing electroplating which applies electricity between a positive electrode plate and a rotating negative electrode drum which are disposed to in the electrolytic solution be spaced apart from each other; and

forming a protective layer on the copper layer,

wherein, while the electroplating is performed, an interval between the positive electrode plate and the rotating negative electrode drum is maintained to be in a range of 5 to 15 mm, a difference between a maximum interval and a minimum interval of the positive electrode plate and the rotating negative electrode drum in a width direction of the copper layer is maintained to be less than 0.2 mm, total organic carbon (TOC) in the electrolytic solution is maintained at 50 ppm or less, and a concentration of silver (Ag) in the electrolytic solution is maintained at 25 ppm or less.

14. (Withdrawn) The method of claim 13, wherein the electroplating is performed by applying a current density of 30 to 80 A/dm^2 between the positive electrode plate and the rotating negative electrode drum.

15. (Withdrawn) The method of claim 13, wherein the preparing of the electrolytic solution comprises:

performing a heat treatment on a copper wire;

pickling the heat-treated copper wire; and

introducing the pickled copper wire into sulfuric acid.

16. (Withdrawn) The method of claim 15, wherein:

the copper wire is heat-treated at a temperature of 600 to 900 °C for 2 to 6 hours, and

the heat-treated copper wire is pickled by being immersed in an acidic solution containing 8 to 10 wt% of sulfuric acid and 1 to 2 wt% of hydrogen peroxide and then being washed with water.

17. (Withdrawn) The method of claim 13, wherein, while the electroplating is performed, continuous filtration for removing solid impurities from the electrolytic solution is performed at a flow rate of 31 to 45 m^3/hr.

18. (Withdrawn) The method of claim 13, wherein the electrolytic solution further comprises chloride ions capable of precipitating silver (Ag) in the form of AgC1 to prevent the concentration of silver (Ag) from exceeding 25 ppm by silver (Ag) being introduced into the electrolytic solution while the electroplating is performed.

19. (Withdrawn) The method of claim 13, wherein the electrolytic solution further comprises an organic additive selected from a group consisting of hydroxyethyl cellulose (HEC), organic sulfides, organic nitrides, and thiourea-based compounds.

20. (Withdrawn) The method of claim 13, wherein the forming of the protective layer comprises immersing the copper layer in an antirust solution containing 0.5 to 1.5 g/L of chromium (Cr).

REMARKS

This Response is submitted in response to the Final Office Action dated March 20, 2020. Claims 1, 2, and 4 to 20 are currently pending in this application. Claims 1, 2, and 4 to 12 stand rejected. Claims 13 to 20 were previously withdrawn. Favorable reconsideration of this application is respectfully requested in view of the following remarks.

The Office Action states that:

> Claims 1, 2 and 4-12 are rejected under 35 U.S.C. 103 as being unpatentable over Iwama et al. (US 2008/0176144 "Iwama") in view of Oguro (US 2013/0071755 "Oguro"), Laser and Optics User's Manual (2002), Lee et al. (US 2016/0260980 "Lee"), and Kohiki (US 2013/0256140 "Kohiki")
>
> * * *
>
> Claim 3 is rejected under 35 U.S.C. 103 as being unpatentable over Iwama et al. (US 2008/0176144 "Iwama") in view of Oguro (US 2013/0071755 "Oguro"), Laser and Optics User's Manual (2002), Lee et al. (US 2016/0260980 "Lee"), and Kohiki (US 2013/0256140 "Kohiki"), and further in view of Hirose et al. (US 2008/0050652 "Hirose")

Office Action, pages 2, 6. Applicant notes that claim 3 was previously cancelled, and the subject matter of original claim 3 was incorporated into independent claims 1, 8, and 12. Therefore, Applicant will understand that **claims 1, 2, and 4 to 12 are rejected under 35 U.S.C. § 103** as being unpatentable over U.S. Patent Publication No. 2008/0176144 to Iwama et al. ("Iwama") in view of U.S. Patent Publication No. 2013/0071755 to Oguro ("Oguro"), Laser and Optics User's Manual (2002), U.S. Patent Publication No. 2016/0260980 to Lee et al. ("Lee"), and U.S. Patent Publication No. 2013/0256140 to Kohiki ("Kohiki"), **and further in view of U.S. Patent Publication No. 2008/0050652 to Hirose et al. ("Hirose")**.

Overall, in the current Office Action, the Examiner merely repeats the same arguments that the Examiner made in the previous Office Action. *Compare* March 20, 2020 Office Action, pages 2-7 *with* September 6, 2019 Office Action, pages 3-8. Although the Response to Arguments Section is newly added, the arguments made in this section are also similar to the previous arguments:

March 20, 2020 Office Action, page 7	March 20, 2020 Office Action, page 6; September 6, 2019 Office Action, page 8
As Hirose teaches a surface roughness of 1.5 µm to 5 µm (Hirose in 0026), absent of unexpected results it is maintained that the peak count or peaks which rise above 0.5 µmis an optimizable parameter for a result-effective variable, as Hirose teaches that a surface roughness of 1.5 µm to 5 µm directly affects adhesion and cracking on expansion. (Hirose in 0026) This teaching by Hirose is asserted to refute applicant's allegation that one of ordinary skill in the art would have no reason to optimize the claimed peak count ranges.	To this end, **as Hirose teaches a surface roughness of 1.5 µm to 5 µm (Hirose in 0026), absent of unexpected results it is asserted that the peak count is an optimizable parameter for a resulteffective variable**. *In re Boesch,* 617 F.2d 272,205 USPQ 215 (CCPA 1980).

While the Examiner additionally asserts that "as Hirose teaches that **a surface roughness of 1.5 µm to 5 µm directly affects adhesion and cracking on expansion**," and that "it is noted that Hirose similarly teaches 'enhanced adhesion'. (Hirose in 0026)," such a **circular** argument is not enough to rebut Applicant's previous response. In the previous response, Applicant argued that:

> Applicant respectfully submits that none of the cited art discloses the claimed peak count ranges. Hirose merely discloses a surface roughness of 1.5 µm to 5 µm, however, Hirose fails to disclose the relationship between "peak count (Pc)" and "surface roughness."
>
> It appears that the Examiner also concedes that none of the cited art discloses the claimed peak count ranges, but the Examiner seems to allege that it is an obvious matter of routine optimization. Applicant respectfully disagrees.
>
> Applicant respectfully submits that one of ordinary skill in the art would not have arrived at the present claims as an obvious matter of routine optimization. In this regard, MPEP § 2144.05.II.B states that "**[a] particular parameter must first be recognized as a result-effective variable, i.e., a variable which achieves a recognized result, before the determination of the optimum or workable ranges of said variable might be characterized as routine experimentation**." See In re Antonie, 559 F.2d 618 (CCPA 1977). Furthermore, the Board of Patent Appeals and Interferences has recognized that **the cited prior art needs to recognize a variable as a result-effective variable for the claimed purpose to support a conclusion of obviousness**. See Ex parte Collison, Appeal No. 2010-002734 (BPAI February 29, 2012).

> One of ordinary skill in the art would have no reason to optimize the claimed peak count ranges, because Hirose fail to teach that the peak count of the surfaces of the electrolytic copper foil has any particular effect. That is, nothing in Hirose recognizes the peak count as variables that achieve any recognized result. In contrast, the Specification specifically teaches that the claimed peak count ranges would ensure sufficient adhesion between the electrolytic copper foil and the active material layers and good coating uniformity of the negative electrode active material. See Specification, paragraphs [0067], [0068].

December 6, 2019 Response, page 9.

As pointed out in the previous response, MPEP § 2144.05.II.B specifically states that "[a] particular parameter must first be recognized as a result-effective variable, i.e., a variable which achieves a recognized result, before the determination of the optimum or workable ranges of said variable might be characterized as routine experimentation." In the current Office Action, the Examiner fails to identify anything in the Hirose reference that recognizes "the peak count" as a result-effective variable and, thus, the Office does not shift the burden of proof to Applicant.

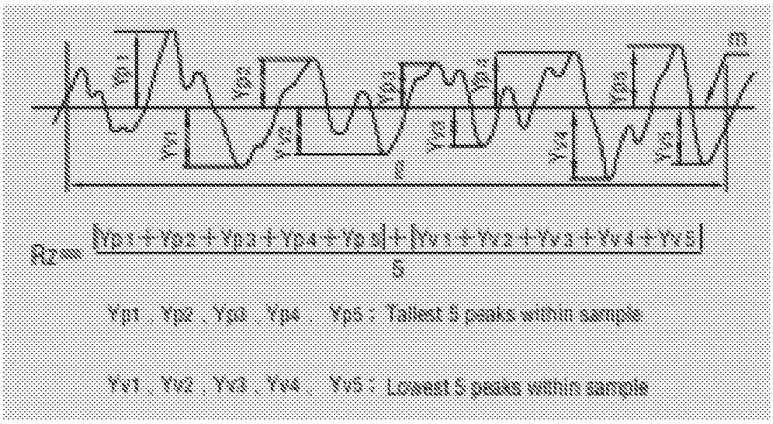
Although the Examiner identified "adhesion" and "cracking," these are merely an effect/result that may be controlled by changing the surface roughness and/or peak count. The mere disclosure of such effect/result cannot be an evidence that the specific parameter at issue in this case, namely "**peak count**", is "recognized as a result-effective variable," in Hirose. If anything, given the total lack of any disclosure of a peak count value in Hirose, one skilled in the art facing a problem of further improving the adhesion and cracking would have been merely motivated to make workmanship improvements in relation to the **surface roughness** in view of Hirose.

The Examiner further states that: "As set forth in the prior Office action, the term 'peak count' was given its broadest reasonable construction." Office Action, page 7. However, Applicant notes that MPEP 2111 specifically states that "[t]he broadest reasonable interpretation does not mean the broadest possible interpretation."

Applicant respectfully submits that the surface roughness disclosed in Hirose is totally different from the peak count (Pc) of the present disclosure. Hirose discloses surface roughness Rz. According to paragraph [0026] of Hirose, the surface roughness Rz is ten-point mean roughness, and the method of measuring ten-point mean roughness (Rz) is well-described in JIS B0601 (1994), available at https://th.misumi-ec.com/pdf/tech/mold/09_mo1517.pdf as follows:

Ten-point mean roughness (Rz)

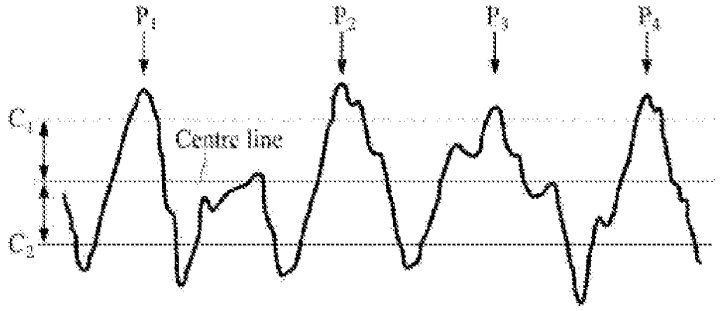
A section of standard length is sampled from the mean line on the roughness chart. The distance between the peaks and valleys of the sampled line is measured in the y direction. Then, the average peak is obtained among 5 tallest peaks (Yp), as is the average valley between 5 lowest valleys (Yv). The sum of these two values is expressed in micrometer(μm).



Id.

However, the peak count (Pc) of the present disclosure is measured differently. For example, paragraph [0065] of the Specification states:

> [0065] In the present invention, the "peak count (Pc)" may be obtained by measuring peak counts (Pc) of any three points on the surface of the electrolytic copper foil 110 and calculating an average value of measured values of the peak counts (Pc). The peak count (Pc) of each of the points is the number of effective peaks P1, P2, P3, and P4 which rise above a 0.5 μm upper criteria line C1 per 4 mm unit sample length in a surface roughness profile obtained according to U.S. standard ASME B46.1-2009. In this case, at least one valley deeper than a −0.5 μm lower criteria line C2 exists between adjacent effective peaks among the effective peaks. When there is no valley deeper than the −0.5 μm lower criteria line C2 between adjacent peaks which rise above the upper criteria line C1, all of the adjacent peaks may not be "effective peaks" used for measuring the peak count (Pc), and relatively lower peaks among the peaks are ignored when obtaining the number of "effective peaks."



<Fig. 2, Present Application>

As shown above, the peak count (Pc) of the present disclosure is totally different from the surface roughness (Rz) disclosed in Hirose.

In addition, as discussed above, paragraphs [0067]-[0068] of the Specification set forth the reason of restricting peak count (Pc) to be 3 to 92, as follows:

> [0067] When the peak count (Pc) is less than 3, an active specific surface area of the electrolytic copper foil 110 which may come in contact with the negative electrode active material is too small to ensure sufficient adhesion between the electrolytic copper foil 110 and the active material layers 120 a and 120 b.
> [0068] On the other hand, when, the peak count (Pc) is more than 92 or the surface roughness (Rz) is more than 3.5 pun, coating uniformity of the negative electrode active material is lowered due to too many surface irregularities, and thus the adhesion between the electrolytic copper foil 110 and the active material layers 120 a and 120 b is significantly lowered.

If the Office desired to argue that the above-discussed features of independent claims 1, 8, and 12 are an **inherent** characteristic of Hirose, such an attempt is improper at least because it is not in compliance with the Office's own procedures. For example, the Office failed to provide "some evidence or scientific reasoning to establish the reasonableness of the examiner's belief that the [] limitation is an **inherent** characteristic of the prior art before the burden is shifted to the applicant to disprove the inherency." *See Ex parte Skinner*, 2 USPQ2d 1788, 1789 (BP AI 1986); MPEP 2112 ("In relying upon the theory of inherency, the examiner must provide a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art." (emphasis in original)). Applicant respectfully submits that there is no guarantee that the copper foil of Hirose ***necessarily*** has a peak count of the claimed range simply because the copper foil of Hirose may have surface roughness that falls within the claimed range.

If the Office intends to maintain the rejection, Applicant respectfully requests that the Office provide specific evidence that the copper foil of Hirose ***necessarily*** has a peak count of the claimed range. For at least these reasons, Applicant respectfully submits that the Office fails to state a *prima facie* case of obviousness over the cited art.

Accordingly, Applicant respectfully submits that independent claims 1, 8 and 12 are patentable over the cited art. Claims 2, 4 to 7, 9 to 11, each directly depend from independent claims 1 or 8, and are allowable for substantially the same reasons as independent claims 1 and 8.

In view of the foregoing amendments and remarks, Applicant respectfully submits that this application is now in condition for allowance. Accordingly, a timely Notice of Allowance to this effect is earnestly solicited. Nevertheless, the Examiner is invited to contact the undersigned representative by telephone prior to issuing a subsequent Office Action to discuss any outstanding issues with this application in the event that the foregoing amendments and remarks fail to advance the present application to allowance.

The Office is hereby authorized to charge any underpayment of fees, or credit any overpayments, to Deposit Account No. 02-1818.

Respectfully submitted,

K&L Gates LLP

BY /Matthew S. Dicke/
Matthew S. Dicke
Reg. No. 58,819
Customer No. 29178
312-578-5415

Dated: June 17, 2020

Doc Code: A.NE.AFCP
Document Description: After Final Consideration Pilot Program Request

PTO/SB/434 (05-13)

CERTIFICATION AND REQUEST FOR CONSIDERATION UNDER THE AFTER FINAL CONSIDERATION PILOT PROGRAM 2.0

Practitioner Docket No.:	Application No.:	Filing Date:
0313221.00013	15/696,360	September 6, 2017
First Named Inventor:	**Title:**	
Seung Min KIM	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR M	

APPLICANT HEREBY CERTIFIES THE FOLLOWING AND REQUESTS CONSIDERATION UNDER THE AFTER FINAL CONSIDERATION PILOT PROGRAM 2.0 (AFCP 2.0) OF THE ACCOMPANYING RESPONSE UNDER 37 CFR 1.116.

1. The above-identified application is (i) an original utility, plant, or design nonprovisional application filed under 35 U.S.C. 111(a) [a continuing application (*e.g.*, a continuation or divisional application) is filed under 35 U.S.C. 111(a) and is eligible under (i)], or (ii) an international application that has entered the national stage in compliance with 35 U.S.C. 371(c).
2. The above-identified application contains an outstanding final rejection.
3. Submitted herewith is a response under 37 CFR 1.116 to the outstanding final rejection. The response includes an amendment to at least one independent claim, and the amendment does not broaden the scope of the independent claim in any aspect.
4. This certification and request for consideration under AFCP 2.0 is the only AFCP 2.0 certification and request filed in response to the outstanding final rejection.
5. Applicant is willing and available to participate in any interview requested by the examiner concerning the present response.
6. This certification and request is being filed electronically using the Office's electronic filing system (EFS-Web).
7. Any fees that would be necessary consistent with current practice concerning responses after final rejection under 37 CFR 1.116, *e.g.*, extension of time fees, are being concurrently filed herewith. [There is no additional fee required to request consideration under AFCP 2.0.]
8. By filing this certification and request, applicant acknowledges the following:
    - Reissue applications and reexamination proceedings are not eligible to participate in AFCP 2.0.
    - The examiner will verify that the AFCP 2.0 submission is compliant, *i.e.*, that the requirements of the program have been met (see items 1 to 7 above). For compliant submissions:
        - The examiner will review the response under 37 CFR 1.116 to determine if additional search and/or consideration (i) is necessitated by the amendment and (ii) could be completed within the time allotted under AFCP 2.0. If additional search and/or consideration is required but cannot be completed within the allotted time, the examiner will process the submission consistent with current practice concerning responses after final rejection under 37 CFR 1.116, *e.g.*, by mailing an advisory action.
        - If the examiner determines that the amendment does not necessitate additional search and/or consideration, or if the examiner determines that additional search and/or consideration is required and could be completed within the allotted time, then the examiner will consider whether the amendment places the application in condition for allowance (after completing the additional search and/or consideration, if required). If the examiner determines that the amendment does not place the application in condition for allowance, then the examiner will contact the applicant and request an interview.
            - The interview will be conducted by the examiner, and if the examiner does not have negotiation authority, a primary examiner and/or supervisory patent examiner will also participate.
            - If the applicant declines the interview, or if the interview cannot be scheduled within ten (10) calendar days from the date that the examiner first contacts the applicant, then the examiner will proceed consistent with current practice concerning responses after final rejection under 37 CFR 1.116.

Signature	Date
/Matthew S. Dicke/	June 17, 2020
Name (Print/Typed) Matthew S. Dicke	**Practitioner Registration No.** 58819

***Note**: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. Submit multiple forms if more than one signature is required, see below*.*

☐ * Total of _____ forms are submitted.

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.

Electronic Acknowledgement Receipt	
EFS ID:	39742299
Application Number:	15696360
International Application Number:	
Confirmation Number:	7466
Title of Invention:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Seung Min KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/US Patent Mail
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313221.00013
Receipt Date:	17-JUN-2020
Filing Date:	06-SEP-2017
Time Stamp:	12:59:20
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		0313221-00013_RespFinal.pdf	250949 40f251f5075a83266af4989bc95c8542039d1804	yes	12

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Response After Final Action	1	1
	Claims	2	6
	Applicant Arguments/Remarks Made in an Amendment	7	12

Warnings:					
Information:					
2	After Final Consideration Program Request	0313221-00013_AFPP.pdf	226275 229879985b652cd7478e234442384a3af5dadb8c	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	477224		

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/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
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 15/696,360	Filing Date 09/06/2017	☐ 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 $80 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $420 =	
☐ 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

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT	06/17/2020	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 19	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 4	Minus	*** 4	= 0		x $460 =	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

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ 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.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/DIANE FLOYD/
*** 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.	

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.

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/696,360	09/06/2017	Seung Min KIM	0313221.00013	7466

24573 7590 03/20/2020

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

EXAMINER
ANTHONY, JULIAN

ART UNIT	PAPER NUMBER
1722	

NOTIFICATION DATE	DELIVERY MODE
03/20/2020	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):

USpatentmail@klgates.com

Office Action Summary	Application No. 15/696,360	Applicant(s) KIM, Seung Min	
	Examiner JULIAN ANTHONY	Art Unit 1722	AIA (FITF) Status Yes

-- 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 12-6-19.

☐ 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) 1-20 is/are pending in the application.

5a) Of the above claim(s) 13-20 is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☑ Claim(s) 1-12 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

Remarks

This Office action is responsive to applicant's amendment filed on December 6, 2019.

Claim Rejections - 35 USC § 103

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

> A patent for a claimed invention may not be obtained, notwithstanding that the claimed invention is not identically disclosed as set forth in section 102, if the differences between the claimed invention and the prior art are such that the claimed invention as a whole would have been obvious before the effective filing date of the claimed invention to a person having ordinary skill in the art to which the claimed invention pertains. Patentability shall not be negated by the manner in which the invention was made.

Claims 1, 2 and 4-12 are rejected under 35 U.S.C. 103 as being unpatentable over Iwama et al. (US 2008/0176144 "Iwama") in view of Oguro (US 2013/0071755 "Oguro"), Laser and Optics User's Manual (2002), Lee et al. (US 2016/0260980 "Lee"), and Kohiki (US 2013/0256140 "Kohiki")

For claims 1, 8 and 12: Iwama teaches an electrolytic copper foil including a first surface and a second surface opposite the first surface, the electrolytic copper foil comprising a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface. (Iwama in 0036-0040) For claims 8 and 12, Iwama further teaches the electrolytic copper foil comprising copper as a current collector for a lithium ion secondary battery. (Iwama in 0003, 0006, 0036)

Iwama does not explicitly teach a first protective layer on the matte surface of the copper layer and a second protective layer on the shiny surface of the copper layer. However, Oguro in the same field of endeavor teaches chromate anti-rust layers applied to both sides of a copper

foil. (Oguro in 0085) The skilled artisan would find obvious to modify Iwama with a first protective layer on the matte surface of the copper layer and a second protective layer on the shiny surface of the copper layer. The motivation for such a modification is to inhibit corrosion and raise the rust-prevention of the copper foil. (Oguro in 0135) Iwama's copper layer hence modified teaches or at least suggests a first protective layer on the matte surface of the copper layer and a second protective layer on the shiny surface of the copper layer.

Iwama does not explicitly teach a coefficient of thermal expansion of the electrolytic foil which ranges from 16 to 22 μm /(m▪°C). However, the Laser and Optics User's Manual teaches that copper has a thermal expansion coefficient of 16.5 ppm/°C and higher, which is equal to 16.5 μm /(m▪°C), which teaches or at least suggests the claimed range of 16 to 22 μm /(m▪°C). In view of the Laser and Optics User's Manual, it would naturally flow for copper to have a coefficient of thermal expansion within applicant's claimed range, *inherently*, absent of a showing by applicant that the claimed invention distinguishes over the reference. *In re Best*, 195 USPQ at 433, footnote 4 (CCPA 1977) and *In re Spada*, 15 USPQ 2d 1655 (Fed. Cir. 1990) Where the claimed and prior art products are identical or substantially identical in structure or composition, or are produced by identical or substantially identical processes, a prima facie case of either anticipation or obviousness has been established. *In re Best*, 562 F.2d 1252, 1255, 195 USPQ 430, 433 (CCPA 1977). "When the PTO shows a sound basis for believing that the products of the applicant and the prior art are the same, the applicant has the burden of showing that they are not." *In re Spada*, 911 F.2d 705, 709, 15 USPQ2d 1655, 1658 (Fed. Cir. 1990). Therefore, the prima facie case can be rebutted by evidence showing that the prior art products do not necessarily possess the characteristics of the claimed product. *In re Best*, 562 F.2d at 1255, 195 USPQ at 433. As to the thermal expansion being measured using a thermomechanical

analyzer (TMA) while heating the electrolytic copper foil from 30 ºC to 190 ºC at a speed of 5 ºC/min, the examiner notes that these limitations have not been given patentable weight within the context of claim 1, as such limitations are considered process limitations which fail to further limit or give patentable scope to the electrolytic copper foil.

Iwama does not explicitly teach a tensile strength of the electrolytic copper foil ranging from 21 to 36 kgf/mm^2. However, Lee in the same field of endeavor teaches a tensile strength of electrolytic copper foil as 85% to 99% of the tensile strength (40 kgf/mm^2 to 70 kgf/mm^2) before a heat treatment step, the lower endpoint equating to 34 kgf/mm^2 which overlaps with applicant's claimed range. (Lee in 0018) Furthermore, the extent that the claimed prior art range and the prior art range do not overlap are considered close enough that one skilled in the art would have expected them to have the same properties, thereby establishing a *prima facie* case of obviousness. *Titanium Metals Corp. of America v. Banner*, 778 F.2d 775, 227 USPQ 773 (Fed. Cir. 1985) Applicant is invited to submit unexpected results to render the claims unobvious. (MPEP 2131.03) The skilled artisan would find obvious to modify Iwama so that the electrolytic copper foil has a tensile strength ranging from 21 to 36 kgf/mm^2. The motivation for such a modification is for high mechanical strength. (Lee in 0051)

Iwama does not explicitly teach a weight deviation of the electrolytic copper foil is 5% or less. However, Kohiki in the same field of endeavor teaches a weight deviation of 0.05 g/dm^2 or less, which relative to a foil weight of 2.75 g/dm^2 equates to a weight deviation of 1.8%. (Kohiki in 0068) The skilled artisan would find obvious to modify the electrolytic copper foil of Iwama to have a weight deviation of 5% or less. The motivation for such a modification is to improve the foil thickness precision. (Kohiki in 0074)

For claim 2: Iwama does not explicitly teach an elongation of 3% or more at room temperature. However, Oguro teaches an elongation rate of 3.5% or more at 25ºC, which teaches or at least suggests an elongation of 3% or more at room temperature. (Oguro in 0193) The skilled artisan would find obvious to modify Iwama with an elongation of 3% or more at room temperature. The motivation for such a modification is to the elongation of the electrolytic foil directly affecting adhesion of the active material. (Oguro in 0194)

For claim 4: In Oguro, the protective layers include a chromium-based solution, which teaches or at least suggests each of the first and second protective layers include at least one of chromium, a silane compound, and a nitrogen compound. (Oguro in 0085-0087)

For claim 5: In Iwama, the electrolytic copper foil has a thickness 10 to 25 μm, which teaches or at least suggests a thickness of 4 to 30 μm to the extent that Iwama's thickness range overlaps therewith. (Iwama in 0045)

For claim 6: In Iwama, each of the first and second surfaces has a surface roughness (R_z) of 2.0 μm and 2.5 μm, respectively, which teaches or at least suggests the claimed range of 3.5 μm or less. (Iwama in 0038)

For claim 7: The Laser and Optics User's Manual teaches a thermal expansion coefficient of 16.5 ppm/ºC and higher, which teaches or at least suggests the claimed range of 16 to 22 μm /(m•ºC).

For claims 9 and 10: The first active material layer comprises Si. (Iwama in 0036, 0048)

For claim 11: As discussed above, Iwama's copper layer modified by Oguro teaches or at least suggests a second protective layer on the shiny surface of the copper layer. Iwama does not explicitly teach a second active material layer on the second protective layer. However, Oguro teaches a second active material layer on the second layer. (Oguro in 0029, 0176, 0286)

The skilled artisan would find obvious to modify Iwama with a second active material on the second protective layer. The motivation for such a modification is for the current collector to have superior properties of electrical conductivity, ease of surface processing for both of the front and back surfaces of the metal foil, adhesion with active material, ultrasonic bondability and uniformly coating a larger amount of active material. (Oguro in 0029, 0286)

Claim 3 is rejected under 35 U.S.C. 103 as being unpatentable over Iwama et al. (US 2008/0176144 "Iwama") in view of Oguro (US 2013/0071755 "Oguro"), Laser and Optics User's Manual (2002), Lee et al. (US 2016/0260980 "Lee"), and Kohiki (US 2013/0256140 "Kohiki"), and further in view of Hirose et al. (US 2008/0050652 "Hirose")

The teachings of Iwama, Oguro, Laser and Optics User's Manual, Lee and Kohiki are discussed above.

As to a peak count of each of the first and second surfaces of the electrolytic copper foil ranging from 3 to 92, applicant's specification defines peak count as the number of effective peaks which rise above 0.5 μm in a surface roughness profile. (specification in [0065]) To this end, as Hirose teaches a surface roughness of 1.5 μm to 5 μm (Hirose in 0026), absent of unexpected results it is asserted that the peak count is an optimizable parameter for a result-effective variable. *In re Boesch,* 617 F.2d 272, 205 USPQ 215 (CCPA 1980) A patent claim can be proved obvious merely by showing that the combination of elements was obvious to try. When there is a design need or market pressure to solve a problem and there are a finite number of identified, predictable solutions, a person of ordinary skill has good reason to pursue the known options within his or her technical grasp. If this leads to the anticipated success, it is likely the product is not of innovation but of ordinary skill and common sense. *KSR Int'l Co. v.*

Teleflex Inc., 550 U.S. 398, 415-421, 82 USPQ2d 1385, 1395-97 (2007) Furthermore, absent of unexpected results it is asserted that surface roughness, and hence the number of effective peaks which rise above 0.5 μm in a surface roughness profile, is an optimizable parameter for a result-effective variable. *In re Boesch,* 617 F.2d 272, 205 USPQ 215 (CCPA 1980) The skilled artisan would find obvious to optimize the peak count of copper in view of Hirose teaching a surface roughness of 1.5 μm to 5 μm directly affecting adhesion and cracking on expansion. (Hirose in 0026)

Response to Arguments

Applicant's arguments filed with the present amendment have been fully considered but they are not persuasive. Applicant submits that none of the cited art discloses the claimed peak count ranges in that Hirose merely discloses a surface roughness of 1.5 μm to 5 μm while failing to disclose the relationship between "peak count (Pc)" and "surface roughness." This argument has been fully considered but is not found persuasive. As set forth in the prior Office action, the term "peak count" was given its broadest reasonable construction and in light of applicant's specification defining peak count as the number of effective peaks which rise above 0.5 μm in a surface roughness profile. (specification in [0065])]) As Hirose teaches a surface roughness of 1.5 μm to 5 μm (Hirose in 0026), absent of unexpected results it is maintained that the peak count or peaks which rise above 0.5 μm is an optimizable parameter for a result-effective variable, as Hirose teaches that a surface roughness of 1.5 μm to 5 μm directly affects adhesion and cracking on expansion. (Hirose in 0026) This teaching by Hirose is asserted to refute applicant's allegation that one of ordinary skill in the art would have no reason to optimize the claimed peak count ranges.

In response to applicant's argument that the claimed peak count ranges ensures sufficient adhesion and good coating uniformity, it is noted that Hirose similarly teaches "enhanced adhesion". (Hirose in 0026) As to good coating uniformity, the fact that applicant has recognized another advantage which would flow naturally from following the suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious. See *Ex parte Obiaya*, 227 USPQ 58, 60 (Bd. Pat. App. & Inter. 1985).

Conclusion

THIS ACTION IS MADE FINAL. Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to JULIAN ANTHONY whose telephone number is (571)272-1289. The examiner can normally be reached on Monday to Friday.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is

encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Cynthia Kelly, can be reached on 571-272-1526. 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.

/Julian Anthony/
Examiner, Art Unit 1722

/CYNTHIA H KELLY/
Supervisory Patent Examiner, Art Unit 1722

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Seung Min KIM
Appl. No.:	15/696,360
Conf. No.:	7466
Filed:	September 6, 2017
Title:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1722
Examiner:	ANTHONY, Julian
Docket No.:	0313221.00013

AMENDMENT AND RESPONSE TO NON-FINAL OFFICE ACTION

VIA ELECTRONIC FILING

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

Dear Commissioner:

In view of the non-final Office Action mailed on September 6, 2019, the following response is submitted, wherein:

Amendments to the Claims begin on page 2 of this paper; and

Remarks begin on page 7 of this paper.

AMENDMENTS TO THE CLAIMS

The following Listing of the Claims replaces all prior Listing(s) of the Claims in the Subject Application.

Listing of Claims:

1. (Currently Amended) An electrolytic copper foil, which includes a first surface and a second surface opposite the first surface, the electrolytic copper foil comprising:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

wherein:

a coefficient of thermal expansion of the electrolytic copper foil, which is measured using a thermomechanical analyzer (TMA) while heating the electrolytic copper foil from 30°C to 190°C at a speed of 5°C/min, ranges from 16 to 22 ~~pm~~μm/(m•°C),

a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190 °C for 1 hour, ranges from 21 to 36 kgf/mm^2, [[and]]

a weight deviation of the electrolytic copper foil is 5% or less, and

a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92.

2. (Original) The electrolytic copper foil of claim 1, having an elongation of 3% or more at room temperature.

3. (Cancelled) .

4. (Original) The electrolytic copper foil of claim 1, wherein each of the first and second protective layers includes at least one of chromium (Cr), a silane compound, and a nitrogen compound.

5. (Original) The electrolytic copper foil of claim 1, having a thickness of 4 to 30 μm.

6. (Currently Amended) The electrolytic copper foil of claim 1, wherein each of the first and second surfaces has a surface roughness (R_z) of 3.5 ~~pm~~μm or less.

7. (Original) The electrolytic copper foil of claim 1, having a coefficient of thermal expansion of 17.3 to 22 μm/(m•°C).

8. (Currently Amended) A secondary battery electrode comprising:

an electrolytic copper foil including a first surface and a second surface opposite the first surface; and

a first active material layer on the first surface of the electrolytic copper foil,

~~wherein:~~wherein the electrolytic copper foil comprises:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

wherein a coefficient of thermal expansion of the electrolytic foil, which is measured using a TMA while heating the electrolytic copper foil from 30 °C to 190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m•°C),

wherein a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190°C for 1 hour, ranges from 21 to 36 kgf/mm^2, [[and]]

wherein a weight deviation of the electrolytic copper foil is 5% or less, and

wherein a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92.

9. (Currently Amended) The secondary battery electrode of claim 8, wherein the first active material layer includes at least one active material selected from [[a]] the group consisting of carbon, a metal (Me) such as Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni, or Fe, an alloy containing the metal (Me), an oxide of the metal (MeO_x), and a composite of the metal (Me) and carbon.

10. (Original) The secondary battery electrode of claim 8, wherein the first active material layer comprises Si.

11. (Original) The secondary battery electrode of claim 8, further comprising a second active material layer on the second protective layer.

12. (Currently Amended) A secondary battery comprising:

a cathode;

an anode including a secondary battery electrode;

an electrolyte configured to provide an environment in which lithium ions may move between the cathode and the anode; and

a separator configured to electrically insulate the cathode from the anode,

wherein the secondary battery electrode comprises:

an electrolytic copper foil including a first surface and a second surface opposite the first surface; and

a first active material layer on the first surface of the electrolytic copper foil,

wherein the electrolytic copper foil comprises:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

wherein a coefficient of thermal expansion of the electrolytic foil, which is measured using a TMA while heating the electrolytic copper foil from 30 °C to 190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m•°C),

wherein a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190°C for 1 hour, ranges from 21 to 36 kgf/mm^2, [[and]]

wherein a weight deviation of the electrolytic copper foil is 5% or less, and

wherein a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92.

13. (Withdrawn) A method of manufacturing a secondary battery electrolytic copper foil, the method comprising:

preparing an electrolytic solution containing 70 to 90 g/L of copper ions and 80 to 130 g/L of sulfuric acid;

forming a copper layer by performing electroplating which applies electricity between a positive electrode plate and a rotating negative electrode drum which are disposed to in the electrolytic solution be spaced apart from each other; and

forming a protective layer on the copper layer,

wherein, while the electroplating is performed, an interval between the positive electrode plate and the rotating negative electrode drum is maintained to be in a range of 5 to 15 mm, a difference between a maximum interval and a minimum interval of the positive electrode plate and the rotating negative electrode drum in a width direction of the copper layer is maintained to be less than 0.2 mm, total organic carbon (TOC) in the electrolytic solution is maintained at 50 ppm or less, and a concentration of silver (Ag) in the electrolytic solution is maintained at 25 ppm or less.

14. (Withdrawn) The method of claim 13, wherein the electroplating is performed by applying a current density of 30 to 80 A/dm^2 between the positive electrode plate and the rotating negative electrode drum.

15. (Withdrawn) The method of claim 13, wherein the preparing of the electrolytic solution comprises:

performing a heat treatment on a copper wire;

pickling the heat-treated copper wire; and

introducing the pickled copper wire into sulfuric acid.

16. (Withdrawn) The method of claim 15, wherein:

the copper wire is heat-treated at a temperature of 600 to 900 °C for 2 to 6 hours, and

the heat-treated copper wire is pickled by being immersed in an acidic solution containing 8 to 10 wt% of sulfuric acid and 1 to 2 wt% of hydrogen peroxide and then being washed with water.

17. (Withdrawn) The method of claim 13, wherein, while the electroplating is performed, continuous filtration for removing solid impurities from the electrolytic solution is performed at a flow rate of 31 to 45 m^3/hr.

18. (Withdrawn) The method of claim 13, wherein the electrolytic solution further comprises chloride ions capable of precipitating silver (Ag) in the form of AgC1 to prevent the concentration of silver (Ag) from exceeding 25 ppm by silver (Ag) being introduced into the electrolytic solution while the electroplating is performed.

19. (Withdrawn) The method of claim 13, wherein the electrolytic solution further comprises an organic additive selected from a group consisting of hydroxyethyl cellulose (HEC), organic sulfides, organic nitrides, and thiourea-based compounds.

20. (Withdrawn) The method of claim 13, wherein the forming of the protective layer comprises immersing the copper layer in an antirust solution containing 0.5 to 1.5 g/L of chromium (Cr).

REMARKS

This Response is submitted in response to the non-final Office Action dated September 6, 2019. Claims 1 to 12 stand rejected. Claims 13 to 20 were previously withdrawn. Claims 1 and 9 are objected to. Claims 1, 6, 8, 9, and 12 are amended, and claim 3 has been cancelled without prejudice or disclaimer. No new matter has been added by the amendments. Favorable reconsideration of this application is respectfully requested in view of the following remarks.

Claims 1 and 9 are objected to. The Examiner explains that:

> Claims 1 and 9 are objected to because of the following informalities:
>
> 1. In claim 1 at line 8, it is suggested to change "the electrolytic foil" to --the electrolytic copper foil--.
> 2. In claim 9 at line 2, it is suggested to change "selected from a group consisting of" to --selected from the group consisting of--, in order to more properly comply with Markush-claim format.

Office Action, page 2. In response, claims 1 and 9 are amended to address the objections, as suggested by the Examiner.

Accordingly, Applicant respectfully requests that the objection of claims 1 and 9 be reconsidered and withdrawn.

Claims 1 to 12 are rejected under 35 U.S.C. § 112(a) or 35 U.S.C. § 112 (pre-AIA), first paragraph. The Examiner alleges that the specification, while being enabling for a surface roughness of 16 to 22 μm /(m▪°C) and 3.5 μm or less, does not reasonably provide enablement for a surface roughness of 16 to 22 pm /(m▪°C) and 3.5 pm or less. Office Action, page 3.

In response, claims 1 and 6 are amended to replace "pm" with "μm."

Accordingly, Applicant respectfully requests that the rejections under 35 U.S.C. §112(a) or 35 U.S.C. § 112 (pre-AIA), first paragraph with respect to claims 1 to 12 be reconsidered and withdrawn.

Claims 1, 2, and 4 to 12 are rejected under 35 U.S.C. § 103 as being unpatentable over U.S. Patent Publication No. 2008/0176144 to Iwama et al. ("Iwama") in view of U.S. Patent Publication No. 2013/0071755 to Oguro ("Oguro"), Laser and Optics User's Manual (2002), U.S. Patent

Publication No. 2016/0260980 to Lee et al. ("Lee"), and U.S. Patent Publication No. 2013/0256140 to Kohiki ("Kohiki"). Claim 3 is rejected under 35 U.S.C. § 103 as being unpatentable over Iwama, Oguro, Laser and Optics User's Manual (2002), Lee, and Kohiki, and further in view of U.S. Patent Publication No. 2008/0050652 to Hirose et al. ("Hirose").

In this Response, claim 1 has been amended to incorporate the subject matter of former claim 3. Amended claim 1 recites, in relevant part, "a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92." Independent claims 8 and 12 are amended similarly.

In the Office Action, the Examiner alleges that:

> As to a peak count of each of the first and second surfaces of the electrolytic copper foil ranging from 3 to 92, applicant's specification defines peak count as the number of effective peaks which rise above 0.5 μm in a surface roughness profile. (specification in [0065]) To this end, as Hirose teaches a surface roughness of 1.5 μm to 5 μm (Hirose in 0026), absent of unexpected results it is asserted that the peak count is an optimizable parameter for a result-effective variable. *In re Boesch*, 617 F.2d 272, 205 USPQ 215 (CCPA 1980) A patent claim can be proved obvious merely by showing that the combination of elements was obvious to try. When there is a design need or market pressure to solve a problem and there are a finite number of identified, predictable solutions, a person of ordinary skill has good reason to pursue the known options within his or her technical grasp. If this leads to the anticipated success, it is likely the product is not of innovation but of ordinary skill and common sense. *KSR Int'l Co. v. Teleflex Inc.*, 550 U.S. 398, 415-421, 82 USPQ2d 1385, 1395-97 (2007) Furthermore, absent of unexpected results it is asserted that surface roughness, and hence the number of effective peaks which rise above 0.5 μm in a surface roughness profile, is an optimizable parameter for a result-effective variable. *In re Boesch*, 617 F.2d 272, 205 USPQ 215 (CCPA 1980) The skilled artisan would find obvious to optimize the peak count of copper in view of Hirose teaching a surface roughness of 1.5 μm to 5 μm directly affecting adhesion and cracking on expansion. (Hirose in 0026)

Office Action, page 8.

Applicant respectfully submits that none of the cited art discloses the claimed peak count ranges. Hirose merely discloses a surface roughness of 1.5 μm to 5 μm, however, Hirose fails to disclose the relationship between "peak count (Pc)" and "surface roughness."

It appears that the Examiner also concedes that none of the cited art discloses the claimed peak count ranges, but the Examiner seems to allege that it is an obvious matter of routine optimization. Applicant respectfully disagrees.

Applicant respectfully submits that one of ordinary skill in the art would not have arrived at the present claims as an obvious matter of routine optimization. In this regard, MPEP § 2144.05.II.B states that "**[a] particular parameter must first be recognized as a result-effective variable, i.e., a variable which achieves a recognized result, before the determination of the optimum or workable ranges of said variable might be characterized as routine experimentation**." See In re Antonie, 559 F.2d 618 (CCPA 1977). Furthermore, the Board of Patent Appeals and Interferences has recognized that **the cited prior art needs to recognize a variable as a result-effective variable for the claimed purpose to support a conclusion of obviousness**. See Ex parte Collison, Appeal No. 2010-002734 (BPAI February 29, 2012).

One of ordinary skill in the art would have no reason to optimize the claimed peak count ranges, because Hirose fail to teach that the peak count of the surfaces of the electrolytic copper foil has any particular effect. That is, nothing in Hirose recognizes the peak count as variables that achieve any recognized result. In contrast, the Specification specifically teaches that the claimed peak count ranges would ensure sufficient adhesion between the electrolytic copper foil and the active material layers and good coating uniformity of the negative electrode active material. See Specification, paragraphs [0067], [0068].

For at least these reasons, Applicant respectfully submits that independent claims 1, 8 and 12 are patentable over the cited art. Claims 2, 4 to 7, 9 to 11, each directly depend from independent claims 1 or 8, and are allowable for substantially the same reasons as independent claims 1 and 8.

In view of the foregoing amendments and remarks, Applicant respectfully submits that this application is now in condition for allowance. Accordingly, a timely Notice of Allowance to this effect is earnestly solicited. Nevertheless, the Examiner is invited to contact the undersigned representative by telephone prior to issuing a subsequent Office Action to discuss any outstanding

issues with this application in the event that the foregoing amendments and remarks fail to advance the present application to allowance.

The Office is hereby authorized to charge any underpayment of fees, or credit any overpayments, to Deposit Account No. 02-1818.

Respectfully submitted,

K&L Gates LLP

BY /Matthew S. Dicke/
Matthew S. Dicke
Reg. No. 58,819
Customer No. 29178
312-578-5415

Dated: December 6, 2019

Electronic Acknowledgement Receipt	
EFS ID:	37953631
Application Number:	15696360
International Application Number:	
Confirmation Number:	7466
Title of Invention:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Seung Min KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/US Patent Mail
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313221.00013
Receipt Date:	06-DEC-2019
Filing Date:	06-SEP-2017
Time Stamp:	16:19:59
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		0313221-00013_RespNFOA.pdf	189949 48ce3bdf0957c9dfb43353b3270fbf2ae8555b63	yes	10

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Amendment/Req. Reconsideration-After Non-Final Reject	1	1
	Claims	2	6
	Applicant Arguments/Remarks Made in an Amendment	7	10
Warnings:			
Information:			
	Total Files Size (in bytes):	189949	

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/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 15/696,360	Filing Date 09/06/2017	☐ 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 $80 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $420 =	
☐ 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

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT	12/06/2019	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 19	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 4	Minus	*** 4	= 0		x $460 =	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

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ 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.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/GOIGA N DUCKETT/
*** 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.	

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.

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/696,360	09/06/2017	Seung Min KIM	0313221.00013	7466

24573 7590 09/06/2019

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

EXAMINER	
ANTHONY, JULIAN	

ART UNIT	PAPER NUMBER
1722	

NOTIFICATION DATE	DELIVERY MODE
09/06/2019	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):

USpatentmail@klgates.com

Office Action Summary	Application No. 15/696,360	Applicant(s) KIM, Seung Min	
	Examiner JULIAN ANTHONY	Art Unit 1722	AIA (FITF) Status Yes

-- 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 6-28-19.

☐ 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) 1-20 is/are pending in the application.

5a) Of the above claim(s) 13-20 is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☑ Claim(s) 1-12 is/are rejected.

8) ☑ Claim(s) 1 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 1-25-19, 1-23-19, 3-12-18, 9-6-17.

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

4) ☐ Other: _____.

DETAILED ACTION

Notice of Pre-AIA or AIA Status

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Election/Restrictions

Claims 13-20 are withdrawn from further consideration pursuant to 37 CFR 1.142(b) as being drawn to a nonelected invention, there being no allowable generic or linking claim. Election was made **without** traverse in the reply filed on June 28, 2019.

Information Disclosure Statement

The IDS filed on 1-25-19, 1-23-19, 3-12-18 and 9-6-17 have been considered by the examiner.

Claim Objections

Claims 1 and 9 are objected to because of the following informalities:

1. In claim 1 at line 8, it is suggested to change "the electrolytic foil" to --the electrolytic copper foil--.
2. In claim 9 at line 2, it is suggested to change "selected from a group consisting of" to --selected from the group consisting of--, in order to more properly comply with Markush-claim format.

Appropriate correction is required.

Claim Rejections - 35 USC § 112

The following is a quotation of the first paragraph of 35 U.S.C. 112(a):

> (a) IN GENERAL.—The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same, and shall set forth the best mode contemplated by the inventor or joint inventor of carrying out the invention.

The following is a quotation of the first paragraph of pre-AIA 35 U.S.C. 112:

> The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same, and shall set forth the best mode contemplated by the inventor of carrying out his invention.

Claims 1-12 are rejected under 35 U.S.C. 112(a) or 35 U.S.C. 112 (pre-AIA), first paragraph, because the specification, while being enabling for a surface roughness of 16 to 22 μm /(m▪°C) and 3.5 μm or less, does not reasonably provide enablement for a surface roughness of 16 to 22 pm /(m▪°C) and 3.5 pm or less. The specification does not enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the invention commensurate in scope with these claims. See claim 1 at line 10, claim 6 at line 2, in comparison to par. [0021], [0050], [0066] and [0068] of the specification. For purposes of claim interpretation the claims are examined as if a limitation to 16 to 22 μm /(m▪°C) and 3.5 μm or less is recited in the claims.

Claims 2-12 are rejected under 35 U.S.C. 112(a) or 35 U.S.C. 112 (pre-AIA), first paragraph, as being dependent upon a rejected base claim.

Claim Rejections - 35 USC § 103

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

> A patent for a claimed invention may not be obtained, notwithstanding that the claimed invention is not identically disclosed as set forth in section 102, if the differences between the claimed invention and the prior art are such that the claimed invention as a whole would have been obvious before the effective filing date of the claimed invention to a person having ordinary skill in the art to which the claimed invention pertains. Patentability shall not be negated by the manner in which the invention was made.

Claims 1, 2 and 4-12 are rejected under 35 U.S.C. 103 as being unpatentable over Iwama et al. (US 2008/0176144 "Iwama") in view of Oguro (US 2013/0071755 "Oguro"), Laser and Optics User's Manual (2002), Lee et al. (US 2016/0260980 "Lee"), and Kohiki (US 2013/0256140 "Kohiki")

For claims 1, 8 and 12: Iwama teaches an electrolytic copper foil including a first surface and a second surface opposite the first surface, the electrolytic copper foil comprising a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface. (Iwama in 0036-0040) For claims 8 and 12, Iwama further teaches the electrolytic copper foil comprising copper as a current collector for a lithium ion secondary battery. (Iwama in 0003, 0006, 0036)

Iwama does not explicitly teach a first protective layer on the matte surface of the copper layer and a second protective layer on the shiny surface of the copper layer. However, Oguro in the same field of endeavor teaches chromate anti-rust layers applied to both sides of a copper foil. (Oguro in 0085) The skilled artisan would find obvious to modify Iwama with a first protective layer on the matte surface of the copper layer and a second protective layer on the shiny surface of the copper layer. The motivation for such a modification is to inhibit corrosion and raise the rust-prevention of the copper foil. (Oguro in 0135) Iwama's copper layer hence modified teaches or at least suggests a first protective layer on the matte surface of the copper layer and a second protective layer on the shiny surface of the copper layer.

Iwama does not explicitly teach a coefficient of thermal expansion of the electrolytic foil which ranges from 16 to 22 μm /(m▪°C). However, the Laser and Optics User's Manual teaches

that copper has a thermal expansion coefficient of 16.5 ppm/ºC and higher, which is equal to 16.5 µm /(m▪ºC), which teaches or at least suggests the claimed range of 16 to 22 µm /(m▪ºC). In view of the Laser and Optics User's Manual, it would naturally flow for copper to have a coefficient of thermal expansion within applicant's claimed range, *inherently*, absent of a showing by applicant that the claimed invention distinguishes over the reference. *In re Best*, 195 USPQ at 433, footnote 4 (CCPA 1977) and *In re Spada*, 15 USPQ 2d 1655 (Fed. Cir. 1990) Where the claimed and prior art products are identical or substantially identical in structure or composition, or are produced by identical or substantially identical processes, a prima facie case of either anticipation or obviousness has been established. *In re Best*, 562 F.2d 1252, 1255, 195 USPQ 430, 433 (CCPA 1977). "When the PTO shows a sound basis for believing that the products of the applicant and the prior art are the same, the applicant has the burden of showing that they are not." *In re Spada*, 911 F.2d 705, 709, 15 USPQ2d 1655, 1658 (Fed. Cir. 1990). Therefore, the prima facie case can be rebutted by evidence showing that the prior art products do not necessarily possess the characteristics of the claimed product. *In re Best*, 562 F.2d at 1255, 195 USPQ at 433. As to the thermal expansion being measured using a thermomechanical analyzer (TMA) while heating the electrolytic copper foil from 30 ºC to 190 ºC at a speed of 5 ºC/min, the examiner notes that these limitations have not been given patentable weight within the context of claim 1, as such limitations are considered process limitations which fail to further limit or give patentable scope to the electrolytic copper foil.

Iwama does not explicitly teach a tensile strength of the electrolytic copper foil ranging from 21 to 36 kgf/mm^2. However, Lee in the same field of endeavor teaches a tensile strength of electrolytic copper foil as 85% to 99% of the tensile strength (40 kgf/mm^2 to 70 kgf/mm^2) before a heat treatment step, the lower endpoint equating to 34 kgf/mm^2 which overlaps with applicant's

claimed range. (Lee in 0018) Furthermore, the extent that the claimed prior art range and the prior art range do not overlap are considered close enough that one skilled in the art would have expected them to have the same properties, thereby establishing a *prima facie* case of obviousness. *Titanium Metals Corp. of America v. Banner*, 778 F.2d 775, 227 USPQ 773 (Fed. Cir. 1985) Applicant is invited to submit unexpected results to render the claims unobvious. (MPEP 2131.03) The skilled artisan would find obvious to modify Iwama so that the electrolytic copper foil has a tensile strength ranging from 21 to 36 kgf/mm^2. The motivation for such a modification is for high mechanical strength. (Lee in 0051)

Iwama does not explicitly teach a weight deviation of the electrolytic copper foil is 5% or less. However, Kohiki in the same field of endeavor teaches a weight deviation of 0.05 g/dm^2 or less, which relative to a foil weight of 2.75 g/dm^2 equates to a weight deviation of 1.8%. (Kohiki in 0068) The skilled artisan would find obvious to modify the electrolytic copper foil of Iwama to have a weight deviation of 5% or less. The motivation for such a modification is to improve the foil thickness precision. (Kohiki in 0074)

For claim 2: Iwama does not explicitly teach an elongation of 3% or more at room temperature. However, Oguro teaches an elongation rate of 3.5% or more at 25ºC, which teaches or at least suggests an elongation of 3% or more at room temperature. (Oguro in 0193) The skilled artisan would find obvious to modify Iwama with an elongation of 3% or more at room temperature. The motivation for such a modification is to the elongation of the electrolytic foil directly affecting adhesion of the active material. (Oguro in 0194)

For claim 4: In Oguro, the protective layers include a chromium-based solution, which teaches or at least suggests each of the first and second protective layers include at least one of chromium, a silane compound, and a nitrogen compound. (Oguro in 0085-0087)

For claim 5: In Iwama, the electrolytic copper foil has a thickness 10 to 25 μm, which teaches or at least suggests a thickness of 4 to 30 μm to the extent that Iwama's thickness range overlaps therewith. (Iwama in 0045)

For claim 6: In Iwama, each of the first and second surfaces has a surface roughness (R_z) of 2.0 μm and 2.5 μm, respectively, which teaches or at least suggests the claimed range of 3.5 μm or less. (Iwama in 0038)

For claim 7: The Laser and Optics User's Manual teaches a thermal expansion coefficient of 16.5 ppm/ºC and higher, which teaches or at least suggests the claimed range of 16 to 22 μm /(m•°C).

For claims 9 and 10: The first active material layer comprises Si. (Iwama in 0036, 0048)

For claim 11: As discussed above, Iwama's copper layer modified by Oguro teaches or at least suggests a second protective layer on the shiny surface of the copper layer. Iwama does not explicitly teach a second active material layer on the second protective layer. However, Oguro teaches a second active material layer on the second layer. (Oguro in 0029, 0176, 0286) The skilled artisan would find obvious to modify Iwama with a second active material on the second protective layer. The motivation for such a modification is for the current collector to have superior properties of electrical conductivity, ease of surface processing for both of the front and back surfaces of the metal foil, adhesion with active material, ultrasonic bondability and uniformly coating a larger amount of active material. (Oguro in 0029, 0286)

Claim 3 is rejected under 35 U.S.C. 103 as being unpatentable over Iwama et al. (US 2008/0176144 "Iwama") in view of Oguro (US 2013/0071755 "Oguro"), Laser and Optics User's

Manual (2002), Lee et al. (US 2016/0260980 "Lee"), and Kohiki (US 2013/0256140 "Kohiki"), and further in view of Hirose et al. (US 2008/0050652 "Hirose")

The teachings of Iwama, Oguro, Laser and Optics User's Manual, Lee and Kohiki are discussed above.

As to a peak count of each of the first and second surfaces of the electrolytic copper foil ranging from 3 to 92, applicant's specification defines peak count as the number of effective peaks which rise above 0.5 μm in a surface roughness profile. (specification in [0065]) To this end, as Hirose teaches a surface roughness of 1.5 μm to 5 μm (Hirose in 0026), absent of unexpected results it is asserted that the peak count is an optimizable parameter for a result-effective variable. *In re Boesch,* 617 F.2d 272, 205 USPQ 215 (CCPA 1980) A patent claim can be proved obvious merely by showing that the combination of elements was obvious to try. When there is a design need or market pressure to solve a problem and there are a finite number of identified, predictable solutions, a person of ordinary skill has good reason to pursue the known options within his or her technical grasp. If this leads to the anticipated success, it is likely the product is not of innovation but of ordinary skill and common sense. *KSR Int'l Co. v. Teleflex Inc.*, 550 U.S. 398, 415-421, 82 USPQ2d 1385, 1395-97 (2007) Furthermore, absent of unexpected results it is asserted that surface roughness, and hence the number of effective peaks which rise above 0.5 μm in a surface roughness profile, is an optimizable parameter for a result-effective variable. *In re Boesch,* 617 F.2d 272, 205 USPQ 215 (CCPA 1980) The skilled artisan would find obvious to optimize the peak count of copper in view of Hirose teaching a surface roughness of 1.5 μm to 5 μm directly affecting adhesion and cracking on expansion. (Hirose in 0026)

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to JULIAN ANTHONY whose telephone number is 571-272-1289. The examiner can normally be reached on Monday to Friday.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Cynthia Kelly, can be reached on 571-272-1526. 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.

/JONATHAN G JELSMA/
Primary Examiner, Art Unit 1722

/Julian Anthony/
Examiner, Art Unit 1722

Notice of References Cited	Application/Control No. 15/696,360	Applicant(s)/Patent Under Reexamination KIM, Seung Min	
	Examiner JULIAN ANTHONY	Art Unit 1722	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-20080176144-A1	07-2008	Iwama; Masayuki	H01M4/134	429/338
*	B	US-20130071755-A1	03-2013	Oguro; Ryoichi	C23C30/00	429/245
*	C	US-20160260980-A1	09-2016	Lee; Sun Hyoung	H01M4/661	1/1
*	D	US-20130256140-A1	10-2013	Kohiki; Michiya	C25D1/04	205/50
*	E	US-20080050652-A1	02-2008	Hirose; Takakazu	H01M2/0275	429/200
	F					
	G					
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	I					
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	K					
	L					
	M					

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	Laser and Optics User's Manual, Chapter 17 Material Expansion Coefficients, pp. 1-12 (Year: 2002)
	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.

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/696,360	KIM, Seung Min
	Examiner	**Art Unit**
	JULIAN ANTHONY	1722

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

CLAIMS

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

CLAIM		DATE								
Final	Original	08/30/2019	08/30/2019							
	1	✓	O							
	2	✓								
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	13	N								
	14	N								
	15	N								
	16	N								
	17	N								
	18	N								
	19	N								
	20	N								

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/696,360	KIM, Seung Min
	Examiner	Art Unit
	JULIAN ANTHONY	1722

CPC - Searched*		
Symbol	Date	Examiner

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
EAST class/keyword search	08/19/2019	

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S63	1	("20080176144").PN.	US-PGPUB; USPAT	OR	OFF	2019/08/26 16:23
S62	35	electrolytic adj copper and roughness with ".mu.m" and electrode and peak same valley	US-PGPUB; USPAT	OR	ON	2019/08/26 14:31
S61	237	electrolytic adj copper and roughness with ".mu.m" and electrode not circuit	US-PGPUB; USPAT	OR	OFF	2019/08/26 14:30
S58	153	electrolytic with copper and roughness with peak	US-PGPUB; USPAT	OR	OFF	2019/08/26 14:05
S46	1	("20040029006").PN.	US-PGPUB; USOCR	OR	OFF	2019/08/26 13:30
S44	349	electrolytic with copper and copper with peak	US-PGPUB; USPAT	OR	OFF	2019/08/26 12:51
S43	1	("6372113").PN.	USPAT; USOCR	OR	OFF	2019/08/26 11:11
S42	1	("6732113").PN.	USPAT; USOCR	OR	OFF	2019/08/26 11:10
S41	84	electrolytic adj copper same peak	US-PGPUB; USPAT	OR	OFF	2019/08/26 10:28
S40	220	electrolytic same copper same peak	US-PGPUB; USPAT	OR	OFF	2019/08/26 10:28
S39	3	electrolytic same copper same peak adj count	US-PGPUB; USPAT	OR	OFF	2019/08/26 10:28
S38	3	electrolytic adj copper same peak adj count	US-PGPUB; USPAT	OR	OFF	2019/08/19 14:26
S37	181	roughness with peak adj count	US-PGPUB; USPAT	OR	OFF	2019/08/19 14:25
S36	47	electrolytic with copper with thermal adj expansion and electrolytic	US-PGPUB; USPAT	OR	OFF	2019/08/16 15:10

S35	1212	copper with thermal adj expansion and electrolytic	US-PGPUB; USPAT	OR	OFF	2019/08/16 15:05
S34	10	copper with thermal adj expansion and electrolytic	EPO; JPO	OR	OFF	2019/08/16 15:03
S33	3	electrolytic adj copper with thermal adj expansion	EPO; JPO	OR	OFF	2019/08/16 14:54
S32	812	copper with thermal adj expansion	EPO; JPO	OR	OFF	2019/08/16 14:54
S31	96	H01M$.cpc. and copper with thermal adj expansion	US-PGPUB; USPAT	OR	OFF	2019/08/16 14:49
S30	7	H01M$.cpc. and copper adj foil with thermal adj expansion	US-PGPUB; USPAT	OR	OFF	2019/08/16 14:47
S29	594	copper adj foil with thermal adj expansion	US-PGPUB; USPAT	OR	OFF	2019/08/16 14:46
S28	1258	copper adj foil same thermal adj expansion	US-PGPUB; USPAT	OR	OFF	2019/08/16 14:46
S26	237	electrolytic adj copper with weight	US-PGPUB; USPAT	OR	OFF	2019/08/15 19:25
S25	733	electrolytic adj copper same weight	US-PGPUB; USPAT	OR	OFF	2019/08/15 19:25
S24	93	electrolytic adj copper same weight with (more less)	US-PGPUB; USPAT	OR	OFF	2019/08/15 18:46
S23	0	electrolytic adj copper same weight with ("or less")	US-PGPUB; USPAT	OR	OFF	2019/08/15 18:46
S22	0	electrolytic adj copper same weight with ("or more")	US-PGPUB; USPAT	OR	OFF	2019/08/15 18:46
S21	3	electrolytic adj copper same weight with (variance deviation)	US-PGPUB; USPAT	OR	OFF	2019/08/15 18:45
S20	3	electrolytic adj copper same weight adj deviation	US-PGPUB; USPAT	OR	OFF	2019/08/15 18:44
S19	833	electrolytic adj copper same kgf$ weight adj deviation	US-PGPUB; USPAT	OR	OFF	2019/08/15 18:44
S18	114	electrolytic adj copper same kgf$ same (heat heating)	US-PGPUB; USPAT	OR	OFF	2019/08/15 17:09
S17	277	electrolytic adj copper same kgf$	US-PGPUB; USPAT	OR	OFF	2019/08/15 17:07

S15	148	electrolytic adj copper same thermal adj expansion	US-PGPUB; USPAT	OR	OFF	2019/08/15 14:32
S13	14	H01M$.cpc. and electrolytic adj copper and (protective protects) with (chromium Cr silane nitrogen)	US-PGPUB; USPAT	OR	OFF	2019/08/14 19:09
S12	497	H01M$.cpc. and electrolytic adj copper and protective	US-PGPUB; USPAT	OR	OFF	2019/08/14 16:45
S11	148	electrolytic adj copper same thermal adj expansion	US-PGPUB; USPAT	OR	OFF	2019/08/14 14:40
S8	41	peak adj count and copper and electrolytic	US-PGPUB; USPAT	OR	OFF	2019/08/14 14:23
S7	17	roughness with peak adj count and copper and electrolytic	US-PGPUB; USPAT	OR	OFF	2019/08/14 14:21
S6	45	roughness with peak adj count and copper	US-PGPUB; USPAT	OR	OFF	2019/08/14 14:17
S3	3	H01M$.cpc. and electrolytic adj copper same peak adj count	US-PGPUB; USPAT	OR	OFF	2019/08/14 14:16
S2	188	H01M$.cpc. and electrolytic adj copper with surface adj roughness	US-PGPUB; USPAT	OR	OFF	2019/08/13 19:52
S1	1307	H01M$.cpc. and electrolytic adj copper	US-PGPUB; USPAT	OR	OFF	2019/08/13 19:50

EAST Search History (Interference)

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Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
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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	15696360
Filing Date	2017-09-06
First Named Inventor	Seung Min KIM
Art Unit	1725
Examiner Name	CONLEY, OI K
Attorney Docket Number	0313221.00013

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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
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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]
	1	2013-181236	JP	A	2013-09-12	JX NIPPON MINING & METALS CORP		
	2	2013-175488	JP	A	2013-09-05	LS MTRON LTD		
	3	2001-140091	JP	A	2001-05-22	MITSUI MINING & SMELTING CO LTD		

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	First Named Inventor	Seung Min KIM
	Art Unit	1725
	Examiner Name	CONLEY, OI K
	Attorney Docket Number	0313221.00013

	4	2000-182623	JP	A	2000-06-30	NIPPON DENKAI KK			

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	1	Japanese Office Action for related Japanese Application No. 2017-162283; action dated October 23, 2018; (2 pages)	
	2	UNKNOWN; "The Chemical Dictionary"; October 20, 1989; page 1233; (4 pages)	

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Examiner Signature	/JULIAN ANTHONY/	Date Considered	08/19/2019

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Attorney Docket Number	0313221.00013

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See attached certification statement.

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☒ A certification statement is not submitted herewith.

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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	/Matthew S. Dicke/	Date (YYYY-MM-DD)	2019-01-23
Name/Print	Matthew S. Dicke	Registration Number	58819

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.**

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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.

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Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

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Approved for use through 11/30/2020. OMB 0651-0031
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(Not for submission under 37 CFR 1.99)

Application Number	15696360
Filing Date	2017-09-06
First Named Inventor	Seung Min KIM
Art Unit	1725
Examiner Name	RIDLEY, BASIA ANNA
Attorney Docket Number	0313070.00025

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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
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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
	1	20040104117	A1	2004-06-03	YANG JEOM- SIK, ET AL.	

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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]
	1	3943214	JP	B	2007-04-13	JAPAN ENERGY CORP		
	2	2660359	EP	A1	2013-11-06	FURUKAWA ELECTRIC CO LTD.		
	3	2011108442	JP	A	2011-06-02	JX NIPPON MINING & METALS CORP		

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	First Named Inventor	Seung Min KIM
	Art Unit	1725
	Examiner Name	RIDLEY, BASIA ANNA
	Attorney Docket Number	0313070.00025

	4	2009116432	WO	A1	2009-09-24	NIPPON MINING CO., ET AL.		
	5	2871266	EP	A1	2015-05-13	JX NIPPON MINING & METALS CORP		

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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	European Search Report for related European Application No. 17189147.6; report dated February 23, 2018; (8 pages)	

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Examiner Signature	/JULIAN ANTHONY/	Date Considered	08/19/2019

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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

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Signature	/Matthew S. Dicke/	Date (YYYY-MM-DD)	2018-03-12
Name/Print	Matthew S. Dicke	Registration Number	58819

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Doc code: IDS
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	Application Number	
	Filing Date	
	First Named Inventor	Seung Min KIM
	Art Unit	
	Examiner Name	
	Attorney Docket Number	P11491US

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	1	10-2002-0012118	KR	A	2002-02-15	MITSUI MINING & SMELTING CO., LTD.		☓
	2	10-2010-0125044	KR	A	2010-11-30	LS MTRON LTD		☒
	3	2012-022939	JP	A	2012-02-02	LS MTRON LTD		☒

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	Examiner Name	
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SIGNATURE

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Signature	/Taeksoo Lee/	Date (YYYY-MM-DD)	2017-09-06
Name/Print	Taeksoo Lee	Registration Number	61976

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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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Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	15696360
Filing Date	2017-09-06
First Named Inventor	Seung Min KIM
Art Unit	1725
Examiner Name	CONLEY, OI K
Attorney Docket Number	0313221.00013

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	1	104114751	CN	A	2014-10-22	JX NIPPON MINING & METALS CORP		
	2	200946719	TW	A	2009-11-16	NIPPON MINING CO		

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15696360
	Filing Date	2017-09-06
	First Named Inventor	Seung Min KIM
	Art Unit	1725
	Examiner Name	CONLEY, OI K
	Attorney Docket Number	0313221.00013

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	Taiwanese Office Action for related Taiwanese Application No. 106134727; action dated November 14, 2018; (5 pages)	

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EXAMINER SIGNATURE

Examiner Signature	/JULIAN ANTHONY/	Date Considered	08/19/2019

*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.

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15696360
Filing Date	2017-09-06
First Named Inventor	Seung Min KIM
Art Unit	1725
Examiner Name	CONLEY, OI K
Attorney Docket Number	0313221.00013

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	/Matthew S. Dicke/	Date (YYYY-MM-DD)	2019-01-25
Name/Print	Matthew S. Dicke	Registration Number	58819

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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).

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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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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 15/696,360	Filing Date 09/06/2017	☐ 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 $80 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $420 =	
☐ 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

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT	06/28/2019	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 20	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 4	Minus	*** 4	= 0		x $460 =	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

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ 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.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/NINA RATANAVONG/
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The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

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Electronic Acknowledgement Receipt	
EFS ID:	36442636
Application Number:	15696360
International Application Number:	
Confirmation Number:	7466
Title of Invention:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Seung Min KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/US Patent Mail
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313221.00013
Receipt Date:	28-JUN-2019
Filing Date:	06-SEP-2017
Time Stamp:	12:55:26
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	Response to Election / Restriction Filed	0313221-00013_RespRestriction.pdf	96495 c1ad973e79e855894792a6c73e197435fd93f77e	no	8

Warnings:

Information:	
Total Files Size (in bytes):	96495

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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.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Seung Min KIM
Appl. No.:	15/696,360
Conf. No.:	7466
Filed:	September 6, 2017
Title:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1613
Examiner:	LEE, SIN J
Docket No.:	0313221.00013

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

RESPONSE TO RESTRICTION REQUIREMENT

Examiner:

This Response is submitted in reply to the Restriction Requirement dated May 3, 2019;

A **Listing of Claims** begins on page 2 of this paper.

Remarks begin on page 8 of this paper.

WHAT IS CLAIMED IS:

1. (Original) An electrolytic copper foil, which includes a first surface and a second surface opposite the first surface, the electrolytic copper foil comprising:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

wherein:

a coefficient of thermal expansion of the electrolytic foil, which is measured using a thermomechanical analyzer (TMA) while heating the electrolytic copper foil from 30°C to 190°C at a speed of 5°C/min, ranges from 16 to 22 pm/(m•°C),

a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190 °C for 1 hour, ranges from 21 to 36 kgf/mm^2, and

a weight deviation of the electrolytic copper foil is 5% or less.

2. (Original) The electrolytic copper foil of claim 1, having an elongation of 3% or more at room temperature.

3. (Original) The electrolytic copper foil of claim 1, wherein a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92.

4. (Original) The electrolytic copper foil of claim 1, wherein each of the first and second protective layers includes at least one of chromium (Cr), a silane compound, and a nitrogen compound.

5. (Original) The electrolytic copper foil of claim 1, having a thickness of 4 to 30 μm.

6. (Original) The electrolytic copper foil of claim 1, wherein each of the first and second surfaces has a surface roughness (R_z) of 3.5 pm or less.

7. (Original) The electrolytic copper foil of claim 1, having a coefficient of thermal expansion of 17.3 to 22 μm/(m•°C).

8. (Original) A secondary battery electrode comprising:

an electrolytic copper foil including a first surface and a second surface opposite the first surface; and

a first active material layer on the first surface of the electrolytic copper foil,

wherein:

the electrolytic copper foil comprises:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

a coefficient of thermal expansion of the electrolytic foil, which is measured using a TMA while heating the electrolytic copper foil from 30 °C to 190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m•°C),

a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190°C for 1 hour, ranges from 21 to 36 kgf/mm^2, and

a weight deviation of the electrolytic copper foil is 5% or less.

9. (Original) The secondary battery electrode of claim 8, wherein the first active material layer includes at least one active material selected from a group consisting of carbon, a metal (Me) such as Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni, or Fe, an alloy containing the metal (Me), an oxide of the metal (MeO_x), and a composite of the metal (Me) and carbon.

10. (Original) The secondary battery electrode of claim 8, wherein the first active material layer comprises Si.

11. (Original) The secondary battery electrode of claim 8, further comprising a second active material layer on the second protective layer.

12. (Original) A secondary battery comprising:

a cathode;

an anode including a secondary battery electrode;

an electrolyte configured to provide an environment in which lithium ions may move between the cathode and the anode; and

a separator configured to electrically insulate the cathode from the anode,

wherein the secondary battery electrode comprises:

an electrolytic copper foil including a first surface and a second surface opposite the first surface; and

a first active material layer on the first surface of the electrolytic copper foil,

wherein the electrolytic copper foil comprises:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

a coefficient of thermal expansion of the electrolytic foil, which is measured using a TMA while heating the electrolytic copper foil from 30 °C to 190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m•°C),

a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190°C for 1 hour, ranges from 21 to 36 kgf/mm^2, and

a weight deviation of the electrolytic copper foil is 5% or less.

13. (Withdrawn) A method of manufacturing a secondary battery electrolytic copper foil, the method comprising:

preparing an electrolytic solution containing 70 to 90 g/L of copper ions and 80 to 130 g/L of sulfuric acid;

forming a copper layer by performing electroplating which applies electricity between a positive electrode plate and a rotating negative electrode drum which are disposed to in the electrolytic solution be spaced apart from each other; and

forming a protective layer on the copper layer,

wherein, while the electroplating is performed, an interval between the positive electrode plate and the rotating negative electrode drum is maintained to be in a range of 5 to 15 mm, a difference between a maximum interval and a minimum interval of the positive electrode plate and the rotating negative electrode drum in a width direction of the copper layer is maintained to be less than 0.2 mm, total organic carbon (TOC) in the electrolytic solution is maintained at 50 ppm or less, and a concentration of silver (Ag) in the electrolytic solution is maintained at 25 ppm or less.

14. (Withdrawn) The method of claim 13, wherein the electroplating is performed by applying a current density of 30 to 80 A/dm^2 between the positive electrode plate and the rotating negative electrode drum.

15. (Withdrawn) The method of claim 13, wherein the preparing of the electrolytic solution comprises:

performing a heat treatment on a copper wire;

pickling the heat-treated copper wire; and

introducing the pickled copper wire into sulfuric acid.

16. (Withdrawn) The method of claim 15, wherein:

the copper wire is heat-treated at a temperature of 600 to 900 °C for 2 to 6 hours, and

the heat-treated copper wire is pickled by being immersed in an acidic solution containing 8 to 10 wt% of sulfuric acid and 1 to 2 wt% of hydrogen peroxide and then being washed with water.

17. (Withdrawn) The method of claim 13, wherein, while the electroplating is performed, continuous filtration for removing solid impurities from the electrolytic solution is performed at a flow rate of 31 to 45 m^3/hr.

18. (Withdrawn) The method of claim 13, wherein the electrolytic solution further comprises chloride ions capable of precipitating silver (Ag) in the form of AgC1 to prevent the concentration of silver (Ag) from exceeding 25 ppm by silver (Ag) being introduced into the electrolytic solution while the electroplating is performed.

19. (Withdrawn) The method of claim 13, wherein the electrolytic solution further comprises an organic additive selected from a group consisting of hydroxyethyl cellulose (HEC), organic sulfides, organic nitrides, and thiourea-based compounds.

20. (Withdrawn) The method of claim 13, wherein the forming of the protective layer comprises immersing the copper layer in an antirust solution containing 0.5 to 1.5 g/L of chromium (Cr).

REMARKS

This Response is submitted in reply to the Restriction Requirement dated May 3, 2019. The Examiner is requiring the Applicant to elect one of the following inventions:

I. Claims 1-12, drawn to an electrolytic copper foil; or

II. Claims 13-20, drawn to a method of manufacturing a secondary battery electrolytic copper foil.

Applicant hereby elects Group I, including claims 1 to 12, without traverse for examination on the merits. Favorable consideration is respectfully requested.

Respectfully submitted,

K&L Gates LLP

BY /Matthew S. Dicke/
Matthew S. Dicke
Reg. No. 58,819
Customer No. 29178
312-578-5415

Dated: June 28, 2019

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/696,360	09/06/2017	Seung Min KIM	0313221.00013	7466

24573 7590 05/03/2019

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

EXAMINER
LEE, SIN J

ART UNIT	PAPER NUMBER
1722	

NOTIFICATION DATE	DELIVERY MODE
05/03/2019	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):

USpatentmail@klgates.com

Office Action Summary	**Application No.** 15/696,360	**Applicant(s)** KIM, Seung Min	
	Examiner SIN J LEE	**Art Unit** 1722	**AIA (FITF) Status** Yes

-- 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 2 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 9/6/2017.

☐ 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) 1-20 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) _____ is/are rejected.

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

9) ☑ Claim(s) 1-20 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: _____.

Election/Restrictions

1. Restriction to one of the following inventions is required under 35 U.S.C. 121:

I. Claims 1-12, drawn to an electrolytic copper foil, classified in H01M 4/662.

II. Claims 13-20, drawn to a method of manufacturing a secondary battery electrolytic copper foil, classified in C25D 3/38.

2. The inventions are independent or distinct, each from the other because: Inventions I and II are related as process of making and product made. The inventions are distinct if either or both of the following can be shown: (1) that the process as claimed can be used to make another and materially different product or (2) that the product as claimed can be made by another and materially different process (MPEP § 806.05(f)). In the instant case, the copper foil of Group I can be manufactured by repeatedly rolling and annealing a copper ingot (which was obtained by melting and casting) a plurality of times and then surface-treating the copper foil.

3. Restriction for examination purposes as indicated is proper because all the inventions listed in this action are independent or distinct for the reasons given above and there would be a serious search and/or examination burden if restriction were not required because one or more of the following reasons apply:

. The inventions have acquired a separate status in the art in view of their different classification.

. The inventions require a different field of search (e.g., searching different classes/subclasses or electronic resources, or employing different search strategies or search queries).

4. **Applicant is advised that the reply to this requirement to be complete must include (i) an election of a invention to be examined** even though the requirement may be traversed (37 CFR 1.143) **and (ii) identification of the claims encompassing the elected invention.**

The election of an invention may be made with or without traverse. To reserve a right to petition, the election must be made with traverse. If the reply does not distinctly and specifically point out supposed errors in the restriction requirement, the election shall be treated as an election without traverse. Traversal must be presented at the time of election in order to be considered timely. Failure to timely traverse the requirement will result in the loss of right to petition under 37 CFR 1.144. If claims are added after the election, applicant must indicate which of these claims are readable upon the elected invention.

