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
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APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/307,069	11/19/2019	10480090	0313221.00005	9113

24573 7590 10/30/2019

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

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

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

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

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

LS Mtron Ltd., Anyang-si, Gyeonggi-do, KOREA, REPUBLIC OF;
Dae Young KIM, Yongin-si, KOREA, REPUBLIC OF;
Seung Min KIM, Osan-si, KOREA, REPUBLIC OF;

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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
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	
	Filing Date	
	First Named Inventor	Dae Young KIM
	Art Unit	
	Examiner Name	
	Attorney Docket Number	P11304US

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

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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
Change(s) applied to document, /C.H.J./ 8/2/2019	1	20150340639	A1	2015-11-26	MITSUI MINING & SMELTING CO., LTD	Matsuura
	2	20160260981	A1	2016-09-08	ILJIN MATERIALS CO., LTD	Lee et al.
	3	20140193660	A1	2014-07-10	CHANG CHUN PETROCHEMICAL CO., LTD.	Tsai et al.
	4	20010051282	A1	2001-12-13	Charles B. YATES 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]

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /AU/

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/307,069	10/27/2016	Dae Young KIM	0313221.00005	9113

24573 7590 10/28/2019

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

EXAMINER	
USYATINSKY, ALEXANDER	

ART UNIT	PAPER NUMBER
1727	

NOTIFICATION DATE	DELIVERY MODE
10/28/2019	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

Response to Rule 312 Communication	Application No. 15/307,069	Applicant(s)
	Examiner	Art Unit

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

1. ☒ The amendment filed on *27 September 2019* under 37 CFR 1.312 has been considered, and has been:

a) ☒ entered.

b) ☐ entered as directed to matters of form not affecting the scope of the invention.

c) ☐ disapproved because the amendment was filed after the payment of the issue fee.
Any amendment filed after the date the issue fee is paid must be accompanied by a petition under 37 CFR 1.313(c)(1) and the required fee to withdraw the application from issue.

d) ☐ disapproved. See explanation below.

e) ☐ entered in part. See explanation below.

Kimberly Payne

PUBLISHING DIVISION

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/307,069	10/27/2016	Dae Young KIM	0313221.00005	9113

24573 7590 08.06/2019

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

EXAMINER
USYATINSKY, ALEXANDER

ART UNIT	PAPER NUMBER
1727	

NOTIFICATION DATE	DELIVERY MODE
08/06/2019	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):

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UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents
United States Patent and Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450
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Application No. : 15307069
Applicant : Kim
Filing Date : 10/27/2016
Date Mailed : 08/06/2019

NOTICE TO FILE CORRECTED APPLICATION PAPERS

Notice of Allowance Mailed

This application has been accorded an Allowance Date and is being prepared for issuance. The application, however, is incomplete for the reasons below.

Applicant is given two (2) months from the mail date of this Notice within which to respond. This time period for reply is extendable under 37 CFR 1.136(a) for only TWO additional MONTHS.

The informalities requiring correction are indicated in the attachment(s). If the informality pertains to the abstract, specification (including claims) or drawings, the informality must be corrected with an amendment in compliance with 37 CFR 1.121 (or, if the application is a reissue application, 37 CFR 1.173). Such an amendment may be filed after payment of the issue fee if limited to correction of informalities noted herein. See Waiver of 37 CFR 1.312 for Documents Required by the Office of Patent Publication, 1280 Off. Gaz. Patent Office 918 (March 23, 2004). In addition, if the informality is not corrected until after payment of the issue fee, for purposes of 35 U.S.C. 154(b)(1)(iv), "all outstanding requirements" will be considered to have been satisfied when the informality has been corrected. A failure to respond within the above-identified time period will result in the application being ABANDONED.

See attachment(s).

A copy of this notice MUST be returned with the reply. Please address response to "Mail Stop Issue Fee, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450".

/Chris Harmon/
Publication Branch
Office of Data Management
(571) 272-4200

Application No. 15307069

IDENTIFICATION OF APPLICATION DEFICIENCIES IN APPLICATION FILED ON OR AFTER SEPTEMBER 16, 2012

[X] Applicant must provide legible text for the following item(s).

- [X] Specification filed 10/27/2016, page(s) 7 line 13.
- [ ] Claims filed , claim(s) .
- [ ] Other: .

[ ] Applicant must provide missing information on the following page(s) of the specification by amending the specification to add the missing text. No new matter may be added.
Page/line no(s).

[ ] The specification refers to one or more applications by attorney docket number and does not show the U.S. application number(s). Applicant must supply the U.S. application number in place of each attorney docket number.
Page/line no(s).

[ ] Applicant must provide an Abstract of the Disclosure.

[ ] The Application Data Sheet (ADS dated) does not supply the inventor's city and/or does not supply the inventor's U.S. state and/or does not supply the inventor's country. Applicant must submit a signed, in accordance with 37 CFR 1.76(e) and 1.33(b), application data sheet that corrects this deficiency. To be in compliance with 37 CFR 1.76, the corrected application data sheet must identify the information being changed by using underlining for additions and strikethroughs or brackets for deletions.

[ ] Other:

ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an electrolytic copper foil, a current collector including the same, an electrode including the same, a secondary battery including the same, and a method for manufacturing the same.

2. Description of Related Art

Secondary batteries are energy conversion devices which are capable of storing electrical energy in chemical form and of converting into electrical energy to generate electricity when needed. They are also called "rechargeable batteries" because they can be charged repeatedly.

Secondary batteries are more economically and environmentally advantageous than single-use primary batteries and include lead storage batteries, nickel cadmium secondary batteries, nickel hydride secondary batteries, lithium secondary batteries and the like.

Lithium secondary batteries can store greater energy relative to size and weight, as compared to other secondary batteries. Accordingly, lithium secondary batteries are preferred in the field of information communicative apparatuses which require portability and mobility as essential factors and have an extended applicability as energy storage devices for hybrid cars and electric cars.

Lithium secondary batteries are repeatedly used in each cycle including charge

and discharge. When a certain device is operated with a completely charged lithium secondary battery, the lithium ion secondary battery should have a high charge/discharge capacity in order to increase an operation time of the device. Accordingly, there is a continuous demand for research to satisfy users' increasing needs for charge/discharge capacity of lithium secondary batteries.

Meanwhile, although secondary batteries have a sufficiently high charge/discharge capacity, when charge/discharge capacity of the secondary batteries is rapidly decreased (that is, when capacity maintenance is low or lifespan is short) with repeated charge/discharge cycles, users frequently need to change secondary batteries, causing users' discomfort and energy waste.

SUMMARY OF THE INVENTION

Therefore, the present invention is directed to an electrolytic copper foil, a current collector including the same, an electrode including the same, a secondary battery including the same and a method of producing the same capable of preventing these limitations and drawbacks of the related art.

An aspect of the present invention is to provide an electrolytic copper foil which is capable of securing a secondary battery with high capacity maintenance.

Another aspect of the present invention is to provide a current collector which is capable of securing a secondary battery with high capacity maintenance.

Further another aspect of the present invention is to provide an electrode which is capable of securing a secondary battery with high capacity maintenance.

Further another aspect of the present invention is to provide a secondary battery with high capacity maintenance.

Yet another aspect of the present invention is to provide a method of producing

an electrolytic copper foil which is capable of securing a secondary battery with high capacity maintenance.

Additional aspects and features of the present invention will be set forth in part in the description which follows and in part will become apparent to those having ordinary skill in the art upon examination of the following or may be learned from practice of the invention. The objectives and other advantages of the invention may be realized and attained by the structure particularly pointed out in the written description and claims.

In accordance with the one aspect of the present invention, there is provided an electrolytic copper foil for a secondary battery, the electrolytic copper foil comprising a first surface and a second surface opposite to the first surface, wherein each of the first and second surfaces has a peak count roughness R_{pc} of 10 to 100, wherein the peak count roughness R_{pc} of each of the first and second surfaces is an average of peak count roughness R_{pc} values measured at randomly-selected three points, the peak count roughness R_{pc} of each point is the number of effective peaks which rise above an upper criteria line of 0.5 μm per unit sampling length of 4 mm in a surface roughness profile obtained according to steel-iron test schedule (SEP 1940), and there is at least one valley deeper than a lower criteria line of -0.5 μm between adjacent ones of the effective peaks.

In accordance with another aspect of the present invention, there is provided a current collector for a secondary battery, the current collector comprising an electrolytic copper foil having a first surface and a second surface, each having a peak count roughness R_{pc} of 10 to 100 and a protective layer disposed on the electrolytic copper foil, wherein the protective layer includes at least one of chromate, benzotriazole and a silane compound.

In accordance with further another aspect of the present invention, there is provided an electrode for a secondary battery, the electrode comprising a current

collector having a first surface and a second surface, each having a peak count roughness R_{pc} of 10 to 100, and an active material layer disposed on the current collector, wherein the active material layer includes at least one active material selected from the group consisting of: carbon; metal (Me) of Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni or Fe; an alloy containing the metal; an oxide of the metal (MeO_x); and a complex of the metal and carbon.

In accordance with further another aspect of the present invention, there is provided a secondary battery including a cathode, an anode, an electrolyte for providing an environment enabling the lithium ions to move between the cathode and the anode, and a separator for electrically insulating the cathode from the anode, wherein the anode includes a current collector a current collector having a first surface and a second surface, each having a peak count roughness R_{pc} of 10 to 100, and an active material layer disposed on the current collector.

In accordance with yet another aspect of the present invention, there is provided a method of producing an electrolytic copper foil by allowing a current to flow between a cathode plate and a rotational anode drum spaced from each other in an electrolytic solution so as to electrodeposit a copper on the rotational anode drum, the method comprising heat-treating a copper wire, acid-cleaning the heat-treated copper wire, dipping the acid-cleaned copper wire in the electrolytic solution, conducting electroplating, while the copper wire is dipped in the electrolytic solution, by allowing a current to flow between the cathode plate and the rotational anode drum, and conducting continuous filtration to remove solid impurities from the electrolytic solution during the electroplating.

General description related to the present invention given above serves to illustrate or disclose the present invention and should not be construed as limiting the

scope of the present invention.

ADVANTAGEOUS EFFECTS

According to the present invention, long-lifespan secondary batteries which are capable of maintaining high charge/discharge capacity for a long time in spite of repetition of charge/discharge cycles can be produced. Accordingly, electronic product consumers' discomfort and energy waste resulting from frequent change of secondary batteries can be minimized.

BRIEF DESCRIPTION OF DRAWINGS

The accompanying drawings, which are included to provide a further understanding of the invention and are incorporated in and constitute a part of this application, illustrate embodiment(s) of the invention and together with the description serve to explain the principle of the invention. In the drawings:

FIG. 1 is a sectional view of an electrode for a secondary battery according to an embodiment of the present invention; and

FIG. 2 illustrates a surface roughness profile obtained according to steel-iron test schedule (SEP 1940) specification.

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, embodiments according to the present invention will be described in detail with reference to the annexed drawings.

Those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims. Accordingly, the present invention includes

modifications and alterations which fall within the scope of inventions as claimed and equivalents thereto.

A lithium ion secondary battery includes a cathode, an anode, an electrolyte for providing an environment enabling the lithium ions to move between the cathode and the anode, and a separator for electrically insulating the cathode from the anode to prevent unnecessary consumption of electrons because of movement of electrons generated in one electrode to the other electrode.

FIG. 1 is a sectional view of an electrode for secondary batteries according to an embodiment of the present invention.

As shown in FIG. 1, the electrode for secondary batteries 100 according to an embodiment of the present invention includes a current collector 110 and an active material layer 120. FIG. 1 illustrates the active material layer 120 which is formed on both of the upper and lower surfaces of the current collector 110, but the present invention is not limited thereto and the active material layer 120 may be formed only on one surface of the current collector 110.

In general, in a lithium secondary battery, an aluminum foil is used as a cathode current collector coupled to a cathode active material and a copper foil is used as an anode current collector coupled to an anode active material.

According to an embodiment of the present invention, the electrode for secondary batteries 100 is an anode, the current collector 110 is an anode current collector and the active material layer 120 includes an anode active material.

The current collector 110 of the present invention which is an anode current collector, includes an electrolytic copper foil 111 having a thickness of 3 to 20 μm and a tensile strength of 30 to 60 kgf/mm^2. In addition, as shown in FIG. 1, the current collector 110 may further include a protective layer 112 disposed on the electrolytic

copper foil 111. FIG. 1 illustrates the protective layer 112 which is formed on both of the upper and lower surfaces of electrolytic copper foil 111, but the present invention is not limited thereto and the protective layer 112 may be formed only on one surface of the electrolytic copper foil 111.

The electrolytic copper foil 111 of the present invention may be formed on a rotational anode drum by electroplating, thereby having a first surface (also called a "shiny surface") 111a which contacts the rotational anode drum in the process of electroplating and a second surface (also called a "matte surface") 111b opposite to the first surface.

In general, the shiny surface 111a has a lower roughness than the matte surface 111b, but the present invention is not limited thereto and the shiny surface 111a may have a roughness equal to or higher than the matte surface 111b. Here, roughness of the shiny surface 111a and the matte surface 111b means a ten-point mean roughness (R_{zJIS})

The active material layer 120 contains, as an anode active material, at least one active material selected from the group consisting of: carbon; metal (Me) of Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni or Fe; an alloy containing the metal; an oxide of the metal (MeO_x); and a complex of the metal and carbon.

In order to increase charge/discharge capacity of secondary batteries, the active material layer 120 may be formed using a mixture of anode active materials containing a predetermined amount of Si.

Meanwhile, as a result of repeated charge/discharge of secondary batteries, the active material layer 120 alternately contracts and expands, which induces separation of the active material layer 120 from the current collector 110, causing deterioration in charge/discharge efficiency of secondary batteries. Accordingly, in order for the secondary electrodes to secure predetermined levels of capacity maintenance and lifespan

(that is, in order to prevent deterioration in charge/discharge efficiency of secondary batteries), the current collector 110 should have excellent coatability to the active material so that adhesion strength between the current collector 110 and the active material layer 120 can be increased.

In a broad sense, as the ten-point mean roughness R_{zJIS} of the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 decreases, deterioration in charge/discharge efficiency of the secondary battery including the current collector 110 decreases.

Accordingly, each of the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 according to an embodiment of the present invention has a ten-point mean roughness R_{zJIS} of 2 μm or less. When the shiny surface 111a or the matte surface 111b has a ten-point mean roughness R_{zJIS} exceeding 2 μm, contact uniformity between the current collector 110 and the active material layer 120 does not reach a desired level and the secondary battery thus cannot satisfy a capacity maintenance of 90% or higher required in the art.

However, the present applicant found that an electrolytic copper foil 111 the shiny surface 111a and the matte surface 111b of which have a ten-point mean roughness R_{zJIS} of 2 μm or less does not always secure capacity maintenance of the secondary battery, of 90% or higher. That is, a low ten-point mean roughness R_{zJIS} (for example, 2 μm or less) of the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 cannot be a sufficient condition for capacity maintenance of the secondary battery of 90% or higher.

In particular, it was found that there is less correlation between the ten-point mean roughness R_{zJIS} of the electrolytic copper foil 111 and capacity maintenance of the secondary battery when the active material layer 120 contains Si for high capacity of the

secondary battery.

As a result of repeated research, the present applicant found that a peak count roughness R_{pc} of the electrolytic copper foil 111 is an important factor in stably securing capacity maintenance of 90% or higher.

Hereinafter, the peak count roughness R_{pc} of the electrolytic copper foil 111 will be described with reference to FIG. 2.

As used herein, the peak count roughness R_{pc} of each of the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 means an average of peak count roughness R_{pc} values obtained at three randomly-selected points, and the peak count roughness R_{pc} of each point is the number of effective peaks P_1, P_2, P_3 and P_4 which rise above an upper criteria line C1 of 0.5 μm per unit sampling length of 4 mm in the surface roughness profile obtained according to steel-iron test schedule (SEP 1940). In this case, there is at least one valley deeper than a lower criteria line C2 of -0.5 μm between adjacent ones of the effective peaks. If there is no valley deeper than the lower criteria line C2 of -0.5 μm between adjacent peaks rising above the upper criteria line C1, all of the adjacent peaks cannot be "effective peaks" used for measurement of the peak count roughness R_{pc} and relatively lower one is excluded in determining the number of "effective peaks".

According to the present invention, the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 have a peak count roughness R_{pc} of 10 to 100, respectively.

When the peak count roughness R_{pc} is less than 10, capacity maintenance of the secondary battery is deteriorated. This is because the stress caused during the charge/discharge of the secondary battery is concentrated on mountains which locally protrude.

Furthermore, when the peak count roughness R_{pc} exceeds 100, capacity maintenance of the secondary battery is also deteriorated. This is because the active material cannot be uniformly coated on the electrolytic copper foil 111 due to the excessive number of mountains.

The difference in peak count roughness R_{pc} between the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 is preferably 60 or less because, according to an embodiment of the present invention, both surfaces of the current collector 110 are coated with the active material. When the difference in the peak count roughness R_{pc} exceeds 60, capacity maintenance of the secondary battery is deteriorated due to difference in surface appearance between both surfaces 111a and 111b.

As described above, the current collector 110 for secondary batteries of the present invention may further include a protective layer 112 on the electrolytic copper foil 111. The protective layer 112 may be formed by anticorrosion treatment of the electrolytic copper foil 111. That is, the electrolytic copper foil 111 of the present invention may be used as the current collector, but is preferably subjected to anticorrosion treatment using chromate, benzotriazole and/or a silane compound. The anticorrosion treatment prevents corrosion of the electrolytic copper foil 111, improves heat resistance and enhances adhesive strength to the active material layer 120, thus inhibiting deterioration in charge/discharge efficiency of secondary batteries.

Hereinafter, a method of producing an electrolytic copper foil according to an embodiment of the present invention will be described in detail.

A deposition machine used for producing the electrolytic copper foil 111 includes an electrolytic bath containing an electrolytic solution, and a rotational anode drum and a cathode plate spaced from each other in the electrolytic solution.

The electrolytic copper foil 111 is produced by adding a small amount of organic

additive such as hydroxyethyl cellulose (HEC), organic sulfide, organic nitride, and/or thiourea-based compound to an electrolytic solution containing 50 to 100 g/L of a copper ion, 50 to 150 g/L of sulfuric acid and 50 ppm or less of chlorine ions, and then depositing copper on the surface of the rotational anode drum at a current density of 10 to 80 A/dm^2 at 40 to 60℃.

The ten-point mean roughness R_{zJIS} and the peak count roughness R_{pc} of the shiny surface 111a of the electrolytic copper foil 111 depend on a polishing level of the surface of the rotational anode drum (the surface on which copper is deposited by electroplating).

According to the present invention, in order for the shiny surface 111a to have a peak count roughness R_{pc} of 10 to 100 and a ten-point mean roughness R_{zJIS} of 2 μm or less, the surface of the rotational anode drum is polished with a #800 to #1500 grit polishing brush.

The ten-point mean roughness R_{zJIS} and the peak count roughness R_{pc} of the matte surface 111b of the electrolytic copper foil 111 depend on the composition of the electrolytic solution (particularly, concentrations of organic impurities and metal impurities), used for electroplating, the current density of electroplating and the like.

According to the present invention, in order for the matte surface 111b to have a peak count roughness R_{pc} of 10 to 100 and a ten-point mean roughness R_{zJIS} of 2 μm or less, the concentrations of organic impurities and metal impurities in the electrolytic solution are controlled to 1 g/L or less and 10 g/L or less, respectively, and the electroplating is conducted at a current density of 10 to 80 A/dm^2.

In addition, according to the present invention, in order to control concentrations of organic impurities and metal impurities in the electrolytic solution controlled to 1 g/L or less and 10 g/L or less, respectively, organic substances are burned by thermal treatment at a high temperature of 600 to 800℃ (for example, about 700℃) and then

cleaned with an acid before addition of a highly pure copper wire to the electrolytic solution. In addition, continuous filtration is performed to remove solid impurities including organic impurities and metal impurities from the electrolytic solution during electroplating, thereby maintaining concentrations of organic impurities and metal impurities in the electrolytic solution at 1 g/L or less and at 10 g/L or less, respectively.

Subsequently, a protective layer 112 is formed on the shiny surface 111a and/or the matte surface 111b of the electrolytic copper foil 111 by anticorrosion treatment using chromate, benzotriazole (BTA) and/or a silane compound, thereby producing the current collector 110 of the present invention.

For example, the protective layer 112 can be formed by dipping the electrolytic copper foil 111 in 1 to 10 g/L of a potassium dichromate solution at room temperature for 2 to 20 seconds.

Subsequently, the current collector 110 is coated with at least one active material selected from the group consisting of: carbon; metal (Me) of Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni or Fe; an alloy containing the metal (Me); oxides of the metal (Me) (MeO_x); and a complex of the metal (Me), to produce an electrode (that is, anode) for secondary batteries of the present invention.

For example, 100 parts by weight of carbon as an anode active material, 1 to 3 parts by weight of styrene butadiene rubber (SBR) and 1 to 3 parts by weight of carboxymethyl cellulose (CMC) are mixed and produced into a slurry using distilled water as a solvent. Subsequently, the slurry is applied to a thickness of 20 to 60 μm onto the current collector 110 using a doctor blade and pressed at 110 to 130℃ and at a pressure of 0.5 to 1.5 ton/cm^2.

A lithium secondary battery can be produced using the electrode (anode) for secondary batteries of the present invention produced by the method as described above,

in combination with an ordinary cathode, electrolyte and separator.

Hereinafter, the present invention will be described in more detail with reference to the following examples and comparative Examples. The following examples are only given for better understanding of the present invention and should not be construed as limiting the scope of the present invention.

* Production of Electrolytic copper foil

Examples 1 to 4 and Comparative Examples 1 to 4

Electrolytic copper foils were produced under the same conditions except that i) whether or not a copper wire was subjected to heat treatment and what the heat treatment temperature was, ii) whether or not continuous filtration is conducted during electroplating, and/or iii) the grit of polishing brush used for surface polishing of the rotational anode drum are changed as shown in the following Table 1.

Subsequently, the peak count roughness R_{pc} of the shiny surface and matte surface of the electrolytic copper foils was measured using a MahrSurf M300 roughness tester available from Mahr company and results are shown in the following Table 1.

As described above, the peak count roughness R_{pc} of the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 means an average of peak count roughness R_{pc} values obtained at three randomly-selected points, the peak count roughness R_{pc} of each point is the number of effective peaks which rise above an upper criteria line C1 of 0.5 μm per unit sampling length of 4 mm in the surface roughness profile obtained according to the steel-iron test schedule (SEP 1940).

If there is no valley deeper than a lower criteria line C2 of -0.5 μm between adjacent peaks rising above the upper criteria line C1, relatively lower one is excluded in

determining the number of "effective peaks".