Should applicant traverse on the ground that the inventions are not patentably distinct, applicant should submit evidence or identify such evidence now of record showing the inventions to be obvious variants or clearly admit on the record that this is the case. In either instance, if the examiner finds one of the inventions unpatentable over the prior art, the evidence or admission may be used in a rejection under 35 U.S.C. 103 or pre-AIA 35 U.S.C. 103(a) of the other invention.

5. Any inquiry concerning this communication or earlier communications from the examiner should be directed to SIN J LEE whose telephone number is (571)272-1333. The examiner can normally be reached on M-F 9am-5:30pm.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview,

applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Cynthia H Kelly can be reached on 571-272-1526. 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.

/SIN J LEE/
Primary Examiner, Art Unit 1722
April 30, 2019

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/696,360	KIM, Seung Min
	Examiner	Art Unit
	SIN J LEE	1722

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

CLAIMS										
☐ Claims renumbered in the same order as presented by applicant					☐ CPA		☐ T.D.		☐ R.1.47	
CLAIM		DATE								
Final	Original	04/30/2019								
	1	÷								
	2	÷								
	3	÷								
	4	÷								
	5	÷								
	6	÷								
	7	÷								
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	19	÷								
	20	÷								

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
Approved for use through 07/31/2016. 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.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	15696360
Filing Date	2017-09-06
First Named Inventor	Seung Min KIM
Art Unit	1725
Examiner Name	CONLEY, OI K
Attorney Docket Number	0313221.00013

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
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FOREIGN PATENT DOCUMENTS Remove

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]
	1	104114751	CN	A	2014-10-22	JX NIPPON MINING & METALS CORP		
	2	200946719	TW	A	2009-11-16	NIPPON MINING CO		

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NON-PATENT LITERATURE DOCUMENTS Remove

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15696360
	Filing Date	2017-09-06
	First Named Inventor	Seung Min KIM
	Art Unit	1725
	Examiner Name	CONLEY, OI K
	Attorney Docket Number	0313221.00013

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	Taiwanese Office Action for related Taiwanese Application No. 106134727; action dated November 14, 2018; (5 pages)	

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

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	15696360
	Filing Date	2017-09-06
	First Named Inventor	Seung Min KIM
	Art Unit	1725
	Examiner Name	CONLEY, OI K
	Attorney Docket Number	0313221.00013

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	/Matthew S. Dicke/	Date (YYYY-MM-DD)	2019-01-25
Name/Print	Matthew S. Dicke	Registration Number	58819

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.**

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.

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.

Espacenet

Bibliographic data: CN104114751 (A) — 2014-10-22

Ultrathin copper foil, method for producing same, and ultrathin copper layer

Inventor(s): KOHIKI MICHIYA ± (KOHIKI MICHIYA)

Applicant(s): JX NIPPON MINING & METALS CORP ± (JX NIPPON MINING & METALS CORPORATION)

Classification: - international: ***C25D1/04; C25D7/06; H05K1/09***
- cooperative: **C25D1/04**; **C25D1/22**; **C25D5/10**; **C25D5/12**; **C25D7/0614**; **C25D7/0621**; **C25D7/0635**; **H05K1/09**; C25D3/12; C25D3/38; H05K2201/0355; H05K2203/1545; H05K3/025; Y10T428/12438; Y10T428/24917

Application number: CN20128069847 20121225 Global Dossier

Priority number(s): WO2012JP83531 20121225 ; JP20120152823 20120706

Also published as: EP2871266 (A1) EP2871266 (A4) HK1198549 (A1) JP2014015650 (A) JP5175992 (B1) more

Abstract of CN104114751 (A)

Provided is an ultrathin copper foil which has improved thickness accuracy of an ultrathin copper layer on a supporting copper foil. An ultrathin copper foil which is provided with a supporting copper foil, a releasing layer that is laminated on the supporting copper foil, and an ultrathin copper layer that is laminated on the releasing layer. The thickness accuracy of the ultrathin copper layer as determined by a weight thickness method is 3.0% or less.

(19)中华人民共和国国家知识产权局

(12)发明专利申请

(10)申请公布号 CN 104114751 A
(43)申请公布日 2014.10.22

(21)申请号 201280069847.4
(22)申请日 2012.12.25
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WO2014/006781 JA 2014.01.09
(71)申请人 JX日矿日石金属株式会社
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(74)专利代理机构 中国专利代理(香港)有限公司 72001
代理人 孔青 李炳爱
(51)Int.Cl.
C25D 1/04(2006.01)
C25D 7/06(2006.01)
H05K 1/09(2006.01)

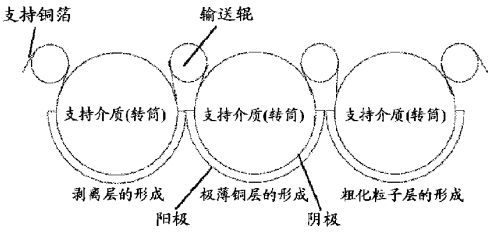
权利要求书1页 说明书7页 附图2页

(54)发明名称

极薄铜箔及其制备方法以及极薄铜层

(57)摘要

本发明提供提高了支持铜箔上的极薄铜层的厚度精度的极薄铜箔。本发明提供极薄铜箔，其为具备支持铜箔、层压于支持铜箔上的剥离层和层压于剥离层上的极薄铜层的极薄铜箔，其中，采用重量厚度法测定的上述极薄铜层的厚度精度为3.0%以下。



CN 104114751 A

1. 极薄铜箔，其为具备支持铜箔、层压于支持铜箔上的剥离层和层压于剥离层上的极薄铜层的极薄铜箔，其中，

采用重量厚度法测定的上述极薄铜层的厚度精度为 3.0% 以下。

2. 极薄铜箔，其为具备支持铜箔、层压于支持铜箔上的剥离层和层压于剥离层上的极薄铜层的极薄铜箔，其中，

采用四探针法测定的上述极薄铜层的厚度精度为 10.0% 以下。

3. 权利要求 1 或 2 的极薄铜箔，其中，在上述极薄铜层表面具有粗化粒子层。

4. 极薄铜箔的制备方法，所述方法为通过处理以辊对辊输送方式在长度方向输送的长条状支持铜箔的表面，制备具备支持铜箔、层压于支持铜箔上的剥离层和层压于剥离层上的极薄铜层的极薄铜箔的方法，包括

在用输送辊输送的支持铜箔的表面形成剥离层的工序，和

在用转筒支持用输送辊输送的形成有上述剥离层的支持铜箔的同时通过电镀在上述剥离层表面形成极薄铜层的工序。

5. 权利要求 4 的极薄铜箔的制备方法，其中，形成上述剥离层的工序通过在用转筒支持用输送辊输送的上述支持铜箔的同时通过电镀在上述支持铜箔表面形成极薄铜层来进行。

6. 权利要求 4 或 5 的极薄铜箔的制备方法，其中，进一步包括在用输送辊输送的上述支持铜箔的极薄铜层表面形成粗化粒子层的工序。

7. 权利要求 6 的极薄铜箔的制备方法，其中，形成上述粗化粒子层的工序通过在用转筒支持用输送辊输送的上述支持铜箔的同时通过电镀在上述极薄铜层表面形成粗化粒子层来进行。

8. 极薄铜层，其为在层压于支持铜箔上的剥离层上层压、用以与上述支持铜箔和上述剥离层一同构成极薄铜箔的、由电解铜箔形成的极薄铜层，其中，

采用重量厚度法测定的厚度精度为 3.0% 以下。

9. 极薄铜层，其为在层压于支持铜箔上的剥离层上层压、用以与上述支持铜箔和上述剥离层一同构成极薄铜箔的、由电解铜箔形成的极薄铜层，其中，

采用四探针法测定的厚度精度为 10.0% 以下。

10. 权利要求 8 或 9 的极薄铜层，其为在层压于支持铜箔上的剥离层上层压、用以与上述支持铜箔和上述剥离层一同构成极薄铜箔的、由电解铜箔形成的极薄铜层，其中，

在表面具有粗化粒子层。

11. 印刷线路板，其使用权利要求 1~3 中任一项的极薄铜箔制备。

12. 印刷线路板，其使用权利要求 8~10 中任一项的极薄铜层。

极薄铜箔及其制备方法以及极薄铜层

技术领域

[0001] 本发明涉及极薄铜箔及其制备方法以及极薄铜层。更具体而言，本发明涉及可用作精细图案用途的印刷线路板的材料的极薄铜箔及其制备方法以及极薄铜层。

背景技术

[0002] 近年来，随着半导体电路的高集成化，印刷线路板中也要求精细电路。通常的精细电路形成方法为在极薄铜层上形成布线回路后，用硫酸－过氧化氢类蚀刻剂蚀刻除去极薄铜层的技术（MSAP：Modified-Semi-Additive-Process（模拟半加成工艺））。因此，优选极薄铜层的厚度均匀。

[0003] 在这里，电镀的箔厚精度大幅受阳极－阴极间的电极间距离影响。通常的极薄铜层形成方法是在支持铜箔（12~70μm）上形成剥离层，进而在其表面形成极薄铜层（0.5~10.0μm）和粗化粒子。对于形成支持铜箔以后的工序，目前采用如图1的对支持铜箔无转筒支持的曲折送箔方式进行（专利文献1）。

[0004] 先前技术文献

专利文献

专利文献1：日本特开2000-309898号公报。

发明内容

[0005] 发明所要解决的课题

但是，由于通过电镀形成的极薄铜层的厚度精度大幅受阳极－阴极间的电极间距离影响，所以当采用这样的对支持铜箔无转筒支持的曲折送箔方式时，由于电解液和送箔张力等的影响，难以固定电极间距离，产生厚度的变化增大的问题。

[0006] 因此，本发明的课题在于，提供提高了支持铜箔上的极薄铜层的厚度精度的极薄铜箔。

[0007] 解决课题的手段

为达成上述目的，本发明人在反复深入研究时着眼于支持铜箔以后的工序的送箔方式，发现通过非曲折而以转筒为支持介质的送箔方式，可确保一定的电极间距离，提高极薄铜层的厚度精度。

[0008] 本发明以上述见解为基础完成，在一个侧面，本发明为极薄铜箔，所述铜箔为具备支持铜箔、层压于支持铜箔上的剥离层和层压于剥离层上的极薄铜层的极薄铜箔，其中，采用重量厚度法测定的上述极薄铜层的厚度精度为3.0%以下。

[0009] 在另一个侧面，本发明为极薄铜箔，所述铜箔为具备支持铜箔、层压于支持铜箔上的剥离层和层压于剥离层上的极薄铜层的极薄铜箔，其中，采用四探针法测定的上述极薄铜层的厚度精度为10.0%以下。

[0010] 在本发明所涉及的极薄铜箔的一个实施方案中，在上述极薄铜层表面具有粗化粒子层。

[0011] 在又一个侧面，本发明为极薄铜箔的制备方法，所述制备方法为通过处理以辊对辊输送方式在长度方向输送的长条状支持铜箔的表面，制备具备支持铜箔、层压于支持铜箔上的剥离层和层压于剥离层上的极薄铜层的极薄铜箔的方法，包括：在用输送辊输送的支持铜箔的表面形成剥离层的工序，和在用转筒支持用输送辊输送的形成有上述剥离层的支持铜箔的同时通过电镀在上述剥离层表面形成极薄铜层的工序。

[0012] 对于本发明的极薄铜箔的制备方法，在一个实施方案中，形成上述剥离层的工序通过在用转筒支持用输送辊输送的上述支持铜箔的同时通过电镀在上述支持铜箔表面形成极薄铜层来进行。

[0013] 对于本发明的极薄铜箔的制备方法，在另一个实施方案中，进一步包括在用输送辊输送的上述支持铜箔的极薄铜层表面形成粗化粒子层的工序。

[0014] 对于本发明的极薄铜箔的制备方法，在又一个实施方案中，形成上述粗化粒子层的工序通过在用转筒支持用输送辊输送的上述支持铜箔的同时通过电镀在上述极薄铜层表面形成粗化粒子层来进行。

[0015] 在又一个侧面，本发明为极薄铜层，所述铜层为在层压于支持铜箔上的剥离层上层压、用以与上述支持铜箔和上述剥离层一同构成极薄铜箔的、由电解铜箔形成的极薄铜层，其中，采用重量厚度法测定的厚度精度为 3.0% 以下。

[0016] 在又一个侧面，本发明为极薄铜层，所述铜层为在层压于支持铜箔上的剥离层上层压、用以与上述支持铜箔和上述剥离层一同构成极薄铜箔的、由电解铜箔形成的极薄铜层，其中，采用四探针法测定的厚度精度为 10.0% 以下。

[0017] 在一个实施方案中，本发明的极薄铜层为在层压于支持铜箔上的剥离层上层压、用以与上述支持铜箔和上述剥离层一同构成极薄铜箔的、由电解铜箔形成的极薄铜层，其中，在表面具有粗化粒子层。

[0018] 在又一个侧面，本发明为使用本发明的极薄铜箔制备的印刷线路板。

[0019] 在又一个侧面，本发明为使用本发明的极薄铜层的印刷线路板。

[0020] 发明的效果

根据本发明，可提供提高了支持铜箔上的极薄铜层的厚度精度的极薄铜箔。

附图说明

[0021] [图 1] 示出现有的曲折送箔方式的示意图。

[0022] [图 2] 示出本发明的实施方案 1 所涉及的极薄铜箔制备方法所涉及的送箔方式的示意图。

[0023] [图 3] 示出本发明的实施方案 2 所涉及的极薄铜箔制备方法所涉及的送箔方式的示意图。

[0024] [图 4] 示出本发明的实施方案 3 所涉及的极薄铜箔制备方法所涉及的送箔方式的示意图。

[0025] 实施发明的最佳方式

<1. 支持铜箔>

本发明中可使用的支持铜箔典型地可以轧制铜箔或电解铜箔的形态提供。通常，电解铜箔通过从硫酸铜电镀浴中电解析出铜在钛或不锈钢转筒上而制备，轧制铜箔重复利用轧

辊的塑性加工和热处理而制备。作为铜箔的材料，除韧铜或无氧铜之类的高纯度铜以外，亦可使用例如含 Sn 铜，含 Ag 铜，添加 Cr、Zr 或 Mg 等的铜合金，添加 Ni 和 Si 等的科森类铜合金之类的铜合金。需说明的是，在本说明书中当单独使用术语“铜箔”时亦包含铜合金箔。

[0026] 对于在本发明中可使用的支持铜箔的厚度亦无特殊限制，只要适宜调节为在发挥作为支持铜箔的作用方面合适的厚度即可，例如可设为 12μm 以上。但是，若过厚，则生产成本升高，所以通常优选设为 35μm 以下。因此，支持铜箔的厚度典型地为 12~70μm，更典型地为 18~35μm。

[0027] <2. 剥离层>

在支持铜箔上设置剥离层。剥离层可使用镍、镍 - 磷合金、镍 - 钴合金、铬等形成。剥离层为将支持铜箔由极薄铜层剥下时剥离的部分，但亦可具有防止铜成分由支持铜箔向极薄铜层扩散的屏障效果。

[0028] 当使用电解铜箔作为支持铜箔时，从减少小孔的观点出发优选在低粗糙度面设置剥离层。剥离层可利用电镀、喷镀、CVD、物理蒸镀等方法设置。

[0029] <3. 极薄铜层>

在剥离层之上设置极薄铜层。极薄铜层可通过利用硫酸铜、焦磷酸铜、氨基磺酸铜、氰化铜等的电解浴的电镀形成，由于可使用普通的电解铜箔，可在高电流密度下形成铜箔，所以优选硫酸铜浴。极薄铜层的厚度无特殊限制，但通常比支持铜箔薄，例如为 12μm 以下。典型地为 0.5~10μm，更典型地为 1~5μm。

[0030] <4. 粗化处理>

在极薄铜层的表面，例如为使与绝缘基板的粘附性良好等而可通过实施粗化处理设置粗化粒子层。粗化处理例如可通过用铜或铜合金形成粗化粒子来进行。粗化处理可为精细处理。粗化粒子层可为由选自铜、镍、钴和锌的任一单体或含有任一种以上单体的合金构成的层。另外，可在进行粗化处理后或不进行粗化处理，用镍、钴、铜、锌的单体或合金形成二次粒子或三次粒子和 / 或防锈层，进而对其表面实施铬酸盐处理、硅烷偶联剂处理等处理。即，可在粗化粒子层的表面形成选自防锈层、铬酸盐处理层和硅烷偶联剂处理层的 1 种以上的层，也可在极薄铜层的表面形成选自防锈层、铬酸盐处理层和硅烷偶联剂处理层的 1 种以上的层。

[0031] <5. 极薄铜箔>

极薄铜箔具备支持铜箔、在支持铜箔上形成的剥离层和在剥离层之上层压的极薄铜层。极薄铜箔自身的使用方法为本领域技术人员所熟知，例如将极薄铜层的表面与纸基底酚醛树脂、纸基底环氧树脂、合成纤维布基底环氧树脂、玻璃布 - 纸复合基底环氧树脂、玻璃布 - 玻璃无纺布复合基底环氧树脂和玻璃布基底环氧树脂、聚酯薄膜、聚亚胺薄膜等绝缘基板粘合，在热压粘合后剥下载体，将与绝缘基板粘合的极薄铜层蚀刻成作为目标的导体图案，最终可制备印刷线路板。在本发明所涉及的极薄铜箔的情况下，剥离部位主要为剥离层与极薄铜层的界面。

[0032] <6. 极薄铜箔的制备方法>

接着，对本发明所涉及的极薄铜箔的制备方法进行说明。图 2 为示出本发明的实施方案 1 所涉及的极薄铜箔制备方法所涉及的送箔方式的示意图。本发明的实施方案 1 所涉及的极薄铜箔的制备方法为：通过处理以辊对辊输送方式在长度方向输送的长条状支持铜箔

的表面，制备具备支持铜箔、层压于支持铜箔上的剥离层和层压于剥离层上的极薄铜层的极薄铜箔的方法。本发明的实施方案 1 所涉及的极薄铜箔的制备方法包括以下工序：在用转筒支持用输送辊输送的支持铜箔的同时通过电镀在支持铜箔表面形成极薄铜层的工序，在用转筒支持形成有剥离层的支持铜箔的同时通过电镀在剥离层表面形成极薄铜层的工序，和在用转筒支持支持铜箔的同时通过电镀在极薄铜层表面形成粗化粒子层的工序。在各工序中用转筒支持的支持铜箔的处理面兼作阴极，在此转筒与设置使与转筒相对的阳极之间的电镀液中进行各种电镀。

[0033] 在本发明中，为了以辊对辊输送方式输送长条状支持铜箔，在对支持铜箔的长度方向施加张力的同时进行输送。张力可通过将各输送辊与驱动马达连接等来施加扭矩而调整。支持铜箔的输送张力优选 0.01~0.2kg/mm。若输送张力不足 0.01kg/mm，则与转筒的粘附力弱，难以将各层形成所希望的厚度。另外，虽然亦取决于装置的结构，但易产生滑脱等问题，此外支持铜箔的卷绕缓慢，易产生卷偏等问题。另一方面，若输送张力超过 0.2kg/mm，则即使支持铜箔稍微错位，也易产生折皱，从装置管理的观点出发亦不优选。另外，卷绕紧，易产生紧绕皱褶等。支持铜箔的输送张力更优选为 0.02~0.1kg/mm。

[0034] 在实施方案 1 中，剥离层和粗化粒子层均在用转筒支持支持铜箔的同时通过电镀形成，但并不限定于此。例如，作为实施方案 2，如图 3 所示，粗化粒子层的形成可通过采用现有的对支持铜箔无转筒支持的曲折送箔方式的电镀来形成。另外，作为实施方案 3，如图 4 所示，剥离层和粗化粒子层的形成均可通过采用现有的对支持铜箔无转筒支持的曲折送箔方式的电镀来形成。但是，由于实施方案 2 和 3 不如实施方案 1 那样以采用转筒的送箔方式进行全部工序，所以与实施方案 1 相比，难以固定电镀时的电极间距离，剥离层和 / 或粗化粒子层的厚度精度差。

[0035] 如上所述，由于本发明用转筒支持支持铜箔，所以电镀时的阳极 - 阴极间的电极间距离稳定。因此，可良好地抑制形成的层的厚度变化，从而可制备具有厚度精度高的极薄铜层的极薄铜箔。

[0036] 对于这样制备的极薄铜箔，采用重量厚度法测定的极薄铜层的厚度精度为 3.0% 以下、优选 2.0% 以下，厚度精度极好。需说明的是，下限无需特别限定，例如为 0.05% 以上或 0.1% 以上或 0.2% 以上。

[0037] 在这里，对利用重量厚度法的厚度精度测定方法进行说明。首先，在测定支持铜箔和极薄铜箔的重量后，剥下极薄铜层，再次测定支持铜箔的重量，将前者与后者之差定义为极薄铜层的重量。将作为测定对象的极薄铜层片制成用挤压机冲压而成的 3cm 四边形片材。为调查重量厚度精度，在各个水平下均求得合计 60 个点的极薄铜层片的重量厚度测定值的平均值和标准偏差（σ），其中，宽度方向上等间隔 10 个点，长度方向上 6 个点（间隔 4cm）。需说明的是，重量厚度精度的计算式为下式：

厚度精度 (%)=(3σ ×100) / 平均值

此测定方法的重复精度为 0.2%。

[0038] 另外，对于这样制备的极薄铜箔，采用四探针法测定的极薄铜层的厚度精度为 10.0% 以下，优选 6.0% 以下，厚度精度极好。需说明的是，下限无需特别限定，例如为 0.05% 以上或 0.5% 以上或 0.7% 以上或 1.0% 以上。

[0039] 在这里，对利用四探针法的厚度精度测定方法进行说明。首先，在通过用四探针测

定厚度电阻来求得支持铜箔和极薄铜箔的厚度后，剥下极薄铜层，再次根据支持铜箔的厚度电阻测定厚度，将前者与后者之差定义为极薄铜层的厚度。为调查厚度精度，在各个水平下均在宽度方向上以 5mm 的间隔进行测定，求得合计 280 个测定点的平均值和标准偏差（σ）。需说明的是，利用四探针的厚度精度的计算式为下式：

厚度精度 (%)=(3σ×100)/ 平均值

此测定方法的重复精度为 1.0%。

实施例

[0040] 以下通过本发明的实施例对本发明进行更详细的说明，但本发明不因这些实施例而受到任何限定。

[0041] 1. 极薄铜箔的制备

作为支持铜箔，制备表 1 中记载的厚度的长条状支持铜箔。实施例 1、3、5~7、10、13、15、16，比较例 1、2 的铜箔使用电解铜箔 (JX 日矿日石金属公司制 JTC)，实施例 2、4、8、9、11、12、14，比较例 3 的铜箔使用轧制铜箔 (JX 日矿日石金属公司制韧铜箔 (JIS-H3100-C1100))。对此铜箔的光泽面，在以下条件下用辊对辊型连续生产线根据以下条件进行表 1 中记载的剥离层、极薄铜层和粗化粒子层的各形成处理。在这里，实施例 1~3 根据上述图 4 中示出的实施方案 3 所涉及的方式制备，实施例 4~9 根据上述图 3 中示出的实施方案 2 所涉及的方式制备，实施例 10~16 根据上述图 2 中示出的实施方案 1 所涉及的方式制备。另外，比较例 1~3 根据上述图 1 中示出的现有方式制备。

[0042] （剥离层的形成）

(A) 曲折送箔方式

- 阳极：不溶性电极
- 阴极：支持铜箔的处理面
- 电极间距离（示出于表 1 中）
- 电镀液组成 ($NiSO_4$：100g/L)
- 电镀液 pH：6.7
- 电镀的浴温：40℃
- 电镀的电流密度：5A/dm^2
- 电镀时间：10 秒
- 支持铜箔的输送张力：0.05kg/mm

(B) 转筒送箔方式

- 阳极：不溶性电极
- 阴极：在直径为 100cm 的转筒上支持的支持铜箔的表面
- 电极间距离（示出于表 1 中）
- 电镀液组成 ($NiSO_4$：100g/L)
- 电镀液 pH：6.7
- 电镀的浴温：40℃
- 电镀的电流密度：5A/dm^2
- 电镀时间：10 秒

• 支持铜箔的输送张力 :0.05kg/mm

(极薄铜层的形成)

(A) 曲折送箔方式

• 阳极 :不溶性电极

• 阴极 :支持铜箔的处理面

• 电极间距离 (示出于表 1 中)

• 电镀液组成 (Cu :50g/L, H_2SO_4 :50g/L, Cl :60ppm)

• 电镀的浴温 :45℃

• 电镀的电流密度 :30A/dm^2

• 支持铜箔的输送张力 :0.05kg/mm

(B) 转筒送箔方式

• 阳极 :不溶性电极

• 阴极 :在直径为 100cm 的转筒上支持的支持铜箔的表面

• 电极间距离 (示出于表 1 中)

• 电镀液组成 (Cu :100g/L, H_2SO_4 :80g/L, Cl :60ppm

• 电镀的浴温 :55℃

• 电镀的电流密度 :30A/dm^2

• 支持铜箔的输送张力 :0.05kg/mm

(粗化粒子层的形成)

(A) 曲折送箔方式

• 阳极 :不溶性电极

• 阴极 :支持铜箔的处理面

• 电极间距离 (示出于表 1 中)

• 电镀液组成 (Cu :10g/L, H_2SO_4 :50g/L)

• 电镀的浴温 :40℃

• 电镀的电流密度 :30A/dm^2

• 支持铜箔的输送张力 :0.05kg/mm

(B) 转筒送箔方式

• 阳极 :不溶性电极

• 阴极 :在直径为 100cm 的转筒上支持的支持铜箔的表面

• 电极间距离 (示出于表 1 中)

• 电镀液组成 (Cu :20g/L, H_2SO_4 :50g/L)

• 电镀的浴温 :40℃

• 电镀的电流密度 :30A/dm^2

• 支持铜箔的输送张力 :0.05kg/mm

2. 极薄铜箔的评价

对于如上得到的极薄铜箔,根据以下方法实施厚度精度的评价。将结果示出于表 1 中。

[0043] < 利用重量厚度法的厚度精度的评价 >

首先,在测定支持铜箔和极薄铜箔的重量后,剥下极薄铜层,再次测定支持铜箔的重

量，将前者与后者之差定义为极薄铜层的重量。将作为测定对象的极薄铜层片制成用挤压机冲压而成的 3cm 四边形片材。为调查重量厚度精度，在各个水平下均求得合计 60 个点的极薄铜层片的重量厚度测定值的平均值和标准偏差（σ），其中，宽度方向上等间隔 10 个点，长度方向上 6 个点（间隔 4cm）。需说明的是，重量厚度精度的计算式为下式：

厚度精度 (%)=(3σ×100)/平均值

此测定方法的重复精度为 0.2%。

[0044] 另外，重量计使用 A&D Co., Ltd.（株式会社エー・アンド・デイ）制 HF-400，挤压机使用 Noguchi Press Co., Ltd.（野口プレス株式会社）制 HAP-12。

[0045] <利用四探针法的厚度精度的评价>

在通过用四探针测定厚度电阻来求得支持铜箔和极薄铜箔的厚度后，剥下极薄铜层，再次根据支持铜箔的厚度电阻测定厚度，将前者与后者之差定义为极薄铜层的厚度。为调查厚度精度，在各个水平下均在宽度方向上以 5mm 的间隔求得合计 280 个测定点的平均值和标准偏差（σ）。需说明的是，利用四探针的厚度精度的计算式为下式：

厚度精度 (%)=(3σ×100)/平均值

此测定方法的重复精度为 1.0%。

[0046] 另外，四探针使用 OXFORD INSTRUMENTS 公司制 CMI-700。

[0047] [表 1]

	箔厚 (μm)	剥离层的形成		极薄层的形成		粗化粒子层的形成		厚度精度(%)	
		方式	电极间距离 (mm)	形成方法	电极间距离 (mm)	形成方法	电极间距离 (mm)	重量厚度法	四探针法
实施例 1	3	曲折	50	转筒	8	曲折	50	2.55	9.18
实施例 2	5	曲折	50	转筒	8	曲折	50	1.58	8.32
实施例 3	2	曲折	50	转筒	8	曲折	50	2.86	9.68
实施例 4	3	转筒	8	转筒	8	曲折	50	2.45	8.89
实施例 5	5	转筒	8	转筒	8	曲折	50	1.45	8.12
实施例 6	2	转筒	8	转筒	8	曲折	50	2.65	9.63
实施例 7	3	转筒	8	转筒	8	曲折	50	2.45	8.89
实施例 8	5	转筒	8	转筒	8	曲折	50	1.45	8.12
实施例 9	2	转筒	8	转筒	8	曲折	50	2.45	9.32
实施例 10	3	转筒	8	转筒	8	转筒	8	1.56	6.54
实施例 11	5	转筒	8	转筒	8	转筒	8	1.04	5.63
实施例 12	2	转筒	8	转筒	8	转筒	8	1.89	7.04
实施例 13	5	转筒	5	转筒	5	转筒	5	0.50	2.67
实施例 14	2	转筒	5	转筒	5	转筒	5	0.81	4.03
实施例 15	3	转筒	5	转筒	5	转筒	5	0.72	3.31
实施例 16	12	转筒	5	转筒	5	转筒	5	0.31	1.02
比较例 1	3	曲折	50	曲折	50	曲折	50	4.56	15.36
比较例 2	5	曲折	50	曲折	50	曲折	50	3.12	12.11
比较例 3	2	曲折	50	曲折	50	曲折	50	4.89	16.22

（评价结果）

实施例 1~16，对于极薄铜层，利用重量厚度法的厚度精度均为 3% 以下，并且利用四探针法的厚度精度均为 10% 以下，良好地抑制了厚度变化。

[0048] 比较例 1~3，对于极薄铜层，利用重量厚度法的厚度精度均超过 3%，并且利用四探针法的厚度精度均超过 10%，厚度变化大。

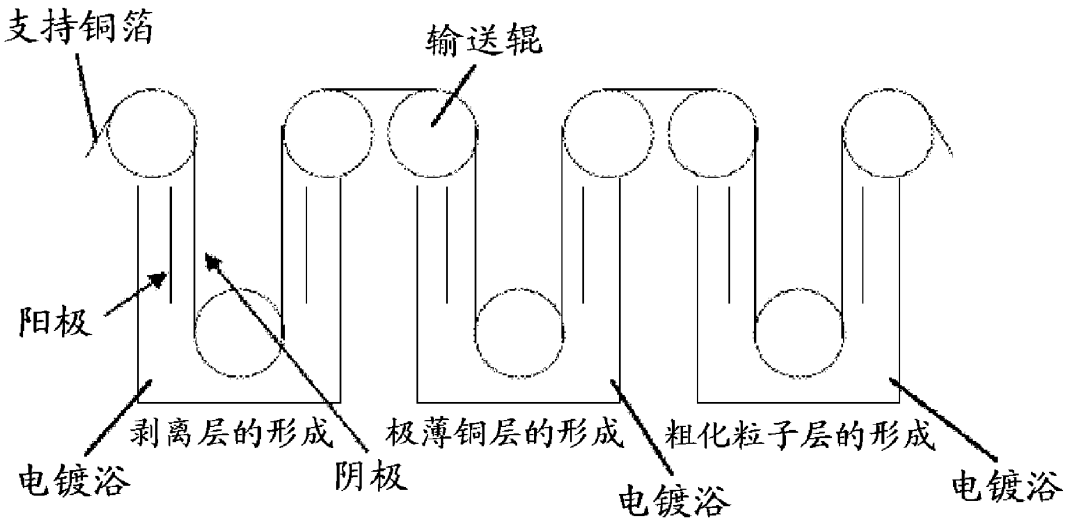

支持铜箔
输送辊
阳极
剥离层的形成
极薄铜层的形成
粗化粒子层的形成
电镀浴
阴极
电镀浴
电镀浴

图 1

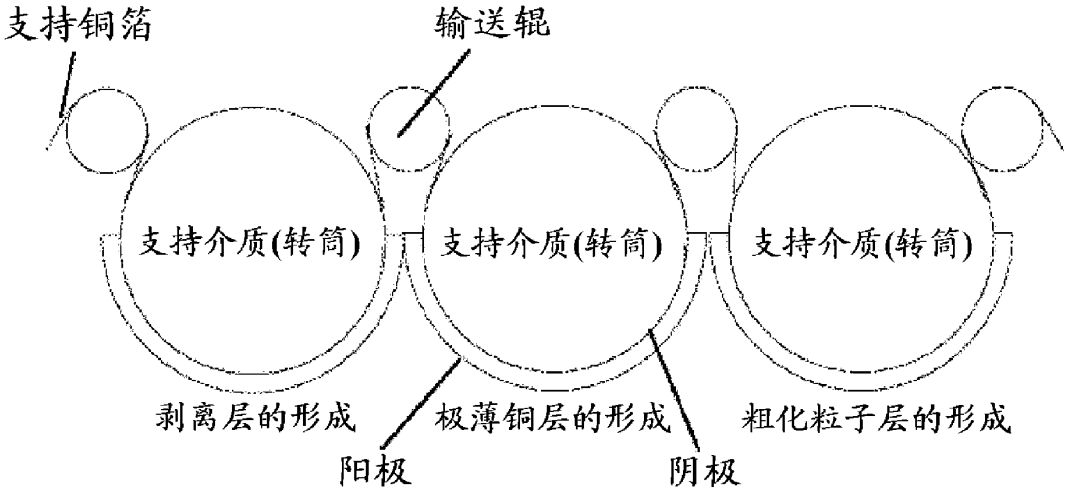

支持铜箔
输送辊
支持介质(转筒)
支持介质(转筒)
支持介质(转筒)
剥离层的形成
阳极
极薄铜层的形成
阴极
粗化粒子层的形成

图 2

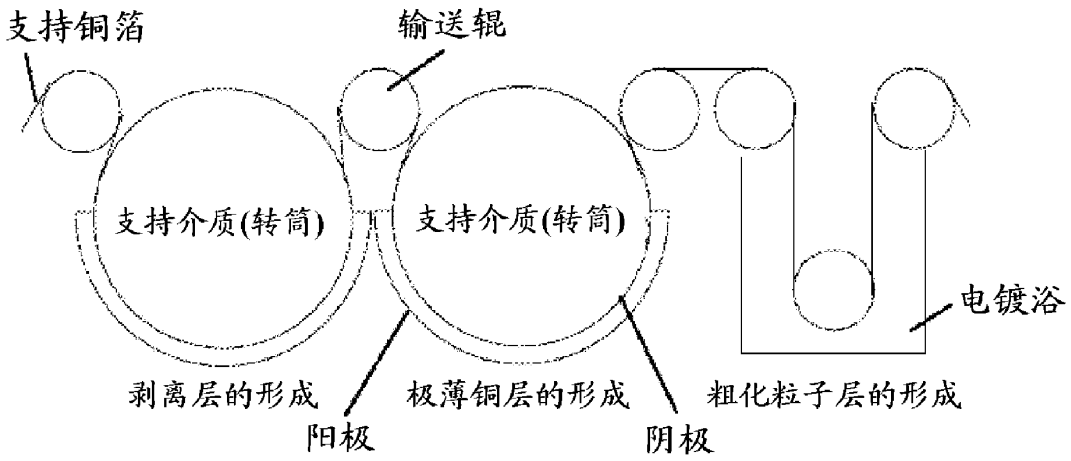

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电镀浴
剥离层的形成
阳极
极薄铜层的形成
阴极
粗化粒子层的形成

图 3

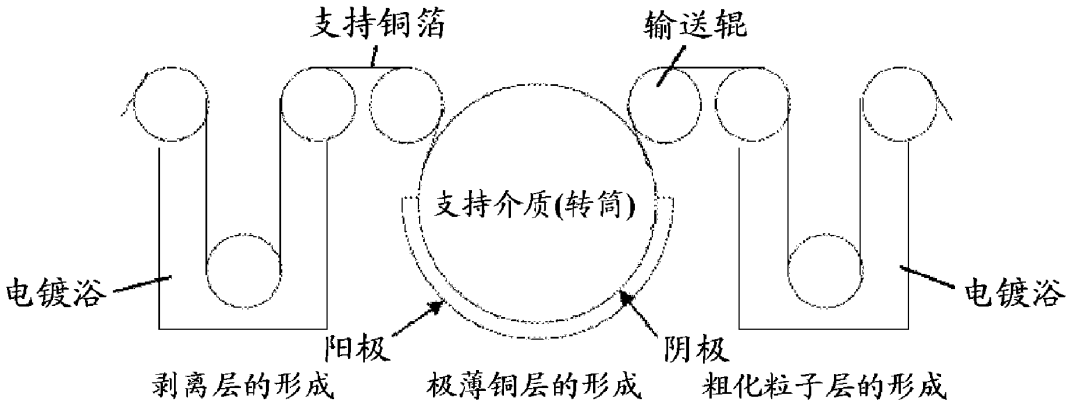

支持铜箔
输送辊
支持介质(转筒)
电镀浴
电镀浴
阳极
阴极
剥离层的形成
极薄铜层的形成
粗化粒子层的形成

图 4

Espacenet

Bibliographic data: TW200946719 (A) — 2009-11-16

Electrolytic solution for producing electrolytic copper foil

Inventor(s): HANABUSA MIKIO [JP] ± (HANABUSA, MIKIO)

Applicant(s): NIPPON MINING CO [JP] ± (NIPPON MINING & METALS CO., LTD)

Classification: - international: ***B32B15/08; C25C1/12; C25D1/04; C25D3/38; H05K1/09***
- cooperative: **C25D1/04**; **C25D1/20**; **C25D3/38**; H05K1/09

Application number: TW20090107962 20090312

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Abstract of TW200946719 (A)

An electrolytic copper solution for producing an electrolytic copper foil is provided which can improve elongation properties while reducing the profile of the rough surface. The electrolytic solution for electrolytic-copper foil production is a sulfuric-acid-acidified aqueous copper sulfate solution containing: bromide ions derived from bromine, an inorganic acid thereof, an inorganic salt thereof, or a mixture of these; a glue; and chloride ions.

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申請實體審查：有 申請專利範圍項數：11 項 圖式數：0 共 21 頁

(54)名稱
電解銅箔製造用之電解液

(57)摘要

本發明提供一種能夠一邊達成粗面的低起伏化，一邊提升延伸特性之電解銅箔製造用的銅電解液。其係含有作為電解銅箔製造用電解液之溴離子(係源自於溴、溴的無機酸、溴的無機鹽、或者是此等之混合物)、膠與氯離子之硫酸酸性硫酸銅水溶液。

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六、發明說明：

【發明所屬之技術領域】

本發明係關於一種電解銅箔的製造所使用之銅電解液。又，本發明係關於一種電解銅箔的製造方法。進一步，本發明係關於一種覆銅積層板的製造方法。

【先前技術】

印刷電路板係於各種電子機器的運作上所不可或缺的零件，一般而言，印刷電路板係經由以下之製造步驟所製造而成。首先，透過接著劑，或者是不使用接著劑，於高溫高壓下，將銅箔積層接著於合成樹脂板、薄膜等之絕緣基材來製造覆銅積層板。接著，於印刷用來形成目的回路所需要的回路之後，施行除去不要部份的蝕刻處理。最後，焊接所需要的電子零件，作為各種的印刷電路板。

銅箔當中雖然有電解銅箔與壓延銅箔，然而從接著強度等之觀點來看，印刷電路板用所使用的銅箔，大部份為電解銅箔。電解銅箔的基本，係以電解銅或者是具有與其相等之純度的電線廢料作為原料，將原料溶解於硫酸銅水溶液中來調製電解浴，藉由電解反應，連續地將銅電沈積於作為陰極被浸漬於浴中之回轉桶的周圍面，將已經變成既定之厚度的電沈積物，自回轉桶剝離，來製造生箔。之後，為了因應對於印刷電路板用銅箔品質之要求，針對與樹脂基材接著之面(粗面)及非接著面(光澤面)分別施行了眾多的處理(表面處理)。

伴隨著近年之電子機器的小型化、高性能化之需求的增加，搭載零件的高密度封裝化或信號的高頻率化也有所進展，印刷電路板相對地被要求了導體圖案的微細化(細節距化)或高頻率對應等。因此，關於印刷電路板所使用之銅箔，被要求要能夠因應如此之印刷電路板的高性能化之特性。具體而言，印刷電路板所使用之銅箔被要求了需為無針孔，從尺寸安定性的觀點來看抗張力要高，從防止龜裂的觀點來看延伸率要高，然後，為了對應如上述之導體圖案的微細化(細節距化)或高頻率對應等，印刷電路板所使用之銅箔特別被要求粗面的低起伏(low profile)化。

粗面的低起伏化，已知可藉由將膠添加於電解液來達成。膠對於針孔的防止或回轉桶的保護皆能夠發揮功效。然而，若讓膠的添加量增加下去，則在高溫下的延伸會有降低之問題。因此，期望能夠在活用膠所賦予之低起伏化或針孔的防止等優點的同時，提升在高溫下的延伸特性。

關於此點，例如，於日本專利特公昭 49-31415 號公報中，記載了將添加了聚亞烷基乙二醇或膠質劑之中的任 1 種或 2 種、與進一步添加了氯離子 5～100mg/L 之酸性銅電鍍液作為電解液使用，藉此能夠得到硬度及韌性優異，且針孔少的銅箔。氯離子被認為具有促進電沈積結晶的微細化，防止微小針孔的發生的效果。

於日本專利特開平 8-53789 號公報中，記載了於硫脲中加入特定量之高分子多醣類與膠的三元系添加劑的組合，被認為能夠達成低起伏化、在常溫及高溫中的延伸率高、

而且能有效取得抗張力高的電解銅箔，公報中記載：「一種電解銅箔的製造方法，其特徵在於，作為其添加劑，使用了含有以下成份的電解液：0.05～2.0 重量 ppm 的硫脲或者是該衍生物；0.08～12 重量 ppm 的高分子多醣類；及分子量 10000 以下且 0.03～4.0 重量 ppm 的膠」。

又，於日本專利特開平 7-278866 號公報中，記載了電解液中的膠濃度較慣用的量 2～10ppm 較少，具體而言，有效量為 0.5ppm 以下，如此一來，可以大幅地改善電解銅箔在高溫下的延伸。又，公報中記載，除非添加氯離子 20～100ppm，否則銅箔的基本特性會不穩定。

[專利文獻 1] 日本專利特公昭 49-31415 號公報

[專利文獻 2] 日本專利特開平 8-53789 號公報

[專利文獻 3] 日本專利特開平 7-278866 號公報

【發明內容】

發明所欲解決之課題

在日本專利特開平 8-53789 號公報中，雖然將硫脲的添加視為必要，但正如同該公報中也有指出，硫脲的效果及弊害很大，須要精密地控制其添加量。又，有機物的硫脲在分解的時候，有各種分解物存在，此等之分解物對於銅箔特性也會造成各種影響，而難以得到安定的特性。

在日本專利特開平 7-278866 號公報降低膠濃度的結果，在高溫下的延伸雖然獲得改善，但會出現桶使用週期變短的問題。亦即，膠雖然具有將初期的核發生均一化的

效果，但當膠濃度較小時，則該效果會變弱。當在降低膠濃度的狀態下繼續使用桶時，則桶表面的電阻落差會變大。隨著桶表面的電阻落差變大，初期的核發生不均一的情況會變得很明顯，變成龜裂狀的缺陷，於箔中產生針孔。

又，根據本發明之發明者眾人的檢討結果，在膠與氯離子的系統中，無論是在高溫下的延伸特性、表面粗度，皆不能說是足夠的特性。

因此，本發明的課題，係提供一種即使不降低膠的濃度，也能夠提升延伸特性之其他種電解銅箔製造用的銅電解液。又，本發明的另一課題，係提供一種延伸特性優異之電解銅箔的製造方法。本發明進一步的課題，係提供一種具備如此之銅電銅箔的覆銅積層板的製造方法。

用以解決課題之手段

本發明之發明者眾人為了解決上述課題，致力檢討的結果，發現在溴離子與氯離子共存於銅電解液中的情況下，在常溫及高溫下的延伸會獲得改善。因此，藉由在電解銅箔製造用的銅電解液之中，添加能夠供給溴離子的溴化合物與能夠供給氯離子的氯化物，可謀求改善延伸特性。

因此，於本發明之一側面，係提供一種硫酸酸性硫酸銅水溶液，其含有溴離子、膠、與氯離子來作為電解銅箔製造用的電解液。

於本發明之電解液之一特定實施形態，電解液中之溴離子的濃度為 0.25～200mg/L(ppm)。

於本發明之電解液之其他的一特定實施形態，溴離子係源自於溴、溴的無機酸、溴的無機鹽、或者是此等之混合物。

於本發明之電解液之進一步其他的一特定實施形態，電解液中的溴離子係源自於鹼金屬鹽及鹼土金屬鹽。

於本發明之電解液之一特定實施形態，電解液中的氯離子之濃度為 2.5～200mg/L。

於本發明之電解液之一特定實施形態，電解液中的膠之濃度為 1～10mg/L。

又，於本發明之其他的一側面，係一種電解銅箔的製造方法，其中，包括將上述的硫酸酸性硫酸銅水溶液作為電解液使用，將銅電沈積於陰極上之步驟；與將電沈積之銅自陰極剝除之步驟。

於本發明之電解銅箔的製造方法之一特定實施形態，係以溫度 45～70℃ 的電解液、30～150A/dm^2 的電流密度將銅電沈積於陰極上。

又，於本發明之進一步的其他的一側面，係一種覆銅積層板的製造方法，其中，包括使用上述之電解銅箔的製造方法得到電解銅箔之步驟；與讓該銅箔的粗面側面向絕緣基板，將該銅箔積層於絕緣基板之步驟。

又，本發明之進一步的其他的一側面，係含有 Br 之電解銅箔。

又，本發明之進一步的其他的一側面，係一種含有 Br 之電解銅箔的製造方法，其中，包括將上述之硫酸酸性硫

酸銅水溶液作為電解液使用，將銅電沈積於陰極上之步驟；與將電沈積之銅自陰極剝除之步驟。

發明效果

根據本發明，可製造一種粗面能夠低起伏且具有高度的延伸特性之電解銅箔。

【實施方式】

1.電解液

(1)硫酸酸性硫酸銅水溶液

本發明中，用以製造電解銅箔所使用之電解液為硫酸酸性的硫酸銅水溶液。雖然作為用以製造電解銅箔之電解液而使用硫酸酸性硫酸銅水溶液已被廣為所知而不需要特別說明，但一般而言係以 $CuSO_4 \cdot 5H_2O$ 與 H_2SO_4 作為主成份，一般而言含有 Cu：60～110g/L、H_2SO_4：50～150g/L、典型為含有 Cu：80～120g/L、H_2SO_4：80～105g/L。

(2)溴離子

本發明之電解液含有溴離子，其供給源為溴、溴的無機酸、溴的無機鹽、或者是此等之混合物。當不存在氯離子的情況下，即便讓含有膠的電解液含有溴離子，雖然和含有氯離子的情況相同不論是在高溫下的延伸特性、表面粗度皆無法得到足夠的特性，但因為溴離子被包含於含有膠與氯離子之電解液中，所得到之電解銅箔的延伸及表面粗度會獲得改善。亦即，雖然溴離子單獨存在的時候，對

延伸率或表面粗度幾乎沒有改善效果，但藉由讓溴離子與氯離子在電解液中共存，會出現延伸率及表面粗度改善的相乘效果。

又，因為本發明中溴離子係由溴、溴的無機酸、溴的無機鹽、或者是此等之混合物所供給，故不須要擔心溴離子會如同有機物那樣分解，在能夠得到安定的特性這點也有利。

溴能夠以液體溴或溴水的形態提供給電解液。作為溴的無機酸，除了溴化氫酸(HBr)之外，可舉出諸如溴酸($HBrO_3$)或亞溴酸($HBrO_2$)等之溴的含氧酸，此等能夠作為水溶液來供給。作為溴的無機鹽，可舉出諸如溴化鈉(NaBr)、溴化鉀(KBr)、溴化鈣($CaBr_2$)、溴化鎂($MgBr_2$)等之鹼金屬鹽及鹼土金屬鹽。亦可為上述含氧酸的鹼金屬鹽或鹼土金屬鹽。溴離子的供給源從安定性、容易處理的觀點來看，以鹼金屬鹽、鹼土金屬鹽為較佳。

如同前述，雖然一直以來含有氯離子之電解液已為人所知悉，但氯離子的功用係在於防止針孔。另一方面，於本發明所使用之溴雖然與氯同樣為鹵素，但對於延伸特性的改善，進一步對於表面粗度的降低等特異的效果能夠發揮功效。溴對於抗張力也幾乎沒有不良的影響。

當添加於電解液之溴離子濃度過低時，則降低表面粗度的效果較差。而即使溴離子濃度升高，因已得到充份的改善效果，故其效果只能維持一定程度。因此，電解液中的溴離子(Br^-)濃度較佳為設為 0.25～200mg/L，更佳為設為

10～200mg/L，最佳為設為 50～100mg/L。

已知添加的溴離子最終會被攝入電解銅箔中，而於本發明之電解銅箔之一特定實施態樣，所得到之電解銅箔含有 Br。

(3)膠

如同上述，膠具有粗面的低起伏化、針孔的防止、回轉桶的保護的優點。一般而言，電解液中所添加的膠之濃度範圍為 0.1～20mg/L。從充份享受所謂粗面的低起伏化、針孔的防止、回轉桶的保護之膠所帶來的優點的觀點來看，電解液中的膠濃度較佳為設為 0.25～10mg/L，更佳為設為 2.0～5.0mg/L。

於本發明所使用的膠，典型為以明膠作為主成份、分子量為 500～250000 左右者，例如，可以從獸・魚類的骨頭・皮・腱・腸等利用水解來製造。低分子側的膠，可以使用酵素、酸或鹼分解一般的膠取得。本發明中所使用的膠，從桶的保護之觀點來看，較佳為數量平均分子量 1000～75000 者，更佳為數量平均分子量 2000～50000 者。

(4)氯離子

本發明之電解液含有氯離子。氯離子讓電沈積結晶的結晶方位產生變化，藉由形成山形的表面形狀來加粗表面粗度，具有防止針孔發生的效果。作為氯離子的供給源並沒有特別的限制，除了鹽酸(HCl)之外，可以像是氯化鈉(NaCl)、氯化鉀(KCl)、氯化鈣($CaCl_2$)、氯化鎂($MgCl_2$)之類的無機鹽的形態來添加。亦可以氯水的形態來添加。在此

等之中以容易的觀點來看，較佳為以稀鹽酸的形態供給氯離子。

雖然當氯離子在電解液中的濃度過低時會無法得到充份的效果，但反過來當氯離子在電解液中的濃度過高時表面形狀會破壞，容易發生異常析出。因此，電解液中的氯離子的濃度，較佳為設為 2.5～200mg/L，更佳為設為 10～100mg/L，最佳為設為 25～75mg/L。

(5)其他的添加物

一般而言，為了製造電解銅箔，透過將各種添加劑添加於所使用的電解液，來謀求電解銅箔的特性提升，但會妨害本發明之電解液中 Br^-所帶來的特性提升效果，或抵銷 Br^-所帶來的特性提升效果的添加劑最好不要添加。例如，雖然已知磷酸系化合物、胺化合物、有機硫化合物(例：硫脲)等作為添加劑，但若將如此之添加劑添加於本發明之電解液中時，因為會造成高溫下的機械特性降低的不良影響，故最好還是不要讓本發明之電解液含有如此之添加劑。其中，因為高分子多醣類、聚乙二醇之類的添加劑對於 Br 添加所帶來的特性提升效果不會造成不良影響，或者就算會造成不良影響程度也很輕微，故可適宜使用。

2.電解銅箔的製造

電解銅箔可以使用本發明之電解液依照常法來製造。亦即，可以藉由將上述的硫酸酸性硫酸銅水溶液作為電解液使用，讓銅電沈積於陰極上，將電沈積的銅從陰極剝除來製造電解銅箔。更具體而言，可以使用表面經研磨的回

轉金屬製陰極桶，與配置於該陰極桶大約下半部的位置、包圍該陰極桶四周的不溶性金屬陽極(anode)，在讓前記陰極桶與陽極之間的電解液流動的同時，在此等之間施加電位讓銅電沈積於陰極桶上，於形成既定的厚度時從該陰極桶剝除電沈積的銅連續地製造銅箔。作為銅箔的厚度，雖然並沒有特別的限制，但如果是細節距用的銅箔，一般是設為 18μm 以下。如此所得之銅箔進一步經過表面處理步驟及切斷步驟成為銅箔製品。表面處理步驟一般是進行粗化處理、耐熱層形成及/或防鏽層形成等。

其中，為了讓本發明之電解液中所含之溴離子的效果發揮到最大限度，在一定的電解條件下讓電解銅箔電沈積較為理想。

首先，較佳的電解液的溫度為 40～75℃、更佳為 45～70℃。當電解液的溫度過低時，則會容易變成焦沉積，而無法取得正常的銅箔。反言之，當電解液的溫度過高時，則膠的分解會加快，分解物的累積會變多，而變得容易發生機械特性的降低。

又，電流密度較佳為 30～150A/dm^2，更佳為 60～130A/dm^2。當電流密度過低時則生產速度會變慢，而生產性會降低。反言之，當電流密度過高時則會容易變成焦沉積，而無法取得正常的銅箔。

3.覆銅積層板的製造

使用以上述的方法所製造出來的銅箔製品，可以依照常法製造覆銅積層板。具體而言，可以藉由讓該銅箔的粗

面側面向絕緣基板，將該銅箔積層於絕緣基板來製造覆銅積層板。

作為讓銅箔與絕緣基板接著的方法，例如，有加熱加壓的方法、使用接著劑的方法、將成為絕緣基板之聚合物的前驅物分散於溶劑塗佈之後使其產生加熱聚合反應等方法。

積層了銅箔的絕緣基板，只要是具有可適用於印刷電路板(PCB)的特性者並沒有特別受到限制，例如，剛性 PCB 用，可以使用紙基材苯酚樹脂、紙基材環氧樹脂、合成纖維布基材環氧樹脂、玻璃布・紙複合基材環氧樹脂、玻璃布・玻璃不織布複合基材環氧樹脂及玻璃布基材環氧樹脂等，FPC 用可以使用聚酯膜或聚醯亞胺膜等。

藉由依照常法加工覆銅積層板，可以形成各種印刷配線板，進一步可以形成印刷電路板。

【實施例】

以下，紹介本發明之實施例以期能進一步理解本發明及其優點，但本發明並非被限定於此等之實施例。

試驗例 1(Br^-的濃度變化所造成的影響)

於 Cu：90g/L、H_2SO_4：80g/L 的硫酸酸性硫酸銅水溶液添加膠(數量平均分子量 20000)、溴化鉀及鹽酸來調製電解液，於鉻製陰極桶(外徑 0.64m)上，連續製造厚度為 18μm 的電解銅箔。

使用以下的方法測定電解液中的膠、溴離子及氯離子

於電解液中的濃度。針對各例，於表 1 表示其測定結果。

＜膠＞

CVS 分析裝置(北斗電工公司製)

對於已知的膠濃度，以 CVS 法(cyclic voltammetric stripping method)從測定的銅在電解液中溶解所發生的庫倫量來作成檢測線，藉由與使用實際的電解液測定到的 CVS 的值加以比較來決定膠濃度。

＜溴離子＞

離子層析(DIONEX 公司製、型式 ICS-2000)

＜氯離子＞

離子層析(DIONEX 公司製、型式 ICS-2000)

所得到之電解銅箔的粗面側的表面粗度 Ra、Rt 及 Rz(μm)，係根據 JISB0601 使用小坂研究所公司製型式 SE-3C 來進行測定，室溫抗張力(Kgf/mm^2)、室溫延伸(%)、高溫抗張力(Kgf/mm^2)、高溫延伸(%)，係根據 IPC-TM650 使用島津製作所公司製型式 AGS-H-500N 來進行測定。針對各例，於表 1 表示測定結果。

桶使用週期係以下述的方式來評價。將厚度 18μm 箔連續地製箔，每 6 個小時調查有無周期性的針孔，將周期性的針孔變成有 5 個以上時作為桶使用週期。

試驗例 2(膠的濃度變化所造成的影響)

將試驗例 1 的 No.2 作為基準，調查改變電解液中的膠濃度時的電解銅箔的特性變化。於表 2 表示其結果。

試驗例 3(氯離子變化所造成的影響)

調查改變電解液中的氯離子濃度時的電解銅箔的特性變化。於表 3 表示其結果。

[表 1]

					室溫		高溫(180℃)					桶使用週期
No.	Br (mg/L)	Cl (mg/L)	膠 (mg/L)	液溫 (℃)	抗張力 (kgf/mm²)	延伸率 (%)	抗張力 (kgf/mm²)	延伸率 (%)	Ra	Rt	Rz	(時間)
1	0.25	60	2.0	55	36.8	9.3	22.4	4.1	0.50	3.67	3.10	306
2	1	60	2.0	55	37.1	10.1	22.7	4.9	0.50	3.60	3.00	306
3	10	60	2.0	55	37.3	11.2	22.4	6.1	0.50	3.60	3.08	318
4	30	60	2.0	55	37.2	15.3	21.8	4.8	0.47	3.57	2.87	318
5	50	60	2.0	55	37.4	15.9	21.4	10.3	0.46	3.40	2.83	336
6	100	60	2.0	55	38.3	16.3	21.9	11.3	0.47	3.38	2.77	330
7	200	60	2.0	55	38.8	15.8	21.6	10.9	0.48	3.42	2.85	330
8(比較)	0	60	2.0	55	36.7	8.8	21.1	2.3	0.62	4.38	3.93	300

[表 2]

					室溫		高溫(180℃)					桶使用週期
No.	Br (mg/L)	Cl (mg/L)	膠 (mg/L)	液溫 (℃)	抗張力 (kgf/mm²)	延伸率 (%)	抗張力 (kgf/mm²)	延伸率 (%)	Ra	Rt	Rz	(時間)
3	10	60	2.0	55	37.3	11.2	22.4	6.1	0.50	3.60	3.08	318
8	10	60	1.0	55	37.2	10.8	22.2	5.8	0.50	3.62	3.11	306
9	10	60	5.0	55	37.4	11.5	22.5	5.7	0.49	3.59	2.97	330
10	10	60	10.0	55	37.7	10.6	22.8	5.4	0.50	3.60	3.00	336
11	10	60	0.2	55	37.2	9.8	21.9	5.6	0.48	3.63	3.03	174
12	10	60	15.0	55	38.3	8.2	22.9	1.9	0.47	3.58	2.87	348
13(比較)	0	60	0.2	55	37.3	8.3	21.8	5.2	0.47	3.87	3.31	96

[表 3]

					室溫		高溫(180℃)					桶使用週期
No.	Br (mg/L)	Cl (mg/L)	膠 (mg/L)	液溫 (℃)	抗張力 (kgf/mm²)	延伸率 (%)	抗張力 (kgf/mm²)	延伸率 (%)	Ra	Rt	Rz	(時間)
14	50	2.5	2.0	60	36.8	15.6	21.9	11.2	0.46	3.37	2.87	300
15	50	10	2.0	60	36.3	15.2	21.8	10.9	0.46	3.39	2.89	306
16	50	25	2.0	60	36.1	15.3	21.4	11.0	0.48	3.42	3.06	312
17	50	50	2.0	60	36.2	15.3	21.1	10.8	0.47	3.38	2.98	324
18	50	75	2.0	60	36.0	15.6	21.3	10.7	0.46	3.43	3.12	318
19	50	100	2.0	60	35.9	14.8	20.9	9.6	0.48	3.48	3.01	288
20	50	200	2.0	60	36.1	14.5	21.1	9.4	0.49	3.50	3.22	276
21(比較)	50	0	2.0	60	45.3	8.8	21.3	2.5	0.47	4.38	3.98	306
22(比較)	0	0	2.0	60	60	8.7	20.7	12.1	0.45	3.25	2.65	296
23(比較)	0	50	2.0	60	35.8	8.9	21.1	2.4	0.61	4.27	3.80	288

考察

從表 1 中可以得知，藉由於含有 Cl^-的電解液添加 Br^-，不會對桶使用週期或表面粗度造成不良影響，且可以改善室溫及高溫下的延伸率。又，隨著 Br 濃度增加延伸率也會提昇，大致以 100mg/L 效果達到飽和。

從表 2 中可以得知，藉由讓膠的濃度適當化，可讓桶使用週期及所得到的銅箔特性提升。

從表 3 中可以得知，所添加的 Cl^-以極低的濃度即可。從 No.21 與 No.22 的比較可以得知，單獨添加 Br^-的效果並不大。

電解銅箔中 Br 的有無

針對從 No.1，5，7 所得到的電解銅箔，使用 TOF-SIMS(Hitachi High-Tech Trading Corporation. 型式 TOF-SIMS IV)調查銅箔裡是否含有 Br。其結果，從任一的電解銅箔中皆檢測出 10^5 數量級(ion counts)的 Br 強度。

【圖式簡單說明】

無

【主要元件符號說明】

無

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發明專利說明書

（本說明書格式、順序，請勿任意更動，※記號部分請勿填寫）

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一、發明名稱：(中文/英文)

電解銅箔製造用之電解液

二、中文發明摘要：

本發明提供一種能夠一邊達成粗面的低起伏化，一邊提升延伸特性之電解銅箔製造用的銅電解液。其係含有作為電解銅箔製造用電解液之溴離子(係源自於溴、溴的無機酸、溴的無機鹽、或者是此等之混合物)、膠與氯離子之硫酸酸性硫酸銅水溶液。

三、英文發明摘要：

無

七、申請專利範圍：

1.一種硫酸酸性硫酸銅水溶液，其中，含有作為電解銅箔製造用電解液之溴離子、膠與氯離子。

2.如申請專利範圍第1項之硫酸酸性硫酸銅水溶液，其中，溴離子的濃度為0.25～200mg/L。

3.如申請專利範圍第1項或第2項之硫酸酸性硫酸銅水溶液，其中，溴離子係源自於溴、溴的無機酸、溴的無機鹽、或者是此等之混合物。

4.如申請專利範圍第3項之硫酸酸性硫酸銅水溶液，其中，溴離子係源自於鹼金屬鹽及鹼土金屬鹽。

5.如申請專利範圍第1項或第2項之硫酸酸性硫酸銅水溶液，其中，電解液中的氯離子之濃度為2.5～200mg/L。

6.如申請專利範圍第1項或第2項之硫酸酸性硫酸銅水溶液，其中，電解液中的膠之濃度為1～10mg/L。

7.一種電解銅箔的製造方法，其中包括：

將申請專利範圍第1～6項中任一項之硫酸酸性硫酸銅水溶液作為電解液使用，將銅電沈積於陰極上之步驟；以及

將電沈積之銅自陰極剝除之步驟。

8.如申請專利範圍第7項之電解銅箔的製造方法，其中，係以溫度45～70℃的電解液、30～150A/m^2的電流密度將銅電沈積於陰極上。

9.一種覆銅積層板的製造方法，其中包括：

使用申請專利範圍第7項或第8項之電解銅箔的製造

方法得到電解銅箔之步驟；以及

讓該銅箔的粗面側面向絕緣基板，將該銅箔積層於絕緣基板之步驟。

10.含有 Br 之電解銅箔。

11.一種電解銅箔之製造方法，係用以製造申請專利範圍第 10 項之電解銅箔，其中包括：

將申請專利範圍第 1～6 項中任一項之硫酸酸性硫酸銅水溶液作為電解液使用，將銅電沈積於陰極上之步驟；以及

將電沈積之銅自陰極剝除之步驟。

八、圖式：

（無）

方法得到電解銅箔之步驟；以及

讓該銅箔的粗面側面向絕緣基板，將該銅箔積層於絕緣基板之步驟。

10.含有 Br 之電解銅箔。

11.一種電解銅箔之製造方法，係用以製造申請專利範圍第 10 項之電解銅箔，其中包括：

將申請專利範圍第 1～6 項中任一項之硫酸酸性硫酸銅水溶液作為電解液使用，將銅電沈積於陰極上之步驟；以及

將電沈積之銅自陰極剝除之步驟。

八、圖式：

（無）

四、指定代表圖：

(一)本案指定代表圖為：第（　無　）圖。

(二)本代表圖之元件符號簡單說明:

無

五、本案若有化學式時，請揭示最能顯示發明特徵的化學式：

無

Electronic Acknowledgement Receipt

EFS ID:	34958304
Application Number:	15696360
International Application Number:	
Confirmation Number:	7466
Title of Invention:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Seung Min KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/Samantha Lingo
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313221.00013
Receipt Date:	25-JAN-2019
Filing Date:	06-SEP-2017
Time Stamp:	12:35:00
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	00013_IDS_Trans.pdf	81459 7cb9168d0536d88f1e97c6844163e4d2db60ed27	no	3

Warnings:

Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	00013_PTOsb08.pdf	1035086 c4ede773fd748bc7617ee2b5621abb47c17c18ec	no	4
Warnings:					
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3	Foreign Reference	CN104114751A.pdf	864186 93f9b76db27556920d8288fb9a2c0e503e37c84a	no	12
Warnings:					
Information:					
4	Foreign Reference	TW200946719A.pdf	817840 0434f39578a8eb2e7d8f2bcb4417bbac5930a785	no	22
Warnings:					
Information:					
5	Other Reference-Patent/App/Search documents	OP17-KF-012-US-00_TW_OA.pdf	745674 90ce70264b23a40d7b1c4eea3014f3b3c77c6a0b	no	5
Warnings:					
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		Total Files Size (in bytes):	3544245		

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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.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Seung-Min KIM
Appl. No.:	15/696,360
Conf. No.:	7466
Filed:	September 6, 2017
Title:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1725
Examiner:	CONLEY, OI K
Docket No.:	0313221.00013

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

INFORMATION DISCLOSURE STATEMENT TRANSMITTAL LETTER

Sir:

Submitted herewith is an Information Disclosure Statement for consideration in the above-identified application. In accordance with the provisions of 37 C.F.R. 1.56, 37 C.F.R. 1.97, and 37 C.F.R. 1.98, Applicants request that a citation and examination of the references cited on the enclosed SB08 form be made during the course of examination of the above-identified application for United States patent.

This Information Disclosure Statement is submitted as follows:

Submission without Certification

[X] Within three months of filing of a national application; within three months of the date of entry of the national stage as set forth in 37 C.F.R. §1.491 in an international application; before the mailing date of a first Office Action on the merits, or before the mailing of a first Office Action after the filing of a Request for Continued Examination.

[ ] After the period specified above, but before the mailing date of a Final Action under 37 CFR 1.113, a Notice of Allowance under 37 CFR 1.311, or an Action that otherwise closes prosecution in the application and is accompanied by payment of the fee set forth in 37 CFR 1.17(p).

Submission with Certification

[ ] Within three months of filing of a national application; within three months of the date of entry of the national stage as set forth in 37 C.F.R. §1.491 in an international application; before the mailing date of a first Office Action on the merits, or before the mailing of a first Office Action after the filing of a Request for Continued Examination.

[ ] After the period specified above, but before the mailing date of a Final Action under 37 CFR 1.113, a Notice of Allowance under 37 CFR 1.311, or an Action that otherwise closes prosecution in the application and is accompanied by the Certification specified in 37 CFR 1.97(e) which is set forth below.

[ ] After the mailing date of a Final Action under 37 CFR 1.113, a Notice of Allowance under 37 CFR 1.311, or an Action that otherwise closes prosecution in the application and is accompanied by the fee set forth in 37 CFR 1.17(p) and the Certification specified in 37 CFR 1.97(e) which is set forth below.

Certification under 37 CFR 1.97(e)

[ ] The undersigned counsel for applicant(s) hereby certifies that each item of information contained in the accompanying 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.

[ ] The undersigned counsel for applicant(s) hereby certifies that no item of information contained in the accompanying Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the undersigned, after making reasonable inquiry, no item of information contained in the accompanying 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.

Statement under 37 CFR 1.704(d)

[ ] The undersigned counsel for applicant(s) hereby states that each item of information contained in the accompanying Information Disclosure Statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and/or is a communication that was issued by a patent office in a counterpart foreign or international application or by the Office, and this communication was not received by any individual designated in § 1.56(c) more than **thirty days** prior to the filing of the information disclosure statement.

[ ] A copy of a Search Report from a corresponding foreign patent application is enclosed.

[ ] The Commissioner is hereby authorized to charge the amount of $240.00 to cover the required fee to Deposit Account No. 02-1818.

[X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-1818.

Respectfully submitted,

K&L GATES LLP

BY /Matthew S. Dicke/
Matthew S. Dicke
Reg. No. 58819
Customer No. 24573
Phone: (312) 578-5415

Dated: January 25, 2019

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
Approved for use through 07/31/2016. OMB 0651-0031
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	15696360
	Filing Date	2017-09-06
	First Named Inventor	Seung Min KIM
	Art Unit	1725
	Examiner Name	CONLEY, OI K
	Attorney Docket Number	0313221.00013

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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
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FOREIGN PATENT DOCUMENTS Remove

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]
	1	2013-181236	JP	A	2013-09-12	JX NIPPON MINING & METALS CORP		
	2	2013-175488	JP	A	2013-09-05	LS MTRON LTD		
	3	2001-140091	JP	A	2001-05-22	MITSUI MINING & SMELTING CO LTD		

EFS Web 2.1.17

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15696360
	Filing Date	2017-09-06
	First Named Inventor	Seung Min KIM
	Art Unit	1725
	Examiner Name	CONLEY, OI K
	Attorney Docket Number	0313221.00013

	4	2000-182623	JP	A	2000-06-30	NIPPON DENKAI KK			

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]
	1	Japanese Office Action for related Japanese Application No. 2017-162283; action dated October 23, 2018; (2 pages)	
	2	UNKNOWN; "The Chemical Dictionary"; October 20, 1989; page 1233; (4 pages)	

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

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	15696360
	Filing Date	2017-09-06
	First Named Inventor	Seung Min KIM
	Art Unit	1725
	Examiner Name	CONLEY, OI K
	Attorney Docket Number	0313221.00013

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	/Matthew S. Dicke/	Date (YYYY-MM-DD)	2019-01-23
Name/Print	Matthew S. Dicke	Registration Number	58819

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.**

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.

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.

Espacenet

Bibliographic data: JP2000182623 (A) — 2000-06-30

ELECTROLYTIC COPPER FOIL, COPPER FOIL FOR CURRENT COLLECTOR OF SECONDARY BATTERY, AND SECONDARY BATTERY

Inventor(s): HARIGAYA KOICHI; NOGUCHI HIDEO; KOBAYASHI KATSUMI; ASO KAZUYOSHI ± (HARIGAYA KOICHI, ; NOGUCHI HIDEO, ; KOBAYASHI KATSUMI, ; ASO KAZUYOSHI)

Applicant(s): NIPPON DENKAI KK ± (NIPPON DENKAI KK)

Classification: **- international:** ***C25D1/04; H01M10/28; H01M4/64; H01M4/66;*** (IPC1-7): C25D1/04; H01M10/28; H01M10/40; H01M4/64

- cooperative:

Application number: JP19980353213 19981211

Priority number(s): JP19980353213 19981211

Also published as: JP3850155 (B2)

Abstract of JP2000182623 (A)

PROBLEM TO BE SOLVED: To provide an electrolytic copper foil used as a current collector of a secondary battery, excellent in the tensile strength and in the rate of elongation at a room temp. and after being heated and a secondary battery equipped with a current collector consisting of such copper foil excellent in overcharging test characteristics. SOLUTION: An electrolytic copper foil containing not more than 5 ppm carbon and not more than 3 ppm sulfur is used as a current collector of a secondary battery, which is furnished with a negative electrode and positive electrode of such a structure that an electrode constituting substance layer is formed on the surface of current collector in plane form, wherein at least one of the plane current collectors of the positive and negative electrodes consists of the electrolytic copper foil.

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報**（Ａ）　(11)特許出願公開番号
特開2000－182623
（P2000－182623A）
(43)公開日　平成12年６月30日(2000.6.30)

(51)Int.Cl.⁷	識別記号	ＦＩ		テーマコード*（参考）
Ｈ０１Ｍ　4/64		Ｈ０１Ｍ　4/64	Ａ	５Ｈ０１７
Ｃ２５Ｄ　1/04	３１１	Ｃ２５Ｄ　1/04	３１１	５Ｈ０２８
Ｈ０１Ｍ　10/28		Ｈ０１Ｍ　10/28	Ｚ	５Ｈ０２９
10/40		10/40	Ｚ	

審査請求　未請求　請求項の数５　ＯＬ　（全　６　頁）

(21)出願番号　特願平10－353213

(22)出願日　平成10年12月11日(1998.12.11)

(71)出願人　000232014
日本電解株式会社
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(72)発明者　野口　英男
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(74)代理人　100086494
弁理士　穂高　哲夫

最終頁に続く

(54)【発明の名称】　電解銅箔、二次電池の集電体用銅箔及び二次電池

(57)【要約】
【課題】　二次電池用の集電体として好適に用いられる常温及び加熱後の引張り強さに優れ、かつ常温及び加熱後の伸び率に優れた電解銅箔、二次電池の集電体として用いた場合、過充電試験特性に優れた二次電池が得られる二次電池の集電体用銅箔及び過充電試験特性に優れた二次電池を提供する。
【解決手段】　銅箔中の炭素含有量が５ｐｐｍ以下であり、かつ硫黄含有量が３ｐｐｍ以下である電解銅箔、この電解銅箔からなる二次電池の集電体用銅箔及び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が上記の電解銅箔である二次電池。

【特許請求の範囲】
【請求項１】　銅箔中の炭素含有量が５ｐｐｍ以下であり、かつ硫黄含有量が３ｐｐｍ以下であることを特徴とする電解銅箔。
【請求項２】　銅箔中の酸素含有量が５ｐｐｍ以下であり、かつ窒素含有量が０．５ｐｐｍ以下である請求項１記載の電解銅箔。
【請求項３】　銅箔中の炭素、硫黄、酸素、窒素及び水素の合計含有量が１５ｐｐｍ以下である請求項１又は２記載の電解銅箔。
【請求項４】　請求項１、２又は３記載の電解銅箔からなることを特徴とする二次電池の集電体用銅箔。
【請求項５】　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が請求項１、２又は３記載の電解銅箔であることを特徴とする二次電池。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は引張り強さ、伸び率に優れた電解銅箔、この銅箔からなる二次電池の集電体用銅箔及びこの銅箔を用いた二次電池に関する。
【０００２】
【従来の技術】近年、携帯電子機器の進展は著しく、例えば、電話、ノート型パソコン、カメラ一体型ＶＴＲ、電子スチルカメラなどが普及し、その電源として、ニッケル・カドミウム電池、ニッケル・水素電池、リチウムイオン電池などの二次電池が広く使用されるようになってきた。
【０００３】とりわけ、リチウムイオン電池は、エネルギー密度、作動電圧が大きく、充放電を伴うサイクル寿命特性に優れていることが注目されている。このリチウムイオン電池の構造は、一般に、正極集電体、例えば２０μｍ程度の厚さを持つアルミニウム箔の両面に、正極活物質、例えば、$LiCoO_2$の粉末をバインダーと非水溶媒で混練し、ペースト状にしたものを塗布し、乾燥、圧着一体化させた正極と、負極集電体、例えば１０μｍ程度の厚さを持つ銅箔を使用して、負極活物質、例えば炭素粉末を正極と同様にバインダーと非水溶媒で混練してペースト状にしたものを塗布し、乾燥、圧着一体化させた負極とからなり、この正極と負極との両極の間に絶縁性を有する多孔質セパレータを介して、順次重ね合わせ、円筒形に巻き上げられている。更にこの両極が円筒缶に収納され、非水電解液が注入され、スイッチ素子、安全弁、端子などの部材を設けて二次電池として組み立てられている。
【０００４】前記するように負極集電体には、導電性に優れる金属箔、例えば、銅箔が多用されている。銅箔には製法の異なる圧延銅箔、電解銅箔が知られている。電解銅箔は、圧延銅箔に比べて量産性に優れ、比較的製造コストも安価である利点から、圧延銅箔と同様に二次電池の負極集電体材料として使用されるようになってきた。
【０００５】電解銅箔は、一般に、硫酸－硫酸銅水溶液を電解液として用い、一定速度で回転する円筒型陰極と、これと対向配置させて設けた陽極との間に前記電解液を供給し、通電しながら回転する陰極面に銅を析出させ、所定厚みとなった銅箔を陰極面上から剥がしとり製造される。
【０００６】この電解銅箔の機械的、物理的特性は、当然のことながら、電解液の組成、必要に応じて加えられる各種の薬剤（添加剤）、また、電流密度、電解液供給量などの電解条件に依存し、添加剤を適量添加することにより、引張り強さ、伸び率が制御できることは知られている。
【０００７】ところで、二次電池に強く要請される特性の一つとして、安全性の点から過充電が行われる際、集電体（銅箔）が経時的に劣化し、亀裂を生じたりあるいは破断するなどの不具合が生じないことが必要である。しかしながら、従来の電解銅箔では、過充電後の集電体（銅箔）の破断状態を表す過充電試験特性を十分に満足させることはできなかった。
【０００８】
【発明が解決しようとする課題】本発明の目的は、二次電池用の集電体として好適に用いられる常温及び加熱後の引張り強さに優れ、かつ常温及び加熱後の伸び率に優れた電解銅箔を提供することにある。
【０００９】本発明の他の目的は、二次電池の集電体として用いた場合、過充電試験特性に優れた二次電池が得られる二次電池の集電体用銅箔を提供することにある。
【００１０】本発明の他の目的は、過充電試験特性に優れた二次電池を提供することにある。
【００１１】
【課題を解決するための手段】すなわち、本発明は、銅箔中の炭素含有量が５ｐｐｍ以下であり、かつ硫黄含有量が３ｐｐｍ以下であることを特徴とする電解銅箔に関する。
【００１２】本発明はまた、上記の電解銅箔からなることを特徴とする二次電池の集電体用銅箔に関する。
【００１３】本発明はまた、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が上記の電解銅箔であることを特徴とする二次電池に関する。
【００１４】
【発明の実施の形態】本発明の電解銅箔は、銅箔中の炭素含有量が５ｐｐｍ以下であり、かつ硫黄含有量が３ｐｐｍ以下であることを特徴とする。このように銅箔中の炭素含有量及び硫黄含有量を制御することにより、常温及び加熱後の引張り強さに優れ、かつ常温及び加熱後の

伸び率に優れた電解銅箔が得られる。銅箔中の炭素含有量が５ｐｐｍを超えると加熱後における伸び率が低下する。また、硫黄含有量が３ｐｐｍを超えると加熱後の伸び率が低下する。炭素含有量の好ましい範囲は０．１～４ｐｐｍであり、硫黄含有量の好ましい範囲は０．１～２ｐｐｍである。

【００１５】さらに、本発明の電解銅箔は、銅箔中の酸素含有量が５ｐｐｍ以下であり、かつ窒素含有量が０．５ｐｐｍ以下であることが好ましい。銅箔中の酸素含有量が５ｐｐｍを超えると加熱後の伸び率が低下する傾向にあり、窒素含有量が０．５ｐｐｍを超えると加熱後の伸び率が低下する傾向がある。酸素含有量のより好ましい範囲は０．１～４ｐｐｍであり、窒素含有量のより好ましい範囲は０．１～０．４ｐｐｍである。

【００１６】さらに、本発明の電解銅箔は、銅箔中の炭素、硫黄、酸素、窒素及び水素の合計含有量が１５ｐｐｍ以下であることが好ましい。この不純物の合計量が１５ｐｐｍを超えると常温における引張り強さ及び加熱後の伸び率が低下する傾向がある。炭素、硫黄、酸素、窒素及び水素の合計含有量は１０ｐｐｍ以下であることが更に好ましい。

【００１７】本発明において、炭素、硫黄、酸素、窒素及び水素の測定は元素分析装置により行われる。炭素及び硫黄の含有量の測定は、堀場製作所製ＥＭＩＡ－８２０により行なうことができ、酸素及び窒素の含有量の測定は、堀場製作所製ＥＭＧＡ－６２０により行なうことができ、水素の含有量の測定は、堀場製作所製ＥＭＧＡ－５２１により行なうことができる。

【００１８】上記のように不純物含有量が制御された本発明の銅箔は、例えば、電解銅箔製造に用いられる電解液として有機系不純物を高度に除去したものを用いて電解処理することにより得られる。

【００１９】電解液中の不純物を高度に除去する方法としては、電解液製造に用いられる原料である銅線を６００～９００℃で３０～６０分間焼成して用いる方法、硫酸などを用いて銅線を洗浄する方法、高純度の銅線材、硫酸銅、硫酸を用いる方法、電解液中に通常使用される各種添加剤、例えばチオ尿素、アラビアゴム、ゼラチン、膠などを使用しない方法、使用する水として蒸留水又は純水を使用する方法など、あるいはこれらを適宜組み合わせる方法等が挙げられる。

【００２０】その他に、電解液を活性炭ろ過装置により処理したり、オゾン発生装置により液中に存在する有機物を酸化分解したりして、電解液中の不純物を除去する方法等が挙げられる。

【００２１】上記の方法により得られた不純物が高度に除去された電解液を用いて電解銅箔を製造することにより、所定の元素含有量の電解銅箔が得られる。

【００２２】本発明の電解銅箔は、銅箔中の炭素含有量及び硫黄含有量が前記範囲内にあり、常温及び加熱後の引張り強さに優れ、かつ常温及び加熱後の伸び率に優れ、二次電池の集電体として好適に用いられる。

【００２３】本発明の電解銅箔の表面には必要に応じて、粗面化処理層や、防錆のためにクロメート処理層などの防錆層が設けられていてもよい。

【００２４】本発明の二次電池は、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たものであり、本発明の電解銅箔を正極及び負極の集電体の少なくとも一方、好ましくは負極集電体として使用している。このように、本発明の電解銅箔を集電体として用いることにより、過充電試験特性に優れた二次電池が得られる。その理由は、本発明の電解銅箔は、従来の電解銅箔と比べて、加熱後の銅箔の強度を表す引き裂き伝播時間が長く、二次電池の過充電試験の箔破れが起こりにくくなるからである。

【００２５】本発明の二次電池の負極の電極構成物質としては、熱分解炭素類、コークス類、グラファイト類、金属リチウム、リチウム合金、ポリアセチレン、ポリピロールなどを使用することができる。

【００２６】本発明の二次電池の正極の電極構成物質としては、特に制限はなく、$LiNiO_2$、$LiCoO_2$、$LiMn_2O_4$等を単独、又は混合して使用することができる。

【００２７】電解液としては、$LiClO_4$、$LiPF_6$等のリチウム塩を、例えば炭酸エチレン、炭酸ジメチルなどの非水系溶剤に溶解したいわゆる有機系電解液をポリフッ化ビニリデン等の高分子固体電解質に含ませた電解液などを使用することができる。

【００２８】セパレータとしては、例えばポリエチレン、ポリプロピレン等のポリオレフィンを主成分とした不織布、クロス、微孔フィルム又はこれらを組み合わせたものを使用することができる。

【００２９】なお、円筒型リチウムイオン電池の一例の一部断面正面図を図１に示す。

【００３０】

【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。

【００３１】実施例１

（１）電解銅箔の製造

銅原料である市販の銅線を７００℃で１時間焼成し、更に１００ｇ／ｌ　硫酸水溶液を用いて２０分間酸洗処理し、銅線に付着する不純物を除去した。次いでこの焼成処理及び酸洗処理された銅線を硫酸に溶解し、硫酸銅溶液を得た。この硫酸銅溶液を活性炭を用いたろ過装置によりろ過して下記組成の電解液を得た。なお、硫酸としては精製硫酸を使用した。

硫酸銅（$CuSO_4 \cdot 5H_2O$）　２８０ｇ／ｌ

硫酸（H_2SO_4）　８０ｇ／ｌ

この電解液を用いて、貴金属酸化物被覆チタンを陽極、

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、厚さ１０μｍの電解銅箔を製造した。得られた銅箔をサンプルとして銅箔中の不純物量の測定及び下記の特性試験を行い、その結果を表１に示す。

（ａ）引張り強さ

常温（２３℃）及び１３０℃で１５時間加熱後の引張り強さをＪＩＳ　Ｃ　６５１１に基づいて測定した。

（ｂ）伸び率

常温（２３℃）及び１３０℃で１５時間加熱後の伸び率をＪＩＳ　Ｃ　６５１１に基づいて測定した。

（ｃ）引き裂き伝播時間

１３０℃で１５時間加熱後の引張り強さ試験（クロスヘッドスピード２．０ｍｍ／分、チャートスピード２００ｍｍ／分）における箔の亀裂開始から破断完了までの時間（秒）を測定した。

【００３２】（２）リチウムイオン電池の製造

図１は、円筒形リチウムイオン電池の一部断面正面図を示し、１は正極、２は負極、３はセパレータ、４は正極リード、５は負極リード、６は正極蓋、７は電池缶及び８はガスケットである。

【００３３】図１に示すリチウムイオン電池は以下のようにして作製した。正極活物質としては、$LiCoO_2$を９０重量部、導電助剤として平均粒径が１μｍの黒鉛を５重量部、及び結着剤としてポリフッ化ビニリデン（ＰＶＤＦ）を５重量部添加して、これにＮ－メチル－２－ピロリドンを５重量部加え正極用合剤ペーストを調製した。同様に負極活物質としてピッチ系炭素繊維９０重量部及び結着剤としてＰＶＤＦを１０重量部添加して、これにＮ－メチル－２－ピロリドンを１０重量部混合して負極用合剤ペーストを得た。

【００３４】次に正極用合剤ペーストを厚みが２０μｍのアルミニウム箔の両面に塗布し、１２０℃で１０分間予備乾燥し、ローラープレスによって電極を加圧成形した後１３０℃で１５時間真空乾燥し、厚みを１６０μｍとした。単位面積当たりの正極合剤（ペーストから溶剤を除いたもの）塗布量は、２５ｍｇ／ｃｍ^{2}であり、幅が５４ｍｍで長さが４３７ｍｍの大きさに切り出して正極１を作製した。但し正極１の両端の長さ１０ｍｍは、正極用合剤が塗布されておらず、アルミニウム箔が露出されており、この一方に正極リード４を、超音波接合によって圧着した。

【００３５】一方負極用合剤ペーストを、厚みが１０μｍの実施例１で得た銅箔の両面に塗布し、その後１２０℃で１０分間予備乾燥し、ローラープレスによって電極を加圧成形した後１３０℃で１５時間真空乾燥し、厚みを２００μｍとした。単位面積当たりの負極用合剤（ペーストから溶剤を除いたもの）の塗布量は、１３ｍｇ／ｃｍ^{2}であり、幅が５６ｍｍで長さが４８０ｍｍの大きさに切り出して、負極２を作製した。これを正極１と同様に、負極２の長さ１０ｍｍの部分は、負極用合剤が塗布されておらず、銅箔が露出しており、この一方に負極リード５を超音波接合により圧着した。

【００３６】セパレータ３は、厚みが２５μｍ、幅が５８ｍｍのポリエチレン製の微孔膜を用いた。次いで図１に示すように正極１、セパレータ３、負極２及びセパレータ３の順で重ね合わせ、これを捲回して電極群とした。これを電池缶に挿入して、負極リード５を缶底に溶接し、正極蓋６を加締るための絞り部を設けた。この後体積比で１：１の炭酸エチレンと炭酸ジメチルの混合溶媒に六フッ化リン酸リチウムを１モル／リットルで溶解させた電解液を電池缶７に注入した後、正極リード４を正極蓋６に溶接した後、正極蓋６をとりつけてリチウムイオン電池を得た。

【００３７】過充電試験

得られたリチウムイオン電池を用いて、直流２Ａで４０分間及び直流３Ａで３０分間の過充電後、それぞれ電池を解体し、負極銅箔の巻き終わり箇所（５ｃｍ×５ｃｍ、２５ｃｍ^2）を目視観察し銅箔破れの有無を調べその個数を測定した。その結果を表１に示す。

【００３８】実施例２

電解銅箔の製造において、硫酸銅溶液（電解液）を作製するにあたり、銅線の焼成処理を行わなかった以外は、実施例１と同様にして電解銅箔を製造した。この銅箔を用いて、実施例１と同様に銅箔中の不純物量の測定及び（ａ）引張り強さ、（ｂ）伸び率、（ｃ）引き裂き伝播時間の各特性試験を行い、その結果を表１に示した。また、この銅箔を用いて実施例１と同様にしてリチウムイオン電池を製造し、実施例１と同様に過充電試験を行いその結果を表１に示した。

【００３９】実施例３

電解銅箔の製造において、硫酸銅溶液（電解液）を作製するにあたり、銅線の酸洗処理を行わなかった以外は、実施例１と同様にして電解銅箔を製造した。この銅箔を用いて、実施例１と同様に銅箔中の不純物量の測定及び（ａ）引張り強さ、（ｂ）伸び率、（ｃ）引き裂き伝播時間の各特性試験を行い、その結果を表１に示した。また、この銅箔を用いて実施例１と同様にしてリチウムイオン電池を製造し、実施例１と同様に過充電試験を行いその結果を表１に示した。

【００４０】比較例１

電解銅箔の製造において、硫酸銅溶液（電解液）を作製するにあたり、銅線に焼成処理及び酸洗処理を行わなかったこと、及び電解液にゼラチンを０．５ｐｐｍ含有させたこと以外は、実施例１と同様にして電解銅箔を製造した。この銅箔を用いて、実施例１と同様に銅箔中の不純物量の測定及び（ａ）引張り強さ、（ｂ）伸び率、（ｃ）引き裂き伝播時間の各特性試験を行い、その結果を表１に示した。また、この銅箔を用いて実施例１と同様にしてリチウムイオン電池を製造し、実施例１と同様

に過充電試験を行いその結果を表１に示した。

【００４１】比較例２

電解銅箔の製造において、硫酸銅溶液（電解液）を作製するにあたり、電解液にゼラチンを３ｐｐｍ、塩素イオンを２０ｐｐｍ含有させたこと以外は、実施例１と同様にして電解銅箔を製造した。この銅箔を用いて、実施例１と同様に銅箔中の不純物量の測定及び（ａ）引張り強さ、（ｂ）伸び率、（ｃ）引き裂き伝播時間の各特性試験を行い、その結果を表１に示した。また、この銅箔を用いて実施例１と同様にしてリチウムイオン電池を製造し、実施例１と同様に過充電試験を行いその結果を表１に示した。

【００４２】比較例３

電解銅箔の製造において、硫酸銅溶液（電解液）を作製するにあたり、電解液にゼラチンを１０ｐｐｍ含有させたこと以外は、実施例１と同様にして電解銅箔を製造した。この銅箔を用いて、実施例１と同様に銅箔中の不純物量の測定及び（ａ）引張り強さ、（ｂ）伸び率、（ｃ）引き裂き伝播時間の各特性試験を行い、その結果を表１に示した。また、この銅箔を用いて実施例１と同様にしてリチウムイオン電池を製造し、実施例１と同様に過充電試験を行いその結果を表１に示した。

【００４３】比較例４

市販の厚さ１０μｍの圧延銅箔［Ｃ１１００（ＪＩＳ Ｈ ３１１０、タフピッチ銅）、Ｃｕ９９．９０％以上］を用いて実施例１と同様にしてリチウムイオン電池を製造し、実施例１と同様に評価試験を行いその結果を表１に示した。

【００４４】

【表１】

	銅箔中不純物含有量 (ppm)					
	C	S	O	N	H	合計
実施例1	1.9	1.8	3.5	0.4	0.5	8.1
実施例2	2.8	1.8	3.6	0.5	0.5	9.2
実施例3	3.8	1.8	3.5	0.4	0.5	10.0
比較例1	7.9	2.2	4.2	0.9	0.6	15.8
比較例2	9.3	2.3	10.6	1.5	0.9	24.6
比較例3	46.4	15.0	88.5	19.0	9.0	177.9
比較例4	−	-	−	−	−	−

	引張り強さ (kgf/mm^2)		伸び率 (%)		引き裂き伝播時間 (秒)	過充電試験箔破れ数 (個)	
	常温	加熱後	常温	加熱後	加熱後	2.0A	3.0A
実施例1	57.1	23.2	7.0	26.6	9.0	0	0
実施例2	57.8	24.0	6.8	25.6	8.2	0	0
実施例3	59.2	24.1	6.8	25.1	8.0	2	3
比較例1	36.7	32.0	12.0	15.8	0.2	15	18
比較例2	37.8	37.0	8.7	8.5	0.2	52	53
比較例3	56.1	53.2	5.2	3.9	0.1	49	52
比較例4	42.0	15.9	1.4	12.8	7.8	3	6

実施例１～３において、本発明の電解銅箔は銅箔中の不純物の合計量が１５ｐｐｍ以下に低減されているので、銅箔特性の引張り強さ、伸び率を同時に高めている。特に常温引張り強さが５５ｋｇｆ／ｍｍ^{2}以上、加熱後伸び率が２５％以上を保持している。また、引き裂き伝播時間が長く、かつ電池の過充電試験において破断防止に優れている。

【００４５】一方、比較例１～３においては、銅箔中の不純物の合計量が１５ｐｐｍを超えていることから常温及び加熱後における引張り強さ、伸び率を本発明のよう

に高められず、二次電池としての過充電試験から明らかなように、信頼性を欠くものである。また、比較例４（圧延銅箔）では、特に加熱後の引張り強さ及び常温伸び率が本発明の銅箔に比べて低い傾向を示し、過充電試験の評価では本発明の銅箔を使用したものより若干劣っていることが判った。

【００４６】

【発明の効果】本発明の電解銅箔は、常温及び加熱後の引張り強さに優れ、かつ常温及び加熱後の伸び率に優れ、二次電池用の集電体銅箔として好適に用いられる。

【００４７】また、本発明の二次電池用の集電体銅箔を用いると、過充電試験特性に優れた二次電池を得ることができる。

【００４８】また、本発明の二次電池は、過充電試験特性特性に優れたものである。

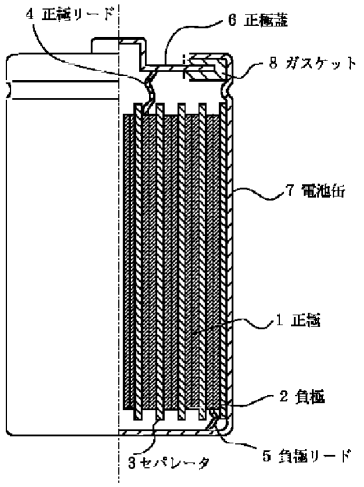
【図面の簡単な説明】

【図１】円筒形リチウムイオン電池の一部断面正面図である。

【符号の説明】

１　正極
２　負極
３　セパレータ
４　正極リード
５　負極リード
６　正極蓋
７　電池缶
８　ガスケット

【図１】



フロントページの続き

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(54)ELECTROLYTIC COPPER FOIL WITH CARRIER FOIL AND COPPER-CLAD LAMINATE USING THE ELECTROLYTIC COPPER FOIL WITH CARRIER FOIL

(57)Abstract

PROBLEM TO BE SOLVED: To stabilize the peel strength of the carrier foil of the electrolytic copper foil with carrier foil using an organic agent in a joining-interface layer at a lower level and to facilitate the peeling of the carrier foil.

SOLUTION: This electrolytic copper foil with carrier foil is obtained by forming an organic joining-interface layer on the surface of a carrier foil layer and forming an electrolytic copper foil layer on the joining-interface layer. In this case, the difference between the thermal expansion coefficient of the material constituting the carrier foil layer and that of the of the material constituting the electrolytic copper foil layer is controlled to ≥4×10-7 /deg.

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最終頁に続く

(54)【発明の名称】　キャリア箔付電解銅箔及びそのキャリア箔付電解銅箔を用いた銅張積層板

(57)【要約】
【課題】　接合界面層に有機剤を用いたキャリア箔付電解銅箔の、キャリア箔の引き剥がし強度を、より低位で安定させ、キャリア箔の引き剥がし作業を容易化させる。
【解決手段】　キャリア箔層の表面に有機接合界面層を形成し、その有機接合界面層上に電解銅箔層を形成したキャリア箔付電解銅箔において、キャリア箔層を構成する素材の熱膨張率と電解銅箔層を構成する素材の熱膨張率との差が４×１０$^{-7}$／ｄｅｇ．以上であることを特徴とするキャリア箔付電解銅箔とする。

【特許請求の範囲】
【請求項１】　キャリア箔層の表面に有機接合界面層を形成し、その有機接合界面層上に電解銅箔層を形成したキャリア箔付電解銅箔において、
キャリア箔層を構成する素材の熱膨張率と電解銅箔層を構成する素材の熱膨張率との差が４×１０－７／ｄｅｇ．以上であることを特徴とするキャリア箔付電解銅箔。
【請求項２】　キャリア箔層を構成する素材は、ＩＰＣ規格のグレード１～３に分類される電解銅箔であり、電解銅箔層を構成する素材は、ＩＰＣ規格のベリーロープロファイル（Ｖタイプ）に分類される電解銅箔である請求項１に記載のキャリア箔付電解銅箔。
【請求項３】　請求項１又は請求項２に記載のキャリア箔付電解銅箔を用いた銅張積層板。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、主にプリント配線板等に用いるキャリア箔付電解銅箔に関する。
【０００２】
【従来の技術】従来より、キャリア箔付電解銅箔は、広く電気、電子産業の分野で用いられるプリント配線板製造の基礎材料として用いられてきた。一般に、電解銅箔はガラス－エポキシ基材、フェノール基材、ポリイミド等の高分子絶縁基材と熱間プレス成形にて張り合わされ銅張積層板とし、高密度プリント配線板製造に用いられてきた。
【０００３】この熱間成形プレスは、銅箔、Ｂステージに硬化させたプリプレグ（基材）、その他スペーサーとなる鏡板とを多段に積層し、高温雰囲気下で高圧をかけ、銅箔とプリプレグとを熱圧着するものである（以下、この工程を「プレス成形」と称する場合がある。）。このとき銅箔に皺が存在すると、皺部において銅箔にクラックが生じ、プリプレグの樹脂が染み出したり、後のエッチング工程であるプリント配線板製造工程にて形成回路の断線を起こす原因となることもある。キャリア箔付電解銅箔は、キャリア箔を用いることで電解銅箔側への皺の発生を防止できるのである。
【０００４】キャリア箔付電解銅箔は、一般にピーラブルタイプとエッチャブルタイプに大別することが可能である。違いを一言で言えば、ピーラブルタイプはプレス成形後にキャリア箔を引き剥がして除去するタイプのものであり、エッチャブルタイプとは、プレス成形後にキャリア箔をエッチング法にて除去するタイプのものである。本明細書は、ピーラブルタイプのキャリア箔付電解銅箔について記載している。
【０００５】従来のピーラブルタイプは、プレス成形後、そのキャリア箔の引き剥がし強度の値が極めて不安定であり、一般的に５０～３００ｇｆ／ｃｍの範囲が良好な範囲とされてきた。一方で、極端な場合には、キャリア箔が引き剥がせないという事態も生じ、目的の引き剥がし強度が得られにくいと言う欠点を有していた。この欠点は、キャリア箔付電解銅箔が広く一般用途に普及する際の最大の障害となっていた。
【０００６】キャリア箔の引き剥がし強度が不安定になる原因は、次のように考えられてきた。従来のキャリア箔付電解銅箔は、ピーラブルタイプとエッチャブルタイプとの別に関わらず、キャリア箔と電解銅箔との間に、亜鉛に代表される金属系の接合界面層を形成したものである。ピーラブルタイプとするか、エッチャブルタイプとするかの作り分けは、キャリア箔の種類により僅かな差違はあるが、接合界面層に存在させる金属量を制御することで行われてきた。
【０００７】金属系の接合界面層の形成は、所定の金属元素を含む溶液を電気分解して電析で行うものが主であり、電気化学的手法が採用されてきた。ところが、電気化学的手法は、極めて微量な析出量制御が困難で、他の技術的手法に比べ再現性の点では劣るものである。しかも、ピーラブルタイプとなるかエッチャブルタイプとなるかの必要析出量の境界は、即ち接合界面層に存在する金属量の僅かな相違でしかないため、安定した性能を引き出すことは困難なものと考えられる。
【０００８】更に、キャリア箔を引き剥がすのは、一般に１８０℃以上の温度で、高圧をかけ、しかも１～３時間のプレスの終了後であるため、接合界面層はキャリア箔や電解銅箔と相互拡散を起こすことが考えられる。このことは、むしろ接合強度を高める方向に作用するものであり、引き剥がし強度が不安定になる一因と考えられる。
【０００９】これらの問題点を解決するため、本件発明者等は、キャリア箔層と電解銅箔層との接合界面層にＣＢＴＡ等の有機系剤を用いた有機接合界面を相互拡散バリアとして備えたキャリア箔付電解銅箔及びその製造方法の提唱を行ってきた。
【００１０】
【発明が解決しようとする課題】しかしながら、本件発明者等の提唱してきた接合界面層に有機系剤を用いたキャリア箔付電解銅箔は、キャリア箔が引き剥がせないという不良の発生は完全に解消することが可能となり、３ｇｆ／ｃｍ～２００ｇｆ／ｃｍの範囲での引き剥がしが可能となってきたものの、キャリア箔付電解銅箔を用いて銅張積層板を製造した後に、更に、キャリア箔が安定して容易に引き剥がせ、そのキャリア箔の引き剥がし強度にバラツキのない銅箔に対する要求が強まってきた。
【００１１】一方で、キャリア箔付電解銅箔のメリットは、キャリア箔と電解銅箔とがあたかもラミネートされ、貼り合わされたような状態である点にある。即ち、キャリア箔と電解銅箔とが貼り合わされたような状態を、キャリア箔付電解銅箔とプリプレグ（基材）と熱間プレス成形を経て銅張積層板を製造し、少なくともプリ

ント回路を形成するエッチング工程の直前まで維持することで、電解銅箔表面への異物混入及び電解銅箔層の損傷を防止できる点にある。

【００１２】従って、銅張積層板を製造する熱間プレス成形以前の段階で、キャリア箔付電解銅箔のハンドリング時にキャリア箔と電解銅箔とが剥離することは、容認できることではない。そして、当該熱間プレス成形後も、単に容易に引き剥がせるというだけでなく、確実にエッチング工程にはいる前段階まで、キャリア箔が張り付いた状態を維持し、銅張積層板の銅箔表面をコンタミネーション、異物付着等から保護しなければならないのである。

【００１３】

【課題を解決するための手段】そこで、本件発明者等は、鋭意研究の結果、上述のような市場の要求に応えるためには、確実にエッチング工程にはいる前段階まで、キャリア箔が張り付いた状態を維持し、キャリア箔と電解銅箔との剥離強度を可能な限り低くすることを考えれば３ｇｆ／ｃｍ～１００ｇｆ／ｃｍの範囲の引き剥がし強度に制御すべきとの判断を行った。

【００１４】その結果、キャリア箔と電解銅箔との接合界面層に用いる有機系剤の種類、当該接合界面層の形成方法等の接合界面形成技術の改良を行うのとは異なる見地より、キャリア箔付電解銅箔を構成する主要素材であるキャリア箔と電解銅箔との素材物性の組み合わせに着目して課題を解決することとしたのである。特に、素材物性の中でも、キャリア箔付電解銅箔が用いられる銅張積層板の製造過程が熱間プレス成形を採用するため一定の熱応力が加わることになる。そこで、熱膨張率に着目して、以下に説明する本件発明を完成させるに至ったのである。

【００１５】請求項１には、キャリア箔層の表面に有機接合界面層を形成し、その有機接合界面層上に電解銅箔層を形成したキャリア箔付電解銅箔において、キャリア箔層を構成する素材の熱膨張率と電解銅箔層を構成する素材の熱膨張率との差が４×１０⁻７／ｄｅｇ．以上であることを特徴とするキャリア箔付電解銅箔としている。

【００１６】請求項１に記載の発明は、本件発明者等が研究を重ねた結果、キャリア箔層を構成する素材の熱膨張率と電解銅箔層を構成する素材の熱膨張率との差が４×１０⁻７／ｄｅｇ．以上であると、銅張積層板の製造に用いたピーラブルタイプのキャリア箔付電解銅箔のキャリア箔が、極めて容易に引き剥がせることを見いだした。即ち、キャリア箔層と電解銅箔層との受けた熱履歴の中での熱膨張挙動が同じであれば、有機接合界面を介して、キャリア箔層と電解銅箔層との結合状態も弾性限の範囲内で保持され、有機接合界面層での剥離を助長するものとはならない。しかしながら、ここに述べた「キャリア箔層を構成する素材の熱膨張率と電解銅箔層を構成する素材の熱膨張率との差が４×１０⁻７／ｄｅｇ．以上」となると、一般的に考えられる銅張積層板製造プロセスにおける熱履歴によって、キャリア箔層と電解銅箔層との有機接合界面を介してズレを起こそうとする熱応力が働くことになり、より容易に剥離可能な状態に導くことが出来るのである。ここに述べた当該構成素材の熱膨張率との差が４×１０⁻７／ｄｅｇ．以上となると、本件発明の達成しようとする３～１００ｇｆ／ｃｍの範囲の引き剥がし強度に制御できるのである。このときの熱膨張率の差とは、電解銅箔層から見て、キャリア箔層が膨張する場合でも、収縮する場合であっても、４×１０⁻７／ｄｅｇ．以上であればよいと判断できるものである。

【００１７】ここで、「４×１０⁻７／ｄｅｇ．以上」という表現を用いているが、上限の範囲を不明確なままにした記載ではない。キャリア箔層を構成する素材及び負荷される温度が決まれば、その熱膨張率と電解銅箔層を構成する素材との熱膨張率との差として、必然的に一定の上限値が定まるからである。

【００１８】また、本請求項においては、キャリア箔層の表面に有機接合界面層を形成し、その有機接合界面層上に電解銅箔層を形成したキャリア箔付電解銅箔を対象としている。従って、キャリア箔層と電解銅箔層との間に存在する有機剤は、キャリア箔層及び電解銅箔層と相互に結合する形状をなし、有機接合界面層は接着層としての役割をも有している。このため、キャリア箔層と電解銅箔層との間に有機接合界面層が存在するため、当該キャリア箔付電解銅箔が銅張積層板の製造過程で一定の熱衝撃を受けても、有機接合界面層に適正な有機剤を用いれば、キャリア箔層と電解銅箔層との熱膨張率の違いによる剥離挙動を緩和する方向に働くため、キャリア箔層と電解銅箔層との自然剥離に到ることは防止できるものと考えられる。

【００１９】ここで言うキャリア箔付電解銅箔は、図１に示したような模式断面を持つものである。即ち、キャリア箔層（以下、単に「キャリア箔」と称する場合がある。）と電解銅箔層（以下、単に「電解銅箔」と称する場合がある。）とは、有機接合界面を介して、あたかもラミネートされたが如き形態となっている。一般にＦＲ－４基板を例に取れば、キャリア箔付電解銅箔と絶縁層を構成するプリプレグ若しくは内層プリント配線板とを積層し、１８０℃前後の雰囲気中でプレス成形することで銅張積層板を製造する目的として用いられるのである。

【００２０】そして、本発明におけるキャリア箔には、有機系の素材若しくは無機系の金属素材等を用いることが可能であり、電解銅箔との組み合わせにより、熱膨張率の差が４×１０⁻７／ｄｅｇ．以上であればよいのである。ところが、キャリア箔のリサイクリングの容易性、製造安定性を考慮すれば、請求項２に記載したよう

に電解銅箔を主に用いるものとすることが有利である。係る場合、本件発明に係るキャリア箔付電解銅箔の電解銅箔とキャリア箔とは、同じ電解銅箔ではあるけれど、その物性、特に熱膨張率が異なる種類のものを組み合わせて用いなければならない。

【００２１】そこで、以下の説明の理解をより容易にするために、電解銅箔の種類について、説明することとする。電解銅箔の分類に関しては、国際的に通用する種々の規格の中にそれぞれ別個に存在するが、ここでは最も広く一般的に用いられるＩＰＣ（The Institute for Interconnecting and Packaging Electronic Circuits）規格に基づいた分類として説明するものとする。

【００２２】ＩＰＣ規格によれば、電解銅箔は、その伸び率、引張り強さ等の基本物性的観点より、グレード１～グレード３のいずれかに分類される。グレード１を通常銅箔、グレード２をハイダクタイル箔として分類しているが、今日において、当業者間ではグレード１及び２に属する電解銅箔を一般に通常電解銅箔と称する（以下、ここで示した意味合いにおいて「通常電解銅箔」と称する。）。そして、グレード３に属する電解銅箔を一般にＨＴＥ箔と称する。このＨＴＥ箔は、１８０℃雰囲気中で３％以上の熱間伸び率を有する銅箔の総称として用いられるもので、グレード１及び２に属する通常電解銅箔では熱間伸び率が２％に満たない点で大きな差異を有するものである。

【００２３】更に、今日のプリント配線板関連業界においては、グレード３に分類される銅箔であっても、熱間伸びが３％～１８％程度の電解銅箔（以下、単に「ＨＴＥ箔」と称する。）と、熱間伸びが１８～５０％程度の電解銅箔（以上及び以下において、この銅箔を「Ｓ－ＨＴＥ箔」と称する。）とを明確に区別して、用途に応じて使い分けを行っているのが現実である。

【００２４】ここで言うＨＴＥ箔とＳ－ＨＴＥ箔との根本的な違いは、双方とも９９．９９％前後の純度を持つ電解析出銅にて構成されているものであるが、その析出結晶の持つ性格が異なるのである。銅張積層板の製造プロセスにおいては、銅箔を基材と張り付ける熱間プレス成型時に、電解銅箔に対して少なくとも１８０℃×６０分程度の加熱がなされる。この加熱後の結晶組織を光学顕微鏡で観察すると、ＨＴＥ箔に再結晶化は見られないが、Ｓ－ＨＴＥ箔には再結晶化が起きていることが認められる。

【００２５】これは銅箔の物性をコントロールするため、電解条件である溶液組成、溶液濃度、溶液の沪過処理方法、溶液温度、添加剤、電流密度等の条件を変更して製造が行われ、その析出結晶の結晶学的性質が異なるためと考えられる。特に、再結晶化が容易に起こりやすい銅箔であるほど、他の銅箔に比べ、その結晶内部には高密度に転移が内蔵され、しかも、その転移は強固に固着しておらず、僅かの熱量で素早く転移の再配列がおこり、より再結晶化が起こりやすくなっているものと考えられる。

【００２６】また、ＩＰＣ規格の中には、銅張積層板とする際の基材と接着する銅箔表面のプロファイルの持つ粗さにより分類を行っている。その分類は、ＩＰＣ規格に定めるＩＰＣ－ＴＭ－６５０に定めた試験方法でものであって、特に粗さを規定しない通常プロファイル箔（Ｓタイプ）、最大粗さが１０．２μm以下を保証することの出来るロープロファイル箔（Ｌタイプ箔）、最大粗さが５．１μm以下を保証することの出来るベリーロープロファイル箔（Ｖタイプ）の３種類である。

【００２７】この内、Ｓタイプ及びＬタイプはともかくとして、Ｖタイプに属する銅箔を電解法で得ようとすると、電解溶液の不純物の低減、電解条件等に特殊な工夫を行い、一般に光学顕微鏡で観察される柱状の析出組織に比べ、析出結晶のグレインサイズが極めて細かく、数百倍程度の光学顕微鏡倍率では捉えることの出来ないものとしなければならない。従って、ここで言うＶタイプの電解銅箔は、極めて細かな結晶粒を有するため、結晶粒の微細化による効果として引張り強さ、硬度が高いものであり、他の銅箔とは明らかに異なる結晶組織を有しているのである。

【００２８】上述のような結晶構造の持つ性質の差異により、銅箔の持つ物性もそれぞれに異なり、熱膨張率も、上述した銅箔の種類により微妙に異なってくる。そのため、キャリア箔付電解銅箔のキャリア箔として物性、特に熱膨張率を考慮して適正な電解銅箔を用いれば、キャリア箔付電解銅箔の電解銅箔層を構成する電解銅箔とは異なる熱膨張率を持つものとすることが出来るのである。

【００２９】請求項２に記載したキャリア箔層を構成する素材であって、ＩＰＣ規格のグレード１～３に分類される電解銅箔とは、上述の通常電解銅箔、ＨＴＥ箔、Ｓ－ＨＴＥ箔とを意味するものである。そして、電解銅箔層を構成する素材は、ＩＰＣ規格のベリーロープロファイル（Ｖタイプ）に分類される極めて微細な結晶粒を有する電解銅箔である。表１には、これらの銅箔の熱膨張率を測定して得られた熱膨張係数（α）の実測値を示すものとする。そして、表２には、表１に示した電解銅箔層とキャリア箔層との熱膨張係数（α）の差の絶対値をまとめて表示している。この測定には、理学電機株式会社の熱機械分析装置であるＴＭＡ標準型ＣＮ８０９８Ｆ１を用いた。

【００３０】

【表１】

測定温度		熱膨張係数（α） X10⁻⁵			
		電解銅箔層	キャリア箔層		
	℃	Vタイプ	HTE	S-HTE	通常銅箔
昇温	50	1.355	0.969	1.395	1.453
	100	1.491	1.137	1.527	1.689
	150	1.601	1.411	1.649	1.860
	200	1.594	1.734	1.654	1.939
降温	150	1.649	1.757	1.595	2.264
	100	1.523	1.820	1.481	2.261
	50	1.515	2.240	1.477	4.637

【００３１】

【表２】

測定温度		熱膨張係数（α）の差 X10⁻⁵		
		(電解銅箔層の値) - (キャリア箔の値) の絶対値		
	℃	(Vタイプ) - (HTE)	(Vタイプ) - (S-HTE)	(Vタイプ) - (通常銅箔)
昇温	50	0.386	0.040	0.098
	100	0.354	0.036	0.198
	150	0.190	0.048	0.259
	200	0.140	0.060	0.345
降温	150	0.108	0.054	0.615
	100	0.297	0.042	0.738
	50	0.725	0.038	3.122

【００３２】この表２に示したように、（電解銅箔層の値）－（キャリア箔の値）の熱膨張係数の絶対値が求められる。そして、キャリア箔にＳ－ＨＴＥ箔を用いた場合の熱膨張係数の差の絶対値の平均は、昇温過程で０．０４６×１０⁻⁵／ｄｅｇ．、降温過程で０．０４９×１０⁻⁵／ｄｅｇ．である。キャリア箔にＨＴＥ箔を用いた場合の熱膨張係数の差の絶対値の平均は、昇温過程で０．２６８×１０⁻⁵／ｄｅｇ．、降温過程で０．３１８×１０⁻⁵／ｄｅｇ．である。キャリア箔にグレード１に相当する通常電解銅箔を用いた場合の熱膨張係数の差の絶対値の平均は、昇温過程で０．２２５×１０⁻⁵／ｄｅｇ．、降温過程で１．２０５×１０⁻⁵／ｄｅｇ．である。

【００３３】銅張積層板の熱間成形プレス過程においてキャリア箔層と電解銅箔層とが受ける熱履歴の中で、両者の熱膨張挙動が同じであれば、有機接合界面を介してキャリア箔層と電解銅箔層との結合状態も段制限の範囲内に保持され、有機接合界面層での剥離を助長するものとはならない。即ち、熱間成形プレス過程において、熱膨張率の差が大きな程、熱膨張による剥離挙動が起こりやすく、熱膨張係数の差が小さいほど剥離しにくくなるものと言える。よって、熱膨張率の値と該剥離強度との関係を論ずる場合には、前温度域でのデータを比較し、熱膨張率の差が４×１０⁻⁷／ｄｅｇ．を満足させる必要がある。ところが、表２から明らかなように降温過程と昇温過程とを比較すると、昇温過程での熱膨張率の差が小さくなっている。よって、昇温過程で条件を満たせば、降温過程においても満たしていると判断される。

【００３４】以上の３種のキャリア箔を用いた場合の実証テストにおいて、キャリア箔として、より容易に引き剥がせるのは、ＨＴＥ箔及び通常電解銅箔をキャリア箔に用いた場合と言える。これは、表２に示した結果から考えられるように電解銅箔層を構成するＶタイプの銅箔との熱膨張係数の差がＳ－ＨＴＥ箔に比べ大きくなるためといえる。これは、Ｓ－ＨＴＥ箔は１８０℃前後の温度で再結晶化するため、加熱状態において、ＨＴＥ箔に比べ、電解銅箔層の熱膨張挙動に追随しやすくなり、有機接合界面層における剥離挙動が起こりにくくなるためと考えられる。従って、熱膨張係数の差が大きな程、熱膨張による剥離挙動が起こりやすくなるものと言える。

【００３５】ここでは、本件発明者等が行った研究の中で見いだすことの出来た代表的な値を示しており、ここに掲げた材質で構成したキャリア箔付電解銅箔は、本件発明の目的とするところのキャリア箔と電解銅箔との剥離強度を、銅張積層板に熱間プレス加工後に３ｇｆ／ｃｍ～１００ｇｆ／ｃｍの範囲とすることが出来るのである。更に、本件発明者は研究を重ねデータを蓄積した結果、昇温過程における電解銅箔層とキャリア箔層との熱膨張係数の差の平均が０．０４×１０⁻⁵／ｄｅｇ．以上あれば、キャリア箔の目的の引き剥がし強度が得られ

ることが明らかになってきた。

【００３６】そこで、キャリア箔に電解銅箔を用いる場合には、請求項２に記載したようにキャリア箔にグレード１～３箔を用い、電解銅箔層をＶタイプのものとすることで電解銅箔層とキャリア箔層との熱膨張係数の差が０．０４×１０$^{-5}$／ｄｅｇ．以上という条件をクリアして、キャリア箔が銅張積層板を得るための熱間プレス加工後に３ｇｆ／ｃｍ～１００ｇｆ／ｃｍの範囲の力で引き剥がせるのである。

【００３７】そして、ここで有機接合界面の形成に用いる有機剤は、窒素含有有機化合物、硫黄含有有機化合物及びカルボン酸の中から選択される１種又は２種以上からなるものを用いることが好ましい。以下に具体的に述べる有機剤は、本件発明の目的を達成し、現段階において、銅張積層板に加工して以降の、プリント配線板の製造工程として存在する、種々のレジスト塗布、エッチング工程、種々のメッキ処理、表面実装等の工程において悪影響のないことが確認できたものである。

【００３８】窒素含有有機化合物、硫黄含有有機化合物及びカルボン酸のうち、窒素含有有機化合物には、置換基を有する窒素含有有機化合物を含んでいる。具体的には、窒素含有有機化合物としては、置換基を有するトリアゾール化合物である１，２，３－ベンゾトリアゾール（以下、「ＢＴＡ」と称する。）、カルボキシベンゾトリアゾール（以下、「ＣＢＴＡ」と称する。）、Ｎ’，Ｎ’－ビス（ベンゾトリアゾリルメチル）ユリア（以下、「ＢＴＤ－Ｕ」と称する。）、１Ｈ－１，２，４－トリアゾール（以下、「ＴＡ」と称する。）及び３－アミノ－１Ｈ－１，２，４－トリアゾール（以下、「ＡＴＡ」と称する。）等を用いることが好ましい。

【００３９】硫黄含有有機化合物には、メルカプトベンゾチアゾール（以下、「ＭＢＴ」と称する。）、チオシアヌル酸（以下、「ＴＣＡ」と称する。）及び２－ベンズイミダゾールチオール（以下、「ＢＩＴ」と称する）等を用いることが好ましい。

【００４０】カルボン酸は、特にモノカルボン酸を用いることが好ましく、中でもオレイン酸、リノール酸及びリノレイン酸等を用いることが好ましい。

【００４１】以上及び以下において、電解銅箔（電解銅箔層）とは、図２に示す断面からみると、一般にプリント配線板とした際の導電性を確保するためバルク銅層と絶縁基板との接着安定性を確保するための表面処理層であるアンカー用微細銅粒及び防錆層とからなるものである。ただし、本発明の性格上、発明の実施の形態を除き、表面処理層の話は省略して記載している。

【００４２】以上に述べたキャリア箔付電解銅箔を製造するにあたり、キャリア箔上に有機剤を用いて有機接合界面層を形成し、更に電解銅箔層となる銅成分を電着させる製造方法を採用するのである。

【００４３】そして、請求項３に記載の請求項１又は請求項２に記載のキャリア箔付電解銅箔を用いた銅張積層板は、そのキャリア箔の引き剥がし作業が極めて小さな力で円滑に素早く行えるため、より一層の作業効率の向上を図ることが可能となる。しかも、キャリア箔が３ｇｆ／ｃｍ～１００ｇｆ／ｃｍの範囲の安定した力で行えるため、キャリア箔の引き剥がし作業の機械による自動化をも図れるものとなる。

【００４４】

【発明の実施の形態】以下、本発明に係るキャリア箔付電解銅箔の製造方法及びその銅箔を用いて銅張積層板を製造し、その評価結果を示すことにより、発明の実施の形態について説明する。ここではキャリア箔に電解銅箔を用いた場合を中心に説明するものとする。なお、図面中の符号については可能な限り、同一の物を指し示す場合には同一の符号を用いている。以下、図１及び図２を参照しつつ、説明する。

【００４５】第１実施形態：本実施形態においては、キャリア箔付電解銅箔１であって、図１に示したものに関して説明する。そして、ここで用いた製造装置２は、図２として示したものであり、巻き出されたキャリア箔３が、電解銅箔層５の形成工程を蛇行走行するタイプのものである。ここでは、キャリア箔３に１８μｍ厚のグレード３に分類されるＨＴＥ箔であって、表面処理を施していない電解銅箔を用い、光沢面４側へ３μ厚の電解銅箔層５形成したのである。以下、各種の槽を直列に連続配置した順序に従って、製造条件の説明を行う。

【００４６】巻き出されたキャリア箔３は、最初に酸洗処理槽６に入る。酸洗処理槽６の内部には濃度１５０ｇ／ｌ、液温３０℃の希硫酸溶液が満たされており、浸漬時間３０秒として、キャリア箔３に付いた油脂成分を除去し、表面酸化被膜の除去を行った。

【００４７】酸洗処理槽６を出たキャリア箔３は、接合界面形成槽７に入ることになる。接合界面形成槽７の中には、濃度５ｇ／ｌのＣＢＴＡを含む、液温４０℃、ｐＨ５の水溶液で満たした。従って、キャリア箔３は、走行しつつ当該溶液中に３０秒浸漬され、キャリア箔３表面に接合界面層８を形成した。

【００４８】接合界面層８の形成がなされると、続いて、その界面上にＶタイプの電解銅箔層のバルク銅層９の形成が行われる。バルク銅の形成槽１０内には、濃度７０ｇ／ｌ硫酸、６３．５ｇ／ｌ銅（硫酸銅・５水和物）、液温４０℃の硫酸銅溶液を満たした。そして、当該溶液中を、接合界面層８を形成したキャリア箔３が通過する間に、バルク銅層９を形成する銅成分を当該接合界面上に均一且つ平滑に電析させるため、接合界面層８を形成したキャリア箔３の片面に対し、図２中に示すように、平板のアノード電極１１を平行配置し、電流密度５Ａ／ｄｍ^{2}の平滑メッキ条件で１５０秒間電解した。このとき、キャリア箔３自体をカソード分極するため、蛇行走行するキャリア箔３と接触するテンションロール

１２の少なくとも１つは、電流の供給ロールとして用いた。

【００４９】バルク銅層９形成が終了すると、次にはバルク銅層９の表面に微細銅粒１３を形成する工程として、表面処理槽１４にキャリア箔３は入ることになる。表面処理槽１４内で行う処理は、バルク銅層９の上に微細銅粒１３を析出付着させる工程１４Ａと、この微細銅粒１３の脱落を防止するための被せメッキ工程１４Ｂとで構成される。

【００５０】バルク銅層９の上に微細銅粒１３を析出付着させる工程１４Ａでは、前述のバルク銅の形成槽１０で用いたと同様の硫酸銅溶液であって、濃度が１００ｇ／ｌ硫酸、１８ｇ／ｌ銅、液温２５℃、電流密度１０Ａ／ｄｍ^{2}のヤケメッキ条件で１０秒間電解した。このとき、平板のアノード電極１１は、バルク銅層９を形成したキャリア箔３の面に対し、図２中に示すように平行配置した。

【００５１】微細銅粒１３の脱落を防止するための被せメッキ工程１４Ｂでは、前述のバルク銅の形成槽１０で用いたと同様の硫酸銅溶液であって、濃度１５０ｇ／ｌ硫酸、６５ｇ／ｌ銅、液温４５℃、電流密度１５Ａ／ｄｍ^{2}の平滑メッキ条件で２０秒間電解した。このとき、平板のアノード電極１１は、微細銅粒１３を付着形成したキャリア箔３の面に対し、図２中に示すように平行配置した。

【００５２】防錆処理槽１５では、防錆元素として亜鉛を用いて防錆処理を行った。ここでは、アノード電極として亜鉛板を用いた溶解性アノード１６として、防錆処理槽１５内の亜鉛の濃度バランスを維持するものとした。ここでの電解条件は、硫酸亜鉛浴を用い、７０ｇ／ｌ硫酸、２０ｇ／ｌ亜鉛の濃度とし、液温４０℃、電流密度１５Ａ／ｄｍ^{2}とした。

【００５３】防錆処理が終了すると、最終的にキャリア箔３は、乾燥処理部１７で電熱器により雰囲気温度１１０℃に加熱された炉内を４０秒かけて通過し、完成したキャリア箔付電解銅箔１としてロール状に巻き取った。以上の工程でのキャリア箔の走行速度は、２．０ｍ／ｍｉｎとし、各槽毎の工程間には、約１５秒間の水洗可能な水洗層１８を設けて洗浄し、前処理工程の溶液の持ち込みを防止している。

【００５４】このキャリア箔付電解銅箔１と、１５０μｍ厚のＦＲ－４のプリプレグ２枚とを用いて両面銅張積層板を製造し、キャリア箔層３と電解銅箔層５との接合界面８における引き剥がし強度を測定した。その結果、接合界面層８の厚さは平均１０ｎｍであり、キャリア箔層３と電解銅箔層５との熱膨張係数の差は０．２６８×１０$^{-5}$／ｄｅｇ．で、当該引き剥がし強度は加熱前４．０ｇｆ／ｃｍ、１８０℃で１時間加熱後は４．２ｇｆ／ｃｍであった。

【００５５】第２実施形態：　本実施形態においては、キャリア箔付電解銅箔１であって、図１に示したものに関して説明する。そして、ここで用いた製造装置２は、図２として示したものであり、巻き出されたキャリア箔３が、電解銅箔層５の形成工程を蛇行走行するタイプのものである。ここでは、キャリア箔３に１８μｍ厚のグレード３に分類されるＳ－ＨＴＥ箔であって、表面処理を施していない析離箔を用い、光沢面４側へ３μ厚の電解銅箔層５形成したのである。

【００５６】この第２実施形態においては、第１実施形態とキャリア箔が異なるのみで、その他の実施内容は第１実施形態と同様であるため重複した記載となるため、ここでの説明は省略する。

【００５７】このキャリア箔付電解銅箔１と、１５０μｍ厚のＦＲ－４のプリプレグ２枚とを用いて両面銅張積層板を製造し、キャリア箔層３と電解銅箔層５との接合界面８における引き剥がし強度を測定した。その結果、接合界面層８の厚さは平均１０ｎｍであり、キャリア箔層３と電解銅箔層５との熱膨張係数の差は０．０４６×１０$^{-5}$／ｄｅｇ．で、当該引き剥がし強度は加熱前７０．４ｇｆ／ｃｍ、１８０℃で１時間加熱後は７０．８ｇｆ／ｃｍであった。

【００５８】第３実施形態：　本実施形態においては、キャリア箔付電解銅箔１であって、図１に示したものに関して説明する。そして、ここで用いた製造装置２は、図２として示したものであり、巻き出されたキャリア箔３が、電解銅箔層５の形成工程を蛇行走行するタイプのものである。ここでは、キャリア箔３に１８μｍ厚のグレード１に分類される通常銅箔であって、表面処理を施していない析離箔を用い、光沢面４側へ３μ厚の電解銅箔層５形成したのである。

【００５９】この第３実施形態においては、第１実施形態とキャリア箔が異なるのみで、その他の実施内容は第１実施形態と同様であるため重複した記載となるため、ここでの説明は省略する。

【００６０】このキャリア箔付電解銅箔１と、１５０μｍ厚のＦＲ－４のプリプレグ２枚とを用いて両面銅張積層板を製造し、キャリア箔層３と電解銅箔層５との接合界面８における引き剥がし強度を測定した。その結果、接合界面層８の厚さは平均１０ｎｍであり、キャリア箔層３と電解銅箔層５との熱膨張係数の差は０．２２５×１０$^{-5}$／ｄｅｇ．で、当該引き剥がし強度は加熱前５．８ｇｆ／ｃｍ、１８０℃で１時間加熱後は６．５ｇｆ／ｃｍであった。

【００６１】

【発明の効果】本発明に係るキャリア箔付電解銅箔は、キャリア箔層と電解銅箔層との界面での剥離が非常に小さな３ｇｆ／ｃｍ～１００ｇｆ／ｃｍの範囲の力で容易に行えるため、従来のピーラブルタイプのキャリア箔付電解銅箔では不可能であった、キャリア箔の引き剥がし安定性を維持することができる。このような特性が得ら

れることで、初めてキャリア箔の引き剥がしの自動化が可能となり、銅張積層板の生産歩留まりを大きく改善することが可能となる。

【図面の簡単な説明】

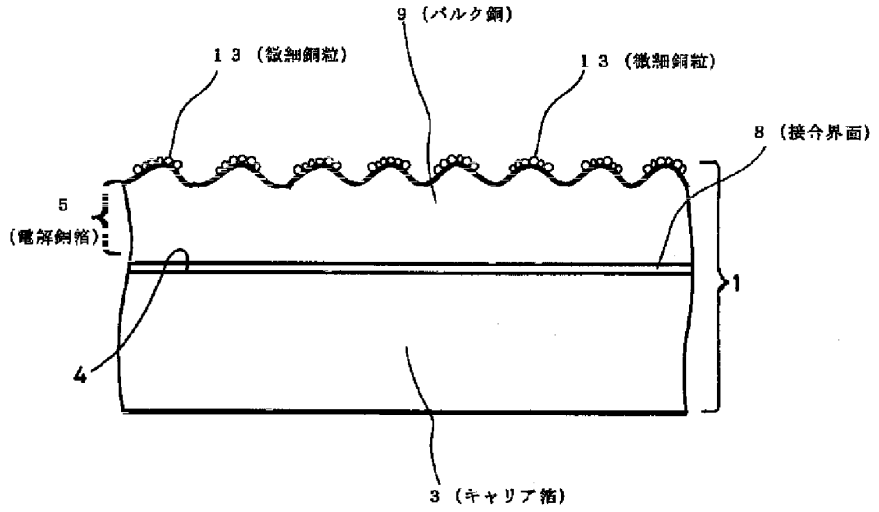
【図１】キャリア箔付電解銅箔の断面模式図。

【図２】キャリア箔付電解銅箔の製造装置の模式断面。

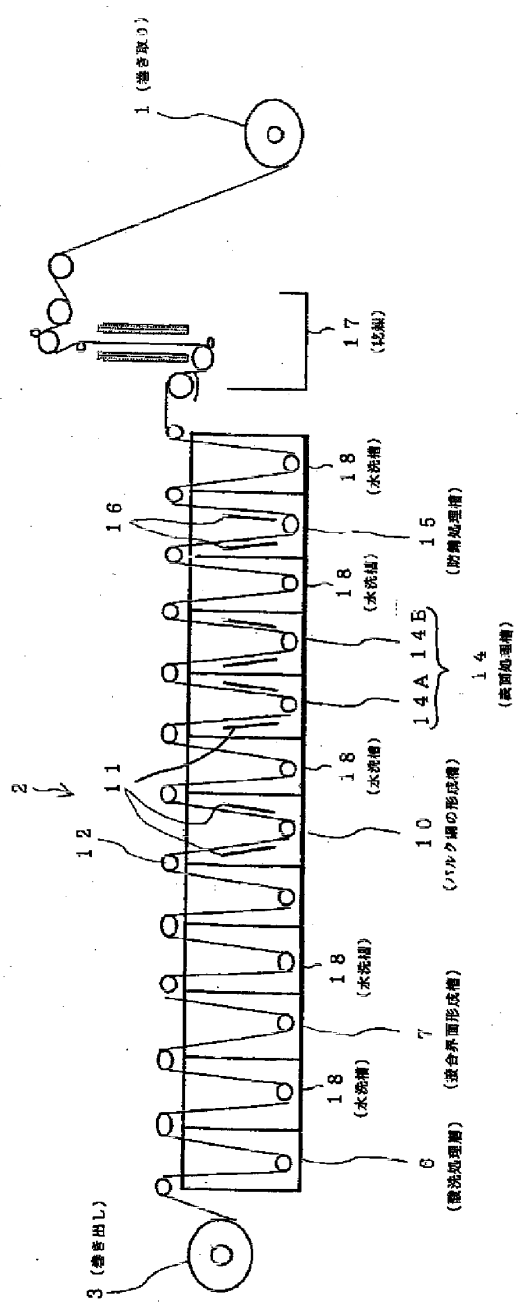
【符号の説明】

1	キャリア箔付電解銅箔
2	キャリア箔付電解銅箔の製造装置
3	キャリア箔（キャリア箔層）
4	光沢面
5	電解銅箔（電解銅箔層）
6	酸洗処理槽
7	接合界面形成槽
8	接合界面（接合界面層）
9	バルク銅（バルク銅層）
１０	バルク銅の形成槽
１１	アノード電極
１２	テンションロール
１３	微細銅粒
１４	表面処理槽
１５	防錆処理槽
１６	亜鉛溶解性アノード
１７	乾燥処理部
１８	水洗槽

【図１】



【図2】


1 (巻き取り)
17 (比較)
18 (水洗槽)
16
15 (防錆処理槽)
14A 14B
14 (表面処理槽)
2
11
12
10 (バルク層の形成槽)
7 (混合界面形成槽)
6 (撥洗処理槽)
3 (巻き出し)

フロントページの続き

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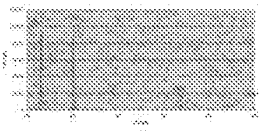
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(54)COPPER FOIL FOR CURRENT COLLECTOR OF LITHIUM SECONDARY BATTERY

(57)Abstract

PROBLEM TO BE SOLVED: To provide copper foil for a current collector of a lithium secondary battery with a crystal structure capable of decreasing the generation of wrinkles on a surface of the copper foil.

SOLUTION: A copper foil for a current collector of a lithium secondary battery has weight deviation of 3% or less and tensile strength of 30 to 40 kgf/mm2. The copper foil has a crystal 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) 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%.

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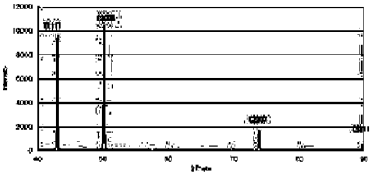
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(54)【発明の名称】リチウム二次電池の集電体用銅箔

(57)【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、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。
【選択図】図２



【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１または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１～３のいずれか一項に記載のリチウム二次電池の集電体用銅箔。
【発明の詳細な説明】
【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、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。
【００１１】
表面粗度（Ｒｚ‐ＪＩＳ）が２μｍ以下であることが望ましい。
【００１２】
延伸率が３～２０％であることが望ましい。
【００１３】
銅箔厚さが１～３５μｍであることが望ましい。
【発明の効果】
【００１４】
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】
【００１５】
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】

【００１６】

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。

【００１７】

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。

【００１８】

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。

【００１９】

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。

【００２０】

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$_0$（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。

【００２１】

【数１】

$$TC(hkl) \geq \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{n}\sum\frac{I(hkl)}{I_0(hkl)}}$$

【００２２】

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。

【００２３】

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。

【００２４】

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。

【００２５】

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。

【００２６】

【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	41.6	0.9	2
比較例９	電解銅箔	8	76	25	50	25	31.8	3.4	5

【００２７】

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。

【００２８】

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。

【００２９】

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】

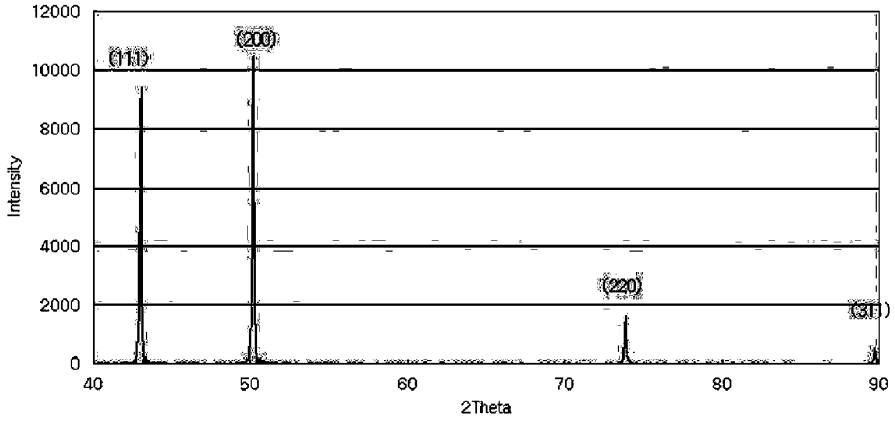
【００３０】

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。

【図１】



【図２】


12000
10000
8000
6000
4000
2000
0
Intensity
(111)
(200)
(220)
(311)
40
50
60
70
80
90
2Theta

フロントページの続き

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Ｆターム(参考) 5H017 AA03 CC01 EE00 EE01 HH01 HH03

Espacenet

Bibliographic data: JP2013181236 (A) — 2013-09-12

ELECTROLYTIC COPPER FOIL AND NEGATIVE ELECTRODE COLLECTOR FOR SECONDARY BATTERY

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Application number: JP20120047397 20120302 Global Dossier

Priority number (s): JP20120047397 20120302

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Abstract of JP2013181236 (A)

PROBLEM TO BE SOLVED: To provide an electrolytic copper foil which has high normal tensile strength and whose tensile strength is hardly deteriorated after thermal history, in regard to an electrolytic copper foil used as a negative electrode collector for a lithium ion secondary battery.SOLUTION: An electrolytic copper foil is produced by using a sulfuric acid-based copper electrolytic solution containing glue in an amount of 6-11 ppm by mass and performing electrolysis at a ratio to limiting current density of 0.14-0.16 to make electrodeposition onto a rotating cathode drum made of titanium or stainless steel. The electrolytic copper foil has a normal tensile strength of 500-750 MPa and a tensile strength of ≥350 MPa after heating at 400°C for 1 hour.

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Ｆターム(参考)　4K023 AA19 BA06 CB40 DA07
5H017 AA03 AS01 AS10 BB01 BB15 BB16 BB19 CC03 EE01 EE08 HH01 HH03 HH08 HH10

(54)【発明の名称】電解銅箔及び二次電池用負極集電体

(57)【要約】　（修正有）
【課題】リチウムイオン二次電池負極集電体として用いられる電解銅箔に関し、常態抗張力が高く、熱履歴後の抗張力低下が小さい電解銅箔を提供する。
【解決手段】ニカワを６～１１質量ｐｐｍ含む硫酸系銅電解液を使用し、対限界電流密度比を０．１４～０．１６として電解し、チタン製またはステンレス製の回転カソードドラム上に電着させて製造される、常態抗張力が５００～７５０ＭＰａであり、４００℃で１時間加熱後の抗張力が３５０ＭＰａ以上である電解銅箔。
【選択図】なし

【特許請求の範囲】
【請求項１】
常態抗張力が５００～７５０ＭＰａであり、４００℃で１時間加熱後の抗張力が３５０ＭＰａ以上である電解銅箔。
【請求項２】
常態抗張力が５００～７５０ＭＰａであり、４００℃で１時間加熱後の抗張力が４５０ＭＰａ以上である電解銅箔。
【請求項３】
常態抗張力が５００～７５０ＭＰａであり、４００℃で１時間加熱後の抗張力が常態抗張力の５０％以上である電解銅箔。
【請求項４】
常態抗張力が５００～７５０ＭＰａであり、４００℃で１時間加熱後の抗張力が常態抗張力の６５％以上である電解銅箔。
【請求項５】
常態抗張力が５００～７５０ＭＰａであり、４００℃で１時間加熱後の銅粒子径が０．５０μｍ以下である電解銅箔。
【請求項６】
伸び率が４％以上である請求項１～５の何れか一項に記載の電解銅箔。
【請求項７】
伸び率が６％以上である請求項１～５の何れか一項に記載の電解銅箔。
【請求項８】
ニカワを６～１１質量ｐｐｍ含む銅電解液を使用し、対限界電流密度比を０．１４～０．１６として電解することを含む請求項１～７の何れか一項に記載の電解銅箔の製造方法。
【請求項９】
請求項１～７の何れか一項に記載の電解銅箔より構成される二次電池用負極集電体。
【請求項１０】
請求項９に記載の負極集電体を備えた二次電池。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は電解銅箔に関し、特に、電解銅箔を材料とした二次電池用負極集電体に関する。
【背景技術】
【０００２】
リチウムイオン電池はエネルギー密度が高く、比較的高い電圧を得ることができるという特徴を有し、ノートパソコン、ビデオカメラ、デジタルカメラ、携帯電話等の小型電子機器用に多用されている。電気自動車や一般家庭の分散配置型電源といった大型機器の電源としての利用も実用段階となっている。
【０００３】
リチウムイオン電池の電極体は一般に、正極、セパレータ及び負極が幾十にも巻回又はラミネートされたスタック構造を有している。このうち、負極は銅箔でできた負極集電体とその表面に設けられた負極活物質から主として構成される。
【０００４】
近年、リチウムイオン二次電池の高密度化及び高容量化に伴い、負極活物質の体積伸縮量も増加しているため、集電体に求められる耐力が高くなっている。特にＳｉやＳｎなどを用いた合金系活物質は充電反応による体積膨張が従来の炭素と比較し、数倍から数十倍である。また、合金系活物質のバインダー種は密着力を要する為、ポリイミド等の高いガラス転移温度を有する有機系溶剤が使用される。ガラス転移温度の高いバインダーでは硬化に高温を要する為、加熱後に耐力低下の少ない集電体が求められることになる。

【０００５】
そこで、特許第３８５０１５５号（特許文献１）では、常温及び加熱後の引張強さ及び伸び率の向上を目的として、銅箔中の不純物含有量が少なく且つ常態抗張力の高い電解銅箔の例が記載されている。特開２００８－１０１２６７号公報（特許文献２）及び特開２００９－２９９１００号公報（特許文献３）では、加熱後の屈曲性能を高く維持するために、常態抗張力が高く、熱履歴後の抗張力低下も少ない電解銅箔の例が開示されている。
【先行技術文献】
【特許文献】
【０００６】
【特許文献１】特許第３８５０１５５号公報
【特許文献２】特開２００８－１０１２６７号公報
【特許文献３】特開２００９－２９９１００号公報
【発明の概要】
【発明が解決しようとする課題】
【０００７】
しかしながら、特許文献１に記載された電解銅箔は、銅箔中の不純物含有量が少なく、常態抗張力は高いが、熱履歴後の抗張力低下が大きいという問題があり、二次電池負極体用銅箔に求められる特性としては十分ではない。また、特許文献２及び特許文献３に記載された電解銅箔は、常態抗張力が高く、１８０℃加熱後の初期抗張力の低下も少ないが、それ以上の高温加熱による抗張力推移が不明であり、しかも抗張力を高める為、銅箔中の不純物取り込み量を多くしていることで、ＬｉＢ用負極集電体として最重要項目の一つである導体抵抗特性を低下させているので、この用途への使用はふさわしくない。
【０００８】
上記課題に鑑み、本発明は、常態抗張力が高く、熱履歴後の抗張力低下が小さい電解銅箔を提供することを課題の一つとする。また、本発明はそのような電解銅箔の製造方法を提供することを別の課題の一つとする。更に、本発明はそのような電解銅箔を材料とした二次電池用負極集電体を提供することを別の課題の一つとする。
【課題を解決するための手段】
【０００９】
上記課題を解決するために、本発明者は、製箔時の対限界電流密度比及び電解液中のニカワ濃度を最適化することで、加熱軟化による銅粒子の肥大化が抑制され、加熱後でも小粒径を保持することが分かった。そして、これによって得られた電解銅箔は、常態抗張力が高く且つ熱履歴後の抗張力の低下が少ないことが分かった。
【００１０】
かかる知見を基礎として完成した本発明は一側面において、常態抗張力が５００～７５０ＭＰａであり、４００℃で１時間加熱後の抗張力が３５０ＭＰａ以上である電解銅箔である。
【００１１】
本発明は別の一側面において、常態抗張力が５００～７５０ＭＰａであり、４００℃で１時間加熱後の抗張力が４５０ＭＰａ以上である電解銅箔である。
【００１２】
本発明は更に別の一側面において、常態抗張力が５００～７５０ＭＰａであり、４００℃で１時間加熱後の抗張力が常態抗張力の５０％以上である電解銅箔である。
【００１３】
本発明は更に別の一側面において、常態抗張力が５００～７５０ＭＰａであり、４００℃で１時間加熱後の抗張力が常態抗張力の６５％以上である電解銅箔である。
【００１４】
本発明は更に別の一側面において、常態抗張力が５００～７５０ＭＰａであり、４００℃で１時間加熱後の銅粒子径が０．５０μｍ以下である電解銅箔である。
【００１５】

本発明に係る電解銅箔の一実施形態においては、伸び率が４％以上である。

【００１６】

本発明に係る電解銅箔の別の一実施形態においては、伸び率が６％以上である。

【００１７】

本発明は更に別の一側面において、ニカワを６～１１質量ｐｐｍ含む銅電解液を使用し、対限界電流密度比を０．１４～０．１６として電解することを含む本発明に係る電解銅箔の製造方法である。

【００１８】

本発明は更に別の一側面において、本発明に係る電解銅箔より構成される二次電池用負極集電体である。

【００１９】

本発明は更に別の一側面において、本発明に係る負極集電体を備えた二次電池である。

【発明の効果】

【００２０】

本発明に係る電解銅箔は、常態抗張力が高く、熱履歴後の抗張力低下が小さい。そのため、本発明に係る電解銅箔は耐熱性が求められる二次電池負極集電体として好適に利用できる。

【発明を実施するための形態】

【００２１】

本発明に係る電解銅箔の特徴の一つは、常態抗張力が高いという点である。具体的には、本発明に係る電解銅箔は一実施形態において、常態抗張力が５００～７５０ＭＰａである。常態抗張力は高い方がプレス加工やスリット加工する際に有利であるため、好ましくは６００ＭＰａ以上であり、より好ましくは６３０ＭＰａ以上である。但し、極端に常態抗張力を高くすると今度は熱履歴後の抗張力保持率が低下する傾向が見られ、また、伸び特性に悪影響が及ぶので、好ましくは７５０ＭＰａ以下であり、より好ましくは７００ＭＰａ以下である。

【００２２】

本発明において、「常態抗張力」とは、常温（２３℃）においてＩＰＣ-ＴＭ-６５０に基づく引張強さ試験をした場合の値を示す。

【００２３】

本発明に係る電解銅箔のもう一つの特徴は、４００℃というかなりの高温で１時間加熱した後の抗張力保持率が高いという点である。これは、見方を変えれば、加熱を加えても銅粒子の肥大化による軟化現象が生じにくく、加熱後でも小粒径を保持することができるということを意味する。従来、１８０℃×１時間や１３０℃×１５時間という低温側での耐熱性の改善を試みた先行技術が特許文献１及び２に記載されているものの、本発明のように高温側での耐熱性を実現できている例は本発明者の知る限り存在しない。

【００２４】

具体的には、本発明に係る電解銅箔は一実施形態において、４００℃で１時間加熱後の抗張力が３５０ＭＰａ以上であり、好ましくは４００ＭＰａ以上である。

また、４００℃で１時間加熱後の抗張力の上限は特に規定する必要はないが、例えば６００ＭＰａ以下であり、例えば５８０ＭＰａ以下であり、例えば５５０ＭＰａ以下である。

【００２５】

本発明に係る電解銅箔は別の一実施形態において、４００℃で１時間加熱後の抗張力が初期抗張力の５０％以上であり、好ましくは６０％以上である。上限は特に設定されないが、典型的には９５％以下であり、より典型的には９０％以下、更により典型的には８５％以下、例えば８０％以下である。

【００２６】

本発明において、「４００℃で１時間加熱後の抗張力」とは、４００℃で１時間の加熱後、常温（２３℃）まで放冷してからＩＰＣ-ＴＭ-６５０に基づく引張強さ試験をした場

合の値を示す。

【００２７】

また、本発明に係る電解銅箔は更に別の一実施形態において、４００℃で１時間加熱後の銅粒子径が０．５０μｍ以下であり、好ましくは０．４５μｍ以下であり、より好ましくは０．３０μｍ以下である。また、４００℃で１時間加熱後の銅粒子径の下限は特に規定する必要はないが、一実施形態においては０．０１μｍ以上であり、別の一実施形態においては０．０５μｍ以上であり、更に別の一実施形態においては０．０７μｍ以上である。

【００２８】

本発明において、「４００℃で１時間加熱後の銅粒子径」とは、４００℃で１時間の加熱後、常温（２３℃）まで放冷後の、ＦＩＢ－ＳＩＭ断面写真から切断法よって測定した値を指す。

【００２９】

本発明に係る電解銅箔の更にもう一つの特徴は、抗張力が高く且つ一定以上の伸び率を有するものである。強度と伸び率には逆相関の関係があり、強度が高いものは伸び率は低く発現するものが一般的である。抗張力が高く且つ一定以上の伸び率を保有することで、充放電の際に活物質の大きな体積変化に伴う箔にかかる大きな応力を吸収することに有利な効果を発揮するばかりでなく、更には製造工程での運箔性向上による生産性増加等の有益な効果も発現するものである。

伸び率は電解銅箔の厚みによっても異なるが、厚さ６～２０μｍ程度の電解銅箔であれば、伸び率４％以上、典型的には６％以上、より典型的には６～１０％、例えば６～９％もの大きな伸び率が得られる。高強度及び高耐熱性でありながら伸び性にも優れるというのは、二次電池負極集電体用電解銅箔として使用する場合において、充放電の際に活物質の大きな体積変化に伴う箔にかかる大きな応力を吸収することに有利な効果を発揮するものである。本発明において、「伸び率」とは、常温（２３℃）においてＩＰＣ－ＴＭ－６５０に基づく引張強さ試験をしたときに、試験片が破断した際の伸び率を指す。

伸び率（％）＝（Ｌ－Ｌｏ）／Ｌｏ×１００

Ｌｏ：試験前の試料長さ　Ｌ：破断時の試料長さ変形量を示す。

【００３０】

電解銅箔の厚みは、以下に制限されないが、二次電池負極集電体用電解銅箔として用いる場合には、例えば２０μｍ以下、好ましくは１８μｍ以下、更に好ましくは１５μｍ以下とすれば上記の特性を十分に得ることができる。厚みの下限値も以下に制限されるものではないが、例えば６μｍ以上である。

【００３１】

本発明に係る電解銅箔を製造する場合は、電解槽中に、ニカワを６～１１質量ｐｐｍ添加した硫酸系銅電解液を入れ、対限界電流密度比を０．１４～０．１６としてカソードに電着することにより行うことが好ましい。例えば、電解槽の中に、直径約３０００ｍｍ、幅約２５００ｍｍのチタン製又はステンレス製の回転カソードドラムと、ドラムの周囲に３～１０ｍｍ程度の極間距離を置いて電極を配置した電解銅箔製造装置を用いて製造することができる。硫酸系銅電解液は典型的には銅濃度：８０～１１０ｇ／Ｌ、硫酸濃度：７０～１１０ｇ／Ｌとすることができる。

【００３２】

ニカワ濃度は１１質量ｐｐｍ超だと、伸び率が低下する傾向となる一方で、６質量ｐｐｍ未満だと加熱後の抗張力が低くなるため、６～１１質量ｐｐｍが最適である。

【００３３】

対限界電流密度比は０．１６超だと、加熱後の抗張力が低くなる一方で、０．１４未満だと初期抗張力が低くなることから、０．１４～０．１６が好ましい。本発明において、対限界電流密度比は、次式により算出する。

対限界電流密度比＝実際の電流密度／限界電流密度

限界電流密度は、銅濃度、硫酸濃度、給液速度、極間距離、電解液温度によって変化す

るが、本検討では、正常めっき（銅が層状に析出している状態）と粗化めっき（焼けメッキ、銅が結晶状（球状や針状や樹氷状等）に析出している状態、凹凸がある。）との境界の電流密度を限界電流密度と定義し、ハルセル試験にて正常めっきとなる限界（焼けメッキとなる直前）の電流密度（目視判断）を限界電流密度とした。

具体的にはハルセル試験において、銅濃度、硫酸濃度、電解液温度を銅箔の製造条件に設定し、ハルセル試験を行う。そして、当該電解液組成、電解液温度における銅層形成状態（銅が層状に析出しているか結晶状に形成しているか）を調査する。そして、株式会社山本鍍金試験器製の電流密度早見表に基づいて、テストピースの正常めっきと粗化めっきの境界が存在する箇所のテストピースの位置から、当該境界の位置における電流密度を求めた。そして、当該境界の位置における電流密度を限界電流密度と規定した。これにより、当該電解液組成、電解液温度での限界電流密度が分かる。一般的には極間距離が短いと、限界電流密度が高くなる傾向にある。実施例において、ハルセル試験に使用したテストピースは株式会社山本鍍金試験器製のハルセル試験用横銅板とした。

なお、従来は銅箔粒子の形状を整えるため対限界電流密度比を０．１７以上として電解銅箔を製造するのが通例であった。ハルセル試験の方法は例えば「めっき実務読本」　丸山　清　著　日刊工業新聞社　１９８３年６月３０日の１５７ページから１６０ページに記載されている。

【００３４】

電解銅箔の表面又は裏面、さらには両面には、防錆処理を行うことが好ましい。防錆処理は、限定的ではないが、クロム酸化物単独の皮膜処理或いはクロム酸化物と亜鉛／亜鉛酸化物との混合物皮膜処理が挙げられる。クロム酸化物と亜鉛／亜鉛酸化物との混合物皮膜処理とは、亜鉛塩または酸化亜鉛とクロム酸塩とを含むめっき浴を用いて電気めっきにより亜鉛または酸化亜鉛とクロム酸化物とより成る亜鉛－クロム基混合物の防錆層を被覆する処理である。

【００３５】

めっき浴としては、代表的には、$K_2Cr_2O_7$、$Na_2Cr_2O_7$等の重クロム酸塩やCrO_3等の少なくとも一種と水酸化アルカリ並びに酸の混合水溶液が用いられる。また、上記水溶液と水溶性亜鉛塩、例えばＺｎＯ 、$ZnSO_4・7H_2O$など少なくとも一種との混合水溶液も用いることができる。

【００３６】

防錆処理前に必要に応じて粗化処理を施すことができる。粗化粒子として、銅、コバルト、ニッケルの１種のめっき又はこれらの２種以上の合金めっきを形成することができる。通常、銅、コバルト、ニッケルの３者の合金めっきにより、粗化粒子を形成する。さらに、二次電池用負極集電体用銅箔は、耐熱性及び耐候（耐食）性を向上させるために、表裏両面の粗化処理面上に、コバルト－ニッケル合金めっき層、亜鉛－ニッケル合金めっき層、銅－亜鉛合金めっき層、クロメート層から選択した一種以上の防錆処理層又は耐熱層及び／又はシランカップリング層を形成することが望ましい。なお、粗化粒子を形成しないで、コバルト－ニッケル合金めっき層、亜鉛－ニッケル合金めっき層、銅－亜鉛合金めっき層、クロメート層から選択した一種以上の防錆処理層又は耐熱層及び／又はシランカップリング層を形成しても良い。

【００３７】

必要に応じ、銅箔と活物質との接着力の改善を主目的として、防錆層上の両面もしくは析出面にシランカップリング剤を塗布するシラン処理が施してもよい。このシラン処理に使用するシランカップリング剤としては、オレフィン系シラン、エポキシ系シラン、アクリル系シラン、アミノ系シラン、メルカプト系シランを挙げることができるが、これらを適宜選択して使用することができる。塗布方法は、シランカップリング剤溶液のスプレーによる吹付け、コーターでの塗布、浸漬、流しかけ等いずれでもよい。

【００３８】

（電池の構成）

本発明に係る電解銅箔は二次電池負極集電体として好適に使用することができる。一般

に二次電池は、負極、正極、正極及び負極を絶縁するためのセパレータ、並びに非水もしくは水系電解質を有しており、これらが電池ケースによって収容された構造となっている。また、電解質がポリマー電解質である場合にはセパレータは不要である。

【００３９】

（負極）

負極は、本発明の負極集電体と、負極集電体の片面もしくは両面に形成される負極活物質含有層より一般に構成される。負極活物質としては、リチウムの吸蔵放出が可能な炭素質物、金属、金属化合物（金属酸化物、金属硫化物、金属窒化物）、リチウム合金などが挙げられる。

前記炭素質物としては、黒鉛、コークス、炭素繊維、球状炭素、熱分解気相炭素質物、樹脂焼成体などの黒鉛質材料もしくは炭素質材料；熱硬化性樹脂、等方性ピッチ、メソフェーズピッチ系炭素、メソフェーズピッチ系炭素繊維、メソフェーズ小球体などに５００～３０００℃で熱処理を施すことにより得られる黒鉛質材料又は炭素質材料等が挙げられる。

前記金属としては、リチウム、アルミニウム、マグネシウム、すず、けい素等が挙げられる。

前記金属酸化物としては、すず酸化物、ケイ素酸化物、リチウムチタン酸化物、ニオブ酸化物、タングステン酸化物等が挙げられる。前記金属硫化物としては、すず硫化物、チタン硫化物等が挙げられる。前記金属窒化物としては、リチウムコバルト窒化物、リチウム鉄窒化物、リチウムマンガン窒化物等が挙げられる。

リチウム合金としては、リチウムアルミニウム合金、リチウムすず合金、リチウム鉛合金、リチウムケイ素合金等が挙げられる。

本発明に係る電解銅箔は、上述したように常態抗張力が高く、熱履歴後の抗張力低下が小さいので、特に体積膨張が大きく、バインダーの硬化に高温を要するＳｉやＳｎなどを用いた合金系活物質を負極活物質として使用した場合に特に有利である。

【００４０】

負極活物質含有層にはバインダーや流動性調整剤（典型的には増粘剤）などの添加剤を含有させることができる。例えば、ポリフッ化ビニリデン（ＰＶＤＦ）、ポリテトラフルオロエチレン（ＰＴＦＥ）、ポリフッ化ビニリデンーヘキサフルオロプロピレン共重合体（ＰＶＤＦ－ＨＦＰ）等のフッ素含有ポリマー；スチレンブタジエンゴム（ＳＢＲ）、アクリル系ゴム（例えば、（メタ）アクリル酸エステルを主構成単量体とするゴム）、フッ素系ゴム（例えば、フッ化ビニリデン系ゴム、テトラフルオロエチレン－プロピレン共重合体ゴム）、ポリブタジエン、エチレン－プロピレン－ジエン共重合体（ＥＰＤＭ）およびスルホン化ＥＰＤＭ等のゴム類；アクリル系樹脂（例えば、（メタ）アクリル酸エステルを主構成単量体とする樹脂、ポリアクリル酸等）；カルボキシメチルセルロース（ＣＭＣ）、ジアセチルセルロース、ヒドロキシプロピルセルロース等のセルロース系ポリマー；ポリビニルアルコール；ポリエチレンオキサイド等のポリアルキレンオキサイド；ポリイミド等の各種ポリマーから適宜選択される一種または二種以上のポリマー材料を添加することができる。中でも、ＣＭＣ及びＳＢＲを含む混合物が好ましい。当該混合物を使用することによって、負極活物質と集電体との密着性をより高くすることができる。

負極活物質含有層には、導電剤を含有させることができる。導電剤としては、アセチレンブラック、粉末状膨張黒鉛などのグラファイト類、炭素繊維粉砕物、黒鉛化炭素繊維粉砕物等が挙げられる。

【００４１】

（正極）

正極は、正極集電体と、前記正極集電体の片面もしくは両面に形成される正極活物質含有層より一般に構成される。

正極集電体としては、アルミニウム板、アルミニウムメッシュ材等が挙げられる。

正極活物質含有層は、例えば、活物質と結着剤とを含有する。正極活物質としては、二酸化マンガン、二硫化モリブデン、$LiCoO_2$、$LiNiO_2$、$LiMn_2O_4$等のカルコ

ゲン化合物が挙げられる。これらのカルコゲン化合物は、２種以上の混合物で用いても良い。特に、リチウムイオン二次電池用にはリチウム遷移金属複合酸化物が多用される。

正極活物質含有層には、負極活物質含有層と同様に、結着剤や流動性調整剤（典型的には増粘剤）などの添加剤を含有させることができる。具体例は負極活物質含有層で述べた通りである。

活物質含有層には、導電補助材としてアセチレンブラック、粉末状膨張黒鉛などのグラファイト類、炭素繊維粉砕物、黒鉛化炭素繊維粉砕物、等をさらに含有することができる。

【００４２】

（セパレータ）

正極と負極の間には、セパレータを配置することができる。セパレータとしては、例えば２０～３０μｍの厚さを有するポリエチレン多孔質フィルム、ポリプロピレン多孔質フィルム等を用いることができる。非水電解質として、固体又はゲル状などのポリマー電解質を使用する場合は、セパレータを省略することもできる。

【００４３】

（非水電解質）

非水電解質は、非水溶媒と、この非水溶媒に溶解される電解質とを含む非水電解液の形態とすることができる。

非水溶媒としては、エチレンカーボネート、ジメチルカーボネート、メチルエチルカーボネート、ジエチルカーボネート、γ－ブチロラクトン、プロピオン酸メチル等が挙げられる。使用する非水溶媒の種類は、１種類もしくは２種類以上にすることが可能である。

電解質としては、過塩素酸リチウム（ＬｉＣｌＯ$_4$）、六フッ化リン酸リチウム（ＬｉＰＦ$_6$）、四フッ化硼酸リチウム（ＬｉＢＦ$_4$）、六フッ化砒素リチウム（ＬｉＡｓＦ$_6$）等が挙げられる。電解質は、単独でも混合物の形態でも使用することができる。

また、非水電解質は、固体又はゲル状などのポリマー電解質の形態とすることもできる。

【実施例】

【００４４】

以下に本発明の実施例を示すが、以下の実施例に本発明が限定されることを意図するものではない。

【００４５】

電解槽の中に、直径約３１３３ｍｍ、幅２４７６．５ｍｍのチタン製の回転ドラムと、ドラムの周囲に５ｍｍ程度の極間距離を置いて電極を配置した。この電解槽の中に、表１に記載濃度のニカワを添加した硫酸銅水溶液を導入した。そして、表１に記載の対限界電流密度比に調節し、回転ドラムの表面に銅を析出させ、回転ドラムの表面に析出した銅を剥ぎ取り、連続的に表１に記載の厚みを有する発明例及び比較例の電解銅箔を製造した。

得られた各電解銅箔に対して、先述した測定条件に従い、常態抗張力、４００℃で１時間加熱後の抗張力、４００℃で１時間加熱後の抗張力の常態抗張力に対する比（保持率）、伸び率、４００℃で１時間加熱後の銅粒子径、を評価した。結果を表１に示す。

【００４６】

【表１】

	箔厚	対限界電流密度比	ニカワ濃度	抗張力			伸び率	粒子径
				常態	加熱後	初期抗張力保持率		
	(μm)	(-)	(質量ppm)	(MPa)	(MPa)	(%)	(%)	(μm)
発明例1	12	0.15	6	632	370	58.6	8.4	0.35
発明例2	12	0.16	6	672	355	52.9	8.7	0.41
発明例3	10	0.16	8	705	405	57.4	5.6	0.29
発明例4	15	0.15	8	685	423	61.8	8.4	0.25
発明例5	10	0.15	10	730	450	61.6	7.4	0.20
発明例6	10	0.14	10	704	503	71.4	6.5	0.14
発明例7	10	0.14	11	713	537	75.3	6.0	0.09
比較例1	15			672			8.8	
比較例2	10	0.15		617		48.3	8.3	0.56
比較例3	10		6	743			7.3	
比較例4	12	0.16			470	60.0	3.5	0.22
比較例5	12					67.3	9.1	
比較例6	15		6	684			8.4	

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First Named Inventor/Applicant Name:	Seung Min KIM
Customer Number:	24573
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Warnings:					
Information:					
5	Foreign Reference	JP2001140091A.pdf	602310 619cc20c46427f9d51634185ae9f0ea79b0fd9b7	no	11
Warnings:					
Information:					
6	Foreign Reference	JP2013175488A.pdf	328231 e61b1a235655e510c6e3baeb18fc268f6c4e3740	no	9
Warnings:					
Information:					
7	Foreign Reference	JP2013181236A.pdf	477064 6a29143247604ba6c870f8f6a103421242e2a993	no	10
Warnings:					
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8	Non Patent Literature	TheChemicalDictionary.pdf	7812400 eec5a74d13687033a180ad5436aadfbb7dda04ce	no	4
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			Total Files Size (in bytes):	11022431	

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Seung-Min KIM
Appl. No.:	15/696,360
Conf. No.:	7466
Filed:	September 6, 2017
Title:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1725
Examiner:	CONLEY, OI K
Docket No.:	0313221.00013

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

INFORMATION DISCLOSURE STATEMENT TRANSMITTAL LETTER

Sir:

Submitted herewith is an Information Disclosure Statement for consideration in the above-identified application. In accordance with the provisions of 37 C.F.R. 1.56, 37 C.F.R. 1.97, and 37 C.F.R. 1.98, Applicants request that a citation and examination of the references cited on the enclosed SB08 form be made during the course of examination of the above-identified application for United States patent.