TABLE 1

	Heat treatment temperature of copper wire (℃)	Whether continuous filtration is conducted	Grit of polishing brush (#)	R_{pc} of matte surface (count)	R_{pc} of shiny surface (count)	Difference in R_{pc} (count)
Ex. 1	720	○	1200	13	42	29
Ex. 2	700	○	1400	20	24	4
Ex. 3	680	○	800	39	98	59
Ex. 4	660	○	1000	98	89	9
Comp. Ex. 1	810	○	1600	8	9	1
Comp. Ex. 2	-	○	700	112	128	16
Comp. Ex. 3	-	×	1200	181	47	134
Comp. Ex. 4	670	○	600	47	139	92

* Production of secondary battery

Examples 5 to 8 and Comparative Examples 5 to 8

The electrolytic copper foils of Examples 1 to 4 and Comparative Examples 1 to 4 were dipped in 10 g/L of a potassium dichromate solution for 10 seconds to obtain current collectors including a protective layer formed on an electrolytic copper foil. Subsequently, 100 parts by weight of commercially available carbon as an anode active material was mixed with 2 parts by weight of SBR and 2 parts by weight of CMC, and a slurry was produced using distilled water as a solvent. The slurry was applied to a thickness of 50 μm on the current collectors having a width of 10 cm using a doctor blade, dried at 120℃ and pressed at a pressure of 1 ton/cm^2 to produce 8 anodes for secondary batteries.

8 secondary batteries were produced using the anodes for secondary batteries thus

produced in combination with an electrolytic solution and a cathode for secondary batteries. The electrolytic solution and the cathode were prepared as follows.

$LiPF_6$ as a solute was dissolved in a non-aqueous organic solvent containing a mixture of ethylene carbonate (EC) and ethylene methyl carbonate (EMC) in a ratio of 1:2 to prepare a 1M basic electrolytic solution, and 99.5% by weight of the basic electrolytic solution was mixed with 0.5% by weight of succinic anhydride, to prepare the electrolytic solution.

In addition, lithium manganese oxide ($Li_{1.1}Mn_{1.85}Al_{0.05}O_4$) was mixed with an orthorhombic crystal structure of lithium manganese oxide (o-$LiMnO_2$) in a weight ratio of 90:10 to produce a cathode active material. The cathode active material, carbon black and polyvinylidene fluoride (PVDF) as a binder were mixed in a weight ratio of 85:10:5 and was further mixed with NMP as an organic solvent to prepare a slurry. The slurry was applied onto opposite surfaces of an aluminum foil with a thickness of 20 μm, followed by drying to produce the cathode.

Capacity maintenance was measured for 8 secondary batteries of Examples 5 to 8 and Comparative Example 5 to 8 thus produced according to the following method and results are shown in Table 2.

* Discharge capacity maintenance of secondary battery

A capacity per weight (g) of the cathode was measured at a charge operating voltage of 4.3V and a discharge operating voltage of 3.4V, charge/discharge test was conducted 50 cycles at 50℃ and at a current density of 0.2C to evaluate high temperature lifespan, and discharge capacity maintenance was calculated in accordance with the following Equation 1:

Equation 1

Discharge capacity maintenance (%) = (50th discharge capacity/1st discharge capacity) × 100

For reference, the discharge capacity maintenance of secondary batteries required in the art is 90% or higher.

TABLE 2

	R_{pc} of matte surface of electrolytic copper foil (count)	R_{pc} of shiny surface of electrolytic copper foil (count)	Difference in R_{pc} between two surfaces of electrolytic copper foil (count)	Discharge capacity maintenance of secondary battery (%)
Ex. 5	13	42	29	95
Ex. 6	20	24	4	97
Ex. 7	39	98	59	93
Ex. 8	98	89	9	94
Comp. Ex. 5	8	9	1	84
Comp. Ex. 6	112	128	16	85
Comp. Ex. 7	181	47	134	85
Comp. Ex. 8	47	139	92	87

From Table 2, it can be seen that, when at least one of the shiny surface and the matte surface of the electrolytic copper foil has a peak count roughness R_{pc} exceeding 100 (count), discharge capacity maintenance of the secondary battery produced using such electrolytic copper foil cannot satisfy 90% or higher required in the art (Comparative Examples 6-8). This is considered because the active material is not uniformly coated on the electrolytic copper foil due to excessively many mountains.

In addition, it can be seen that, when at least one of the shiny surface and the matte surface of the electrolytic copper foil has a peak count roughness R_{pc} less than 100

(count), discharge capacity maintenance of the secondary battery produced using such electrolytic copper foil cannot satisfy 90% or higher required in the art (Comparative Example 5). This is considered because stress is concentrated on mountains which locally protrude upon charge/discharge of the secondary battery.

Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

Electronic Acknowledgement Receipt	
EFS ID:	37300099
Application Number:	15307069
International Application Number:	
Confirmation Number:	9113
Title of Invention:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Dae Young KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/US Patent Mail
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313221.00005
Receipt Date:	27-SEP-2019
Filing Date:	27-OCT-2016
Time Stamp:	16:51:48
Application Type:	U.S. National Stage under 35 USC 371

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	0313221-00005_RespCorrectAppPapers.pdf	76245 faa9661c5452b6087e217f6cca7290ea3ae9f200	no	1

Warnings:

Information:					
2	Miscellaneous Incoming Letter	notice.pdf	96992 5a444b90bcc37b524eab67dbbe03fd74a1e19d8d	no	3
Warnings:					
Information:					
3	Specification	0313221-00005_SubSpec-.pdf	12330491 0953a59a45ac3334c04e424df96ca004dc7ef9c8	no	17
Warnings:					
Information:					
			Total Files Size (in bytes):	12503728	

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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

Applicants:	Dae Young KIM
Appl. No.:	15/307,069
Conf. No.:	9113
Filed:	October 27, 2016
Title:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1727
Examiner:	USYATINSKY, ALEXANDER
Docket No.:	0313221.00005

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

RESPONSE TO NOTICE TO FILE CORRECTED APPLICATION PAPERS

Sir:

This Response is to the Notice to File Corrected Application Papers dated August 6, 2019. The Notice to File Corrected Application Papers indicated that the specification provided illegible text on page 7, line 13. By way of this amendment, Applicant submits a legible copy of the specification, including the aforementioned page and line number. No new matter has been added.

Please charge Deposit Account No. 02-1818 for any fees due in connection with this Response. If such a transaction is made, please reference attorney docket no. 0313221.00005.

Respectfully submitted,

K&L Gates LLP

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

Dated: September 27, 2019

UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/307,069	10/27/2016	Dae Young KIM	0313221.00005	9113

24573 7590 08/06/2019

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

EXAMINER	
USYATINSKY, ALEXANDER	

ART UNIT	PAPER NUMBER
1727	

NOTIFICATION DATE	DELIVERY MODE
08/06/2019	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

UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents
United States Patent and Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450
www.uspto.gov

Application No. : 15307069
Applicant : Kim
Filing Date : 10/27/2016
Date Mailed : 08/06/2019

NOTICE TO FILE CORRECTED APPLICATION PAPERS

Notice of Allowance Mailed

This application has been accorded an Allowance Date and is being prepared for issuance. The application, however, is incomplete for the reasons below.

Applicant is given two (2) months from the mail date of this Notice within which to respond. This time period for reply is extendable under 37 CFR 1.136(a) for only TWO additional MONTHS.

The informalities requiring correction are indicated in the attachment(s). If the informality pertains to the abstract, specification (including claims) or drawings, the informality must be corrected with an amendment in compliance with 37 CFR 1.121 (or, if the application is a reissue application, 37 CFR 1.173). Such an amendment may be filed after payment of the issue fee if limited to correction of informalities noted herein. See Waiver of 37 CFR 1.312 for Documents Required by the Office of Patent Publication, 1280 Off. Gaz. Patent Office 918 (March 23, 2004). In addition, if the informality is not corrected until after payment of the issue fee, for purposes of 35 U.S.C. 154(b)(1)(iv), "all outstanding requirements" will be considered to have been satisfied when the informality has been corrected. A failure to respond within the above-identified time period will result in the application being ABANDONED.

See attachment(s).

A copy of this notice MUST be returned with the reply. Please address response to "Mail Stop Issue Fee, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450".

/Chris Harmon/
Publication Branch
Office of Data Management
(571) 272-4200

Application No. 15307069

IDENTIFICATION OF APPLICATION DEFICIENCIES
IN APPLICATION FILED ON OR AFTER SEPTEMBER 16, 2012

[X] Applicant must provide legible text for the following item(s).

- [X] Specification filed 10/27/2016, page(s) 7 line 13.
- [ ] Claims filed , claim(s) .
- [ ] Other: .

[ ] Applicant must provide missing information on the following page(s) of the specification by amending the specification to add the missing text. No new matter may be added.
Page/line no(s).

[ ] The specification refers to one or more applications by attorney docket number and does not show the U.S. application number(s). Applicant must supply the U.S. application number in place of each attorney docket number.
Page/line no(s).

[ ] Applicant must provide an Abstract of the Disclosure.

[ ] The Application Data Sheet (ADS dated) does not supply the inventor's city and/or does not supply the inventor's U.S. state and/or does not supply the inventor's country. Applicant must submit a signed, in accordance with 37 CFR 1.76(e) and 1.33(b), application data sheet that corrects this deficiency. To be in compliance with 37 CFR 1.76, the corrected application data sheet must identify the information being changed by using underlining for additions and strikethroughs or brackets for deletions.

[ ] Other:

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 07/19/2019
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.
15/307,069	10/27/2016	Dae Young KIM	0313221.00005	9113

TITLE OF INVENTION: ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, 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	10/21/2019

EXAMINER	ART UNIT	CLASS-SUBCLASS
USYATINSKY, ALEXANDER	1727	429-249000

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 August 1, 2019

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

Electronic Patent Application Fee Transmittal				
Application Number:	15307069			
Filing Date:	27-Oct-2016			
Title of Invention:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME			
First Named Inventor/Applicant Name:	Dae Young KIM			
Filer:	Matthew S. Dicke/Meg Boinski			
Attorney Docket Number:	0313221.00005			
Filed as Large Entity				
Filing Fees for U.S. National Stage under 35 USC 371				
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:	36751179
Application Number:	15307069
International Application Number:	
Confirmation Number:	9113
Title of Invention:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Dae Young KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/US Patent Mail
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313221.00005
Receipt Date:	01-AUG-2019
Filing Date:	27-OCT-2016
Time Stamp:	13:49:37
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$1000
RAM confirmation Number	E201981D49496151
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	Issue Fee Payment (PTO-85B)	0313221-00005_IssueFee.pdf	1654837 d9c8369ce66306199aa0988143beb878f8696b58	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30470 147f1fe5c4275678836c1ac8883dd0802f2e531b	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	1685307		

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.

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NOTICE OF ALLOWANCE AND FEE(S) DUE

24573 7590 07/19/2019

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EXAMINER
USYATINSKY, ALEXANDER

ART UNIT	PAPER NUMBER
1727	

DATE MAILED: 07/19/2019

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/307,069	10/27/2016	Dae Young KIM	0313221.00005	9113

TITLE OF INVENTION: ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, 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	10/21/2019

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.

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Commissioner for Patents
P.O. Box 1450
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By fax, send to: (571)-273-2885

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

24573 7590 07/19/2019

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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

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

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/307,069	10/27/2016	Dae Young KIM	0313221.00005	9113

TITLE OF INVENTION: ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, 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	10/21/2019

EXAMINER	ART UNIT	CLASS-SUBCLASS
USYATINSKY, ALEXANDER	1727	429-249000

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
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www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/307,069	10/27/2016	Dae Young KIM	0313221.00005	9113

24573 7590 07/19/2019

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

EXAMINER	
USYATINSKY, ALEXANDER	
ART UNIT	PAPER NUMBER
1727	

DATE MAILED: 07/19/2019

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.** 15/307,069	**Applicant(s)** KIM et al.	
	Examiner ALEXANDER USYATINSKY	**Art Unit** 1727	**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 Remarks/Amendments from 04/08/2019.
   ☐ 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 1-11 . 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 areply 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 _____.

/Alexander Usyatinsky/
Primary Examiner, Art Unit 1727

EXAMINER'S AMENDMENT/COMMENT/REASONS FOR ALLOWANCE

Examiner's Comment

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

2. The rejection of claim 7 under 35 U.S.C. § 112 (b) set forth in the Office Action of 01/10/2019 is withdrawn in response to the Amendments filed on 04/08/2019.

3. The objection to claim 3 set forth in the Office Action of 01/10/2019 is withdrawn in response to the Amendments filed on 04/08/2019.

EXAMINER'S AMENDMENT

4. 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.

The application has been amended as follows:

Claims 12-16 are cancelled by Examiner as being drawn to non-elected invention without traverse (see Response to Election/ Restriction from 12/17/2018).

Reasons for Allowance

5. The following is an examiner's statement of reasons for allowance: Applicant arguments filed on 04/08/2019 overcome the Rejections of Office Action from 01/10/2019. The closest prior art of record- US 2004/0029006, US 20130108922, US 2001005182, US 20140193660, US 20030129497 US 20130108922 - us fail to teach or suggest the combination of limitations of claim 1.

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."

Allowable Claims

6. **Claims 1-11** are allowed over prior art of record.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to ALEXANDER USYATINSKY whose telephone number is (571)270-7703. The examiner can normally be reached on IFP.

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, Barbara Gilliam can be reached on 5712721330. 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.

/Alexander Usyatinsky/
Primary Examiner, Art Unit 1727

Notice of References Cited	Application/Control No. 15/307,069	Applicant(s)/Patent Under Reexamination KIM et al.	
	Examiner ALEXANDER USYATINSKY	Art Unit 1727	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-20010051282-A1	12-2001	YATES, CHARLES B.	C25D1/04	428/607
*	B	US-20140193660-A1	07-2014	Tsai; Chen-Ping	C25D1/04	428/606
*	C	US-20030129497-A1	07-2003	Yamamoto, Hironori	H01M4/131	429/246
*	D	US-20130108922-A1	05-2013	Shinozaki; Kensaku	H01M4/13	429/211
	E					
	F					
	G					
	H					
	I					
	J					
	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	
	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.

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/307,069	KIM et al.
	Examiner	Art Unit
	ALEXANDER USYATINSKY	1727

CPC - Searched*		
Symbol	Date	Examiner
C25D1/04 H01M4/66 H01M4/661 H01M4/665 H01M10/052 Y02P70/54 Y02E60/122 Y02T10/7011	07/14/2019	AU

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
Inventors name searched Palm and East	07/14/2019	AU
East search history attached	07/14/2019	AU

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner
	C25D1/04 H01M4/66 H01M4/661 H01M4/665 H01M10/052 Y02P70/54 Y02E60/122 Y02T10/7011	07/14/2019	AU
		07/14/2019	AU

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/307,069	KIM et al.
	Examiner	Art Unit
	ALEXANDER USYATINSKY	1727

CPC						
Symbol					Type	Version
C25D	/	1	/	04	F	2013-01-01
H01M	/	4	/	66	I	2013-01-01
H01M	/	10	/	052	I	2013-01-01
H01M	/	4	/	661	I	2013-01-01
H01M	/	4	/	665	I	2013-01-01
Y02E	/	60	/	122	A	2013-01-01
Y02T	/	10	/	7011	A	2013-01-01
Y02P	/	70	/	54	A	2015-11-01

CPC Combination Sets							
Symbol					Type	Set	Ranking	Version
	/		/					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	11	
/Alexander Usyatinsky/ Primary Examiner, Art Unit 1727	14 July 2019	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office — Part of Paper No.: 20190712

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/307,069	KIM et al.
	Examiner	**Art Unit**
	ALEXANDER USYATINSKY	1727

INTERNATIONAL CLASSIFICATION				
CLAIMED				
H01M	/	4	/	66

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	11	
/Alexander Usyatinsky/ Primary Examiner, Art Unit 1727	14 July 2019	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office — Part of Paper No.: 20190712

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/307,069	KIM et al.
	Examiner	**Art Unit**
	ALEXANDER USYATINSKY	1727

☐ 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
1	1	10	10												
2	2	11	11												
3	3		12												
4	4		13												
5	5		14												
6	6		15												
7	7		16												
8	8														
9	9														

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	11	
/Alexander Usyatinsky/ Primary Examiner, Art Unit 1727	14 July 2019	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office Part of Paper No.: 20190712

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	5	("20010051282" | "20140193660" | "20160260981" | "20150340639" | "5431803").PN.	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L2	3	L1 and ((copper near foil) same anode)	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L3	821	((("KIM") near3 ("Dae") near3 ("Young")) OR (("KIM") near3 ("Seung") near3 ("Min"))).INV.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	OFF	2019/07/14 18:33
L4	34	L3 and foil	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L5	1	L4 and (SEP near "1940")	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L6	1	L4 and "R.sub.pc"	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L7	12	foil and "R.sub.pc"	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L8	1	L7 and (SEP near "1940")	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L9	7	L7 and value	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L10	1	L7 and valley	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L11	3	(foil same "R.sub.pc")	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L12	0	((cuirrent near collector) same "R.sub.pc")	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L13	0	((cuirrent near collector) and "R.sub.pc")	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L14	2	("20180119301").PN.	US-PGPUB; USPAT; USOCR; DERWENT	OR	OFF	2019/07/14 18:33
L15	17	L4 and ((copper near foil) same anode)	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L16	0	429/ccls. not 429/400-535.ccls.	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L17	0	429/$ccls. not 429/400-535.ccls.	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L18	57593	429/$.ccls. not 429/400-535.ccls.	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L19	2724	L18 and ((copper near foil) same anode)	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L20	2106	L18 and ((copper near foil) with anode)	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L21	4048	L18 and (anode with active near	US-PGPUB;	OR	OFF	2019/07/14

		material) with (metal or alloy or silicon)	USPAT			18:33
L22	158	L18 and ((anode with active near material) with (metal or alloy or silicon) with (copper near foil))	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L23	21	L18 and ((anode with active near material) with ((metal or alloy or silicon) with carbon) with (copper near foil))	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L24	0	L20 and ((first near surface) same (second near surface) same (roughness with ratio))	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L25	1	L20 and ((first near surface) same (second near surface) same (roughness with difference))	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L26	0	L25 and (shiny same matte)	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L27	0	L25 and (shiny same matte)	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L28	0	L25 and (shiny and matte)	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L29	5	L18 and (shiny with matte)	US-PGPUB; USPAT	OR	OFF	2019/07/14 18:33
L30	201216	(C25D1/04 H01M4/66 H01M4/661 H01M4/665 H01M10/052 Y02P70/54 Y02E60/122 Y02T10/7011)".CPC"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	OR	OFF	2019/07/14 18:33
S20	2105	S18 and ((copper near foil) with anode)	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:48

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L31	1	(electrolytic copper foil secondary battery average first surface second opposite peak count roughness (Rpc or "R.sub.pc") measured randomly-selected three points effective rise above upper criteria line (per near unit) sampling length profile steel-iron test schedule (SEP "1940") one valley deeper lower adjacent).CLM.	US-PGPUB; USPAT	AND	OFF	2019/07/14 19:01
L32	0	"L30" and (electrolytic copper foil secondary battery average first surface second opposite peak count roughness (Rpc or "R.sub.pc") measured randomly-selected three points effective rise above upper criteria line (per near unit) sampling length profile steel-iron test schedule (SEP "1940") one valley deeper lower adjacent).CLM.	US-PGPUB; USPAT	AND	OFF	2019/07/14 19:04
L33	0	"L30" and (electrolytic copper foil secondary battery average first surface second opposite peak count roughness (Rpc or "R.sub.pc") measured randomly-selected three points effective rise above upper criteria line (per near unit) sampling length profile steel-iron test schedule (SEP "1940") one valley deeper lower adjacent)	US-PGPUB; USPAT	AND	OFF	2019/07/14 19:04

L34	1	(electrolytic copper foil secondary battery average first surface second opposite peak count roughness (Rpc or "R.sub.pc") measured randomly-selected three points effective rise above upper criteria line (per near unit) sampling length profile steel-iron test schedule (SEP "1940") one valley deeper lower adjacent)	US-PGPUB; USPAT	AND	OFF	2019/07/14 19:05
L35	1	(electrolytic copper foil secondary battery average first surface second opposite peak count roughness (Rpc or "R.sub.pc") measured randomly-selected three points effective rise above upper criteria line (per near unit) sampling length profile steel-iron test schedule (SEP near "1940") one valley deeper lower adjacent)	US-PGPUB; USPAT	AND	OFF	2019/07/14 19:06

7/ 14/ 2019 7:07:11 PM
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventors: Dae Young KIM et al.	)	**Examiner:** Alexander Usyatinsky
Serial No.: 15/307,069	)	**Art Unit:** 1727
Filing Date: October 27, 2016	)	**Atty. Docket No.:** 0313221.00005
Confirmation No.: 9113	)	

Title: ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

AMENDMENT AND RESPONSE TO NON-FINAL OFFICE ACTION

VIA ELECTRONIC FILING

Mail Stop: Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In view of the non-final Office Action mailed on January 10, 2019, the following response is submitted, wherein:

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

Remarks begin on page 6 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. (Original) An electrolytic copper foil for a secondary battery, the electrolytic copper foil comprising:

a first surface; and

a second surface opposite to the first surface,

wherein each of the first and second surfaces has a peak count roughness Rpc of 10 to 100,

wherein the peak count roughness Rpc of each of the first and second surfaces is an average of peak count roughness Rpc values measured at randomly-selected three points,

the peak count roughness Rpc of each point is the number of effective peaks which rise above an upper criteria line of 0.5 μm per unit sampling length of 4 mm in a surface roughness profile obtained according to steel-iron test schedule (SEP 1940), and

there is at least one valley deeper than a lower criteria line of -0.5 μm between adjacent ones of the effective peaks.

2. (Original) The electrolytic copper foil according to claim 1, wherein a difference in peak count roughness Rpc between the first and second surfaces is 60 or less.

3. (Currently Amended) The electrolytic copper foil according to claim 1, wherein each of the first and second surfaces has a ten-point mean roughness [[Rpc]] $\underline{R_{ZJIS}}$ of 2 μm or less.

4. (Original) The electrolytic copper foil according to claim 1, wherein the electrolytic copper foil has a thickness of 3 to 20 μm and tensile strength of 30 to 60 kgf/mm^2.

5. (Previously Presented) A current collector for a secondary battery, the current collector comprising:

the electrolytic copper foil according to claim 1; and

a protective layer disposed on the electrolytic copper foil,

wherein the protective layer comprises at least one of chromate, benzotriazole and a silane compound.

6. (Original) The current collector according to claim 5, wherein the protective layer is formed on the first and second surfaces of the electrolytic copper foil.

7. (Currently Amended) An electrode for a secondary battery, the electrode comprising:

a current collector comprising the electrolytic copper foil according to claim 1; and

an active material layer disposed on the current collector;

wherein the active material layer comprises at least one active material selected from the group consisting of: carbon; a metal (Me) of Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni or Fe; an alloy containing the metal; an oxide of the metal (MeO_x); and a ~~complex~~ chemical compound of the metal and carbon.

8. (Original) The electrode according to claim 7, wherein the active material layer comprises Si.

9. (Original) the electrode according to claim 7, wherein the current collector further comprises a protective layer comprising at least one of chromate, benzotriazole and a silane compound, and

wherein the protective layer is interposed between the electrolytic copper foil and the active material layer.

10. (Previously Presented) A secondary battery comprising:

a cathode;

an anode;

an electrolyte for providing an environment enabling lithium ions to move between the cathode and the anode; and

a separator for electrically insulating the cathode from the anode,

wherein the anode comprises:

a current collector comprising the electrolytic copper foil according to claim 1; and

an active material layer disposed on the current collector.