This Information Disclosure Statement is submitted as follows:

Submission without Certification

[X] Within three months of filing of a national application; within three months of the date of entry of the national stage as set forth in 37 C.F.R. §1.491 in an international application; before the mailing date of a first Office Action on the merits, or before the mailing of a first Office Action after the filing of a Request for Continued Examination.

[ ] After the period specified above, but before the mailing date of a Final Action under 37 CFR 1.113, a Notice of Allowance under 37 CFR 1.311, or an Action that otherwise closes prosecution in the application and is accompanied by payment of the fee set forth in 37 CFR 1.17(p).

Submission with Certification

[ ] Within three months of filing of a national application; within three months of the date of entry of the national stage as set forth in 37 C.F.R. §1.491 in an international application; before the mailing date of a first Office Action on the merits, or before the mailing of a first Office Action after the filing of a Request for Continued Examination.

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Certification under 37 CFR 1.97(e)

[ ] The undersigned counsel for applicant(s) hereby certifies that each item of information contained in the accompanying 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.

[ ] The undersigned counsel for applicant(s) hereby certifies that no item of information contained in the accompanying Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the undersigned, after making reasonable inquiry, no item of information contained in the accompanying 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.

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[ ] The undersigned counsel for applicant(s) hereby states that each item of information contained in the accompanying Information Disclosure Statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and/or is a communication that was issued by a patent office in a counterpart foreign or international application or by the Office, and this communication was not received by any individual designated in § 1.56(c) more than **thirty days** prior to the filing of the information disclosure statement.

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[ ] The Commissioner is hereby authorized to charge the amount of $240.00 to cover the required fee to Deposit Account No. 02-1818.

[X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-1818.

Respectfully submitted,

K&L GATES LLP

BY /Matthew S. Dicke/
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Dated: January 23, 2019

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
15/696,360	09/06/2017	Seung Min KIM	0313070.00025

CONFIRMATION NO. 7466

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

PUBLICATION NOTICE

OC000000098745752

Title:EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

Publication No.US-2018-0102546-A1
Publication Date:04/12/2018

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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/.

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(Not for submission under 37 CFR 1.99)

Application Number	15696360
Filing Date	2017-09-06
First Named Inventor	Seung Min KIM
Art Unit	1725
Examiner Name	RIDLEY, BASIA ANNA
Attorney Docket Number	0313070.00025

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	1	3943214	JP	B	2007-04-13	JAPAN ENERGY CORP		
	2	2660359	EP	A1	2013-11-06	FURUKAWA ELECTRIC CO LTD.		
	3	2011108442	JP	A	2011-06-02	JX NIPPON MINING & METALS CORP		

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15696360
	Filing Date	2017-09-06
	First Named Inventor	Seung Min KIM
	Art Unit	1725
	Examiner Name	RIDLEY, BASIA ANNA
	Attorney Docket Number	0313070.00025

	4	2009116432	WO	A1	2009-09-24	NIPPON MINING CO., ET AL.		
	5	2871266	EP	A1	2015-05-13	JX NIPPON MINING & METALS CORP		

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	1	European Search Report for related European Application No. 17189147.6; report dated February 23, 2018; (8 pages)	

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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.

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15696360
	Filing Date	2017-09-06
	First Named Inventor	Seung Min KIM
	Art Unit	1725
	Examiner Name	RIDLEY, BASIA ANNA
	Attorney Docket Number	0313070.00025

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

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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.

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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	/Matthew S. Dicke/	Date (YYYY-MM-DD)	2018-03-12
Name/Print	Matthew S. Dicke	Registration Number	58819

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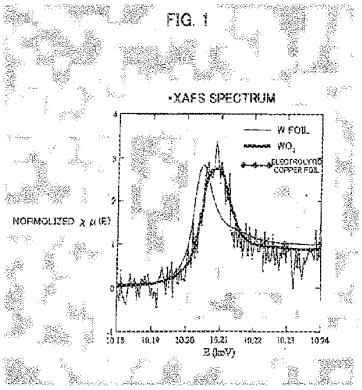
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(54) ELECTROLYTIC COPPER ALLOY FOIL, METHOD FOR PRODUCING SAME, ELECTROLYTIC SOLUTION USED FOR PRODUCTION OF SAME, NEGATIVE ELECTRODE COLLECTOR FOR SECONDARY BATTERIES USING SAME, SECONDARY BATTERY, AND ELECTRODE OF SECONDARY BATTERY

(57) Provision of an electrolytic copper alloy foil having large mechanical strength in an ordinary state and showing resistant to heat deterioration even when it is heated to 300°C or more. That electrolytic copper foil is an electrolytic copper alloy foil which contains tungsten and has a remainder (balance) comprised of copper. Preferably, that electrolytic copper foil incorporates tungsten into copper foil as a copper alloy, has a tensile strength at ordinary temperature of 650 MPa, has a tensile strength after heat treatment at 300°C for 1 hour of 450 MPa or more, and has a conductivity of 80% or more. Further preferably, the electrolytic copper foil has an elongation at ordinary temperature of 2.5% or more and an elongation after treatment at 300°C for 1 hour of 3.5% or more. The electrolytic copper foil is produced by adding a thiourea compound, tungsten salt, and chloride ions to a sulfuric acid-copper sulfate electrolyte and performing electrolytic deposition.

FIG. 1



EP 2 660 359 A1

Description

Technical Field

[0001] The present invention relates to an electrolytic copper alloy foil which has an electrolytic deposition surface with a low profile and provides a large mechanical strength and which is resistant to change in mechanical strength even if heated at a high temperature, and to a method of production of the same.
Further, the present invention relates to an electrolytic copper alloy foil forming-use electrolyte for forming the electrolytic copper alloy foil.
Note that, here, the "mechanical strength" indicates the tensile strength, 0.2% yield strength, and so on.

[0002] The present invention further relates to a rigid printed circuit board which uses the electrolytic copper alloy foil as a conductive material, a flexible printed circuit board, an electromagnetic wave shield material, and so on.
Further, the present invention relates to a secondary cell which uses the electrolytic copper alloy foil as a secondary cell-use current collector, deposits an active material on the current collector to form a secondary cell-use electrode, and includes the electrode.

Background Art

[0003] A copper foil is used in a rigid printed circuit board, a flexible printed circuit board, an electromagnetic wave shield material, acurrent collector of a cell, and other various fields.

[0004] Among these fields, in the field of printed circuit boards (flexible circuit boards, hereinafter referred to as "FPCs") which are bonded to a polyimide film, in hard disk (hereinafter, referred to as "HDD") suspension materials or tape automated bonding (hereinafter, referred to as "TAB") materials, improvement of the strength of the copper foil has been requested.

[0005] The suspensions which are mounted on HDDs have mostly changed from the conventionally used wire type suspensions to the wiring-integrated type suspensions in which buoyancy and positional accuracy of the flying head to the storage medium of the disk are stable along with the increase of the capacity of HDDs.

[0006] This wiring-integrated type suspension includes the following three types.

a. A so-called FSA (flex suspension aggregation) type obtained by working a flexible printed board and using a binder for bonding
b. A so-called CIS (circuit integrated suspension) type obtained by shaping a precursor of a polyimide resin, amic acid, then imidizing it and further plating the polyimide to thereby form wiring.
c. A so-called TSA (trace suspension aggregation) type obtained by etching a laminate comprised of stainless steel foil, polyimide resin, and copper foil to thereby work it to a predetermined shape

[0007] A TSA suspension enables easy formation of a flying lead by laminating a copper alloy foil having a high strength and has a high degree of freedom in shaping, is relatively cheap, and is good in dimensional precision, so is being widely used.

[0008] A laminate formed according to the TSA method is produced by using as materials a stainless steel foil of a thickness of about 12 to 30 μm, a polyimide layer of a thickness of about 5 to 20 μm, and a copper alloy foil of a thickness of about 7 to 14 μm.

[0009] In the production of the laminate, first, a polyimide resin solution is coated on the base member of stainless steel foil. After coating, the solvent is removed by preheating, then heat treatment is further carried out for imidization. Then, the copper alloy foil is superimposed on the imidized polyimide resin layer and the aggregation is hot pressed at a temperature of about 300°C for lamination to thereby produce a laminate comprised of a stainless steel layer, polyimide layer, and copper alloy layer.

[0010] At the time of this heating at about 300°C, the stainless steel foil does not exhibit almost any dimensional change. However, if using a conventional electrolytic copper foil, the electrolytic copper foil is annealed at a temperature of about 300°C, increasingly recrystallizes, and softens, so changes in dimensions. For this reason, the laminate warps after lamination, so the precision of dimensions of the product is lowered.
In order not to cause warping in the laminate after lamination, provision of a copper alloy foil in which the dimensional change at the time of heating is as small as possible has been desired.

[0011] Further, in a TAB material, in the same way as the HDD suspension material, raising of the strength of the copper foil and lowering of the roughness of the foil surface have been demanded.
In a TAB product, a plurality of terminals of an IC chip are directly bonded to inner leads (flying leads) arranged in a device hole located at the substantial center of the product. This bonding is carried out by using a bonding system for instantaneous electrical heating and application of a constant bonding pressure. At this time, it suffers from the disad-

vantage that the inner leads obtained by etching of the electrolytic copper foil are pulled and stretched by the bonding pressure.

Further, if the strength of the electrolytic copper foil is low, it plastically deforms to cause slack in the inner leads. In remarkable cases, there is a possibility of breakage.

Accordingly, in order to make the line width of the inner leads finer, it is demanded that the electrolytic copper foil which is used have a roughened surface which is roughened to a low degree and have a high strength.

[0012] In this case as well, it is necessary that the copper foil have a high strength in an ordinary state (ordinary temperature/ ordinary pressure state) and have a high strength even after heating. When it is used for TAB, there is used an FPC comprised of two layers or three layers formed by bonding copper foils and polyimide to each other. In a three-layer FPC, when bonding polyimide to the copper foils, an epoxy binder is used and the members are bonded to each other at a temperature of around 180°C. Further, in a two-layer FPC using a polyimide binder, bonding is carried out at a temperature of around 300°C.

[0013] Even if the electrolytic copper foil has a large mechanical strength in the ordinary state, there is no meaning if the electrolytic copper foil is softened when bonded to polyimide. The conventional high strength electrolytic copper foil has a large mechanical strength in the ordinary state and does not change much at all in mechanical strength even when it is heated at approximately 180°C. However, when it is heated at about 300°C, it is annealed and increasingly recrystallizes, therefore it is rapidly softened and falls in mechanical strength. Such copper foil is unsuitable for the purpose of TAB.

[0014] Further, copper foil is used as a current collector for use for a cell such as a lithium ion secondary cell. A lithium ion secondary cell is basically configured by a positive electrode, a negative electrode, and an electrolyte. The negative electrode is formed by coating a negative active material layer on the surface of the copper foil used as the current collector. The method of formation of the negative electrode generally carries out by: the method of dissolving a negative active material and binder resin (added for the purpose of binding the active material and copper foil substrate) in a solvent to form a slurry, coating this on the copper foil substrate, drying it at a temperature not less than a curing temperature of the binder resin, and then pressing.

[0015] As the binder resin, polyvinylidene fluoride (PVDF), styrene butadiene rubber, and so on are widely used. Active materials comprised of high theoretical capacity silicon-, tin-, or germanium alloy-based materials and the like have come into focus along with the increase of cell capacity in recent years. These have very large rates of expansion of volume along with insertion/desorption of lithium at the time of charging/discharging. The above-mentioned binder resins are insufficient in strength. Therefore, a polyimide resin, which has a high bonding strength with a copper substrate, has been preferably used. However, a polyimide resin has a very high curing temperature such as about 300°C unlike the binder resin explained above, therefore a negative current collector (copper foil) durable against this heating condition has been demanded.

[0016] In this way, in both of the FPC field and secondary cell field, a polyimide resin having a very high curing temperature such as about 300°C has begun to be used as the binder, therefore a copper foil durable against this heating condition has been demanded.

[0017] On the other hand, to obtain electrolytic copper foil which has a surface to be bonded to the polyimide resin base material with a low profile and which is excellent in mechanical strength as well, various studies such as shown below have been carried out.

For example, Patent Literature (PLT) 1, Japanese Patent No. 4120806, discloses, as a copper foil which is optimal for use for a printed circuit board and use for a negative electrode current collector for secondary cell use, a low roughened surface electrolytic copper foil which has a roughened surface which has a surface roughness Rz of 2.0 μm or less and is uniformly roughened to a low degree and which has an elongation at 180°C of 10.0% or more.

Further, PLT 1 discloses that the above electrolytic copper foil can be obtained by using an sulfuric acid-copper sulfate aqueous solution as the electrolyte and adding polyethylene imine or its derivative, a sulfonate of active organic sulfur, and chlorine ions.

[0018] PLT 2, Japanese Patent No. 4273309, discloses an electrolytic copper foil in which the surface roughness Rz is 2.5 μm or less, the tensile strength at 25°C measured within 20 minutes from the point of time of completion of electrodeposition is 820 MPa or more, and a rate of fall of the tensile strength at 25°C measured when 300 minutes have passed from the point of completion of electrodeposition with respect to the tensile strength at 25°C measured within 25 minutes from the point of completion of electrodeposition is 10% or less.

Further, PLT 2 discloses that the above electrolytic copper foil can be obtained by using an aqueous solution containing copper sulfate and sulfuric acid as the electrolyte and adding hydroxyethyl cellulose, polyethylene imine, a sulfonate of an active organic sulfur compound, acetylene glycol, and chlorine ions.

[0019] PLT 3, Japanese Patent No. 3270637, discloses a controlled, low profile electrolytic copper foil comprised of an electrolytic copper foil having a particle structure free from columnar crystals and twin boundaries and having a mean particle size of up to 10 μm wherein the particle structure is a particle structure which is substantially uniform and randomly oriented.

In this electrolytic copper foil, the maximum tensile strength at 23°C is within a range of 87,000 to 120,000 psi (600 MPa to 827 MPa) and the ultimate elongation at 180°C is 25,000 to 35,000 psi (172 MPa to 241 MPa).

[0020] In the case of the electrolytic copper foils disclosed in the above PLTs 1 to 3, the mechanical strength in the ordinary state is large in all instances, but the mechanical strength remarkably falls in a case where they are heated at a high temperature of 300°C or more.

[0021] In the case of the electrolytic copper foils disclosed in the above PLTs 1 to 3, all use an electrolyte containing copper sulfate and sulfuric acid and all use organic compounds as additives though the types of additives are different (hereinafter referred to as "organic additives").

Many organic additives usually have the effect of suppressing crystal growth. It is considered that the crystals are incorporated into the grain boundaries.

In this case, the larger the amount of the organic additive incorporated into the grain boundaries, the more improved the mechanical strength tends to become that disclosed in Non-Patent Literature (NPLT) 1: Shoji Shiga, Metal Surface Technology, Vol. 31, No. 10, p. 573 (1980)).

[0022] When the organic additive which has been incorporated into the grain boundaries is heated at a high temperature of 300°C or more, the organic additive decomposes. As a result, it is considered that the mechanical strength is lowered.

[0023] On the other hand, as copper foil satisfying the above demands, use is made of rolled copper alloy foil. Rolled copper alloy foil is not annealed much at a temperature of about 300°C, has a small dimensional change at the time of heating, and has a small change of mechanical strength as well.

However, rolled copper foil is expensive compared with electrolytic copper foil, and it is difficult to satisfy demands on width, thickness, etc. with it.

[0024] Therefore, to obtain electrolytic copper foil which has a surface to be bonded to the polyimide resin base material with a low profile and which is excellent in mechanical strength as well, the present inventors attempted to develop an electrolytic copper alloy foil which is improved in the heat resistance of the copper foil by adding tungsten to the copper foil and is suitable for applications which use a polyimide resin as a binder resin.

However, tungsten is a metal which is very hard to incorporate into electrolytic copper foil.

[0025] PLT 4 (Japanese Patent No. 3238278) and PLT 5 (Japanese Patent Publication No. 9-67693 A1) disclose addition of tungsten to the electrolyte for forming the electrolytic copper foil.

PLTs 4 and 5 relate to copper foil for a printed circuit and disclose in their examples to form foil by an electrolyte obtained by adding 20 to 100 mg/liter of tungsten (W) and chlorine ions (chloride ions) to the electrolyte and that the formed copper foil does not have pinholes, is excellent in adhesion with the resin substrate, and has a high hot-rolling elongation at 180°C. However, there is no description that tungsten was incorporated into the copper foil, that is, that a Cu-W alloy foil was produced.

[0026] In this regard, an electrolyte containing copper sulfate and sulfuric acid is used as the electrolyte of the electrolytic copper foil. Various additives are added to the plating bath for the purpose of glossing and smoothing the copper foil surface, reducing stress of the copper foil, and so on. When no additives are used, the surface morphology, mechanical properties, etc. demanded from the copper foil are not obtained, therefore the importance of additives is very high. In particular, a copper sulfate plating bath is a simple acidic solution, therefore has a poor uniform electrodeposition property, so production of a preferred electrolytic copper foil without any additives is difficult. As additives used in the copper sulfate plating bath, chlorine ions, polyoxyethylene-based surfactants, smoothening agents, organic sulfates, or another gloss agents, glue, gelatin, etc. are proposed and used.

[0027] Unless chlorine or other additives are added to the copper sulfate plating bath, plating is concentrated at high current portions in which electricity easily flows (portions near anode, end of cathode, tip ends of pointed objects, etc.) and a generally called "burning state (where the plating surface becomes more uneven)" occurs. For this reason, about 20 to 100 mg/liter of chlorine ions are added in the usual copper sulfate plating. When the chlorine ions become less than 20 mg/liter, for the above reason, burning easily occurs. Conversely, when it exceeds 80 mg/liter, the leveling action is too strong, therefore "dull deposition" occurs in low current portions (in small holes etc.).

[0028] However, when there are chlorine ions in the electrolyte, it becomes difficult to mix a specific metal into the copper foil to change the characteristics of the copper foil. That is, with an electrolyte free from chlorine ions, it is possible to mix another metal into the copper foil. The characteristics of the copper foil can be changed by mixing (alloying) another metal, but it becomes hard to mix another metal into the copper foil if chlorine ions enter the electrolyte, and it becomes extremely difficult to change the characteristics of the copper foil by another metal.

[0029] For example, PLTs 4 and 5 disclose a method of producing an electrolytic copper foil by an electrolyte obtained by adding tungsten into a sulfuric acid-copper sulfate electrolyte and further adding glue and chlorine ions and describe, as the effect thereof, that the production of copper foil having a hot-rolling elongation at 180°C of 3% or more and a large surface roughness, but with few pinholes is possible.

[0030] Therefore, the present inventors repeated the experiment of adding tungsten into the sulfuric acid-copper sulfate electrolyte and further adding glue and chlorine ions and could produce copper foil with the characteristics aimed at by the electrolytic copper foil disclosed in PLT 4 of a hot-rolling elongation at 180°C of 3% or more, a large roughness of

the roughened surface, and few pinholes. However, when heat treating this copper foil at 300°C for 1 hour, it was learned that the mechanical strength could not be kept. As a result of analysis of this copper foil, it was clarified that tungsten did not form eutectoids in the electrically deposited copper.

[0031] That is, in the method of PLTs 4 and 5, the electrodeposition was carried out by an electrolyte obtained by adding tungsten to a sulfuric acid-copper sulfate electrolyte and further adding 10 mg/liter or less of glue and 20 to 100 mg/liter of chlorine ions. Therefore, an electrolytic copper alloy foil in which eutectoids of tungsten did not form in the copper foil and in which a high mechanical strength was kept even if it was heated at 300°C could not be produced.

Citations List

Patent Literature (PLT)

[0032]

PLT1: Japanese Patent No. 4120806
PLT2: Japanese Patent No. 4273309
PLT3: Japanese Patent No. 3270637
PLT4: Japanese Patent No. 3238278
PLT5: Japanese Patent Publication No. 9-67693 A1
PLT6: Japanese Patent No. 3238278
PLT7: Japanese Patent Publication No. 9-67693 A1

Non-Patent Literature (NPLT)

[0033] NPLT 1: Shoji Shiga, Metal Surface Technology, Vol. 31, No. 10, p. 573 (1980)

Summary of Invention

Technical Problem

[0034] The present inventors overcame the problems explained above and, by incorporating tungsten into the copper alloy in the copper foil, succeeded in forming an electrolytic copper alloy foil with a tensile strength at ordinary temperature of 650 MPa or more, a tensile strength after heat treatment at 300°C for 1 hour of 450 MPa or more, and a conductivity of 80% or more.

Further, the present inventors enabled use of a polyimide binder for example for a HDD suspension material and TAB material or for an active material of an Si or Sn alloy active material which repeatedly greatly expands and contracts and succeeded in developing as a conductor (copper foil) an electrolytic copper alloy foil which will not deform or break.

[0035] An object of the present invention is to provide an electrolytic copper alloy foil having a tensile strength at ordinary temperature of 650 MPa or more, a tensile strength after heat treatment at 300°C for 1 hour of 450 MPa or more, and a conductivity of 80% or more.

Further, another object of the present invention is to provide an electrolytic copper alloy foil excellent in mechanical strength in applications in the field of printed circuit boards bonded to polyimide film.

Further, still another object of the present invention is to provide a copper alloy foil in a lithium ion secondary cell using an Si or Sn alloy active material in which an adhesion between the collector (copper foil) and the active material is maintained by the polyimide binder even against large expansion and contraction of the Si or Sn alloy active material and in which the current collector (copper foil) will not deform or break.

Solution to Problem

[0036] An electrolytic copper alloy foil of the present invention is an electrolytic copper alloy foil containing tungsten. Preferably all or a portion of the tungsten is incorporated as an oxide.

[0037] Further, according to the present invention, there is provided an electrolytic copper alloy foil containing tungsten and has a remainder (balance) substantially comprised of copper. Note that, the above "remainder (balance) is substantially comprised of copper" means that the copper contains unavoidable impurities or contains a small amount of additives.

[0038] Preferably, it is an electrolytic copper alloy foil in which a peak intensity ratio I<220>/I<200> obtained by X-ray diffraction between the peak intensity I<220> of the crystal orientation <220> and the peak intensity I<200> of the crystal orientation <200> is 1.2 or more.

Further preferably, the electrolytic copper alloy foil contains 0.0001 to 0.060 wt% or tungsten.

[0039] Further, according to the present invention, there is provided an electrolytic copper alloy foil containing 0.001 to 0.055 wt% of tungsten, having a tensile strength at ordinary temperature of 650 MPa or more, and having a tensile strength after treatment at 300°C for 1 hour of 450 MPa or more.

[0040] Further, according to the present invention, there is provided an electrolytic copper alloy foil containing 0.001 to 0.055 wt% of tungsten, having a tensile strength at ordinary temperature of 650 MPa or more, having a tensile strength after treatment at 300°C for 1 hour of 450 MPa or more, and having a conductivity of 80% or more.

[0041] Preferably it further contains chlorine ions.

[0042] Further preferably, the content of the chlorine is 0.005 to 0.040 wt%.

[0043] Preferably the electrolytic copper alloy foil has an elongation at ordinary temperature of 2.5% or more and an elongation after treatment at 300°C for 1 hour of 3.5% or more.

[0044] According to the present invention, there is provided a negative electrode current collector used for secondary cell which uses the electrolytic copper alloy foil disclosed in any of above.

[0045] Further, according to the present invention, there is provided an electrode for secondary cell use in which an electrolytic copper alloy foil disclosed in any of the above is used as a negative electrode current collector for a secondary cell and in which an active material containing as a principal ingredient silicon, germanium, tin, or alloyed compound of the same is deposited on the surface.

[0046] According to the present invention, there is provided a secondary cell using the above electrode for secondary cell use.

[0047] According to the present invention, there is provided a method of production of an electrolytic copper alloy foil used for producing an electrolytic copper alloy foil containing tungsten and has a remainder (balance) comprised of copper, comprising the steps of adding a thiourea compound, tungsten salt, and chlorine ions to a sulfuric acid-copper sulfate electrolyte as additives, and performing electrolytic deposition.

[0048] Further, according to the present invention, there is provided a method of production of a copper alloy foil containing 0.001 to 0.055 wt% of tungsten, having a tensile strength at ordinary temperature of 650 MPa or more, having a tensile strength after treatment at 300°C for 1 hour of 450 MPa or more, and having a conductivity of 80% or more, wherein the copper alloy foil is formed by a copper sulfate electrolyte obtained by adding, as additives, 10 to 1,000 ppm of tungsten, 1 to 20 ppm of at thiourea compound, and 1 to 100 ppm of chlorine ions to the copper sulfate electrolyte.

[0049] According to the present invention, there is provided an electrolyte for forming an electrolytic copper foil containing copper sulfate, sulfuric acid, and chlorine ions and having tungsten or a tungsten compound and thiourea organic additive added to it.

[0050] Preferably, the electrolyte has 10 to 1,000 ppm of tungsten or a tungsten compound as tungsten, 1 to 20 ppm of a thiourea compound, and 1 to 100 ppm of chlorine ions added to it.

[0051] Further preferably, the thiourea compound added to the electrolyte is any of thiourea, N,N-diethylthiourea, tetramethylthiourea, and ethylene thiourea.

[0052] Further preferably, the electrolyte has at least one of ammonia ions and nitrate ions added to it.

[0053] According to the present invention, there is provided an electrolytic copper alloy foil which is electrolytically formed by using the electrolyte for forming electrolytic copper alloy foil described above.

Advantageous Effects of Invention

[0054] According to the present invention, an electrolytic copper alloy foil having a large mechanical strength in an ordinary state and resistant to heat deterioration even by heating at 300°C or more can be provided.

Brief Description of Drawings.

[0055] [FIG. 1] FIG. 1 is an XAFS spectrum diagram of an electrolytic copper alloy foil of the present invention.

Description of Embodiments

[0056] An electrolytic copper alloy foil of the present invention is an electrolytic copper alloy foil (Cu-W alloy foil) containing tungsten and having a remainder (balance) comprised of copper.

The amount of tungsten contained in the electrolytic copper alloy foil is preferably within a range from 0.0001 to 0.060 wt%. The reason for why the content of tungsten is preferably controlled to 0.0001 wt% or more is that there is almost no effect of addition of tungsten if the content is less than 0.0001 wt%. On the other hand, the reason for making the amount of addition of tungsten preferably 0.060 wt% or less is that the effect is already saturated even when it is added over 0.060 wt% and no effect of improvement of physical properties is seen.

[0057] That is, the copper alloy foil obtained by adding tungsten in an amount less than 0.0001 wt% tends to fall in mechanical strength after heating at 300°C for 1 hour in the same way as the case where tungsten is not contained. The larger the amount of addition of tungsten, the smaller the drop of the strength after heating at 300°C for 1 hour.

However, when the content becomes larger to a certain extent, the effect is saturated. Accordingly, the upper limit of the amount of addition is about 0.060 wt%.

[0058] The inventors of the present invention repeated various experiments in order to produce a Cu-W alloy foil. As a result, in an electrolyte containing chlorine ions, tungsten was not incorporated into the formed copper foil even when a large amount of tungsten was added into the solution. Naturally, the mechanical strength of the copper foil formed by such an electrolyte at ordinary temperature and after heating was not improved.

However, the inventors discovered that even if chlorine ions are added to the electrolyte, if a thiourea compound is added to the solution, according to the foil formation conditions, tungsten is incorporated into the foil.

When analyzing the factors of incorporation of tungsten into the copper foil based on such a discovery, the following result was obtained: the tungsten is incorporated into the copper foil if the ratio between the peak intensity I<220> in the crystal orientation <220> and the peak intensity I<200> in the crystal orientation <200> which is obtained by the X-ray diffraction of the copper foil, that is, the peak intensity ratio I<220>/I<200>, is 1.2 or more.

[0059] By forming the electrolytic copper alloy foil under the following conditions based on such a discovery, the inventors succeeded in the production of an electrolytic copper alloy foil excellent in heat resistance.

That is, by forming a copper alloy foil having a tensile strength after heating at 300°C for 1 hour of 450 MPa or more by the following basic electrolytic bath composition and electrolytic conditions, an electrolytic copper alloy foil in which the peak intensity ratio obtained by the X-ray diffraction of the electrolytic copper alloy foil, i.e., I<220>/I<200>, becomes 1.2 or more and in which tungsten is incorporated as a Cu-W alloy into the foil can be produced.

Basic electrolytic bath composition:

[0060]

Cu=50 to 150 g/liter
H_2SO_4=20 to 200 g/liter
Cl=1 to 100 ppm
Sodium tungstate (as tungsten)=10 to 1,000 ppm
Thiourea compound=3 to 20 ppm
Electrolytic conditions:
Current density=30 to 100 A/dm^2
Solution temperature=30 to 70°C

[0061] The additives added to the sulfuric acid-copper sulfate electrolyte are as follows.

Additive A: Thiourea compound
Additive B: Tungsten salt
Additive C: Chlorine ions

[0062] Additive A: A thiourea compound is an organic compound having the following structure.



Examples of thiourea compounds are thiourea, N,N-diethylthiourea, tetramethylthiourea, and ethylene thiourea. However, these only exemplify ones used in the examples which will be explained later. Any compound is useable so far as the compound has the structural characteristics as explained above and exhibits the same effects.

[0063] Additive B: A tungsten salt is dissolved in the electrolyte containing copper sulfate and sulfuric acid. There can be mentioned sodium tungstate, ammonium tungstate, potassium tungstate, etc.

[0064] Additive C: The additive of chlorine ions is selected from among compounds which dissolve in an electrolyte containing copper sulfate and sulfuric acid. There can be mentioned hydrochloric acid, sodium chloride, potassium chloride, and so on.

[0065] The reason for use of a thiourea compound as an organic additive is that these compounds easily change to the structure of [=S] in the solution. The [=S] structure is adsorbed at the copper with a high priority to form an adsorbed layer of organic molecules. By adsorption of tungsten oxide onto the adsorbed layer, tungsten is incorporated into the foil together with the thiourea compound.

The tungsten exists as an oxide in an acidic solution. However, by electrodeposition of copper using an electrolyte containing chlorine, the copper-precipitated surface is coated by the chlorine ions, therefore the tungsten oxide is not

adsorbed to the copper, so incorporation of tungsten into the foil does not occur. When a thiourea compound is added to the electrolyte, the [=S] structure is adsorbed onto the copper with a higher priority than the chlorine ions, and an adsorbed layer of organic molecules is formed on the copper. It is believed that tungsten is incorporated into the foil together with the thiourea compound by adsorption of the tungsten oxide onto the adsorbed layer.

[0066] In this way, the electrolytic copper alloy foil of the present invention is formed from an electrolyte containing tungsten, a thiourea compound, and chlorine in a sulfuric acid-copper sulfate electrolyte by electrolytic deposition. It is considered that, if electrolytically depositing copper in this sulfuric acid-copper sulfate electrolyte containing tungsten, a thiourea compound, and chlorine, the tungsten oxide is adsorbed at the grain boundaries of the copper together with the thiourea compound, the growth of crystal nuclei is suppressed, and refinement of crystal grains is caused (lowering of profile), and an electrolytic copper alloy foil provided with a large mechanical strength in an ordinary state is formed.

[0067] Further, the inventors of the present invention repeated various experiments for producing Cu-W alloy foil. As a result, with an electrolyte containing chlorine ions, even when a large amount of tungsten was added into the solution, incorporation of tungsten into the electrolytic copper foil did not occur. Further, as disclosed in PLTs 4 and 5, even when tungsten and glue were added to the electrolyte containing chlorine ions, incorporation of tungsten into the electrolytic copper foil did not occur.

Naturally, the electrolytic copper foil formed by such an electrolyte was greatly lowered in mechanical strength after heating at a high temperature of about 300°C.

However, the inventors discovered that if a thiourea compound is added to the electrolyte, even if chlorine ions are contained, according to the foil formation conditions, tungsten is incorporated into the foil.

[0068] When analyzing the factors of incorporation of tungsten into copper foil based on such discovery, result as obtained that incorporation of tungsten was promoted if the peak intensity ratio obtained by the X-ray diffraction of the copper foil, i.e., I<220>/I<200>, was 1.2 or more.

[0069] It is considered that the tungsten oxide at the grain boundaries of this copper alloy foil remains at the grain boundaries as tungsten oxide as it is without bonding with or being absorbed at the bulk copper crystal.

Accordingly, it is considered that, even if electrolytic copper alloy foil containing tungsten is heated at a high temperature of about 300°C, the tungsten oxide remains at the grain boundaries and acts to prevent fine crystals of the copper from recrystallization and the crystals from coarsening due to heat.

[0070] Accordingly, the electrolytic copper foil of the present invention exhibits excellent characteristics which are not seen in electrolytic copper foils produced by a sulfuric acid-copper sulfate electrolyte using organic additives hitherto such as a low profile and a small drop of mechanical strength even after heating at a high temperature of about 300°C.

[0071] It is considered that a thiourea compound which is added to a sulfuric acid-copper sulfate electrolyte forms a complex in the electrolyte together with the metal elements and chlorine.

When tungsten is not added, the metal element added to the electrolyte for forming electrolytic copper foil is copper. Accordingly, a copper- thiourea compound is formed in the electrolyte containing copper sulfate and sulfuric acid. When the electrolytic copper foil is formed by the electrodeposition of copper by this electrolyte, an electrolytic copper foil in which the copper-thiourea compound is adsorbed at the grain boundaries, the growth of crystal nuclei is suppressed, the crystal grains are made finer, and a large mechanical strength is provided in the ordinary state is formed.

[0072] However, in this copper foil, the substance existing at the grain boundaries is a copper-thiourea compound, therefore the copper is bonded to the bulk copper crystals or adsorbed, and the substance at the grain boundaries becomes only the thiourea compound. Therefore, it is considered that decomposition occurs when the foil is exposed to a high temperature of about 300°C and, as a result, the mechanical strength falls.

[0073] The reason for the remarkable drop in the tensile strength in the case of heating at a high temperature of about 300°C is considered to be that, as described above, the compound existing in the grain boundaries is an organic compound, and an organic compound is easily decomposed by heating at about 300°C, therefore the mechanical strength falls.

[0074] In the method disclosed in PLTs 1 to 3, different organic compounds are used for the electrolytic deposition to produce electrolytic copper foils. However, all of them are produced from a sulfuric acid-copper sulfate electrolyte containing an organic additive and chlorine, and it is the organic compound ingredient that is adsorbed at the grain boundaries of the electrolytic copper foil. Therefore, the reason for the remarkable drop in the mechanical strength in the case where such an electrolytic copper foil is exposed to a high temperature of 300°C or more is considered to be that all of the compounds adsorbed at the grain boundaries are organic compounds which are easily decomposed by heating at a high temperature of 300°C or more.

[0075] Contrary to this, the present invention uses an electrolyte obtained by further adding tungsten, a thiourea compound, and chlorine ions to an electrolyte containing copper sulfate and sulfuric acid for copper electrodeposition to form a copper alloy foil, therefore the tungsten oxide is adsorbed onto the copper together with the thiourea compound. An electrolytic copper alloy foil in which the growth of crystal nuclei is suppressed by the adsorbed tungsten oxide and thiourea compound, the crystal grains are made finer, and large mechanical strength is provided in an ordinary state is formed.

[0076] In this way, in the electrolytic copper alloy foil of the present invention, the tungsten oxide and thiourea compound are at the grain boundaries. Therefore, unlike the case of a copper-thiourea compound, it is considered that the tungsten oxide is not bonded with or adsorbed at the bulk copper crystals, but the tungsten oxide and thiourea compound remain as they are at the grain boundaries. For this reason, even if the foil is exposed to a high temperature of about 300°C, the tungsten oxide remains at the grain boundaries and acts to prevent the fine crystals of copper from recrystallizing due to heat and the crystals from coarsening.

[0077] The amount of tungsten added into the electrolyte is preferably 10 to 1,000 ppm. The reason for setting the amount of addition of tungsten to 10 ppm or more is that the effect of including tungsten does not appear when the amount is less than this and the effect such as improvement of the tensile strength is not improved even if tungsten is contained exceeding 1,000 ppm. Accordingly, the amount of addition of tungsten is preferably set to 10 to 1,000 ppm.

[0078] As explained above, it is extremely difficult to squarely incorporate tungsten into copper foil by an electrolyte obtained by adding chlorine ions. In the present invention, however, by adding a thiourea compound, incorporation of tungsten into the copper foil was successful.

The reason for why the amount of the thiourea compound added is set to 3 ppm to 20 ppm is that a prescribed amount of tungsten cannot be incorporated into the copper foil if the amount is less than 3 ppm, therefore the tensile strength after heating at 300°C for 1 hour becomes 450 MPa or less, while tungsten enters into the copper foil too much if the thiourea compound is added exceeding 20 ppm, therefore the tensile strength becomes too high or elongation becomes small, so property which is not preferred appears. Therefore, the preferred range of the amount of addition is 3 ppm to 20 ppm.

[0079] The amount of addition of chlorine ions is 1 to 100 ppm. This is because if the addition of chlorine ions is less than 1 ppm, many pinholes are formed in the foil, therefore this is not preferred, while when the chlorine ions are added exceeding 100 ppm, the inconvenience that the surface roughness becomes remarkably large is manifested. Accordingly, preferably the amount of chlorine ion is controlled to the range of 1 to 100 ppm, particularly preferably 15 to 50 ppm.

[0080] The electrolytic copper alloy foil is formed by using a copper sulfate solution obtained by adding the above prescribed amounts of tungsten, the thiourea compound, and chlorine ions as the electrolyte, using titanium coated with a precious metal oxide as the anode, using a rotary drum made of titanium as a cathode, and performing electrolytic treatment under conditions of a current density of 30 to 100 A/dm^2 and solution temperature of 30 to 70°C.

By forming the foil under such conditions, the peak intensity ratio I<220>/I<200> obtained by X-ray diffraction can be made 1.2 or more, and incorporation of tungsten into the electrolytic copper foil can be promoted.

[0081] Preferably, the mechanical strength after heating at 300°C for 1 hour of the electrolytic copper alloy foil formed by adding ammonium ions or nitrate ions to the electrolyte of the present invention can be further improved.

The amount of the ammonium ions added to the electrolyte is suitably 1 to 15 g/liter, while the amount of the nitrate ions is suitably 50 to 200 mg/liter. When further improving the mechanical strength after the heat treatment, preferably ammonia ions or nitrate ions are added to the electrolyte.

[0082] By using the electrolyte and forming the foil with the proper current density and solution temperature, an electrolytic copper alloy foil in which the tensile strength after heating at 300°C for 1 hour is 450 MPa or more, the elongation after heating at 300°C for 1 hour is 3.5% or more, and the conductivity is 80% or more can be produced.

[0083] As explained above, the current collector (copper foil) forming the negative electrode current collector of the lithium ion secondary cell must be durable against the usual heat treatment of 300°C for 1 hour when using a polyimide binder. That is, the surface of the current collector for lithium ion secondary cell use is coated with an active material composition made into a paste state by adding a solvent or the like to a mixture of an active material, conductive material, and binder and the result is dried to obtain a negative electrode of the lithium ion secondary cell. In that drying process, a heat treatment at 300°C for 1 hour is needed. As the copper foil which is durable against the heating conditions in this drying process and durable against the expansion and contraction by the charging-discharging cycle of the active material, a performance satisfying the conditions of a tensile strength after heating at 300°C for 1 hour of 450 MPa or more and elongation of 3.5% or more is necessary.

[0084] Further, Si, Sn, and other active materials have a poor electron conductivity compared with an active material such as carbon. If the conductivity of the active material is bad, the internal resistance of the electrode rises, therefore the cycle characteristics deteriorate. For this reason, a conductivity of 80% or more is demanded from the copper foil as the current collector.

The Cu-W alloy foil of the present invention satisfies the various characteristics demanded by the current collector for secondary cell use described above. Accordingly, by using such an electrolytic copper alloy foil as the current collector, depositing silicon, germanium, tin, or an alloyed compound of them or an active material containing them as principal ingredients on the current collector to form an electrode and assembling the electrode, a lithium ion secondary cell having excellent performance can be produced.

Examples

<Example A>

[0085] Electrolytes containing copper sulfate and sulfuric acid obtained by adding copper, sulfuric acid, chlorine ion, tungsten, and thiourea organic additives in the amounts shown in Table 1 were used to form electrolytic copper alloy foils under the following electrolytic conditions using a precious metal oxide-coated titanium as the anode and a rotary drum made of titanium as the cathode:

Electrolytic conditions

Current density: 30 to 100 A/dm^2

Temperature: 30 to 70°C

[0086] Note that, "after heating" means after heating at 300°C for 1 hour in an inert gas atmosphere

[0087]

[Table 1]

			Solution concentration					Foil-form condition	Content in alloy foil		Copper foil characteristics					Cell performance
			Cu	H_2SO_4	Cl	Organic matter	W	Current density	W	Cl	Strength at ord. temp.	Strength after heating	Elongation at ord. temp.	Elongation after heating	Conductivity	Deformation of foil
		Organic compound	g/l	g/l	ppm	ppm	ppm	A/dm^2	Wt%	Wt%	MPa	MPa	%	%	%	
Ex. (optimal range)	1-1	Thiourea	70	50	30	2.0	100	40	0.0180	0.0200	650	496	2.8	6.2	92	No wrinkles or other changes
	1-2		70	50	10	6.5	30	40	0.0050	0.0100	720	465	2.5	6.8	94	No wrinkles or other changes
	1-3		100	90	10	15.0	200	40	0.0253	0.0132	650	530	3.5	4.9	80	No wrinkles or other changes
	1-4		50	40	30	3.0	30	40	0.0140	0.0230	660	510	2.5	5.1	93	No wrinkles or other

																changes
	1-5	Ethylene thiourea	70	50	30	5.0	100	40	0.0230	0.0200	720	520	3.3	4.6	87	No wrinkles or other changes
	1-6		70	50	30	3.0	150	40	0.0212	0.0200	660	480	4.3	6.1	90	No wrinkles or other changes
	1-7		100	90	10	20.0	1000	40	0.0545	0.0160	830	601	4.2	3.9	80	No wrinkles or other changes
	1-8		70	50	30	7.0	80	40	0.0208	0.0230	738	510	3.3	4.2	90	No wrinkles or other changes
	1-9		70	50	50	5.0	100	40	0.0130	0.0330	680	475	4.7	7.1	89	No wrinkles or other changes
	1-10	Tetra-methyl thiourea	70	50	30	6.0	10	40	0.0017	0.0080	710	454	3.3	7.3	97	No wrinkles or other changes
	1-11		70	50	10	6.0	30	40	0.0040	0.0160	740	463	2.5	6.9	90	No wrinkles or other changes
	1-12		100	90	90	9.0	50	40	0.0120	0.0280	750	450	3.1	7.0	93	No wrinkles or other

																changes
	1-13		50	40	50	3.0	10	40	0.0015	0.0230	650	452	3.6	7.1	97	No wrinkles or other changes
	1-14		70	50	30	3.0	10	60	0.0010	0.0170	680	450	3.4	6.8	95	No wrinkles or other changes
	1-15	N,N-diethyl thiourea	70	50	30	5.0	100	40	0.0180	0.0180	652	476	2.9	6.9	86	No wrinkles or other changes
	1-16		90	65	10	13.0	200	40	0.0460	0.0080	730	530	3.4	4.5	80	No wrinkles or other changes
	1-17		70	50	50	7.0	100	40	0.0192	0.0400	663	479	3.2	7.2	87	No wrinkles or other changes
Ex. (good Rang e)	1-18	Thiourea	70	50	30	1.5	8	40	0.0003	0.0223	500	320	4.3	4.8	83	Wrinkles
	1-19		100	90	4	22.0	1010	40	0.0560	0.0050	535	410	5.2	8.3	75	Wrinkles
	1-20		70	50	30	1.5	100	40	0.0150	0.0230	500	400	4.3	4.8	81	Wrinkles
	1-21		70	50	80	4.0	50	40	0.0001	0.0350	520	360	4.3	4.6	83	Wrinkles
	1-22	Ethylene thiourea	70	50	30	3.0	45	40	0.0004	0.0302	640	400	2.6	3.4	88	Wrinkles
	1-23		70	50	8	22.0	1010	40	0.0580	0.0071	800	440	3	3.5	70	Some wrinkles
	1-24	Tetra-	70	50	30	1.5	30	80	0.0003	0.0182	600	445	4.8	6.3	81	Some

		methyl														wrinkles
	1-25	thiourea	70	50	5	21.0	1010	40	0.0592	0.0055	580	428	3.3	4.4	72	Wrinkles
	1-26		70	50	60	12.0	7	80	0.0002	0.0054	630	300	3.7	6	82	Wrinkles
	1-27	N,N-diethyl thiourea	70	50	5	21.0	1010	40	0.0570	0.0110	660	425	2.8	3.5	71	Some wrinkles

Rustproofing

[0088] The electrolytic copper alloy foils formed in this way were treated for rustproofing under the following conditions. The formed electrolytic copper alloy foils (untreated copper alloy foils) were dipped in an aqueous solution of 1 g/liter of CrO_3 for 5 seconds to apply chromate treatment, then were washed by water and then dried.
Note that, here, a chromate treatment was carried out, but naturally a benzotriazole treatment or silane coupling agent treatment may be carried out or silane coupling agent treatment may be carried out after the chromate treatment.

<Comparative Example>

[0089] Electrolytes containing copper sulfate and sulfuric acid obtained by adding copper, sulfuric acid, chlorine, tungsten, a thiourea organic additive, or glue in the amounts shown in Table 2 were used to form electrolytic copper alloy foils under the following electrolytic conditions by using precious oxide-coated titanium as the anode and a rotary drum made of titanium as the cathode.

Electrolytic conditions

Current density: 10 to 40 A/dm^2

Temperature: 30 to 70°C

[0090] The copper foils formed in this way were treated on their surfaces in the same way as the examples.
[0091]

[Table 2]

			Solution concentration					Foil-form Conditions	Content in alloy foil		Copper foil characteristics					Cell performance
			Cu	H_2SO_4	Cl	Organic matter	W	Current density	W	Cl	Strength at ord. temp.	Strength after heating	Elongation at ord. Temp.	Elongation after heating	Conductivity	Deformation of foil
		Organic compound	g/l	g/l	ppm	ppm	ppm	A/dm^2	wt%	wt%	MPa	MPa	%	%	%	
Comp. ex.	1-1	Ethylene thiourea	70	50	30	1.5	100	10	0	0.0200	430	210	6.1	7.8	90	Large deformation
	1-2	N,N-diethyl thiourea	70	50	30	1.5	8	40	0	0.0150	440	230	4.1	6.2	90	Large deformation
	1-3	Glue	70	50	30	100.0	200	40	0	0.0011	420	205	2.7	4.1	98	Large deformation
	1-4		70	50	30	3.0	200	40	0	0.0010	400	200	2.5	3.5	99	Large deformation

The prepared copper foils were tested as follows.

Measurement of content of tungsten in copper alloy foil

[0092] The tungsten content was found by dissolving a constant weight of electrolytic copper alloy foil by acid, then measuring tungsten in the solution by ICP emission spectrum analysis.
Used apparatus: ICPS-7000 (Shimadzu Corporation)

Measurement of tensile strength and elongation of copper alloy foil

[0093] The tensile strength and elongation of the copper alloy foil were measured for foils before heating and after heating based on the IPC-TM-650.
Used apparatus: AG-1 (Shimadzu Corporation)

Measurement of conductivity

[0094] The conductivity was calculated by first measuring the resistance value of 20×200 mm length copper foil, then dividing the measured resistance value by the cross-sectional area of the copper foil.

[0095] The resistance value was measured based on JIS-K6271 by the four-terminal method (current-voltage method).

Measurement of chlorine content

[0096] The chlorine content was calculated by dissolving a constant weight of electrolytic copper alloy foil by acid, then assaying the chlorine in the solution by titration of silver nitrate.

Analysis of tungsten

[0097] The chemical bonding state and electron state of the tungsten contained in the electrolytic copper alloy were analyzed by the XAFS (X-ray absorption fine structure) method. In the XAFS method, samples were irradiated by X-rays while changing the X-ray energy. From the obtained X-ray absorption spectrum, the chemical bonding state and electron state in the samples werere analyzed.
Other than this, as the technique of obtaining the X-ray absorption spectrum, there are a transmission method of finding the X-ray absorption spectrum from the intensity of the incident X-rays and the intensity of the transmitted X-rays and a fluorescence method of measuring the intensity of the fluorescence X-rays emitted from the sample along with the absorption of the X-rays.
When a metal material or other additive element is the subject for analysis, the amount of addition is very small. Therefore it is difficult to obtain the XAFS spectrum by the transmission method. It is the fluorescence method described above that is effective in such a case. The characteristic feature of the fluorescence method resides in that a wide irradiation area of X-rays can be taken from its optical axis system, therefore XAFS measurement is possible even for elements which are very small in amount.
The present measurement was carried out for the purpose of learning the chemical bonding state and electron state of tungsten in high strength copper foil. Since the amount of tungsten is very small and it is difficult to obtain the XAFS spectrum by the transmission method, the fluorescence method was selected.
For measurement, use was made of the Engineering Science Research Beamline BL14B2 of SPring-8. The energy range of the measured X-rays was made 10000 to 10434 eV. Within this energy range, there is an L3-absorption end (10207eV) of tungsten, therefore this is suitable for the purpose of the present measurement.

An example of the measurement will be shown in FIG. 1.

[0098] As the measurement sample, copper foil (Example 23) containing 0.058 wt% of tungsten was prepared. Further, for comparison, tungsten foil and WO_3 were prepared. The measurement time was made 4 hours per sample. The spectrum of the tungsten-containing copper foil had a peak in an energy region almost coincident with the spectrum of not tungsten, but WO_3. Therefore, it was seen that the tungsten element in the electrolytic copper foil was contained in the oxide state. As a result of measurement for examples based on this result, it was confirmed that tungsten was contained in the oxide state.

Cell performance test

[0099] Next, using the electrolytic copper foils formed in the examples as the current collectors, lithium secondary cells were prepared, and cycle life tests were carried out.
A powder-shaped Si alloy active material (mean particle diameter: 0.1 μm to 10 μm) in a ratio (weight ratio) of 85 and a binder (polyimide) in a ratio of 15 were mixed, and the mixture was dispersed in N-methylpyrrolidone (solvent) to form an active material slurry.
Then, this slurry was coated on the two surfaces of the prepared electrolytic copper foil having a thickness of 12 μm. The foil was dried and then press formed by a roller press machine. After that, it was annealed at 300°C for 1 hour under a nitrogen atmosphere to form a negative electrode. In this negative electrode, the film thicknesses of the negative electrode mixture at the two surfaces after shaping were the same 20 μm.

Preparation of lithium secondary cell

[0100] In a glovebox in an argon atmosphere, three-electrode type cells for evaluation use were constructed by the following configuration.
Negative electrode: Si alloy negative electrode prepared as described above
Counter electrode, reference electrode: Lithium foil
Electrolyte: 1 mol/liter of $LiPF_6$/EC+DEC (3:7 vol%)

[0101] The constructed cells were taken out of the box into the atmosphere and were measured for charging/discharging life in the atmosphere at 25°C.
Charging was carried out by a constant current up to 0.02V with respect to the standard single-electrode potential reference of Li. After that, charging was ended at the point of time when the current of CV (constant potential as it was) was lowered by 0.05C. Discharge was carried out up to 1.5V (Li reference) with the constant current by 0.1C. Charging/discharging was repeated with the same current corresponding to 0.1C.
For evaluation of the charging/discharging performances, after performing 100 cycles of charging/discharging, the cells were disassembled and deformation and breakage of foil were checked for. The results thereof are shown in Tables 1 and 2.
The tungsten content of the tungsten-containing electrolytic copper foil is preferably 0.0001 to 0.060 wt%, particularly preferably 0.001 to 0.055 wt%. When out of this range, wrinkles were formed after the charging/discharging test.

[0102]

[Table 3]

	Electrolyte			Foil-form condition	Characteristics of copper foil				Cell characteristics	
	Organic additive	Organicadditive concentration (ppm)	W concentration in bath (ppm)	Current density (A/dm^2)	I (220) / I (200)	W content in alloy foil (wt%)	Tensile strength before heating (MPa)	Tensile strength after heating (MPa)	Cycle life	Deformation of foil
Ex. 2-1	Thiourea	3	10	20	5.3	0.003 5	660	462	113	Good
Ex. 2-2				40	7.4	0.006 6	676	468	123	Good
Ex. 2-3				60	1.6	0.001 9	673	454	105	Good
Ex. 2-4		10	100	20	8.0	0.020 8	670	483	139	Good
Ex. 2-5				40	9.3	0.024 1	709	496	153	Good
Ex. 2-6				60	4.0	0.015 7	702	472	131	Good
Ex. 2-7		20	1000	20	10.6	0.037 2	763	537	162	Good
Ex. 2-8				40	11.9	0.046 9	758	563	168	Good
Ex. 2-9				60	4.5	0.022 4	755	510	157	Good
Ex. 2-10	Ethylene thiourea	3	10	20	6.1	0.006 7	649	468	124	Good
Ex. 2-11				40	7.7	0.007 7	667	476	133	Good
Ex. 2-12				60	4.8	0.004 3	661	465	115	Good

(continued)

	Electrolyte			Foil-form condition	Characteristics of copper foil				Cell characteristics	
	Organic additive	Organicadditive concentration (ppm)	W concentration in bath (ppm)	Current density (A/dm^2)	I (220) / I (200)	W content in alloy foil (wt%)	Tensile strength before heating (MPa)	Tensile strength after heating (MPa)	Cycle life	Deformation of foil
Ex. 2-13		10	10	20	6.6	0.008 1	720	509	150	Good
Ex. 2-14				40	8.1	0.010 4	740	513	160	Good
Ex. 2-15				60	3.4	0.004 1	745	507	142	Good
Ex. 2-16			100	20	8.8	0.022 0	721	514	158	Good
Ex. 2-17				40	9.4	0.025 8	748	520	163	Good
Ex. 2-18				60	6.1	0.017 5	742	509	148	Good
Ex. 2-19			1000	20	9.0	0.028 9	734	559	167	Good
Ex. 2-20				40	12.3	0.050 3	756	609	173	Good
Ex. 2-21				60	7.2	0.024 8	756	543	168	Good
Ex. 2-22		20	1000	20	12.9	0.051 8	775	609	180	Good
Ex. 2-23				40	13.2	0.053 3	788	610	179	Good
Ex. 2-24				60	8.1	0.028 4	786	557	164	Good
Ex. 2-25	N,N-diethy l thiourea	3	10	20	5.1	0.004 2	655	468	115	Good
Ex. 2-26				40	7.0	0.006 3	670	473	133	Good
Ex. 2-27				60	2.2	0.001 6	684	452	105	Good
Ex. 2-28		10	100	20	7.5	0.020 3	701	504	147	Good
Ex. 2-29				40	9.5	0.025 0	739	519	160	Good
Ex. 2-30				60	3.3	0.013 9	737	475	132	Good
Ex. 2-31		20	1000	20	9.3	0.030	741	558	165	Good

(continued)

	Electrolyte			Foil-form condition	Characteristics of copper foil			Cell characteristics	
	Organic additive	Organic additive concentration (ppm)	W concentration in bath (ppm)	Current density (A/dm^2)	I (220) / I (200)	W content in alloy foil (wt%)	Tensile strength before heating (MPa)	Tensile strength after heating (MPa)	Cycle life	Deformation of foil
						g				
Ex. 2-32				40	11.2	0.045 4	750	680	170	Good
Ex. 2-33				60	3.3	0.019 5	754	543	167	Good
Ex. 2-34	Tetra-methyl thiourea	3	10	20	2.1	0.001 4	693	453	106	Good
Ex. 2-35				40	3.4	0.002 1	691	466	130	Good
Ex. 2-36				60	1.2	0.001 0	680	452	103	Good

[0103]

[Table 4]

	Electrolyte			Foil- form condition	Copper foil				Cell characteristics	
	Organic additive	Organic additive concentration (ppm)	W concentration in bath (ppm)	Current density (A/dm^2)	I (220) / I (200)	W content in alloy foil (wt%)	Tensile strength before heating (MPa)	Tensile strength after heating (MPa)	Cycle life	Deformation of foil
Comp. Ex. 2-1	Thiourea	3	50	80	0.7	0	754	351	73	×
Comp. Ex. 2-2		20	200	10	0.9	0	310	211	81	×
Comp. Ex. 2-3	Ethylene thiourea	3	50	80	0.8	0	748	350	72	×
Comp. Ex. 2-4		20	200	10	0.9	0	321	227	79	×
Comp. Ex. 2-5	N,N-diethyl thiourea	3	50	80	0.9	0	757	349	70	×
Comp. Ex. 2-6		20	200	10	0.8	0	309	201	82	×
Comp. Ex. 2-7	Glue	3	50	20	0.4	0	359	185	41	×
Comp. Ex. 2-8				40	0.7	0	407	198	49	×
Comp. Ex. 2-9				60	0.3	0	362	189	42	×
Comp. Ex. 2-10		10	100	20	0.5	0	361	195	47	×
Comp. Ex. 2-11				40	0.7	0	417	206	52	×

(continued)

	Electrolyte			Foil- form condition	Copper foil				Cell characteristics	
	Organic additive	Organic additive concentration (ppm)	W concentration in bath (ppm)	Current density (A/dm^2)	I (220) / I (200)	W content in alloy foil (wt%)	Tensile strength before heating (MPa)	Tensile strength after heating (MPa)	Cycle life	Deformation of foil
Comp. Ex. 2-12				60	0.4	0	358	188	40	×
Comp. Ex. 2-13		20	200	20	0.2	0	369	205	53	×
Comp. Ex. 2-14				40	0.9	0	423	210	58	×
Comp. Ex. 2-15				60	0.7	0	361	195	49	×

<Example B>

[0104] The following bath composition was set as the basic bath composition of the electrolyte containing copper sulfate and sulfuric acid.
Cu=50 to 150 g/liter
H_2SO_4=20 to 200 g/liter
Cl=1 to 100 ppm
Organic additives shown in Table 5=3 to 20 ppm

[0105]

[Table 5]

Thiourea
Ethylene thiourea
N,N-diethylthiourea
Tetramethylthiourea

[0106] In the above bath, as additives, sodium tungstate and the thiourea, ethylene thiourea, N,N-diethylthiourea, and tetramethylthiourea shown in Table 5 were added so as to obtain the concentrations shown in Table 3 and electrolytic copper alloy foils were formed to a thickness of 12 μm with current densities shown in Table 3.

[0107] The electrolytic copper alloy foils formed in this way were treated for rust proofing under the following conditions. The formed electrolytic copper alloy foils (untreated copper alloy foils) were dipped in 1 g/liter of CrO_3 aqueous solution for 5 seconds to apply the chromate treatment, were washed with water, and then were dried.
Note that, the chromate treatment was carried out here, but naturally benzotriazole treatment or silane coupling agent treatment may be carried out or silane coupling agent treatment may be carried out after the chromate treatment.
The copper alloy foils prepared in this way were measured and tested as follows. The results thereof are shown in Table 3.

(1) Measurement of crystal orientation (XRD)

[0108] The crystal orientation of the copper foil was measured by X-ray diffraction (XRD).
Used apparatus: RAD-B (Rigaku Corporation)
Conditions: CuKα
Scanning method: θ-2θ
Tube voltage: 40 kV
Tube current: 20 mA
Measurement range: 20 to 100

(2) Measurement of tungsten content in foil (ICP)

[0109] The tungsten content in the copper alloy foil was obtained by dissolving a constant amount of copper alloy foil by acid, then diluting this by distilled water and measuring the thus prepared sample by using inductively coupled plasma (ICP) atomic emission spectrometry.
Used apparatus: ICPS-700 (Shimadzu Corporation)

(3) Measurement of tensile strength

[0110] The tensile strength of the copper alloy foil was measured based on the IPC-TM-650 for the foil before heating and after heating.
Used apparatus: AG-I (Shimadzu Corporation)

(4) Cell performance test

[0111] Next, using the electrolytic copper foils formed in the examples as the current collectors, lithium secondary cells were prepared, and cycle life tests were carried out.
A powder-shaped Si alloy active material (mean particle diameter: 0.1 μm to 10 μm) in a ratio (weight ratio) of 85 and a binder (polyimide) in a ratio of 15 were mixed, and the mixture was dispersed in N-methylpyrrolidone (solvent) to form

an active material slurry.
Then, this slurry was coated on the two surfaces of the prepared electrolytic copper foil having a thickness of 12 μm. The foil was dried and then press formed by a roller press machine. After that, it was annealed at 300°C for 1 hour under a nitrogen atmosphere to form a negative electrode. In this negative electrode, the film thicknesses of the negative electrode mixture at the two surfaces after shaping were the same 20 μm.

Preparation of lithium secondary cell

[0112] In a glovebox in an argon atmosphere, three-electrode type cells for evaluation use were constructed by the following configuration.
Negative electrode: Si alloy negative electrode prepared as described above
Counter electrode, reference electrode: Lithium foil
Electrolyte: 1 mol/liter of $LiPF_6$/EC+DEC (3:7 vol%)
[0113] The constructed cells were taken out of the box into the atmosphere and were measured for charging/discharging life in the atmosphere at 25°C.
Charging was carried out by a constant current up to 0.02V with respect to the standard single-electrode potential reference of Li. After that, charging was ended at the point of time when the current of CV (constant potential as it was) was lowered by 0.05C. Discharge was carried out up to 1.5V (Li reference) with the constant current by 0.1C. Charging/discharging was repeated with the same current corresponding to 0.1C.
For evaluation of the charging/discharging performances, the number of cycles until the discharge capacity reached 70% of the discharge capacity in the first cycle was measured. An electrode having a cycle number of 100 or more was judged as useable in practice and deemed as a passing level. The numbers of cycles of electrodes produced under different conditions are shown in Table 3 and Table 4.
[0114] Further, the cells were disassembled after the end of the charging/discharging tests and the electrodes (copper foils) used as the materials of the negative electrode current collectors were checked for any deformation. The results are indicated as "Good" for cells without wrinkles and other deformation and as "Poor" for cells with wrinkles and other deformation deemed as not passing.

(Comparative Examples 1 to 15)

[0115] The following bath composition was used as the basic bath composition of the electrolyte containing copper sulfate and sulfuric acid. Cu=50 to 150 g/liter
H_2SO_4=20 to 200 g/liter
Cl=1 to 100 ppm
[0116] In the above bath, in the same way as the examples, as additives, sodium tungstate and thiourea, ethylene thiourea, N,N-diethylthiourea, and glue were added so as to obtain the concentrations shown in Table 4, and electrolytic copper foils were formed to a thickness of 12 μm with current densities shown in Table 4.
[0117] The formed copper foils were evaluated in the same way as the examples and were measured for the crystal orientation of the foil, tungsten concentration in the foil, tensile strengths before and after the heat treatment, and cell characteristics. The results thereof are shown in Table 4.
[0118] Table 3 shows the results of evaluation of the copper foils prepared in Examples 1 to 36. It can be confirmed that the peak intensity ratio I<220>/I<200> obtained by X-ray diffraction changes in each sample due to the change of the additive concentration and current density. In all of the copper foils shown in Table 3, the peak intensity ratio obtained by the X-ray diffraction, i.e., I<220>/I<200>, is 1.2 or more. By being controlled to a crystal orientation where tungsten is easily incorporated, in the foil, tungsten is incorporated into the foil in an amount of 0.001 wt% to 0.055 wt%.
[0119] It is seen that when the amount of tungsten in the electrolytic bath is increased, the amount of tungsten incorporated into the foil tends to increase. Further, it was seen that the tensile strength after heating is 450 MPa or more and the heat resistance is excellent.
When looking at the tensile strength after heating at 300°C for 1 hour, in all foils, it was 450 MPa or more. The heat resistance was excellent, and no deformation of foil could be confirmed after the cycle test under all conditions either. More preferably, under conditions giving an amount of incorporation of tungsten of 0.001 wt% or more, the tensile strength after heating at 300°C for 1 hour was 450 MPa or more, the heat resistance was more excellent, and the number of cycles of the cell was 100 or more or usable in practice, so preferred characteristics were exhibited. Further, among them, in a foil having an amount of incorporation of tungsten larger than 0.055 wt%, the foil easily breaks and formation of foil is difficult, therefore the most preferred amount of incorporation of tungsten in the foil is 0.001 to 0.055 wt%.
[0120] Table 4 shows the results of evaluation of Comparative Examples 1 to 15.
The copper foils in Comparative Examples 1 to 6 show the results of samples prepared by using the same electrolyte as that for the examples but under different electrodeposition conditions (current density). However, it was confirmed

that the peak intensity ratio obtained by the X-ray diffraction, i.e., I<220>/I<200>, was less than 1.2, and a crystal orientation considered to contribute to the incorporation of tungsten was not exhibited. Further, the amount of incorporation of tungsten was less than 0.0001 wt% which was the detection limit for all irrespective of the tungsten concentration in the electrolytic bath, therefore almost no tungsten was incorporated. It was clarified that the tensile strength after heating at 300°C for 1 hour was 450 MPa or less and that the heat resistance was very low.

[0121] Further, the copper foils in Comparative Examples 7 to 15 formed by adding glue which is generally used as an additive did not show a crystal orientation whereby the peak intensity ratio obtained by X-ray diffraction, i.e. I<220>/I<200>, became 1.2 or more under any electrolytic condition. In all samples, the amount of incorporation of tungsten was 0 wt% and the tensile strength after heating was 250 MPa, therefore a very low heat resistance was shown.

In cells using the electrolytic copper foils of the comparative examples, after the cycle tests, deformation was seen in all electrolytic copper foils. Further, the numbers of cycles of the cells were 85 or less, so the characteristics were not preferred.

[0122] By the Cu-W alloy foil having the above characteristics, the excellent effects are exhibited that it is possible to provide an electrolytic copper foil free from breakage of the current collector (copper foil) while keeping the adhesion between the collector (copper foil) and the active material in the face of large expansion and contraction of the silicon or tin alloy active material and it is possible to provide an excellent lithium secondary cell by using the electrolytic copper foil as a negative electrode current collector.

<Example C>

[0123] In the present example, as the electrolyte, a copper sulfate solution prepared to have a copper concentration of 50 to 150 g/liter, a free sulfuric acid concentration of 20 to 200 g/liter, and a chlorine ion concentration of 1 to 100 ppm was used as the basic solution. The thiourea compound used as the additive and its added concentration and the tungsten concentration are shown in Table 6 together so that they can be compared with the comparative examples.

[0124] Setting of chlorine concentration of the basic solution to 100ppm or less was made since no difference was seen in the mechanical characteristic of the foil even when it was added exceeding 100ppm.

[0125] In the present example, copper alloy foils of 12 μm were produced by using the above electrolyte. The production conditions are a current density of 30 to 100 A/dm^2 and a temperature of 30 to 70°C.

The tungsten contents in the produced copper foils were calculated by dissolving a constant weight of electrolytic copper alloy foil by acid and finding the amount of tungsten in the solution by ICP atomic emission spectrometry.

The tensile strengths and elongations of the copper alloy foils were measured based on IPC-TM-650 for foils before heating and after heating. The results are shown in Table 6 together with the comparative examples. Used apparatus: AG-I (Shimadzu Corporation)

[0126]

[Table 6]

		Organic additive		W	W	Copper foil characteristic		
		Name of compound	Concentration in solution	Concentration in solution	content in alloy foil	Strength at ordinary temperature	Strength after heat treatment	Conductivity
			Ppm	ppm	wt%	MPa	MPa	%
Ex.	3-1		3	60	0.0090	661	464	90
	3-2		7	50	0.0090	689	503	89
	3-3		10	50	0.0100	773	517	88
	3-4		5	100	0.0100	727	538	86
	3-5		7	100	0.0110	750	520	85
	3-6	Ethylene thiourea	10	100	0.0120	793	549	85
	3-7		5	150	0.0150	723	536	86
	3-8		7	150	0.0170	750	555	85
	3-9		10	150	0.0180	788	561	85
	3-10		5	200	0.0180	701	509	82
	3-11		7	200	0.0180	726	512	81
	3-12		10	200	0.0190	751	499	80
	3-13	Thiourea	20	100	0.0150	708	453	82
	3-14	N,N-diethyl thiourea	10	100	0.0130	733	503	83
	3-15	Tetramethyl thiourea	6	10	0.0010	720	490	92
	3-16	*7 g/l of ammonium ions contained in Examples 1 to 4			0.0110	730	545	86
	3-17	*130 mg/l of nitrate ions contained in Examples 1 to 4			0.0100	731	540	88

(continued)

		Organic compound		W	W	Copper foil characteristics		
		Name of compound	Concentration in solution	Concentration in solution	content in alloy foil	Strength at ordinary temperature	Strength after heat treatment	Conductivity
			ppm	ppm	wt%	MPa	MPa	%
Comp. ex.	3-1	No organic additive	-	100	0	428	208	99
	3-1	Glue	3	100	0	440	210	97

[0127] From the evaluation results shown in Table 6, the electrolytic copper alloy foils in Examples 3-1 to 3-15 have mechanical strengths after heating at 300°C for 1 hour exceeding 450 MPa. It is proved that the adhesion between the collector and the active material is maintained by the polyimide binder and the current collector is not broken despite large expansion and contraction of the Si or Sn alloy active material.

[0128] Example 3-16 is produced by using an electrolyte comprised of the electrolyte of Example 3-4 further containing 7 g/liter of ammonium ions. Further, Example 3-17 is produced by using an electrolyte comprised of the electrolyte of Example 3-4 further containing 130 mg/liter of nitrate ions.
The electrolytic copper alloy foils in Example 3-16 and Example 3-17 are increased in mechanical strength after heating at 300°C for 1 hour compared with Example 3-4. When the mechanical strength after heat treatment is to be further improved, preferably use is made of an electrolyte containing ammonia ions or nitrate ions.

Comparative Examples

[0129] In Comparative Example 3-1, tungsten is added to the basic solution. The mechanical strength in the ordinary state is large, but the mechanical strength is remarkably lowered after heating at 300°C for 1 hour. Further, when measuring the amount of tungsten in this copper foil, it is less than the lower limit of detection, i.e., 0.0001 wt%.
When containing chlorine ions in the electrolyte, precipitation of tungsten was suppressed and the electrolytic copper foil was formed, but an electrolytic copper alloy foil comprised of Cu-W alloy was not formed.