11. (Original) The secondary battery according to claim 10, further comprising a protective layer comprising at least one of chromate, benzotriazole and a silane compound,

wherein the protective layer is interposed between the electrolytic copper foil and the active material layer.

12. (Withdrawn) A method of producing an electrolytic copper foil by allowing a current to flow between a cathode plate and a rotational anode drum spaced from each other in an electrolytic solution so as to electrodeposit a copper of the rotational anode drum, the method comprising:

heat-treating a copper wire;

acid-cleaning the heat-treated copper wire;

dipping the acid-cleaned copper wire in the electrolytic solution;

conducting electroplating, while the copper wire is dipped in the electrolytic solution, by allowing a current to flow between the cathode plate and the rotational anode drum; and

conducting continuous filtration to remove solid impurities from the electrolytic solution during the electroplating.

13. (Withdrawn) The method according to claim 12, wherein concentrations of organic impurities and metal impurities in the electrolytic solution during the electroplating are maintained at 1g/L or less and 10 g/L or less, respectively.

14. (Withdrawn) The method according to claim 12, wherein the heat-treatment of the copper wire is carried out at 600 to 800°C.

15. (Withdrawn) The method according to claim 12, wherein the electrolytic solution comprises 50 to 100 g/L of a copper ion, 50 to 150 g/L of sulfuric acid, 50 ppm or less of a chlorine ion and an organic additive.

16. (Withdrawn) The method according to claim 15, wherein the organic additive is hydroxyethyl cellulose (HEC), organic sulfide, organic nitride, a thiourea compound, or a mixture of two or more thereof.

REMARKS

This Response is submitted in reply to the Non-Final Office Action dated January 10, 2019. Claims 1 to 16 are currently pending in the application. Claims 12 to 16 were previously withdrawn from consideration. Claims 1 to 11 stand rejected. Claims 3 and 7 are amended. No new matter has been added by the amendments. Favorable reconsideration of this application is respectfully requested in view of the following remarks.

Claim 3 is objected to because of informalities. Applicant has amended claim 3 to address the objection, as suggested by the Examiner.

Accordingly, Applicant respectfully requests that the objection to claim 3 be withdrawn.

Claim 7 is rejected under 35 U.S.C. § 112(b) as being indefinite. The Examiner explains that:

> 7. In claim 7 it is unclear what kind of composition claimed by the term complex of the metal and carbon a chemical compound (carbide) or mechanical mixture. For examination purposes said term is interpreted either chemical compounds or mechanical mixture.

Office Action, page 3. In response, without acquiescing to the merits of the rejection and solely to further prosecution of the present application, Applicant has amended claim 7 to recite "chemical compound of the metal and carbon."

Accordingly, Applicant respectfully requests that the rejection under 35 U.S.C. §112(b) with respect to claim 7 be reconsidered and withdrawn.

Claims 1 to 11 are rejected under 35 U.S.C. § 103 as being unpatentable over U.S. Patent Publication No. 2004/0029006 to Otsuka ("Otsuka"). Alternatively, claim 2 is rejected under 35 U.S.C. § 103 as being unpatentable over Otsuka in view of U.S. Patent Publication No. 2013/0108922 to Shinozaki ("Shinozaki"). Applicant respectfully traverses the obviousness rejections of these claims in view of the following remarks.

With respect to the consideration and determination of obviousness, the Supreme Court in *Graham v. John Deere*, 383 U.S. 1, 148 USPQ 459 (1966), stated:

> Under § 103, the scope and content of the prior art are to be determined; differences between the prior art and the claims at issue are to be ascertained; and the level of ordinary skill in the pertinent art resolved. Against this background,

> the obviousness or non-obviousness of the subject matter is determined. Such secondary considerations as commercial success, long felt but unsolved needs, failure of others, etc., might be utilized to give light to the circumstances surrounding the origin of the subject matter sought to be patented. As indicia of obviousness or non-obviousness, these inquiries may have relevancy.

According to MPEP § 2141, it is Office policy to follow *Graham v. John Deere Co.* in the consideration and determination of obviousness under 35 U.S.C. § 103. A determination of obviousness under § 103 requires the determination of the following factual inquiries: (1) determining the scope and content of the prior art; (2) ascertaining the differences between the prior art and the claims at issue; (3) resolving the level of ordinary skill in the pertinent art; and (4) evaluating evidence of secondary considerations, if any.

Based on the above factual inquiries, the Office must first consider all claim limitations. *See MPEP § 2143.03*. And with all limitations considered, a determination of obviousness requires that all claim limitations be taught or suggested by the cited references. *See CMFT Inc. v. Yieldup Int'l Corp.,* 349 F3d 1333, 68 USPQ 1940, 1947 (Fed. Cir. 2003) (citing *In re Royka*, 490 F.2d 981, 985, 180 USPQ 580 (CCPA 1974)). When the Office asserts a combination of elements present in the cited references, it must identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way that the claimed invention does. *See KSR Int'l Co. v. Teleflex Inc.*, 127 S. Ct. 1727, 82 USPQ2d 1385, 1396 (2007). In addition to the above criteria, a reference must be considered in its entirety, *i.e.*, as a whole, including portions that would lead away from the claimed invention. *W. L. Gore & Assocs., Inc. v. Garlock, Inc.*, 721 F.2d 1540, 220 USPQ 303 (Fed. Cir. 1983), *cert. denied*, 469 U.S. 851 (1984). Furthermore, the key to supporting any rejection under 35 U.S.C. § 103 is a "clear articulation of the reason(s) why the claimed invention would have been obvious." *See MPEP § 2142*.

The Supreme Court in *KSR International Co. v. Teleflex Inc.*, 127 S. Ct. 1727, 1741 (2007) noted that the analysis supporting a rejection under 35 U.S.C. § 103 should be made explicit because "rejections on obviousness cannot be sustained with mere conclusory statements. Instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness." *KSR*, 127 S. Ct. at 1741 (quoting *In re Kahn*, 441 F.3d 977, 988 (Fed. Cir. 2006)).

"It is [also] impermissible to use the claimed invention as an instruction manual or 'template' to piece together the teachings of the prior art so that the claimed invention is rendered obvious." *In re Fritch*, 972 F.2d 1260, 1266, 23 USPQ2d 1780, 1783 (Fed. Cir. 1992) (citing *In re Gorman*, 933 F.2d 982, 987, 18 USPQ2d 1885, 1888 (Fed. Cir. 1991)). In other words, "'[o]ne cannot use hindsight reconstruction to pick and choose among isolated disclosures in the prior art to deprecate the claimed invention.'" *In re Fritch*, 972 F.2d at 1266, 23 USPQ2d at 1783 (quoting *In re Fine*, 837 F.2d 1071, 1075, 5 USPQ2d 1596, 1600 (Fed.Cir.1988)).

Furthermore, if an independent claim is nonobvious under 35 U.S.C. § 103, then any claim depending therefrom is nonobvious. *In re Fine*, 837 F.2d 1071, 5 USPQ2d 1596 (Fed. Cir. 1988).

Pending claim 1 recites, in relevant part:

> **wherein each of the first and second surfaces has a peak count roughness Rpc of 10 to 100,**
>
> **wherein the peak count roughness Rpc of each of the first and second surfaces is an average of peak count roughness Rpc values measured at randomly-selected three points,**
>
> **the peak count roughness Rpc of each point is the number of effective peaks which rise above an upper criteria line of 0.5 μm per unit sampling length of 4 mm in a surface roughness profile obtained according to steel-iron test schedule (SEP 1940), and**
>
> **there is at least one valley deeper than a lower criteria line of -0.5 μm between adjacent ones of the effective peaks**.

Applicant respectfully submits that none of the cited art discloses the above-discussed distinguishing features of claim 1. In the Office Action, the Examiner also concedes that Otsuka does not disclose the above-discussed features recited in claim 1. For example, the Examiner states that:

> 12. Otsuka does not expressly discloses ach of the first and second surfaces has a peak count roughness Rpc of 10 to 100, wherein the peak count roughness Rpc of each of the first and second surfaces is an average of peak count roughness Rpc values measured at randomly-selected three points, the peak count roughness Rpc of each point is the number of effective peaks which rise above an upper criteria line of 0.5 μm

> per unit sampling length of 4 mm in a surface roughness profile obtained according to steel-iron test schedule (SEP 1940), and there is at least one valley deeper than a lower criteria line of -0.5 μm between adjacent ones of the effective peaks.

Office Action, page 4. However, the Examiner merely states that:

> 13. However, Otsuka teaches that Rz in the experiment 1 and 3 equal 1.3 μm and 1.2 μm respectively (within claim range, **re claim 3**), and distance between peaks of base foil peal is a least 5 μm. Therefore, common structural parameters for the claimed foil and foil of Otsuka are substantially similar. Moreover, a retention rate (the characteristic connected to the roughness of the current collector) are substantially the same for the foil of the instant Application and the foil of Otsuka. In addition, Otsuka teaches that the roughness of the foil and relative roughness of the first and second surfaces affect a physical property of the electrode and working parameters of a battery and, as such a result effective variable. It has been held by the courts that discovering an optimum value or workable ranges of a result-effective variable involves only routine skill in the art, and thus not novel. *In re Boesch*, 617 F.2d 272, 205 USPQ 215 (CCPA 1980). See MPEP 2144.05. It would have been obvious to one of ordinary skill of art at the time the invention was made to optimize the roughness of the foil of Otsuka in order to improve physical characteristics of the electrode and working characteristics of the battery.

Office Action, pages 4-5. It appears that the Examiner alleges that the peak count roughness (Rpc) of claim 1 is an inherent/implicit characteristic of the "Rz" or "distance between peaks" of Otsuka. Applicant respectfully disagrees.

Applicant notes that the MPEP 2112 states that "[i]n 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 the above-recited features (e.g., peak count roughness Rpc of 10 to 100) of independent claim 1, do

not necessarily flow from the disclosure of Otsuka (e.g., Rz of 1.3 and 1.2 μm, or distance between peaks of at least 5 μm). For example, the Specification specifically states that:

> However, the present applicant found that an electrolytic copper foil 111 the shiny surface 111 a and the matte surface 111 b of which have a ten-point mean roughness RzJIS of 2 μm or less does not always secure capacity maintenance of the secondary battery, of 90% or higher. That is, a low ten-point mean roughness RzJIS (for example, 2 μm or less) of the shiny surface 111 a and the matte surface 111 b of the electrolytic copper foil 111 cannot be a sufficient condition for capacity maintenance of the secondary battery of 90% or higher.
>
> * * *
>
> **As a result of repeated research, the present applicant found that a peak count roughness Rpc of the electrolytic copper foil 111 is an important factor in stably securing capacity maintenance of 90% or higher.**

Specification, paragraphs [0039], [0041]. That is, unlike a peak count roughness (Rpc) of the claimed range (i.e., 10 to 100), the roughness RzJIS or Rz (e.g., 2 μm or less) cannot be a sufficient condition for capacity retention rate of a secondary battery of 90% or higher, **which means that the roughness (Rz) range disclosed in Otsuka cannot guarantee a peak count roughness (Rpc) of the claimed range (i.e., 10 to 100).** Thus, even though the electrolytic copper foil of Otsuka has Rz of 1.3 μm or 1.2 μm, it does not necessarily have 'peak count roughness (Rpc)' of claimed range (i.e., 10 to 100).

Moreover, the claimed peak count roughness (Rpc) is also a parameter which is totally different from the distance between peaks of Otsuka and cannot be inferred therefrom at all for following reasons.

First, the 'peak' of claim 1 is totally different from the 'peak' of Otsuka. As defined in claim 1, the 'peak' of claim 1 is a peak shown in a 'surface roughness profile' obtained by measuring the surface roughness of a copper foil according to steel-iron test schedule (SEP 1940). On the other hand, the 'peak' of Otsuka is a protrusion shown in a 'photograph' taken at a magnification of X2000 by an electron microscope. See Otsuka, paragraph [0036] ("Further, the minimum distance between peaks Ds of the base foil peak was measured from a photograph taken at a magnification of X2000 by an electron microscope. ...").

Second, even if it is assumed that the 'peak' of Otsuka has a similar meaning as the 'peak' of claim 1, claim 1 is still distinguished from Otsuka in that what is limited in claim 1 is the number of 'effective peaks' rather than that of "all peaks." That is, in claim 1, only the peaks

that satisfy the conditions as defined in claim 1 are counted as "effective peaks." On the other hand, in Otsuka, the minimum distance between the peaks is determined with respect to all the peaks existing or shown in the photograph taken by an electron microscope.

Therefore, the Examiner has not established a *prima facie* case of obviousness because none of the cited references explicitly or implicitly teach or suggest an electrolytic copper foil having a peak count roughness (Rpc) of the claimed range.

For at least these reasons, Applicant respectfully submits that independent claim 1 is patentable over the cited art. Claims 2 to 11, each ultimately depend from or incorporate independent claim 1, and are allowable for substantially the same reasons as independent claim 1.

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,

/Matthew S. Dicke/

Matthew S. Dicke
Reg. No. 58,819
Customer No. 35884
Telephone No. 312-578-5415

Dated: April 8, 2019

Electronic Acknowledgement Receipt	
EFS ID:	35655506
Application Number:	15307069
International Application Number:	
Confirmation Number:	9113
Title of Invention:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Dae Young KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/Elias Santiago
Filer Authorized By:	Matthew S. Dicke
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Application Type:	U.S. National Stage under 35 USC 371

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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		00005_RespNFOA.pdf	223012 c3c369dd3ee3064007a336eb0b952917478 66583	yes	11

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Amendment/Req. Reconsideration-After Non-Final Reject	1	1
	Claims	2	5
	Applicant Arguments/Remarks Made in an Amendment	6	11
Warnings:			
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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.
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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)
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 15/307,069	Filing Date 10/27/2016	☐ To be Mailed

ENTITY: ☑ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED - PART I

	(Column 1)	(Column 2)			
FOR	NUMBER FILED	NUMBER EXTRA		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A		N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A		N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*		x $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

AMENDMENT	04/08/2019	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 16	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 2	Minus	*** 3	= 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

AMENDMENT		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $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".	/MARCUS A PRIDGEN/
*** 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.**

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/307,069	10/27/2016	Dae Young KIM	0313221.00005	9113

24573 7590 01/10/2019

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

EXAMINER	
USYATINSKY, ALEXANDER	

ART UNIT	PAPER NUMBER
1727	

NOTIFICATION DATE	DELIVERY MODE
01/10/2019	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. 15/307,069	Applicant(s) KIM et al.	
	Examiner ALEXANDER USYATINSKY	Art Unit 1727	AIA 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 12/17/2018.

☐ 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) 1-16 is/are pending in the application.

5a) Of the above claim(s) 12-16 is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☑ Claim(s) 1-11 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 10/27/2016 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 12/18/2018, 10/26/2018, 05/08/2018, 10/27/2016

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

4) ☐ Other: _____.

DETAILED ACTION

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

Priority

2. Acknowledgement has been made of applicant's claim for priority under 35 USC 119 (a-d). The certified copy has been filed on 10/27/2016.

Information Disclosure Statement

3. The Information Disclosure Statement (IDS) filed 12/18/2018, 10/26/2018, 05/08/2018, 10/27/2016 have been placed in the application file and the information referred to therein has been considered.

Drawings

The drawings received 10/27/2016 are acceptable for examination purposes.

Election/Restrictions

4. Applicant's election without traverse of Group I claims 1-11 in the reply filed on 12/17/2018 is acknowledged.

Claim Objections

5. Claim 3 is objected to because of the following informalities: typo, should be R_{zJIS}. Appropriate correction is required.

Claim Rejections - 35 USC § 112

The following is a quotation of 35 U.S.C. 112(b):

> (b) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.

6. Claim 7 is rejected under 35 U.S.C. 112(b) as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention.

7. In claim 7 it is unclear what kind of composition claimed by the term complex of the metal and carbon a chemical compound (carbide) or mechanical mixture. For examination purposes said term is interpreted either chemical compounds or mechanical mixture.

Claim Rejections - 35 USC § 103

8. 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.

9. This application currently names joint inventors. In considering patentability of the claims the examiner presumes that the subject matter of the various claims was commonly owned as of the effective filing date of the claimed invention(s) absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and effective filing dates of each claim that was not commonly owned as of the effective filing date of the later invention in order for the examiner to consider the applicability of 35 U.S.C. 102(b)(2)(C) for any potential 35 U.S.C. 102(a)(2) prior art against the later invention.

10. Claims 1-11 are rejected under 35 U.S.C. 103 as being unpatentable over US 2004/0029006 to Otsuka (Otsuka).

11. **Regarding claims 1 and 2,** Otsuka discloses an electrolytic copper foil for a secondary battery (Title, Abstract), the electrolytic copper foil comprising a first surface and a second surface opposite to the first surface, having 10 point roughness less than 2.5 μm (re claim 3).

12. Otsuka does not expressly discloses ach of the first and second surfaces has a peak count roughness Rpc of 10 to 100, wherein the peak count roughness Rpc of each of the first and second surfaces is an average of peak count roughness Rpc values measured at randomly-selected three points, the peak count roughness Rpc of each point is the number of effective peaks which rise above an upper criteria line of 0.5 μm per unit sampling length of 4 mm in a surface roughness profile obtained according to steel-iron test schedule (SEP 1940), and there is at least one valley deeper than a lower criteria line of -0.5 μm between adjacent ones of the effective peaks.

13. However, Otsuka teaches that Rz in the experiment 1 and 3 equal 1.3 μm and 1. 2 μm respectively (within claim range, **re claim 3**), and distance between peaks of base foil peal is a least 5 μm. Therefore, common structural parameters for the claimed foil and foil of Otsuka are substantially similar. Moreover, a retention rate (the characteristic connected to the roughness of the current collector) are substantially the same for the foil of the instant Application and the foil of Otsuka. In addition, Otsuka teaches that the roughness of the foil and relative roughness of the first and second surfaces affect a physical property of the electrode and working parameters of a battery and, as such a result effective variable It has been held by the courts that discovering an optimum

value or workable ranges of a result-effective variable involves only routine skill in the art, and thus not novel. *In re Boesch*, 617 F.2d 272, 205 USPQ 215 (CCPA 1980). See MPEP 2144.05. It would have been obvious to one of ordinary skill of art at the time the invention was made to optimize the roughness of the foil of Otsuka in order to improve physical characteristics of the electrode and working characteristics of the battery.

14. **Regarding claim 3**, Otsuka discloses in the experiment 1 and 3 equal 1.3 μm and 1. 2 μm respectively. It is noted that a specific example in the prior art which is within a claimed range anticipates the range. See MPEP 2131.03

15. **Regarding claim 4**, Otsuka discloses a tensile strength as 40 kg/mm^2 (claim 1) and foil thickness 12 μm (para 35). It is noted that a specific example in the prior art which is within a claimed range anticipates the range. See MPEP 2131.03

16. **Regarding claim 5**, Otsuka discloses current collector for a secondary battery the current collector comprising the electrolytic copper foil and a protective layer disposed on the electrolytic copper foil, wherein the protective layer comprises at least one of chromate, and a silane compound (para 37).

17. **Regarding claim 6**, Otsuka discloses he protective layer is formed on the first and second surfaces of the electrolytic copper foil (para 37). Since the foil was immersed into solution, the layer necessarily formed on both sides.

18. **Regarding claim 7**, Otsuka discloses graphite as an electrode active material (para 38).

19. **Regarding claim 8**, Otsuka discloses the claimed invention except for Si as electrode active material. It would have been obvious to one having ordinary skill in the art at the time the invention was filed to choose Si the electrode active material, since it

has been held to be within the general skill of a worker in the art to select a known material on the basis of its suitability for the intended use as a matter of obvious design choice. *In re Leshin,* 125 USPQ 416.

20. **Regarding claim 9**, Otsuka discloses the current collector further comprises a protective layer comprising a chromate or silane compound, and wherein the protective layer is interposed between the electrolytic copper foil and the active material layer (para 37). Since the foil was immersed into solution before applying a slurry containing the electrode active material. That necessarily will provide a protective layer between the electrolytic copper foil and the active material layer.

21. **Regarding claims 10,** Otsuka discloses a secondary battery (para 38) comprising a cathode ($LiCoO_2$ on Al-current collector), an anode (graphite on Cu-foil) an electrolyte for providing an environment enabling lithium ions to move between the cathode and the anode (para 40) and a separator for electrically insulating the cathode from the anode, wherein the anode comprise; and an active material layer graphite) disposed on the current collector.

22. **Regarding claim 11**, Otsuka discloses the current collector further comprises a protective layer comprising a chromate or silane compound, and wherein the protective layer is interposed between the electrolytic copper foil and the active material layer (para 37). Since the foil was immersed into solution before applying a slurry containing the electrode active material. That necessarily will provide a protective layer between the electrolytic copper foil and the active material layer.

23. **Alternatively claim 2 are rejected under 35 U.S.C. 103 as being unpatentable over US 2004/0029006 to Otsuka in view of US 20130108922 to Shinozaki (Shinozaki).**

24. **Regarding claim 2**, Otsuka discloses the invention as discussed above as applied to claim 1 and incorporated therein. Otsuka does not expressly disclose that a difference in peak count roughness Rpc between the first and second surfaces is 60 or less.

25. Shinozaki a lithium ion secondary battery, which uses a negative electrode wherein an active material is deposited on an electrolytic copper foil current collector and the surface-roughened layers on both surfaces have a surface roughness Rz of 1.0-5 μm and a surface roughness R_a of 0.25-0.7 μm, with the R_z difference between the front and back surfaces being within 3 μm and the Ra differences between the front and back surfaces being within 0.3 μm. Shinozaki also teaches that when difference of surface roughness between first and second surfaces of the copper foil is small it result in preventing drop in charge/discharge efficiency of the battery (para 4). Therefore Shinozaki clearly teaches that difference of surface roughness between first and second surfaces is a result effective variable. It has been held by the courts that discovering an optimum value or workable ranges of a result-effective variable involves only routine skill in the art, and thus not novel. *In re Boesch*, 617 F.2d 272, 205 USPQ 215 (CCPA 1980). See MPEP 2144.05. It would have been obvious to one of ordinary skill of art at the time the invention was filed to optimize (or minimize) the difference in difference of surface roughness between first and second surfaces in order to avoid drop in the charge/discharge efficiency of the battery. Based on Otsuka and Shinozaki

disclosure such optimization can be done by skilled artisan as a result of routine experimentation.

Conclusion

23. Any inquiry concerning this communication or earlier communications from the examiner should be directed to ALEXANDER USYATINSKY whose telephone number is (571)270-7703. The examiner can normally be reached on IFP.

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, Barbara Gilliam can be reached on 5712721330. 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.

/Alexander Usyatinsky/
Primary Examiner, Art Unit 1727

Notice of References Cited	Application/Control No. 15/307,069	Applicant(s)/Patent Under Reexamination KIM et al.	
	Examiner ALEXANDER USYATINSKY	Art Unit 1727	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-20040029006-A1	02-2004	Otsuka, Hideo	C25D1/04	429/220
*	B	US-20130108922-A1	05-2013	Shinozaki; Kensaku	H01M4/13	429/211
	C					
	D					
	E					
	F					
	G					
	H					
	I					
	J					
	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	
	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.

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/307,069	KIM et al.
	Examiner	Art Unit
	ALEXANDER USYATINSKY	1727

CPC - Searched*		
Symbol	Date	Examiner
C25D1/04 H01M4/66 H01M4/661 H01M4/665 H01M10/052 Y02P70/54 Y02E60/122 Y02T10/7011	12/25/2018	AU

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
Inventors name searched Palm and East	12/25/2018	AU
East search history attached	12/25/2018	AU

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
L1	5	("20010051282" | "20140193660" | "20160260981" | "20150340639" | "5431803").PN.	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:32
L2	3	1 and ((copper near foil) same anode)	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:33
L3	772	((("KIM") near3 ("Dae") near3 ("Young")) OR (("KIM") near3 ("Seung") near3 ("Min"))).INV.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	OFF	2018/12/25 20:35
L4	28	L3 and foil	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:35
L5	1	L4 and (SEP near "1940")	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:35
L6	1	L4 and "R.sub.pc"	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:35
L7	12	foil and "R.sub.pc"	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:35
L8	1	L7 and (SEP near "1940")	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:35
L9	7	L7 and value	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:35
L10	1	L7 and valley	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:35
L11	3	(foil same "R.sub.pc")	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:35
L12	0	((cuirrent near collector) same "R.sub.pc")	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:35
L13	0	((cuirrent near collector) and "R.sub.pc")	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:35
L14	2	("20180119301").PN.	US-PGPUB; USPAT; USOCR; DERWENT	OR	OFF	2018/12/25 20:35
L15	13	4 and ((copper near foil) same anode)	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:37
L16	0	429/ccls. not 429/400-535.ccls.	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:44
L17	0	429/$ccls. not 429/400-535.ccls.	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:45
L19	57567	429/$.ccls. not 429/400-535.ccls.	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:46
L20	2723	19 and ((copper near foil) same anode)	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:48
L21	2105	19 and ((copper near foil) with anode)	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:48
L22	4046	19 and (anode with active near	US-PGPUB;	OR	OFF	2018/12/25

		material) with (metal or alloy or silicon)	USPAT			20:50
L23	158	19 and ((anode with active near material) with (metal or alloy or silicon) with (copper near foil))	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:51
L24	21	19 and ((anode with active near material) with ((metal or alloy or silicon) with carbon) with (copper near foil))	US-PGPUB; USPAT	OR	OFF	2018/12/25 20:53
L25	0	21 and ((first near surface) same (second near surface) same (roughness with ratio))	US-PGPUB; USPAT	OR	OFF	2018/12/25 21:57
L26	1	21 and ((first near surface) same (second near surface) same (roughness with difference))	US-PGPUB; USPAT	OR	OFF	2018/12/25 21:59
L27	0	26 and (shiny same matte)	US-PGPUB; USPAT	OR	OFF	2018/12/25 22:09
L29	0	26 and (shiny same matte)	US-PGPUB; USPAT	OR	OFF	2018/12/25 22:10
L30	0	26 and (shiny and matte)	US-PGPUB; USPAT	OR	OFF	2018/12/25 22:11
L31	5	19 and (shiny with matte)	US-PGPUB; USPAT	OR	OFF	2018/12/25 22:11
L32	186285	(C25D1/04 H01M4/66 H01M4/661 H01M4/665 H01M10/052 Y02P70/54 Y02E60/122 Y02T10/7011)".CPC"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	OR	OFF	2018/12/25 22:56

EAST Search History (Interference)

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12/25/2018 11:02:48 PM
C:\Users\ausyatinsky\Documents\EAST\Workspaces\15307069.wsp

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	15307069
Filing Date	2016-10-27
First Named Inventor	Dae Young KIM
Art Unit	1727
Examiner Name	USYATINSKY, ALEXANDER
Attorney Docket Number	0313221.00005

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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	2011129633	WO	A2	2011-10-20	ILJIN MATERIALS CO., LTD.		
	2	2014033917	WO	A1	2014-03-06	JX NIPPON MINING & METALS CORPORATION		
	3	2006299320	JP	A	2006-02-11	LS CABLE LTD.		

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /AU/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15307069
	Filing Date	2016-10-27
	First Named Inventor	Dae Young KIM
	Art Unit	1727
	Examiner Name	USYATINSKY, ALEXANDER
	Attorney Docket Number	0313221.00005

	4	104846407	CN	A	2015-08-19	LINGBAO WASON COPPER FOIL CO		

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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	~~Taiwanese Notice of Allowance for related Taiwanese Application No. 105119103, action dated February 6, 2018,~~ (8 pages)	

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EXAMINER SIGNATURE

Examiner Signature	/Alexander Usyatinsky/ (12/25/2018)	Date Considered	12/25/2018

*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	15307069
	Filing Date	2016-10-27
	First Named Inventor	Dae Young KIM
	Art Unit	1727
	Examiner Name	USYATINSKY, ALEXANDER
	Attorney Docket Number	0313221.00005

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)	2018-05-08
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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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.

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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	15307069
Filing Date	2016-10-27
First Named Inventor	Dae Young KIM
Art Unit	1727
Examiner Name	USYATINSKY, ALEXANDER
Attorney Docket Number	0313221.00005

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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	2007105635	WO	A1	2009-07-30	UNKNOWN		
	2	2012151106	JP	A	2012-08-09	FURUKAWA ELECTRIC CO LTD.		
	3	2012022939	JP	A	2012-02-02	LS MTRON LTD		

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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	Japanese Office Action for related Japanese Application No. 2017-561829; action dated December 11, 2018; (3 pages)	

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EXAMINER SIGNATURE

Examiner Signature	/Alexander Usyatinsky/ (12/25/2018)	Date Considered	12/25/2018

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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)	2018-12-18
Name/Print	Matthew S. Dicke	Registration Number	58819

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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.

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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Bibliographic Data

Application No: 15/307,069

Foreign Priority claimed: (●) Yes ( ) No

35 USC 119 (a-d) conditions met: [☑] Yes [ ] No | [ ] Met After Allowance

Verified and Acknowledged: /Alexander Usyatinsky/ | [ ]

Examiner's Signature | Initials

Title: ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
10/27/2016	429	1727	0313221.00005
RULE			

APPLICANTS

LS Mtron Ltd., Anyang-si, Gyeonggi-do, KOREA, REPUBLIC OF

INVENTORS

Dae Young KIM Yongin-si, KOREA, REPUBLIC OF

Seung Min KIM Osan-si, KOREA, REPUBLIC OF

CONTINUING DATA

This application is a 371 of PCT/KR2016/004449 04/28/2016

FOREIGN APPLICATIONS

KOREA, REPUBLIC OF 10-2015-0090000 06/24/2015

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P.O. Box 1135
CHICAGO, IL 60690
UNITED STATES

FILING FEE RECEIVED

$1,480

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
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	Application Number	
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	First Named Inventor	Dae Young KIM
	Art Unit	
	Examiner Name	
	Attorney Docket Number	P11304US

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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	20150340639	A1	2015-11-26	MITSUI MINING & SMELTING CO., LTD	
	2	20160260981	A1	2016-09-08	ILJIN MATERIALS CO., LTD	
	3	20140193660	A1	2014-07-10	CHANG CHUN PETROCHEMICAL CO., LTD.	
	4	20010051282	A1	2001-12-13	Charles B. YATES et al.	

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	Examiner Name	
	Attorney Docket Number	P11304US

	1	2000-182623	JP	A	2000-06-30	NIPPON DENKAI KK		☒
	2	2014-135175	JP	A	2014-07-24	MITSUI MINING & SMELTING CO LTD	Also published as US Patent Application Publication No. US 2015-0340639	☒
	3	10-1449342	KR	B1	2014-10-13	ILJIN M ATERIALS CO., LTD.	Also published as US Patent Application Publication No. US 2016-0260981	☒
	4	10-2014-0090069	KR	A	2014-07-16	CHANG CHUN PETROCHEM ICAL CORPORATION	Also published as US Patent Application Publication No. US 2014-0193660	☒

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	1	Search Report for International Application No. PCT/KR2016/004449	

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EXAMINER SIGNATURE

Examiner Signature	/Alexander Usyatinsky/ (01/05/2019)	Date Considered	01/05/2019

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Signature	/Taeksoo Lee/	Date (YYYY-MM-DD)	2016-10-26
Name/Print	Taeksoo Lee	Registration Number	61976

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	1	5431803		1995-07-11	DIFRANCO, ET AL.	

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	1	3067199	EP	A1	2016-09-14	IJIN MATERIALS CO., LTD		
	2	2660359	EP	A1	2013-11-06	FURUKAWA ELECTRIC CO., LTD		
	3	1876266	EP	A1	2008-01-09	MITSUI MINING & SMELTING CO., LTD		

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	4	20001011684	JP	A	2001-01-16	UNKNOWN		
	5	3850155	JP	A	2006-11-29	NIPPON DENKAI KK	Also published as JP2000-182623	
	6	1480563	CN	A	2004-03-10	FURUKAWA CIRCUIT FOIL		

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	1	Chinese Office Action for related Chinese Application No. 201680000680.4; action dated August 1, 2018; (8 pages)	
	2	European Search Report for related European Application No. 16814576.1; report dated October 17, 2018; (9 pages)	

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Examiner Signature	/Alexander Usyatinsky/ (12/25/2018)	Date Considered	12/25/2018

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Signature	/Matthew S. Dicke/	Date (YYYY-MM-DD)	2018-10-26
Name/Print	Matthew S. Dicke	Registration Number	58819

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Application Number	15307069
Filing Date	2016-10-27
First Named Inventor	Dae Young KIM
Art Unit	1727
Examiner Name	USYATINSKY, ALEXANDER
Attorney Docket Number	0313221.00005

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	1	2007105635	WO	A1	2009-07-30	UNKNOWN		
	2	2012151106	JP	A	2012-08-09	FURUKAWA ELECTRIC CO LTD.		
	3	2012022939	JP	A	2012-02-02	LS MTRON LTD		

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
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	Art Unit	1727
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Name/Print	Matthew S. Dicke	Registration Number	58819

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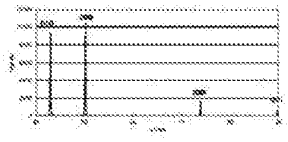
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(22)Date of filing	15.07.2010
(71)Applicant	LS MTRON LTD
(72)Inventor	KIM DAE-YON LEE BYON-KWAN CHOE SUN-JUN



(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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(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2012-22939
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(51)Int.Cl.			F I			テーマコード（参考）
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審査請求 有　請求項の数 7　ＯＬ　（全 8 頁）

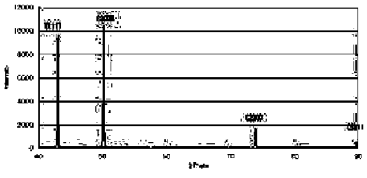
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(71)出願人　509023012
エル　エス　エムトロン　リミテッド
ＬＳ　Ｍｔｒｏｎ　Ｌｔｄ.
大韓民国，　ギョンギ－ド，　アニャン－シティー，　ドン－アン－グ，　ホゲ－ドン，　１０２６－６
１０２６－６，　Ｈｏｇｙｅ－ｄｏｎｇ，　Ｄｏｎｇ－ａｎ－ｇｕ，　Ａｎｙａｎｇ－ｃｉｔｙ，　Ｇｙｅｏｎｇｇｉ－ｄｏ，　Ｒｅｐｕｂｌｉｃ　ｏｆ　Ｋｏｒｅａ
(74)代理人　100080621
弁理士　矢野　寿一郎

最終頁に続く

(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。（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】

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

【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 [㎛]	(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	76	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】

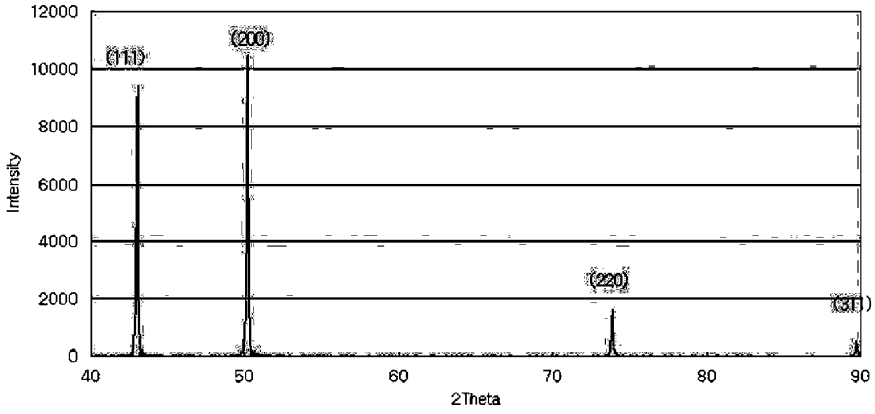
【００３２】

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

フロントページの続き

(72)発明者 キム，デーヨン
大韓民国 ４３５－７６０ キョンギード，クンポーシ，オゲムードン，ハルラ ２ーチャ アパートメント，４１５－１１０１
(72)発明者 リ，ビョンークァン
大韓民国 ４６７－７４１ キョンギード，イチョンーシ，ソンジェンードン，シニル アパートメント，２０１－１０２
(72)発明者 チェ，スンージュン
大韓民国 ４４２－１５０ キョンギード，スウォンーシ，パルタルーグ，ファセードン，ビュンサン ブラン プレアンサップ，１０６－４０４

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(71)Applicant	FURUKAWA ELECTRIC CO LTD:THE
(72)Inventor	SUZUKI AKITOSHI SHINOZAKI KENSAKU

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(54)LITHIUM ION SECONDARY BATTERY, NEGATIVE ELECTRODE FOR THE BATTERY, AND ELECTROLYTIC COPPER FOIL FOR COLLECTOR OF THE NEGATIVE ELECTRODE FOR THE BATTERY

(57)Abstract

PROBLEM TO BE SOLVED: To provide electrolytic copper foil for a negative electrode for a lithium ion secondary battery capable of constituting a lithium ion secondary battery prevented from decreasing in capacity maintenance factor over repeated cycles of charge and discharge to achieve a long life, and preventing deformation of a negative electrode collector.
SOLUTION: The electrolytic copper foil constitutes a negative electrode collector of a lithium

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(33)優先権主張国　日本国(JP)

(71)出願人　000005290
古河電気工業株式会社
東京都千代田区丸の内二丁目２番３号
(74)代理人　100094053
弁理士　佐藤　隆久
(72)発明者　鈴木　昭利
東京都千代田区丸の内２丁目２番３号　古河電気工業株式会社内
(72)発明者　篠崎　健作
東京都千代田区丸の内２丁目２番３号　古河電気工業株式会社内

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(54)【発明の名称】リチウムイオン二次電池、該電池用負極電極、該電池負極集電体用電解銅箔

(57)【要約】
【課題】充放電サイクルを繰り返しても容量保持率の低下が起こらず高寿命で、負極集電体が変形しないリチウムイオン二次電池を作成可能なリチウムイオン二次電池負極用電解銅箔を供給することを目的とする。
【解決手段】本発明のリチウムイオン二次電池の負極集電体を構成する電解銅箔であって、該電解銅箔は２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上であり、該電解銅箔の活物質層を設ける表面は防錆処理が施され、或いは粗化処理され防錆処理が施されている。また本発明は前記電解銅箔を集電体とするリチウムイオン二次電池用電極、該電極を負極としたリチウムイオン二次電池である。
【選択図】なし

【特許請求の範囲】
【請求項１】
リチウムイオン二次電池の負極集電体を構成するリチウムイオン二次電池負極集電体用電解銅箔であって、該電解銅箔はＳ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上であり、該電解銅箔の活物質層を設ける表面は防錆処理が施されているリチウムイオン二次電池負極集電体用電解銅箔。
【請求項２】
リチウムイオン二次電池の負極集電体を構成するリチウムイオン二次電池負極集電体用電解銅箔であって、該電解銅箔はＳ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上であり、該電解銅箔の活物質層を設ける表面は粗化処理が施され、さらに防錆処理が施されているリチウムイオン二次電池負極集電体用電解銅箔。
【請求項３】
前記電解銅箔の表面を粗化処理して形成する表面が、めっき法により銅を主成分とする粒子を付着して粗化した表面であることを特徴とする請求項２に記載のリチウムイオン二次電池負極電極集電体用電解銅箔。
【請求項４】
前記電解銅箔の表面を粗化処理して形成する表面が、銅のやけめっきによる粒粉状銅めっき層と、該粒粉状銅めっき層上にその凹凸形状を損なわない緻密な銅めっき（被せめっき）で形成した銅めっき層とで形成された表面である請求項２に記載のリチウムイオン二次電池負極電極集電体用銅箔。
【請求項５】
前記電解銅箔の表面を粗化して形成する表面が、エッチング法により粗化した表面であることを特徴とする請求項２に記載のリチウムイオン二次電池負極集電体用電解銅箔。
【請求項６】
リチウムイオン二次電池の負極電極であって、該負極電極は、Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上で、その少なくとも一方の表面を防錆処理してなる電解銅箔を集電体とし、該集電体の前記防錆処理がなされた面に活物質層が形成されているリチウムイオン二次電池の負極電極。
【請求項７】
リチウムイオン二次電池の負極電極であって、該負極電極は、Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上で、その少なくとも一方の表面を粗化処理し、防錆処理してなる電解銅箔を集電体とし、該集電体の前記防錆処理がなされた面に活物質層が形成されているリチウムイオン二次電池の負極電極。
【請求項８】
前記活物質層が、活物質、バインダー、溶媒を混練りしスラリー状としたものを負極集電体に塗布、乾燥、プレスしたものであることを特徴とする請求項６又は７に記載のリチウムイオン二次電池の負極電極。
【請求項９】
前記活物質層がカーボン、シリコン、ゲルマニウム、または錫を主成分とする活物質で形成されている請求項６～８のいずれかに記載のリチウムイオン二次電池の負極電極。
【請求項１０】
正極及び負極を備えるリチウムイオン二次電池であって、前記負極電極はＳ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上で、その少なくとも一方の表面を防錆処理してなる電解銅箔を集電体とし、該集電体の前記防錆処理がなされた面に活物質層が形成されているリチウムイオン二次電池。

【請求項１１】
正極及び負極を備えるリチウムイオン二次電池であって、前記負極はＳ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上で、その少なくとも一方の表面が粗化処理され、防錆処理されてなる電解銅箔を集電体とし、該集電体の前記防錆処理がなされた面に活物質層が形成されているリチウムイオン二次電池。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、正極と、負極集電体の表面に負極活物質層が形成された負極と、非水電解質とを備えるリチウムイオン二次電池、該二次電池に用いる電極、ならびに該電極の集電体を構成する電解銅箔に関するものである。
【背景技術】
【０００２】
正極と、両面が平滑な銅箔からなる負極集電体の表面に負極活物質層としてカーボン粒子を塗布、乾燥し、さらにプレスした負極と、非水電解質を備えるリチウムイオン二次電池は現在、携帯電話、ノートタイプパソコン等に使用されている。このリチウムイオン二次電池の負極には、電解により製造された、いわゆる「未処理銅箔」に防錆処理を施したものが使用されている。
【０００３】
前記リチウムイオン二次電池用負極集電体としての銅箔には、特許文献１に示すように、粗面の粗さを小さくして、さらにＳ面（光沢面）とＭ面（粗面）との間における表面粗さの差を小さくした銅箔を用いることにより、電池の充放電効率の低下を抑えている。
【０００４】
上記のような粗面の粗さを小さくして、さらにＳ面とＭ面との表面粗さの差を小さくした電解銅箔は、硫酸銅－硫酸電解液に各種水溶性高分子物質、各種界面活性剤、各種有機イオウ系化合物、塩化物イオンなどを適宜選定して添加することによって製造されている。
例えば、特許文献１には、硫酸銅－硫酸電解液にメルカプト基を持つ化合物、塩化物イオン、並びに分子量１００００ 以下の低分子量膠及び高分子多糖類を添加したものにより製造した電解銅箔を用いた負極集電体が開示されている。
上記製造方法で製造した電解銅箔は、その銅箔の表面にカーボン粒子が塗布され乾燥した後、さらにプレスされて負極となる。
この電解銅箔は引張強さが３００～３５０Ｎ／ｍｍ^{2}であり、前記カーボン粒子を活物質とした負極用銅箔として使用する場合には適度な伸びと併せて好適な材料である。
また、特許文献２には硫酸銅－硫酸電解液から製造した電解銅箔が開示されている。
【０００５】
ところで近年、リチウムイオン二次電池の高容量化を目的として、充電の際に電気化学的にリチウムと合金化するアルミニウム、シリコン、錫などを負極活物質として用いるリチウムイオン二次電池が提案されている（特許文献３参照）。
【０００６】
高容量化を目的としたリチウムイオン二次電池用電極（負極）は、ＣＶＤ法やスパッタリング法により、銅箔などの集電体の上に、例えばシリコンを非晶質シリコン薄膜や微結晶シリコン薄膜として堆積し形成している。このような方法で作成した活物質の薄膜層は集電体に密着するため、良好な充放電サイクル特性を示すことが見出されている（特許文献４参照）。
また、最近では粉末シリコンあるいはシリコン化合物をイミド系のバインダーと共に有機溶媒によりスラリー状にして銅箔上に塗布し、乾燥、プレスする形成方法も開発されている。（特許文献５参照）
【０００７】

しかし、このようなリチウムイオン二次電池用電極においては、例えばシリコン活物質は充電時にリチウムイオンを吸蔵することによりその体積が約４倍膨張する。さらに放電時にはリチウムイオンを放出して収縮する。

こうした充放電に伴う活物質層体積の膨張及び収縮により、活物質が微粉化して集電体から剥離する現象が見られる。

また該活物質層が集電体と密着しているため、充放電の繰り返しにより活物質層の体積が膨張及び収縮すると、集電体に大きな応力が働き、集電体にしわが発生し、さらに多数回充放電を繰り返すと、集電体を構成する箔が破断するといった問題があった。

【０００８】

活物質が微粉化して集電体から剥離すると、電池のサイクル充放電効率の低下が発生する。

また、集電体にしわなどの変形が生じると、正極と負極が短絡しやすくなるという問題が生じる。

また、集電体の破断が起こると長時間安定した電池性能を維持することができないという問題が生じる。

【０００９】

従来こうした問題に対して、本発明者等は、引張強さが高く、破断伸びが大きい銅箔を採用することを提案している。例えば、引張り強さが４００Ｎ／ｍｍ^{2}以上で、伸びが４．５％～１３％であり、表面粗さＲａが０．０１～１μｍである電解銅箔を採用してリチウムイオン二次電池を構成することを提案した。（特許文献６）

特許文献６では活物質層にシリコン活物質を使用している例が記載されている。

しかし、シリコン活物質を使用し、集電体である銅箔に熱がかかるような場合、例えばシリコン活物質を使用して、ポリイミド系のバインダーを使用した場合、乾燥、キュアの温度は、２００℃から４００℃に及ぶ場合がある。