[0130] In Comparative Example 3-2, a copper foil was prepared based on PLT 4 (Japanese Patent No. 3238278). The film was formed by a composition obtained by further adding glue to the electrolyte of Comparative Example 3-1. In this copper foil, the mechanical strength in the ordinary state is small and the mechanical strength remarkably falls after heating at 300°C for 1 hour. When measuring the amount of tungsten in this copper foil, it was less than the lower limit of detection, i.e., 0.0001 wt%.
Glue was added to the electrolyte, but glue does not have [=S]. Therefore, it is believed that, due to the glue, an adsorbed layer of organic molecules could not be formed on the copper by adsorption with a higher priority than the chlorine ions, therefore the tungsten oxide was not adsorbed onto the copper, incorporation of tungsten into the foil did not occur, and an electrolytic Cu-W alloy foil was not formed.

<Example D>

[0131] In the present example, after preparing the electrolytic copper alloy foils, HDD suspension use substrates having a configuration of stainless steel foil, a polyimide resin layer, and an electrolytic copper alloy foil were prepared and were evaluated for characteristics.

Preparation of electrolytic copper alloy foils and electrolytic copper foils

[Example 4-1]

[0132] As a sulfuric acid-copper sulfate electrolyte, the following bath was used as the basic bath composition.
Cu=50 to 150 g/liter
H_2SO_4=20 to 200 g/liter
Thiourea=3 to 20 ppm
Sodium tungstate (as tungsten)=10 to 1,000 ppm
Chlorine ions=1 to 100 ppm
After electrodeposition under the following conditions by using this electrolyte and forming an untreated copper alloy foil, roughening treatment and surface treatment same as those for an electrolytic copper foil F2-WS made by Furukawa Electric Co., Ltd. were carried out to produce an electrolytic copper alloy foil having a thickness of 9 μm.
Current density=30 to 100 A/dm^2
Temperature=30 to 70°C

[Example 4-2]

[0133] An electrolyte composition of the same conditions as those for Example 1 but only using the following thiourea compound was used.
Ethylene thiourea=1 to 20 ppm
After electrodeposition under the same conditions as those in Experiment 1 by using this electrolyte to form an untreated copper alloy foil, the same roughening treatment and surface treatment as those for electrolytic copper foil F2-WS made by Furukawa Electric Co., Ltd. were carried out to produce an electrolytic copper alloy foil having a thickness of 9 μm.

[Example 4-3]

[0134] An electrolyte composition of the same conditions as those for Example 1 but only using the following thiourea compound was used.

N,N-diethylthiourea=1 to 20 ppm

After electrodeposition under the same conditions as those in Experiment 1 by using this electrolyte to form an untreated copper alloy foil, the same roughening treatment and surface treatment as those for electrolytic copper foil F2-WS made by Furukawa Electric Co., Ltd. were carried out to produce an electrolytic copper alloy foil having a thickness of 9 μm.

[Comparative Example 4-1]

[0135] An electrolytic copper foil F2-WS made by Furukawa Electric Co., Ltd. having a thickness of 9 μm was prepared.

[Comparative Example 4-2]

[0136] An electrolytic copper foil HLA made by Nippon Denkai, Ltd. having a thickness of 9 μm was prepared.

[0137] Using the electrolytic copper alloy foils and electrolytic copper foils prepared in above examples and comparative examples, HDD suspension use substrates having configurations of stainless steel foil, a polyimide resin layer, and electrolytic copper alloy foil or electrolytic copper foil were prepared.

Synthesis of polyimide resin

Synthesis Example 1

[0138] In order to synthesize a polyimide resin having a low thermal expansion property with a linear expansion coefficient of 30 ppm/K or less, 9.0 mol of DADMB was weighed and was dissolved in 25.5 kg of a solvent DMAc while stirring it in a 40 liter planetary mixer. Then, 8.9 mol of BPDA was added and stirring was continued at room temperature for 3 hours to perform a polymerization reaction to thereby obtain a viscous solution of a polyimide precursor A. The thermal expansion coefficient after imidization of the polyimide precursor A according to the present Synthesis Example was 13 ppm/K.

Synthesis Example 2

[0139] In order to synthesize a polyimide resin having a glass transition temperature of 300°C or less, 6.3 mol of DADMB was weighed and was dissolved in 25.5 kg of a solvent DMAc while stirring it in a 40 liter planetary mixer. Then, 6.4 mol of BPDA was added and stirring was continued at room temperature for 3 hours to perform a polymerization reaction to thereby obtain a viscous solution of a polyimide precursor B. The glass transition temperature by a dynamic viscoelastic property measurement device after imidization of the polyimide precursor B according to the present Synthesis Example was 225°C.

[0140] Note that, abbreviations used here are as follows.

DADMB: 4,4'-diamino-2,2'-dimethylbiphenyl

DMAc: N,N-dimethylacetamide

BPDA: 3,3',4,4'-biphenyl tetracarboxylic dianhydride

BAPP: 2,2'-bis[4-(4-aminophenoxy)phenyl]propane

Preparation of HDD suspension use substrate

[0141] (a) A solution of the polyimide precursor B obtained in Synthesis Example 2 was coated on stainless steel foil (made by Nippon Steel & Sumitomo Metal Corporation, SUS304, tension annealed product, thickness: 20 μm) so that the thickness after hardening became 1 μm and was dried at 110°C for 3 minutes. (b) After that, a solution of the polyimide precursor A obtained in Synthesis Example 1 was coated on that so that the thickness after hardening became 7.5 μm and (c) was dried at 110°C for 10 minutes, and (d) a solution of the polyimide precursor B obtained in Synthesis Example 2 was further coated on that so that the thicknesses after hardening became 1.5 μm and (e) was dried at 110°C for 3 minutes. (f) After that, the imidization was completed by further performing stepwise heat treatment in several stages within a range of 130 to 360°C for 3 minutes for each to thereby obtain a laminate of a polyimide resin layer having a thickness of 10 μm on stainless steel. Note that, the polyimide resin layer of the first layer and the polyimide resin layer of the third layer were made the same.

Next, the electrolytic copper alloy foils or electrolytic copper foils shown in the examples and comparative examples

were superimposed on each other and were hot pressed using a vacuum press machine under conditions of surface pressure of 15 Mpa, a temperature of 320°C, and a pressing time of 20 minutes to obtain the targeted laminates.

Measurement of peel strength

[0142] For the adhesive strength of the metal foil and polyimide resin, a polyimide resin layer was formed on stainless steel foil, then electrolytic copper alloy foil or electrolytic copper foil was further hot-pressed to prepare a laminate having metallic foils on the two surfaces. This was worked to a predetermined shape to thereby prepare a measurement use sample having a line width of 1/8 inch. This sample was adhered to a fixed plate at the SUS foil side and copper alloy foil or copper foil side, then a tensile tester was used to measure the peel strength in a direction of 90 degrees for each metallic foil.

Measurement of warp

[0143] The laminate was worked to prepare a disc having a diameter of 65 mm. This was allowed to stand at 23°C and a humidity of 50% for 24 hours, then the location with the greatest warping when placed on a desk was measured by a vernier micrometer.

Measurement of linear thermal expansion coefficient

[0144] For measurement of the linear thermal expansion coefficient, a thermomechanical analyzer (Seiko Instruments Inc.) was used. The sample was raised in temperature up to 255°C at a rate of 20°C/min, was held at that temperature for 10 minutes, then was further cooled at a constant rate of 5°C/min. A mean thermal expansion coefficient (linear thermal expansion coefficient) from 240°C to 100°C at the time of cooling was calculated.

[0145] The results are shown in Table 7. HDD suspension use substrates having the configuration of stainless steel foil, polyimide resin layer, and electrolytic copper alloy foil using electrolytic copper alloy foils shown in Examples 4-1 to 4-3 sufficiently satisfy the required characteristics as the suspension substrate materials.

[0146]

[Table 7]

		Example			Comparative Example	
		4-1	4-2	4-3	4-1	4-2
Thickness	μm	9	9	9	9	9
W content in alloy foil	wt%	0.009	0.010	0.012	-	-
Strength at ordinary temperature	MPa	655	771	787	320	510
Strength after heating	MPa	461	510	550	225	208
Elongation at ordinary temperature	%	2.8	3.5	3.3	8.5	6.0
Elongation after heating	%	4.0	4.3	4.9	11.8	16.0
Conductivity	%	90	88	85	98	98
Polyimide thermal expansion coefficient	ppm/K	22.3	22.3	22.3	22.3	22.3
Stainless steel-polyimide peel strength	kN/m	1.5	1.5	1.5	1.5	1.5
Copper foil-polyimide peel strength	kN/m	1.4	1.4	1.4	1.4	1.1
Warping	mm	2.8	2.5	2.3	21.5	23.5

[0147] As explained above, according to the present invention, there can be provided an electrolytic copper alloy foil having a large mechanical strength in an ordinary state and resistant to heat deterioration even when it is heated at 300°C or more.

Further, according to the present invention, there can be provided an electrolytic copper alloy foil excellent as a current collector for a lithium ion secondary cell and there can be provided an excellent secondary cell by using the current

collector.

Industrial Applicability

[0148] An electrolytic copper alloy foil of the present invention is preferred as a printed circuit board material from which a large mechanical strength is demanded even after heating, for example, an HDD suspension material or component material in the field of a TAB material.

[0149] Further, it can be preferably used not only as the material of a printed circuit board, but also as a component material in the field in which large mechanical strength and conductivity are demanded even after heating at a high temperature.

Claims

1. An electrolytic copper alloy foil containing tungsten.

2. An electrolytic copper alloy foil wherein all or a portion of tungsten is incorporated as an oxide.

3. An electrolytic copper alloy foil containing tungsten and having a remainder (balance) substantially comprised of copper.

4. An electrolytic copper alloy foil containing 0.0001 to 0.060 wt% of tungsten.

5. An electrolytic copper alloy foil containing 0.001 to 0.055 wt% of tungsten, having a tensile strength at ordinary temperature of 650 MPa or more, and having a tensile strength after treatment at 300°C for 1 hour of 450 MPa or more.

6. An electrolytic copper alloy foil containing 0.001 to 0.055 wt% of tungsten, having a tensile strength at ordinary temperature of 650 MPa or more, having a tensile strength after treatment at 300°C for 1 hour of 450 MPa or more, and having a conductivity of 80% or more.

7. An electrolytic copper alloy foil containing 0.001 to 0.055 wt% of tungsten, having a tensile strength at ordinary temperature of 650 MPa or more, having a tensile strength after treatment at 300°C for 1 hour of 450 MPa or more, having an elongation at ordinary temperature of 2.5% or more, and having an elongation after treatment at 300°C for 1 hour of 3.5% or more.

8. An electrolytic copper alloy containing tungsten and chlorine.

9. An electrolytic copper alloy foil containing 0.0001 to 0.060 wt% of tungsten, and 0.005 to 0.050 wt% of chlorine.

10. An electrolytic copper alloy foil containing 0.0001 to 0.0060wt% of tungsten, and having a peak intensity ratio I<200>/I<220> obtained by X-ray diffraction between a peak intensity I<220> of a crystal orientation I<220> and a peak intensity I<200> of a crystal orientation I<200> of 1.2 or more.

11. A negative electrode current collector used for lithium ion secondary cell which uses an electrolytic copper alloy foil as set forth in any one of claims 1 to 10.

12. An electrode used for lithium ion secondary cell which uses an electrolytic copper alloy foil as set forth in any one of claims 1 to 10 as a negative electrode current collector and deposits silicon, germanium, tin, or an alloyed compound of the same or an active material containing them as principal ingredients on the surface thereof.

13. A lithium ion secondary cell using an electrolytic copper alloy foil as set forth in any one of claims 1 to 10 as a current collector.

14. A method of production of an electrolytic copper alloy foil for producing an electrolytic copper alloy foil which contains tungsten and has a remainder (balance) comprised of copper comprising the steps of:

    adding a thiourea compound, tungsten salt, and chlorine ions to a sulfuric acid-copper sulfate electrolyte as additives; and

performing electrolytic deposition.

15. A method of production of a copper alloy foil containing 0.001 to 0.055 wt% of tungsten, having a tensile strength at ordinary temperature of 650 MPa or more, having a tensile strength after treatment at 300°C for 1 hour of 450 MPa or more, and having a conductivity of 80% or more, wherein
the copper alloy foil is formed by a copper sulfate electrolyte obtained by adding, as additives, 10 to 1,000 ppm of tungsten, 1 to 20 ppm of at thiourea compound, and 1 to 100 ppm of chlorine ions to the copper sulfate electrolyte.

16. An electrolyte for forming an electrolytic copper foil which contains copper sulfate, sulfuric acid, and chlorine ions and has tungsten or a tungsten compound and thiourea organic additive added to it.

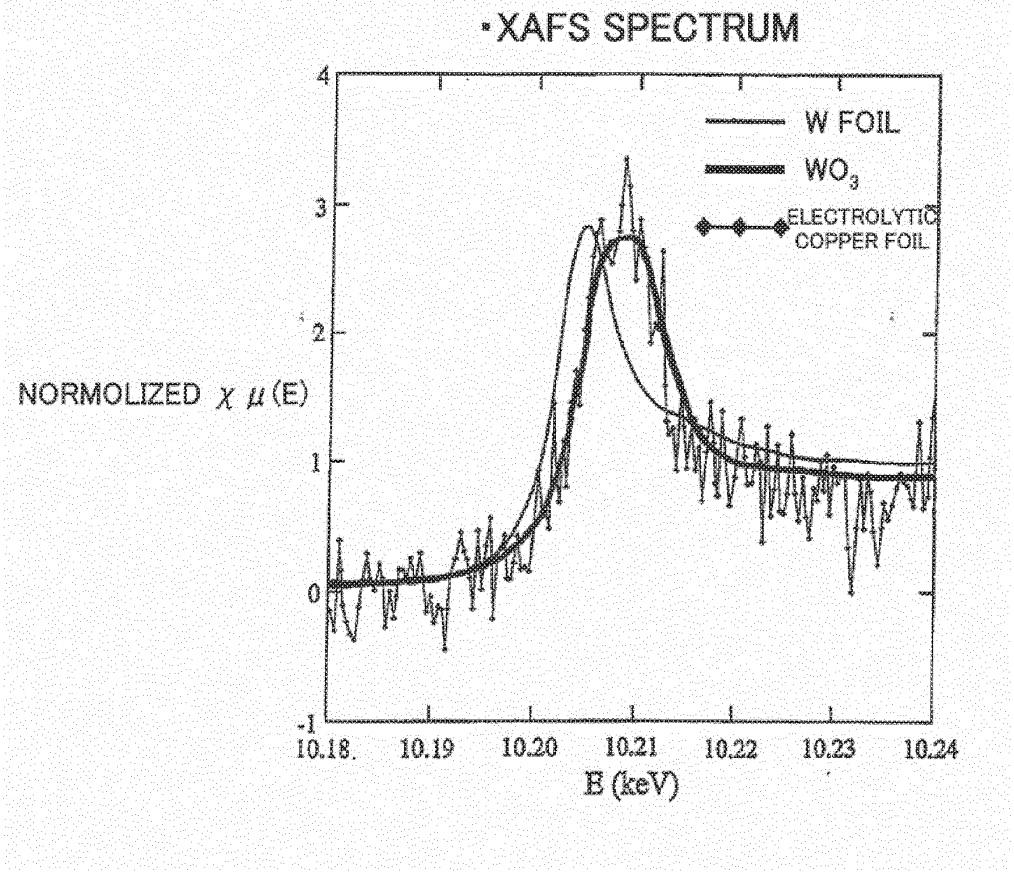
17. The electrolyte for forming an electrolytic copper foil as set forth in claim 16, wherein the electrolyte has 10 to 1,000 ppm of tungsten or a tungsten compound as tungsten, 1 to 20 ppm of a thiourea compound, and 1 to 100 ppm of chlorine ions added to it.

18. The electrolyte for forming an electrolytic copper foil as set forth in claim 16 or 17, wherein the thiourea compound added to the electrolyte is any of thiourea, N,N-diethylthiourea, tetramethylthiourea, and ethylene thiourea.

19. An electrolyte for forming an electrolytic copper alloy foil formed by adding at least one of ammonia ions or nitrate ions to the electrolyte as set forth in any of claims 16 to 18.

20. An electrolytic copper alloy foil electrolytic formed by using the electrolyte for forming an electrolytic copper alloy foil as set forth in any one of claims 17 to 19.

FIG. 1


XAFS SPECTRUM
W FOIL
WO3
ELECTROLYTIC COPPER FOIL
NORMOLIZED χ μ (E)
4
3
2
1
0
-1
10.18
10.19
10.20
10.21
10.22
10.23
10.24
E (keV)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/069368

A. CLASSIFICATION OF SUBJECT MATTER
C25D1/00(2006.01)i, *C22C9/00*(2006.01)i, *C25D1/04*(2006.01)i, *H01B5/02*(2006.01)i, *H01B13/00*(2006.01)i, *H01M4/38*(2006.01)i, *H01M4/66*(2006.01)i, *H05K1/09*(2006.01)i
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25D1/00, C22C9/00, C25D1/04, H01B5/02, H01B13/00, H01M4/38, H01M4/66, H05K1/09

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2012
Kokai Jitsuyo Shinan Koho 1971-2012 Toroku Jitsuyo Shinan Koho 1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 7-278867 A (Nikko Gould Foil Co., Ltd.), 24 October 1995 (24.10.1995), examples & JP 3238278 B2	1-20
A	JP 9-67693 A (Nikko Gould Foil Co., Ltd.), 11 March 1997 (11.03.1997), examples (Family: none)	1-20
A	JP 10-330983 A (Fukuda Metal Foil & Powder Co., Ltd.), 15 December 1998 (15.12.1998), entire text & GB 9811653 A0 & GB 2325673 A & US 6231742 B1	1-20

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
22 October, 2012 (22.10.12)	30 October, 2012 (30.10.12)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/069368

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11-152593 A (Japan Energy Corp.), 08 June 1999 (08.06.1999), entire text & JP 3943214 B2	1-20
A	JP 2004-263296 A (Furukawa Techno-Research Co., Ltd.), 24 September 2004 (24.09.2004), claim 3 & US 2004/0157080 A1 & EP 1448036 A1 & KR 10-2004-0073376 A & JP 2004-263300 A & CN 1551710 A & DE 602004012910 D	1-20

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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- JP 4273309 B **[0018] [0032]**
- JP 3270637 B **[0019] [0032]**
- JP 3238278 B **[0025] [0032] [0130]**
- JP 9067693 A **[0025] [0032]**

Non-patent literature cited in the description

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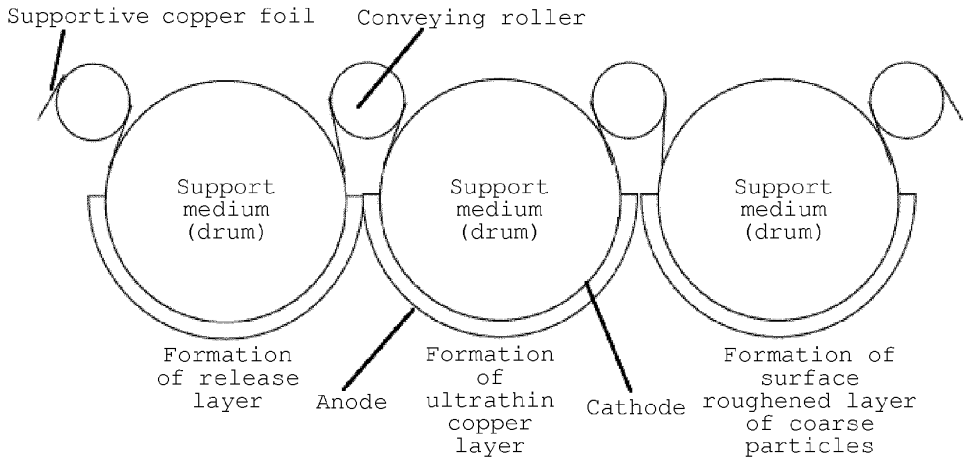
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(54) ULTRATHIN COPPER FOIL, METHOD FOR PRODUCING SAME, AND ULTRATHIN COPPER LAYER

(57) Provided is an utrathin copper foil which has improved thickness accuracy of an ultrathin copper layer on a supporting copper foil. An ultrathin copper foil which is provided with a supporting copper foil, a releasing layer that is laminated on the supporting copper foil, and an ultrathin copper layer that is laminated on the releasing layer. The thickness occuracy of the ultrathin copper layer as determined by a weight thickness method is 3.0% or less.

FIG. 2



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Description

Technical Field

[0001] The present invention relates to an ultrathin copper foil and a method of manufacturing the same, and an ultrathin copper layer. In further detail, the present invention relates to an ultrathin copper foil used as a material of a printed circuit board for fine pattern applications and to a method of manufacturing the same, and to an ultrathin copper layer.

Background Art

[0002] In recent years, fine-line circuitry is demanded in a printed circuit board as the density of semiconductor integrated circuits is increased. A common method of producing fine-line circuitry is the modified semi-additive process (MSAP) of which circuits are formed on an ultrathin copper layer, followed by removing the ultrathin copper layer through an etch process with a sulfuric acid/hydrogen peroxide type etchant. Therefore, the ultrathin copper layer is preferably uniform in thickness.

[0003] Herein, accuracy of the thickness of the electroplated copper foil strongly depends on the interelectrode distance between anode and cathode. A common method of forming an ultrathin copper layer involves formation of a release layer on a supportive copper foil (12 to 70μm thick), on the surface of which an ultrathin copper foil layer (0.5 to 10.0 μm thick) and coarse particles by surface roughening are then formed. In the past the step after formation of the supportive copper foil uses the conveying system for the supportive copper foil in the form of zigzag path without a drum to support it as illustrated in Fig. 1. (Patent Literature 1)

Citation List

Patent Literature

[0004] Patent Literature 1: JP 2000-309898 A

Summary of Invention

Technical Problem

[0005] However, since accuracy of the thickness of the ultrathin copper layer formed by electrolytic plating strongly depends on the interelectrode distance between anode and cathode, use of such a conveying system for a supportive copper foil as the form of zigzag path without a drum to support the supportive copper foil makes it difficult to keep the interelectrode distance constant because of effects such as the electrolyte and tension for conveying the supportive copper foil, causing the problem of larger variations in thickness.

[0006] The purpose of the present invention is to provide an ultrathin copper foil in which accuracy of the thickness of the ultrathin copper layer on a supportive copper foil is improved.

Solution to Problem

[0007] To realize the purpose described above the present inventors performed extensive investigation and found that in focusing on the steps after formation of a supportive copper foil, accuracy of the thickness of an ultrathin copper layer can be improved by keeping the interelectrode distance constant using a drum instead of a zigzag path as a support medium for conveying the ultrathin copper foil.

[0008] The present invention is completed based on the findings described above, and in one aspect, the invention relates to an ultrathin copper foil comprising a supportive copper foil, a release layer superposed on the supportive copper foil, and an ultrathin copper layer superposed on the release layer, and it relates to the ultrathin copper foil with accuracy of the thickness of the ultrathin copper layer to be 3.0% or less when measured with the weight method.

[0009] In another aspect the present invention relates to an ultrathin copper foil comprising a supportive copper foil, a release layer superposed on the supportive copper foil, and an ultrathin copper layer superposed on the release layer, and it relates to the ultrathin copper foil with accuracy of the thickness of the ultrathin copper layer to be 10.0% or less when measured with the four-point probe method.

[0010] In one embodiment of an ultrathin copper foil related to the present invention there is the surface roughened layer of coarse particles on the surface of the ultrathin copper layer.

[0011] Further in another aspect of the present invention it relates to a method of manufacturing an ultrathin copper

foil comprising a supportive copper foil, a release layer superposed on the supportive copper foil, and an ultrathin copper layer superposed on the release layer by treating the surface of the belt-like shaped supportive copper foil conveyed by the roll-to-roll conveyance process in the length direction, and to a manufacture method of the ultrathin copper foil including a step of forming a release layer on the surface of the supportive copper foil conveyed by a conveying roller and a step of forming an ultrathin copper layer on the surface of the release layer by electrolytic plating while supporting with a drum the supportive copper foil on which the release layer is formed and which is conveyed by a conveying roller.

[0012] In one embodiment of a manufacture method of an ultrathin copper foil in the present invention a step of forming the release layer involves formation of an ultrathin copper layer on the surface of the supportive copper foil by electrolytic plating while supporting with a drum the supportive copper foil conveyed by a conveying roller.

[0013] In another embodiment a manufacture method of an ultrathin copper foil in the present invention further includes a step of forming a surface roughened layer of coarse particles on the surface of an ultrathin copper layer of the supportive copper foil conveyed with a conveying roller.

[0014] In another embodiment of a manufacture method of an ultrathin copper foil in the present invention a step of forming the surface roughened layer of coarse particles further includes formation of the surface roughened layer of coarse particles on the surface of the ultrathin copper layer by electrolytic plating while supporting with a drum the supportive copper foil conveyed with a conveying roller.

[0015] In another aspect of the present invention it further relates to an ultrathin copper layer of an electrolytic copper foil superposed on a release layer which is superposed on a supportive copper foil, constituting the ultrathin copper foil together with the supportive copper foil and the release layer and to the ultrathin copper layer with accuracy of the thickness to be 3.0% or less when measured with the weight method.

[0016] In another aspect of the present invention it further relates to an ultrathin copper layer of an electrolytic copper foil superposed on a release layer which is superposed on a supportive copper foil, constituting the ultrathin copper foil together with the supportive copper foil and the release layer and to the ultrathin copper layer with accuracy of the thickness to be 10.0% or less when measured with the four-point probe method.

[0017] In one embodiment an ultrathin copper layer of the present invention is the ultrathin copper layer of electrolytic copper foil superposed on a release layer which is superposed on the supportive copper foil, constituting the ultrathin copper foil together with the supportive copper foil and the release layer, and having a surface roughened layer of coarse particles on the surface of the ultrathin copper layer.

[0018] In another aspect of the present invention it further relates to a printed circuit board manufactured using the ultrathin copper foil of the present invention.

[0019] In another aspect of the present invention it further relates to a printed circuit board using the ultrathin copper layer of the present invention.

Advantageous Effects of Invention

[0020] According to the present invention an ultrathin copper foil can be provided, of which accuracy of the thickness of an ultrathin copper layer on a supportive copper foil is improved.

Brief Description of Drawings

[0021]

Fig. 1 is a schematic diagram of illustrating the conventional conveying system for a copper foil in the form of a zigzag path.

Fig. 2 is a schematic diagram of illustrating the conveying system for a copper foil related to a manufacture method of an ultrathin copper foil related to embodiment 1 of the present invention.

Fig. 3 is a schematic diagram of illustrating the conveying system for a copper foil related to a manufacture method of an ultrathin copper foil related to embodiment 2 of the present invention.

Fig. 4 is a schematic diagram of illustrating the conveying system for a copper foil related to a manufacture method of an ultrathin copper foil related to embodiment 3 of the present invention.

Description of Embodiments

1. Supportive copper foil

[0022] A supportive copper foil usable in the present invention is typically provided in the form of a rolled copper foil and an electrolytic copper foil. Generally an electrolytic copper foil is manufactured by electrolytic plating of copper sulfate in a plating bath to deposit on a titanium or stainless steel drum, whereas a rolled copper foil is manufactured by

repeating the plastic deformation and heat treatment of the foil material with a press roll. Materials for a copper foil used can include, in addition to high purity copper such as tough pitch copper and oxygen-free copper, for example, Sn-added copper, Ag-added copper, and a copper alloy such as a Cr-, Zr- or Mg-added copper alloy, and a Corson-type copper alloy in which Ni and Si are added. When the term "copper foil" is used independently in the present description, a copper alloy foil is included.

[0023] The thickness of a supporting copper foil usable in the present invention is not particularly limited, and the thickness may be appropriately chosen to properly serve its function as a supportive copper foil, and for example, the thickness can be 12 μm or more. However, in general the thickness is preferably 35 μm or less since production cost becomes higher when too thick. Therefore, the thickness of a supportive copper foil is typically from 12 to 70 μm, more typically from 18 to 35 μm.

2. Release layer

[0024] A release layer is provided on a supportive copper foil. The release layer can be formed using nickel, nickel-phosphorous alloy, nickel-cobalt alloy, chromium, and the like. The release layer is the part released when the supportive copper foil is peeled from the ultrathin copper layer, and can have the effects of a barrier to prevent copper in the supportive copper foil fromdiffusing into the ultrathin copper layer.

[0025] When an electrolytic copper foil is used as the supportive copper foil, a release layer is preferably provided on the low-roughness surface from the viewpoint of reducing pinholes. The release layer can be provided using processes such as plating, sputtering, chemical vapor deposition (CVD), and physical vapor deposition.

3. Ultrathin copper layer

[0026] An ultrathin copper layer is provided on a release layer. The ultrathin copper layer can be formed by electrolytic plating using a plating bath of copper sulfate, copper pyrophosphate, copper sulfamate, and copper cyanide, and a copper sulfate bath is preferred since it is used for production of an electrolytic copper foil and the copper foil can be formed with high current density. The thickness of the ultrathin copper layer is not particularly limited, and generally thinner than the supportive copper foil, for example, 12 μm or less. Typically the thickness is from 0.5 to 10 μm, more typically from 1 to 5 μm.

4. Surface roughening treatment

[0027] A surface roughened layer of coarse particles can be provided on the surface of an ultrathin copper layer by surface roughening treatment, for example, in order to improve adhesion to an insulating substrate. Surface roughening can be performed, for example, by forming coarse particles of copper or copper alloy. Surface roughening may form fine particles. The surface roughened layer may be the layer including either elemental substance selected from a group consisted of copper, nickel, cobalt, and zinc or an alloy containing one or more of any one of the elements in the group. Or after surface roughening treatment or without surface roughening treatment secondary particles and tertiary particles of the elemental substance or alloy of nickel, cobalt, copper, and zinc and/or an anticorrosion layer are formed and then the surface treatment such as the chromate treatment and the silane coupling treatment is performed. That is, one type or more of layers selected from the group consisted of the anticorrosion layer, the chromate treatment layer, and the silane coupling treatment layer may be formed on the surface of the surface roughened layer of coarse particles or one type or more of layers selected from the group consisted of the anticorrosion layer, the chromate treatment layer, and the silane coupling treatment layer may be formed on the surface of the ultrathin copper layer.

5. Ultrathin copper foil

[0028] An ultrathin copper foil is comprising a supportive copper foil, a release layer formed on the supportive copper foil, and an ultrathin copper layer superposed on the release layer. The way to use the ultrathin copper foil itself is well known to those skilled in the art, and for example, the surface of the ultrathin copper layer is laminated to an insulating substrate such as phenol resin impregnated paper base, epoxy resin impregnated paper base, epoxy resin impregnated synthetic fabric base, epoxy resin impregnated composite base of fiberglass and paper, epoxy resin impregnated composite base of fiberglass fabric and fiberglass nonwoven fabric, epoxy resin impregnated fiberglass fabric base, a polyester film, andapolyimidefilmandheat-pressed, followed by peeling the carrier and etching the ultrathin copper layer adhered to the insulating substrate to form a targeted conductor pattern, thereby manufacturing a printed circuit board. In the ultrathin copper foil related to the present invention, release site is mainly at the interface between the release layer and the ultrathin copper layer.

6. Manufacture method of an ultrathin copper foil

[0029] A manufacture method of an ultrathin copper foil related to the present invention will next be described. Fig. 2 is a schematic diagram of illustrating the conveying system for a copper foil related to a manufacture method of the ultrathin copper foil related to embodiment 1 of the present invention. The manufacture method of the ultrathin copper foil related to embodiment 1 of the present invention is a method of manufacturing the ultrathin copper foil comprising a supportive copper foil, a release layer superposed on the supportive copper foil, and an ultrathin copper layer superposed on the release layer by treating the surface of the belt-like shaped supportive copper foil conveyed by the roll-to-roll conveyance process in the length direction. A manufacture method of the ultrathin copper foil related to embodiment 1 of the present invention includes a step of forming by electrolytic plating an ultrathin copper layer on the surface of the supportive copper foil while supporting with a drum the supportive copper foil conveyed by a conveying roller, a step of forming by electrolytic plating the ultrathin copper layer on the surface of the release layer while supporting with a drum the supportive copper foil on which the release layer is formed, and a step of forming by electrolytic plating the surface roughened layer of coarse particles on the surface of the ultrathin copper layer while supporting the supportive copper foil with a drum. In each step the treatment surface of the supportive copper foil supported with the drum simultaneously serves as cathode, and electrolytic plating process in each step proceeds in the copper plating solution between the drum and the anode placed opposite to the drum.

[0030] In the present invention the supportive copper foil is conveyed while applying tension to the supportive copper foil in the length direction, since the belt-like shaped supportive copper foil is conveyed by the roll-to-roll conveyance process. Tension can be adjusted by applying the torque created by connecting each conveying roller to a drive motor. Tension of conveying the supportive copper foil is preferably from 0.01 to 0.2 kg/mm. When tension for conveying the supportive copper foil is below 0.01 kg/mm, the contact force to the drum is too weak, making it difficult to adjust the thickness of each layer to the desired thickness. Also problems such as slipping are likely to occur depending on the structure of equipment and a supportive copper foil roll further slacks, thereby likely to cause problems such as the winding slippage. On one hand, when tension for conveying the supportive copper foil exceeds 0.2 kg/mm, slight misalignment of the supportive copper foil is likely to create creases and folds so that it is not preferred from the viewpoint of managing equipment. When a roll is wound too hard, tight winding is likely to cause wrinkles. Tension for conveying the supportive copper foil is more preferably from 0.02 to 0.1 kg/mm.

[0031] In embodiment 1 both the release layer and the surface roughened layer are formed by electrolytic plating while supporting the supportive copper foil with a drum, but the invention is not limited by that embodiment. For example, as illustrated in Fig. 3 as embodiment 2, a surface roughened layer of coarse particles may be formed by electrolytic plating using the conventional conveying system for the copper foil in the form of the zigzag path without supporting the supporting copper foil with a drum. As illustrated in Fig. 4 as embodiment 3, both the release layer and the surface roughened layer of coarse particles may also be formed by electrolytic plating using the conventional conveying system for the copper foil in the form of zigzag path without supporting the supporting copper foil with a drum. However, since in embodiments 2 and 3 the drum for the conveying system of the supportive copper foil is not used in every step as in embodiment 1, it is difficult to make constant the interelectrode distance in electrolytic plating as compared to embodiment 1, resulting in lower accuracy in controlling the thickness of the release layer and/or the surface roughened layer of coarse particles.

[0032] As described above, the present invention keeps constant the interelectrode distance between anode and cathode in electrolytic plating by supporting a supportive copper foil with a drum. Therefore, variations in the thickness of the copper foil layer formed are prevented enabling preparation of an ultrathin copper foil with an ultrathin copper layer having the thickness in high accuracy.

[0033] The ultrathin copper foil thus prepared has high accuracy in the thickness of the ultrathin copper layer measured with the weight method to be 3.0% or less, preferably 2.0% or less resulting in the highly accurate thickness. The lower limit of accuracy is not required to set inparticular, and for example, 0.05% or more, or 0.1% or more, or 0.2% or more.

[0034] A measurement method for determining accuracy of the thickness by the weight method will be herein described. Firstly the total weight of a supportive copper foil and an ultrathin copper foil is measured and then an ultrathin copper layer is peeled off to reweigh the supportive copper foil to assign the weight difference between the former and the latter as the weight of the ultrathin copper layer. A sample piece of an ultrathin copper layer is obtained as the measuring object by punching out the ultrathin copper foil into a 3 cm x 3 cm sheet with the press. To study accuracy of the thickness determined from the weight, the thickness of the ultrathin copper layer in each standard is determined by the weight method at 10 points at equal space in the width direction and 6 points (spacing of 4 cm) in the length direction, a total of 60 points to calculate the mean and the standard deviation (σ). The formula for calculating accuracy of the thickness is given as follows.

$$\text{Accuracy in thickness } (\%) = 3\sigma \times 100/\text{mean}$$

[0035] Repeat accuracy of the measurement method is 0.2%.

[0036] An ultrathin copper foil thus prepared has accuracy of the thickness of the ultrathin copper layer determined by the four-point probe method to be 10.0% or less, preferably 6.0% or less, resulting in the highly accurate thickness. The lower limit of accuracy is not required to set in particular, and for example, 0.05% or more, or 0.5% or more, or 0.7% or more, or 1.0% or more.

[0037] A measurement method for determining accuracy of the thickness with the four-point probe method will be herein described. The total thickness of the supportive copper foil and the ultrathin copper foil is determined by measuring the resistivity with the four-point probe and then the ultrathin copper layer is peeled off to redetermine the resistivity of the supportive copper foil for determining its thickness to assign the difference between the former and the latter as the thickness of the ultrathin copper layer.To study accuracy of the thickness, the thickness of the ultrathin copper layer in each standard is determined at a spacing of 5 mm in the width direction to calculate the mean and the standard deviation (σ) at total of 280 measuring points. The formula for calculating accuracy of the thickness with the four point probe is given as follows.

$$\text{Accuracy in thickness } (\%) = 3\sigma \times 100/\text{mean}$$

[0038] Repeat accuracy of the measurement method is 1.0%.

Examples

[0039] Hereinafter, the present invention will be described in further detail below in accordance with the examples, but is in no way limited by the examples.

1. Manufacture of ultrathin copper foil

[0040] Belt-like shaped supportive copper foils with the thickness described in Table were prepared as the supportive copper foil. Electrolytic copper foils of JTC (manufactured by JX Nippon Mining & Metals Corporation) were used as the copper foil in Examples 1, 3, 5-7, 10, 13, 15, and 16 and Comparative Examples 1 and 2, whereas rolled copper foils of tough pitch copper JIS H3100 C1100 (manufactured by JX Nippon Mining & Metals Corporation) were used as the copper foil in Examples 2, 4, 8, 9, 11, 12, and 14 and Comparative Example 3. On the shiny surface of the copper foil were formed the release layer, the ultrathin copper layer, and the surface roughened layer of coarse particles under the condition described in Table 1 using the continuous roll-to-roll fabrication line. Herein, copper foils in Examples 1-3 were prepared in accordance with the system related to embodiment 3 illustrated in Fig. 4 described above, those in Examples 4-9 were prepared in accordance with embodiment 2 illustrated in Fig. 3 described above, and those in Examples 10-16 were prepared in accordance with embodiment 1 illustrated in Fig. 2 described above. Copper foils in Comparative Examples 1-3 were prepared in accordance with the conventional system illustrated in Fig. 1 described above.

Preparation of release layer

(A) Conveying system for copper foil in accordance with zigzag path

[0041]

- Anode: insoluble electrode
- Cathode: treated surface of supportive copper foil
- Interelectrode distance (indicated in Table 1)
- Composition of electrolytic plating solution: $NiSO_4$ 100 g/L
- pH of electrolytic plating solution: 6.7
- Temperature of electrolytic plating bath: 40°C
- Current density for electrolytic plating: 5 A/dm^2
- Electrolytic plating time: 10 seconds
- Tension in conveying a supportive copper foil: 0.05 kg/mm (B) Conveying system of copper foil with drums
- Anode: insoluble electrode
- Cathode: surface of a supportive copper foil supported with a drum of 100 cm diameter.
- Interelectrode distance (indicated in Table 1)
- Composition of electrolytic plating solution: $NiSO_4$ 100 g/L

- pH of electrolytic plating solution: 6.7
- Temperature of electrolytic plating bath: 40°C
- Current density for electrolytic plating: 5 A/dm^2
- Electrolytic plating time: 10 seconds
- Tension in conveying a supportive copper foil: 0.05 kg/mm

Preparation of ultrathin copper layer

(A) Conveying system for copper foil in accordance with zigzag path

[0042]

- Anode: insoluble electrode
- Cathode: treated surface of a supportive copper foil
- Interelectrode distance (indicated in Table 1)
- Composition of electrolytic plating solution: Cu: 50 g/L, H_2SO_4: 50 g/L, and Cl: 60 ppm
- Temperature of electrolytic plating bath: 45°C
- Current density for electrolytic plating: 30 A/dm^2
- Tension in conveying a supportive copper foil: 0.05 kg/mm (B) Conveying system of copper foil with drums
- Anode: insoluble electrode
- Cathode: surface of a supportive copper foil supported with a drum of 100 cm diameter
- Interelectrode distance (indicated in Table 1)
- Composition of electrolytic plating solution: Cu: 100 g/L, H_2SO_4: 80 g/L, and Cl: 60 ppm
- Temperature of electrolytic plating bath: 55°C
- Current density for electrolytic plating: 30 A/dm^2
- Tension in conveying a supportive copper foil: 0.05 kg/mm

Preparation of surface roughened layer of coarse particles

(A) Conveying system for copper foil in accordance with zigzag path

[0043]

- Anode: insoluble electrode
- Cathode: treated surface of supportive copper foil
- Interelectrode distance (indicated in Table 1)
- Composition of electrolytic plating solution: Cu: 10 g/L and H_2SO_4: 50 g/L
- Temperature of electrolytic plating bath: 40°C
- Current density for electrolytic plating: 30 A/dm^2
- Tension in conveying a supportive copper foil: 0.05 kg/mm (B) Conveying system of copper foil with a drum
- Anode: insoluble electrode
- Cathode: surface of supportive copper foil supported with a drum of 100 cm diameter
- Interelectrode distance (indicated in Table 1)
- Composition of electrolytic plating solution: Cu: 20 g/L and H_2SO_4: 50 g/L
- Temperature of electrolytic plating bath: 40°C
- Current density for electrolytic plating: 30 A/dm^2
- Tension in conveying a supportive copper foil: 0.05 kg/mm

2. Evaluation of ultrathin copper foil

[0044] Accuracy of the thickness of ultrathin copper foils obtained as described above was evaluated using the following method. Results are shown in Table 1.

Evaluation of accuracy of the thickness determined by the weight method

[0045] Firstly the total weight of a supportive copper foil and an ultrathin copper foil is measured and then an ultrathin copper layer is peeled off to reweigh the supportive copper foil to assign the weight difference between the former and the latter as the weight of the ultrathin copper layer. The ultrathin copper foil was punched out into a 3 cm x 3 cm sheet

with the press yielding a sample piece for determining the weight of an ultrathin copper layer. To study accuracy of the thickness determined from the weight, the thickness of the ultrathin copper layer in each standard is determined by the weight method at 10 points with equal space in the width direction and 6 points (spacing of 4 cm) in the length direction, a total of 60 points to calculate the mean and the standard deviation (σ). The formula for calculating accuracy of the thickness is given as follows.

$$\text{Accuracy in thickness (\%)} = 3\sigma \times 100/\text{mean}$$

[0046] Repeat accuracy of the measurement method is 0.2%.

[0047] A balance HF-400 (manufacture by A & D Company, Ltd.) was used as a balance and a press HAP-12 (manufactured by NOGUCHI PRESS Co., Ltd.) was used as the press.

Evaluation of accuracy of the thickness determined by the four-point probe method

[0048] The thickness of the supportive copper foil and the ultrathin copper foil is determined by measuring the resistivity with the four-point probe and then the ultrathin copper layer is peeled off to remeasure the resistivity of the supportive copper foil for determining its thickness to assign the difference between the former and the latter as the thickness of the ultrathin copper layer. To study accuracy of the thickness, the thickness of the ultrathin copper layer in each standard is determined at a spacing of 5 mm in the width direction, a total of 280 measuring points to calculate the mean and the standard deviation (σ). The formula for calculating accuracy of the thickness determined by measuring the resistivity with the four point probe is given as follows.

$$\text{Accuracy in thickness (\%)} = 3\sigma \times 100/\text{mean}$$

[0049] Repeat accuracy of the measurement method is 1.0%.

[0050] A four point probe CMI-700 (manufactured by Oxford Instruments PLC) was used as the four point probe.

Table 1

	Foil thickness (μm)	Release layer		Ultrathin layer (mm)		Surface roughened layer of coarse particles		Accuracy of thickness (%)	
		Conveying system	Interelectrode distance (mm)	Conveying system	Interelectrode distance (mm)	Conveying system	Interelectrode distance (mm)	Weight method	Four-point probe method
Example 1	3	zigzag	50	drum	8	zigzag	50	2.55	9.18
Example 2	5	zigzag	50	drum	8	zigzag	50	1.58	8.32
Example 3	2	zigzag	50	drum	8	zigzag	50	2.86	9.68
Example 4	3	drum	8	drum	8	zigzag	50	2.45	8.89
Example 5	5	drum	8	drum	8	zigzag	50	1.45	8.12
Example 6	2	drum	8	drum	8	zigzag	50	2.65	9.63
Example 7	3	drum	8	drum	8	zigzag	50	2.45	8.89
Example 8	5	drum	8	drum	8	zigzag	50	1.45	8.12
Example 9	2	drum	8	drum	8	zigzag	50	2.54	9.32
Example 10	3	drum	8	drum	8	drum	8	1.56	6.54
Example 11	5	drum	8	drum	8	drum	8	1.04	5.63
Example 12	2	drum	8	drum	8	drum	8	1.89	7.04
Example 13	5	drum	5	drum	5	drum	5	0.50	2.67
Example 14	2	drum	5	drum	5	drum	5	0.81	4.03
Example 15	3	drum	5	drum	5	drum	5	0.72	3.31
Example 16	12	drum	5	drum	5	drum	5	0.31	1.02
Comparative Example 1	3	zigzag	50	zigzag	50	zigzag	50	4.56	15.36
Comparative Example 2	5	zigzag	50	zigzag	50	zigzag	50	3.12	12.11
Comparative Example 3	2	zigzag	50	zigzag	50	zigzag	50	4.89	16.22

Results of evaluation

[0051] In Examples 1-16 accuracy of the thickness of the ultrathin copper layer is 3% or less in every one by the weight method and 10% or less in every one by the four-point probe method, indicating variation of the thickness is effectively prevented.

[0052] In Comparative Examples 1-3 accuracy of the thickness exceeds 3% in every one by the weight method and exceeds 10% in every one by the four-point probe method, indicating large variation in the thickness.

Claims

1. An ultrathin copper foil comprising a supportive copper foil, a release layer superposed on the supportive copper foil, and an ultrathin copper layer superposed on the release layer, wherein
accuracy of the thickness of the ultrathin copper layer measured with the weight method is 3.0% or less.

2. An ultrathin copper foil comprising a supportive copper foil, a release layer superposed on the supportive copper foil, and an ultrathin copper layer superposed on the release layer, wherein
accuracy of the thickness of the ultrathin copper layer measured with the four-point probe method is 10.0% or less.

3. The ultrathin copper foil according to claim 1 or 2, having a surface roughened layer of coarse particles on the surface of the ultrathin copper layer.

4. A method of manufacturing an ultrathin copper foil comprising a supportive copper foil, a release layer superposed on the supportive copper foil, and an ultrathin copper layer superposed on the release layer by treating the surface of the belt-like shaped supportive copper foil conveyed in the length direction with the roll-to-roll conveying system, comprising:

   a step of forming the release layer on the surface of the supportive copper foil conveyed by a conveying roller and a step of forming an ultrathin copper layer on the surface of the release layer by electrolytic plating while supporting with a drum the supportive copper foil on which the release layer is formed and which is conveyed by a conveying roller.

5. The manufacture method of an ultrathin copper foil according to claim 4, wherein the step of forming the release layer is performed by forming the release layer on the surface of the supportive copper foil by electrolytic plating while supporting with a drum the supportive copper foil conveyed by a conveying roller.

6. The manufacture method of the ultrathin copper foil according to claim 4 or 5, further comprising a step of forming the surface roughened layer of coarse particles on the surface of the ultrathin copper layer of the supportive copper foil conveyed by a conveying roller.

7. The manufacture method of the ultrathin copper foil according to claim 6, wherein the step of forming the surface roughened layer of coarse particles is performed by forming a surface roughened layer of coarse particles on the surface of the ultrathin copper layer by electrolytic plating while supporting with a drum the supportive copper foil conveyed by a conveying roller.

8. An ultrathin copper layer comprising an electrolytic copper foil superposed on a release layer superposed on a supportive copper foil and constituting an ultrathin copper foil together with the supportive copper foil and the release layer, wherein
accuracy of the thickness of the ultrathin copper layer measured with the weight method is 3.0% or less.

9. An ultrathin copper layer comprising an electrolytic copper foil superposed on a release layer superposed on a supportive copper foil and constituting an ultrathin copper foil together with the supportive copper foil and the release layer, wherein
accuracy of the thickness of the ultrathin copper layer measured with the four-point probe method is 10.0% or less.

10. The ultrathin copper layer comprising electrolytic copper foil according to claim 8 or 9, superposed on the release layer superposed on the supportive copper foil and constituting the ultrathin copper foil together with the supportive copper foil and the release layer, and

having a surface roughened layer of coarse particles on the surface of the ultrathin copper layer.

11. A printed circuit board manufactured using the ultrathin copper foil according to any one of claims 1 to 3.

12. A printed circuit board using the ultrathin copper layer according to any one of claims 8 to 10.

FIG. 1

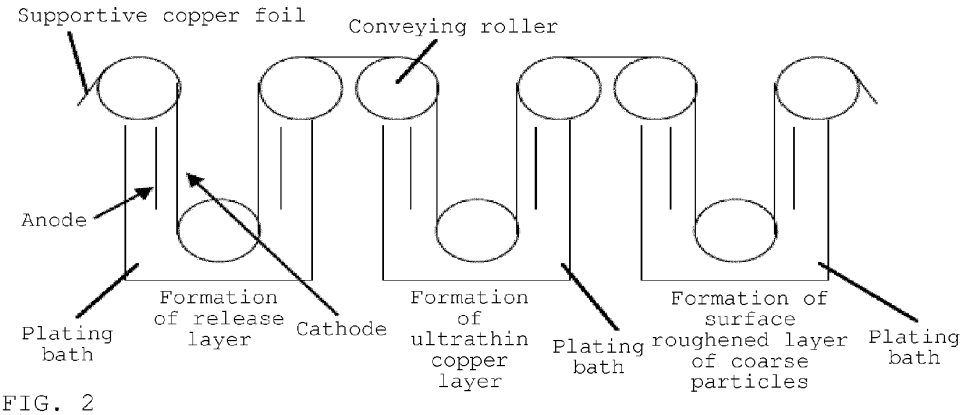


FIG. 2

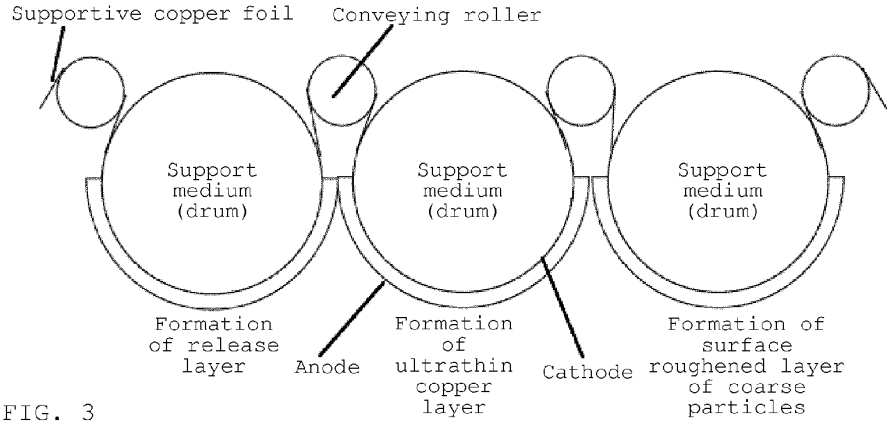


FIG. 3

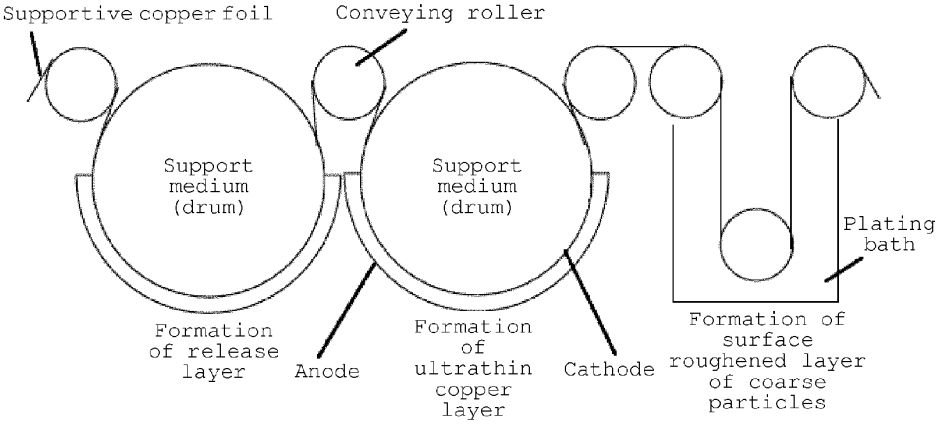
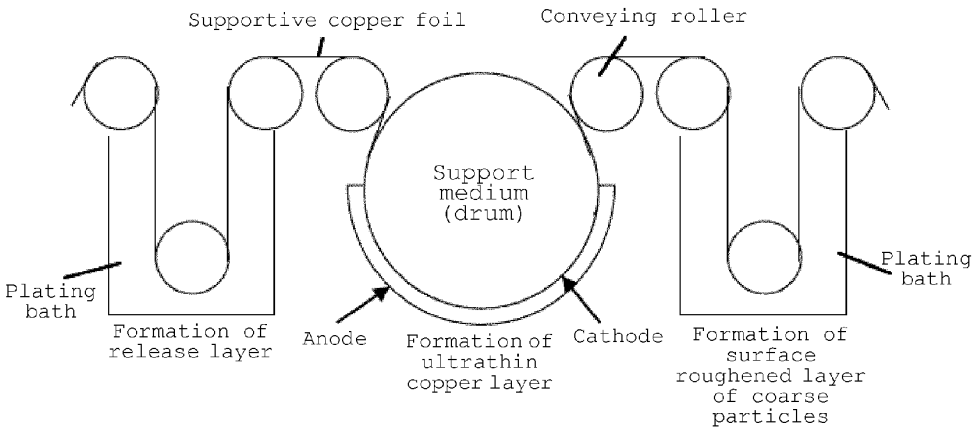


FIG. 4


Supportive copper foil
Conveying roller
Support medium (drum)
Plating bath
Plating bath
Formation of release layer
Anode
Formation of ultrathin copper layer
Cathode
Formation of surface roughened layer of coarse particles

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/083531

A. CLASSIFICATION OF SUBJECT MATTER
C25D1/04(2006.01)i, *C25D7/06*(2006.01)i, *H05K1/09*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25D1/04, C25D7/06, H05K1/09

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2013
Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	JP 8-209396 A (Ishifuku Metal Industry Co., Ltd.), 13 August 1996 (13.08.1996), & WO 1997/034029 A1 & CA 2248777 A & EP 887441 A1 & CN 1214088 A & US 6051118 A & TW 389795 B	1-12
A	JP 61-87889 A (Kawasaki Steel Corp.), 06 May 1986 (06.05.1986), (Family: none)	1-12

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
01 March, 2013 (01.03.13)	12 March, 2013 (12.03.13)
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/083531

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2004-35985 A (Kawasaki Heavy Industries, Ltd.), 05 February 2004 (05.02.2004), (Family: none)	1-12
A	JP 2004-131821 A (Kawasaki Heavy Industries, Ltd.), 30 April 2004 (30.04.2004), (Family: none)	1-12
A	WO 2012/046804 A1 (The Furukawa Electric Co., Ltd.), 12 April 2012 (12.04.2012), & TW 201229322 A	1-12

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Patent documents cited in the description

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Detail Image

CLAIMS DETAILED DESCRIPTION

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CLAIMS

(57)[Claim(s)]
[Claim 1]
Electrolytic copper foil containing 20-5200 ppm silver.
[Claim 2]
A manufacturing method of the electrolytic copper foil according to claim 1 characterized by using a sulfuric acid copper sulfate solution which added a silver salt meltable to the electrolysis solution as an electrolysis solution so that silver ion concentration in the electrolysis solution may be set to 1-50 ppm.

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最終頁に続く

(54)【発明の名称】銀を含む電解銅箔

(57)【特許請求の範囲】

【請求項1】

２０～５２００ｐｐｍの銀を含む電解銅箔。

【請求項2】

電解液として、該電解液中の銀イオン濃度が１～５０ｐｐｍとなるように該電解液に可溶な銀塩を添加した硫酸酸性硫酸銅溶液を使用することを特徴とする請求項１に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、プリント回路基板（ＰＣＢ）の製造に用いられる電解銅箔に関するものであり、特には２０～５２００ｐｐｍの銀を含有させることにより室温及び１８０℃での機械的特性を向上させた電解銅箔に関する。

【０００２】

【従来の技術】

電解銅箔は、回転するカソードとそれに対向するアノードとの間に電解液を流しながら電圧を加え、そして銅を回転するカソード上に析出させ、そして所定厚さとなった析出銅をカソードから剥ぎ取ることにより製造される。電解液は銅イオンと硫酸イオンを含有し、これに有機添加剤を加えて、また塩素イオン濃度を管理することにより銅箔の特性を制御している。

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【０００３】
例えば、特開平４－５０１８８７号は、ゼラチン（具体的には、ニカワ）及び活性硫黄含有成分（具体的には、チオ尿素）を添加することにより、低プロファイルで、かつ、ＩＰＣ１級又は３級と同等以上の特性を持つ銅箔の製造について記載する。
特開平５－５０２０６２号は、塩素イオンを２０ｐｐｍ以下、ゼラチン（具体的には、ニカワ）及び／又は活性硫黄含有成分（具体的には、チオ尿素）を微量（具体的には、０～４ｐｐｍ）添加することにより、高温（１８０℃）での伸び率５．５％以上、室温での引張り強度の大きい（６００００ｐｓｉ以上）銅箔を製造することを記載する。
更に、特開平８－５３７８９号は、０．０５～２．０ｐｐｍのチオ尿素若しくはその誘導体、０．０８～１２ｐｐｍの高分子多糖類及び分子量１００００以下の膠を０．０３～４ｐｐｍ添加することにより、ロープロファイルで、常温及び高温における伸び率が高く、かつ抗張力が高い銅箔の製造について記載する。
このように、ニカワ、チオ尿素等の有機物を添加することにより、銅箔の室温及び／又は高温での機械的特性の改善がなされてきた。
【０００４】
しかしながら、ニカワ、チオ尿素等の有機物は、電解酸化等により分解され、電解液中でその濃度を一定に保つことが難しい、或いは、分解物の影響により製造される銅箔の特性が一定のものを得ることが難しい、更には、分解物の影響により電解銅箔の特性が悪化する場合もある等の問題点があった。
例えば、チオ尿素は熱および電解により分解し、この分解物は電析物である銅箔の性質、例えば室温での抗張力、および１８０℃での破断伸びを低下させ、特性に悪影響を与える。
銅箔の抗張力は取扱い易さを表す１つの指標であり、この値が低くなると、一般に銅箔は柔らかく、取扱いの際にシワができ易くなる。シワができた銅箔をＰＣＢに用いると、シワの部分で電気的な接触不良が発生する場合がある。
近年の電子機器の小型、軽量化に伴い、より高密度の電子回路の形成が求められ、これに応えるために、複数の基板を張り合わせた積層板が広く用いられているが、この積層板の作製には、約１８０℃の熱を約１時間かけて基板と銅箔を張り合わせる工程がある。この工程では、基板と銅箔の熱膨張率の違いから、銅箔の１８０℃破断伸びが小さいと、銅箔が基板の膨張に追随することができずにクラックが発生し、電気的な接触不良が発生する場合がある。
【０００５】
このため電解液中の有機物、特に、ニカワについては、その濃度管理のために過剰分を活性炭等で除去することが一般的に行われてきた。
又、チオ尿素については、特願平８－２８４６１８号において、電解液中に金属銅を添加することにより、チオ尿素及び／又はその分解物を除去することにより濃度管理を行うことが提案されている。
【０００６】
【発明が解決しようとする課題】
このようにニカワ、チオ尿素等の有機物の添加は、銅箔の特性を向上させることが出来るという反面、その濃度管理及び分解物の除去が必要であり、銅箔の特性を一定に保つことが難しいという問題点があった。
従って、本発明の課題は、こうした有機物の添加に頼ることなく室温及び高温での特性に優れた銅箔を製造することである。
【０００７】
【課題を解決するための手段】
そこで、これら課題を解決するため、本発明者等が鋭意検討した結果、濃度管理が容易な無機イオン、特には、銅箔に取り込まれても銅の電気的特性を損なわない銀イオンを添加することで、室温及び高温での特性に優れた銅箔を製造することが出来ることを見出した。電解銅箔に銀を２０～５２００ｐｐｍ共析させることにより、電解銅箔の機械特性が向

上する。
かくして、本発明は２０～５２００ｐｐｍの銀を含む電解銅箔を提供する。
【０００８】
【発明の実施の形態】
電解銅箔は、円筒状の回転するカソードとカソードに沿ってカソードとほぼ一定の距離に保たれて配置されるアノードとの間に銅イオンと硫酸イオンを含有する硫酸酸性硫酸銅溶液から成る電解液を流し、カソードに銅が電析するように有効な量の電圧を印加し、回転するカソード周囲に銅を電着していくことにより製造される。所定の厚さとなった薄膜はカソードからはぎ取られる。カソード面側がシャイニー面を構成しそして電着面側がマット面を構成する。
【０００９】
硫酸酸性硫酸銅溶液の銅イオン濃度は一般に７０～１２０ｇ／ｌでありそして硫酸濃度は一般に５０～１２０ｇ／ｌである。
電流密度Ｄｋは特には限定されず、通常範囲、５０～２００Ａ／ｄｍ^2、特には１００～１５０Ａ／ｄｍ^{2}で十分である。
硫酸酸性硫酸銅溶液の液温度もまた特には限定されるものではなく、通常４０～８０℃、特には５０～６０℃範囲に管理される。
硫酸酸性硫酸銅溶液の液流速もまた特には限定されるものではなく、通常１．５ｍ／ｓｅｃ以上、好ましくは２．０～５ｍ／ｓｅｃとされる。
【００１０】
本発明に従えば、電解液中に銀を含有させ、銀を電解銅箔中に共析させることにより、２０～５２００ｐｐｍの銀を含む電解銅箔を製造する。電解液中に銀イオンを１～５０ｐｐｍの範囲で添加することにより、電解銅箔中の銀濃度を２０～５２００ｐｐｍに管理することができる。電解銅箔中の銀濃度が２０ｐｐｍ未満の場合には、室温及び１８０℃での機械特性を向上させる効果が少ない。又、５２００ｐｐｍを超える場合には、機械特性を向上させる効果が少なくなる上、銀添加のコストが高くなり経済的に不利となる。銀イオンは、電解液に可溶な銀塩、例えば硫酸銀の形で電解液中に添加することができる。
銀を電解銅箔中に含ませることにより、室温の伸び率を損なうことなく、室温の抗張力を増大させ、また１８０℃での抗張力及び伸び率を増大させることができる。
【００１１】
【実施例】
表１は、電解液中に銀イオンを１～５０ｐｐｍを添加し、電流密度：１２０Ａ／ｄｍ^2、電解液温度：５７℃、液流速：２ｍ／ｓｅｃとした場合の電解銅箔中に共析する銀濃度並びに室温及び１８０℃での機械的性質（抗張力及び伸び率）を調べた結果である。
【００１２】
【表１】

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表１：電解銅箔に共析する銀濃度、室温および180 ℃での機械特性

試料番号	電解液中の銀濃度（ppm）	電解箔中の銀濃度（ppm）	室温での機械特性		180 ℃での機械特性	
			抗張力（kg/mm²）	伸び率（%）	抗張力（kg/mm²）	伸び率（%）
1	0	0	49.7	7.2	17.7	17.4
2	1	20	48.4	7.2	21.6	22.8
3	5	220	52.4	7.4	24.5	28.0
4	10	630	51.1	9.0	26.1	36.6
5	20	1800	53.8	7.2	28.7	25.0
6	30	2500	55.0	6.6	30.2	30.0
7	50	5200	50.1	7.4	33.3	23.0

【００１３】
この結果、銀が共析することにより、室温の伸び率を損なうことなく、室温の抗張力は、増大していることが分かる。また、１８０℃の抗張力は、大きく増大し、１８０℃伸び率も、銀濃度５２００ｐｐｍでも銀を含まないものより大きいことが分かる。特に、銀箔中の銀濃度２０～２５００ｐｐｍのものは１８０℃抗張力及び伸び率も無添加より大きく優れている。

【００１４】
【発明の効果】
濃度管理が容易な無機イオンとして銅箔に取り込まれても銅の電気的特性を損なわない銀イオンを添加することで、室温及び１８０℃での機械的特性に優れた銅箔を製造することが出来る。

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特開平０５－１３８２０６（ＪＰ，Ａ）
特開昭６３－０１４８８６（ＪＰ，Ａ）
日本伸銅協会，銅および銅合金の基礎と工業技術，日本，日本伸銅協会，１９９４年１０月３１日，改訂版，ｐ．４２３－４２７

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APPLICANT : JX NIPPON MINING & METALS CORP;

INVENTOR : HATANO TAKATSUGU;

INT.CL. : H01M 4/66 (2006.01), H01M 4/133 (2010.01), H01M 4/134 (2010.01), H01M 10/0566 (2010.01), H01M 10/052 (2010.01), H01B 5/02 (2006.01), C22C 9/02 (2006.01), C22F 1/08 (2006.01), C22F 1/00 (2006.01)

TITLE : ROLLED COPPER FOIL AND NEGATIVE ELECTRODE COLLECTOR USING THIS, NEGATIVE ELECTRODE PLATE, AND SECONDARY BATTERY

ABSTRACT : PROBLEM TO BE SOLVED: To provide a rolled copper foil suitable as a negative electrode collector material of a secondary battery and a negative electrode collector using this, a negative electrode plate, and a battery.

SOLUTION: The rolled copper foil for secondary battery negative electrode collector is a copper alloy foil of oxygen-free copper base which contains Sn of 0.05-0.22 mass% and the rest is Cu and impurities and in which the Sn concentration in the surface oxidized film is 0.16-1.5 mass% and which has excellent cycle characteristics. The copper foil may contain Ag of 0.1 mass% or less and preferably has a tensile strength of 480 MPa or more and a conductivity of 80% IACS or more, and maintains the tensile strength of 400 MPa of more after annealing for 30 minutes at 300°C. The secondary battery using this copper foil as a current collector of the negative electrode plate is superior in charge and discharge cycle life.

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5H017 AA03 AS10 BB06 CC01 DD05 EE01 HH00 HH01 HH07 HH08 HH09 HH10

最終頁に続く

(54)【発明の名称】圧延銅箔、並びにこれを用いた負極集電体、負極板及び二次電池

(57)【要約】
【課題】二次電池の負極集電体材料として好適な圧延銅箔、並びにそれを用いた負極集電体、負極板及び電池。
【解決手段】０．０５～０．２２質量％のＳｎを含有し残部Ｃｕ及び不純物からなる無酸素銅ベースの銅合金箔であり、表面酸化膜中のＳｎ濃度が０．１６～１．５質量％である良好なサイクル特性を有する二次電池用負極集電体用圧延銅箔。この銅箔は、０．１質量％以下のＡｇを含有してもよく、好ましくは４８０ＭＰａ以上の引張り強さ及び８０％ＩＡＣＳ以上の導電率を有し、３００℃で３０分間焼鈍後に４００ＭＰａ以上の引張り強さを維持する。この銅箔を負極板の集電体として用いた二次電池は、充放電サイクル寿命に優れる。
【選択図】　なし

【特許請求の範囲】
【請求項１】
０．０５～０．２２質量％のＳｎを含有し残部Ｃｕ及び不純物からなる無酸素銅ベースの銅合金箔であり、表面酸化膜中のＳｎ濃度が０．１６～１．５質量％であることを特徴とする、良好なサイクル特性を有する二次電池用負極集電体用圧延銅箔。
【請求項２】
更に０．１質量％以下のＡｇを含有することを特徴とする請求項１記載の圧延銅箔。
【請求項３】
４８０ＭＰａ以上の引張り強さ及び８０％ＩＡＣＳ以上の導電率を有する請求項１又は２記載の圧延銅箔であり、３００℃で３０分間加熱後に４００ＭＰａ以上の引張り強さを維持することを特徴とする圧延銅箔。
【請求項４】
請求項１～３いずれか１項記載の圧延銅箔より構成される負極集電体。
【請求項５】
請求項４に記載の負極集電体の少なくとも片面に、炭素質材料または黒鉛質材料を主成分とする負極活物質層を有する負極板。
【請求項６】
請求項４に記載の負極集電体の少なくとも片面に、金属リチウム、金属すず、すず化合物、けい素単体、及びけい素化合物からなる群から選ばれた少なくとも１種以上を含有する活物質層を有する負極板。
【請求項７】
請求項５又は６記載の負極板が、リチウム遷移金属複合酸化物を正極活物質の主成分とする正極板とセパレータを介して絶縁配置された極板群、非水電解液、並びに極板群及び非水電解液を収容する電池ケースとから構成される二次電池。
【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をはじめとする二次電池の負極集電体材料として好適な圧延銅箔、並びにそれを用いた負極集電体、負極板及び電池に関する。
【背景技術】
【０００２】
携帯電話、ノート型パソコン等のポータブル機器の普及に伴い、小型で高容量の二次電池の需要が伸びている。また、電気自動車やハイブリッド車等に用いられる中・大型の二次電池の需要も急増している。二次電池のなかでも、リチウムイオン二次電池は、軽量でエネルギー密度が高いことから多くの分野で使用されている。
リチウムイオン二次電池としては、アルミニウム箔に$LiCoO_2$、$LiNiO_2$、$LiMn_2O_4$等の化合物をコーティングしたものを正極として用い、銅箔に炭素質材料等を活物質としてコーティングしたものを負極に用いるものが知られている（図２）。
【０００３】
銅箔には圧延銅箔と電解銅箔がある。圧延銅箔は、強度、疲労特性等の点で二次電池負極板の材料として優れている。二次電池負極板材料として市販されている圧延銅箔の多くは、タフピッチ銅（ＪＩＳ－Ｃ１１００）を素材とするものである。タフピッチ銅とは、１００～５００質量ｐｐｍの酸素を含有する純銅であり、銅分は９９．９０質量％以上に規格化されている（以下、質量ｐｐｍ及び質量％をそれぞれｐｐｍ及び％と表記する）。
圧延銅箔の製造プロセスでは、タフピッチ銅の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、最後に最終冷間圧延で、例えば３５～５μｍの範囲の所定の厚みに仕上げる。
【０００４】
一般的に、銅箔負極板は、電解銅箔や圧延銅箔を用いて次のプロセスで製造される。
（１）活物質と結着剤とを溶剤に混練分散したペーストを、集電体となる銅箔の片面もし

くは両面に塗布して負極板材とする。
（２）１５０～３００℃の温度で数時間から数十時間加熱し乾燥する。
（３）必要に応じ、負極板材に加圧する。
（４）せん断加工を施し、所定形状の負極板へ成型する。
せん断加工の例としては、プレス機による打ち抜き加工、シャーリングによる切断加工、丸刃スリッターによる切断加工等がある。
【０００５】
タフピッチ銅または無酸素銅を素材とする従来の圧延銅箔は、上記（２）乾燥工程において再結晶を起こして銅箔強度が低下（軟化）し、引張強さが２００ＭＰａ近くまで低下する。このような軟らかい銅箔は、電池製造工程での負極板の巻き取り、巻回による極板群の製造時に高張力の負荷がかけられて箔切れを起こしやすくなる。
又、リチウムイオン二次電池では、充電時にはリチウムイオンが正極から負極に移動し、放電時にはリチウムイオンが負極から正極に移動する。リチウムイオンの移動に伴って負極活物質が膨張収縮するため、銅箔は充放電によって機械的な繰り返しストレスを受ける。そのため、軟化した銅箔は充放電による機械的な繰り返しストレスを受けて変形し、銅箔表面に塗布された活物質が剥離しやすいと共に、銅箔自体も損傷しやすくなる。
【０００６】
また、二次電池の小型化に伴い、負極集電体である銅箔の薄肉化が進んでいる。銅箔が薄肉化すると、電池製造において活物質の塗布時に高張力の負荷がかけられて箔切れを起こしやすくなると共に、上記軟化による箔切れが更に発生しやすくなる。従って、最終圧延加工後の製品（圧延上がり）においてより高い引張強さを有すると共に、軟化による箔切れも起こさない銅箔が求められている。
このような課題に対応するため、タフピッチ銅を素材とする圧延銅箔に替わり、銅合金を素材とする圧延銅箔（以下、銅合金箔）が提案されている。
【０００７】
特開２０００－３０３１２８（特許文献１）では、無酸素銅にＣｒ、Ｚｎ、Ａｇ、Ｃａ、Ｓｎ、ＳｂまたはＢｉを５０または１００ｐｐｍ添加した銅合金箔が開示されている。
特開２０００－１３３２７６（特許文献２）では、Ｚｎを１０～３５％の範囲で含有する銅合金箔が開示されている。
特開平１１－３３９８１１（特許文献３）では、Ｃｕ－０．１％Ｆｅ－０．０３％Ｐ、Ｃｕ－０．３％Ｃｒ－０．２５％Ｓｎ－０．２％Ｚｎ及びＣｕ－０．１％Ｎｉを素材とする銅合金箔が開示されている。
特開２０００－３２８１５９（特許文献４）では、０．００２～０．４５重量％のＰを含有し、これに０．００６～０．２５重量％のＦｅまたは／及び０．００５～０．２５重量％のＡｇを添加した銅合金箔が開示されている。これら合金は、りん脱酸銅をベースとしており、Ｐの特性への弊害を発現させないようにＰ濃度を制限している。
特開２００３－２８６５２８（特許文献５）では、０．０６３～０．２３１％のＳｎを含有し、水素濃度と酸素濃度を適正に調整した銅合金箔が開示されている。この銅箔はピンホールと屈曲寿命が改善されており、リチウムイオン二次電池の負極集電体にも使用できる。
【先行技術文献】
【特許文献】
【０００８】
【特許文献１】特開２０００－３０３１２８号公報
【特許文献２】特開２０００－１３３２７６号公報
【特許文献３】特開平１１－３３９８１１号公報
【特許文献４】特開２０００－３２８１５９号公報
【特許文献５】特開２００３－２８６５２８号公報
【発明の概要】
【発明が解決しようとする課題】

【０００９】
特許文献１の銅合金箔は４６０～４８０ＭＰａの引張強さを有しているが、その耐熱性は、２００℃で３０分の熱履歴後の４００～４３０ＭＰａの引張強さを目標にしており、更に高温でも引張強さを維持する銅箔は目的とされていなかった。特許文献２では実施例の中で最も導電率が高い合金はＣｕ－１０％Ｚｎ（ＪＩＳ－Ｃ２２００）であり、その導電率は４４％ＩＡＣＳに過ぎない（日本伸銅協会：伸銅品データブック（１９９７））。特許文献３のＦｅ－Ｐ、Ｃｒ等の析出物が形成される銅合金箔では、より高い強度と耐熱性が得られるものの、箔が脆くなり極薄箔への圧延が困難であった。そして、Ｆｅ－Ｐ粒子が析出するＣｕ－Ｆｅ－Ｐ合金、及びＣｒ粒子が析出するＣｕ－Ｃｒ－Ｓｎ－Ｚｎ合金では、５５０ＭＰａの引張強さが得られているが、Ｃｕ－Ｎｉ合金の引張強さは、ぎりぎり５００ＭＰａに達するレベルである。特許文献４で使用されるＡｇは高価なために添加量が制限されることに加え、３００℃で５分の熱履歴後の引張強さを目標にしており、更に長時間でも引張強さを維持する銅箔は目的とされていなかった。
本発明者らの検討結果によれば、従来の負極集電体用銅合金箔のなかでは、特許文献５の無酸素銅をベースとするＣｕ－Ｓｎ合金が、比較的特性、製造性、コストのバランスに優れていたが、二次電池の充放電サイクル特性という点では充分なものではなかった。
【００１０】
近年、リチウムイオン二次電池の性能に対する要求は高度化している。これに伴い、負極集電体用の圧延銅箔に対しては、高張力が付加される製造工程中や、二次電池充放電のストレスを受けた際に、箔に破れが生じず、活物質が剥離しない性能が更に強く求められている。
本発明はＣｕ－Ｓｎ合金箔を改良することにより、リチウムイオン二次電池をはじめとする二次電池の負極集電体材料として好適な、充放電サイクル寿命に優れる圧延銅箔、並びにこれを用いた負極集電体、負極板及び二次電池を提供することを目的とする。
【課題を解決するための手段】
【００１１】
本発明者は、上記課題を解決すべく鋭意研究した結果、下記発明をなすに至った。
（１）０．０５～０．２２質量％のＳｎを含有し残部Ｃｕ及び不純物からなる無酸素銅ベースの銅合金箔であり、表面酸化膜中のＳｎ濃度が０．１６～１．５質量％であることを特徴とする、良好なサイクル特性を有する二次電池用負極集電体用圧延銅箔。
（２）更に０．１質量％以下のＡｇを含有することを特徴とする（１）記載の圧延銅箔。
（３）４８０ＭＰａ以上の引張り強さ及び８０％ＩＡＣＳ以上の導電率を有する（１）又は（２）記載の圧延銅箔であり、３００℃で３０分間加熱後に４００ＭＰａ以上の引張り強さを維持することを特徴とする圧延銅箔。
（４）上記（１）～（３）いずれか１項記載の圧延銅箔より構成される負極集電体。
（５）上記（４）に記載の負極集電体の少なくとも片面に、炭素質材料または黒鉛質材料を主成分とする負極活物質層を有する負極板。
（６）上記（４）に記載の負極集電体の少なくとも片面に、金属リチウム、金属すず、すず化合物、けい素単体、及びけい素化合物からなる群から選ばれた少なくとも１種以上を含有する活物質層を有する負極板。
（７）上記（５）又は（６）記載の負極板が、リチウム遷移金属複合酸化物を正極活物質の主成分とする正極板とセパレータを介して絶縁配置された極板群、非水電解液、並びに極板群及び非水電解液を収容する電池ケースとから構成される二次電池。
【図面の簡単な説明】
【００１２】
【図１】発明例６の試料表面における、ＳｎおよびＯ濃度の深さ方向のプロファイルである。
【図２】一般的な二次電池の構造を示す概略図である。
【発明を実施するための形態】
【００１３】