こうした場合には特許文献６に示した電解銅箔では集電体としての機能を充分に発揮できないことが判明した。

【先行技術文献】

【特許文献】

【００１０】

【特許文献１】特許第３７４２１４４号公報
【特許文献２】特許第３８５０１５５号公報
【特許文献３】特開平１０－２５５７６８号公報
【特許文献４】特開２００２－０８３５９４号公報
【特許文献５】特開２００７－２２７３２８号公報
【特許文献６】ＷＯ２０１０－１１０２０５号

【発明の概要】

【発明が解決しようとする課題】

【００１１】

リチウムイオン二次電池用電極として上述したようにシリコン、ゲルマニウム、または錫を主成分とする活物質層を集電体上に形成した負極電極を用いた場合、活物質が微粉化して集電体から剥離する場合がある。また、充放電反応に伴い活物質層の体積が膨張・収縮し、集電体に大きな応力が働き、集電体にしわなどの変形を生じさせる場合がある。さらに多数回充放電を繰り返すと集電体としての箔が破断するという問題があった。

活物質が微粉化して集電体から剥離すると、電池の充放電サイクル効率の低下が発生する。集電体にしわなどの変形が生じると、正極と負極が短絡しやすいという問題を生じる。また、集電体に破断が起こると長時間安定した電池性能を維持することができない。

【００１２】

本発明は例えばシリコン、ゲルマニウム、または錫を主成分とする活物質層を集電体上に形成した負極電極を用いたリチウムイオン二次電池において、充放電サイクル効率に優れ、さらに集電体にしわが発生せず、また集電体の破断も起こらない長時間安定した性能

を維持できるリチウムイオン二次電池を提供することを目的とし、該二次電池用の電極、ならびに該電極の集電体を構成する電解銅箔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】

【００１３】

本発明のリチウムイオン二次電池負極集電体用電解銅箔は、Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、該電解銅箔を２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上であり、該電解銅箔の活物質層を設ける表面に防錆処理が施されていることを特徴とする。

【００１４】

また、本発明のリチウムイオン二次電池の負極集電体を構成するリチウムイオン二次電池負極集電体用電解銅箔は、Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、該電解銅箔を２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上であり、該電解銅箔の活物質層を設ける表面は粗化処理され、さらに防錆処理が施されていることを特徴とする。

【００１５】

前記電解銅箔の表面は、めっき法により銅を主成分とする粒子を付着して粗化した表面、または銅のやけめっきによる粒粉状銅めっき層と、該粒粉状銅めっき層上にその凹凸形状を損なわない緻密な銅めっき（被せめっき）で形成した銅めっき層とで形成した表面、或いはエッチング法により粗化した表面である。

【００１６】

本発明のリチウムイオン二次電池の負極電極は、Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上で、その少なくとも一方の表面を防錆処理してなる電解銅箔を集電体とし、該集電体の前記防錆処理がなされた面に活物質層が形成されていることを特徴とする。

【００１７】

また、本発明のリチウムイオン二次電池の負極電極は、Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上で、その少なくとも一方の表面を粗化し、防錆処理してなる電解銅箔を集電体とし、該集電体の前記防錆処理がなされた面に活物質層が形成されていることを特徴とする。

【００１８】

前記活物質層は、前記集電体に活物質、バインダー、溶媒を混練りしスラリー状として塗布、乾燥、プレスして堆積する。

前記活物質層はカーボン、シリコン、ゲルマニウム、または錫を主成分とする活物質で形成されていることを特徴とする。

【００１９】

本発明のリチウムイオン二次電池は、Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上で、その少なくとも一方の表面を防錆処理してなる電解銅箔を集電体とし、該集電体の前記防錆処理がなされた面に活物質層が形成されている電極を負極電極とすることを特徴とする。

【００２０】

本発明のリチウムイオン二次電池は、Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上で、その少なくとも一方の表面が粗化され、防錆処理されてなる電解銅箔を集電体とし、該集電体の前記防錆処理がなされた面に活物質層が形成されている電極を負極電極とすることを特徴とする。

【発明の効果】

【００２１】

本発明のリチウムイオン二次電池は、該電池の負極集電体に前記電解銅箔を使用することにより、充放電により集電体にしわ等の変形が発生せず、正極と負極の短絡を防ぐことができ、また集電体が破断しないため長時間にわたり安定した性能のリチウムイオン二次電池を提供することができる。

【発明を実施するための形態】

【００２２】

本発明のリチウムイオン二次電池負極集電体用電解銅箔は、Ｓ面とＭ面ともに表面粗さＲｚが０．８～２．８μｍで、２００～４００℃で０．５～１．５時間加熱処理後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上で、伸びが２．５％以上ある電解銅箔の少なくとも一方の面に防錆処理、或いは粗化と防錆処理を施した電解銅箔である。

【００２３】

本発明のリチウムイオン二次電池の負極集電体は、Ｓ面とＭ面ともに表面粗さＲｚ：０．８～２．８μｍで、２００～４００℃で０．５～１．５時間加熱処理後にその０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上ある電解銅箔の少なくとも一方の面に防錆処理、或いは粗化と防錆処理を施した電解銅箔を集電体として用いる。

【００２４】

また、本発明のリチウムイオン二次電池用負極電極は、Ｓ面とＭ面ともに表面粗さＲｚ：０．８～２．８μｍで、２００～４００℃で０．５～１．５時間加熱後の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上で、少なくとも一方の面に防錆処理、或いは粗化と防錆処理が施された電解銅箔を集電体とし、該集電体の防錆処理がなされた面に負極構成活物質層が施されている。

前記電解銅箔を集電体とし、該集電体表面に活物質層を施しリチウムイオン二次電池の負極電極とすることで、集電体がリチウムの吸蔵・放出に伴う活物質層の膨張・収縮による応力を受けても、電池の充放電サイクル効率の低下が小さく、集電体としてしわ等の変形、破断等が生じることがない。

【００２５】

従来のカーボン系の負極構成活物質層を形成する場合は、負極活物質であるカーボン、バインダーであるポリフッ化ビニリデン樹脂、溶媒であるＮ－メチルピロリドンからなるペーストを作り銅箔の両面に塗布、乾燥を行う。

この場合は、１５０℃前後の温度で乾燥を行う。１５０℃前後の温度では電解銅箔の引張強さ、０．２％耐力、伸びはほとんど変化しない。例えば前述した特許文献１に記載されている、硫酸銅－硫酸電解液にメルカプト基を持つ化合物、塩化物イオン、並びに分子量１００００ 以下の低分子量膠及び高分子多糖類を添加した電解液を使って製造した電解銅箔は、１０μｍ箔の室温での引張強さは３００～３５０Ｎ／ｍｍ^{2}であるが、１５０℃前後の温度で乾燥を行ってもその性能はほとんど変化しない。

さらに前記のようにカーボン活物質の場合は充放電時にその体積膨張がせいぜい１０％程度であるため、充放電サイクル効率が著しく小さくなったり、充放電による集電体の変形が起こったり破断したりするというようなことはない。

【００２６】

また、前述した特許文献２に記載されている、硫酸銅－硫酸電解液から製造した１０μｍ厚さの電解銅箔は、室温での引張強さは５７０Ｎ／ｍｍ^{2}前後、伸びは７％前後であるが、１５０℃前後の温度で乾燥を行うとその性能は変化し、引張強さは２３０Ｎ／ｍｍ^{2}前後、伸びは２５％前後になる。しかし、カーボン活物質の場合は充放電時にその体積膨張がせいぜい１０％程度であるため、上記のような引張強さが小さく、伸びが大きい箔でも充放電サイクル効率が著しく小さくなったり、充放電による集電体の変形が起こったり破断したりするというようなことはない。

【００２７】

これに対して活物質としてシリコン（ケイ素系）を使う場合は、充放電時の活物質の膨張、収縮を防ぐためにバインダーにポリイミド系の樹脂を使う場合がある。この場合乾燥、キュア温度はカーボン系の活物質を使う場合より高く、２００℃～４００℃程度の温度

で０．５～１．５時間ほど乾燥、キュアを行う。
こうした高温で加熱を行うと、前記特許文献１及び特許文献２の電解銅箔では箔が焼鈍され軟化して、充放電サイクル効率が著しく小さくなり、充放電時の活物質の膨張収縮により箔に変形、破断が発生しやすくなる。
【００２８】
箔が変形する場合、箔には降伏点以上の応力がかかったと考えることができる。降伏点とは弾性から塑性に変わるところの応力である。箔に弾性領域の応力がかかっても変形が起こることはない。しかし、塑性領域の応力がかかった場合は変形する。
【００２９】
従って、乾燥、キュアにより箔が加熱された後であっても、降伏点が大きい箔の場合は、充放電により活物質が膨張収縮し、集電体である箔に応力がかかった場合でも変形が起こる可能性は極めて低い。
【００３０】
従って、前記特許文献６に記載されているように、室温において引張り強さが４００Ｎ／ｍｍ^{2}以上、伸びが４．５％～１３％ある電解銅箔を用いたとしても、必ずしも充放電による膨張、収縮で箔に変形が起こらない、とは言えない。乾燥、キュアによる加熱後でも降伏点が大きい箔こそ、箔変形を起こさない箔であると言える。
【００３１】
ここで、降伏点は引張試験により測定を行うが、電解銅箔の場合はこの点がはっきりしない。こうした場合、通常０．２％ひずみが発生したときの値をとり降伏点に代用する。これを０．２％耐力と呼んでいる。
【００３２】
電解銅箔の場合、室温において大きな０．２％耐力をもつことが、加熱後でも大きな降伏点をもつことと必ずしも一致するわけではない。例えば表２の比較例２に示した箔は特許文献２をもとに作成した箔であるが、室温では高い引張強さ（５１０Ｎ／ｍｍ^2）と０．２％耐力（３４５Ｎ／ｍｍ^2）を持つが、加熱後には焼鈍され軟化して引張り強さ（２０４Ｎ／ｍｍ^2）、０．２％耐力（１０２Ｎ／ｍｍ^2）と小さい箔になってしまう。
【００３３】
特許文献６に記載されているように、室温における引張強さが４００Ｎ／ｍｍ^{2}以上ある材料でも、加熱により焼鈍され０．２％耐力が小さくなる材料では意味がない。加熱した後の０．２％耐力がある一定の値以上を有することが重要である。
また伸びが小さい場合には、充放電サイクルを多数回繰り返すうちに充放電サイクル効率の低下が大きい傾向がある。
充放電サイクル効率の低下を小さくするためには、０．２％耐力で２５０Ｎ／ｍｍ^{2}以上必要で、伸びが２．５％以上必要である。
【００３４】
本発明のリチウムイオン二次電池負極集電体用電解銅箔は、負極構成活物質層を形成し２００～４００℃で０．５～１．５時間加熱処理後にその０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上ある未処理銅箔の少なくとも一方の面に防錆処理、或いは粗化と防錆処理を施した材料を集電体として用いるので、リチウムの吸蔵・放出に伴う活物質層の膨張・収縮による応力を受けても、集電体としてしわ等の変形、破断等が生じることがない。
【００３５】
リチウムイオン二次電池は充電放電サイクルを繰り返すと容量維持率は低下する。この容量維持率（充放電サイクル効率）の低下が少ないほど高性能なリチウムイオン二次電池と言うことができる。
この特性に影響する要因として、０．２％耐力、伸びがあることは既に述べたとおりであるが、その他に負極活物質自体の劣化、電解液の分解による活物質表面への皮膜の形成、活物質の亀裂発生、或いは活物質－銅箔間の剥離等がある。
このうち銅箔が原因と考えられるものは活物質－銅箔間の剥離である。

【００３６】
活物質－銅箔間の剥離原因として、０．２％耐力、伸びとともに、表面粗さもひとつの要因となる。
表面粗さの適正な範囲はＲｚで０．８～２．８μｍである。Ｒｚが０．８μｍを下回ると効果がなく、またＲｚを２．８μｍ以上にしても効果が飽和してしまったり、かえって充放電時の容量維持率が悪くなったりする。そのため、表面粗さＲｚが０．８～２．８μｍの電解銅箔（集電体）上に活物質層を形成することが効果的である。
【００３７】
本発明において、引張強さ、０．２％耐力、伸びは、日本工業規格（ＪＩＳ Ｋ ６２５１）に定められた方法により、測定した値である。
また、表面粗さＲｚは、日本工業規格（ＪＩＳ Ｂ ０６０１－１９９４）に定められた十点平均粗さであり、例えば触針式表面粗さ計により測定した値である。
【００３８】
本発明のリチウムイオン二次電池負極集電体用電解銅箔は、上記電解銅箔上に負極構成活物質層を形成し、Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で加熱処理後にその０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上ある電解銅箔の少なくとも一方の面に防錆処理して集電体として用いるので、リチウムの吸蔵・放出に伴う活物質薄膜の膨張・収縮による応力を受けても、電池の充放電サイクル効率の低下、集電体としてしわ等の変形、破断等が生じることがない。
【００３９】
また、本発明のリチウムイオン二次電池負極集電体用電解銅箔は、上記電解銅箔上に負極構成活物質層を形成し、Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で０．５～１．５時間加熱処理後にその０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上ある電解銅箔を用い、少なくとも一方の面を粗化し、防錆処理を施して集電体として用いるので、電池の充放電サイクル効率の低下、リチウムの吸蔵・放出に伴う活物質薄膜の膨張・収縮による応力を受けても、集電体としてしわ等の変形、破断等が生じることがない。
【００４０】
集電体用電解銅箔としては、電池の充放電サイクル効率の低下、リチウムの吸蔵・放出に伴う活物質層の膨張・収縮による応力によるしわ等の変形、破断等に対して、Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で０．５～１．５時間加熱処理後にその０．２％耐力が２５０Ｎ／ｍｍ^{2}以上であることとともに、伸びが２．５％以上であることも重要な要素である。
【００４１】
Ｓ面とＭ面ともに、Ｒｚ：０．８～２．８μｍであり、２００～４００℃で０．５～１．５時間加熱処理後にその０．２％耐力が２５０Ｎ／ｍｍ^{2}以上であっても、伸びが２．５％より小さなものでは、集電体としてしわ等の変形、破断等は発生しないが、電池の充放電サイクル効率の低下は大きくなる傾向が見られる。
【００４２】
本発明のリチウムイオン二次電池負極集電体用電解銅箔は、硫酸－硫酸銅水溶液を電解液とし、白金属元素又はその酸化物元素で被覆したチタンからなる不溶性陽極と該陽極に対向させて設けられたチタン製陰極ドラムとの間に該電解液を供給し、陰極ドラムを一定速度で回転させながら、両極間に直流電流を通電することにより陰極ドラム表面上に銅を析出させ、析出した銅を陰極ドラム表面から引き剥がし、連続的に巻き取る方法により製造される。
【００４３】
本発明のリチウムイオン二次電池負極集電体用電解銅箔は、硫酸－硫酸銅電解液に次のＡ又はＢ－３のいずれかの有機添加剤、及び塩化物イオンを添加し製造することができる。
Ａ：チオ尿素又はチオ尿素誘導体から選ばれた一種以上の添加剤

Ｂ：Ｂ－１；チオ尿素又はチオ尿素誘導体
　Ｂ－２；ニカワ、ゼラチン、ポリエチレングリコール、ポリプロピレングリコール、デンプン、セルロース系水溶性高分子（カルボキシルメチルセルロース、ヒドロキシエチルセルロース等）等の高分子多糖類、ポリエチレンイミン、ポリアクリルアミド
　Ｂ－３；Ｂ－１及びＢ－２からそれぞれ選ばれた一種以上の添加剤の組み合わせ

【００４４】

ここで、チオ尿素、チオ尿素誘導体としては、チオ尿素（CH_4N_2S）、Ｎ，Ｎ’－ジメチルチオ尿素（$C_3H_8N_2S$）、Ｎ，Ｎ’－ジエチルチオ尿素（$C_5H_{12}N_2S$）、テトラメチルチオ尿素（$C_5H_{12}N_2S$）、チオセミカルバシド（CH_5N_3S）、Ｎ－アリルチオ尿素（$C_4H_8N_2S$）、エチレンチオ尿素（$C_3H_6N_2S$）等の水溶性のチオ尿素、チオ尿素誘導体があげられる。

【００４５】

なお本明細書においては、製造時に電解銅箔が陰極ドラム表面に接していた側の面を光沢面；「Ｓ面」、逆の面を粗面；「Ｍ面」と称している。

【００４６】

製造された電解銅箔（未処理銅箔）はこのまま集電体として使用することもできるが、多くの場合、クロメート処理、Ｎｉ又はＮｉ合金めっき、Ｃｏ又はＣｏ合金めっき、Ｚｎ又はＺｎ合金めっき、Ｓｎ又はＳｎ合金めっき、或いは上記各種めっき上にさらにクロメート処理を施したもの等の無機防錆処理、ベンゾトリアゾール等の有機防錆処理、シランカップリング剤処理等が施されて、リチウムイオン二次電池負極集電体用電解銅箔として使用される。

上記無機防錆処理、有機防錆処理、シランカップリング剤処理は活物質との密着強度を高め、電池の充放電サイクル効率の低下を防ぐ役割を果たす。

【００４７】

また電解銅箔表面に粗面化処理を行う。この粗面化処理としては、めっき法、エッチング法等が好適に採用できる。

めっき法は、未処理電解銅箔の表面に凹凸を有する薄膜層を形成することにより表面を粗面化する方法である。めっき法としては、電解めっき法及び無電解めっき法が採用することができる。

【００４８】

めっき法による粗面化としては、銅や銅合金などの銅を主成分とするめっき膜を、未処理電解銅箔表面に形成する方法が好ましい。

【００４９】

電気めっきにより粗面化する方法としては、例えば、特許文献７（特公昭５３－３９３７６号公報）に開示された、プリント回路用銅箔に対し一般的に用いられているめっきによる粗面化方法が好ましく用いられる。すなわち、いわゆる「やけめっき」により、粒粉状銅めっき層を形成した後、この粒粉状銅めっき層の上に、その凹凸形状を損なわないように「被せめっき」を行い、実質的に平滑なめっき層を堆積させて粒粉状銅をいわゆるコブ状銅とする粗面化方法である。

【００５０】

エッチング法による粗面化としては、物理的エッチングや化学的エッチングによる方法が適している。物理的エッチングにはサンドブラスト等でエッチングする方法があり、化学エッチングには処理液として、無機または有機酸と酸化剤と添加剤を含有する液が多数提案されている。例えば特許文献８（特許２７４０７６８号公報）では、無機酸＋過酸化水素＋トリアゾールなどの腐食防止剤＋界面活性剤が開示されている。また、特許文献９（特開平１０－９６０８８号公報）には、無機酸＋過酸化物＋アゾール＋ハロゲン化物を含有する液が開示されている。

通常は酸と酸化剤にキレート剤などの添加剤を付与した浴であり、銅の結晶粒界を優先的に溶解するものである。例えば、前記特許文献に開示されている液組成の他に、メック株式会社のＣＺ－８１００、同８１０１、三菱ガス化学株式会社のＣＰＥ－９００などの

市販品が採用できる。

【００５１】

本発明における活物質層は、リチウムを吸蔵・放出する物質であり、リチウムを合金化することにより吸蔵する活物質であることが好ましい。このような活物質材料としては、カーボン、シリコン、ゲルマニウム、錫、鉛、亜鉛、マグネシウム、ナトリウム、アルミニウム、カリウム、インジウムなどが挙げられる。これらの中でも、カーボン、シリコン、ゲルマニウム、及び錫がその高い理論容量から好ましく用いられる。従って、本発明において用いる活物質層は、カーボン、シリコン、ゲルマニウム、または錫を主成分とする層であることが好ましく、特に本発明の電解銅箔を集電体とするリチウムイオン二次電池に好ましく採用できる活物質はシリコンである。

【００５２】

本発明における活物質層は、活物質をバインダー、溶剤とともにスラリー状にして、塗布、乾燥、プレスすることにより形成する方法が望ましい。

【００５３】

本発明においては、集電体は厚みの薄いものであることが好ましく、活物質層は、集電体の片面または両面上に形成することができる。

【００５４】

本発明における活物質層には、予めリチウムが吸蔵または添加されていてもよい。リチウムは、活物質層を形成する際に添加してもよい。すなわち、リチウムを含有する活物質層を形成することにより、活物質層にリチウムを含有させる。また、活物質層を形成した後に、活物質層にリチウムを吸蔵または添加させてもよい。活物質層にリチウムを吸蔵または添加させる方法としては、電気化学的にリチウムを吸蔵または添加させる方法が挙げられる。

【００５５】

本発明のリチウムイオン二次電池において用いる非水電解質は、溶媒に溶質を溶解した電解質である。非水電解質の溶媒としては、リチウムイオン二次電池に使用される溶媒であれば特に限定されないが、例えば、エチレンカーボネート、プロピレンカーボネート、ブチレンカーボネート、ビニレンカーボネートなどの環状カーボネートや、ジメチルカーボネート、ジエチルカーボネート、メチルエチルカーボネートなどの鎖状カーボネートが挙げられる。好ましくは、環状カーボネートと鎖状カーボネートとの混合溶媒が用いられる。また、上記環状カーボネートと、１，２－ジメトキシエタン、１，２－ジエトキシエタンなどのエーテル系溶媒や、γ－ブチロラクトン、スルホラン、酢酸メチル等の鎖状エステル等との混合溶媒を用いてもよい。

【００５６】

非水電解質の溶質としては、リチウムイオン二次電池に用いられる溶質であれば特に限定されるものではなく、例えば、$LiPF_6$、$LiBF_4$、$LiCF_3SO_3$、$LiN(CF_3SO_2)_2$、$LiN(C_2F_5SO_2)_2$、$LiN(CF_3SO_2)(C_4F_9SO_2)$、$LiC(CF_3SO_2)_3$、$LiC(C_2F_5SO_2)_3$、$LiAsF_6$、$LiClO_4$、$Li_2B_{10}Cl_{10}$、$Li_2B_{12}Cl_{12}$などが挙げられる。特に、$LiXFy$（式中、XはP、As、Sb、B、Bi、Al、Ga、またはInであり、XがP、AsまたはSbのときyは６であり、XがB、Bi、Al、Ga、またはInのときyは４である。）と、リチウムペルフルオロアルキルスルホン酸イミド$LiN(C_mF_{2m+1}SO_2)(C_nF_{2n+1}SO_2)$（式中、m及びnはそれぞれ独立して１～４の整数である。）またはリチウムペルフルオロアルキルスルホン酸メチド$LiC(C_pF_{2p+1}SO_2)(C_qF_{2q+1}SO_2)(C_rF_{2r+1}SO_2)$（式中、p、q及びrはそれぞれ独立して１～４の整数である。）との混合溶質が好ましく用いられる。これらの中でも、$LiPF_6$と$LiN(C_2F_5SO_2)_2$との混合溶質が特に好ましく用いられる。

【００５７】

また、非水電解質として、ポリエチレンオキシド、ポリアクリロニトリル、ポリフッ化ビニリデンなどのポリマー電解質に電解液を含浸したゲル状ポリマー電解質や、LiI、

Li_3Nなどの無機固体電解質を用いることができる。

【００５８】

本発明のリチウムイオン二次電池の電解質は、イオン導電性を発現させる溶質としてのＬｉ化合物とこれを溶解・保持する溶媒が電池の充電時や放電時あるいは保存時の電圧で分解しない限り、制約なく用いることができる。