（銅箔の成分）
本発明では、銅箔の強度と耐熱性を改善するために無酸素銅にＳｎを添加している。Ｓｎ濃度が０．０５％以上、好ましくは０．１０％以上であると強度と耐熱性に優れた銅箔が得られる。一方、Ｓｎ濃度が０．２２％を超えると、導電率が低下して二次電池の負極集電体用として不適当になる。より好ましくは０．１５％以下であり、この場合８３％ＩＡＣＳ以上の導電率が安定して得られる。
【００１４】
本発明の銅合金箔は、無酸素銅の溶湯にＳｎを添加することにより溶製する。無酸素銅溶湯の酸素濃度は、通常１０ｐｐｍ以下である。タフピッチ銅溶湯のように１００～５００ｐｐｍの酸素を含む溶湯にＳｎを添加すると、Ｓｎが酸化して酸化すずを形成し、Ｓｎの耐熱性改善効果が得られない。ＳｎはＣｕ中に固溶した状態でＣｕの耐熱性を改善するが、酸化物として析出してしまったＳｎ成分はＣｕの耐熱性改善に寄与しないためである。酸素濃度の調整は、溶湯のカーボン脱酸等の当業者公知の技術により行うことができる。
【００１５】
本発明の銅合金箔は、０．１％以下のＡｇを含有することができる。Ａｇを添加することにより、導電率を低下させずに耐熱性を改善することができる。０．１％を超えるＡｇを添加すると耐熱性はさらに向上するが、製造コストが増加することに加え、延性が低下し箔への圧延加工が難しくなる。より好ましいＡｇ濃度は０．０６％以下である。なお、銅箔の溶解原料となる電気銅は、不可避的不純物として、通常Ａｇを１０ｐｐｍ程度含有する。
【００１６】
（銅箔の特性）
充放電ストレスによる銅箔の変形が生じず、電池の信頼性を更に向上させるには、乾燥工程を経た後に４００ＭＰａ以上の引張強さを保つことが好ましい。本発明で求められる乾燥工程での熱負荷レベルは、３００℃で３０分間の熱処理に相当する。これは従来の熱負荷の基準である２００℃で３０分（特許文献１）、３００℃で５分（特許文献４）などの条件より極めて厳しい条件である。
本発明の圧延銅箔は、３００℃で３０分間加熱後の引張強さが、好ましくは４００ＭＰａ以上、より好ましくは４５０ＭＰａ以上である。ここで、３００℃で３０分間加熱後に４００ＭＰａ以上の引張強さを維持するためには、圧延上がりの状態で、４８０ＭＰａ以上、好ましくは５２０ＭＰａ以上の引張強さを有している必要がある。
Ｓｎ濃度が０．０５％以上であると、上記条件加熱後の引張強さが４００ＭＰａ以上、０．１０％以上であると４５０ＭＰａ以上になる。
【００１７】
タフピッチ銅を素材とする従来の圧延銅箔の導電率は約１００％ＩＡＣＳであるが、素材を銅合金化することにより、銅箔の導電率は低下して電池性能が低下する傾向がある。本発明の圧延銅箔の導電率は、好ましくは８０％ＩＡＣＳ以上、更に好ましくは８３％ＩＡＣＳ以上であり、このレベルであると電池性能は低下しない。
【００１８】
（銅箔の酸化膜）
本発明の表面酸化膜中のＳｎ濃度は、０．１６～１．５質量％である。
ＳｎはＣｕより酸化しやすいため、酸化膜中のＳｎ濃度は母地中のＳｎ濃度と比較して高くなる。銅箔の表面に酸化すずが存在すると、金属化合物等の負極活物質に対する親和性が上昇するため、負極活物質を塗布して負極を製造する工程の作業効率が上昇する利点があることが予測できる。従って、従来技術では、Ｓｎ含有銅箔表面に必然的に存在する酸化すずに対する問題点は特に認識されていなかった。しかし、本発明者は、酸化膜中のＳｎ濃度が１．５％を越えると、酸化膜が脆くなって母地から剥離しやすくなり、銅箔と活物質との結合性が阻害されることを発見した。酸化膜中のＳｎ濃度を１．５％以下に制御することで、銅箔と活物質との密着性が向上し、電池の充放電サイクル寿命が向上した

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一方、酸化膜中のＳｎ濃度を０．１６％未満に調整しようとすると、活物質との密着性以外のところで弊害が生じる。例えば、後述するように、表面に酸化すずを局在させないために酸化雰囲気下で焼鈍を行うと、厚く不均一な酸化膜が生成し、酸洗後の最終圧延では材料破断が頻発する。

本発明の銅合金箔の酸化膜の厚さは１～４ｎｍであり、この範囲であれば酸化膜の厚みが銅箔と活物質との密着性に影響を及ぼすことはない。

本発明では、酸化膜のＳｎ濃度は、ＸＰＳ（Ｘ線光電子分光法）により試料表面をＡｒスパッタリングしてＳｎ濃度プロファイルを測定し、得られたプロファイルの、母地濃度に対応するベースラインよりも表面側に存在する最大ピーク濃度として表される。また、酸化膜の厚さは、上記ＸＰＳのＯ濃度のプロファイルにおいて、表面に濃化したＯが母地のＯ濃度まで低下するときの深さとして表される。

【００１９】

（銅箔の製造方法）

インゴットの溶製では、まずカーボンによる脱酸反応を利用して溶銅中の酸素濃度を１０ｐｐｍ以下に下げ、その後Ｓｎを添加する。溶銅中の酸素濃度が１０ｐｐｍを超える状態でＳｎを添加すると、Ｓｎが酸化し、酸化すずの介在物が生成してしまう。次に、インゴットを熱間圧延により厚さ１０ｍｍ程度の板とし、その後冷間圧延と再結晶焼鈍を繰り返し、最後に冷間圧延で所定厚み（一般的には３５～５μｍ）に仕上げる。厚みが５μｍ以下になると、単位面積当たりの引張強さが高くても破断しやすくなる。一方、３５μｍを超えると、負極板が厚くなるため二次電池を小型化しにくくなる。

再結晶焼鈍は、炉温が３００～８００℃の範囲、焼鈍時間が数秒間～数時間の範囲で、焼鈍後の結晶粒径が所定の大きさ（通常は３～３０μｍ）になる条件で行われる。焼鈍後の材料は、焼鈍中に生成した表面酸化膜を除去するため、硫酸水溶液等を用いて酸洗される。

【００２０】

最終圧延後の銅箔表面酸化膜中のＳｎ濃度を調整する方法は、本発明を限定するものではないが、例えば、最終圧延前の最終再結晶焼鈍における炉内のガス雰囲気を、下記影響を考慮して制御する。

雰囲気の還元性が強い場合、ＳｎがＣｕより酸化しやすい傾向がそのまま要因となってＣｕが酸化せずにＳｎが優先的に酸化し、Ｓｎリッチな酸化膜が形成される。焼鈍後の酸洗の際、Ｃｕの酸化物は酸に溶けやすいが、Ｓｎの酸化物は酸に溶けにくいため、酸化膜中のＳｎ濃度はさらに高くなる。焼鈍で生成した酸化膜は、最終圧延において部分的に割れたり剥離したりする場合もあるが、そのほとんどは箔製品の表面に残留する。

一方、雰囲気の酸化性が強いと、ＳｎとＣｕとの酸化傾向の差を区別できないほどＳｎとＣｕが同程度の速度で酸化され、酸化膜中のＣｕ／Ｓｎ濃度比が母地中のＣｕ／Ｓｎ濃度比に近付くものの、酸化膜が厚く不均一に成長する。このため酸洗後の材料表面に凹凸やピットが生じ、箔への圧延において銅箔にピンホールが生じたり銅箔が破断したりする。

【００２１】

好ましい最終圧延加工度は８０～９８％であり、より好ましくは８５～９５％である。ここで圧延加工度ｒは、ｒ＝（t_0－ｔ）／t_0（ｔ：圧延後の厚み、t_0：圧延前の厚み）とする。最終冷間圧延の加工度が８０％未満であると、圧延上がりの引張り強さを４８０ＭＰａ以上に調整することが難しくなる。また、最終冷間圧延の加工度が９８％を超えると、銅箔の耐熱性が低下し、３００℃で３０分間加熱後に４００ＭＰａ以上の引張強さを維持することが難しくなる。これは極度に蓄積される加工歪が再結晶を促進するためである。

【００２２】

（電池の構成）

本発明に関わる負極板及び二次電池は、上記銅箔を負極集電体として用いることを特徴

とするものであり、これ以外の構成については限定されず、一般に用いられている公知のものを用いることができる。

【００２３】

（負極）

負極は、本発明の負極集電体と、負極集電体の片面もしくは両面に形成される負極活物質より構成される。負極活物質としては、リチウムの吸蔵放出が可能な炭素質物、金属、金属化合物（金属酸化物、金属硫化物、金属窒化物）、リチウム合金などが挙げられる。

前記炭素質物としては、黒鉛、コークス、炭素繊維、球状炭素、熱分解気相炭素質物、樹脂焼成体などの黒鉛質材料もしくは炭素質材料；熱硬化性樹脂、等方性ピッチ、メソフェーズピッチ系炭素、メソフェーズピッチ系炭素繊維、メソフェーズ小球体などに５００～３０００℃で熱処理を施すことにより得られる黒鉛質材料または炭素質材料；等が挙げられる。

前記金属としては、リチウム、アルミニウム、マグネシウム、すず、けい素等が挙げられる。

前記金属酸化物としては、すず酸化物、ケイ素酸化物、リチウムチタン酸化物、ニオブ酸化物、タングステン酸化物等が挙げられる。前記金属硫化物としては、すず硫化物、チタン硫化物等が挙げられる。前記金属窒化物としては、リチウムコバルト窒化物、リチウム鉄窒化物、リチウムマンガン窒化物等が挙げられる。

リチウム合金としては、リチウムアルミニウム合金、リチウムすず合金、リチウム鉛合金、リチウムケイ素合金等が挙げられる。

【００２４】

負極活物質含有層には結着剤を含有させることができる。結着剤としては、カルボキシメチルセルロース（ＣＭＣ）及びスチレンブタジエン（ＳＢＲ）を含む混合物が挙げられる。ＣＭＣ及びＳＢＲを含む結着剤を使用することによって、負極活物質と集電体との密着性をより高くすることができる。

負極活物質含有層には、導電剤を含有させることができる。導電剤としては、アセチレンブラック、粉末状膨張黒鉛などのグラファイト類、炭素繊維粉砕物、黒鉛化炭素繊維粉砕物、等が挙げられる。

【００２５】

（正極）

正極は、正極集電体と、前記正極集電体の片面もしくは両面に形成される正極活物質含有層より構成される。

正極集電体としては、アルミニウム板、アルミニウムメッシュ材等が挙げられる。

正極活物質含有層は、例えば、活物質と結着剤とを含有する。正極活物質としては、二酸化マンガン、二硫化モリブデン、$LiCoO_2$、$LiNiO_2$、$LiMn_2O_4$等のカルコゲン化合物が挙げられる。これらのカルコゲン化合物は、２種以上の混合物で用いても良い。結着剤としては、フッ素系樹脂、ポリオレフィン樹脂、スチレン系樹脂、アクリル系樹脂のような熱可塑性エラストマー系樹脂、またはフッ素ゴムのようなゴム系樹脂を用いることができる。

活物質含有層には、導電補助材としてアセチレンブラック、粉末状膨張黒鉛などのグラファイト類、炭素繊維粉砕物、黒鉛化炭素繊維粉砕物、等をさらに含有することができる。

【００２６】

（セパレータ）

正極と負極の間には、セパレータか、固体もしくはゲル状の電解質層を配置することができる。セパレータとしては、例えば２０～３０μｍの厚さを有するポリエチレン多孔質フィルム、ポリプロピレン多孔質フィルム等を用いることができる。

【００２７】

（非水電解質）

非水電解質には、液状、ゲル状もしくは固体状の形態を有するものを使用することがで

きる。また、非水電解質は、非水溶媒と、この非水溶媒に溶解される電解質とを含むことが望ましい。

非水溶媒としては、エチレンカーボネート、ジメチルカーボネート、メチルエチルカーボネート、ジエチルカーボネート、γ－ブチロラクトン等が挙げられる。使用する非水溶媒の種類は、１種類もしくは２種類以上にすることが可能である。

電解質としては、過塩素酸リチウム（$LiClO_4$）、六フッ化リン酸リチウム（$LiPF_6$）、四フッ化硼酸リチウム（$LiBF_4$）、六フッ化砒素リチウム（$LiAsF_6$）等が挙げられる。電解質は、単独でも混合物の形態でも使用することができる。

【実施例】

【００２８】

（圧延銅箔の作製）

カーボン脱酸により酸素濃度を調整した溶銅にＳｎを添加した後、幅が５００ｍｍ、厚みが２００ｍｍのインゴットに鋳造した。このインゴットを８５０℃で３時間加熱し、熱間圧延により厚み１０ｍｍの板にした。次に、表面の酸化スケールを研削除去し、冷間圧延により１．５ｍｍの板とした。その後、再結晶焼鈍と冷間圧延を繰り返して、最終の圧延で厚みを１８～６μｍに仕上げた。

再結晶焼鈍は連続焼鈍ラインを用いて行った。炉温を７００℃とし、焼鈍後の結晶粒径が１０μｍになるように、材料の通板速度（炉内の滞留時間）を調整した。

最終圧延の加工度を変化させるために、最終焼鈍（最終冷間圧延直前の焼鈍）を施す板厚を予め調整した。

銅箔表面の酸化膜中のＳｎ濃度を、最終再結晶焼鈍における炉内のガス雰囲気の酸化還元雰囲気を、下記手法により適宜制御することにより調整した。用いた連続焼鈍炉は、ブタンガスと空気との混合ガスを燃焼させて熱源とする炉であり、炉内の雰囲気はＣＯ、CO_2、O_2、N_2の混合ガスである。ブタンガスと空気との混合比を変化させることにより、ＣＯ濃度とCO_2濃度との比（CO/CO_2）を調整した。CO/CO_2比が大きくなると還元性雰囲気となり、CO/CO_2比が小さくなると酸化性雰囲気となる。炉から出た後の材料は１０質量％硫酸水溶液で酸洗処理した。最終圧延後に得られた圧延銅箔について、下記評価を行った。

【００２９】

（成分）

銅箔母地中の酸素濃度を不活性ガス溶融－赤外線吸収法で、Ｓｎ及びＡｇ濃度をＩＣＰ－質量分析法で分析した。ここで、Ｓｎ及びＡｇ分析には銅箔試料を用いたが、Ｏ分析には１．５ｍｍの板から採取した試料を用いた。これは、箔試料では質量に対する表面積の比率が非常に大きいため（例えば１ｇの試料の場合、厚さ１．５ｍｍの板の表面積は１．５cm^2に対し、厚さ１０μｍの箔の表面積は２２０cm^2）、銅箔試料を用いて酸素を分析すると、表面の酸化膜及び吸着水膜中の酸素が加算され、酸素分析値が銅箔中の酸素濃度より５０ｐｐｍ程度増加するためである。なお、箔試料を用い、これが無酸素銅ベースの箔であることを判定するためには、試料の金属組織を観察し、酸化物粒子が存在しないこと（直径２μｍ以上の酸化物粒子が０．０１個／mm^2以下）を確認すればよい。なお、分析限界は１ｐｐｍであるが表中の表示は、質量％の小数点以下２桁までとした。

【００３０】

（引張強さ、導電率）

負極活物質の乾燥工程を模して圧延銅箔試料を３００℃で３０分間加熱した。加熱前及び加熱後の試料に対し、ＩＰＣ(Institute for Interconnecting and Packaging Electronics Circuits)規格、ＩＰＣ－ＴＭ－６５０；Ｍｅｔｈｏｄ　２．４．１９に準じて引張強さを求めた。試験片は、幅１２．７ｍｍ、長さ１５０ｍｍとし、試験片の長さ方向が圧延方向と平行になるように採取した。引張り速度は５０ｍｍ／ｍｉｎとした。

圧延上がり（加熱前）の試料に対し引張り試験用の試験片を用い、四端子法により２０℃での導電率を求めた。

【００３１】

（酸化膜）
ＸＰＳ（Ｘ線光電子分光法）を用い、試料表面をＡｒスパッタリングしながらＯ及びＳｎを分析することにより、試料表層におけるＯ及びＳｎの濃度プロファイルを測定した。測定条件は次の通りである。
装置：アルバック・ファイ株式会社製５６００ＭＣ、到達真空度：１．４×１０$^{-7}$Ｐａ、励起源：単色化ＡｌＫα、出力：２１０Ｗ、検出面積：８００μｍφ、入射角：４５度、取り出し角：４５度、中和銃なし。
（スパッタ条件）イオン種：Ａｒ＋、加速電圧：３ｋＶ、掃引領域：３ｍｍ×３ｍｍ、レート：SiO_2換算で２．０ｎｍ／ｍｉｎ。
後述する発明例６での測定結果を図１に示す。Ｓｎ濃度プロファイルにおけるＳｎのピーク値は０．８％であり、この値を酸化膜中のＳｎ濃度とした。また、Ｏ濃度のプロファイルより酸化膜の厚みを読み取ると１．８ｎｍとなる。ここで、酸化膜の厚さは、図中に点線で示すように、Ｏ濃度曲線の裾の部分に接線を引き、この接線が母地のＯ濃度（この場合はゼロ質量％）と交わる深さとした。

【００３２】
（サイクル寿命）
図２に示す円筒型のリチウムイオン二次電池を以下の手順で作製し、サイクル寿命を測定した。
（１）負極活物質として鱗片状黒鉛粉末５０重量部、結着剤としてスチレンブタジエンゴム５重量部、そして増粘剤としてカルボキシルメチルセルロース１重量部に対して水９９重量部に溶解した増粘剤水溶液２３重量部を、混錬分散して負極用ペーストを得た。この負極用ペーストを圧延銅箔試料表面にドクターブレード方式で厚さ２００μｍに両面塗布し、３００℃で３０分間加熱し乾燥した。加圧して厚さを１６０μｍに調整した後、せん断加工により成型し負極板６を得た。
（２）正極活物質として$LiCoO_2$粉末５０重量部、導電剤としてアセチレンブラック１．５重量部、結着剤としてＰＴＦＥ５０重量％水性ディスパージョン７重量部、増粘剤としてカルボキシルメチルセルロース１重量％水溶液４１．５重量部を、混練分散して正極用ペーストを得た。この正極用ペーストを、厚さ３０μｍのアルミニウム箔からなる集電体上にドクターブレード方式で厚さ約２３０μｍに両面塗布して２００℃で１時間加熱し乾燥した。加圧して厚さを１８０μｍに調整した後、せん断加工により成型し正極板５を得た。
（３）正極板５と負極板６とを、厚さ２０μｍのポリプロピレン樹脂製の微多孔膜からなるセパレータ７を介して絶縁した状態で渦巻状に巻回した電極群を電池ケース８に収容した。
（４）負極板６から連接する負極リード９を、前記ケース８と下部絶縁板１０を介して電気的に接続した。同様に正極板５から連接する正極リード３を、封口板１の内部端子に上部絶縁板４を介して電気的に接続した。これらの後、非水電解液を注液し、封口板１と電池ケース８とを絶縁ガスケット２を介してかしめ封口して、直径１７ｍｍ、高さ５０ｍｍサイズで電池容量が７８０ｍＡｈの円筒型リチウムイオン二次電池を作製した。
（５）電解液は、エチレンカーボネート３０体積％、エチルメチルカーボネート５０体積％、プロピオン酸メチル２０体積％の混合溶媒中に、電解質としてヘキサフルオロリン酸リチウム（$LiPF_6$）を１．０モル溶かした電解液を所定量注液した。この電解液を正極活物質層及び負極活物質層内に含浸させた。

【００３３】
作製した電池を用い、充放電サイクル特性を評価した。２０℃の環境下で充放電を行い、３サイクル目における放電容量を初期容量とし、初期容量に対して放電容量が８０％に低下するまでサイクル数を計数し、これをサイクル寿命とした。充電条件：４．２Ｖで２時間の定電流－定電圧充電を行い、電池電圧が４．２Ｖに達するまでは５５０ｍＡ（０．７ＣｍＡ）の定電流充電を行った後、さらに電流値が減衰して４０ｍＡ（０．０５ＣｍＡ）になるまで充電した。放電条件：７８０ｍＡ（１ＣｍＡ）の定電流で３．０Ｖの放電終

止電圧まで放電した。サイクル寿命が６００回以上になった場合に良好なサイクル特性が得られたと判定した。

【００３４】

評価結果を表１に示す。発明例３～１０、１２～１３、１５～１８、２０～２２、２６～３０は０．０５～０．２２質量％のＳｎを含有し、８０％ＩＡＣＳ以上の導電率と４８０ＭＰａ以上の引張り強さを有し、３００℃で３０分間焼鈍後にも４００ＭＰａ以上の引張り強さを維持している。また表面酸化膜中のＳｎ濃度が１．５％以下である。その結果、６００回以上の良好なサイクル寿命が得られている。

比較例１、２、発明例３～１０及び比較例１１では、銅合金中のＳｎ濃度の効果を検討している。

発明例３～１０は本発明の範囲内のＳｎ濃度であり、目的とする特性が得られた。発明例３、４はＳｎ濃度が低いため熱履歴後の引張強さにやや劣る。発明例９、１０はＳｎ濃度が高いため導電率がやや低い。

比較例１は従来の無添加無酸素銅であり、活物質乾燥工程における３００℃での３０分間の熱履歴により、銅箔の引張強さが２００ＭＰａ近くまで低下した。また、比較例２は無酸素銅にＳｎを添加したものの添加量が０．０５％未満であったため、３００℃での３０分間の熱履歴後、引張強さが４００ＭＰａを下回った。熱履歴後の引張強さが低いため、比較例１及び２の銅箔は、充放電の繰り返しストレスを受けて変形し、銅箔表面に塗布された活物質が剥離した。その結果、サイクル寿命が６００回に満たなかった。一方、比較例１１は０．２２％を超えるＳｎを添加したために導電率が８０％ＩＡＣＳを下回ってしまい、発熱や電圧損失により目的とする二次電池を製造できなくなる。

【００３５】

発明例１２及び１３はＡｇを好ましい範囲で添加して、導電率を低下させることなく耐熱性を向上させており、３００℃で３０分間加熱後の引張強さが、同量のＳｎを添加した発明例９よりも高い。

比較例１４は酸素が１０ｐｐｍを超えたものであり、添加したＳｎの一部が酸化して酸化すずとなった。このため、３００℃で３０分間加熱後の引張強さが４００ＭＰａを下回った。更に、充放電の繰り返しストレスを受けた際に酸化すずを起点として銅箔にクラックが生じて銅箔が変形し活物質が剥離した結果、サイクル寿命が６００回を大きく下回った。

発明例１５～１８は、発明例５～７の箔厚１０μｍに対して６μｍと１２μｍの箔厚としても、酸化膜の厚さが１～４ｎｍの範囲内であれば箔厚に関係なく目的とする効果を得られることを示す。

【００３６】

比較例１９、発明例２０～２２及び比較例２３及び２４では、表面酸化膜中のＳｎ濃度の効果を検討している。

発明例２０～２２は本発明の範囲内の表面酸化膜中Ｓｎ濃度であり、目的とする特性が得られた。

比較例１９では、最終焼鈍の際のＣＯ／CO_2比を０．１未満として雰囲気の酸化性が強くしたところ、表面酸化膜中のＳｎ濃度は低いが厚く不均一な酸化膜が生成し、酸洗で酸化膜を溶解した後の表面に顕著な凹凸が生じた。次工程の最終圧延で、この凹凸に起因して材料が破断し、特性を評価できなかった。表中「＊１」は評価不能を示す。

比較例２３及び２４では、最終焼鈍の際のＣＯ／CO_2比が０．３を超え雰囲気の還元性が強くなりすぎ、表面酸化膜のＳｎ濃度が１．５％を超えた。この酸化膜は脆いため銅箔と活物質との結合性が阻害され、充放電の繰り返しストレスを受けた際に活物質が銅箔から剥離し、サイクル寿命が６００回に満たなかった。

【００３７】

比較例２５、発明例２６～３０及び比較例３１では、最終圧延加工度の効果を検討している。

発明例２６～３０は適正な最終圧延加工度を採用したため、目的とする特性が得られた

。発明例２６は加工度がやや低く、発明例３０は加工度がやや高いため熱履歴後の引張強さにやや劣る。

比較例２５は加工度が８０％未満であったため、圧延上がりの引張強さが４８０ＭＰａ未満となり、この影響により、３００℃で３０分間の熱履歴を受けた後の引張強さが４００ＭＰａを下回った。比較例３１は加工度が９８％を超えたため、焼鈍軟化が促進され３００℃で３０分間の熱履歴を受けた後の引張強さが４００ＭＰａを下回った。比較例２５及び３１の銅箔は、充放電の繰り返しストレスを受けて変形し、銅箔表面に塗布された活物質が剥離した。その結果、サイクル寿命が６００回に満たなかった。

【００３８】

【表１】

	箔厚	Sn	Ag	O	最終圧延加工度	最終焼鈍の雰囲気	酸化膜厚	酸化膜のSn濃度	導電率	圧延上がりの引張強さ	300℃30分焼鈍後引張強さ	サイクル
	μm	質量%	質量%	質量ppm	%	CO/CO_2	nm	質量%	%IACS	MPa	MPa	回
比較例1	10	0.00	0.00	4	90	0.24	2.0	0.00	99	428	216	521
比較例2	10	0.03	0.00	3	90	0.15	1.5	0.33	96	476	375	563
発明例3	10	0.05	0.00	2	90	0.12	1.6	0.09	94	498	404	615
発明例4	10	0.07	0.00	3	90	0.15	2.4	0.23	92	527	431	637
発明例5	10	0.10	0.00	1	90	0.11	2.2	0.14	89	545	452	650
発明例6	10	0.12	0.00	3	90	0.22	1.8	0.80	88	548	462	664
発明例7	10	0.15	0.00	4	90	0.18	2.5	0.43	85	555	468	658
発明例8	10	0.18	0.00	3	90	0.10	1.2	0.24	83	558	475	663
発明例9	10	0.20	0.00	5	90	0.25	3.0	0.87	82	563	479	645
発明例10	10	0.22	0.00	2	90	0.20	2.2	0.52	80	567	480	670
比較例11	10	0.25	0.00	5	90	0.28	3.1	1.26	77	568	482	641
発明例12	10	0.20	0.05	1	90	0.25	1.4	0.98	82	585	493	666
発明例13	10	0.20	0.09	4	90	0.22	1.9	0.76	81	568	508	657
比較例14	10	0.07	0.00	25	90	0.20	2.3	0.59	93	466	391	394
発明例15	6	0.11	0.00	4	90	0.18	2.0	0.53	89	548	455	658
発明例16	6	0.14	0.00	5	90	0.26	1.8	0.86	86	552	468	639
発明例17	12	0.13	0.00	6	90	0.20	1.7	0.80	87	549	460	630
発明例18	12	0.15	0.00	3	90	0.21	1.6	0.74	85	557	473	649
比較例19	18	0.12	0.00	3	90	0.08	1.6	0.15	*1	*1	*1	*1
発明例20	18	0.12	0.00	3	90	0.11	1.8	0.18	88	550	459	662
発明例21	18	0.12	0.00	4	90	0.23	2.2	0.90	88	549	460	654
発明例22	18	0.12	0.00	1	90	0.30	1.9	1.41	88	553	462	618
比較例23	18	0.12	0.00	2	90	0.35	2.3	1.77	88	548	460	558
比較例24	18	0.12	0.00	2	90	0.48	3.6	3.10	88	547	461	418
比較例25	9	0.12	0.00	2	75	0.12	2.7	0.21	89	437	390	550
発明例26	9	0.12	0.00	1	80	0.14	1.9	0.24	89	483	432	629
発明例27	9	0.12	0.00	3	85	0.12	1.6	0.18	88	520	451	669
発明例28	9	0.12	0.00	2	90	0.11	1.5	0.16	88	547	460	663
発明例29	9	0.12	0.00	3	95	0.12	2.4	0.20	88	568	463	658
発明例30	9	0.12	0.00	4	98	0.15	2.3	0.27	87	587	439	632
比較例31	9	0.12	0.00	3	99	0.13	1.8	0.23	86	590	379	497

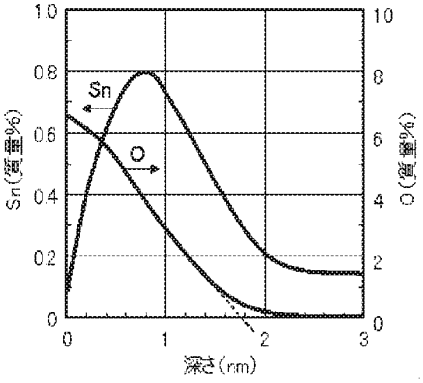
【符号の説明】

【００３９】

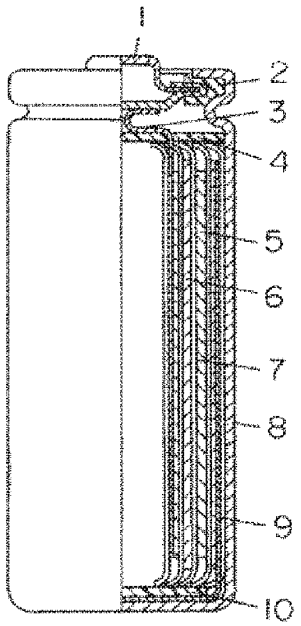
１：封口板
２：絶縁ガスケット
３：正極リード
４：上部絶縁板
５：正極板
６：負極板

７：セパレータ
８：電池ケース
９：負極リード
１０：下部絶縁板

【図１】



【図２】



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			C22F	1/00	630G	
			C22F	1/00	661C	
			C22F	1/00	613	
			C22F	1/00	681	
			C22F	1/00	682	
			C22F	1/00	683	
			C22F	1/00	685Z	
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			C22F	1/00	691C	
			C22F	1/00	694A	

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— 国際調査報告 (条約第 21 条(3))

(54) Title: ELECTROLYTIC SOLUTION FOR PRODUCING ELECTROLYTIC COPPER FOIL

(54) 発明の名称: 電解銅箔製造用の電解液

(57) Abstract: An electrolytic copper solution for producing an electrolytic copper foil is provided which can improve elongation properties while reducing the profile of the rough surface. The electrolytic solution for electrolytic-copper foil production is a sulfuric-acid-acidified aqueous copper sulfate solution containing: bromide ions derived from bromine, an inorganic acid thereof, an inorganic salt thereof, or a mixture of these; a glue; and chloride ions.

(57) 要約: 粗面のロープロファイル化を達成しながら、伸び特性を向上させることのできる電解銅箔製造用の銅電解液を提供する。電解銅箔製造用の電解液としての、臭素、その無機酸、その無機塩、又はこれらの混合物に由来する臭化物イオンと、膠と、塩化物イオンとを含有する硫酸酸性硫酸銅水溶液。

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明 細 書

電解銅箔製造用の電解液

技術分野

[0001] 本発明は電解銅箔の製造に使用される銅電解液に関する。また、本発明は電解銅箔の製造方法に関する。更に、本発明は銅張積層板の製造方法に関する。

背景技術

[0002] プリント回路板は、各種電子機器を作動させる上で欠かせない部品であるが、一般に次のような製造工程を経て製造される。まず、合成樹脂ボード、フィルム等の絶縁基材に接着剤を介して或いは接着剤を使用せずに高温高圧下で銅箔を積層接着して銅張積層板を製造する。次に、目的とする回路を形成するべく必要な回路を印刷した後、不要部を除去するエッチング処理を施す。最後に、所要の電子部品を半田付けして、種々のプリント回路板とする。

[0003] 銅箔には電解銅箔と圧延銅箔とがあるが、プリント回路板用に使用される銅箔は、その接着強度等の観点から、大部分が電解銅箔である。電解銅箔は、電気銅又はそれと同等の純度を有する電線スクラップを原料とし、それを硫酸銅水溶液中に溶解させて電解浴を調製し、浴中に浸漬されるカソードとしての回転ドラムの周面に電解反応により連続的に銅を電着させ、所定の厚さとなった電着物を回転ドラムから剥離し、生箔を製造することを基本とする。その後、プリント回路板用銅箔に対する品質要求に応じて、樹脂基材と接着される面(粗面)と非接着面(光沢面)とでそれぞれに多くのトリート処理(表面処理)がなされる。

[0004] 近年の電子機器の小型化、高性能化ニーズの増大に伴い搭載部品の高密度実装化や信号の高周波化が進展し、プリント回路板に対して導体パターンの微細化(ファインピッチ化)や高周波対応等が求められている。そのため、プリント回路板に使用される銅箔について、そのようなプリント回路板の高性能化に応えることのできる特性が求められる。具体的には、ピンホールがないこと、寸法安定性の観点から抗張力が高いこと、クラック防止の観点から伸び率が高いことが要求され、そして、上述したような導体パターンの微細化(ファインピッチ化)や高周波対応等に対応するために、特に

粗面のローブロファイル化が要求される。

[0005] 粗面のローブロファイル化は、膠を電解液に添加することで達成されることが知られている。膠はピンホールの防止や回転ドラムを保護する点でも有用である。ところが、膠の添加量を増加させていくと、高温での伸びが低下するという問題がある。そのため、膠によって与えられるローブロファイル化やピンホールの防止といった利点を生かしながら、高温での伸び特性を向上させることが望まれる。

[0006] この点に関し、例えば、特公昭49－31415号公報にはポリアルキレングリコール又は膠質剤の内何れか1種又は両種と、更に塩素イオン5～100mg／Lとを添加した酸性銅電鍍液を電解液として使用することで、硬さ及び靭性に優れ、ピンホールの少ない銅箔が得られることが記載されている。塩素イオンは電着結晶の微細化を促進し、微小ピンホールの発生を防止する役割を果たすとされている。

[0007] 特開平8－53789号公報には、チオ尿素に特定量の高分子多糖類と膠を加えた三元系添加剤の組み合わせが、ローブロファイル化され、常温及び高温における伸び率が高く、そして抗張力が高い電解銅箔を得る上で有効であるとし、「添加剤として、0．05～2．0重量ppmのチオ尿素もしくはその誘導体;0．08～12重量ppmの高分子多糖類;及び分子量10，000以下であって0．03～4．0重量ppmの膠を含有する電解液を用いることを特徴とする電解銅箔の製造方法」が記載されている。

[0008] また、特開平7－278866号公報には、電解液中の膠濃度を慣行的に使用されてきた量である2～10ppmより少なく、具体的には0．5ppm以下にすることが有効であり、これによって電解銅箔の高温伸びが大幅に改善することが記載されている。また、塩化物イオンを20～100ppm添加しなければ銅箔の基本的特性が一定とならないことが記載されている。

特許文献1:特公昭49－31415号公報

特許文献2:特開平8－53789号公報

特許文献3:特開平7－278866号公報

発明の開示

発明が解決しようとする課題

[0009] 特開平8－53789号公報ではチオ尿素の添加を必要としているが、当該公報でも

指摘されているようにチオ尿素はその効果及び弊害が大きく、精密に添加量を制御する必要がある。また、有機物であるチオ尿素が分解した場合、種々の分解物が存在し、これらの分解物が銅箔特性に与える影響も種々であり、安定した特性を得るのが困難になっている。

[0010] 特開平7－278866号公報では膠濃度を低くした結果、高温での伸びが改善されたが、ドラムライフが短くなるという問題がある。すなわち、膠は初期の核発生を均一化する効果があるが、膠濃度が小さいとその効果が少なくなる。膠濃度を下げた状態でドラムを使用し続けると、ドラム表面の抵抗バラツキが大きくなる。ドラム表面の抵抗バラツキが大きくなるにつれて初期の核発生の不均一が顕著となり、クラック状の欠陥となって、箔にピンホールが生じる。

[0011] また、本発明者の検討結果によれば、膠と塩化物イオンの系では、高温での伸び特性、表面粗さにいずれもが十分な特性とはいえない。

[0012] そこで、本発明は、膠の濃度を下げなくても伸び特性を向上させることのできる別の電解銅箔製造用の銅電解液を提供することを課題とする。また、本発明は伸び特性に優れた電解銅箔の製造方法を提供することを別の課題とする。本発明はそのような銅電銅箔を備えた銅張積層板の製造方法を提供することを更に別の課題とする。

課題を解決するための手段

[0013] 本発明者は上記課題を解決すべく、鋭意検討したところ、銅電解液中に臭化物イオンと塩化物イオンが共存する場合に、常温及び高温の伸びが改善することを見出した。そのため、電解銅箔製造用の銅電解液において、臭化物イオンを供給することのできる臭素化合物と塩化物イオンを供給することのできる塩素化合物を添加することにより、伸び特性の改善を図ることが可能となる。

[0014] 従って、本発明は一側面において、電解銅箔製造用の電解液としての、臭化物イオンと、膠と、塩化物イオンとを含有する硫酸酸性硫酸銅水溶液である。

[0015] 本発明に係る電解液は一実施形態において、電解液中の臭化物イオンの濃度が0.25～200mg／L(ppm)である。

[0016] 本発明に係る電解液は別の一実施形態において、臭化物イオンが臭素、その無機酸、その無機塩、又はこれらの混合物に由来する。

[0017] 本発明に係る電解液は更に別の一実施形態において、電解液中の臭化物イオンがアルカリ金属塩およびアルカリ土類金属塩に由来する。

[0018] 本発明に係る電解液は一実施形態において、電解液中の塩化物イオンの濃度が2．5～200mg／Lである。

[0019] 本発明に係る電解液は一実施形態において、電解液中の膠の濃度が1～10mg／Lである。

[0020] また、本発明は別の一側面において、上記の硫酸酸性硫酸銅水溶液を電解液として用い、銅を陰極上に電着させる工程と、

電着した銅を陰極から剥ぎ取る工程と、

を含む電解銅箔の製造方法である。

[0021] 本発明に係る電解銅箔の製造方法は一実施形態において、電解液の温度45～70℃、電流密度30～150A／dm^2、で銅を陰極上に電着させる。

[0022] また、本発明は更に別の一側面において、上記の電解銅箔の製造方法を用いて電解銅箔を得る工程と、

該銅箔の粗面側を絶縁基板に対向させて、該銅箔を絶縁基板に積層する工程と、

を含む銅張積層板の製造方法である。

[0023] また、本発明は更に別の一側面において、Brを含有する電解銅箔である。

[0024] また、本発明は更に別の一側面において、上記の硫酸酸性硫酸銅水溶液を電解液として用い、銅を陰極上に電着させる工程と、

電着した銅を陰極から剥ぎ取る工程と、

を含むBrを含有する電解銅箔の製造方法である。

発明の効果

[0025] 本発明によれば、粗面がロープロファイルであり、且つ高い伸び特性を有する電解銅箔を製造することができる。

発明を実施するための最良の形態

[0026] 1．電解液

(1)硫酸酸性硫酸銅水溶液

本発明において、電解銅箔を製造するために使用する電解液は硫酸酸性の硫酸

銅水溶液である。電解銅箔を製造するための電解液として硫酸酸性硫酸銅水溶液を使用することは周知であり、特に説明を要しないが、一般に$CuSO_4 \cdot 5H_2O$とH_2SO_4を主成分とし、一般にはCu:60～110g／L、H_2SO_4:50～150g／L、典型的にはCu:80～120g／L、H_2SO_4:80～105g／Lを含有する。

[0027] (2)臭化物イオン

本発明に係る電解液は臭化物イオンを含有し、その供給源は臭素、その無機酸、その無機塩、又はこれらの混合物である。塩化物イオンの不在下で臭化物イオンを膠を含む電解液に含有させても塩化物イオンを含有させた場合と同様に、高温での伸び特性、表面粗さの何れも十分な特性が得られないが、臭化物イオンが膠と塩化物イオンを含有する電解液中に含まれることで、得られる電解銅箔の伸び及び表面粗さが改善する。すなわち、臭化物イオン単独では伸び率や表面粗さへの改善効果はほとんどないが、臭化物イオンと塩化物イオンとが電解液中で共存することによって、伸び率および表面粗さが改善することという相乗効果が現れるのである。

また、本発明では臭化物イオンを臭素、その無機酸、その無機塩、又はこれらの混合物から供給しているので、有機物のように分解する心配はなく、安定した特性が得られるという点でも有利である。

[0028] 臭素は液体臭素や臭素水の形態で電解液に供給することができる。臭素の無機酸としては臭化水素酸(HBr)のほか、臭素酸($HBrO_3$)や亜臭素酸($HBrO_2$)のような臭素のオキソ酸が挙げられ、これらは水溶液として供給することができる。臭素の無機塩としては、臭化ナトリウム(NaBr)、臭化カリウム(KBr)、臭化カルシウム($CaBr_2$)、臭化マグネシウム($MgBr_2$)のようなアルカリ金属塩及びアルカリ土類金属塩が挙げられる。上記オキソ酸のアルカリ金属塩又はアルカリ土類金属塩でもよい。臭化物イオンの供給源は安定性、取り扱いの容易の観点からアルカリ金属塩、アルカリ土類金属塩とするのが好ましい。

[0029] 前述したように、これまで塩化物イオンを含有する電解液は知られていたが、塩化物イオンはピンホールの防止の役割を果たすものであった。一方、本発明に使用する臭素は塩素と同じハロゲンであるが、伸び特性の改善、更には表面粗さの低減という異質な効果を奏するのである。臭素は抗張力に対する悪影響もほとんどない。

[0030] 電解液に添加する臭化物イオン濃度は低すぎると表面粗さを低減する効果が少ない。臭化物イオン濃度が高くても改善の効果は十分得られるが、ある程度の効果で一定となってしまう。従って、電解液中の臭化物イオン(Br^-)濃度は、0.25～200mg／Lとするのが好ましく、10～200mg／Lとするのがより好ましく、50～100mg／Lとするのが最も好ましい。

[0031] 添加した臭化物イオンは最終的に電解銅箔に取り込まれ得ることが分かっており、本発明に係る電解銅箔の一実施態様において、得られた電解銅箔はBrを含有する。

[0032] (3)膠

上述したように、膠には粗面のロープロファイル化、ピンホールの防止、回転ドラムの保護といった利点を有する。一般に、電解液中に添加される膠は0.1～20mg／Lの濃度範囲である。粗面のロープロファイル化、ピンホールの防止、回転ドラムの保護といった膠による利点を十分に享受する観点から、電解液中の膠濃度は、0.25～10mg／Lとするのが好ましく、2.0～5.0mg／Lとするのがより好ましい。

[0033] 本発明に使用する膠は、典型的にはゼラチンを主成分とする分子量が500～250000程度のものであり、例えば獣・魚類の骨・皮・腱・腸などから加水分解により製造することができる。低分子側の膠は、酵素、酸又はアルカリで一般的な膠を分解することで得ることができる。本発明において使用する膠は、ドラムの保護の観点から、数平均分子量1000～75000のものが好ましく、数平均分子量2000～50000のものがより好ましい。

[0034] (4)塩化物イオン

本発明に係る電解液は塩化物イオンを含有する。塩化物イオンは電着結晶の結晶方位を変化させ、山形の表面形状を形成することで表面粗さを粗くするが、ピンホールの発生を防止する効果がある。塩化物イオンの供給源としては特に制限はないが、塩酸(HCl)のほか、塩化ナトリウム(NaCl)、塩化カリウム(KCl)、塩化カルシウム($CaCl_2$)、塩化マグネシウム($MgCl_2$)のような無機塩の形態で添加することができる。塩素水の形態で添加することもできる。これらの中でも取り扱いの容易の観点から、希塩酸の形態で塩化物イオンを供給するのが好ましい。

[0035] 塩化物イオンは電解液中での濃度が低すぎるとその効果が十分に得られないが、逆に高すぎると表面形状が荒れて、異常析出が発生しやすい。従って、電解液中での塩化物イオンの濃度は、2．5～200mg／Lとするのが好ましく、10～100mg／Lとするのがより好ましく、25～75mg／Lとするのが最も好ましい。

[0036] (5)その他の添加物

一般に、電解銅箔を製造するために、使用する電解液には各種の添加剤を添加することで、得られる電解銅箔の特性向上を図っているが、本発明に係る電解液にはBr^-による特性向上効果を妨害したり、打ち消したりしてしまう添加剤は添加しないのが好ましい。例えば、リン酸系化合物、アミン化合物、有機硫黄化合物(例:チオ尿素)なども添加剤として知られているが、このような添加剤を本発明に係る電解液に添加すると、高温での機械特性を低下させるといった悪影響を与えるため、本発明に係る電解液には含有させないのが好ましい。但し、高分子多糖類、ポリエチレングリコールのような添加剤はBr添加による特性向上効果に悪影響を及ぼさないか及ぼしたとしても軽微であるので、適宜使用可能である。

[0037] 2．電解銅箔の製造

電解銅箔は、本発明に係る電解液を用い、常法に従って製造することができる。すなわち、上記の硫酸酸性硫酸銅水溶液を電解液として用い、銅を陰極上に電着させ、電着した銅を陰極から剥ぎ取ることにより製造することができる。より具体的には、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とができる。銅箔の厚みとしては特に制限はないが、ファインピッチ用の銅箔であれば18μm以下とするのが一般的である。このようにして得た銅箔には更に表面処理工程及び切断工程を経て銅箔製品となる。表面処理工程では粗化処理、耐熱層形成及び／又は防錆層形成等を行うのが一般的である。

[0038] 但し、本発明に係る電解液中に含まれる臭化物イオンの効果を最大限に発揮する

ために、一定の電解条件下で電解銅箔を電着させるのが好ましい。

まず、好ましい電解液の温度は40～75℃、より好ましくは45～70℃である。電解液の温度が低すぎるとやけめっきになりやすく、正常な銅箔が得られない。逆に高すぎると膠の分解が速く、分解物の蓄積が多くなり、機械特性の低下が生じやすくなる。

また、好ましい電流密度は30～150A／dm^2、より好ましくは60～130A／dm^2である。電流密度が低すぎると生産スピードが遅くなり、生産性が低下する。逆に高すぎるとやけめっきになり、正常な銅箔が得られない。

[0039] 3. 銅張積層板の製造

上記のように製造された銅箔製品を用いて、常法に従って銅張積層板を製造することができる。具体的には、該銅箔の粗面側を絶縁基板に対向させて、該銅箔を絶縁基板に積層することで銅張積層板を製造することができる。

[0040] 銅箔と絶縁基板を接着させる方法としては、例えば、加熱加圧する方法、接着剤を用いる方法、絶縁基板となるポリマーの前駆体を溶剤に分散して塗布したのちに加熱重合反応させるもの等がある。

[0041] 銅箔が積層される絶縁基板はプリント回路板(PCB)に適用可能な特性を有するものであれば特に制限を受けないが、例えば、リジッドPCB用に紙基材フェノール樹脂、紙基材エポキシ樹脂、合成繊維布基材エポキシ樹脂、ガラス布・紙複合基材エポキシ樹脂、ガラス布・ガラス不織布複合基材エポキシ樹脂及びガラス布基材エポキシ樹脂等を使用し、FPC用にポリエステルフィルムやポリイミドフィルム等を使用する事ができる。

[0042] 銅張積層板を常法によって加工することで、各種のプリント配線板、更にはプリント回路板を形成することができる。

実施例

[0043] 以下、本発明及びその利点をより理解するために実施例を紹介するが、本発明はこれらの実施例に限定されるものではない。

[0044] 試験例1(Br^-の濃度変化による影響)

Cu:90g／L、H_2SO_4:80g／Lの硫酸酸性硫酸銅水溶液に膠(数平均分子量200

00)、臭化カリウム及び塩酸を添加して電解液を調製し、クロム製陰極ドラム(外径0.64m)上に、厚さ18μmの電解銅箔を連続製造した。

[0045] 電解液中の膠、臭化物イオン及び塩化物イオンの電解液中の濃度は以下の方法で測定した。各例について、測定結果を表1に示す。

＜膠＞

CVS分析装置(北斗電工社製)

既知の膠濃度に対して、CVS法(cyclic voltammetric stripping method)にて測定した銅が電解液中で溶解することにより発生するクーロン量から検量線を作成し、実際の電解液にてCVSを測定した値を比較することにより、膠濃度を決定した。

＜臭化物イオン＞

イオンクロマトグラフ(DIONEX社製、型式ICS－2000)

＜塩化物イオン＞

イオンクロマトグラフ(DIONEX社製、型式ICS－2000)

[0046] 得られた電解銅箔の粗面側の表面粗さRa、Rt及びRz(μm)は、JISB0601に準じて小坂研究所社製型式SE－3Cを用いて測定し、室温抗張力(kgf／mm^2)、室温伸び(%)、高温抗張力(kgf／mm^2)、高温伸び(%)、はIPC－TM650に準じて島津製作所社製型式AGS－H－500Nを用いて測定した。各例について、測定結果を表1に示す。

[0047] ドラムライフは以下のように評価した。厚さ18μm箔を連続的に製箔し、6時間毎に周期的なピンホールの有無を調べ、周期的なピンホールが5個以上になったときをドラムライフとした。

[0048] 試験例2(膠の濃度変化による影響)

試験例1のNo.2を基準にして、電解液中の膠濃度を変化させたときの電解銅箔の特性変化を調べた。結果を表2に示す。

[0049] 試験例3(塩化物イオン変化による影響)

電解液中の塩化物イオン濃度を変化させたときの電解銅箔の特性変化を調べた。結果を表3に示す。

[0050] [表1]

					室温		高温(180℃)				ドラムライフ
No.	Br (mg/L)	Cl (mg/L)	膠 (mg/L)	液温 (℃)	抗張力 (kgf/mm²)	伸び率 (%)	抗張力 (kgf/mm²)	伸び率 (%)	Ra	Rt	Rz	(時間)
1	0.25	60	2.0	55	36.8	9.3	22.4	4.1	0.50	3.67	3.10	306
2	1	60	2.0	55	37.1	10.1	22.7	4.9	0.50	3.60	3.00	306
3	10	60	2.0	55	37.3	11.2	22.4	6.1	0.50	3.60	3.08	318
4	30	60	2.0	55	37.2	15.3	21.8	4.8	0.47	3.57	2.87	318
5	50	60	2.0	55	37.4	15.9	21.4	10.3	0.46	3.40	2.83	336
6	100	60	2.0	55	38.3	16.3	21.9	11.3	0.47	3.38	2.77	330
7	200	60	2.0	55	38.8	15.8	21.6	10.9	0.48	3.42	2.85	330
8(比較)	0	60	2.0	55	36.7	8.8	21.1	2.3	0.62	4.38	3.93	300

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[0051] [表2]

No.	Br (mg/L)	Cl (mg/L)	膠 (mg/L)	液温 (℃)	室温 抗張力 (kgf/mm²)	室温 伸び率 (%)	高温(180℃) 抗張力 (kgf/mm²)	高温(180℃) 伸び率 (%)	Ra	Rt	Rz	ドラムライフ (時間)
3	10	60	2.0	55	37.3	11.2	22.4	6.1	0.50	3.60	3.08	318
8	10	60	1.0	55	37.2	10.8	22.2	5.8	0.50	3.62	3.11	306
9	10	60	5.0	55	37.4	11.5	22.5	5.7	0.49	3.59	2.97	330
10	10	60	10.0	55	37.7	10.6	22.8	5.4	0.50	3.60	3.00	336
11	10	60	0.2	55	37.2	9.8	21.9	5.6	0.48	3.63	3.03	174
12	10	60	15.0	55	38.3	8.2	22.9	1.9	0.47	3.58	2.87	348
13(比較)	0	60	0.2	55	37.3	8.3	21.8	5.2	0.47	3.87	3.31	96

[0052] [表3]

No.	Br (mg/L)	Cl (mg/L)	膠 (mg/L)	液温 (℃)	室温 抗張力 (kgf/mm²)	室温 伸び率 (%)	高温(180℃) 抗張力 (kgf/mm²)	高温(180℃) 伸び率 (%)	Ra	Rt	Rz	ドラムライフ (時間)
14	50	2.5	2.0	60	36.8	15.6	21.9	11.2	0.46	3.37	2.87	300
15	50	10	2.0	60	36.3	15.2	21.8	10.9	0.46	3.39	2.89	306
16	50	25	2.0	60	36.1	15.3	21.4	11.0	0.48	3.42	3.06	312
17	50	50	2.0	60	36.2	15.3	21.1	10.8	0.47	3.38	2.98	324
18	50	75	2.0	60	36.0	15.6	21.3	10.7	0.46	3.43	3.12	318
19	50	100	2.0	60	35.9	14.8	20.9	9.6	0.48	3.48	3.01	288
20	50	200	2.0	60	36.1	14.5	21.1	9.4	0.49	3.50	3.22	276
21(比較)	50	0	2.0	60	45.3	8.8	21.3	2.5	0.47	4.38	3.98	306
22(比較)	0	0	2.0	60	60	8.7	20.7	12.1	0.45	3.25	2.65	296
23(比較)	0	50	2.0	60	35.8	8.9	21.1	2.4	0.61	4.27	3.80	288

[0053] 考察

表1より、Cl^-を含有する電解液にBr^-を添加することで、ドラムライフや表面粗さに悪影響を与えることなく、室温及び高温での伸び率が改善していくことが分かる。また、Br濃度を増加させるにつれて伸び率も上昇し、概ね100mg／Lで効果が飽和していることがわかる。

表2より、膠の濃度を適正化することで、ドラムライフ及び得られる銅箔の特性向上が可能であることが分かる。

表3より、添加するCl^-はかなり低濃度でよいことがわかる。No. 21とNo. 22を比べることにより、Br^-単独添加ではあまり効果が見られないことがわかる。

[0054] 電解銅箔中のBrの有無

No. 1, 5, 7で得られた電解銅箔について、TOF－SIMS（日立ハイテクトレーディング社型式TOF－SIMS IV）により銅箔にBrが含まれるか調べた。その結果、何れの電解銅箔からも10^5オーダー（ion counts）のBr強度が検出された。

請求の範囲

[1] 電解銅箔製造用の電解液としての、臭化物イオンと、膠と、塩化物イオンとを含有する硫酸酸性硫酸銅水溶液。

[2] 臭化物イオンの濃度が0．25～200mg／Lである請求項1記載の硫酸酸性硫酸銅水溶液。

[3] 臭化物イオンが臭素、その無機酸、その無機塩、又はこれらの混合物に由来する請求項1又は2記載の硫酸酸性硫酸銅水溶液。

[4] 臭化物イオンがアルカリ金属塩およびアルカリ土類金属塩に由来する請求項3記載の硫酸酸性硫酸銅水溶液。

[5] 電解液中の塩化物イオンの濃度が2．5～200mg／Lである請求項1～4何れか一項記載の硫酸酸性硫酸銅水溶液。

[6] 電解液中の膠の濃度が1～10mg／Lである請求項1～5何れか一項記載の硫酸酸性硫酸銅水溶液。

[7] 請求項1～6何れか一項記載の硫酸酸性硫酸銅水溶液を電解液として用い、銅を陰極上に電着させる工程と、

電着した銅を陰極から剥ぎ取る工程と、

を含む電解銅箔の製造方法。

[8] 電解液の温度45～70℃、電流密度30～150A／m^2で銅を陰極上に電着させる請求項7記載の製造方法。

[9] 請求項7又は8記載の電解銅箔の製造方法を用いて電解銅箔を得る工程と、

該銅箔の粗面側を絶縁基板に対向させて、該銅箔を絶縁基板に積層する工程と、

を含む銅張積層板の製造方法。

[10] Brを含有する電解銅箔。

[11] 請求項1～6何れか一項記載の硫酸酸性硫酸銅水溶液を電解液として用い、銅を陰極上に電着させる工程と、

電着した銅を陰極から剥ぎ取る工程と、

を含む請求項10記載の電解銅箔の製造方法。

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/054566

A. CLASSIFICATION OF SUBJECT MATTER
C25D3/38(2006.01)i, *C25D1/00*(2006.01)i, *C25D1/04*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25D3/38, C25D1/00, C25D1/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2009
Kokai Jitsuyo Shinan Koho 1971-2009 Toroku Jitsuyo Shinan Koho 1994-2009

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2004-137588 A (Nikko Materials Co., Ltd.), 13 May, 2004 (13.05.04), Claims 1, 3, 5 & WO 2004/035874 A1 & CN 1564880 A & US 2005/0173256 A1 & EP 1568802 A1 & TW 250224 B & US 2007/0042201 A1 & HK 1068655 A	10 1-9,11
X A	WO 2004/059040 A1 (Nikko Materials Co., Ltd.), 15 July, 2004 (15.07.04), Claims 2, 4 & CN 1564881 A & EP 1607495 A1 & US 2006/0011488 A1 & HK 1068654 A & TW 285683 B & US 2008/0075972 A1 & JP 4083171 B	10 1-9,11

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 June, 2009 (09.06.09)	16 June, 2009 (16.06.09)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)

BNSDOCID: <WO_____2009116432A1_I_>

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/054566

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	JP 2009-41096 A (Rohm and Haas Electronic Materials L.L.C.), 26 February, 2009 (26.02.09), Full text & EP 2022875 A & EP 2022875 A2 & US 2009/0038951 A	1-9

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

BNSDOCID: <WO_____2009116432A1_I_>

国際調査報告

国際出願番号 PCT/JP2009/054566

A. 発明の属する分野の分類（国際特許分類（IPC））

Int.Cl. C25D3/38(2006.01)i, C25D1/00(2006.01)i, C25D1/04(2006.01)i

B. 調査を行った分野

調査を行った最小限資料（国際特許分類（IPC））

Int.Cl. C25D3/38, C25D1/00, C25D1/04

最小限資料以外の資料で調査を行った分野に含まれるもの

日本国実用新案公報	1922－1996年
日本国公開実用新案公報	1971－2009年
日本国実用新案登録公報	1996－2009年
日本国登録実用新案公報	1994－2009年

国際調査で使用した電子データベース（データベースの名称、調査に使用した用語）

C. 関連すると認められる文献

引用文献のカテゴリー＊	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する請求項の番号
X A	JP 2004-137588 A (株式会社日鉱マテリアルズ) 2004.05.13, 請求項1, 3, 5 & WO 2004/035874 A1 & CN 1564880 A & US 2005/0173256 A1 & EP 1568802 A1 & TW 250224 B & US 2007/0042201 A1 & HK 1068655 A	10 1-9,11

☑ C欄の続きにも文献が列挙されている。

☐ パテントファミリーに関する別紙を参照。

＊ 引用文献のカテゴリー
「A」特に関連のある文献ではなく、一般的技術水準を示すもの
「E」国際出願日前の出願または特許であるが、国際出願日以後に公表されたもの
「L」優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献（理由を付す）
「O」口頭による開示、使用、展示等に言及する文献
「P」国際出願日前で、かつ優先権の主張の基礎となる出願の日の後に公表された文献
「T」国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの
「X」特に関連のある文献であって、当該文献のみで発明の新規性又は進歩性がないと考えられるもの
「Y」特に関連のある文献であって、当該文献と他の1以上の文献との、当業者にとって自明である組合せによって進歩性がないと考えられるもの
「&」同一パテントファミリー文献

国際調査を完了した日	国際調査報告の発送日
09.06.2009	16.06.2009

国際調査機関の名称及びあて先	特許庁審査官（権限のある職員）	4E	3032
日本国特許庁（ISA/JP） 郵便番号100－8915 東京都千代田区霞が関三丁目4番3号	瀧口 博史 電話番号 03－3581－1101 内線 3425		

様式PCT/ISA/210（第2ページ）（2007年4月）

BNSDOCID: <WO_____2009116432A1_|_>

C（続き）．　関連すると認められる文献

引用文献のカテゴリー＊	引用文献名　及び一部の箇所が関連するときは、その関連する箇所の表示	関連する請求項の番号
X A	WO 2004/059040 A1（株式会社日鉱マテリアルズ）2004.07.15，請求の範囲２，４ & CN 1564881 A & EP 1607495 A1 & US 2006/0011488 A1 & HK 1068654 A & TW 285683 B & US 2008/0075972 A1 & JP 4083171 B	10 1-9,11
P,A	JP 2009-41096 A（ローム・アンド・ハース・エレクトロニック・マテリアルズ，エル．エル．シー．）2009.02.26，全文 & EP 2022875 A & EP 2022875 A2 & US 2009/0038951 A	1-9

様式ＰＣＴ／ＩＳＡ／２１０（第2ページの続き）（２００７年４月）

BNSDOCID: <WO_____2009116432A1_I_>

Electronic Acknowledgement Receipt

EFS ID:	32018890
Application Number:	15696360
International Application Number:	
Confirmation Number:	7466
Title of Invention:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Seung Min KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/Samantha Lingo
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313070.00025
Receipt Date:	12-MAR-2018
Filing Date:	06-SEP-2017
Time Stamp:	16:20:01
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	00025_IDS_Trans.pdf	24733 ab07aa253e7dc5c8ae80287de60e7fdb099dbbae	no	3

Warnings:

Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	00025_PTOsb08.pdf	1034838 156e0659eaa7894e0764d971c003ccc57bf359a1	no	4
Warnings:					
Information:					
3	Other Reference-Patent/App/Search documents	EP_SEARCH.pdf	1011041 43d962b0ef4293af1d64e40d9610fb3eb7cf549c	no	8
Warnings:					
Information:					
4	Foreign Reference	EP2660359.pdf	4427771 2346f222ad3650e90e4aeec5d332caa74aabea4a	no	33
Warnings:					
Information:					
5	Foreign Reference	EP2871266.pdf	334460 035d17d84b1e5a31a59ab0ae5b5bd1f440399aa7	no	16
Warnings:					
Information:					
6	Foreign Reference	JP3943214B.pdf	504378 49bd919e9f108f0f2eba62e94e9deea3e45da4f4	no	6
Warnings:					
Information:					
7	Foreign Reference	JP2011108442.pdf	1466244 cc5e245f80bb406c225059b32f99211895201f350	no	15
Warnings:					
Information:					
8	Foreign Reference	WO2009116432.pdf	1840402 045e9ddb618421b81f1609dcee730824c434fea8	no	19
Warnings:					
Information:					
			Total Files Size (in bytes):	10643867	

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.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Seung Min KIM
Appl. No.:	15/696,360
Conf. No.:	7466
Filed:	September 6, 2017
Title:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1725
Examiner:	RIDLEY, BASIA ANNA
Docket No.:	0313070.00025

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

INFORMATION DISCLOSURE STATEMENT TRANSMITTAL LETTER

Sir:

Submitted herewith is an Information Disclosure Statement for consideration in the above-identified application. In accordance with the provisions of 37 C.F.R. 1.56, 37 C.F.R. 1.97, and 37 C.F.R. 1.98, Applicants request that a citation and examination of the references cited on the enclosed SB08 form be made during the course of examination of the above-identified application for United States patent.

This Information Disclosure Statement is submitted as follows:

Submission without Certification

[X] Within three months of filing of a national application; within three months of the date of entry of the national stage as set forth in 37 C.F.R. §1.491 in an international application; before the mailing date of a first Office Action on the merits, or before the mailing of a first Office Action after the filing of a Request for Continued Examination.

[ ] After the period specified above, but before the mailing date of a Final Action under 37 CFR 1.113, a Notice of Allowance under 37 CFR 1.311, or an Action that otherwise closes prosecution in the application and is accompanied by payment of the fee set forth in 37 CFR 1.17(p).

Submission with Certification

[ ] Within three months of filing of a national application; within three months of the date of entry of the national stage as set forth in 37 C.F.R. §1.491 in an international application; before the mailing date of a first Office Action on the merits, or before the mailing of a first Office Action after the filing of a Request for Continued Examination.

[ ] After the period specified above, but before the mailing date of a Final Action under 37 CFR 1.113, a Notice of Allowance under 37 CFR 1.311, or an Action that otherwise closes prosecution in the application and is accompanied by the Certification specified in 37 CFR 1.97(e) which is set forth below.

[ ] After the mailing date of a Final Action under 37 CFR 1.113, a Notice of Allowance under 37 CFR 1.311, or an Action that otherwise closes prosecution in the application and is accompanied by the fee set forth in 37 CFR 1.17(p) and the Certification specified in 37 CFR 1.97(e) which is set forth below.

Certification under 37 CFR 1.97(e)

[ ] The undersigned counsel for applicant(s) hereby certifies that each item of information contained in the accompanying 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.

[ ] The undersigned counsel for applicant(s) hereby certifies that no item of information contained in the accompanying Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the undersigned, after making reasonable inquiry, no item of information contained in the accompanying 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.

Statement under 37 CFR 1.704(d)

[ ] The undersigned counsel for applicant(s) hereby states that each item of information contained in the accompanying Information Disclosure Statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and/or is a communication that was issued by a patent office in a counterpart foreign or international application or by the Office, and this communication was not received by any individual designated in § 1.56(c) more than **thirty days** prior to the filing of the information disclosure statement.

[X] A copy of a Search Report from a corresponding foreign patent application is enclosed.

[ ] The Commissioner is hereby authorized to charge the amount of $240.00 to cover the required fee to Deposit Account No. 02-1818.

[X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-1818.

Respectfully submitted,

K&L GATES LLP

BY /Matthew S. Dicke/
Matthew S. Dicke
Reg. No. 58819
Customer No. 24573
Phone: (312) 578-5415

Dated: March 12, 2018

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
15/696,360	09/06/2017	Seung Min KIM	0313070.00025

CONFIRMATION NO. 7466

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

POA ACCEPTANCE LETTER

OC000000097413165

Date Mailed: 02/15/2018

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 02/12/2018.

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**.

/afessehaye/

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
15/696,360	09/06/2017	Seung Min KIM	P11491US

CONFIRMATION NO. 7466

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

POWER OF ATTORNEY NOTICE

OC000000097412203

Date Mailed: 02/15/2018

NOTICE REGARDING CHANGE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 02/12/2018.

- 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).

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**.

/afessehaye/

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	15/696,360
Filing Date	09-06-2017
First Named Inventor	Seung Min KIM
Title	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit	1726
Examiner Name	
Attorney Docket Number	0313070.00025

SIGNATURE of Applicant or Patent Practitioner

Signature	/Matthew S. Dicke/	Date (Optional)	2018-02-12
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.**

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Electronic Acknowledgement Receipt

EFS ID:	31766031
Application Number:	15696360
International Application Number:	
Confirmation Number:	7466
Title of Invention:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Seung Min KIM
Customer Number:	86144
Filer:	Matthew S. Dicke/Elias Santiago
Filer Authorized By:	Matthew S. Dicke
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1	Power of Attorney	00025_POA.pdf	288396 24639e85f55467eef5cb47f9a393d800added08d	no	2

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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.

대 한 민 국 특 허 청
KOREAN INTELLECTUAL PROPERTY OFFICE

별첨 사본은 아래 출원의 원본과 동일함을 증명함.

This is to certify that the following application annexed hereto is a true copy from the records of the Korean Intellectual Property Office.

출 원 번 호 : 10-2016-0131979
Application Number

출 원 년 월 일 : 2016년 10월 12일
Filing Date OCT. 12, 2016

출 원 인 : 엘에스엠트론 주식회사
Applicant(s) LS Mtron Ltd.

2017년 09월 26일

특 허 청
COMMISSIONER

제출 일자 : 2016-10-12

【서지사항】

【서류명】 특허출원서

【출원구분】 특허출원

【출원인】

【명칭】 엘에스엠트론 주식회사

【특허고객번호】 1-2008-029030-3

【대리인】

【명칭】 특허법인 천문

【대리인번호】 9-2009-100001-0

【지정된변리사】 오정환

【포괄위임등록번호】 2015-043650-5

【발명의 국문명칭】 핸들링이 용이한 전해동박, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법

【발명의 영문명칭】 Easily Handleable Electrolytic Copper Foil, Electrode Comprising The Same, Secondary Battery Comprising The Same, and Method for Manufacturing The Same

【발명자】

【성명】 김승민

【성명의 영문표기】 KIM SEUNG MIN

【주민등록번호】 770119-1XXXXXX

【우편번호】 18105

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【국적】 KR

【출원언어】 국어

제출 일자 : 2016-10-12

【취지】 위와 같이 특허청장에게 제출합니다.

대리인 특허법인 천문 (서명 또는 인)

【수수료】

【출원료】	0 면	46,000 원
【가산출원료】	32 면	0 원
【우선권주장료】	0 건	0 원
【심사청구료】	0 항	0 원
【합계】	46,000 원	

제출 일자 : 2016-10-12

【발명의 설명】

【발명의 명칭】

핸들링이 용이한 전해동박, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법{Easily Handleable Electrolytic Copper Foil, Electrode Comprising The Same, Secondary Battery Comprising The Same, and Method for Manufacturing The Same}

【기술분야】

<1> 본 발명은 핸들링이 용이한 전해동박, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법에 관한 것이다.

【배경기술】

<2> 이차전지는 전기 에너지를 화학 에너지의 형태로 바꾸어 저장하였다가 전기가 필요할 때 상기 화학 에너지를 전기 에너지로 변환시킴으로써 전기를 발생시키는 에너지 변환 기기의 일종으로서, 재충전이 가능하다는 점에서 “충전식 전지(rechargeable battery)”로도 지칭된다.

<3> 1회용의 일차전지에 비해 경제적으로 그리고 환경적으로 이점을 갖고 있는 이차전지로는 납 축전지, 니켈카드뮴 이차전지, 니켈수소 이차전지, 리튬 이차전지 등이 있다.

<4> 리튬 이차전지는 다른 이차전지들에 비해 크기 및 중량 대비 상대적으로 많은 에너지를 저장할 수 있다. 따라서, 휴대성 및 이동성이 중요한 정보통신기기 분

야의 경우 리튬 이차전지가 선호되고 있으며, 하이브리드 자동차 및 전기 자동차의 에너지 저장 장치로도 그 응용 범위가 확대되고 있다.

<5> 리튬 이차전지는 충전과 방전을 하나의 주기로 하여 반복적으로 사용된다. 완전히 충전된 리튬 이차전지로 어떤 기기를 가동시킬 때, 상기 기기의 가동 시간을 늘리기 위해서는 상기 리튬 이온 이차전지가 높은 충전/방전 용량을 가져야 한다. 따라서, 리튬 이차전지의 충전/방전 용량에 대한 수요자의 나날이 높아지는 기대치(needs)를 만족시키기 위한 연구가 지속적으로 요구되고 있다.

<6> 리튬 이차전지의 용량을 증가시키기 위한 하나의 방법으로서, 탄소 활물질에 Si 또는 Sn이 첨가된 복합 활물질을 이차전지의 음극 제조시 전해동박 상에 도포되는 활물질로서 사용하는 것이 제안되었다. 그러나, 이와 같은 복합 활물질은 리튬 이차전지가 충전 또는 방전될 때 발생하는 열로 인해 급격히 그리고 심하게 팽창하여 전해동박의 파단을 야기한다.또한, 리튬 이차전지의 음극 제조에 일반적으로

<7> 사용되는 10㎛ 이하의 얇은 두께를 갖는 전해동박은 휨(curl) 또는 주름(wrinkle)에 특히 취약한데, 이러한 동박의 휨 또는 주름은 전극 제조시 전해동박 핸들링을 곤란하게 할 뿐만 아니라 심지어는 활물질 코팅 자체를 불가능하게 한다.

【발명의 내용】

【해결하려는 과제】

<8> 따라서, 본 발명은 위와 같은 관련 기술의 제한 및 단점들에 기인한 문제점들을 방지할 수 있는 전해동박, 그것을 포함하는 전극, 그것을 포함하는 이차전지,

및 그것의 제조방법에 관한 것이다.

<9> 본 발명의 일 관점은, 높은 내구성의 이차전지를 담보할 수 있으며 핸들링이 용이한 전해동박을 제공하는 것이다.

<10> 본 발명의 다른 관점은, 높은 내구성의 이차전지를 담보할 수 있는 전극을 제공하는 것이다.

<11> 본 발명의 또 다른 관점은, 높은 내구성을 갖는 이차전지를 제공하는 것이다.

<12> 본 발명의 또 다른 관점은, 높은 내구성의 이차전지를 담보할 수 있으며 핸들링이 용이한 전해동박을 제조하는 방법을 제공하는 것이다.

<13> 위에서 언급된 본 발명의 관점들 외에도, 본 발명의 다른 특징 및 이점들이 이하에서 설명되거나, 그러한 설명으로부터 본 발명이 속하는 기술분야에서 통상의 지식을 가진 자에게 명확하게 이해될 수 있을 것이다.

【과제의 해결 수단】

<14> 위와 같은 본 발명의 일 관점에 따라, 제1 면과 그 반대편의 제2 면을 포함하는 이차전지용 전해동박에 있어서, 상기 제1 면을 향하는 매트면(matte surface) 및 상기 제2 면을 향하는 샤이니면(shiny surface)을 포함하는 구리층; 상기 구리층의 상기 매트면 상의 제1 보호층; 및 상기 구리층의 상기 샤이니면 상의 제2 보호층을 포함하고, 열기계분석기(Thermomechanical Analyzer: TMA)를 이용하여 5℃/min의 속도로 30℃에서 190℃까지 승온시키면서 측정된 상기 전해동박의 열팽창계

수는 16 내지 22 ㎛/(m·℃)이고, 190℃에서 1시간 동안 열처리 후 측정된 상기 전해동박의 인장강도는 21 내지 36 kgf/㎟이며, 상기 전해동박의 중량 편차는 5% 이하인 것을 특징으로 하는, 전해동박이 제공된다.

<15> 상기 전해동박은 상온에서 3% 이상의 연신율을 가질 수 있다.

<16> 상기 전해동박의 상기 제1 및 제2 면들 각각의 피크수(Pc)는 3 내지 92개일 수 있다.

<17> 상기 제1 및 제2 보호층들은 크롬(Cr), 실란 화합물 및 질소 화합물 중 적어도 하나를 포함할 수 있다.

<18> 상기 전해동박은 4 내지 30 ㎛의 두께를 가질 수 있다.

<19> 상기 제1 및 제2 면들은 3.5 ㎛ 이하의 표면조도(R_z)를 가질 수 있다.

<20> 본 발명의 다른 관점에 따라, 제1 면과 그 반대편의 제2 면을 포함하는 전해동박; 및 상기 전해동박의 상기 제1 면 상의 제1 활물질층을 포함하되, 상기 전해동박은, 상기 제1 면을 향하는 매트면 및 상기 제2 면을 향하는 샤이니면을 포함하는 구리층; 상기 구리층의 상기 매트면 상의 제1 보호층; 및 상기 구리층의 상기 샤이니면 상의 제2 보호층을 포함하고, 열기계분석기(TMA)를 이용하여 5℃/min의 속도로 30℃에서 190℃까지 승온시키면서 측정된 상기 전해동박의 열팽창계수는 16 내지 22 ㎛/(m·℃)이고, 190℃에서 1시간 동안 열처리 후 측정된 상기 전해동박의 인장강도는 21 내지 36 kgf/㎟이며, 상기 전해동박의 중량 편차는 5% 이하인 것을

특징으로 하는, 이차전지용 전극이 제공된다.

<21> 상기 제1 활물질층은, 탄소; Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni 또는 Fe의 금속(Me); 상기 금속을 포함하는 합금; 상기 금속의 산화물(MeO_x); 및 상기 금속과 탄소의 복합체로 이루어진 군으로부터 선택되는 하나 이상의 활물질을 포함할 수 있다.

<22> 상기 제1 활물질층은 Si를 포함할 수 있다.

<23> 상기 이차전지용 전극은 상기 제2 보호층 상의 제2 활물질층을 더 포함할 수 있다.

<24> 본 발명의 또 다른 관점에 따라, 양극(cathode); 상기 이차전지용 전극으로 구성된 음극(anode); 상기 양극과 음극 사이에서 리튬 이온이 이동할 수 있는 환경을 제공하는 전해질(electrolyte); 및 상기 양극과 상기 음극을 전기적으로 절연시켜 주는 분리막(separator)을 포함하는 것을 특징으로 하는, 이차전지가 제공된다.

<25> 본 발명의 또 다른 관점에 따라, 70 내지 100 g/L의 구리 이온 및 80 내지 130 g/L의 황산을 포함하는 전해액을 준비하는 단계; 상기 전해액 내에 서로 이격되게 배치된 양극판 및 회전 음극드럼을 통전시키는 전기 도금을 수행함으로써 구리층을 형성시키는 단계; 및 상기 구리층 상에 보호층을 형성시키는 단계를 포함하되, 상기 전기 도금이 수행되는 동안, 상기 양극판과 상기 회전 음극 드럼의 간격은 5 내지 15 mm로 유지되고, 구리층의 폭 방향에 따른 상기 양극판과 상기 회전 음극 드럼의 최대 간격과 최소 간격의 차이는 0.2 mm 미만으로 유지되고, 상기 전

해액 내의 총유기탄소량(Total Organic Carbon: TOC)은 50 ppm 이하로 유지되며, 상기 전해액 내의 은(Ag) 농도는 25 ppm 이하로 유지되는 것을 특징으로 하는, 이차전지용 전해동박의 제조방법이 제공된다.

<26> 상기 전기 도금은 30 내지 80 A/dm^2의 전류밀도를 가함으로써 수행될 수 있다.

<27> 상기 전해액 준비 단계는, 구리 와이어를 열처리하는 단계; 상기 열처리된 구리 와이어를 산세하는 단계; 및 상기 산세된 구리 와이어를 황산에 투입하는 단계를 포함할 수 있다.

<28> 상기 구리 와이어는 600 내지 900℃에서 2 내지 6 시간 동안 열처리될 수 있고, 상기 열처리된 구리 와이어는 8 내지 10 중량%의 황산 및 1 내지 2 중량%의 과산화수소를 포함하는 산성 용액에 침지된 후 물로 세정됨으로써 산세될 수 있다.

<29> 상기 전기 도금이 수행되는 동안, 상기 전해액으로부터 고형 불순물을 제거하기 위한 연속 여과가 31 내지 45 m^3/hr의 유량으로 수행될 수 있다.

<30> 상기 전기 도금이 수행되는 동안 은(Ag)이 상기 전해액으로 유입되어 은(Ag) 농도가 25 ppm을 초과하는 것을 방지하기 위하여, 상기 전해액은 은(Ag)을 AgCl 형태로 침전시킬 수 있는 염소 이온을 더 포함할 수 있다.

<31> 상기 전해액은 하이드록시에틸 셀룰로오스(HEC), 유기 황화물, 유기 질화물, 및 티오요소(thiourea)계 화합물로 구성된 그룹으로부터 선택되는 유기 첨가제를 더 포함할 수 있다.

<32> 상기 보호층 형성 단계는 0.5 내지 1.5 g/L의 Cr을 포함하는 방청액 내에 상기 구리층을 침지시키는 단계를 포함할 수 있다.

<33> 위와 같은 본 발명에 대한 일반적 서술은 본 발명을 예시하거나 설명하기 위한 것일 뿐으로서, 본 발명의 권리범위를 제한하지 않는다.