【００５９】

また、正極に用いる正極活物質としては、$LiCoO_2$、$LiNiO_2$、$LiMn_2O_4$、$LiMnO_2$、$LiCo_{0.5}Ni_{0.5}O_2$、$LiNi_{0.7}Co_{0.2}Mn_{0.1}O_2$などのリチウム含有遷移金属酸化物や、$MnO_2$などのリチウムを含有していない金属酸化物が例示される。また、この他にも、リチウムを電気化学的に挿入・脱離する物質であれば、制限なく用いることができる。

【００６０】

本発明によれば、充放電サイクル効率の低下を抑制でき、充放電により集電体にしわ等の変形、あるいは破断が発生するのを抑制することができ、リチウムイオン二次電池の正極－負極間の短絡を防止し、長期間安定した性能を維持するリチウムイオン二次電池を提供することができる。

【実施例】

【００６１】

以下、本発明を実施例に基づいてさらに詳細に説明するが、本発明は以下の実施例に何ら限定されるものではなく、その要旨を変更しない範囲において適宜変更して実施することが可能なものである。

［実施例１～２９、比較例１～８］

【００６２】

［未処理銅箔の製造］

銅７０～１３０ｇ／ｌ－硫酸８０～１４０ｇ／ｌの酸性銅電解浴に表１に示す組成の添加剤をそれぞれ添加し製箔用電解液を調製した。なお、実施例では塩化物イオン濃度を全て３０ｐｐｍに調整したが、塩化物イオン濃度は電解条件により適宜変更するものであり、この濃度に限定されるものではない。

調製した電解液を用い、アノードには貴金属酸化物被覆チタン電極、カソードにはチタン製回転ドラムを用いて表１に示す電解条件（電流密度、液温）の下に、１８μｍ厚みの未処理銅箔を電解製箔法によって実施例１－２、実施例８－２の銅箔を製造した。同様にして実施例１－１、実施例２～実施例８－１、実施例９～２９については、厚さ２０μｍの未処理銅箔を製造した。

また比較例１～２、比較例５～８も表１に示す組成の電解液により２０μｍとなるように未処理銅箔の製造を行い、比較例３は表１に示す組成の電解液により１８μｍとなるように未処理銅箔の製造を行った。

なお比較例２は特許文献２に準拠して作成した電解銅箔である。

【００６３】

比較例４は、Ｚｒを０．０２％含有し、残部が銅である厚みが２０μｍの圧延銅合金箔を用いた。

【００６４】

【表１】

負極集電体用銅箔作成条件

	A 添加剤種類	A (ppm)	B 添加剤種類	B (ppm)	MPS (ppm)	ゼラチン (ppm)	HEC (ppm)	塩素 (ppm)	電流密度 (A/dm^2)	液温 (℃)	粗化処理	加熱温度 (℃)
実施例1-1	チオ尿素	1～10	-	-	-	-	-	30.0	30～70	40～60	無し	230℃
実施例1-2	チオ尿素	1～10	-	-	-	-	-	30.0	30～70	40～60	有り	230℃
実施例2	N,N'-ジメチルチオ尿素	1～10	-	-	-	-	-	30.0	30～70	40～60	無し	230℃
実施例3	N,N'-ジエチルチオ尿素	1～10	-	-	-	-	-	30.0	30～70	40～60	無し	230℃
実施例4	テトラメチルチオ尿素	1～10	-	-	-	-	-	30.0	30～70	40～60	無し	230℃
実施例5	チオセミカルバジド	1～10	-	-	-	-	-	30.0	30～70	40～60	無し	230℃
実施例6	N-アリルチオ尿素	1～10	-	-	-	-	-	30.0	30～70	40～60	無し	230℃
実施例7	エチレンチオ尿素	1～10	-	-	-	-	-	30.0	30～70	40～60	無し	230℃
実施例8-1	チオ尿素	1～10	ポリアクリルアミド	1～20	-	-	-	30.0	30～70	40～60	無し	230℃
実施例8-2	チオ尿素	1～10	ポリアクリルアミド	1～20	-	-	-	30.0	30～70	40～60	有り	230℃
実施例9	チオ尿素	1～10	ポリアクリルアミド	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例10	チオ尿素	1～10	ポリアクリルアミド	1～20	-	-	-	30.0	30～70	40～60	無し	350℃
実施例11	チオ尿素	1～10	ポリアクリルアミド	1～20	-	-	-	30.0	30～70	40～60	無し	400℃
実施例12	N,N'-ジメチルチオ尿素	1～10	ゼラチン	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例13	N,N'-ジメチルチオ尿素	1～10	ポリエチレングリコール	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例14	N,N'-ジメチルチオ尿素	1～10	デンプン	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例15	N,N'-ジメチルチオ尿素	1～10	ヒドロキシエチルセルロース	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例16	N,N'-ジメチルチオ尿素	1～10	ポリエチレンイミン	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例17	N,N'-ジメチルチオ尿素	1～10	ポリアクリルアミド	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例18	テトラメチルチオ尿素	1～10	ゼラチン	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例19	テトラメチルチオ尿素	1～10	ポリエチレングリコール	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例20	テトラメチルチオ尿素	1～10	デンプン	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例21	テトラメチルチオ尿素	1～10	ヒドロキシエチルセルロース	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例22	テトラメチルチオ尿素	1～10	ポリエチレンイミン	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例23	テトラメチルチオ尿素	1～10	ポリアクリルアミド	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例24	エチレンチオ尿素	1～10	ゼラチン	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例25	エチレンチオ尿素	1～10	ポリエチレングリコール	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例26	エチレンチオ尿素	1～10	デンプン	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例27	エチレンチオ尿素	1～10	ヒドロキシエチルセルロース	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例28	エチレンチオ尿素	1～10	ポリエチレンイミン	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
実施例29	エチレンチオ尿素	1～10	ポリアクリルアミド	1～20	-	-	-	30.0	30～70	40～60	無し	300℃
比較例1	-	-	-	-	1～10	1～20	1～20	30.0	30	40～60	無し	300℃
比較例2	-	-	-	-	-	-	-	-	30	40～60	無し	300℃
比較例3	チオ尿素	1～10	ポリアクリルアミド	1～20	-	-	-	30.0	30～70	40～60	有り	300℃
比較例4	圧延銅合金箔										無し	300℃
比較例5	-	-	-	-	-	2	-	0.3	55	50	無し	180℃
比較例6	-	-	-	-	-	2	-	0.3	55	50	無し	230℃
比較例7	-	-	-	-	-	4	-	0.3	55	50	無し	300℃
比較例8	-	-	-	-	-	10	-	0.5	55	50	無し	300℃

MPS；1－メルカプト3－プロパンスルフォン酸ナトリウム
HEC；ヒドロキシエチルセルロース

【００６５】

［負極集電体の作成］

実施例１－２、８－２、比較例３については、表1に示す電解銅箔の表面に電気めっきにより銅のやけめっきを施し、粒粉状銅めっき層を形成した。さらに、該粒粉状銅めっき層の上にその凹凸形状を損なわないように、緻密な銅めっき（被せめっき）を行い、粒粉状銅と電解銅箔との密着性を向上させた粗面化電解銅箔を作成した。

実施例１－２、実施例８－２、比較例３については上記に記述したように、当初１８μｍの未処理銅箔を作成し、その後２０μｍ厚さになるように電気めっきによる銅のやけめっき、被せめっきを施し粗面化電解銅箔を作成し、クロメート処理を施した後、集電体とした。

これに対して実施例１－１、実施例２～実施例８－１、実施例９～実施例２９及び比較例１～２、比較例５～８については、２０μｍの未処理銅箔を作成し、その後銅のやけめっき、被せめっきは施さず、クロメート処理のみを施して集電体とした。

すなわち、実施例１～２９、比較例１～８は集電体になる時には全て２０μｍになるように厚さを合わせた。

【００６６】

銅箔表面粗面化のための粒粉状めっきの条件、緻密な銅めっき（被せめっき）、クロメート処理の条件は以下のようである。

粒粉状めっき条件：

硫酸銅	８０～１４０ｇ／Ｌ
硫酸	１１０～１６０ｇ／Ｌ
添加剤	適量
液温	３０～６０℃
電流密度	１０～５０Ａ／ｄｍ^2
処理時間	２～２０秒

【００６７】

緻密な銅めっき（被せめっき）条件：

硫酸銅	２００～３００ｇ／Ｌ
硫酸	９０～１３０ｇ／Ｌ
液温	３０～６０℃
電流密度	１０～３０Ａ／ｄｍ^2
処理時間	２～２０秒

【００６８】

クロメート処理条件：

重クロム酸カリウム	１～１０ｇ／Ｌ
浸漬処理時間	２～２０秒

【００６９】

集電体の引張強さ、０．２％耐力、伸び、及び表面粗さＲａ、Ｒｚを表２に示す。

【００７０】

【表２】

銅箔の機械的特性

	S面		M面			室温			加熱後		
	Ra（μm）	Rz（μm）	Ra（μm）	Rz（μm）	引張強さ（N/mm^2）	0.2%耐力（N/mm^2）	伸び（%）	引張強さ（N/mm^2）	0.2%耐力（N/mm^2）	伸び（%）
実施例1-1	0.38	2.15	0.38	2.10	716	531	2.3	528	426	7.8
実施例1-2	0.41	2.65	0.43	2.80	715	529	2.4	525	421	8.0
実施例2	0.39	2.00	0.39	2.30	711	546	4.0	547	436	7.9
実施例3	0.34	1.85	0.37	2.00	713	537	4.7	537	448	8.7
実施例4	0.41	2.10	0.37	1.95	684	519	4.3	516	428	7.8
実施例5	0.34	1.75	0.39	2.00	661	511	4.5	497	400	7.2
実施例6	0.39	2.30	0.32	1.95	658	504	4.1	530	430	5.4
実施例7	0.38	2.15	0.36	2.00	678	493	5.2	511	413	4.1
実施例8-1	0.34	1.90	0.45	2.30	720	487	3.5	653	482	2.7
実施例8-2	0.40	2.65	0.50	2.80	710	475	3.8	645	479	2.8
実施例9	0.37	2.10	0.45	2.20	711	500	3.6	480	404	3.6
実施例10	0.35	1.80	0.45	2.50	710	519	4.2	357	281	8.4
実施例11	0.33	1.90	0.46	2.75	706	493	3.8	292	253	8.4
実施例12	0.39	2.00	0.30	2.20	677	490	5.8	412	336	11.9
実施例13	0.39	2.00	0.40	2.10	673	510	5.4	405	345	13.4
実施例14	0.42	2.65	0.43	2.33	672	500	4.5	411	346	10.4
実施例15	0.35	1.60	0.33	2.10	661	519	4.5	406	348	10.2
実施例16	0.34	1.65	0.40	2.50	666	489	4.6	412	365	13.2
実施例17	0.20	0.80	0.35	2.15	667	519	4.8	413	362	12.9
実施例18	0.34	1.80	0.40	2.50	621	455	3.7	323	274	14.4
実施例19	0.35	2.00	0.41	2.55	671	486	3.2	328	305	12.7
実施例20	0.35	1.65	0.34	2.05	679	426	3.3	355	311	13.0
実施例21	0.34	1.65	0.33	2.05	663	467	3.1	344	317	15.0
実施例22	0.32	1.60	0.30	1.80	748	518	3.2	390	359	14.1
実施例23	0.30	1.01	0.35	2.30	761	513	4.2	430	380	9.7
実施例24	0.34	2.05	0.32	1.70	580	428	5.2	373	325	12.0
実施例25	0.33	2.00	0.27	1.50	589	441	6.4	392	329	13.9
実施例26	0.30	1.80	0.32	1.65	615	462	4.6	377	323	16.5
実施例27	0.33	2.10	0.34	1.90	628	460	5.0	376	322	16.6
実施例28	0.40	2.30	0.38	1.90	638	472	4.2	362	333	16.4
実施例29	0.40	2.40	0.40	1.95	643	481	4.7	386	346	15.8
比較例1	0.28	1.80	0.30	1.40	318	250	13.0	240	150	14.4
比較例2	0.30	1.70	0.35	2.00	510	345	4.5	204	102	13.8
比較例3	0.50	3.50	0.60	4.50	700	470	4.0	640	470	3.5
比較例4	0.10	0.60	0.10	0.60	405	310	2.0	400	305	2.0
比較例5	—	—	0.49	3.41	531	371	6.4	478	360	5.8
比較例6	—	—	0.51	3.56	530	373	7.6	320	248	8.6
比較例7	—	—	0.50	4.00	515	367	5.0	305	226	6.6
比較例8	—	—	0.65	6.00	453	328	3.0	290	218	3.3

【００７１】

なお、引張強さ、０．２％耐力、伸びは、引張試験機（インストロン社製１１２２型）を用いて測定した値である。また、表面粗さＲａ、Ｒｚは、触針式表面粗さ計（小坂研究所製ＳＥ－３Ｃ型）により測定した値である。

【００７２】

活物質については、平均粒子径１００ｎｍのケイ素系粒子を使用した。

活物質６４％に、アセチレンブラック粉（ＡＢ）１６％、ポリアミック酸溶液２０％を混合してスラリーを調製した。次いで、上記電解銅箔に上記スラリーを塗布し、塗工膜をほぼ均一なシートとし、乾燥し、プレス機で圧縮して集電体上に活物質層を密着接合させ、更に減圧乾燥させて試験電極（負極）を作製した。この後、アルゴン雰囲気下において表１に示す各温度で焼結し、２０φに打ち抜き電極とした。

【００７３】

上記の電極を負極とし、金属リチウム箔を対極、参照極として１．３モルの$LiPF_6$／エチレンカーボネート（ＥＣ）＋エチルメチルカーボネート（ＥＭＣ）＋ジメチルカーボネート（ＤＭＣ）（ＥＣ：ＥＭＣ：ＤＭＣ＝２：５：３（体積比））溶液を電解液として、三極セルを作製した。

【００７４】
この三極セルにおける負極の評価を次の方法により温度２５℃で行った。
［充放電試験方法］
Ｃレート算出
試験極中の活物質量によりＣレートを以下の通りに算出した。
Ｓｉ：１Ｃ＝４，０００ｍＡｈ／ｇ
初回条件
充電：０．１Ｃ相当電流で定電流充電し、０．０２Ｖ（対Ｌｉ／Ｌｉ＋）到達後、定電位充電し、充電電流が０．０５Ｃ相当に低下した時点で終了した。
放電：０．１Ｃ相当電流で定電流放電し、１．５Ｖになった時点で終了した。
充放電サイクル条件
初回充放電試験を実施した後、同じ０．１Ｃ相当電流で１００サイクルまで充放電を繰り返した。
【００７５】
上記評価による１００サイクル後の集電体両面の放電容量保持率を表３に示す。
なお、１００サイクル後の放電容量保持率は次式により算出した。
（サイクル後放電容量保持率％）＝［（サイクル後の放電容量）／（最大放電容量）］×１００
【００７６】

【表３】

放電容量維持率としわ発生有無

	放電容量保持率 S面(%)	放電容量保持率 M面(%)	しわの発生
実施例1-1	71	73	無し
実施例1-2	77	78	無し
実施例2	73	75	無し
実施例3	68	72	無し
実施例4	73	70	無し
実施例5	70	68	無し
実施例6	71	68	無し
実施例7	72	72	無し
実施例8-1	74	76	無し
実施例8-2	80	80	無し
実施例9	73	73	無し
実施例10	60	61	無し
実施例11	57	58	無し
実施例12	63	64	無し
実施例13	63	65	無し
実施例14	64	64	無し
実施例15	63	64	無し
実施例16	63	65	無し
実施例17	63	66	無し
実施例18	61	61	無し
実施例19	61	62	無し
実施例20	60	63	無し
実施例21	60	63	無し
実施例22	61	61	無し
実施例23	65	67	無し
実施例24	60	61	無し
実施例25	61	63	無し
実施例26	59	59	無し
実施例27	59	58	無し
実施例28	60	60	無し
実施例29	60	60	無し
比較例1	42	44	有り
比較例2	35	38	有り
比較例3	48	45	無し
比較例4	54	53	無し
比較例5	—	35	無し
比較例6	—	31	無し
比較例7	—	24	無し
比較例8	—	20	無し

【００７７】

また、サイクル後における実施例１～２９、比較例１～８の各リチウムイオン二次電池を解体して、各負極の負極集電体におけるしわの発生の有無を調べ、その結果を表３に合わせて示した。

【００７８】

表１、２に示したように２００～４００℃で３０分加熱後にその０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上ある未処理銅箔を用い、少なくとも一方の面に防錆処理を施した負極集電体表４に示すように充放電サイクルを繰り返しても容量の低下が小さくなる。また、充放電により集電体にしわが発生するのを抑制することができた。

また、２００～４００℃で３０分加熱処理後にその０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上ある未処理銅箔を用い、少なくとも一方の面を粗化処理し、防錆

処理を施した実施例１－２、実施例８－２を負極集電体とした電池は、充放電サイクルを繰り返しても容量の低下は他の実施例と比べてさらに小さくすることができた。

【００７９】

また、比較例１は特許文献１に示した電解銅箔を負極集電体に使用した例であるが、加熱前後の０．２％耐力が小さく、充放電サイクルを繰り返すと容量の著しい低下が発生した。また、充放電を繰り返すと集電体にしわが発生してしまう。

【００８０】

さらに、比較例２は室温で引張強さが大きく、０．２％耐力が大きい箔であるが、加熱により軟化してしまい、０．２％耐力が小さく、充放電サイクルを繰り返すと容量の著しい低下が発生した。また、充放電を繰り返すと集電体にしわが発生してしまう。

【００８１】

比較例３は、表２に示すように表面の粗化処理が粗すぎたため、充放電効率が低下している。これは表面粗さが粗すぎると、活物質が表面凹凸の谷底の部分を埋めることが出来ないためと考えられる。

【００８２】

比較例４は室温で引張強さが大きく、０．２％耐力が大きい箔で、加熱しても軟化しにくい箔であるが、伸びが小さい箔である。充放電を繰り返しても集電体にしわは発生しないが、充放電サイクルを繰り返すと本発明の電解銅箔に比較して容量の低下が大きい。

伸びが大きいと、電池の充放電の繰り返しにより活物質層の体積が膨張及び収縮しても、それを吸収して活物質の集電体からの剥離を抑制し、電池の充放電サイクル効率の低下が抑制できると考えられる。

【００８３】

比較例５～８は、表２に示すように表面の粗さ（比較例５～８は元箔の粗さが粗いのであって粗化処理は行っていない。）が粗すぎたため、比較例３と同様、充放電効率が低下している。表３の放電容量保持率をみると、表面粗さＲｚが大きくなるに従い保持率が低下している。これは表面粗さが粗くなるに従って、活物質が表面凹凸の谷底の部分を埋めることができなくなる傾向を示すものと推察できる。

【００８４】

以上のように、本発明のリチウムイオン二次電池負極集電体として、電解銅箔上に負極構成活物質層を形成し、２００～４００℃で３０分加熱後にその０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上で、少なくとも一方の面に防錆処理を施した電解銅箔を用い、或いは２００～４００℃で３０分加熱処理後にその０．２％耐力が２５０Ｎ／ｍｍ^{2}以上、伸びが２．５％以上ある未処理銅箔を用い、少なくとも一方の面を粗化し防錆処理を施した電解銅箔を用いることで、充放電により集電体にしわ等の変形が発生するのを抑制することができ、リチウムイオン二次電池の正極と負極の短絡を防ぐことができ、充放電サイクルを繰り返しても容量保持率の低下が起こらない高寿命で、小型化可能なリチウムイオン二次電池を提供することができる。

【００８５】

なお、本実施例は活物質がシリコンの場合について記載したが、シリコンの酸化物、カーボン、ゲルマニウム、錫を主成分とする活物質を使った場合でも、充放電により集電体にしわ等の変形が発生するのを抑制することができ、リチウムイオン二次電池の正極と負極の短絡を防ぐことができ、充放電サイクルを繰り返しても容量保持率の低下が起こらない高寿命で、小型化可能なリチウムイオン二次電池を提供することができる。

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SURFACE TREATED ELCTROLYTIC COPPER FOIL AND PROCESS FOR PRODUCING THE SAME

Inventor(s): 土橋 誠, ; 松田 光由, ; 朝長 咲子, ; 酒井 久雄, ; 坂田 智浩, ; 吉岡 淳志, ; 西川 丞, ; 田口 丈雄

Applicant(s): 三井金属鉱業株式会社

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It is an object to provide a surface-treated electro-deposited copper foil which has a low profile at a level equal to or excellent than that of low-profile surface-treated electro-deposited copper foils that have conventionally been supplied to the market and in which waviness affecting the straight line performance of wiring is small, and a method for manufacturing the same. In order to achieve this object, in the surface-treated electro-deposited copper foil, the maximum waviness height (Wmax) of the bonding surface to be bonded with an insulation layer-constituting material to be 0.05 μm to 0.7 μm, the maximum peak to valley height (PV) to be 0.05 to 1.5 μm, and the surface roughness (Rzjis) to be 0.1 μm to 1.0 μm. The electro-deposited copper foil used for the manufacturing of this surface-treated electro-deposited copper foil is manufactured by using a sulfuric acid base copper electrolytic solution obtained by adding 3-mercapto-1-propanesulfonic acid or bis(3-sulfopropyl)disulfide, a quaternary ammonium salt polymer having a cyclic structure, and chlorine, and using a cathode having small surface roughness, under electrolysis conditions of carrying out continuous first-step electrolysis to n-th-step electrolysis at two or more different levels of electric current density.

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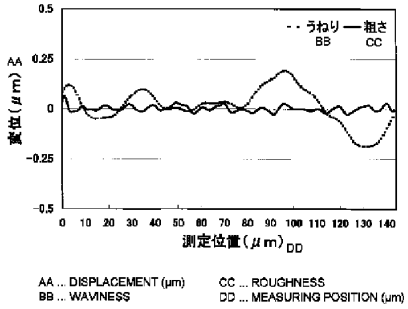
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(71)出願人　000006183
三井金属鉱業株式会社
東京都品川区大崎１丁目１１番１号
(74)代理人　100124327
弁理士　吉村　勝博
(72)発明者　土橋　誠
埼玉県上尾市原市１３３３－２　三井金属鉱業株式会社　総合研究所内
(72)発明者　松田　光由
埼玉県上尾市原市１３３３－２　三井金属鉱業株式会社　総合研究所内
(72)発明者　朝長　咲子
埼玉県上尾市原市１３３３－２　三井金属鉱業株式会社　総合研究所内

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(54)【発明の名称】表面処理電解銅箔及びその製造方法

(57)【要約】
従来市場に供給されてきた低プロファイル表面処理電解銅箔と同レベル以上の低プロファイルを有し、且つ、配線の直線性に影響を与えるうねりの小さな表面処理電解銅箔とその製造方法を提供することを目的とする。この目的を達成するため、絶縁層構成材との接着面の、うねりの最大高低差（Ｗｍａｘ）は０．０５μｍ～０．７μｍ、凹凸の最大高低差（ＰＶ）は０．０５～１．５μｍ、表面粗さ（Ｒｚｊｉｓ）は０．１μｍ～１．０μｍである表面処理電解銅箔とする。この表面処理電解銅箔の製造に用いる電解銅箔は、３－メルカプト－１－プロパンスルホン酸又はビス（３－スルホプロピル）ジスルフィドと環状構造を持つ４級アンモニウム塩重合体と塩素とを添加して得られた硫酸系銅電解液を用い、表面粗さの小さな陰極を用いて、連続する第１ステップ電解から第ｎステップ電解までを、異なる２水準以上の電流密度で実施する電解条件で製造する。



【特許請求の範囲】
【請求項1】
電解銅箔の表面に防錆処理及び／又はシランカップリング剤処理のいずれか１種以上を行った表面処理電解銅箔であって、
　当該表面処理電解銅箔の絶縁層構成材料との接着面のうねりの最大高低差（Ｗｍａｘ）が０．０５μｍ～０．７μｍであることを特徴とする表面処理電解銅箔。
【請求項2】
前記接着面が電解銅箔の析出面側である請求項１に記載の表面処理電解銅箔。
【請求項3】
前記接着面の表面粗さ（Ｒｚｊｉｓ）が、０．１μｍ～１．０μｍである請求項１又は請求項２に記載の表面処理電解銅箔。
【請求項4】
前記接着面の凹凸の最大高低差（ＰＶ）が、０．０５μｍ～１．５μｍである請求項１～請求項３のいずれかに記載の表面処理電解銅箔。
【請求項5】
前記接着面のうねりの最大高低差（Ｗｍａｘ）と凹凸の最大高低差（ＰＶ）との比〔（Ｗｍａｘ）／（ＰＶ）〕が、０．８以上である請求項１～請求項４のいずれかに記載の表面処理電解銅箔。
【請求項6】
請求項１～請求項５のいずれかに記載の表面処理電解銅箔の製造に用いる電解銅箔であって、
　当該電解銅箔の光沢面側の表面粗さ（Ｒｚｊｉｓ）が、０．４μｍ～２．０μｍであることを特徴とする電解銅箔。
【請求項7】
光沢面側の光沢度［Ｇｓ（６０°）］が、７０以上である請求項６に記載の電解銅箔。
【請求項8】
析出面側の表面粗さ（Ｒｚｊｉｓ）が、０．１μｍ～１．０μｍであって、当該析出面側の光沢度［Ｇｓ（６０°）］が４００以上である請求項６又は請求項７に記載の電解銅箔。
【請求項9】
結晶組織の異なる複数層の析出銅層を有する請求項６～請求項８のいずれかに記載の電解銅箔。
【請求項10】
硫酸系銅電解液を用いた電解法により陰極表面に析出させて電解銅箔を製造する方法であって、
　当該電解法は電解に要する時間内において、連続する第１ステップ電解から第ｎステップ電解までを異なる２水準以上の電流密度で実施することを特徴とする請求項６～請求項９のいずれかに記載の電解銅箔を製造する方法。
【請求項11】
前記第１ステップ電解の電流密度は、５０Ａ／ｄｍ^2～４００Ａ／ｄｍ^{2}である請求項１０に記載の電解銅箔の製造方法。
【請求項12】
前記第２ステップ電解～第ｎステップ電解の電流密度は、１５Ａ／ｄｍ^2～９０Ａ／ｄｍ^{2}であって、第１ステップ電解の電流密度よりも小さい請求項１０又は請求項１１に記載の電解銅箔の製造方法。
【請求項13】
前記硫酸系銅電解液は、膠、チオ尿素、ポリアルキレングリコール、アミン化合物、メルカプト基を持つ化合物、塩素イオン、高分子多糖類、ジアリルジアルキルアンモニウム塩と二酸化硫黄との共重合体、オキシエチレン系界面活性剤、ポリエチレンイミン又はその

誘導体、活性硫黄化合物のスルフォン酸塩、環状構造を持つ４級アンモニウム塩重合体から選択された１種類以上の添加剤を含む請求項１０～請求項１２のいずれかに記載の電解銅箔の製造方法。

【請求項14】

前記硫酸系銅電解液は、３－メルカプト－１－プロパンスルホン酸及びビス（３－スルホプロピル）ジスルフィドから選択された少なくとも１種と環状構造を持つ４級アンモニウム塩重合体とを含む請求項１０～請求項１２のいずれかに記載の電解銅箔の製造方法。

【請求項15】

前記硫酸系銅電解液中の３－メルカプト－１－プロパンスルホン酸及び／又はビス（３－スルホプロピル）ジスルフィドの合算濃度は、０．５ｐｐｍ～２００ｐｐｍである請求項１４に記載の電解銅箔の製造方法。

【請求項16】

前記硫酸系銅電解液中は、環状構造を持つ４級アンモニウム塩重合体を１ｐｐｍ～１００ｐｐｍ含有するものである請求項１３に記載の電解銅箔の製造方法。

【請求項17】

前記硫酸系銅電解液中の環状構造を持つ４級アンモニウム塩重合体は、ジアリルジメチルアンモニウムクロライド重合体である請求項１６に記載の電解銅箔の製造方法。

【請求項18】

前記硫酸系銅電解液は、塩素を含むものであって、当該塩素濃度が、５ｐｐｍ～１００ｐｐｍである請求項１３に記載の電解銅箔の製造方法。

【請求項19】

請求項１～請求項５のいずれかに記載の表面処理電解銅箔を絶縁層構成材料と張合わせて得られたことを特徴とする銅張積層板。

【請求項20】

銅を溶解除去後の絶縁層構成材料表面のうねりの高低差（Ｗｍａｘ）が０．０５μｍ～０．７μｍである請求項１９に記載の銅張積層板。

【請求項21】

前記絶縁層構成材料は骨格材を含有するものである請求項１９又は請求項２０に記載のリジッド銅張積層板。

【請求項22】

請求項２１に記載のリジッド銅張積層板を用いて得られたことを特徴とするリジッドプリント配線板。

【請求項23】

前記絶縁層構成材料は可撓性を有するフレキシブル素材で構成したものである請求項１９又は請求項２０に記載のフレキシブル銅張積層板。

【請求項24】

請求項２３に記載のフレキシブル銅張積層板を用いて得られたことを特徴とするフレキシブルプリント配線板。

【発明の詳細な説明】

【技術分野】

【0001】

本件発明は、表面処理電解銅箔、電解銅箔及びその製造方法並びに該表面処理電解銅箔を用いたリジッド銅張積層板、リジッドプリント配線板、フレキシブル銅張積層板及びフレキシブルプリント配線板に関する。特に、プリント配線板などに用いた場合にファインパターン配線の形成性に優れる、絶縁層形成材料との接着面のうねりを小さくした表面処理電解銅箔及びその製造方法に関する。

【背景技術】

【0002】

金属銅は電気の良導体であり、比較的安価で取り扱いも容易であることから、電解銅箔は、プリント配線板の基礎材料として広く使用されている。そして、プリント配線板が多用される電子及び電気機器には小型化、軽量化等の所謂軽薄短小化が求められている。従

来、このような電子及び電気機器の軽薄短小化を実現するためには、信号回路を可能な限りファインピッチ化した配線にする必要があった。そのため、製造者等は、より薄い銅箔を採用して、エッチングで配線を形成する際のオーバーエッチングの設定時間を短縮し、形成する配線のエッチングファクターを向上させることで対応してきた。

【0003】

そして、小型化、軽量化される電子及び電気機器には高機能化の要求も同時に行われている。従って、部品実装における表面実装方式の普及に伴い要求される、限られた基板面積に可能な限り大きな部品実装面積を確保するためにも、プリント配線板には高密度化が要求され、エッチングファクターを良好にする対応が必要とされてきた。その目的で、特にＩＣチップ等の直接搭載を行う所謂インターポーザー基板である、テープ　オートメーティド　ボンディング（ＴＡＢ）基板、チップ　オン　フィルム（ＣＯＦ）基板には、通常のプリント配線板用途を超える低プロファイル電解銅箔が求められてきた。なお、プロファイルとは、プリント配線板用銅箔に関する規格において、銅箔の絶縁層形成材料との接着面の表面粗さ（Ｒｚｊｉｓ）を、ＪＩＳ　Ｂ　０６０１－２００１に準拠してＴＤ方向に測定した値で規定されるものである。そして、低プロファイルとは、接着面の表面粗さ（Ｒｚｊｉｓ）が小さいことをいう。

【0004】

このような問題を解決すべく、特許文献１には、未処理銅箔の析出面の表面粗度Ｒｚが該未処理銅箔の光沢面の表面粗度Ｒｚと同じかそれより小さい箔の析出面上に粗化処理を施して接着面とすることを特徴とする表面処理電解銅箔が開示されている。そして、前記未処理銅箔の製造には、メルカプト基を持つ化合物、塩化物イオン、並びに分子量１００００以下の低分子量膠及び高分子多糖類を添加した電解液を用いており、具体的にはメルカプト基を持つ化合物は３－メルカプト１－プロパンスルホン酸塩、低分子量膠の分子量は３０００以下、そして高分子多糖類はヒドロキシエチルセルロースであるとしている。

【0005】

また、特許文献２には、硫酸酸性銅めっき液の電気分解による電解銅箔の製造方法において、ジアリルジアルキルアンモニウム塩と二酸化硫黄との共重合体を含有する硫酸酸性銅めっき液を用いることを特徴とする電解銅箔の製造方法が開示されており、当該硫酸酸性銅めっき液には、ポリエチレングリコールと塩素と３－メルカプト－１－スルホン酸とを含有することが好ましいとされている。そして、絶縁基材との張合わせ面（接着面）とする析出面の粗さが小さく、厚さ１０μｍの電解銅箔の場合、十点平均粗さＲｚが１．０μｍ±０．５μｍ程度の低プロファイルが得られるとしている。

【0006】

そして、これらの製造方法を用いて電解銅箔を製造すると、確かに低プロファイルの析出面が形成され、従来の低プロファイル電解銅箔としては十分な特性は有している。

【0007】

【特許文献1】特開平９－１４３７８５号公報

【特許文献2】特開２００４－３５９１８号公報

【発明の開示】

【発明が解決しようとする課題】

【0008】

しかしながら、電子又は電気機器の代表であるパーソナルコンピュータのクロック周波数も急激に上昇し、演算速度が飛躍的に速くなっている。そして、用途についても、従来のコンピュータとしての本来の役割である単なるデータ処理に止まらず、コンピュータ自体をＡＶ機器と同様に使用するケースが多くなってきている。即ち、音楽再生機能のみならず、ＤＶＤの録画再生機能、ＴＶ受像録画機能、テレビ電話機能等が次々に付加されているのである。

【0009】

上記の背景から、パーソナルコンピュータのモニタに対しても、単なるデータモニタではなく、映画等の画像を写しても長時間の視聴に耐えるだけの画質が要求され、更に、安

価に且つ大量に供給することも求められる。そして、現在の当該モニタには液晶モニタが多用されており、この液晶パネルのドライバ素子を実装するに当たっては、前記ＴＡＢ基板やＣＯＦ基板を用いるのが一般的である。よって、モニタのハイビジョン化等を図るためには、前記ドライバ用基板にも、よりファインな配線の形成が求められる。しかし、２０μｍピッチの配線を視野に入れた評価を実施した場合には、前記先行技術により製造された電解銅箔では、表面粗さにおいて優れた低プロファイル特性を有しているが、形成されたファインパターン配線には配線端面の波打ちが大きいことに起因した不具合が発生する傾向がある。そして、同レベルの配線形成が要求されるプラズマディスプレイパネルの電磁波シールド用途においても、設計通りの配線幅が得られないと画面の解像度等が設計値を満足しないなどの問題に繋がってしまう。

【0010】

以上のことから、プリント配線板等に用いる表面処理電解銅箔に対しては、従来の、単に低プロファイルであることを特徴とした表面処理電解銅箔ではなく、むしろ、ファインパターンの形成性が良好な表面処理電解銅箔に対する要求が強く存在していた。

【課題を解決するための手段】

【0011】

そこで、本件発明者らは鋭意研究の結果、Ｒｚｊｉｓを指標としている低プロファイル以外に、ファインパターン形成性の良否を判定する指標として接着面のうねりに着目し、この指標を用いた研究開発により、接着面が低プロファイルで、且つ、うねりが小さな表面処理電解銅箔及びその製造方法に想到した。

【0012】

本件発明に係る表面処理電解銅箔：　本件発明に係る表面処理電解銅箔は、電解銅箔の表面に、防錆処理及び／又はシランカップリング剤処理のいずれか１種以上を行ったものである表面処理電解銅箔であって、前記表面処理電解銅箔における絶縁層構成材料との接着面のうねりの最大高低差（Ｗｍａｘ）が０．０５μｍ～０．７μｍであることを特徴としている。

【0013】

そして、本件発明に係る表面処理電解銅箔は、前記接着面が電解銅箔の析出面側であることが好ましい。

【0014】

また、本件発明に係る表面処理電解銅箔は、前記接着面側の凹凸の最大高低差（ＰＶ）が、０．０５μｍ～１．５μｍであることも好ましい。

【0015】

そして、本件発明に係る表面処理電解銅箔は、前記接着面側の表面粗さ（Ｒｚｊｉｓ）が、０．１μｍ～１．０μｍであることも好ましい。

【0016】

そして、本件発明に係る表面処理電解銅箔は、前記接着面側における接着面のうねりの最大高低差（Ｗｍａｘ）と凹凸の最大高低差（ＰＶ）との比〔（Ｗｍａｘ）／（ＰＶ）〕が、０．８以上であることも好ましい。

【0017】

本件発明に係る電解銅箔：　本件発明に係る電解銅箔は、前記表面処理電解銅箔の製造に用いる電解銅箔であって、当該電解銅箔の光沢面側の表面粗さ（Ｒｚｊｉｓ）が０．４μｍ～２．０μｍであることを特徴としている。

【0018】

そして、本件発明に係る電解銅箔は、光沢面側の光沢度［Ｇｓ（６０°）］が、７０以上であることが好ましい。

【0019】

また、本件発明に係る電解銅箔は、前記析出面側の表面粗さ（Ｒｚｊｉｓ）が、０．１μｍ～１．０μｍであって、当該析出面側の光沢度［Ｇｓ（６０°）］が４００以上であることも好ましい。

【0020】
　また、本件発明に係る電解銅箔は、結晶構造の異なる複数層の析出銅層を有することも好ましい。
【0021】
本件発明に係る電解銅箔の製造方法：　本件発明に係る電解銅箔の製造方法は、硫酸系銅電解液を用いた電解法により陰極表面に析出させて電解銅箔を製造する方法であって、電解に要する時間内において、連続する第１ステップ電解から第ｎステップ電解までを、異なる２水準以上の電流密度で実施することを特徴としている。
【0022】
　そして、本件発明に係る電解銅箔の製造方法では、前記第１ステップ電解の電流密度は、５０Ａ／ｄｍ^2～４００Ａ／ｄｍ^{2}であることが好ましい。
【0023】
　また、本件発明に係る電解銅箔の製造方法では、前記第２ステップ電解～第ｎステップ電解の電流密度は、１５Ａ／ｄｍ^2～９０Ａ／ｄｍ^{2}であって第１ステップ電解の電流密度よりも小さいことが好ましい。
【0024】
本件発明に係る電解銅箔の製造方法に用いる硫酸系銅電解液は、膠、チオ尿素、ポリアルキレングリコール、アミン化合物、メルカプト基を持つ化合物、塩素イオン、高分子多糖類、ジアリルジアルキルアンモニウム塩と二酸化硫黄との共重合体、オキシエチレン系界面活性剤、ポリエチレンイミン又はその誘導体、活性硫黄化合物のスルフォン酸塩、環状構造を持つ４級アンモニウム塩重合体から選択された、１種類以上の添加剤を含むことを特徴としている。
【0025】
　また、前記硫酸系銅電解液は、３－メルカプト－１－プロパンスルホン酸（本件出願では以降「ＭＰＳ」と称する。）及びビス（３－スルホプロピル）ジスルフィド（本件出願では以降「ＳＰＳ」と称する。）から選択された少なくとも１種と、環状構造を持つ４級アンモニウム塩重合体とを含むものであることがより好ましい。
【0026】
　そして、前記硫酸系銅電解液中のＭＰＳ及び／又はＳＰＳの合算濃度は、０．５ｐｐｍ～２００ｐｐｍであることも好ましい。
【0027】
　そして、前記硫酸系銅電解液中の環状構造を持つ４級アンモニウム塩重合体濃度は、１ｐｐｍ～１００ｐｐｍであることも好ましい。
【0028】
　そして、前記硫酸系銅電解液中の環状構造を持つ４級アンモニウム塩重合体は、ジアリルジメチルアンモニウムクロライド（本件出願では以降「ＤＤＡＣ」と称する）重合体であることも好ましい。
【0029】
　また、前記硫酸系銅電解液は塩素を含むものであって、当該塩素濃度が、５ｐｐｍ～１００ｐｐｍであることも好ましい。
【0030】
本件発明に係る銅張積層板：　本件発明に係る銅張積層板は、前記表面処理電解銅箔を絶縁層構成材料と張合わせてなることを特徴としている。
【0031】
　前記銅張積層板は、全面の銅を溶解除去後の絶縁層構成材料表面のうねりの高低差（Ｗｍａｘ）が０．０５μｍ～０．７μｍであることも好ましい。
【0032】
　そして、前記銅張積層板は、絶縁層構成材料が骨格材を含有するものであるリジッド銅張積層板であることも好ましい。
【0033】

また、前記銅張積層板は、絶縁層構成材料が可撓性を有するフレキシブル素材で構成したものであるフレキシブル銅張積層板であることも好ましい。

【0034】

本件発明に係るプリント配線板：　本件発明に係るプリント配線板は、前記リジッド銅張積層板を用いて得られたことを特徴とするリジッドプリント配線板、及び、前記フレキシブル銅張積層板を用いて得られたことを特徴とするフレキシブルプリント配線板である。

【発明の効果】

【0035】

本件発明に係る表面処理電解銅箔は、従来市場に供給されてきた低プロファイル表面処理電解銅箔と同等以上のハイレベルな低プロファイル表面処理電解銅箔であって、且つ、接着面のうねりが小さなものである。従って、接着面に対する低プロファイル及びうねりが小さいことへの要求の顕著な、テープ　オートメーティド　ボンディング（ＴＡＢ）基板やチップ　オン　フィルム（ＣＯＦ）基板のファインピッチ配線の形成材料として好適であり、プラズマディスプレイパネルの電磁波シールドパターンの形成材料としても好適である。

【発明を実施するための最良の形態】

【0036】

本件発明に係る表面処理電解銅箔の形態：　本件発明に係る表面処理電解銅箔は、電解銅箔の表面に防錆処理及び／又はシランカップリング剤処理のいずれか１種以上を行った表面処理電解銅箔であって、絶縁層構成材料との接着面のうねりの最大高低差（Ｗｍａｘ）が０．０５μｍ～０．７μｍである。そして、接着面のうねりの最大高低差（Ｗｍａｘ）のより好ましい範囲は０．０５μｍ～０．５μｍである。本件発明ではうねりを検出する指標として、うねりの最大高低差（Ｗｍａｘ）を採用した。本件明細書において、うねりの最大高低差（Ｗｍａｘ）とは、三次元表面構造解析顕微鏡を用いて得られる試料表面の凹凸に係る情報から、うねりに係る波形データをフィルタを用いて抽出したときの波形データの高低差の最大値（波形の最大ピーク高さと最大バレー深さの和）をいう。なお、本件発明者等は、測定機器としてｚｙｇｏ　Ｎｅｗ　Ｖｉｅｗ　５０３２（ＺＹＧＯ社製）を、そして解析ソフトにはＭｅｔｒｏ　Ｐｒｏ　Ｖｅｒ．８．０．２を用い、低周波フィルタは１１μｍに設定して測定した。

【0037】

具体的には次に示すａ）～ｃ）の手順により測定した。

ａ）試料片の非測定面を試料台に密着させて固定する。

ｂ）試料片の１ｃｍ角の範囲内において１０８μｍ×１４４μｍの視野を６点選択して測定する。

ｃ）６箇所の測定点から得られた値の平均値を試料の代表値として採用する。

【0038】

なお、三次元表面構造解析顕微鏡では、表面形状の実態が面に対する高さの分布として３次元の数値情報で得られる。よって、表面形状の測定装置として採用することが有意義である。また、接着面のうねりだけに着目するのであれば、触針式粗さ計を用いても、得られるうねりの値は線上の高さ変位の分布を表す２次元の数値情報であって、情報不足は否めないが指標たり得る。従って、触針式粗さ計を用いて得られるＲＳｍ（ＪＩＳ　Ｂ０６０１：２００１）は、うねりの周期ととらえることが出来るため、ＲＳｍが大きいとうねりが小さくて平滑な表面であって、ＲＳｍが小さいとうねりが大きく粗い表面であると判断する指標に用いることも出来る。

【0039】

ところで、ＴＡＢやＣＯＦの製造等で一般的に用いられているサブトラクティブ法による配線形成における好適なエッチング条件は、配線間にエッチング残が発生しないように設定されており、異なるエッチング時間で試行して好適時間を求める結果、オーバーエッチング時間が設定されている。このオーバーエッチング時間とは、銅張積層板を構成している表面処理電解銅箔が接着面側に表面粗さ等のばらつきを持っていることを前提とし、

最もエッチングしにくい部分にエッチング残が発生しないように、追加のエッチング時間を設定したものである。しかし、オーバーエッチング時間を設けること自体が配線のサイドウォールを必要以上に溶解してしまうことがあり、エッチングレジストの下部に位置する部分にありながら導体が不必要に溶解してしまう、所謂アンダーカットの原因にもなっている。

【0040】

また、前述のオーバーエッチング時間の設定が必要な、接着面のうねりの大きい表面処理電解銅箔を用いた配線では配線のボトム部分の幅が制御困難になり、これを鳥瞰すると、図１に模式的に示すようにボトム部分に波打ちが生じる。図１のＡ－Ａ’部分の断面を、銅箔と絶縁層構成材料との接着界面のうねりを強調して図２に模式的に示した。この配線断面は絶縁層構成材料Ｆ上に配線Ｗが形成され、配線間に接着面Ｉが露出した形態となっている。この図２に示すように、銅のエッチングでは、溶解していく部分が円又は楕円形状を取ろうとするために、うねりの谷側を向いてエッチングされた部分のサイドウォールSW_Vはボトム部分に尾を引くような断面形状を取り、反面、頂点側を向いているサイドウォールSW_Tは切り立った断面形状になる。その結果、配線を上部から平面的に観察すると、図１に示すように配線のボトム端面に波打ちが生じ、直線性に劣るものとなる。一方、図３に示すように、接着面のうねりの小さい表面処理電解銅箔を用いた配線においては、そのような問題は発生せず、直線性が良好な配線形成が可能となる。

【0041】

そして、電解銅箔に施される防錆処理は、銅張積層板及びプリント配線板の製造過程で支障をきたすことの無いよう、表面処理電解銅箔の表面が酸化腐食することを防止するために実施している。更に、絶縁層構成材料との密着性を阻害せず、可能であれば当該密着性を向上させる構成であることが推奨される。防錆処理に用いられる方法は、ベンゾトリアゾール、イミダゾール等を用いる有機防錆、若しくは亜鉛、クロメート、亜鉛合金等を用いる無機防錆のいずれを採用しても使用目的に適合していれば問題は無い。