【발명의 효과】

<34> 본 발명에 의하면, 롤투롤 공정 중에 전해동박의 휨 및/또는 주름 발생을 방지함으로써 설비의 중단과 재가동의 반복으로 인한 생산성 저하를 방지하고 제조원가를 낮출 수 있다. 또한, 리튬 이차전지의 충/방전시 전해동박의 파단을 방지함으로써 이차전지의 내구성을 크게 향상시킬 수 있다.

<35> 또한, 충방전 사이클의 반복에도 불구하고 높은 충전/방전 용량을 오랫동안 유지할 수 있는 장수명의 이차전지가 제조될 수 있다. 따라서, 이차전지의 빈번한 교체로 인한 전자제품 소비자의 불편 및 자원 낭비를 최소화할 수 있다.

【도면의 간단한 설명】

<36> 첨부된 도면은 본 발명의 이해를 돕고 본 명세서의 일부를 구성하기 위한 것으로서, 본 발명의 실시예들을 예시하며, 발명의 상세한 설명과 함께 본 발명의 원리들을 설명한다.

도 1은 본 발명의 일 실시예에 따른 이차전지용 전극의 단면도이고,

도 2는 ASME B46.1(2009) 규격에 따라 얻어진 표면 조도 프로파일을 예시한다.

【발명을 실시하기 위한 구체적인 내용】

<37> 이하에서는 첨부된 도면을 참조하여 본 발명의 실시예들을 상세하게 설명한다.

<38> 본 발명의 기술적 사상 및 범위를 벗어나지 않는 범위 내에서 본 발명의 다양한 변경 및 변형이 가능하다는 점은 당업자에게 자명할 것이다. 따라서, 본 발명은 특허청구범위에 기재된 발명 및 그 균등물의 범위 내에 드는 변경 및 변형을 모두 포함한다.

<39> 리튬 이온 이차전지는, 양극(cathode), 음극(anode), 상기 양극과 음극 사이에서 리튬 이온이 이동할 수 있는 환경을 제공하는 전해질(electrolyte), 및 하나의 전극에서 발생된 전자가 이차전지 내부를 통해 다른 전극으로 이동함으로써 무익하게 소모되는 것을 방지하기 위하여 상기 양극과 음극을 전기적으로 절연시켜주는 분리막(separator)을 포함한다.

<40> 도 1은 본 발명의 일 실시예에 따른 이차전지용 전극의 단면도이다.

<41> 도 1에 예시된 바와 같이, 본 발명의 일 실시예에 따른 이차전지용 전극(100)은 제1 면(S1)과 그 반대편의 제2 면(S2)을 갖는 전해동박(110), 상기 제1 면(S1) 상의 제1 활물질층(120a), 및 상기 제2 면(S2) 상의 제2 활물질층(120b)을 포함한다. 도 1은 상기 전해동박(110)의 제1 및 제2 면들(S1, S2) 모두 위에 활물질층들(120a, 120b)이 각각 형성된 예를 보여주고 있으나, 본 발명이 이에 국한되는 것은 아니며, 본 발명의 이차전지용 전극(100)은 활물질층으로서 상기 제1 활물질

층(120a)만을 포함할 수도 있다.

<42> 리튬 이차전지에 있어서, 양극 활물질과 결합되는 양극 집전체로서는 알루미늄 호일(foil)이 사용되고 음극 활물질과 결합되는 음극 집전체로서는 전해동박이 사용되는 것이 일반적이다.

<43> 본 발명의 일 실시예에 의하면, 상기 이차전지용 전극(100)은 리튬 이차전지의 음극으로 사용되고, 상기 전해동박(110)은 음극 집전체로서 기능하며, 상기 제1 및 제2 활물질층들(120a, 120b)은 음극 활물질을 포함한다.

<44> 도 1에 예시된 바와 같이, 이차전지의 음극 집전체로서 기능하는 본 발명의 전해동박(110)은 매트면(matte surface)(MS) 및 샤이니면(shiny surface)(SS)을 포함하는 구리층(111), 상기 구리층(111)의 상기 매트면(MS) 상의 제1 보호층(112a), 및 상기 구리층(111)의 상기 샤이니면(SS) 상의 제2 보호층(112b)을 포함한다.

<45> 상기 매트면(MS)은 상기 전해동박(110)의 제1 면(S1)을 향하는 구리층(111)의 면이고, 상기 샤이니면(SS)은 상기 전해동박(110)의 제2 면(S2)을 향하는 구리층(111)의 면이다.

<46> 본 발명의 구리층(111)은 전기도금을 통해 회전 음극드럼 상에 형성될 수 있는데, 상기 샤이니면(SS)은 전기도금 과정에서 상기 회전 음극드럼과 접촉하였던 면을 지칭하고, 상기 매트면(MS)은 상기 샤이니면(SS)의 반대 편 면을 지칭한다.

<47> 샤이니면(SS)이 매트면(MS)에 비해 더 낮은 표면조도(R_z)를 갖는 것이 일반적이기는 하지만 본 발명이 이에 국한되는 것은 아니며 샤이니면(SS)의 표면조도

(R_z)가 매트면(MS)의 표면조도(R_z)와 동일하거나 더 높을 수도 있다.

<48> 상기 제1 및 제2 보호층들(112a, 112b)은 상기 구리층(111)의 부식을 방지하고, 내열성을 향상시키며, 상기 구리층(111)과 활물질층들(120a, 120b) 사이의 접착 강도를 높여 이차 전지의 충방전 효율 저하를 억제시키기 위한 것으로서, 크롬(Cr), 실란 화합물 및 질소 화합물 중 적어도 하나를 포함할 수 있다.

<49> 본 발명에 의하면, 열기계분석기(Thermomechanical Analyzer: TMA)를 이용하여 5℃/min의 속도로 30℃에서 190℃까지 승온시키면서 측정된 상기 전해동박(110)의 열팽창계수(Coefficient of Thermal Expansion)는 16 내지 22 ㎛/(m·℃)이다.

<50> 상기 열팽창계수가 16 ㎛/(m·℃) 미만이면 리튬 이차전지가 충/방전될 때 발생하는 열로 인해 활물질이 급격히 그리고 심하게 팽창하여 전해동박(110)의 파단을 야기한다. 반면, 상기 열팽창계수가 22 ㎛/(m·℃)를 초과하면 리튬 이차전지의 제조 공정 중에 받는 열에 의해 전해동박(110)의 휨 및/또는 주름이 야기되어 전해동박 핸들링이 곤란해질 뿐만 아니라 전극(100) 제조시 활물질 코팅 자체가 불가능해진다.

<51> 본 발명에 의하면, 190℃에서 1시간 동안 열처리 후 측정되는 상기 전해동박(110)의 인장강도는 21 내지 36 kgf/mm^2이다.

<52> 전해동박(110)의 상기 인장강도가 21 kgf/mm^2 미만이면, 전극(100) 및 이차

전지 제조를 위한 롤투롤 공정 중에 상기 전해동박(110)에 가해지는 장력에 의해 쉽게 변형되어 주름이 발생할 위험이 높다. 반면, 전해동박(110)의 상기 인장강도가 36 kgf/mm^2를 초과하면, 리튬 이차전지의 충/방전시 전해동박(110)이 파단될 위험이 높아진다.

<53> 본 발명의 전해동박(110)은 5% 이하의 중량 편차를 갖는다. 본 명세서에서 "중량 편차"는 전해동박(110)의 폭 방향, 즉 TD(Transverse Direction)를 따라 배열된 3개 지점들에서 5cm×5cm의 샘플들을 각각 취한 후 각 샘플의 중량을 측정하여 단위면적당 중량을 산출하고, 3개 샘플의 단위면적당 중량으로부터 표준편차를 산출함으로써 구해질 수 있다.

<54> 전해동박(110)의 상기 중량 편차가 5%를 초과하면, 이차전지 제조를 위한 롤투롤 공정 중에 상기 전해동박(110)에 가해지는 장력에 의해 쉽게 변형되어 주름이 발생할 위험이 높다.

<55> 본 발명의 이차전지용 전해동박(110)은 상온(25±15 ℃)에서 3% 이상, 바람직하게는 3 내지 10 %의 연신율을 가질 수 있다. 전해동박(110)의 연신율이 3% 미만이면, 전극(100) 및 이차전지 제조 과정에서 가해지는 힘에 의해 전해동박(110)이 늘어나지 못하고 찢어질 위험이 커질 뿐만 아니라, 리튬 이차전지의 충/방전시 전해동박(110)이 파단될 위험이 높아진다. 반면, 전해동박(110)의 연신율이 10%를 초과하면 이차전지 제조를 위한 롤투롤 공정 중에 상기 전해동박(110)에 가해지는 장력에 의해 쉽게 변형되어 주름이 발생할 위험이 높다.

<56> 본 발명의 전해동박(110)은 4 내지 30 ㎛의 두께를 가질 수 있다. 전해동박(110)의 두께가 4 ㎛ 미만이면 주름이 쉽게 야기되어 이차전지 제조 공정의 작업성이 저하된다. 반면, 전해동박(110)의 두께가 30 ㎛를 초과하면 고용량의 리튬 이차전지 구현이 어려워진다.

<57> 상기 제1 및 제2 활물질층들(120a, 120b)은, 탄소; Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni 또는 Fe의 금속(Me); 상기 금속을 포함하는 합금; 상기 금속의 산화물(MeO_x); 및 상기 금속과 탄소의 복합체로 이루어진 군으로부터 선택되는 하나 이상의 활물질을 음극 활물질로서 포함한다.

<58> 이차전지의 충방전 용량을 증가시키기 위하여, 상기 활물질층(120a, 120b)은 Si를 소정량 포함한 혼합물일 수 있다.

<59> 한편, 이차전지의 충방전이 반복됨에 따라 활물질층(120a, 120b)의 수축 및 팽창이 번갈아 발생하고, 이것은 상기 활물질층(120a, 120b)과 상기 전해동박(110)의 분리를 유발하여 이차전지의 충방전 효율을 저하시킬 수 있다. 따라서, 이차전지가 일정 수준 이상의 용량 유지율 및 수명을 확보하기 위해서는(즉, 이차전지의 충방전 효율 저하를 억제하기 위해서는), 전해동박(110)이 활물질에 대하여 우수한 코팅성을 가져야 한다. 즉, 상기 전해동박(110)와 활물질층(120a, 120b) 사이의 접착 강도가 높아야 한다.

<60> 일반적으로, 상기 전해동박(110)의 표면조도(R_z) 제어를 통해 전해동박(110)과 활물질층(120a, 120b) 사이의 접착 강도를 향상시킬 수 있다고 알려져 있다.

그러나, 실제로는, 표면조도(R_z)가 적절히 제어된 전해동박(110)이라도 스펙에서 요구되는 전해동박(110)과 활물질층(120a, 120b) 간의 충분한 접착력을 반드시 만족시키는 것은 아니며, 특히, 이차전지의 고용량화를 위하여 상기 활물질층(120a, 120b)이 Si를 포함할 경우 전해동박(110)의 표면조도(R_z)와 이차전지의 용량 유지율 사이의 연관성이 더욱 낮은 것으로 드러났다.

<61> 본 발명에 의하면, 전해동박(110)과 활물질층(120a, 120b) 사이의 충분한 접착력을 확보함에 있어서, 전해동박(110) 표면의 표면조도(R_z)와 함께 상기 표면의 피크수(Peak Count: Pc)가 중요한 인자임이 확인되었다.

<62> 상기 피크수(Pc)는 상기 표면조도(R_z)와 함께 전해동박(110)과 제1 활물질층(120a) 사이의 물리적 결합력에 영향을 미친다. 이하에서는, 도 2를 참조하여 피크수(Pc)를 설명한다.

<63> 본 발명에서 "피크수(Pc)"는 제1 면(S1) 중 임의의 3개 지점들의 피크수(Pc)를 측정하고 그 측정값들의 평균값을 산출함으로써 얻어질 수 있다. 상기 지점들 각각의 피크수(Pc)는 ASME B46.1(2009) 규격에 따라 얻어진 표면 조도 프로파일에서 4㎜의 단위 샘플링 길이당 0.5㎛의 상위 기준선(upper criteria line: C1) 위로 솟아 있는 유효 피크들(P_1, P_2, P_3, P_4)의 개수이다. 이때, 상기 유효 피크들 중 이웃하는 유효 피크들 사이에는 -0.5㎛의 하위 기준선(lower criteria line: C2)보다 깊은 적어도 하나의 골(valley)이 존재한다. 만약, 상위 기준선(C1) 위로 솟아

있는 이웃하는 피크들 사이에 -0.5㎛의 하위 기준선(C2)보다 깊은 골이 하나도 존재하지 않는다면, 상기 이웃하는 피크들 모두가 피크수(Pc)의 측정에 이용되는 "유효 피크"가 될 수는 없으며, "유효 피크" 개수를 구함에 있어서 상기 피크들 중 상대적으로 더 낮은 피크는 무시된다.

<64> 본 발명의 일 실시예에 의하면, 상기 전해동박(110)의 제1 및 제2 면들(S1, S2)의 피크수(Pc)는 각각 3 내지 92개이고, 상기 제1 및 제2 면들(S1, S2)의 표면조도(R_z)는 3.5 ㎛ 이하이다.

<65> 상기 피크수(Pc)가 3개 미만인 경우 음극 활물질과 접촉할 수 있는 전해동박(110)의 활성 비표면적이 너무 적어 전해동박(110)과 활물질층들(120a, 120b) 사이에 충분한 밀착력이 확보될 수 없다.

<66> 반면, 피크수(Pc)가 92개를 초과하거나 표면조도(R_z)가 3.5 ㎛를 초과하는 경우에는, 너무 많은 표면 요철들로 인해 음극 활물질의 코팅 균일성이 저하되고, 이로 인해 전해동박(110)과 활물질층들(120a, 120b) 사이의 밀착력이 현저히 저하된다.

<68> 이하에서는, 본 발명의 일 실시예에 따른 전해동박(110)의 제조방법을 구체적으로 설명한다.

<69> 먼저, 70 내지 100 g/L의 구리 이온 및 80 내지 130 g/L의 황산을 포함하는 전해액을 준비하고, 상기 전해액 내에 서로 이격되게 배치된 양극판 및 회전 음극

드럼을 통전시키는 전기 도금을 수행함으로써 상기 구리층(111)을 형성시킨다.

<70> 본 발명에 의하면, 상기 전기 도금이 수행되는 동안, 상기 전해액 내의 총유기탄소량(Total Organic Carbon: TOC)이 50 ppm 이하로 유지되도록 상기 전해액이 관리된다. 전해액 내의 유기물 함량이 높아질수록 전기도금을 통해 생산되는 구리층(111)의 결정립 내에 유기물이 존재할 가능성이 높아진다. 구리층(111)의 결정립 내의 유기물은 전해동박(110)의 열팽창계수를 16 ㎛/(m · ℃) 미만으로 낮추는 원인이 된다.

<71> 전해액의 총유기탄소량(TOC)을 50 ppm 이하로 유지시키기 위하여, 고순도의 구리 와이어를 열처리하여 유기물을 태우고, 상기 열처리된 구리 와이어를 산세하며, 상기 산세된 구리 와이어를 황산에 투입함으로써 불순물이 전혀 또는 거의 없는 전해액을 준비할 수 있다.

<72> 상기 구리 와이어는 산소 분위기의 전기로에서 600 내지 900℃에서 2 내지 6 시간 동안 열처리될 수 있으며, 상기 열처리된 구리 와이어는 8 내지 10 중량%의 황산 및 1 내지 2 중량%의 과산화수소를 포함하는 산성 용액에 침지된 후 물로 세정됨으로써 산세될 수 있다. 이와 같이 구리 와이어의 표면에 붙어있을지도 모를 유기 불순물을 완벽히 제거함으로써 유기 불순물이 전해액 내로 유입되는 것을 방지할 수 있다.

<73> 본 발명에 의하면, 상기 전기 도금이 수행되는 동안, 상기 전해액 내의 은(Ag) 농도는 25 ppm 이하로 유지된다. 상기 전해액 내의 은(Ag) 농도가 25 ppm을 초과하면 구리층(111)이 형성될 때 은(Ag)이 같이 석출되고, 최종 전해동박(110)의

열팽창계수가 22 ㎛/(m · ℃)를 초과하게 된다.

<74> 상기 전기 도금이 수행될 때 은(Ag)이 상기 전해액으로 유입되어 은(Ag) 농도가 25 ppm을 초과하는 것을 방지하기 위하여, 은(Ag)을 함유하지 않은 구리 와이어를 사용하거나, 은(Ag)을 AgCl 형태로 침전시킬 수 있는 염소 이온을 상기 전해액에 소량(예를 들어, 50 ppm 이하) 포함시킬 수 있다.

<75> 총유기탄소량(TOC) 및 은(Ag) 농도를 상기 범위로 각각 관리함으로써 상기 전해동박(110)의 제1 및 제2 면들(S1, S2)의 피크수(Pc) 및 표면조도(R_z)가 3 내지 92개 및 3.5 ㎛ 이하로 각각 제어될 수 있다.

<76> 본 발명의 방법은, 상기 전기 도금이 수행되는 동안 상기 전해액으로부터 고형 불순물을 제거하기 위한 연속(순환) 여과를 31 내지 45 m^3/hr의 유량으로 수행하는 단계를 더 포함할 수 있다. 상기 유량이 31 m^3/hr 미만이면, 유속이 낮아져 과전압이 증가하고 구리층(111)이 불균일하게 형성된다. 반면, 상기 유량이 45 m^3/hr 를 초과하면, 필터 손상이 유발되어 전해액 내로 이물질이 유입된다.

<77> 선택적으로, 오존 처리를 통해 전해액 내 유기물을 분해함으로써 상기 총유기탄소량(TOC)을 낮출 수도 있다.

<78> 선택적으로, 상기 전기 도금이 수행되는 동안 과산화수소 및 공기를 상기 전해액에 투입함으로써 상기 전해액의 청정도를 향상시킬 수 있다.

<79> 선택적으로, 상기 전해액은 하이드록시에틸 셀룰로오스(HEC), 유기 황화물,

유기 질화물, 및 티오요소(thiourea)계 화합물로 구성된 그룹으로부터 선택되는 유기 첨가제를 더 포함할 수 있다.

<80> 본 발명의 일 실시예에 의하면, 상기 전기 도금은 30 내지 80 A/dm^2의 전류 밀도를 가함으로써 수행될 수 있다.

<81> 본 발명에 의하면, 상기 전해동박(110)이 5% 이하의 중량 편차를 갖도록 하기 위하여, 상기 전기 도금이 수행되는 동안, 상기 양극판과 상기 회전 음극 드럼의 간격은 5 내지 15 ㎜로 유지되고 구리층(111)의 폭 방향에 따른 상기 양극판과 상기 회전 음극 드럼의 최대 간격과 최소 간격의 차이는 0.2 ㎜ 미만으로 유지된다.

<82> 이어서, 위와 같이 제조된 구리층(111)을 0.5 내지 1.5 g/L의 Cr을 포함하는 방청액 내에 침지(예를 들어, 상온에 2 내지 20 초 동안)시킨 후 건조시킴으로써 상기 구리층(111) 상에 보호층(112a, 112b)을 형성시킨다.

<83> 방청액 내 Cr 농도가 0.5 g/L 미만이면, 전해동박(110) 표면의 Cr 전착량(DA_{Cr})이 0.5 mg/m^2 미만이 되어 전해동박(110) 표면의 산화가 유발되고, 상기 전해동박(110)과 활물질층(120a, 120b) 사이의 화학적 결합력이 저하된다.

<84> 반면, 상기 방청액 내 Cr 농도가 1.5 g/L를 초과하면, 전해동박(110) 표면의 Cr 전착량(DA_{Cr})이 3.8 mg/m^2를 초과하게 되어 전해동박(110) 표면의 소수성 특성이 급격히 증가하여 음극 활물질과의 화학적 친화도가 저하되며, 궁극적으로는 전해동

박(110)과 활물질층(120a, 120b) 사이의 밀착력이 저하된다.

<85> 상기 방청액은 실란 화합물과 질소 화합물 중 적어도 1종 이상을 더 포함할 수 있다. 예를 들어, 상기 방청액은 0.5 내지 1.5 g/L의 Cr 및 0.5 내지 1.5 g/L의 실란 화합물을 포함할 수 있다.

<86> 한편, 상기 방청액 내 Cu 농도가 지나치게 높으면 상기 구리층(111) 표면에 전착되는 Cr의 양이 감소한다. 따라서, 본 발명의 일 실시예에 의하면, 상기 방청액 내 구리(Cu)의 농도는 0.1 g/L 이하로 유지된다. 상기 Cu 농도가 0.1 g/L를 초과하면 전해동박(110) 표면의 Cr 전착량(DA_{Cr})이 0.5 mg/m^2 미만이 되어 전해동박(110) 표면의 산화가 유발되고, 상기 전해동박(110)과 활물질층(120a, 120b) 사이의 화학적 결합력이 저하된다.

<87> 한편, 회전 음극드럼 표면(전기도금에 의해 구리가 석출되는 면)의 연마 정도를 조절함으로써 전해동박(110)의 제2 면(S2)의 피크수(Pc) 및 평균조도(R_z)가 3 내지 92 개 및 3.5 ㎛ 이하로 각각 제어될 수 있다.

<88> 본 발명의 일 실시예에 의하면, #800 내지 #1500의 입도(Grit)를 갖는 연마 브러시로 상기 회전 음극드럼의 표면이 연마된다.

<89> 이와 같이 제조된 본 발명의 전해동박(110) 상에 음극 활물질을 코팅함으로써 본 발명의 이차전지용 전극(즉, 음극)이 제조될 수 있다.

<90> 상기 음극 활물질은, 탄소; Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni 또는 Fe의

금속(Me); 상기 금속(Me)을 포함하는 합금; 상기 금속(Me)의 산화물(MeO_x); 및 상기 금속(Me)과 탄소의 복합체로 이루어진 군으로부터 선택될 수 있다.

<91> 예를 들어, 100 중량부의 음극 활물질용 탄소에 1 내지 3 중량부의 스티렌부타디엔 고무(SBR) 및 1 내지 3 중량부의 카르복시메틸 셀룰로오스(CMC)를 혼합한 후 증류수를 용제로 사용하여 슬러리를 조제한다. 이어서, 닥터 블레이드를 이용하여 상기 전해동박(110) 상에 20 내지 100㎛ 두께로 상기 슬러리를 도포하고, 110 내지 130℃에서 0.5 내지 1.5 ton/cm^2의 압력으로 프레스한다.

<92> 이상의 방법으로 제조된 본 발명의 이차전지용 전극(음극)과 함께 통상의 양극, 전해질, 및 분리막을 이용하여 리튬 이차전지를 제조할 수 있다.

<94> 이하에서는, 실시예들 및 비교예들을 통해 본 발명을 구체적으로 설명한다. 다만, 하기의 실시예들은 본 발명의 이해를 돕기 위한 것일 뿐으로, 본 발명의 권리범위가 이들 실시예들로 제한되지 않는다.

<95> 실시예 1 내지 4 및 비교예 1 내지 6

<96> 75 g/L의 구리 및 105 g/L의 황산을 포함하는 전해액을 65 ℃로 유지시키면서 양극판과 회전 음극드럼을 65 ASD의 전류밀도로 통전시킴으로써 구리층을 형성시켰다. 이때, 상기 전해액 내 총유기탄소량(TOC)과 은(Ag) 농도, 그리고 상기 양극판과 회전 음극드럼 사이의 최대 간격과 최소 간격의 차이는 아래의 표 1과 같았다.

<97> 이어서, 상기 구리층을 방청액에 침지시킨 후 건조시킴으로써 전해동박을 완성하였다.

<98> 【표 1】

	전해액 내 TOC 농도 (ppm)	전해액 내 Ag 농도 (ppm)	양극판과 회전 음극드럼 사이의 최대 간격과 최소 간격의 차이 (㎜)
실시예1	45	22	0.18
실시예2	2	3	0.18
실시예3	2	22	0.07
실시예4	47	3	0.07
비교예1	3	32	0.18
비교예2	52	15	0.18
비교예3	15	45	0.07
비교예4	62	3	0.07
비교예5	2	3	0.22
비교예6	45	22	0.32

<99> 위와 같이 제조된 실시예 1-4 및 비교예 1-6의 전해동박들의 열팽창계수, 열처리 후 인장강도, 중량 편차, 연신율, 주름 발생 유무, 및 500회 충/방전 후 파단 여부를 아래와 같이 각각 측정/산출하였고, 그 결과를 아래의 표 2에 나타내었다.

<100> * 열팽창계수[㎛/(m·℃)]

<101> 열기계분석기(Thermomechanical Analyzer: TMA)를 이용하여 5℃/min의 속도로 30℃에서 190℃까지 전해동박의 샘플을 승온시키면서 아래의 식 1에 의해 정의되는 열팽창계수를 측정하였다.

<102> 식 1: $CTE = \Delta L/[L_0 \times \Delta T]$

<103> 여기서, CTE는 열팽창계수이고, L_0는 샘플의 초기 길이(m)이고, ΔL는 샘플

의 길이변화(㎛)이며, ΔT는 온도변화(℃)이다.

<104> * 열처리 후 인장강도(kgf/mm^2)

<105> 전해동박 샘플을 190℃에서 1시간 동안 열처리한 후 만능재료시험기(Universal Testing Machine: UTM)를 이용하여 열처리된 샘플의 인장강도를 측정하였다. 이때, 샘플의 폭은 12.7 mm이었고, 그립(grip)간 거리는 50 mm이었으며, 측정 속도는 50 mm/min이었다.

<106> * 중량 편차(%)

<107> 전해동박의 폭 방향, 즉 TD(Transverse Direction)를 따라 배열된 3개 지점들에서 5cm×5cm의 샘플들을 각각 취한 후 각 샘플의 중량을 측정하여 단위면적당 중량을 산출하고, 3개 샘플의 단위면적당 중량으로부터 표준편차를 산출하였다.

<108> * 연신율(%)

<109> 상온에서 만능재료시험기(UTM)를 이용하여 IPC-TM-650 Test Method Manual에 규정된 방법에 따라 전해동박의 연신율을 측정하였다.

<110> * 주름 발생 유무

<111> 전해동박을 이용하여 이차전지용 음극 및 이차전지를 순차적으로 제조하는 과정에서 상기 전해동박의 주름 발생 여부를 관찰하였다.

<112> * 500회 충/방전 후 음극 파단 여부

<113> 전해동박을 이용하여 제조된 음극을 포함하는 이차전지에 대하여 50℃에서 0.5 C의 충/방전 속도로 500회의 충/방전 실험을 수행한 후 상기 음극의 파단 여부

를 관찰하였다.

<114> 【표 2】

	열팽창계수 [㎛/(m · ℃)]	열처리 후 인장강도 (kgf/mm^2)	중량 편차 (%)	연신율 (%)	주름 발생 유무	500회 충/방전 후 음극 파단 여부
실시예1	20.9	25.6	3.8	5.6	×	×
실시예2	20.3	27.2	3.6	5.3	×	×
실시예3	21.8	22.1	0.7	8.9	×	×
실시예4	17.3	34.5	0.6	4.8	×	×
비교예1	22.4	22.2	3.8	10.3	○	×
비교예2	15.7	35.8	3.8	2.8	×	○
비교예3	22.8	20.5	0.6	10.8	○	×
비교예4	15.3	36.8	0.6	2.6	×	○
비교예5	20.1	26.5	5.2	5.3	○	×
비교예6	21.2	27.2	5.8	5.6	○	×

<115> 위 표 2로부터 알 수 있는 바와 같이, 전기도금 수행할 때 전해액 내 TOC 함량이 50 ppm을 초과한 경우(비교예 2 및 4)에는 16 ㎛/(m · ℃) 미만의 열팽창계수 및 3% 미만의 연신율을 갖는 전해동박이 제조되었고, 이 전해동박으로 제조된 이차전지에 대하여 500회 충/방전 실험을 수행한 결과 음극의 파단이 관찰되었다.

<116> 또한, 전기도금을 수행할 때 전해액 내 Ag 농도가 25 ppm을 초과한 경우(비교예 1 및 3)에는 22 ㎛/(m · ℃)를 초과하는 열팽창계수 및 10%를 초과하는 연신율을 갖는 전해동박이 제조되었고, 이 전해동박으로 전극 및 이차전지를 제조할 때 주름이 발생하였다.

<117> 한편, 양극판과 회전 음극드럼 사이의 최대 간격과 최소 간격의 차이가 0.2 ㎜를 초과한 경우(비교예 5 및 6)에는 5%를 초과하는 중량 편차를 갖는 전해동박이 제조되었고, 이 전해동박으로 전극 및 이차전지를 제조할 때 주름이 발생하였다.

【부호의 설명】

<118>

100: 이차전지 전극

110: 전해동박

111: 구리층

112a: 제1 보호층

112b: 제2 보호층

120a: 제1 활물질층

120b: 제2 활물질층

【특허청구범위】

【청구항 1】

제1 면과 그 반대편의 제2 면을 포함하는 이차전지용 전해동박에 있어서,

상기 제1 면을 향하는 매트면(matte surface) 및 상기 제2 면을 향하는 샤이니면(shiny surface)을 포함하는 구리층;

상기 구리층의 상기 매트면 상의 제1 보호층; 및

상기 구리층의 상기 샤이니면 상의 제2 보호층을 포함하고,

열기계분석기(Thermomechanical Analyzer; TMA)를 이용하여 5℃/min의 속도로 30℃에서 190℃까지 승온시키면서 측정된 상기 전해동박의 열팽창계수는 16 내지 22 ㎛/(m·℃)이고,

190℃에서 1시간 동안 열처리 후 측정된 상기 전해동박의 인장강도는 21 내지 36 kgf/㎟이며,

상기 전해동박의 중량 편차는 5% 이하인 것을 특징으로 하는,

전해동박.

【청구항 2】

제1항에 있어서,

상온에서 3% 이상의 연신율을 갖는 것을 특징으로 하는,

전해동박.

【청구항 3】

제1항에 있어서,

상기 전해동박의 상기 제1 및 제2 면들 각각의 피크수(Pc)는 3 내지 92개인 것을 특징으로 하는,

전해동박.

【청구항 4】

제1항에 있어서,

상기 제1 및 제2 보호층들은 크롬(Cr), 실란 화합물 및 질소 화합물 중 적어도 하나를 포함하는 것을 특징으로 하는,

전해동박.

【청구항 5】

제1항에 있어서,

4 내지 30 ㎛의 두께를 갖는 것을 특징으로 하는,

전해동박.

【청구항 6】

제1항에 있어서,

상기 제1 및 제2 면들은 3.5 ㎛ 이하의 표면조도(R_z)를 갖는 것을 특징으로 하는,

전해동박.

【청구항 7】

제1 면과 그 반대편의 제2 면을 포함하는 전해동박; 및

상기 전해동박의 상기 제1 면 상의 제1 활물질층을 포함하되,

상기 전해동박은,

상기 제1 면을 향하는 매트면 및 상기 제2 면을 향하는 샤이니면을 포함하는 구리층;

상기 구리층의 상기 매트면 상의 제1 보호층; 및

상기 구리층의 상기 샤이니면 상의 제2 보호층을 포함하고,

열기계분석기(TMA)를 이용하여 5℃/min의 속도로 30℃에서 190℃까지 승온시키면서 측정된 상기 전해동박의 열팽창계수는 16 내지 22 ㎛/(m·℃)이고,

190℃에서 1시간 동안 열처리 후 측정된 상기 전해동박의 인장강도는 21 내지 36 kgf/㎟이며,

상기 전해동박의 중량 편차는 5% 이하인 것을 특징으로 하는,

이차전지용 전극.

【청구항 8】

제7항에 있어서,

상기 제1 활물질층은, 탄소; Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni 또는 Fe의

금속(Me); 상기 금속을 포함하는 합금; 상기 금속의 산화물(MeO_x); 및 상기 금속과 탄소의 복합체로 이루어진 군으로부터 선택되는 하나 이상의 활물질을 포함하는,

이차전지용 전극.

【청구항 9】

제7항에 있어서,

상기 제1 활물질층은 Si를 포함하는,

이차전지용 전극.

【청구항 10】

제7항에 있어서,

상기 제2 보호층 상의 제2 활물질층을 더 포함하는 것을 특징으로 하는,

이차전지용 전극.

【청구항 11】

양극(cathode);

상기 제8항 내지 제11항 중 어느 한 항의 이차전지용 전극으로 구성된 음극(anode);

상기 양극과 음극 사이에서 리튬 이온이 이동할 수 있는 환경을 제공하는 전해질(electrolyte); 및

상기 양극과 상기 음극을 전기적으로 절연시켜 주는 분리막(separator)을 포

함하는 것을 특징으로 하는,

이차전지.

【청구항 12】

70 내지 100 g/L의 구리 이온 및 80 내지 130 g/L의 황산을 포함하는 전해액을 준비하는 단계;

상기 전해액 내에 서로 이격되게 배치된 양극판 및 회전 음극드럼을 통전시키는 전기 도금을 수행함으로써 구리층을 형성시키는 단계; 및

상기 구리층 상에 보호층을 형성시키는 단계를 포함하되,

상기 전기 도금이 수행되는 동안, 상기 양극판과 상기 회전 음극 드럼의 간격은 5 내지 15 ㎜로 유지되고, 구리층의 폭 방향에 따른 상기 양극판과 상기 회전 음극 드럼의 최대 간격과 최소 간격의 차이는 0.2 ㎜ 미만으로 유지되고, 상기 전해액 내의 총유기탄소량(Total Organic Carbon: TOC)은 50 ppm 이하로 유지되며, 상기 전해액 내의 은(Ag) 농도는 25 ppm 이하로 유지되는 것을 특징으로 하는,

이차전지용 전해동박의 제조방법.

【청구항 13】

제12항에 있어서,

상기 전기 도금은 30 내지 80 A/dm^2의 전류밀도를 가함으로써 수행되는 것을 특징으로 하는,

이차전지용 전해동박의 제조방법.

【청구항 14】

제12항에 있어서,

상기 전해액 준비 단계는,

구리 와이어를 열처리하는 단계;

상기 열처리된 구리 와이어를 산세하는 단계; 및

상기 산세된 구리 와이어를 황산에 투입하는 단계를 포함하는 것을 특징으로 하는,

이차전지용 전해동박의 제조방법.

【청구항 15】

제14항에 있어서,

상기 구리 와이어는 600 내지 900℃에서 2 내지 6 시간 동안 열처리되고,

상기 열처리된 구리 와이어는 8 내지 10 중량%의 황산 및 1 내지 2 중량%의 과산화수소를 포함하는 산성 용액에 침지된 후 물로 세정됨으로써 산세되는 것을 특징으로 하는,

이차전지용 전해동박의 제조방법.

【청구항 16】

제12항에 있어서,

상기 전기 도금이 수행되는 동안, 상기 전해액으로부터 고형 불순물을 제거

하기 위한 연속 여과를 31 내지 45 m^3/hr의 유량으로 수행하는 단계를 포함하는 것을 특징으로 하는,

이차전지용 전해동박의 제조방법.

【청구항 17】

제12항에 있어서,

상기 전기 도금이 수행되는 동안 은(Ag)이 상기 전해액으로 유입되어 은(Ag) 농도가 25 ppm을 초과하는 것을 방지하기 위하여, 상기 전해액은 은(Ag)을 AgCl 형태로 침전시킬 수 있는 염소 이온을 더 포함하는 것을 특징으로 하는,

이차전지용 전해동박의 제조방법.

【청구항 18】

제12항에 있어서,

상기 전해액은 하이드록시에틸 셀룰로오스(HEC), 유기 황화물, 유기 질화물, 및 티오요소(thiourea)계 화합물로 구성된 그룹으로부터 선택되는 유기 첨가제를 더 포함하는 것을 특징으로 하는

이차전지용 전해동박의 제조방법.

【청구항 19】

제12항에 있어서,

상기 보호층 형성 단계는 0.5 내지 1.5 g/L의 Cr을 포함하는 방청액 내에 상

기 구리층을 침지시키는 단계를 포함하는 것을 특징으로 하는,

이차전지용 전해동박의 제조방법.

제출 일자 : 2016-10-12

【요약서】

【요약】

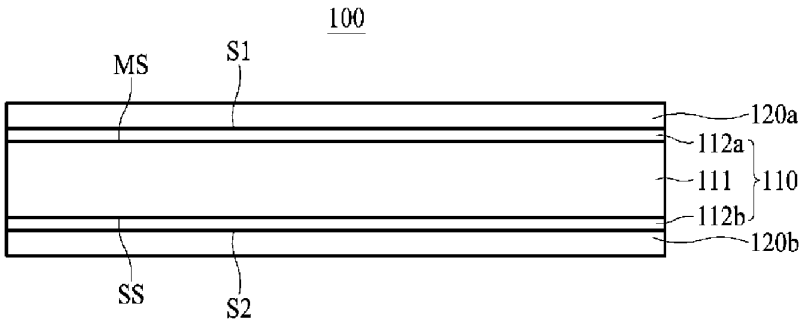
높은 내구성의 이차전지를 담보할 수 있으며 핸들링이 용이한 전해동박, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법이 개시된다. 제1 면 및 그 반대편의 제2 면을 갖는 본 발명의 전해동박은 상기 제1 면을 향하는 매트면 및 상기 제2 면을 향하는 샤이니면을 포함하는 구리층; 상기 구리층의 상기 매트면 상의 제1 보호층; 및 상기 구리층의 상기 샤이니면 상의 제2 보호층을 포함하고, 열기계분석기(TMA)를 이용하여 5℃/min의 속도로 30℃에서 190℃까지 승온시키면서 측정된 상기 전해동박의 열팽창계수는 16 내지 22 ㎛/(m·℃)이고, 190℃에서 1시간 동안 열처리 후 측정된 상기 전해동박의 인장강도는 21 내지 36 kgf/㎟이며, 상기 전해동박의 중량 편차는 5% 이하이다.

【대표도】

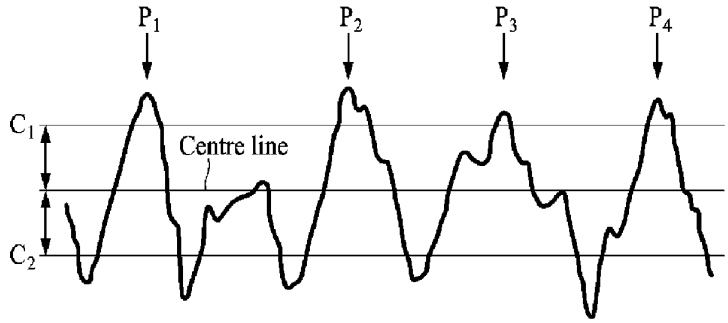
도 1

【도면】

【도 1】


100
MS
S1
120a
112a
111
110
112b
120b
SS
S2

【도 2】


P1
P2
P3
P4
C1
Centre line
C2

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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
15/696,360	09/06/2017	1726	2020	P11491US	20	4

CONFIRMATION NO. 7466

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FILING RECEIPT

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Date Mailed: 09/15/2017

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**

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Power of Attorney: The patent practitioners associated with Customer Number 86144

Domestic Applications for which benefit is claimed - None.
A proper domestic benefit claim must be provided in an Application Data Sheet in order to constitute a claim for domestic benefit. See 37 CFR 1.76 and 1.78.

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.)
REPUBLIC OF KOREA 10-2016-0131979 10/12/2016

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

Request to Retrieve - This application either claims priority to one or more applications filed in an intellectual property Office that participates in the Priority Document Exchange (PDX) program or contains a proper **Request to**

Retrieve Electronic Priority Application(s) (PTO/SB/38 or its equivalent). Consequently, the USPTO will attempt to electronically retrieve these priority documents.

If Required, Foreign Filing License Granted: 09/14/2017

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 15/696,360**

Projected Publication Date: 04/12/2018

Non-Publication Request: No

Early Publication Request: No

Title

EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

Preliminary Class

429

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

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countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

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Title 37, Code of Federal Regulations, 5.11 & 5.15

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PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 15/696,360

APPLICATION AS FILED - PART I

	(Column 1)	(Column 2)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
FOR	NUMBER FILED	NUMBER EXTRA	RATE($)	FEE($)		RATE($)	FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	280
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	600
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	720
TOTAL CLAIMS (37 CFR 1.16(i))	20 minus 20 =	*			OR	x 80 =	0.00
INDEPENDENT CLAIMS (37 CFR 1.16(h))	4 minus 3 =	* 1				x 420 =	420
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	2020

APPLICATION AS AMENDED - PART II

		(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($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	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	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)	OR	RATE($)	ADDITIONAL FEE($)
AMENDMENT B	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	

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Application Number	
Filing Date	
First Named Inventor	Seung Min KIM
Title	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit	
Examiner Name	
Attorney Docket Number	P11491US

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)			

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LS Mtron Ltd.

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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	[signature]	Date (Optional)	Feb. 10, 2015
Name	Kim, YoungHwan		
Title	IP Team Leader		

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EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

[001] This application claims priority to and the benefit of Korean Patent Application No. 10-2016-0131979, filed on October 12, 2016, the disclosure of which is incorporated herein by reference in its entirety.

BACKGROUND

1. Field of the Invention

[002] The present invention relates to an easily handleable electrolytic copper foil, an electrode including the same, a secondary battery including the same, and a method of manufacturing the same.

2. Discussion of Related Art

[003] A secondary battery is a type of energy conversion device that converts electrical energy into chemical energy, stores the chemical energy, and generates electricity by converting the chemical energy into electrical energy when the electricity is needed, and is referred to as a "rechargeable battery."

[004] Lead-acid batteries, nickel cadmium secondary batteries, nickel hydrogen secondary batteries, lithium secondary batteries, and the like are secondary batteries which are economically and environmentally advantageous compared to disposable primary batteries.

[005] Lithium secondary batteries may store a relatively large amount of energy

relative to a size and weight thereof in comparison to other secondary batteries. Therefore, in the field of information communication devices in which portability and mobility are important, the lithium secondary batteries are preferred and an application range thereof is also expanding to energy storage devices for hybrid vehicles and electric vehicles.

[006] Lithium secondary batteries are used by repeatedly performing a cycle including charging and discharging. When operating a certain device with a fully charged lithium secondary battery, the lithium secondary battery should have a high charge and discharge capacity to increase an operating time of the device. Therefore, research to satisfy the ever-increasing expectations (needs) of consumers for charge and discharge capacity of a lithium secondary battery is continuously required.

[007] As a method for increasing capacity of the lithium secondary battery, a method in which a composite active material, in which Si or Sn is added to a carbon active material, is used as an active material to be applied to an electrolytic copper foil when an anode of a secondary battery is manufactured has been proposed. However, such a composite active material rapidly and significantly expands due to heat generated when the lithium secondary battery is charged or discharged, causing breakage of the electrolytic copper foil. Also, an electrolytic copper foil having a thickness of 10 μm or less, which is generally used for manufacturing an anode of a lithium secondary battery, is particularly vulnerable to curling or wrinkling, and the curling or wrinkling of the electrolytic copper foil not only makes handling of the electrolytic copper foil difficult but also makes it impossible to coat the electrolytic copper foil with an active material.

SUMMARY OF THE INVENTION

[008] The present invention is directed to an electrolytic copper foil capable of preventing problems caused by limitations and disadvantages of the related art, an electrode including the same, a secondary battery including the same, and a method of manufacturing the same.

[009] The present invention is directed to an electrolytic copper foil having improved handleability and capable of securing a secondary battery having a high durability.

[0010] The present invention is directed to an electrode capable of securing a secondary battery having a high durability.

[0011] The present invention is directed to a secondary battery having a high durability.

[0012] The present invention is directed to a method of manufacturing an electrolytic copper foil having improved handleability and capable of securing a secondary battery having a high durability.

[0013] In addition to the above-described aspects of the present invention, other features and advantages of the present invention will be described below or will become apparent to those skilled in the art from the following description.

[0014] According to an aspect of the present invention, there is provided an electrolytic copper foil having a first surface and a second surface opposite the first surface, the electrolytic copper foil including a copper layer having a matte surface facing the first surface and a shiny surface facing the second surface, a first protective layer on the matte surface of the copper layer and a second protective layer on the shiny surface of the copper layer, wherein a coefficient of thermal expansion of the electrolytic foil, which is measured using a thermomechanical

analyzer (TMA) while heating the electrolytic copper foil from 30 °C to 190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m·°C), a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190 °C for 1 hour, ranges from 21 to 36 kgf/mm^2, and a weight deviation of the electrolytic copper foil is 5% or less.

[0015] The electrolytic copper foil has an elongation of 3% or more at room temperature.

[0016] A peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92.

[0017] Each of the first and second protective layers includes at least one of chromium (Cr), a silane compound, and a nitrogen compound.

[0018] The electrolytic copper foil has a thickness of 4 to 30 μm.

[0019] Each of the first and second surfaces has a surface roughness (R_z) of 3.5 μm or less.

[0020] The electrolytic copper foil has a coefficient of thermal expansion of 17.3 to 22 μm/(m·°C).

[0021] According to another aspect of the present invention, there is provided a secondary battery electrode including an electrolytic copper foil including a first surface and a second surface opposite the first surface and a first active material layer on the first surface of the electrolytic copper foil, wherein the electrolytic copper foil includes a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface, a first protective layer on the matte surface of the copper layer and a second protective layer on the shiny surface of the copper layer, and wherein a coefficient of thermal expansion of the electrolytic foil, which is measured using a TMA while heating the electrolytic copper foil from 30 °C to

190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m·°C), a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190°C for 1 hour, ranges from 21 to 36 kgf/mm^2, and a weight deviation of the electrolytic copper foil is 5% or less.

[0022] The first active material layer includes at least one active material selected from a group consisting of carbon, a metal (Me) such as Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni, or Fe, an alloy containing the metal (Me), an oxide of the metal (MeO_x), and a composite of the metal (Me) and carbon.

[0023] The first active material layer includes Si.

[0024] The secondary battery electrode further includes a second active material layer on the second protective layer.

[0025] According to still another aspect of the present invention, there is provided a secondary battery including a cathode, an anode including the secondary battery electrode, an electrolyte configured to provide an environment in which lithium ions may move between the cathode and the anode and a separator configured to electrically insulate the cathode from the anode.

[0026] According to yet another aspect of the present invention, there is provided a method of manufacturing a secondary battery electrolytic copper foil, the method including preparing an electrolytic solution containing 70 to 90 g/L of copper ions and 80 to 130 g/L of sulfuric acid, forming a copper layer by performing electroplating which applies electricity between a positive electrode plate and a rotating negative electrode drum which are disposed to in the electrolytic solution be spaced apart from each other and forming a protective layer on the copper layer, wherein, while the electroplating is performed, an interval between the positive electrode plate and the rotating negative electrode drum is maintained to be in a

range of 5 to 15 mm, a difference between a maximum interval and a minimum interval of the positive electrode plate and the rotating negative electrode drum in a width direction of the copper layer is maintained to be less than 0.2 mm, total organic carbon (TOC) in the electrolytic solution is maintained at 50 ppm or less, and a concentration of silver (Ag) in the electrolytic solution is maintained at 25 ppm or less.

[0027] The electroplating is performed by applying a current density of 30 to 80 A/dm^2 between the positive electrode plate and the rotating negative electrode drum.

[0028] The preparing of the electrolytic solution includes performing a heat treatment on a copper wire, pickling the heat-treated copper wire and introducing the pickled copper wire into sulfuric acid.

[0029] The copper wire is heat-treated at a temperature of 600 to 900 °C for 2 to 6 hours and the heat-treated copper wire is pickled by being immersed in an acidic solution containing 8 to 10 wt% of sulfuric acid and 1 to 2 wt% of hydrogen peroxide and then being washed with water.

[0030] While the electroplating is performed, continuous filtration for removing solid impurities from the electrolytic solution is performed at a flow rate of 31 to 45 m^3/hr.

[0031] The electrolytic solution further contains chloride ions capable of precipitating silver (Ag) in the form of AgCl to prevent the concentration of silver (Ag) from exceeding 25 ppm by silver (Ag) being introduced into the electrolytic solution while the electroplating is performed.

[0032] The electrolytic solution further contains an organic additive selected from a group consisting of hydroxyethyl cellulose (HEC), organic sulfides, organic nitrides, and thiourea-based compounds.

[0033] The forming of the protective layer includes immersing the copper layer in an antirust solution containing 0.5 to 1.5 g/L of chromium (Cr).

[0034] The general description of the present invention as described above is merely intended to illustrate or explain the present invention and does not limit the scope of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] The above and other objects, features and advantages of the present invention will become more apparent to those of ordinary skill in the art by describing exemplary embodiments thereof in detail with reference to the accompanying drawings, in which:

[0036] FIG. 1 is a cross-sectional view of a secondary battery electrode according to an embodiment of the present invention;

[0037] FIG. 2 illustrates a surface roughness profile obtained according to U.S. standard ASME B46.1-2009.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0038] Hereinafter, embodiments of the present invention will be described in detail with reference to the accompanying drawings.

[0039] It should be apparent to those skilled in the art that various modifications and alterations can be made in the present invention without departing from the spirit and scope of the invention. Therefore, the present invention includes all modifications and alterations that come within the scope of the invention as defined in the appended claims and equivalents thereof.

[0040] A lithium secondary battery includes a cathode, an anode, an electrolyte,

which provides an environment in which lithium ions may move between the cathode and the anode, and a separator, which electrically insulates the cathode from the anode to prevent electrons generated at one electrode from being inefficiently consumed by moving the electrons to the other electrode through an inside of the secondary battery.

[0041] FIG. 1 is a cross-sectional view of a secondary battery electrode according to an embodiment of the present invention.

[0042] As illustrated in FIG. 1, a secondary battery electrode 100 according to an embodiment of the present invention includes an electrolytic copper foil 110 having a first surface S1 and a second surface S2 opposite the first surface S1, a first active material layer 120a on the first surface S1, and a second active material layer 120b on the second surface S2. In FIG. 1, an example in which the active material layers 120a and 120b are illustrated as being formed on both the first and second surfaces S1 and S2 of the electrolytic copper foil 110, respectively, but the present invention is not limited thereto, and the secondary battery electrode 100 of the present invention may include only one of the first and second active material layers 120a and 120b as an active material layer.

[0043] Generally, in a lithium secondary battery, an aluminum foil is used as a positive electrode current collector coupled to a positive electrode active material, and an electrolytic copper foil is used as a negative electrode current collector coupled to a negative electrode active material.

[0044] According to an embodiment of the present invention, the secondary battery electrode 100 is used as an anode of a lithium secondary battery, the electrolytic copper foil 110 functions as a negative electrode current collector, and each of the first and second active material layers 120a and 120b includes a negative

electrode active material.

[0045] As illustrated in FIG. 1, the electrolytic copper foil 110 of the present invention, which functions as a negative electrode current collector of a secondary battery, includes a copper layer 111 having a matte surface MS and a shiny surface SS, a first protective layer 112a on the matte surface MS of the copper layer 111, and a second protective layer 112b on the shiny surface SS of the copper layer 111.

[0046] The matte surface MS is a surface of the copper layer 111 facing the first surface S1 of the electrolytic copper foil 110, and the shiny surface SS is a surface of the copper layer 111 facing the second surface S2 of the electrolytic copper foil 110.

[0047] The copper layer 111 of the present invention may be formed on a rotating negative electrode drum by electroplating being performed. The shiny surface SS thereof refers to a surface that comes into contact with the rotating negative electrode drum in an electroplating process, and the matte surface MS refers to a surface opposite the shiny surface SS.

[0048] Generally, the shiny surface SS has a lower surface roughness (Rz) than the matte surface MS, but the present invention is not limited thereto, and the surface roughness (Rz) of the shiny surface SS may be higher than or equal to that of the matte surface MS.

[0049] The first and second protective layers 112a and 112b may include at least one of chromium (Cr), a silane compound, and a nitrogen compound and may be formed to prevent corrosion of the copper layer 111, improve heat resistance of the copper layer 111, and suppress the reduction of a charge and discharge efficiency of the secondary battery by increasing an adhesion strength between the copper layer 111 and the active material layers 120a and 120b.

[0050] According to the present invention, a coefficient of thermal expansion of

the electrolytic copper foil 110, which is measured by using a thermomechanical analyzer (TMA) while heating the electrolytic copper coil 110 from 30 °C to 190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m·°C).

[0051] When the coefficient of thermal expansion is less than 16 μm/(m·°C), the electrolytic copper foil 110 may be broken when the active material rapidly and significantly expands due to heat generated during charging and discharging of the lithium secondary battery. On the other hand, when the coefficient of thermal expansion is more than 22 μm/(m·°C), curling and/or wrinkling of the electrolytic copper foil 110 is caused by heat received during the manufacturing process of the lithium secondary battery, which not only makes handling of the electrolytic copper foil difficult but also makes it impossible to coat the electrolytic copper foil 110 with the active material when manufacturing the secondary battery electrode 100.

[0052] Specifically, a volume of the active material expands when the lithium secondary battery is charged or discharged. When the electrolytic copper foil 110 also expands corresponding to the expansion of the volume of the active material, breakage of the electrolytic copper foil 110 may be prevented. Therefore, in order to prevent breakage of the electrolytic copper foil 110 due to the expansion of the volume of the active material, the electrolytic copper foil 110 may have a coefficient of thermal expansion of 16 μm/(m·°C) or more, and more specifically, may have a coefficient of thermal expansion of 17.3 μm/(m·°C) or more. That is, the electrolytic copper foil 110 may have, for example, a coefficient of thermal expansion of 17.3 to 22 μm/(m·°C).

[0053] According to the present invention, a tensile strength of the electrolytic copper foil 110 measured after being heat treated at a temperature of 190 °C for 1 hour ranges from 21 to 36 kgf/mm^2.

[0054] When the tensile strength of the electrolytic copper foil 110 is less than 21 kgf/mm^2, there is a high risk of wrinkling due to the ease of deformation of the electrolytic copper foil 110 caused by a tension applied to the electrolytic copper foil 110 during a roll-to-roll process for manufacturing the secondary battery electrode 100 and the secondary battery. On the other hand, when the tensile strength of the electrolytic copper foil 110 is more than 36 kgf/mm^2, there is a high risk that the electrolytic copper foil 110 is broken when the lithium secondary battery is charged and discharged.

[0055] The electrolytic copper foil 110 of the present invention has a weight deviation of 5% or less. In this specification, the "weight deviation" may be obtained by taking 5 cm x 5 cm samples at three points arranged in a width direction, that is, a transverse direction (TD) of the electrolytic copper foil 110, measuring a weight of each of the samples to calculate a weight per unit area, and then calculating an average weight and a standard deviation of the weights from the weights per unit area of the three samples. That is, the weight deviation is calculated by calculating the "average weight" and the "standard deviation of the weights" from the weights per unit area of the three samples and calculating a ratio (%) of the standard deviation of the weights to the average weight [(standard deviation of weights / average weight) x100].

[0056] When the weight deviation of the electrolytic copper foil 110 is more than 5%, there is a high risk of wrinkling due to the ease of deformation of the electrolytic copper foil 110 caused by the tension applied to the electrolytic copper foil 110 during the roll-to-roll process for manufacturing the secondary battery.

[0057] The secondary battery electrolytic copper foil 110 of the present invention may have an elongation of 3% or more at room temperature (25 ± 15 °C), and

preferably, may have an elongation of 3 to 10%. When the elongation of the electrolytic copper foil 110 is less than 3%, a risk that the electrolytic copper foil 110 may not be stretched and may be torn due to a force applied in the process of manufacturing the secondary battery electrode 100 and the secondary battery is increased, and a risk of breakage of the electrolytic copper foil 110 during charging and discharging of the lithium secondary battery is increased. On the other hand, when the elongation of the electrolytic copper foil 110 is more than 10%, there is a high risk of wrinkling due to the ease of deformation of the electrolytic copper foil 110 caused by the tension applied to the electrolytic copper foil 110 during the roll-to-roll process for manufacturing the secondary battery.

[0058] The electrolytic copper foil 110 of the present invention may have a thickness of 4 to 30 μm. When the thickness of the electrolytic copper foil 110 is less than 4 μm, wrinkles are easily caused and workability of the process of manufacturing the secondary battery is lowered. On the other hand, when the thickness of the electrolytic copper foil 110 is more than 30 μm, it is difficult to implement a high-capacity lithium secondary battery.

[0059] Each of the first and second active material layers 120a and 120b includes at least one active material selected from the group consisting of carbon, a metal such as Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni, or Fe, an alloy containing the metal, an oxide of the metal, and a composite of the metal and carbon as a negative electrode active material.

[0060] In order to increase charge and discharge capacity of the secondary battery, the active material layers 120a and 120b may be a mixture containing a predetermined amount of Si.

[0061] Meanwhile, as charging and discharging of the secondary battery is

repeated, contraction and expansion of the active material layers 120a and 120b occur alternately. This causes separation of the active material layers 120a and 120b from the electrolytic copper foil 110, thereby reducing a charge and discharge efficiency of the secondary battery. Therefore, in order for the secondary battery to have a capacity retention rate and a lifetime of a certain level or more (i.e., in order to suppress deterioration of the charge and discharge efficiency of the secondary battery), the electrolytic copper foil 110 should have an excellent coating property with respect to the active material. That is, adhesion strength between the electrolytic copper foil 110 and the active material layers 120a and 120b should be high.

[0062] Generally, it is known that the adhesion strength between the electrolytic copper foil 110 and the active material layers 120a and 120b may be improved by controlling the surface roughness (Rz) of the electrolytic copper foil 110. However, actually, the electrolytic copper foil 110 whose surface roughness (Rz) is appropriately adjusted does not necessarily satisfy an adhesion force between the electrolytic copper foil 110 and the active material layers 120a and 120b required in a specification. Specifically, it is known that, when the active material layers 120a and 120b include Si to increase the capacity of the secondary battery, a relationship between the surface roughness (Rz) of the electrolytic copper foil 110 and the capacity retention rate of the secondary battery is low.

[0063] According to the present invention, it is known that, when securing the sufficient adhesive force between the electrolytic copper foil 110 and the active material layers 120a and 120b, a peak count (Pc) of the surface, along with the surface roughness (Rz) of the surface of the electrolytic copper foil 110, is an important factor.

[0064] The peak count (Pc), along with the surface roughness (R_z), affects a

physical bonding force between the electrolytic copper foil 110 and the first active material layer 120a. Hereinafter, the peak count (Pc) will be described with reference to FIG. 2.

[0065] In the present invention, the "peak count (Pc)" may be obtained by measuring peak counts (Pc) of any three points on the surface of the electrolytic copper foil 110 and calculating an average value of measured values of the peak counts (Pc). The peak count (Pc) of each of the points is the number of effective peaks P1, P2, P3, and P4 which rise above a 0.5 μm upper criteria line C1 per 4 mm unit sample length in a surface roughness profile obtained according to U.S. standard ASME B46.1-2009. In this case, at least one valley deeper than a -0.5 μm lower criteria line C2 exists between adjacent effective peaks among the effective peaks. When there is no valley deeper than the -0.5 μm lower criteria line C2 between adjacent peaks which rise above the upper criteria line C1, all of the adjacent peaks may not be "effective peaks" used for measuring the peak count (Pc), and relatively lower peaks among the peaks are ignored when obtaining the number of "effective peaks."

[0066] According to an embodiment of the present invention, a peak count (Pc) of each of the first and second surfaces S1 and S2 of the electrolytic copper foil 110 ranges from 3 to 92, and a surface roughness (Rz) of each of the first and second surfaces S1 and S2 is 3.5 μm or less.

[0067] When the peak count (Pc) is less than 3, an active specific surface area of the electrolytic copper foil 110 which may come in contact with the negative electrode active material is too small to ensure sufficient adhesion between the electrolytic copper foil 110 and the active material layers 120a and 120b.

[0068] On the other hand, when, the peak count (Pc) is more than 92 or the

surface roughness (Rz) is more than 3.5 μm, coating uniformity of the negative electrode active material is lowered due to too many surface irregularities, and thus the adhesion between the electrolytic copper foil 110 and the active material layers 120a and 120b is significantly lowered.

[0069] Hereinafter, a method of manufacturing an electrolytic copper foil 110 according to an embodiment of the present invention will be described in detail.

[0070] First, an electrolytic solution containing 70 to 100 g/L of copper ions and 80 to 130 g/L of sulfuric acid is prepared, and the copper layer 111 is formed by applying electricity between a positive electrode plate and a rotating negative electrode drum, which are disposed in the electrolytic solution, to perform an electroplating.

[0071] According to the present invention, while the electroplating is performed, the electrolytic solution is maintained such that total organic carbon (TOC) in the electrolytic solution is maintained at 50 ppm or less. As organic matter content in the electrolytic solution is increased, possibility of the organic matter being present in crystal grains of the copper layer 111 produced through the electroplating is increased. Organic matter in the crystal grains of the copper layer 111 causes the coefficient of thermal expansion of the electrolytic copper foil 110 to be lower than 16 μm/(m·°C).

[0072] In order to maintain total organic carbon (TOC) in the electrolytic solution at 50 ppm or less, a high-purity copper wire is heat-treated to burn organic matter thereon, the heat-treated copper wire is pickled, and an electrolytic solution having little or no impurities may be prepared by introducing the pickled copper wire into sulfuric acid.

[0073] The copper wire may be heat-treated at a temperature of 600 to 900 °C for

2 to 6 hours in an oxygen atmosphere in an electric furnace, and the heat-treated copper wire may be pickled by being immersed in an acidic solution containing 8 to 10 wt% of sulfuric acid and 1 to 2 wt% of hydrogen peroxide and then being washed with water. Thus, organic impurities, which may be attached to a surface of the copper wire, are completely removed, thereby preventing the organic impurities from being introduced into the electrolytic solution.

[0074] According to the present invention, a concentration of silver (Ag) in the electrolytic solution is maintained at 25 ppm or less while the electroplating is performed. When the concentration of silver (Ag) in the electrolytic solution is more than 25 ppm, the silver (Ag) is electrodeposited on the copper layer 111 when the copper layer 111 is formed, and a final coefficient of thermal expansion of the electrolytic copper foil 110 exceeds 22 μm/(m·°C).

[0075] In order to prevent the concentration of silver (Ag) from exceeding 25 ppm by silver (Ag) being introduced into the electrolytic solution when the electroplating is performed, a copper wire not containing silver (Ag) may be used, or the electrolytic solution may include a small amount (e.g., 50 ppm or less) of chloride ions capable of precipitating silver (Ag) in the form of AgCl.

[0076] The peak count (Pc) and the surface roughness (Rz) of each of the first and second surfaces S1 and S2 of the electrolytic copper foil 110 may be respectively controlled to be 3 to 92 and 3.5 μm or less by managing each of TOC and the concentration of silver (Ag) within the above ranges.

[0077] Meanwhile, the method of the present invention may further include performing continuous (or circulating) filtration at a flow rate of 31 to 45 m^3/hr to remove solid impurities from the electrolytic solution while the electroplating is performed. When the flow rate is less than 31 m^3/hr, a flow velocity is lowered,

overvoltage is increased, and the copper layer 111 is not uniformly formed. On the other hand, when the flow rate is more than 45 m^3/hr, a filter is damaged and foreign matter is introduced into the electrolytic solution.

[0078] Optionally, the TOC may be lowered by decomposing organic matter in the electrolytic solution through an ozone treatment.

[0079] Optionally, cleanliness of the electrolytic solution may be improved by introducing hydrogen peroxide and air into the electrolytic solution while the electroplating is performed.

[0080] Optionally, the electrolytic solution may further include an organic additive selected from the group consisting of hydroxyethyl cellulose (HEC), organic sulfides, organic nitrides, and thiourea-based compounds.

[0081] According to an embodiment of the present invention, the electroplating may be performed by applying a current density of 30 to 80 A/dm^2 between the positive electrode plate and the rotating negative electrode drum.

[0082] According to the present invention, in order for the electrolytic copper foil 110 to have a weight deviation of 5% or less, while the electroplating is performed, an interval between the positive electrode plate and the rotating negative electrode drum is maintained to be in a range of 5 to 15 mm, and a difference between a maximum interval and a minimum interval of the positive electrode plate and the rotating negative electrode drum according to a width direction of the copper layer 111 is maintained to be less than 0.2 mm.

[0083] Next, the first and second protective layers 112a and 112b are formed on the copper layer 111 by immersing the copper layer 111 manufactured as described above in an antirust solution containing 0.5 to 1.5 g/L of Cr (e.g., at room temperature for 2 to 20 seconds) and drying the copper layer 111.

[0084] When a concentration of chromium (Cr) in the antirust solution is less than 0.5 g/L, the amount of chromium electrodeposition (DA_{Cr}) of the surface of the electrolytic copper foil 110 is less than 0.5 mg/m^2, oxidation of the surface of the electrolytic copper foil 110 is caused, and the chemical bonding force between the electrolytic copper foil 110 and the active material layers 120a and 120b is lowered.

[0085] On the other hand, when the concentration of chromium (Cr) in the antirust solution is more than 1.5 g/L, the amount of chromium electrodeposition (DA_{Cr}) of the surface of the electrolytic copper foil 110 exceeds 3.8 mg/m^2, the hydrophobic property of the surface of the electrolytic copper foil 110 is significantly increased, and the chemical affinity with the negative electrode active material is lowered, which eventually results in a reduction of the adhesion between the electrolytic copper foil 110 and the active material layers 120a and 120b.

[0086] The antirust solution may further include at least one of a silane compound and a nitrogen compound. For example, the antirust solution may include 0.5 to 1.5 g/L of Cr and 0.5 to 1.5 g/L of a silane compound.

[0087] Meanwhile, when a concentration of copper (Cu) in the antirust solution is too high, the amount of chromium (Cr) electrodeposited on the surface of the copper layer 111 is reduced. Therefore, according to an embodiment of the present invention, the concentration of copper (Cu) in the antirust solution is maintained at 0.1 g/L or less. When the concentration of copper (Cu) is more than 0.1 g/L, the amount of chromium electrodeposition (DA_{Cr}) of the surface of the electrolytic copper foil 110 is less than 0.5 mg/m^2, oxidation of the surface of the electrolytic copper foil 110 is caused, and the chemical bonding force between the electrolytic copper foil 110 and the active material layers 120a and 120b is lowered.

[0088] Meanwhile, the peak count (Pc) and the surface roughness (Rz) of the

second surface S2 of the electrolytic copper foil 110 may be controlled to be 3 to 110 and 0.5 to 2.7 μm, respectively, by adjusting a degree of polishing of a surface (e.g., a surface on which copper is precipitated by performing electroplating) of the rotating negative electrode drum.

[0089] According to an embodiment of the present invention, the surface of the rotating negative electrode drum is polished with an abrasive brush having a particle-size (Grit) of #800 to #1500.

[0090] The secondary battery electrode (i.e., an anode) of the present invention may be manufactured by coating the electrolytic copper foil 110 of the present invention manufactured as described above with the negative electrode active material.

[0091] The negative electrode active material may be selected from the group consisting of carbon, a metal (Me) such as Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni, or Fe, an alloy containing the metal (Me), an oxide of the metal (MeO_x), and a complex of the metal (Me) and carbon.

[0092] For example, 1 to 3 parts by weight of styrene butadiene rubber (SBR) and 1 to 3 parts by weight of carboxymethyl cellulose (CMC) are mixed in 100 parts by weight of carbon for the negative electrode active material, and a slurry is then prepared using distilled water as a solvent. Next, the electrolytic copper foil 110 is coated with the slurry to have a thickness of 20 to 100 μm using a doctor blade and is pressed at a temperature of 110 to 130°C under a pressure of 0.5 to 1.5 ton/cm^2.

[0093] The lithium secondary battery may be manufactured using a conventional cathode, an electrolyte, and a separator together with the secondary battery electrode (or the anode) of the present invention manufactured as described above.

[0094] Hereinafter, the present invention will be described in detail with reference

to examples and comparative examples. However, the following examples are only examples to help understanding of the present invention, and the scope of the present invention is not limited to these examples.

[0095] Examples 1 to 4 and Comparative Examples 1 to 6

[0096] A copper layer was formed by applying electricity between a positive electrode plate and a rotating negative electrode drum at a current density of 65 ASD while maintaining an electrolyte solution containing 75 g/L of copper and 105 g/L of sulfuric acid at a temperature of 65 °C. Here, a TOC in the electrolyte solution, a concentration of silver (Ag), and a difference between a maximum interval and a minimum interval of the positive electrode plate and the rotating negative electrode drum are illustrated in the following Table 1.

[0097] Then, the copper layer was immersed in an antirust solution and dried to prepare an electrolytic copper foil.

[0098] Table 1

	TOC in Electrolyte Solution (ppm)	Concentration of Ag Electrolyte Solution (ppm)	Difference between Maximum Interval and Minimum Interval of Positive Electrode Plate and Rotating Negative Electrode Drum (mm)
Example 1	45	22	0.18
Example 2	2	3	0.18
Example 3	2	22	0.07
Example 4	47	3	0.07
Comparative Example 1	3	32	0.18
Comparative Example 2	52	15	0.18
Comparative Example 3	15	45	0.07
Comparative Example 4	62	3	0.07
Comparative Example 5	2	3	0.22
Comparative Example 6	45	22	0.32

[0099] A coefficient of thermal expansion, a tensile strength after heat treatment, a weight deviation, an elongation, the presence or absence of a wrinkle, and breakage after 500 cycles of charging and discharging of each of the electrolytic copper foils in Examples 1 to 4 and Comparative Example 1 to 6 prepared in the above were measured or calculated as follows, and results thereof are illustrated in the following Table 2.

[00100] * Coefficient of Thermal Expansion [μm/(m·°C)]

[00101] The coefficient of thermal expansion defined by the following Equation 1 was measured using a TMA (Thermomechanical Analyzer) while samples of the electrolytic copper foils were heated from 30 °C to 190 °C at a speed of 5 °C/min.

[00102] Equation 1: $CTE = \Delta L/[L_O \times \Delta T]$

[00103] Here, CTE denotes a coefficient of thermal expansion, L_O denotes an initial length (m) of a sample, ΔL denotes a change (μm) of the length of the sample, and ΔT denotes a temperature change (°C).

[00104] * Tensile Strength after Heat Treatment (kgf/mm^2)

[00105] A sample of the electrolytic copper foil was heat-treated at a temperature of 190 °C for 1 hour and a tensile strength of the heat-treated sample was then measured using a universal testing machine (UTM). In this case, a width of the sample was 12.7 mm, a distance between grips was 50 mm, and a measurement speed was 50 mm/min.

[00106] * Weight Deviation (%)

[00107] 5 cm x 5 cm samples were taken at three points arranged in a width direction (that is, a transverse direction, TD) of the electrolytic copper foil, a weight of each of the samples was then measured to calculate a weight per unit area, and a weight deviation was calculated from the weights per unit area of the three samples.

That is, the weight deviation may be calculated according to Equation 2 after calculating an "average weight" and a "standard deviation of the weights" from the weights per unit area of the three samples.

[00108] Equation 2

$$\text{Weight deviation}\,(\%) = \frac{\text{Standard deviation of weights}}{\text{Average weight}} \times 100$$

[00109] * Elongation (%)

[00110] The elongation of the electrolytic copper foil at room temperature was measured using a UTM according to a method described in the IPC-TM-650 Test Method Manual.

[00111] * Presence or Absence of Wrinkle

[00112] The presence or absence of a wrinkle in the electrolytic copper foil was observed in a process of sequentially manufacturing an anode for a secondary battery and a secondary battery using the electrolytic copper foil.

[00113] * Breakage of Anode after 500 Cycles of Charging and Discharging

[00114] After a charging and discharging test was performed on the secondary battery including the anode manufactured using the electrolytic copper foil 500 times at a temperature of 50°C and at a charging and discharging speed of 0.5 C, it was observed whether the anode was broken.

[00115] Table 2

	Coefficient of Thermal Expansion [㎛/(m·℃)]	Tensile Strength after Heat Treatment (kgf/mm^2)	Weight Deviation (%)	Elongation (%)	Presence of Wrinkle	Breakage of Anode after 500 Cycles of Charging and Discharging
Example 1	20.9	25.6	3.8	5.6	X	X
Example 2	20.3	27.2	3.6	5.3	X	X
Example 3	21.8	22.1	0.7	8.9	X	X
Example 4	17.3	34.5	0.6	4.8	X	X

Comparative Example 1	22.4	22.2	3.8	10.3	O	X
Comparative Example 2	15.7	35.8	3.8	2.8	X	O
Comparative Example 3	22.8	20.5	0.6	10.8	O	X
Comparative Example 4	15.3	36.8	0.6	2.6	X	O
Comparative Example 5	20.1	26.5	5.2	5.3	O	X
Comparative Example 6	21.2	27.2	5.8	5.6	O	X

[00116] As illustrated in Table 2, in a case in which a content of TOC in the electrolyte solution was more than 50 ppm when the electroplating was performed (in Comparative Examples 2 and 4), electrolytic copper foils having a coefficient of thermal expansion of less than 16 μm/(m·°C) and an elongation of less than 3% were manufactured. The charging and discharging test was performed on a secondary battery manufactured by each of the above electrolytic copper foils (Comparative Examples 2 and 4) 500 times, and as a result, breakage of an anode was observed.

[00117] Also, in a case in which a concentration of silver (Ag) in the electrolyte solution was more than 25 ppm when the electroplating was performed (in Comparative Examples 1 and 3), electrolytic copper foils having a coefficient of thermal expansion of more than 22 μm/(m·°C) and an elongation of more than 10% were manufactured. When an electrode and a secondary battery were manufactured by each of the above electrolytic copper foils (Comparative Examples 1 and 3), wrinkles were generated.

[00118] Meanwhile, in a case in which a difference between a maximum interval and a minimum interval of the positive electrode plate and the rotating negative electrode drum was more than 0.2 mm (in Comparative Examples 5 and 6), electrolytic copper foils having a weight deviation of more than 5% was manufactured. When an electrode and a secondary battery were manufactured by

each of the above electrolytic copper foils (Comparative Examples 5 and 6),, wrinkles were generated.

[00119] According to the present invention, since curling and/or wrinkling of an electrolytic copper foil during a roll-to-roll process can be prevented, a reduction of productivity due to repeatedly stopping and re-starting a facility can be prevented and manufacturing costs can be reduced. Also, since breakage of the electrolytic copper foil can be prevented when charging and discharging a lithium secondary battery, durability of the secondary battery can be significantly improved.

[00120] In addition, according to the present invention, despite repetition of a charging and discharging cycle, a long-life secondary battery capable of maintaining a high charge and discharge capacity for a long time can be manufactured. Therefore, inconvenience of consumers of electronic products and resource waste due to the frequent replacement of secondary batteries can be minimized.

WHAT IS CLAIMED IS:

1. An electrolytic copper foil, which includes a first surface and a second surface opposite the first surface, the electrolytic copper foil comprising:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

wherein:

a coefficient of thermal expansion of the electrolytic foil, which is measured using a thermomechanical analyzer (TMA) while heating the electrolytic copper foil from 30 °C to 190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m·°C),

a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190 °C for 1 hour, ranges from 21 to 36 kgf/mm^2, and

a weight deviation of the electrolytic copper foil is 5% or less.

2. The electrolytic copper foil of claim 1, having an elongation of 3% or more at room temperature.

3. The electrolytic copper foil of claim 1, wherein a peak count (Pc) of each of the first and second surfaces of the electrolytic copper foil ranges from 3 to 92.

4. The electrolytic copper foil of claim 1, wherein each of the first and second protective layers includes at least one of chromium (Cr), a silane compound,

and a nitrogen compound.

5. The electrolytic copper foil of claim 1, having a thickness of 4 to 30 μm.

6. The electrolytic copper foil of claim 1, wherein each of the first and second surfaces has a surface roughness (R_z) of 3.5 μm or less.

7. The electrolytic copper foil of claim 1, having a coefficient of thermal expansion of 17.3 to 22 μm/(m·°C).

8. A secondary battery electrode comprising:

an electrolytic copper foil including a first surface and a second surface opposite the first surface; and

a first active material layer on the first surface of the electrolytic copper foil,

wherein:

the electrolytic copper foil comprises:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

a coefficient of thermal expansion of the electrolytic foil, which is measured using a TMA while heating the electrolytic copper foil from 30 °C to 190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m·°C),

a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190°C for 1 hour, ranges from 21 to 36 kgf/mm^2,

and

a weight deviation of the electrolytic copper foil is 5% or less.

9. The secondary battery electrode of claim 8, wherein the first active material layer includes at least one active material selected from a group consisting of carbon, a metal (Me) such as Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni, or Fe, an alloy containing the metal (Me), an oxide of the metal (MeO_x), and a composite of the metal (Me) and carbon.

10. The secondary battery electrode of claim 8, wherein the first active material layer comprises Si.

11. The secondary battery electrode of claim 8, further comprising a second active material layer on the second protective layer.

12. A secondary battery comprising:

a cathode;

an anode including a secondary battery electrode;

an electrolyte configured to provide an environment in which lithium ions may move between the cathode and the anode; and

a separator configured to electrically insulate the cathode from the anode,

wherein the secondary battery electrode comprises:

an electrolytic copper foil including a first surface and a second surface opposite the first surface; and

a first active material layer on the first surface of the electrolytic copper foil,

wherein the electrolytic copper foil comprises:

a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface;

a first protective layer on the matte surface of the copper layer; and

a second protective layer on the shiny surface of the copper layer,

a coefficient of thermal expansion of the electrolytic foil, which is measured using a TMA while heating the electrolytic copper foil from 30 °C to 190 °C at a speed of 5 °C/min, ranges from 16 to 22 μm/(m·°C),

a tensile strength of the electrolytic copper foil, which is measured after a heat treatment at a temperature of 190°C for 1 hour, ranges from 21 to 36 kgf/mm^2, and

a weight deviation of the electrolytic copper foil is 5% or less.

13. A method of manufacturing a secondary battery electrolytic copper foil, the method comprising:

preparing an electrolytic solution containing 70 to 90 g/L of copper ions and 80 to 130 g/L of sulfuric acid;

forming a copper layer by performing electroplating which applies electricity between a positive electrode plate and a rotating negative electrode drum which are disposed to in the electrolytic solution be spaced apart from each other; and

forming a protective layer on the copper layer,

wherein, while the electroplating is performed, an interval between the positive electrode plate and the rotating negative electrode drum is maintained to be in a range of 5 to 15 mm, a difference between a maximum interval and a minimum interval of the positive electrode plate and the rotating negative electrode drum in a

width direction of the copper layer is maintained to be less than 0.2 mm, total organic carbon (TOC) in the electrolytic solution is maintained at 50 ppm or less, and a concentration of silver (Ag) in the electrolytic solution is maintained at 25 ppm or less.

14. The method of claim 13, wherein the electroplating is performed by applying a current density of 30 to 80 A/dm^2 between the positive electrode plate and the rotating negative electrode drum.

15. The method of claim 13, wherein the preparing of the electrolytic solution comprises:

performing a heat treatment on a copper wire;

pickling the heat-treated copper wire; and

introducing the pickled copper wire into sulfuric acid.

16. The method of claim 15, wherein:

the copper wire is heat-treated at a temperature of 600 to 900 °C for 2 to 6 hours, and

the heat-treated copper wire is pickled by being immersed in an acidic solution containing 8 to 10 wt% of sulfuric acid and 1 to 2 wt% of hydrogen peroxide and then being washed with water.

17. The method of claim 13, wherein, while the electroplating is performed, continuous filtration for removing solid impurities from the electrolytic solution is performed at a flow rate of 31 to 45 m^3/hr.

18. The method of claim 13, wherein the electrolytic solution further comprises chloride ions capable of precipitating silver (Ag) in the form of AgCl to prevent the concentration of silver (Ag) from exceeding 25 ppm by silver (Ag) being introduced into the electrolytic solution while the electroplating is performed.

19. The method of claim 13, wherein the electrolytic solution further comprises an organic additive selected from a group consisting of hydroxyethyl cellulose (HEC), organic sulfides, organic nitrides, and thiourea-based compounds.

20. The method of claim 13, wherein the forming of the protective layer comprises immersing the copper layer in an antirust solution containing 0.5 to 1.5 g/L of chromium (Cr).

ABSTRACT

An easily handleable electrolytic copper foil securing a highly durable secondary battery, an electrode including same, a secondary battery including same, and a method of manufacturing same. The electrolytic copper foil including first and second surfaces includes a copper layer including a matte surface facing the first surface and a shiny surface facing the second surface, a first protective layer formed on the matte surface of the copper layer, and a second protective layer formed on the shiny surface of the copper layer. A coefficient of thermal expansion of the electrolyte copper foil measured using thermomechanical analyzer while heating the electrolytic copper foil from 30 to 190 °C at 5 °C/min ranges from 16 to 22 μm/(m·°C), tensile strength of the electrolytic copper foil measured after heat treatment at 190 °C, ranges from 21 to 36 kgf/mm^2, and weight deviation of the electrolytic copper foil is 5% or less.

FIG. 1

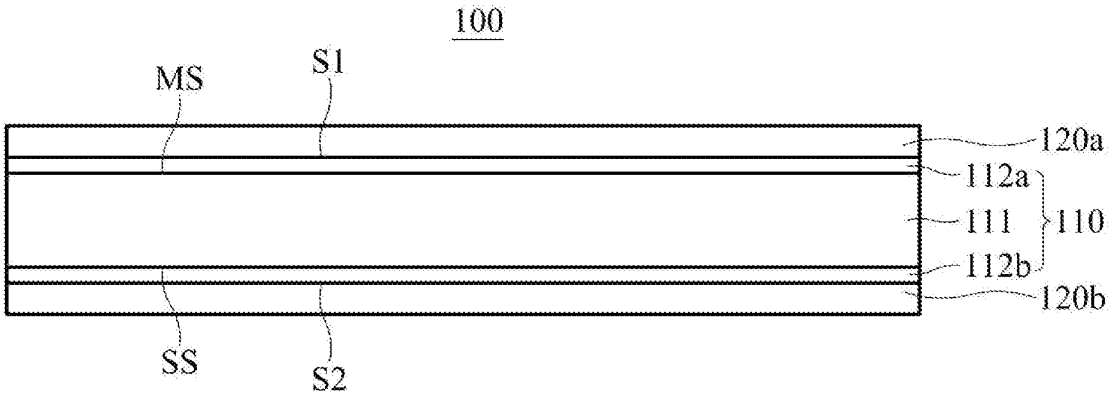
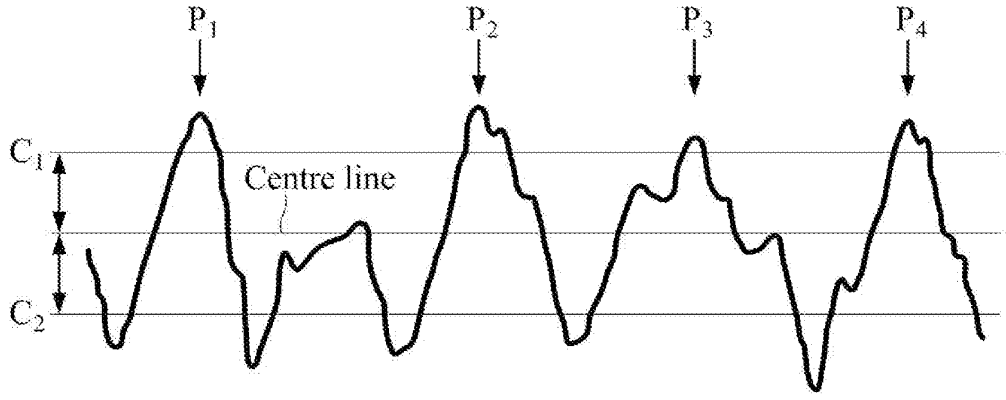

100
MS
S1
120a
112a
111
110
112b
120b
SS
S2

FIG. 2


P1
P2
P3
P4
C1
Centre line
C2

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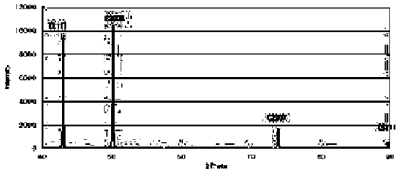
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(54)【発明の名称】リチウム二次電池の集電体用銅箔

(57)【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



【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（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】
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。
【発明の詳細な説明】
【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/mm²]	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	41.6	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】

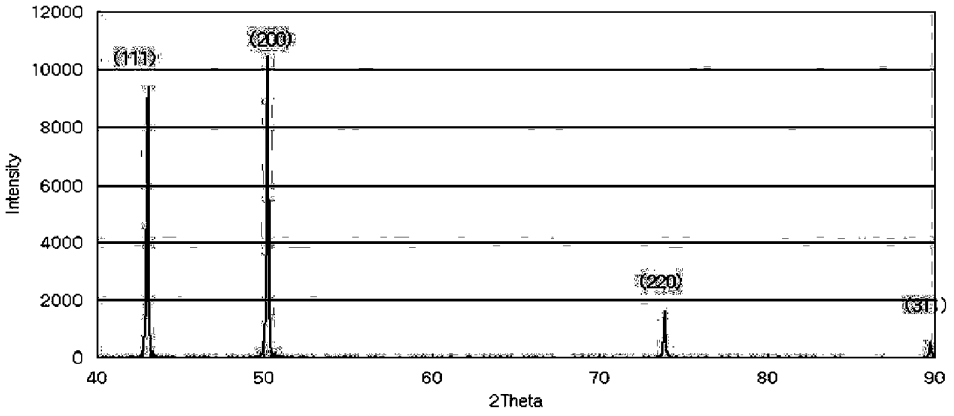
【００３２】

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。

【図１】



【図２】


12000
10000
8000
6000
4000
2000
0
Intensity
(111)
(200)
(220)
(311)
40
50
60
70
80
90
2Theta

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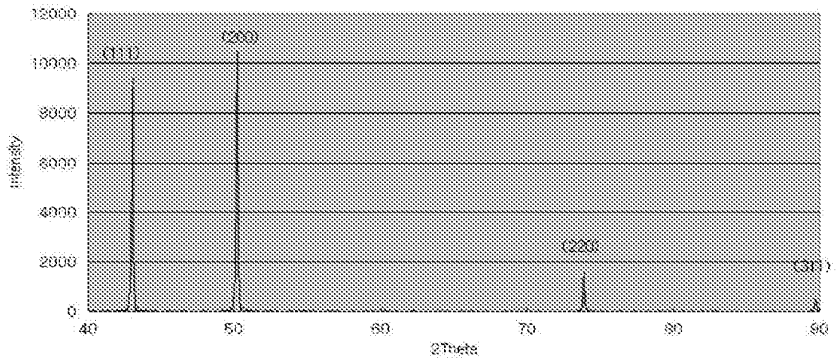
전체 청구항 수 : 총 7 항

(54) 울음특성이 개선된 리튬 이차전지의 집전체용 동박

(57) 요 약

본 발명에 따른 리튬 이차전지 집전체용 동박은, 결정구조에 있어서 (111)면, (200)면, (220)면의 집합조직계수(Texture Coefficient)의 전체 합 중에서 (111)면과 (200)면의 집합조직계수의 합이 차지하는 비율이 60 ~ 85%이며, 상기 (111)면, (200)면, (220)면의 집합조직계수의 전체 합에 대한 (111)면의 집합조직계수의 비율이 18 ~ 38%, (200)면의 집합조직계수의 비율이 28 ~ 62 %, (220)면의 집합조직계수의 비율이 15 ~ 40%이고, 표면조도(R_z-JIS)가 2㎛ 이하이고, 중량편차 특성이 3% 이하이고, 인장강도가 30~40kgf/㎟이고, 연신율이 3~20%이고, 동박두께가 1~35㎛인 것을 특징으로 한다.

대 표 도 - 도2



특허청구의 범위

청구항 1

리튬 이차전지의 집전체로 사용되는 동박에 있어서,

결정구조에 있어서 (111)면, (200)면, (220)면의 집합조직계수(Texture Coefficient)의 전체 합 중에서 (111)면과 (200)면의 집합조직계수의 합이 차지하는 비율이 60 ~ 85%이며, 상기 (111)면, (200)면, (220)면의 집합조직계수의 전체 합에 대한 (111)면의 집합조직계수의 비율이 18 ~ 38%, (200)면의 집합조직계수의 비율이 28 ~ 62 %, (220)면의 집합조직계수의 비율이 15 ~ 40%인 것을 특징으로 하는 리튬 이차전지의 집전체용 동박.

청구항 2

제1항에 있어서,

표면조도(R_z-JIS)가 2㎛ 이하인 것을 특징으로 하는 리튬 이차전지의 집전체용 동박.

청구항 3

제1항에 있어서,

중량편차 특성이 3% 이하인 것을 특징으로 하는 리튬 이차전지의 집전체용 동박.

청구항 4

제1항에 있어서,

인장강도가 30~40kgf/㎟인 것을 특징으로 하는 리튬 이차전지의 집전체용 동박.

청구항 5

제1항에 있어서,

연신율이 3~20%인 것을 특징으로 하는 리튬 이차전지의 집전체용 동박.

청구항 6

제1항에 있어서,

동박두께가 1~35㎛인 것을 특징으로 하는 리튬 이차전지의 집전체용 동박.

청구항 7

리튬 이차전지의 집전체로 사용되는 동박에 있어서,

결정구조에 있어서 (111)면, (200)면, (220)면의 집합조직계수(Texture Coefficient)의 전체 합 중에서 (111)면과 (200)면의 집합조직계수의 합이 차지하는 비율이 60 ~ 85%이며, 상기 (111)면, (200)면, (220)면의 집합조직계수의 전체 합에 대한 (111)면의 집합조직계수의 비율이 18 ~ 38%, (200)면의 집합조직계수의 비율이 28 ~ 62 %, (220)면의 집합조직계수의 비율이 15 ~ 40%이고,

표면조도(R_z-JIS)가 2㎛ 이하이고,

중량편차 특성이 3% 이하이고,

인장강도가 30~40kgf/㎟이고,

연신율이 3~20%이고,

동박두께가 1~35㎛인 것을 특징으로 하는 리튬 이차전지의 집전체용 동박.

명 세 서

발명의 상세한 설명

기 술 분 야

[0001] 본 발명은 리튬 이차전지의 집전체로 사용되는 동박에 관한 것으로서, 더욱 상세하게는 동박 표면에서 울음(Wrinkle)이 발생하는 것을 방지할 수 있는 구조를 가진 리튬 이차전지의 집전체용 동박에 관한 것이다.

배 경 기 술

[0002] 리튬 이차전지는 여타의 이차전지에 비해 상대적으로 에너지 밀도가 높고, 작동전압이 높을 뿐만 아니라 우수한 보존 및 수명특성을 보이는 등 많은 장점이 있어 개인용 컴퓨터, 캠코더, 휴대용 전화기, 휴대용 CD 플레이어, PDA 등 각종 휴대용 전자기기에 널리 사용되고 있다.

[0003] 일반적으로 리튬 이차전지는 전해질을 사이에 두고 배치된 양극 및 음극과, 상기 양극과 음극에 각각 포함된 양극 활물질 및 음극 활물질과, 상기 양극 활물질과 음극 활물질에 각각 접촉하는 양극 집전체 및 음극 집전체를 구비한 구조를 갖는다.

[0004] 리튬 이차전지에 있어서 음극 집전체의 소재로는 주로 동박이 사용되며, 통상적으로 이 동박에는 카본(Carbon)계 슬러리의 활물질이 코팅된다. 여기서, 동박은 전기 도금법으로 전해동박을 제조하는 제박공정과 원박에 박리강도(Peel strength) 등을 부여하기 위한 후처리 공정을 통하여 제조된다. 전기도금에 의해 전해동박의 일면에는 제박기의 드럼(Drum)의 표면형상을 따르는 이른바, 샤이니 면(Shiny side)이 형성되고, 타면에는 산(Mountain) 구조에 의해 상대적으로 조도가 높은 매트면(Matte Side)이 형성된다. 또한, 전해동박은 후처리 공정에서 내식성 및 내변색성을 확보하기 위해 보호성 Coating을 추가로 실시하게 된다.

[0005] 리튬 이차전지는 집전체로 사용되는 동박의 표면 상태에 따라 전지특성이 크게 변하므로 수율의 향상을 위해서는 울음특성(Wrinkle characteristics)과 같은 표면 특성을 개선하는 것이 매우 중요하다.

[0006] 도 1에 도시된 바와 같이 동박의 표면에 울음이 존재할 경우 표면형상의 불균일로 인해 활물질의 균일한 코팅이 이루어지지 않으며, 이로 인해 충,방전 시 단락이 발생하거나 동박으로부터 활물질이 박리되는 현상이 발생하게 된다.

발명의 내용

해결 하고자하는 과제

[0007] 본 발명은 상기와 같은 문제점을 해결하기 위해 창안된 것으로서, 동박표면에서 울음이 발생하는 것을 저감할 수 있는 결정구조를 가진 리튬 이차전지의 집전체용 동박을 제공하는 데 그 목적이 있다.

[0008] 본 발명의 다른 목적은 동박표면에서 울음이 발생하는 것을 보다 효과적으로 저감하기 위해 표면조도(Surface Roughness), 중량편차, 인장강도, 연신율, 두께 등의 인자가 최적화된 리튬 이차전지의 집전체용 동박을 제공하는 데 있다.

과제 해결수단

[0009] 상기와 같은 목적을 달성하기 위해 본 발명에 따른 리튬 이차전지 집전체용 동박은, 결정구조에 있어서 (111)면, (200)면, (220)면의 집합조직계수(Texture Coefficient)의 전체 합 중에서 (111)면과 (200)면의 집합조직계수의 합이 차지하는 비율이 60 ~ 85%이며, 상기 (111)면, (200)면, (220)면의 집합조직계수의 전체 합에 대한 (111)면의 집합조직계수의 비율이 18 ~ 38%, (200)면의 집합조직계수의 비율이 28 ~ 62 %, (220)면의 집합조직계수의 비율이 15 ~ 40%인 것을 특징으로 한다.

[0010] 상기 동박의 표면조도(R_z-JIS)는 2㎛ 이하인 것이 바람직하다.

[0011] 상기 동박의 중량편차 특성은 3% 이하인 것이 바람직하다.

[0012] 상기 동박의 인장강도는 30~40kgf/㎟인 것이 바람직하다.

[0013] 상기 동박의 연신율은 3~20%인 것이 바람직하다.

[0014] 상기 동박의 두께는 1~35㎛인 것이 바람직하다.

효 과

[0015] 본 발명에 따른 리튬 이차전지 집전체용 동박은 표면에 울음이 실질적으로 발생하지 않으므로 활물질의 코팅 시 균일한 코팅면을 형성할 수 있고 단락의 발생을 방지할 수 있다. 또한, 카본계 슬러리와 같은 음극 활물질과의 접촉 시 밀착력이 충분히 확보되어 박리강도가 우수하므로 리튬 이차전지의 용량을 안정적으로 유지할 수 있다.

발명의 실시를 위한 구체적인 내용

[0016] 이하, 첨부된 도면을 참조하여 본 발명의 바람직한 실시예를 상세히 설명하기로 한다. 이에 앞서, 본 명세서 및 청구범위에 사용된 용어나 단어는 통상적이거나 사전적인 의미로 한정해서 해석되어서는 아니되며, 발명자는 그 자신의 발명을 가장 최선의 방법으로 설명하기 위해 용어의 개념을 적절하게 정의할 수 있다는 원칙에 입각하여 본 발명의 기술적 사상에 부합하는 의미와 개념으로 해석되어야만 한다. 따라서, 본 명세서에 기재된 실시예와 도면에 도시된 구성은 본 발명의 가장 바람직한 일 실시예에 불과할 뿐이고 본 발명의 기술적 사상을 모두 대변하는 것은 아니므로, 본 출원시점에 있어서 이들을 대체할 수 있는 다양한 균등물과 변형예들이 있을 수 있음을 이해하여야 한다.

[0017] 본 발명에 따른 리튬 이차전지 집전체용 동박은 결정구조, 표면조도, 중량편차, 인장강도, 연신율 등의 인자가 최적화되어 울름이 발생하지 않는 표면특성을 제공한다.

[0018] 바람직하게, 본 발명에 따른 리튬 이차전지 집전체용 동박은 황산동, 황산 및 염소로 구성된 황산동 도금액을 기본으로 하고, 미량의 유기 첨가제를 첨가하여 제조된다. 여기서 첨가제로는 도금 표면에 광택을 부여하고 미세한 도금층을 얻기 위한 Brightner로서 Sulfide를 함유한 sulphonate계열의 첨가제와, 저조도의 동박을 얻기 위해 첨가하는 leveler로서 분자량 1,000 ~ 100,000정도의 저분자량을 갖는 Gelatin과, 안정적인 저조도를 구현하기 위한 suppressor로서 Cellulose계열의 첨가제가 사용된다. 공정조건으로는 30 ~ 80ASD(A/dm^2)의 전류밀도 및 30 ~ 60℃의 온도에서 제박기의 드럼 표면에 구리를 전착하여 원박을 제조하고, 방청처리를 위해 동박 표면을 크로메이트(Chromate) 처리하는 공정을 거쳐 제조된다.

[0019] 동박의 결정구조는 (111)면, (200)면, (220)면의 집합조직계수(Texture Coefficient)의 전체 합 중에서 (111)면과 (200)면의 집합조직계수의 합이 차지하는 비율이 60 ~ 85%인 조건을 만족해야 한다. 아울러, (111)면, (200)면, (220)면의 집합조직계수(Texture Coefficient)의 전체 합에 대한 (111)면의 집합조직계수의 비율은 18 ~ 38%, (200)면의 집합조직계수의 비율은 28 ~ 62 %, (220)면의 집합조직계수의 비율은 15 ~ 40%의 조건을 만족해야 한다. 이와 같은 결정구조는 동박(100)의 제조를 위한 상술한 전기도금공정 시 전류밀도나 첨가제 등을 제어함으로써 달성될 수 있다.

[0020] 상기 집합조직계수의 수치범위를 벗어나는 경우 동박의 폭 방향으로 울음이 다수 발생하게 되며, 이로 인해 활물질의 코팅 시 동박표면에 대한 활물질의 밀착성이 떨어지는 문제가 있다. 여기서, 집합조직계수(TC)는 X선 회절법(XRD)을 적용하여 도 2에 도시된 바와 같이 각 결정면의 회절강도 피크치(Peak)치를 얻은 후 기준 피크치와 비교하여 아래의 수학식 1을 따르는 범위 내에서 환산함으로써 결정된다. 수학식 1에서 I(hkl)은 (hkl)면에 대한 측정 회절강도를 나타내며, I_0(hkl)은 ASTM(American Society of Testing Materials) 표준 분말형상 회절 데이터의 표준 회절강도를 나타낸다.

수학식 1

$$TC(hkl) \geq \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{n}\sum\frac{I(hkl)}{I_0(hkl)}}$$

[0021]

[0022] 동박의 표면조도(R_z)는 일본공업표준규격(JIS) 기준으로 2㎛ 이하인 조건을 만족해야 한다. 표면조도(R_z)가 2㎛를 초과하는 경우 표면이 불균일하여 리튬 이차전지의 충,방전 시 단락이 발생할 수 있으며, 음극 활물질의 코팅상태가 불균일해지는 문제가 발생하게 된다.

[0023] 동박의 중량편차 특성은 3% 이하의 조건을 만족해야 한다. 중량편차 특성이 3%를 초과하는 경우 동박 표면에 물성 편차가 발생하여 울음 수가 증가하고 집전체의 물성이 불균일해지는 문제가 발생하게 된다. 여기서, 중량편차는 동박을 5㎝×5㎝의 면적으로 절개하여 시편을 만든 후 그 중량을 측정하여 단위면적당 동박 중량값을 환산하고, 동박의 폭 방향을 따라 상기 시편을 절개하는 과정을 반복적으로 수행하여 각 시편에 대한 동박 중량값들

을 측정한 후 표준편차를 계산함으로써 산출한다. 이때 동박은 크로메이트 표면처리를 통해 방청처리된 전해동박을 사용하는 것이 바람직하다.

[0024] 그밖에, 동박의 인장강도는 30~40kgf/㎟, 연신율은 3~20%, 두께는 1~35㎛의 조건을 만족해야 한다. 이와 같은 범위를 벗어나는 경우 동박의 물성 편차가 발생하여 울음 수가 증가하고 집전체의 물성이 불균일해지는 문제가 발생하게 된다.

[0025] 아래의 표 1은 본 발명의 실시예 1 내지 7과 비교예 1 내지 9에 따른 리튬 이차전지 집전체용 동박에 대하여 울음특성을 측정한 결과를 나타낸다. 표 1에서 인장강도는 UTM(Universal Testing Machine)을 이용하여 측정하였으며, 이때 표점거리(Gauge Length)는 5㎝로 설정하였다.

표 1

구분	동박	동박두께 [㎛]	(111)+(200) 비율[%]	(111)비율 [%]	(200)비율 [%]	(220)비율 [%]	인장강도 [kg/㎟]	중량편차 [%]	울음발생수 [ea]
실시예1	전해동박	8	76	26	50	24	32.2	0.4	0
실시예2	전해동박	8	62	31	31	38	33.7	0.7	0
실시예3	전해동박	8	83	32	51	17	34.5	0.8	0
실시예4	전해동박	8	70	20	50	30	32.6	1.6	0
실시예5	전해동박	8	72	35	36	29	32.1	0.4	0
실시예6	전해동박	8	81	22	59	19	37.2	2.6	0
실시예7	전해동박	8	66	36	30	34	33.1	1.2	0
비교예1	전해동박	8	64	16	48	36	36.8	0.5	2
비교예2	전해동박	8	73	41	32	27	33.2	0.9	3
비교예3	전해동박	8	62	37	25	38	31.4	0.5	3
비교예4	전해동박	8	83	19	64	17	37.1	0.9	4
비교예5	전해동박	8	87	34	53	13	33.1	0.7	2
비교예6	전해동박	8	57	26	31	43	32.4	0.8	3
비교예7	전해동박	8	80	30	49	21	27.4	0.6	2
비교예8	전해동박	8	75	23	51	26	41.5	0.9	2
비교예9	전해동박	8	76	25	50	25	31.8	3.4	5

[0026]

[0027] 표 1을 참조하면, 본 발명의 실시예 1 내지 7에 따른 동박은 상술한 집합조직계수 비율, 인장강도, 중량편차, 동박두께의 조건을 모두 만족함에 따라 울음이 발생하지 않는 결과를 보임을 확인할 수 있다. 반면에, 비교예 1 내지 9에 따른 동박은 울음이 다수 발생하여 리튬 이차전지의 집전체로 사용되기에 부적합한 특성을 보임을 확인할 수 있다.

[0028] 본 발명에 따른 리튬 이차전지 집전체용 동박은 집합조직계수 비율의 조건만을 만족해도 울음특성이 종래에 비해 개선될 수 있으나, 비교예 1 내지 9에 나타난 바와 같이 인장강도, 중량편차 등의 다른 조건이 해당 수치범위를 벗어날 경우에는 개선된 특성에 악영향을 미쳐 최종적으로 울음특성의 저하를 초래하므로 상술한 집합조직계수 비율, 인장강도, 중량편차, 동박두께 등의 조건을 모두 만족하는 것이 가장 바람직하다.

[0029] 이상에서 본 발명은 비록 한정된 실시예와 도면에 의해 설명되었으나, 본 발명은 이것에 의해 한정되지 않으며 본 발명이 속하는 기술분야에서 통상의 지식을 가진 자에 의해 본 발명의 기술사상과 아래에 기재될 특허청구범위의 균등범위 내에서 다양한 수정 및 변형이 가능함은 물론이다.

도면의 간단한 설명

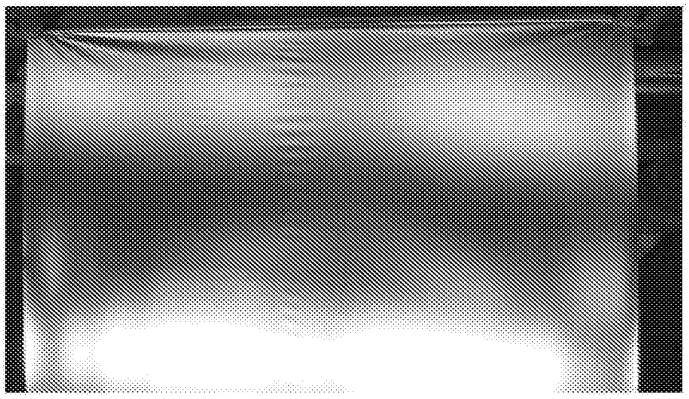
[0030] 본 명세서에 첨부되는 다음의 도면들은 본 발명의 바람직한 실시예를 예시하는 것이며, 상술한 발명의 상세한 설명과 함께 본 발명의 기술사상을 더욱 이해시키는 역할을 하는 것이므로, 본 발명은 그러한 도면에 기재된 사항에만 한정되어 해석되어서는 아니된다.

[0031] 도 1은 종래기술에 따른 리튬 이차전지 집전체용 동박에 울음이 발생한 상태를 보여주는 사진이다.

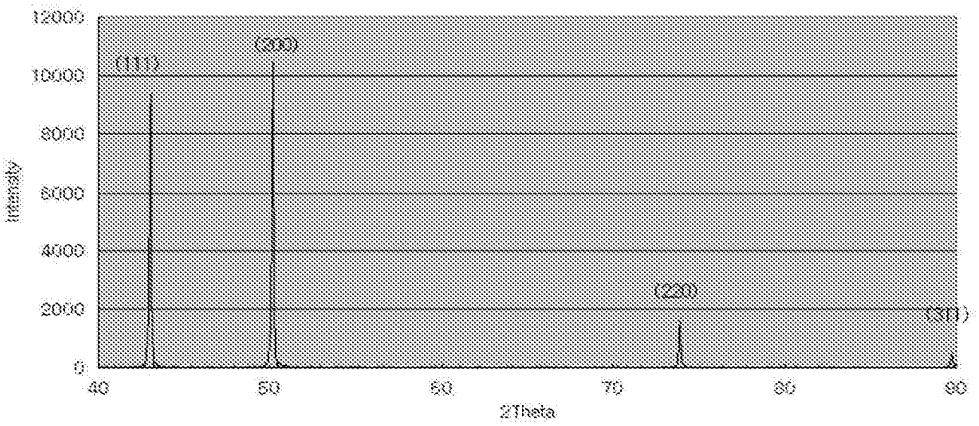
[0032] 도 2는 본 발명에 따른 리튬 이차전지 집전체용 동박의 집합조직계수의 산출을 위해 X선 회절법(XRD)을 실시한 결과를 나타낸 그래프이다.

도면

도면1



도면2


12000
10000
8000
6000
4000
2000
0
Intensity
(111)
(200)
(220)
(311)
40
50
60
70
80
90
2Theta

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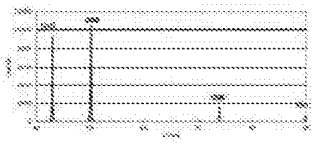
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(71)Applicant	LS MTRON LTD
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(54)COPPER FOIL FOR COLLECTOR OF LITHIUM SECONDARY BATTERY

(57)Abstract
PROBLEM TO BE SOLVED: To provide a copper foil for a collector of a lithium secondary battery with a crystalline structure capable of reducing wrinkles on the surface of the copper foil.
SOLUTION: The copper foil for a collector of a lithium secondary battery has a crystalline structure in which the ratio of the sum of the texture coefficients of surfaces (111) and (200) to the sum total of the texture coefficients of the surfaces (111), (200), and (220) is in the range of 60 to 85%, and the ratio of the texture coefficient of the surface (111) is in the range of 18 to 38%, the ratio of the texture coefficient of the surface (200) is in the range of 28 to 62%, and the ratio of the texture coefficient of the surface (220) is in the range of 15 to 40%, to the sum total of the texture coefficients of the surfaces (111), (200), and (220). The copper foil has the surface roughness (Rz (JIS)) of 2 μm or lower, the weight deviation of 3% or lower, the tensile strength in the range of 30 to 40 kgf/mm2, the drawing rate in the range of 3 to 20%, and the thickness in the range of 1 to 35 μm.

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(74) 대리인 유미특허법인

심사청구 : 없음

(54) 전착 동박 및 전착 동박의 제조 방법

요약

전착 동박(electrodeposited copper foil)을 제조하는 방법은, 구리 농도가 60g/L~85g/L의 범위이고, 유리(遊離) 황산 농도가 100g/L~250g/L의 범위이며, 염화 이온 농도가 1ppm~3ppm의 범위이고, 젤라틴계 첨가제가 0.3ppm~5ppm 첨가된 전해액을 마련하는 단계, 및 30A/dm ^{2} ~75A/dm^{2}의 전류 밀도로 40~60℃에서 상기 전해액을 전기 분해하여 동박을 전착하는 단계를 포함한다.

얻어진 전착 동박은 인장 강도 및 연신율이 우수하다.

전착 동박은 미세 조직 및/또는 주상정(柱狀晶) 조직의 쌍정 조직, 및 쌍정 조직 속에 수용된 염화물(염화 이온)을 포함하고, 전착 동박중의 염화물의 양은 50ppm~180ppm이며, 전해액 중 염화 이온 농도의 40~150배이다.

대표도
도 5

색인어
동장 적층판, 전착 동박, 쌍정 조직, 전해액, 전기 분해

명세서

도면의 간단한 설명

도 1은 쌍정 조직을 포함한 동박(銅薄)의 개략적인 단면도이다.

도 2는 쌍정 계면을 확대한 개략도이다.

도 3은 주상정(columnar crystal) 조직을 포함한 동박의 개략적인 단면도이다.

도 4는 미세 결정 조직을 포함한 동박의 개략적인 단면도이다.

도 5는 본 발명에 따른 전착 동박의 제조 방법에 사용하는 장치의 일례를 나타낸 도이다.

도 6(a) 내지 도 6(d)는 본 발명에 따른 동박의 프로파일(profile) 사진과 비교예에 따른 전착 동박의 SEM(scanning electron microscope, 주사 전자 현미경) 사진이다.

발명의 상세한 설명

발명의 목적

발명이 속하는 기술 및 그 분야의 종래기술

본 발명은 충분한 연신율 및 높은 인장 강도를 가지는 전착 동박 및 그 제조 방법에 관한 것이다. 또한, 본 발명은 전착 동박 등을 이용하여 제조한 동장 적층판(copper-clad laminate) 및 전착 동박 등을 이용하여 제조한 인쇄 배선판에 관한 것이다.

전착 동박의 연속 제조에서, Ti로 된 원통형 드럼을 음극으로 하고, 이와 반대편에 불용성 양극을 배치하고, 산성 황산동(acidic copper sulfate) 등을 용해한 전해액으로 채워진 전기 주조셀을 이용하여 원통형 드럼의 표면에 구리(銅)를 전착시킨다.

이러한 방법으로 제조된 전착 동박을 에폭시 수지 등의 기판에 접착시킨 후, 에칭 등으로 인쇄 회로를 형성하여 인쇄 배선판을 제조한다.

최근에는 전자 장비의 소형화 및 집적화에 따라, 전자 회로를 고밀도로 형성하는 것이 요청된다. 따라서 상호 접착되어 적층된 다수의 인쇄 배선판으로 이루어진 적층 인쇄 배선판이 광범위하게 사용된다.

이러한 인쇄 회로판의 제조 방법은 소자를 260℃ 근방에서 용융 땜납상에 부유시켜 배선판위에 장착하는 방법을 포함한다. 이러한 방법에서, 동박의 고온 연신율(high temperature elongation, HTE)이 작은 경우, 기판과 동박간의 열팽창계수(coefficient of thermal expansion, CTE)가 다르므로 동박이 기판 팽창을 따라갈 수 없어서, 동박에 균열이 생겨 전기 접촉 불량을 야기한 적이 있었다. 따라서 고온에서 인장 강도 및 연신율이 큰 동박이 바람직하다.

동박에 함유된 불순물량을 감소시켜 구리의 재결정성을 향상시킴으로써 전술한 동박의 연신율을 크게 할 수 있다는 것이 알려져 있다.

예를 들면, 일본 특개평 제7-188969호(미심사)에서는 직경이 10㎛이하인 미세 결정이고 무작위 결정 구조를 가지는 실질적으로 균일한 전착 동박의 제조 방법에 대하여 기재하고 있는데, 이러한 방법은 구리 이온, 황산 이온 및 적어도 1종의 유기계 첨가물을 함유하고 염화 이온 농도가 1ppm 미만인 전해액을 전류 밀도가 0.1A/cm ^{2} ~5A/cm^{2}인 조건에서 전기 분해하여 전착 동박을 제조하고 있다.

그러나 이러한 방법으로 제조된 동박은 고온 연신율이 만족스럽지 못한 결점이 있다. 또한, 전해액중의 염화물 농도를 1ppm 미만으로 제어해야 하기 때문에, 방법 제어가 어렵고 원료등으로부터 염화물의 오염을 방지하기가 매우 힘들다. 나아가, 연속 운전 중 전해액의 염화물 농도가 제어 범위를 벗어나는 경우, 제어 범위로 되돌리는 데 장시간이 필요하므로 제조 효율을 저하시킨다.

동박에 함유된 염화물의 양을 특정 범위내로 조정하도록 제어함으로써, 인장 강도 및 연신율이 큰 동박을 제조하는 것이 제안되어 왔다.

예를 들면, 일본 특개평 제10-36992호(미심사)에서는 염화물의 양이 40ppm이하이고, 유황 함유량이 30ppm이하인 전착 동박에 대하여 기재하고 있는데, 이러한 전착 동박은 180℃에서 5%이상의 연신율을 나타낸다. 이 일본 특개평 제10-36992호(미심사)에서는 전술한 전착 동박의 제조 방법에서 5ppm 이하의 염화 이온 및 0.5ppm~2ppm의 티오(thio) 요소(尿素)를 함유한 황산으로 산성화된 황산동 용액으로 이루어진 전해액을 이용하는 것이 기재되어 있다.

그러나 전착 동박의 제조시 티오 요소류 등을 첨가제로 첨가하므로 비용이 많이 든다. 또한 전착 동박의 연신율이 항상 만족스러운 것은 아니다.

또한, 일본 특개평 제10-330983호(미심사)는 염화물을 80ppm~400ppm 함유한 전착 동박에 대하여 기재하고 있는데, 이러한 전착 동박의 비커스(Vickers) 경도는 25℃에서 180~320의 범위에 있고, 220℃에서 30분 동안 열처리 후 전착 동박의 비커스 경도는 150이상이다. 일본 특개평 제10-330983호(미심사)는 전술한 전착 동박의 제조 방법으로서 50mg/L~250mg/L의 염화물, 0.1g/L~1.0g/L의 옥시에틸렌(oxyethylene) 계면 활성제, 1mg/L~10mg/L의 아교 또는 젤라틴(gelatin), 1mg/L~10mg/L의 질소 유기 화합물을 함유한 황산으로 산성화한 황산동 전해액을 사용하는 것에 대하여 기재하고 있다.

그러나 앞서 가재한 전착 동박은 그 제조시에 염화물을 다량 첨가해야 하므로, 제조시 사용되는 장치가 부식될 위험이 있다. 또한 제조된 전착 동박의 결정 구조가 주상정(柱狀晶)이기 때문에, 인장 강도 및 연신율 등의 동박 특성이 항상 만족스러운 것은 아니다.

발명이 이루고자 하는 기술적 과제

본 발명자는 전술한 문제점을 해결하기 위하여 폭넓고 집중적인 연구를 하였다.

그 결과, 1ppm~3ppm의 염화 이온 농도, 60g/L~85g/L의 구리(銅) 농도, 100g/L~250g/L의 유리 황산 농도, 0.3ppm~5ppm의 젤라틴 첨가제 농도를 지닌 전해액을 40℃~60℃에서 30A/dm ^{2} ~75A/dm^{2}의 전류 밀도로 전기 분해하여 제조한 전착 동박은 쌍정 조직을 많이 함유하며, 특히 쌍정 계면에서 염화물이 선택적으로 수용된 것을 발견하였다. 나아가, 이렇게 제조된 전착 동박은 염화물을 50ppm~180ppm 함유하며, 이는 전해액중의 염화 이온 농도의 40~150배이며 인장 강도 및 연신율 등의 특성이 우수하다. 본 발명을 이러한 발견에 기초하여 완성하였다.

본 발명은 인장 강도 및 연신율이 우수한 전착 동박을 제공한다.

본 발명은 또한 이러한 전착 동박을 제조하기 위한 방법을 구비한다.

또한 본 발명은 절연 기판 및 기판 표면상에 적층된 박판을 포함하는 동장 적층판(copper-clad laminate)을 제공하고, 이러한 박판으로부터 제조된 바람직한 배선 패턴을 지닌 인쇄 배선판을 제공한다.

발명의 구성 및 작용

본 발명의 전착 동박을 제조하는 방법은, 구리의 농도가 60g/L~85g/L의 범위이고, 유리 황산 농도가 100g/L~250g/L의 범위이며, 염화 이온 농도가 1ppm~3ppm의 범위이고, 젤라틴계 첨가제의 농도가 0.3ppm~5ppm의 범위인 전해액을 마련하는 단계, 및 30A/dm^2~75A/dm^2 범위의 전류 밀도로 40~60℃의 범위에서 전해액을 전기 분해하여 동박을 전착하는 단계를 포함한다.

본 발명의 전착 동박은 미세 결정 및/또는 주상정(柱狀晶) 결정의 쌍정 조직, 및 쌍정 계면에 수용된 염화물(염화 이온)을 포함하고, 전착 동박중의 염화물의 양은 50ppm~180ppm이고, 이는 전해액중 염화 이온 농도의 40~150배이다.

동장 적층판은 전술한 전착 동박으로 적층된 적어도 하나의 면을 지닌 절연 기판을 포함한다.

동장 적층판상의 전착 동박을 에칭하여 제조한 소정의 배선 패턴을 구비하는 인쇄 배선판은 전술한 전착 동판으로 적층된 적어도 하나의 면을 지닌 절연 기판을 포함한다.

본 발명에 따른 전착 동박 및 그 제조 방법, 동장 적층판 및 인쇄 배선판을 다음에 상세하게 기재한다.

전착 동박의 제조 방법전착 동박의 제조 방법

도 5는 본 발명에 따른 전착 동박의 제조 방법에 사용되는 장치의 일례를 나타낸다. 전해조(4)내에서 원통형 음극 드럼(1)과, 이와 일정한 간격을 두고 원통형 음극 드럼(1)을 따라 배치된 양극(2)과의 사이에, 황산동을 포함한 전해액을 주입한다. 동 전착용 전류를 공급하여 회전하는 음극 드럼(1) 표면에 동을 전착시킨다. 소정 두께에 이른 동박은 연속으로 음극 드럼(1)에서 박리되어 둥근 감기롤(roll winder)(3)에 감긴다.

통상적으로, 얻어진 전착 동박의 음극 드럼쪽은 광택면(윤이 나는 면)이 되고, 전착면쪽은 매트(matte)면(거친 면)이 된다.

본 발명에서는 구리 농도가 60g/L~85g/L, 바람직하게는 60g/L~80g/L이고, 황산 농도가 100g/L~250g/L, 바람직하게는 120g/L~250g/L인 전해액을 사용한다.

이러한 전해액에는 1ppm~3ppm의 염화 이온 농도, 바람직하게는 1.0ppm~2.5ppm, 보다 바람직하게는 1.1ppm~2.5ppm을 함유한다. 본 발명에서는 동박에 염화물이 다량(종래 전착 동박의 4배~20배) 함유되어 있기 때문에, 전해액에 염소를 첨가할 필요가 있다. 통상적으로 염화구리 등의 염화물을 첨가한다. 그러나 염화이온은 동박 제조 방법에서 첨가되는 용수 및 기타 원료로부터 불순물로서 보급되므로 염화물을 전해액에 첨가할 필요는 없다.

또한, 본 발명의 전해액에 젤라틴계 첨가제를 0.3ppm~5ppm, 바람직하게는 0.3ppm~3ppm를 첨가한다. 젤라틴계 첨가제 등의 예는 아교, 젤라틴 등을 들 수 있다. 이러한 젤라틴계 첨가제가 저농도의 염화물에 사용되는 경우, 구리 전착시에 쌍정 조직이 형성되고, 염화물이 쌍정 계면에 결합됨으로써 동박중의 염화물 농도가 증가한다.

본 발명의 전해액은 40℃~60℃의 용해 온도에서 30A/dm^2~75A/dm^{2}의 전류 밀도, 바람직하게는 40A/dm^2~70A/dm^{2}의 전류 밀도, 더욱 바람직하게는 45A/dm^2~70A/dm^{2}의 전류 밀도로 전기 분해된다.

전술한 전해액을 사용하는 방법으로 쌍정 조직을 다량 함유한 전착 동박을 얻을 수 있다. 얻어진 전착 동박은 50ppm~180ppm의 염화물을 포함한다. 이러한 전착 동박은 쌍정 조직 이외에 미세 결정이나 주상정을 포함할 수 있다. 이와 관련하여 전술한 일본 특개평 제10-330983호(미심사)에 기재된 염화 이온 농도가 10ppm~300ppm인 전해액을 사용하는 경우, 얻어진 동박 결정은 주상정이 된다. 한편, 전술한 일본 특개평 제7-188969호(미심사)에 기재된 염화 이온 농도가 1ppm미만인 전해액에서 동박을 제조한 경우, 얻어진 동박에 쌍정 조직은 존재하지 않고, 미세 결정 조직만이 존재한다.

초점이 맞춰진 이온 빔(focused ion beam, FIB)으로 단면 관찰용 동박 시편을 마련한 후, 시편상에 SIM(scanning ion image microscope, 주사 이온 영상 현미경)을 작동시켜 결정 구조를 인식할 수 있다.

도 1을 참조하면, 어느 정도까지 전착 및 성장이 계속되는 경우, 결정 구조의 방위가 갑자기 변경됨에 따라 새로운 결정이 성장하는 것을 반복함으로써 쌍정 조직이 형성된다. 쌍정 조직에서 2개의 결정은 도 2에 나타낸 바와 같이 고정된 결정학적 관계를 유지하면서 상호 접촉한다. 한편, 도 3에 나타낸 바와 같이 한 방향으로 결정을 전착 및 성장시킴으로써 주상정을 형성한다. 나아가, 도 4를 참조하면 무작위 방위를 가진 작은 직경의 결정 전착으로 미세 결정을 형성한다.

본 발명의 전착 동박은 쌍정 조직뿐만 아니라 미세 결정 또는 주상정을 함유한다.

본 발명에 따라 전해액으로부터 전착된 전착 동박의 염화물의 양은 전술한 바와 같이 50ppm~180ppm이다. 이러한 염화물의 양은 염화 이온 농도가 10ppm~50ppm인 전해액에서 제조된 전착 동박(주상정만으로 이루어진 결정) 또는 염화 이온 농도가 1ppm 미만인 전해액에서 제조된 동박(미세 결정으로 이루어진 결정)의 염화물의 양의 약 4~20배이다. 따라서 쌍정 조직, 특히 쌍정 조직 계면에 염화물을 다량 함유하는 것이 명백하다.

본 발명의 전착 동박에 수용된 염화물(ppm)은 전해액중의 염화 이온 농도(ppm)의 40~150배, 바람직하게는 40~140배, 더욱 바람직하게는 50~130배이다.

본 발명의 전술한 방법은 염화물이 수용된 쌍정 조직을 지닌 전착 동박을 얻을 수 있게 한다. 전술한 바와 같이, 얻어진 전착 동박은 온도 상승 중 인장 강도 및 연신율이 크다는 등의 뛰어난 특성을 나타낸다.

또한, 본 발명의 전술한 방법은 다량의 염화물을 첨가하거나 티오 요소 또는 아민(amine)류 등의 첨가제를 첨가할 필요가 없이 전해액의 염소 농도를 용이하게 제어할 수 있으므로, 전착 동박을 높은 효율로 제조할 수 있다. 이와 관련하여 일본 특개평 제10-36992호(미심사)와 같이 티오 요소를 전해액에 첨가하는 경우, 동박에 황이 수용되므로, 얻어진 전착 동박의 결정은 미세 입자를 지닐 뿐만 아니라, 결정에 수용되는 염소량이 적어져서 동박의 연신율이 저하된다.

본 발명의 전술한 방법으로 제조한 전착 동박의 두께 및 표면 거칠기(프로파일)를 전착 동박의 용도에 따라 적절하게 선택한다. 두꺼운 전착 동박을 제조하는 경우, 전해조의 원통형 음극 드럼의 회전 속도를 낮추는 것이 바람직하다.

본 발명의 전술한 방법으로 제조된 전착 동박의 매트면의 표면 거칠기(Rz)는 2.0㎛~5.0㎛, 바람직하게는 2.4㎛~4.5㎛, 더욱 바람직하게는 2.5㎛~4.3㎛, 가장 바람직하게는 2.5㎛~3.2㎛이다.

본 발명으로 얻어진 전착 동박은 우수한 인쇄 배선판의 제조용으로 사용하는 데 적합하다.

즉, 동장 적층판은 절연 기판의 적어도 한 면과 전술한 방법으로 제조한 전착 동박을 적층하여 제조할 수 있다. 또한, 포토레지스트(photoresist)를 노출 및 현상함으로써 얻어진 동장 적층판에 바람직한 패턴을 형성하고 에칭 레지스트로 마스크한 동장 적층판의 전착 동박을 에칭함으로써 인쇄 배선판을 제조할 수 있다. 또한, 차례로 배열하여 제조된 인쇄 배선판을 합치고, 전술한 바와 동일한 방법으로 배선 패턴을 형성함으로써 다층 인쇄 배선판을 제조할 수 있다.

또한 본 발명에 따라 얻어진 전착 동박은 리튬 이온 2차 전지등의 2차 전지용 집전기(collector)로 사용할 수 있다.

제조된 전착 동박을 사용하기 전에, 필요하다면 전착 동박의 매트쪽(동박 전착이 완료된 거친 면) 표면에 입자상의 구리를 형성하는 것이 바람직하다. 이러한 입자상의 구리를 형성하는 처리를 "구상화(nodulation)" 또는 "거칠기 처리(roughening treatment)"라고 한다.

구상화는 매트면(거친 면)이 양극을 향하도록 하여 전착 동박을 배치하고, 구리 이온을 포함하는 도금액중의 매트면에 구리를 전착하는 것을 포함한 처리이다. 통상 이러한 구상화에서는 가열 도금(burn plating), 봉입(차폐) 도금 및 위스커(whisker) 도금을 순차적으로 행한다.

예를 들면, 가열 도금은 전착 동박의 매트면(거친 면)쪽이 양극으로 향하게 하기 위하여 전술한 방법으로 제조한 전착 동박을 배치하고, 다음 조건하에 매트면상에 구리를 도금하는 것을 포함한다.

용액중의 구리 농도 : 5g/L～30g/L,

용액중의 황산 농도 : 50g/L～150g/L,

용액 온도 : 20℃～30℃,

전류 밀도 : 20A/dm^2 ～40A/dm^2 및

도금 시간 : 5～15초

이와 같은 조건하에 전착 동박의 매트면상에 도금한 결과, " 탄도금층(burnt deposit)" 이라고 하는 나무가지형의 구리 전착물이 매트면(거친 면)상에 형성된다.

가열 도금 방법을 거친 매트면은 봉입 도금 방법에 들어간다. 예를 들면, 봉입 도금은 다음과 같은 조건하에 전술한 가열 도금 방법을 거친 후 전착 동박의 매트면상에 구리를 도금하는 방법을 추가로 포함한다.

용액중의 구리 농도 : 40g/L～80g/L,

용액중의 황산 농도 : 50g/L～150g/L,

용액 온도 : 45℃～55℃,

전류 밀도 : 20A/dm^2 ～40A/dm^2 및

도금 시간: 5～15초

전착 동박의 매트면상에 봉입 도금한 결과, " 탄도금층" 을 지닌 매트면상에 입자형의 구리 전착물이 형성된다.

전술한 조건하에 봉입 도금 방법을 거친 매트쪽의 표면은 위스커 도금 방법에 추가로 들어갈 수 있다. 예를 들면, 위스커 도금은 다음과 같은 조건하에 전술한 봉입 도금 방법을 거친 후 매트면상에 구리를 도금하는 방법을 추가로 포함한다.

용액중의 구리 농도 : 5g/L～30g/L,

용액중의 황산 농도 : 30g/L～60g/L,

용액 온도 : 20℃～30℃,

전류 밀도 : 10A/dm^2 ～40A/dm^2 및

도금 시간: 5～15초

전술한 조건하에서 봉입 도금 방법을 거쳐 매트면상에 위스커 도금한 결과, 위스커 모양의 구리가 차폐 도금층(구리 도금층)상에 형성된다.

전착 동박이 2차 전지용 집전기로 사용되는 경우, 전술한 " 구상화" 또는 " 거칠기 처리" 는 반드시 필요하지 않다. 매트면과 광택면간의 표면 거칠기(Rz)의 차가 작은 전착 동박은 2차 전지용 집전기로 사용하는 것이 바람직하다.

따라서 구상화되거나 거칠기 처리된 전착 동박은 부동태(passivation) 처리를 하는 것이 바람직하다.

본 발명에서 채택하는 부동태 처리를 특별히 국한하지 않으며, 예를 들면, 아연 도금 또는 주석 도금 등의 부동태 처리일 수 있다. 이러한 부동태 도금 등에서 예를 들면, 아연 도금은 황산아연, 파이로(pyro)인산아연 등이 용해된 전해액을 사용한다.

부동태 도금후, 부동태 도금 방법을 거친 표면은 크롬산염(chromate)으로 처리하는 것이 바람직하다. 이러한 크롬산염 처리에서 부동태 도금 방법을 거친 전착 동박은 통상적으로 0.2g/L~5g/L의 크롬 무수물을 포함하고 pH값이 9~13으로 조정된 용액에 담그며, 전착 동박의 매트면을 0.1A/dm^2~3A/dm^{2}의 전류 밀도로 처리한다. 처리 시간은 통상 1~8초이다.

크롬산염 처리 후, 전착 동박의 표면은 실란(silane) 결합제로 처리하는 것이 바람직하다.

이러한 실란 결합제 처리에서는 통상적으로 에폭시알콕시실란(epoxyalkoxysilane), 아미노알콕시실란(aminoalkoxysilane), 메타크릴록시알콕시실란(methacryloxyalkoxysilane) 및 메르캅토알콕시실란(mercaptoalkoxysilane) 등의 실란 결합제를 사용한다. 이러한 실란 결합제는 실리콘 원자 0.15mg/m^2~2.0mg/m^2, 바람직하게는 0.3mg/m^2~2.0mg/m^{2}이 전착 동박의 표면에 적용된다.

전술한 구상화, 거칠기 처리, 부동태화, 도금, 크롬산염 처리 및 실란 결합제 처리를 거친 전착 동박은 특히 인쇄 배선 형성용 동박으로서 유용하다.

전착 동박전착 동박

본 발명의 전착 동박에서 50ppm~180ppm 범위의 염화물 또는 염화 이온이 수용된다.

본 발명의 전착 동박은 미세 결정 및/또는 주상정을 지닌 쌍정 조직, 및

쌍정 조직, 특히 쌍정 계면에 선택적으로 수용된 다량의 염화물 또는 염화 이온을 포함한다.

결정 구조는 FIB로써 동박 시편을 마련한 후, 동박 단면을 SIM으로 관찰함으로써 식별할 수 있다.

도 1을 참조하면, 어느 정도까지 전착 및 성장이 계속되는 경우, 결정 구조의 방위가 갑자기 변경되어 새로운 결정이 성장하는 것을 반복함으로써 쌍정 조직이 형성된다. 쌍정 조직에서는 2개의 결정 고체가 도 2에 나타낸 바와 같이 고정된 결정학적 관계를 유지하면서 상호 접촉한다. 한편, 도 3에 나타낸 바와 같이 한 방향으로 결정을 전착 및 성장시킴으로써 주상정을 형성한다. 나아가, 도 4를 참조하면 방위가 없는 미세 직경의 결정 전착으로 미세 결정을 형성한다.

본 발명의 전착 동박은 쌍정 조직뿐만 아니라 미세 결정 또는 주상정을 함유한다.

상온에서 이러한 전착 동박은 45kg/mm^2~65kg/mm^2, 바람직하게는 45kg/mm^2~63kg/mm^2, 더욱 바람직하게는 50kg/mm^2~62kg/mm^{2}의 인장 강도를 가지고, 약 3%~18%, 바람직하게는 3%~15%, 더욱 바람직하게는 6%~15%의 연신율을 가진다.

본 발명의 전착 동박의 두께 및 표면 프로파일을 전착 동박의 용도에 따라 적절하게 선택한다.

본 발명의 전착 동박의 표면 거칠기(Rz)는 바람직하게는 2.0㎛~5.0㎛의 범위, 더욱 바람직하게는 2.4㎛~4.4㎛의 범위이다.

본 발명의 전술한 전착 동박은 높은 인장 강도와 큰 연신율 때문에 인쇄 배선용 동박이나 리튬 이온 2차 전지 등의 2차 전지용 집전기로 사용하는 데 적합하다.

본 발명의 전착 동박은 예를 들면 전술한 방법으로 제조할 수 있다.

동장 적층판 및 이로부터 제조된 인쇄 배선판동장 적층판 및 이로부터 제조된 인쇄 배선판

동장 적층판은 절연 기판의 적어도 한면 위에 절연 접착제를 사용하거나 사용하지 않고 가열 압착(hot press)으로 전술한 전착 동박을 적층함으로써 제조할 수 있다.

동장 적층판의 절연 기판으로서 흔히 전자 기기에서 사용되는 수지 기판을 채택할 수 있다. 예를 들면, 종이/페놀 기판, 종이/에폭시 기판, 유리/에폭시 기판 및 폴리이미드(polyimide) 기판을 사용할 수 있다.

인쇄 배선판은, 예를 들면 얻어진 동장 적층판의 동박 표면에 포토레지스트를 적용한 다음, 포토레지스트(photoresist)를 노출 및 현상함으로써 바람직한 에칭 레지스트 패턴을 형성한 후, 전착 동박을 에칭하여 제조할 수 있다. 그 다음에 절연 기판의 표면을 동박으로 에칭한 배선 패턴으로 피복한다.

나아가 동박으로 에칭한 배선 패턴으로 피복된 표면을 지닌 절연 기판을 포함하는 제조된 인쇄 배선판은 전착 동박으로 절연층을 통하여 추가로 적층할 수 있고, 이러한 전착 동박은 같은 방법으로 에칭할 수 있어서 다층 인쇄 배선판을 형성한다.

실시예실시예

이하, 본 발명을 다음의 실시예에 따라 구체적으로 설명하지만, 본 발명은 이러한 실시예에 국한되지 않는다.

제1 실시예제1 실시예

`전착 동박의 제조전착 동박의 제조

80g/L의 구리 이온 및 250g/L의 유리 황산을 각각 함유하고, 2.7ppm의 염화 이온 및 2ppm의 젤라틴을 각각 추가로 함유한 50℃의 전해액을 도 5에 나타낸 바와 같이 연속해서 전해조(4)에 공급한다. 구리는 60A/dm ^{2}의 전류 밀도로 음극 드럼(1)의 표면에 전착(침전)되며, 음극 드럼(1)으로부터 지속적으로 박리되어 35㎛ 두께의 전착 동박을 얻는다.

인장 강도, 연신율, 동박 전착면(매트면)상의 표면 프로파일 및 얻어진 동박의 염화물의 양을 측정한다.

결과를 표 1에 나타낸다.

얻어진 동박의 결정 구조를 SIM 관찰을 통하여 평가한다. 그 결과, 쌍정 조직을 다량 함유하는 것이 발견되었다.

제2 실시예 및 제3 실시예와 제1 비교예 내지 제3 비교예제2 실시예 및 제3 실시예와 제1 비교예 내지 제3 비교예

전해액 중의 염화 이온 농도가 표 1에 나타낸 바와 같이 변경되는 것을 제외하고, 전착 동박을 제1 실시예에 나타낸 방법과 같은 방법으로 제조하여 평가한다.

또한, 결과를 표 1에 나타낸다.

	전해액중의 염소 농도	인장 강도 (kg/㎟)	연신율(%)	매트면의 표면 거칠기(Rz)(㎛)	구리의 결정 구조	동박중의 염소농도	동박중의 염소 농도 /전해액중의 염소 농도
제1 실시예	2.7	61.7	7.1	4.32	쌍정 + 미세 결정	110	40.7
제2 실시예	1.5	52.3	11.5	3.14	쌍정 + 미세 결정	180	120
제3 실시예	1.1	55.2	8.3	2.74	쌍정 + 미세 결정	66	60
제1 비교예	0.6	53.7	6.3	3.26	미세 결정	23	38
제2 비교예	0.2	49.3	6.5	6.84	미세 결정	17	85
제3 비교예	20	35.0	7.1	8.32	주상정 결정	7	0.35

표 1에 명확히 나타낸 바와 같이, 전해액 중의 염화 이온 농도를 1ppm~3ppm으로 조정함으로써 인장 강도 및 연신율이 큰 전착 동박을 얻을 수 있다.

도 6(a) 내지 도 6(d)는 전해액의 염화 이온 농도가 변경된 것을 제외하고는 제1 실시예와 같은 방법으로 제조한 전착 동박의 SEM 사진이다. 전해액중의 염화 이온 농도가 각각 도 6(a)는 0.8ppm인 경우, 도 6(b)는 1.2 ppm인 경우, 도 6(c)는 2.8ppm인 경우, 도 6(d)는 3.2ppm인 경우를 나타낸다.

이러한 도 6(a) 내지 도 6(d)로부터 명백해지는 바와 같이, 본 발명의 전착 동박은 도 6(b) 및 도 6(c)에 나타낸 것처럼 균일한 표면을 가진다. 한편, 1ppm 미만 또는 3ppm이상의 염화 이온 농도를 가진 전해액을 사용하여 얻어진 전착 동박은 도 6(a) 및 도 6(d)에 나타낸 바와 같이 다량의 원추형 요철을 지닌다.

발명의 효과

본 발명의 방법에 따르면, 1ppm~3ppm의 염화 이온 농도, 65g/L~85g/L의 구리 농도, 100g/L~250g/L의 유리 황산 농도, 0.3ppm~5ppm의 젤라틴 첨가제 농도를 지닌 전해액을 사용하여 30A/dm ^{2} ~75A/dm^2 의 전류 밀도로 40℃~60℃에서 전기 분해함으로써 인장 강도 및 연신율 등의 기계적 특성이 우수한 전착 동박을 제조할 수 있다. 따라서 얻어진 전착 동박은 특히 인쇄 배선판용 동박 또는 리튬 이온 2차 전지 등의 2차 전지용 집전기로서 사용하는 데 적합하다.

본 발명의 전착 동박은 인장 강도 및 연신율 등의 특성이 우수하다. 전착 동박은 특히 인쇄 배선용 동박 또는 리튬 이온 2차 전지 등의 2차 전지용 집전기로 사용하는 데 적합하다.

(57) 청구의 범위

청구항 1.

구리 농도가 60g/L~85g/L의 범위이고, 유리(遊離) 황산 농도가 100g/L~250g/L의 범위이며, 염화(Cl) 이온 농도가 1ppm~3ppm의 범위이고, 젤라틴계 첨가제의 농도가 0.3ppm~5ppm의 범위인 전해액을 마련하는 단계, 및

30A/dm^2 ~75A/dm^2 의 전류 밀도로 40~60℃에서 상기 전해액을 전기 분해하여 동박을 전착하는 단계

를 포함하는 전착 동박(electrodeposited copper foil) 제조 방법.

청구항 2.

제1항에서,

상기 전착 동박은,

미세 결정 및/또는 주상정(柱狀晶) 결정을 지닌 쌍정 조직 및

상기 쌍정 조직 속에 수용된 염화 이온 또는 염화물

을 포함하고,

상기 전착 동박중의 상기 염화물의 양은 50ppm～180ppm의 범위이고, 상기 전해액중의 염화 이온 농도의 40～150배인 전착 동박 제조 방법.

청구항 3.

제1항에서,

상기 전착 동박의 매트(matte)면의 표면 거칠기(Rz)는 2.0㎛～5.0㎛의 범위인 전착 동박 제조 방법.

청구항 4.

미세 결정 및/또는 주상정(柱狀晶) 결정을 지닌 쌍정 조직 및

상기 쌍정 조직 속에 수용된 염화물 또는 염화 이온

을 포함하고,

상기 전착 동박중의 염화물의 양은 50ppm～180ppm의 범위이고, 전해액 중 염화 이온 농도의 40～150배인 전착 동박.

청구항 5.

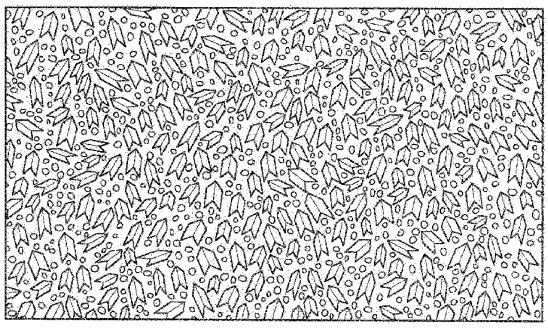
적어도 한 면이 제4항의 전착 동박으로 적층된 절연 기판을 포함하는 동장 적층판(copper-clad laminate).

청구항 6.

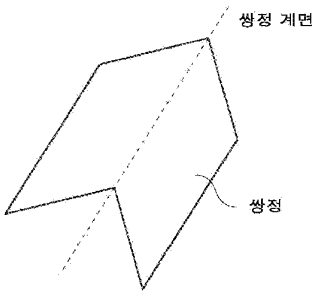
제5항의 동장 적층판상의 전착 동박을 에칭하여 제조한 소정의 배선 패턴을 구비한 인쇄 배선판.

도면

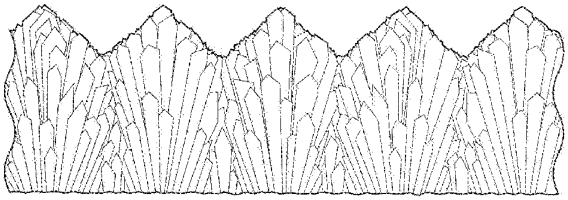
도면 1



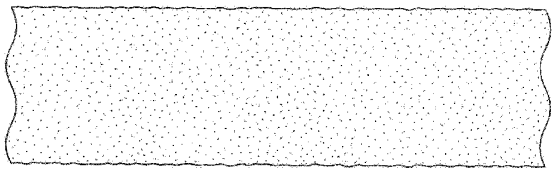
도면 2



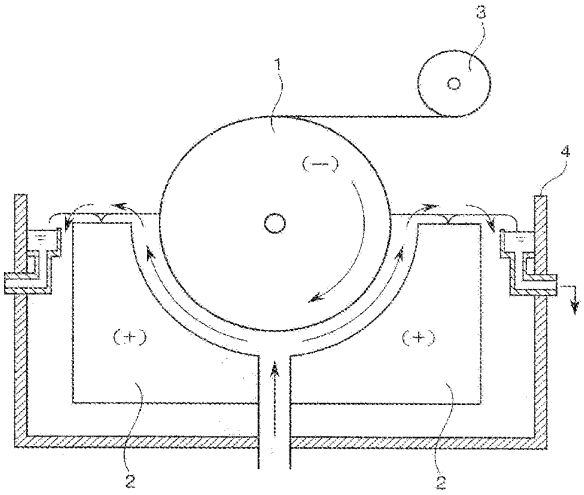
도면 3



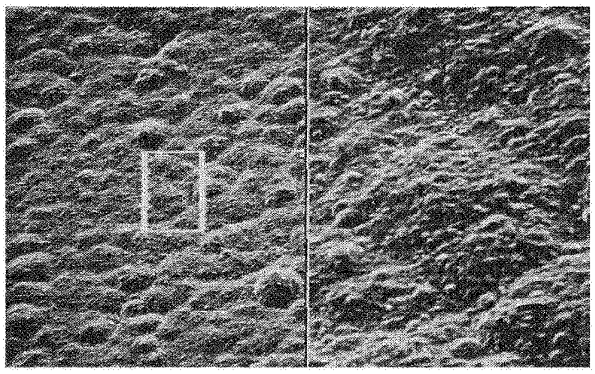
도면 4



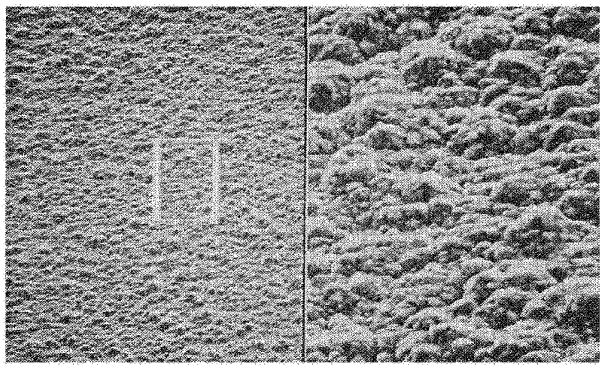
도면 5



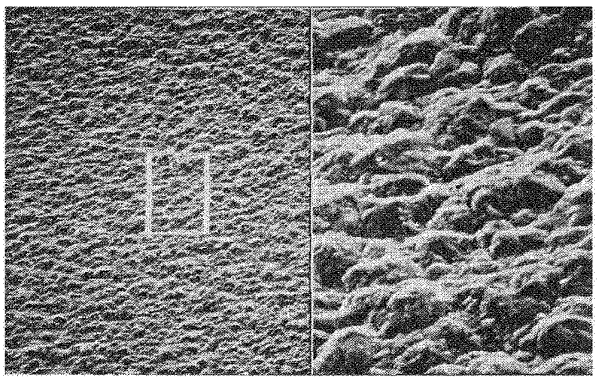
도면 6a



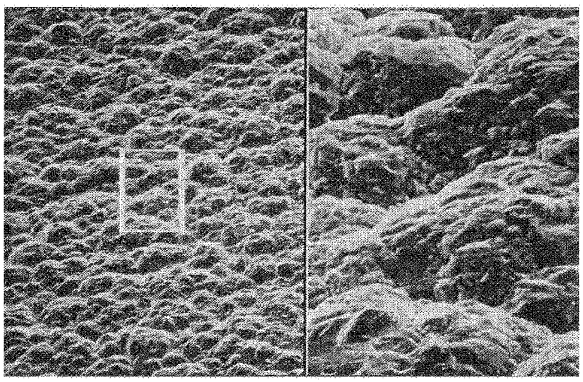
도면 6b



도면 6c

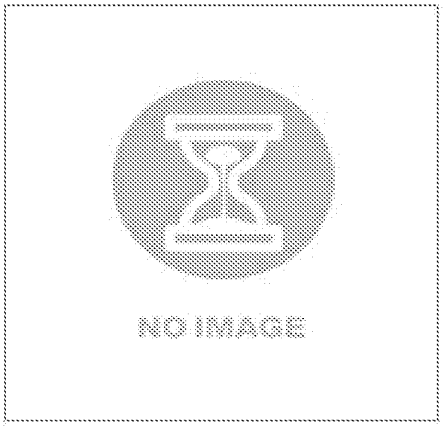


도면 6a



ELECTROLYTIC COPPER FOIL, AND METHOD OF MANUFACTURING THE SAME

(11) Publication No.	1020020012118 A
(43) Publication Date	15.02.2002
(21) Application No.	1020010042844
(22) Application Date	16.07.2001
(30) Priority	04.08.2000 JP 2000 2000237405
(51) Int. Cl.	C25D1/04(01.01.2006)
(52) CPC ⓒ	
(71) Applicant	MITSUI MINING & SMELTING CO., LTD.
(72) Inventor	HIRASAWA YUTAKA TAKAHASHI NAOTOM
Repr. Drawing	

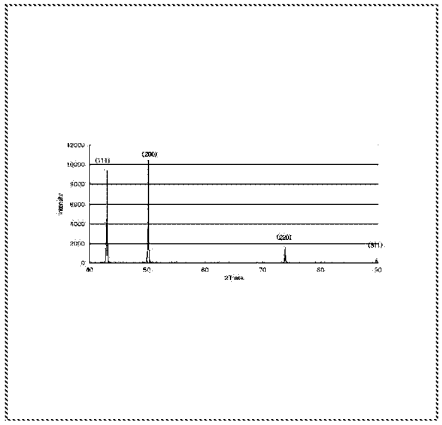


Zoom

Abstract PURPOSE: To provide an electrolytic copper foil having an excellent tensile strength and elongation rate, and a method of manufacturing the same. CONSTITUTION: A twin crystal structure exists in this electrolytic copper foil and chlorine is taken into this twin crystal structure. The concentration of the chlorine included in the copper foil is 50 to 180 ppm. This method of manufacturing the electrolytic copper foil consists of manufacturing the electrolytic copper foil at a liquid temperature of 40 to 60°C and electrolytic current density of 30 to 75 A/dm2 by using an electrolyte which has a copper concentration within the range from 60 to 85 g/L, a sulfuric acid concentration within the range from 100 to 250 g/L, contains chloride ions in an amount of 1 to 3 ppm and is prepared by being added with a gelatin-based additive at an amount of 0.3 to 5 ppm. copyright KIPO & JPO 2002

COPPER FOIL FOR A CURRENT COLLECTOR OF A LITHIUM SECONDARY BATTERY WITH THE IMPROVED WRINKLE PROPERTY, CAPABLE OF PREVENTING THE GENERATION OF A SHORT CIRCUIT

(11) Publication No.	1020100125044 A
(43) Publication Date	30.11.2010
(21) Application No.	1020090044044
(22) Application Date	20.05.2009
(51) Int. CL	H01M4/66(01.01.2006) H01M10/36(01.01.2006)
(52) CPC	
(71) Applicant	LS MTRON LTD.
(72) Inventor	KIM, DAE YOUNG LEE, BYOUNG KWANG CHOI, SEUNG JUN
Repr. Drawing	



Zoom

Abstract PURPOSE: A copper foil for a current collector of a lithium secondary battery is provided to optimize the surface roughness, the weight deflection, the tensile strength, the elongation rate, and the thickness of the foil.CONSTITUTION: A copper foil for a current collector of a lithium secondary battery has 60~85% of the sum rate of the texture coefficient for a first surface(111) and a second surface(200), among the total sum rate of the texture coefficient of the first surface, the second surface, and a third surface(220), in a crystal structure. The surface roughness of the copper foil is less than 2 microns.COPYRIGHT KIPO 2011

Electronic Patent Application Fee Transmittal	
Application Number:	
Filing Date:	
Title of Invention:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Seung Min KIM
Filer:	Taeksoo Lee
Attorney Docket Number:	P11491US

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
UTILITY APPLICATION FILING	1011	1	280	280
UTILITY SEARCH FEE	1111	1	600	600
UTILITY EXAMINATION FEE	1311	1	720	720
Pages:				
Claims:				
INDEPENDENT CLAIMS IN EXCESS OF 3	1201	1	420	420
Miscellaneous-Filing:				
Petition:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**2020**

Electronic Acknowledgement Receipt	
EFS ID:	30280136
Application Number:	15696360
International Application Number:	
Confirmation Number:	7466
Title of Invention:	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Seung Min KIM
Customer Number:	86144
Filer:	Taeksoo Lee
Filer Authorized By:	
Attorney Docket Number:	P11491US
Receipt Date:	06-SEP-2017
Filing Date:	
Time Stamp:	12:01:07
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$2020
RAM confirmation Number	090617INTEFSW12013900
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	Application Data Sheet	P11491_ads.pdf	1822491 bb9d6d7429864381d09196c38f31fae1844af094	no	8
Warnings:					
Information:					
2	Oath or Declaration filed	P11491_dec.pdf	96364 676a686ef2502b24315bfc909256016da1def1a0	no	2
Warnings:					
The page size in the PDF is too large. The pages should be 8.5 x 11 or A4. If this PDF is submitted, the pages will be resized upon entry into the Image File Wrapper and may affect subsequent processing					
Information:					
3	Information Disclosure Statement (IDS) Form (SB08)	P11491_ids.pdf	1034737 5168625299a15571c111aaede1afa616b923bc13	no	4
Warnings:					
Information:					
A U.S. Patent Number Citation or a U.S. Publication Number Citation is required in the Information Disclosure Statement (IDS) form for autoloading of data into USPTO systems. You may remove the form to add the required data in order to correct the Informational Message if you are citing U.S. References. If you chose not to include U.S. References, the image of the form will be processed and be made available within the Image File Wrapper (IFW) system. However, no data will be extracted from this form. Any additional data such as Foreign Patent Documents or Non Patent Literature will be manually reviewed and keyed into USPTO systems.					
4	Power of Attorney	P11491_poa.pdf	1423212 2337689ef2fc454d4fde6e65695fe7af7dd03aa3	no	3
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	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	

	Specification		1	24	
	Claims		25	30	
	Abstract		31	31	
Warnings:					
Information:					
6	Drawings-only black and white line drawings	FIGS.pdf	100496 f5dfd72c7115a77227bff536178cd50bdcf239c5	no	1
Warnings:					
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7	Foreign Reference	JP2012022939.pdf	251287 daaed8419bc9842eba2268362c93ba20f1df26c3	no	8
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8	Foreign Reference	KR1020100125044.pdf	653504 a478636a352d70dbfd0d5b1f48e287b2909e8125	no	6
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9	Foreign Reference	JP2012022939_EN.pdf	158334 283b71d02eeb306df7bc1aa891120ff3f27a520c	no	1
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10	Foreign Reference	KR1020020012118.pdf	6259650 dc1c04fd2ebca5332e442a97d9034f15f3853715	no	13
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12	Foreign Reference	KR1020100125044_EN.pdf	594332 db79597d9be1f8407130153086 9fb6592a79e8d5	no	1
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13	Fee Worksheet (SB06)	fee-info.pdf	36572 734500ee921abd8a7f2cadc6d21b78f7030458bc	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	12946902		

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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.

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. 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 contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	P11491US
	Application Number	
Title of Invention	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME	

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.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

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.)

Inventor Information:

Inventor 1 — Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Seung Min		KIM	

Residence Information (Select One) US Residency ● Non US Residency Active US Military Service

City	Anyang-si	Country of Residence [i]	KR

Mailing Address of Inventor:

Address 1	127, LS-ro, Dongan-gu		
Address 2			
City	Anyang-si, Gyeonggi-do	**State/Province**	
Postal Code	14119	**Country** [i]	KR

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	86144		
Email Address	mail@lrkpatent.com	Add Email	Remove Email

Application Information:

Title of the Invention	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME		
Attorney Docket Number	P11491US	**Small Entity Status Claimed**	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)		**Suggested Figure for Publication (if any)**	

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. 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 contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	P11491US
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Title of Invention	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME	

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	● Customer Number	US Patent Practitioner	◯ Limited Recognition (37 CFR 11.9)
Customer Number	86144		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the "Application Number" field blank.

Prior Application Status			Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button. Add

PTO/AIA/14 (11-15)
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	P11491US
	Application Number	
Title of Invention	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME	

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
10-2016-0131979	KR	2016-10-12	

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button. Add

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

PTO/AIA/14 (11-15)
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Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is 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 State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

PTO/AIA/14 (11-15)
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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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	Application Number	
Title of Invention	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME	

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1 Remove

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. ☒

Organization Name	LS Mtron Ltd.		
Mailing Address Information For Applicant:			
Address 1	127, LS-ro, Dongan-gu		
Address 2			
City	Anyang-si, Gyeonggi-do	**State/Province**	
Country	KR	Postal Code	14119
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button. Add

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

PTO/AIA/14 (11-15)
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Title of Invention	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME	

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

Remove

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		**State/Province**	
Country i		Postal Code	
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button. Add

Signature:

Remove

NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is a **juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	/Taeksoo Lee/			Date (YYYY-MM-DD)	2017-09-06
First Name	Taeksoo	Last Name	Lee	Registration Number	61976

Additional Signature may be generated within this form by selecting the Add button. Add

PTO/AIA/14 (11-15)
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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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This collection of information is required by 37 CFR 1.76. 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 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet 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.**

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 CooperationTreaty.

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.

PTO/AIA/01 (06-12)
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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	EASILY HANDLEABLE ELECTROLYTIC COPPER FOIL, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

As the below named inventor, I hereby declare that:

This declaration is directed to:

- [■] The attached application, or
- [ ] United States application or PCT international application number _____

  filed on _____.

The above-identified application was made or authorized to be made by me.

I believe that 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.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Seung Min KIM Date (Optional): 2019. 9. 1

Signature: _____

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

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 1 minute 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).
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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.
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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.

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	
	Filing Date	
	First Named Inventor	Seung Min KIM
	Art Unit	
	Examiner Name	
	Attorney Docket Number	P11491US

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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
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	1	10-2002-0012118	KR	A	2002-02-15	MITSUI MINING & SMELTING CO., LTD.		☒
	2	10-2010-0125044	KR	A	2010-11-30	LS MTRON LTD		☒
	3	2012-022939	JP	A	2012-02-02	LS MTRON LTD		☒

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Seung Min KIM
	Art Unit	
	Examiner Name	
	Attorney Docket Number	P11491US

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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		
If you wish to add additional non-patent literature document citation information please click the Add button			Add

EXAMINER SIGNATURE			
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	Seung Min KIM
	Art Unit	
	Examiner Name	
	Attorney Docket Number	P11491US

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	/Taeksoo Lee/	Date (YYYY-MM-DD)	2017-09-06
Name/Print	Taeksoo Lee	Registration Number	61976

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.**

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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 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.

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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.