【0042】

次に、防錆処理を施す方法に関して説明する。有機防錆の場合は、有機防錆剤の溶液を用いた浸漬塗布、シャワーリング塗布、電着等の手法を用いることが可能である。無機防錆の場合は、電解法、無電解めっき法、スパッタリング法や置換析出法等を用い、防錆元素を電解銅箔の表面上に析出させることが可能である。

【0043】

また、電解銅箔に施されるシランカップリング剤処理とは、防錆処理が終了した後に、絶縁層構成材料との密着性を化学的に向上させるための処理である。

【0044】

そして、用いるシランカップリング剤は、特に限定を要するものではなく、使用する絶縁層構成材料、プリント配線板製造工程で使用するめっき液等の性状を考慮して選択使用すれば良い。シランカップリング剤処理は、シランカップリング剤溶液を用いた浸漬塗布、シャワーリング塗布、電着等の手法により実施することが可能である。

【0045】

前記表面処理電解銅箔の接着面は、析出面側であることが好ましい。低プロファイルであるという観点だけで見ると、研磨仕上げされている回転陰極表面の転写である光沢面側の方が好ましいように思われる。しかし、回転陰極はその使用中に、酸化物などの化合物皮膜の形成などに起因して、表面状態が不安定になることがあるため、これを防止する目的で表面研磨などの機械加工を実施する必要がある。その結果、表面形状の変化が起こってしまい、同レベルの表面状態を維持することは困難なのである。しかし、平滑めっきを可能とする銅電解液を用いた場合に得られる析出面は、回転陰極表面の凹凸を埋めつつ析出銅被膜が成長するため、回転陰極の表面形状にある程度のばらつきがあっても、安定した表面状態が得られるが故に好ましい。

【0046】

前記表面処理電解銅箔の絶縁層構成材料との接着面の凹凸の最大高低差（ＰＶ）は、０

．０５μｍ～１．５μｍであることが好ましく、より好ましくは０．０５μｍ～０．８μｍである。本件発明で表面形状を検出する指標の一つとして用いている凹凸の最大高低差（ＰＶ）とは、三次元表面構造解析顕微鏡を用いて直接計測された試料表面の最大ピーク高さと最大バレー深さの和である。また、ここで示しているＰＶと前述のＷｍａｘの下限である０．０５μｍは、評価の結果が０．０５μｍを下回った場合に不具合が生じることを意味しているものではなく、本件発明に係る製造方法で得られる表面処理電解銅箔における経験的な下限値として示している。

【0047】

また、前記表面処理電解銅箔の接着面側の表面粗さ（Ｒｚｊｉｓ）は、０．１μｍ～１．０μｍであることが好ましく、０．１μｍ～０．５μｍであることがより好ましい。そして、Ｒｚｊｉｓの測定と同時に得られるＲＳｍは０．１を超えていることが更に好ましい。この表面粗さ（Ｒｚｊｉｓ）は、前述の如くＪＩＳ　Ｂ　０６０１－２００１に準拠してＴＤ方向に測定して得られる数値であるが、本件発明では測定基準長を０．８ｍｍとし、触針には円錐状のダイアモンドスタイラス先端のＲが２μｍのものを用いている。前述のように、波打ちの程度の指標は接着面のうねりの最大高低差（Ｗｍａｘ）であるが、現実の工程を考えてみると、接着面の表面粗さ（Ｒｚｊｉｓ）があるレベルを超えるとオーバーエッチング時間を長くせざるを得なくなる。しかし、前述のように、オーバーエッチング時間が長くなるとアンダーカット現象が顕著になる。従って、表面処理電解銅箔の接着面側の表面粗さ（Ｒｚｊｉｓ）も小さいことが好ましく、上記範囲に調整されていることにより、絶縁層構成材料に張合わせたときに実用上十分な密着性を確保することが可能となる。そして、この範囲であれば、プリント配線板として、実用上十分な耐熱特性、耐薬品性、引き剥がし強さを得ることも可能となる。

【0048】

そして、前記接着面側における、うねりの最大高低差（Ｗｍａｘ）と凹凸の最大高低差（ＰＶ）の比〔（Ｗｍａｘ）／（ＰＶ）〕は、０．８以上であることが好ましい。凹凸の最大高低差（ＰＶ）はうねりを有する表面に存在する粗さを含んだ状態で計測されたものである。従って、当該比〔（Ｗｍａｘ）／（ＰＶ）〕が１に近い値を示すことは、波形の表面に存在する凹凸は〔（ＰＶ）－（Ｗｍａｘ）〕とみなすことが出来ることから、当該凹凸が微細であることを表している。反面、比が小さいことは、当該波形表面に存在している凹凸が大きいことを示す。即ち、比が１に近いほど、絶縁層構成材料に食い込んでいる部分が微細であることを示しており、配線を形成する際に、オーバーエッチングを実質的に必要としないエッチング条件設定が可能となる。

【0049】

本件発明に係る電解銅箔の形態：　本件発明に係る「電解銅箔」とは、何ら表面処理を行っていない状態のものであり、「未処理銅箔」、「析離箔」等と称されることがある。本件明細書では、これを単に「電解銅箔」と称する。この電解銅箔の製造には、一般的に連続生産法が採用されており、ドラム形状をした回転陰極と、その回転陰極の形状に沿って対向配置された、鉛系陽極又は寸法安定性陽極（ＤＳＡ）との間に硫酸系銅電解液を流し、銅を回転陰極の表面に電解析出させ、この析出した銅を箔として回転陰極から連続的に引き剥がして巻き取っている。このようにして得られた電解銅箔は、一定幅で巻き取られたロール状となるため、特性の測定などに際して方向を示すには、回転陰極の回転方向（ウェブの長さ方向）をＭＤ（Ｍａｃｈｉｎｅ　Ｄｉｒｅｃｔｉｏｎ）、ＭＤに対して直角方向である幅方向をＴＤ（Ｔｒａｎｓｖｅｒｓｅ　Ｄｉｒｅｃｔｉｏｎ）といっている。

【0050】

この電解銅箔の、回転陰極と接触した状態から引き剥がされた側の表面形状は、回転陰極表面の形状が転写したものとなり、光沢を有することから、この面を「光沢面」と称する。これに対し、析出側の表面形状は、通常は、析出する銅の結晶成長速度が結晶面ごとに異なるために、山形の凹凸形状を示しており、こちら側を「析出面」と称する。そして、一般的には、電解銅箔に表面処理を施した後の析出面側が、銅張積層板を製造する際の絶縁層構成材料との接着面となる。更に、前述したように、この接着面となる側の表面粗

さが小さいほど優れた低プロファイル電解銅箔なのである。

【0051】

そして、本件発明に係る電解銅箔の、光沢面側の表面粗さ（Ｒｚｊｉｓ）は、０．４μｍ～２．０μｍが好ましく、０．４μｍ～１．８μｍがより好ましい。この表面粗さ（Ｒｚｊｉｓ）は、析出面同様ＪＩＳ　Ｂ　０６０１－２００１に準拠してＴＤ方向に測定して得られる数値である。本件発明では、電解銅箔の光沢面側の表面粗さ（Ｒｚｊｉｓ）を、回転陰極の表面粗さ（Ｒｚｊｉｓ）を管理するための二次指標として規定している。電解銅箔の光沢面側の表面形状が、回転陰極の表面形状の転写であることから指標として用いることが出来るのである。二次指標を用いる理由は、後述するように、回転陰極の表面形状が析出面に与える影響が大きいにもかかわらず、量産中には、使用している回転陰極の表面粗さを測定して管理することが事実上不可能であるからである。

【0052】

そして、前記回転陰極の表面粗さが大きくなると、得られる電解銅箔の析出面の表面粗さが大きくなる傾向があることが経験的に把握されている。即ち、厚い電解銅箔を製造するのであれば、平滑な析出面が得られる銅電解液を用いると回転陰極表面の凹凸を埋めつつ厚くなっていくため大きな問題にはならない。しかし、厚さ２０μｍ以下の電解銅箔において、析出面側の表面粗さ（Ｒｚｊｉｓ）が１．０μｍ以下の析出状態を得るためには、回転陰極表面の表面粗さ（Ｒｚｊｉｓ）が２．０μｍを超えることは好ましくない。そして、厚さ１２μｍで、光沢面側表面粗さ（Ｒｚｊｉｓ）が２．０μｍを超える電解銅箔を用いて得られる表面処理電解銅箔では、その析出面のうねりの最大高低差（Ｗｍａｘ）を測定してみると、０．７μｍを超えてしまう傾向があり好ましくない。

【0053】

そして、前記電解銅箔は光沢面側の光沢度［Ｇｓ（６０°）］は、７０以上であることが好ましい。本件発明では、電解銅箔の析出面の滑らかさの差異を明瞭にとらえるため、光沢度も指標としている。ここでいう光沢度には［Ｇｓ（６０°）］を採用しており、これは、被検体の表面に入射角６０°で測定光を照射し、反射角６０°で跳ね返った光の強度を測定したものである。本件発明における光沢度は、ＪＩＳ　Ｚ　８７４１－１９９７に基づき、日本電色工業株式会社製光沢計ＶＧ－２０００型で測定している。

【0054】

電解銅箔の光沢面では、表面粗さが大きくなるほどＴＤとＭＤの異なる方向から見た凹凸形状の違いが大きくなる。光沢面が回転陰極の表面形状のレプリカ形状であり、回転陰極の製造方法及び回転させながら切削や研磨を行うという機械的表面仕上げ手法等が影響して、回転陰極表面の形状に方向性を持ってしまうためである。従って、回転陰極表面に析出する電解銅箔にＴＤ／ＭＤ方向差を発生させないためには、この回転陰極面のＴＤ／ＭＤ方向差を小さくする必要があり、光沢面側の表面粗さ（Ｒｚｊｉｓ）は小さく、光沢度［Ｇｓ（６０°）］は大きい状態で管理されることが好ましい。具体的には、光沢面側の表面粗さ（Ｒｚｊｉｓ）は、０．４μｍ～２．０μｍ、光沢度［Ｇｓ（６０°）］は、７０以上となるように回転陰極の表面を調整することが好ましい。そして、光沢面側の表面粗さ（Ｒｚｊｉｓ）は０．４μｍ～１．８μｍが、光沢度［Ｇｓ（６０°）］は１００以上がより好ましい。そして、光沢面側の光沢度［Ｇｓ（６０°）］の上限は経験的に５００程度である。

【0055】

また、前記電解銅箔の析出面側の表面粗さ（Ｒｚｊｉｓ）は、０．１μｍ～１．０μｍが好ましく、当該析出面側の光沢度［Ｇｓ（６０°）］は、４００以上であることが好ましい。そして、析出面側の表面粗さ（Ｒｚｊｉｓ）は０．１μｍ～０．５μｍ、光沢度［Ｇｓ（６０°）］は、６００以上がより好ましく、光沢度［Ｇｓ（６０°）］のＴＤ／ＭＤ比が９０％～１１０％であることが更に好ましい。良好な表面状態を有する表面処理電解銅箔を得るためには、ベースである電解銅箔析出面の表面状態が平滑且つ均一であることが必須である。そして、析出面側の光沢度［Ｇｓ（６０°）］の上限は経験的に８００程度である。

【0056】
また、前記電解銅箔は、結晶組織の異なる複数層の析出銅層を有することも好ましい。ここで形成されている複数層の析出銅層は、後述する、電流密度の水準を変えた２ステップ以上を備える電解工程で得られたものであり、図４に見られるように、光沢面側に、より緻密な結晶構造を持つ析出銅層を有する。そして、この緻密な結晶構造を有する銅層が光沢面の全面に亘って一定の厚みで存在していることが、その後の電解ステップで均一で平滑な析出を得るために好ましいのである。
【0057】
一般的な電解銅箔製造に使用している回転陰極の表面は、酸化物などの化合物皮膜が形成されているなどの理由により不均一であり、結果として電析銅の析出サイトに偏りが生じてしまう。即ち、銅が電析している部分には更に優先的に銅析出が進行し、電解銅箔の析出面側にうねりが生じてしまう。特に薄い電解銅箔を製造しようとした場合には、銅電解の開始時から開始直後までの第１ステップ電解工程で形成する銅の初期析出層で、回転陰極の表面を銅で均一に覆ってしまうことが、析出面が低プロファイルで、且つ、うねりの小さな電解銅箔を得るには有効になる。なお、本件発明では、第３ステップ電解以降の電解工程を設けることも可能ではあるが、これらの工程は必要に応じて実施すれば良い。通常は、２層の析出銅層を持つ構成とすれば本件発明の目的は達成される。このようにして得られた電解銅箔には、酸化防止などの理由により前述の表面処理が施されるが、本件発明の目的に沿うためには粗化処理は施さないのが好ましい。
【0058】
本件発明に係る電解銅箔の製造方法の形態：　本件発明に係る電解銅箔の製造方法は、硫酸系銅電解液を用いた電解法により、回転陰極表面に析出させた銅を剥取って電解銅箔を製造する方法であって、連続する第１ステップ電解から第ｎステップ電解（ｎ≧２）までを、異なる２水準以上の電流密度で実施する構成としている。この電解法構成を採用することにより、第１ステップ電解で好ましい形態の初期析出層を形成でき、析出面が低プロファイルで、且つ、うねりの小さな電解銅箔の安定生産が可能になる。
【0059】
そして、前記第１ステップ電解の電流密度は５０Ａ／ｄｍ^2～４００Ａ／ｄｍ^{2}であることが好ましい。この電流密度が５０Ａ／ｄｍ^{2}を下回った場合には、前記初期析出層を均一な電析銅皮膜として得ることが困難になり、４００Ａ／ｄｍ^{2}を上回った場合には、例えば陰極付近で水素が発生し、回転陰極の表面性状の劣化が早まってしまう。そして、効果を一層高めるためには、電流密度を７１Ａ／ｄｍ^{2}以上の設定とすることが好ましい。ところで、ここでいう電流密度は、用いる銅電解液に応じて設定される陽極電流密度（ＤＡ）のことである。本来であれば、析出状態は陰極電流密度（ＤＫ）に左右されるためＤＫで管理すべきであるが、現実的にはＤＫの測定が困難であるため、ＤＡを管理指標としている。
【0060】
また、前記第２ステップ電解以降の電流密度は１５Ａ／ｄｍ^2～９０Ａ／ｄｍ^{2}であって、第１ステップ電解の電流密度よりも小さいことが好ましい。電流密度が１５Ａ／ｄｍ^{2}を下回ると工業的生産性が極度に乏しくなり、そして電流密度が９０Ａ／ｄｍ^{2}を超える場合には得られる電解銅箔の析出面の粗さが大きくなって、低プロファイルで、且つ、うねりの小さな析出面を有する電解銅箔の生産が困難になる傾向にある。そして、より好ましい電流密度は５０Ａ／ｄｍ^2～７０Ａ／ｄｍ^{2}である。
【0061】
本件発明に係る電解銅箔の製造方法で用いる硫酸系銅電解液は、膠、チオ尿素、ポリアルキレングリコール、アミン化合物、メルカプト基を持つ化合物、塩素イオン、高分子多糖類、ジアリルジアルキルアンモニウム塩と二酸化硫黄との共重合体、オキシエチレン系界面活性剤、ポリエチレンイミン又はその誘導体、活性硫黄化合物のスルフォン酸塩、環状構造を持つ４級アンモニウム塩重合体から選択された１種類以上の添加剤を含んでいる。そして、連続する第１ステップ電解から第ｎステップ電解までを、異なる２水準以上の電

流密度で実施する電解工程と、この組成の硫酸系銅電解液との組み合わせにより、本件発明に係る、析出面が低プロファイルであり、且つ、うねりの小さな電解銅箔の安定製造が可能になる。ここで、複数ステップの電解工程における個別の電解条件は、選択した添加剤の構成ごとに予察試験を実施して好適化すべきである。

【0062】

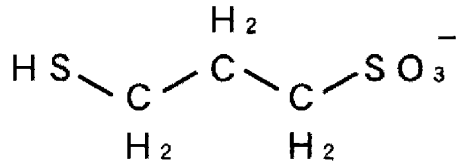
また、前記硫酸系銅電解液は、ＭＰＳ及びＳＰＳから選択された少なくとも１種と、環状構造を持つ４級アンモニウム塩重合体とを含むものであることがより好ましい。その場合において、前記硫酸系銅電解液中のＭＰＳ及び／又はＳＰＳの合算濃度は、０．５ｐｐｍ～２００ｐｐｍであることが好ましい。そして、より好ましい濃度範囲は０．５ｐｐｍ～５０ｐｐｍ、更に好ましい濃度範囲は１ｐｐｍ～２０ｐｐｍである。このＭＰＳ及び／又はＳＰＳの合算濃度が０．５ｐｐｍ未満の場合には、電解銅箔の析出面が粗くなり低プロファイル電解銅箔を得ることが困難となる。一方、ＭＰＳ及び／又はＳＰＳの合算濃度が２００ｐｐｍを越えても得られる電解銅箔の析出面が平滑化する効果は向上せず、むしろ電析状態が不安定化する。従って、析出面が、低プロファイルと小さなうねりとを両立するためには、ＭＰＳとＳＰＳの両方を用いる場合にも、濃度の合算値を上記の範囲とすることが推奨される。

【0063】

なお、本件発明でいうＭＰＳ又はＳＰＳとは、それぞれの塩をも含む意味で使用しており、濃度の記載値は、便宜的に、入手の容易なナトリウム塩としてのＭＰＳナトリウム（本件出願では以降「ＭＰＳ－Ｎａ」と称する）に換算した値としている。そしてＭＰＳは本件発明に係る硫酸系銅電解液中では２量体化することでＳＰＳ構造を取り得るものであり、従ってＭＰＳ及び／又はＳＰＳの合算濃度とは、ＭＰＳ単体やＭＰＳ－Ｎａ等塩類の他、ＳＰＳ－Ｎａとして添加されたもの及びＭＰＳとして電解液中に添加された後ＳＰＳ等に重合化した変性物をも含み、それらのＮａ塩としての換算値である。ＭＰＳの構造式を化１として、ＳＰＳの構造式を化２として以下に示す。これら構造式の比較から、ＳＰＳはＭＰＳの２量体であることがわかる。

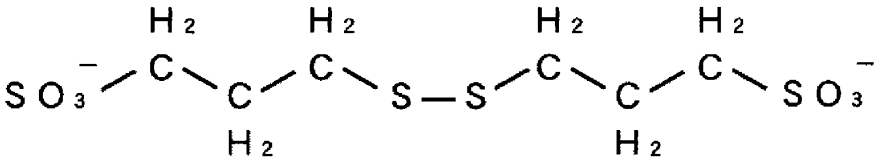
【0064】

【化1】



【0065】

【化2】



【0066】

また、前記硫酸系銅電解液中の環状構造を持つ４級アンモニウム塩重合体濃度は、１ｐｐｍ～１００ｐｐｍが好ましく、より好ましい濃度範囲は１０ｐｐｍ～５０ｐｐｍである。

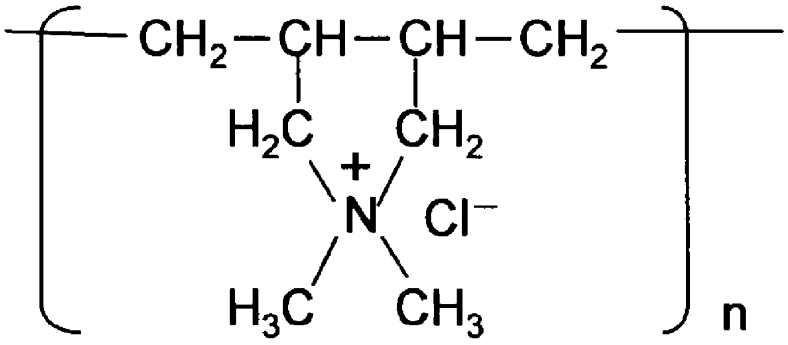
【0067】

前記環状構造を持つ４級アンモニウム塩重合体としては種々のものを用いることが可能であるが、低プロファイルで、且つ、うねりの小さな析出面を形成する効果を考えると、

ＤＤＡＣ重合体を用いることが最も好ましい。ＤＤＡＣは、重合体構造を取る際に環状構造を成すものであり、環状構造の一部は４級アンモニウムの窒素原子で構成されることになる。そして、ＤＤＡＣ重合体には、前記環状構造が５員環や６員環のものなどの複数の形態が存在している。実際に用いる重合体は、合成条件によりそれらのいずれか又は混合物となると考えられているため、ここでは、これら重合体のうち５員環構造を取っている化合物を代表とし、塩素イオンを対イオンとした場合について化３として以下に示す。このＤＤＡＣ重合体とは、化３により明らかなように、ＤＤＡＣが２量体以上の重合体構造を取っているものである。重合体を構成する直鎖部分は、炭素と水素のみから構成されることがより好ましい。

【0068】

【化3】



【0069】

そして、このＤＤＡＣ重合体の、硫酸系銅電解液中の濃度は、１ｐｐｍ～１００ｐｐｍであることが好ましく、より好ましい濃度範囲は１０ｐｐｍ～５０ｐｐｍである。ＤＤＡＣ重合体の硫酸系銅電解液中の濃度が１ｐｐｍ未満の場合には、ＭＰＳ及び／又はＳＰＳの濃度を如何に高めても電析銅の析出面が粗くなり、低プロファイルと小さなうねりとを両立させた析出面を有する電解銅箔を得ることが困難となる。ＤＤＡＣ重合体の硫酸系銅電解液中の濃度が１００ｐｐｍを超えても銅の析出状態が不安定になり、低プロファイルと小さなうねりとを両立させた析出面を有する電解銅箔を得ることが困難となる。

【0070】

また、前記硫酸系銅電解液中の塩素濃度は、５ｐｐｍ～１００ｐｐｍが好ましく、更に好ましい濃度範囲は１０ｐｐｍ～６０ｐｐｍである。この塩素濃度が５ｐｐｍ未満の場合には、電解銅箔の析出面が粗くなり低プロファイルを維持出きなくなる。一方、塩素濃度が１００ｐｐｍを超えても電析状態が安定せず、電解銅箔の析出面が粗くなり、低プロファイルな析出面を形成できなくなる。

【0071】

上記硫酸系銅電解液を用いることにより、製造された電解銅箔は上述のように確かに低プロファイルであり、且つ、高光沢度を有することになる。但し、電解銅箔の析出面側のうねりを低減させることを目的とした場合には電解液の工夫のみで対応できる範囲には限界があるため、前述の如く回転陰極の表面状態の調整や、連続する第１ステップ電解から第ｎステップ電解までを、異なる２水準以上の電流密度で実施する電解法を採用することが重要なのである。

【0072】

本件発明に係る銅張積層板及びプリント配線板の形態：　本件発明に係る銅張積層板は、前記表面処理電解銅箔を絶縁層構成材料と張合わせてなる銅張積層板である。そして本件発明にいう銅張積層板は、片面銅張積層板、両面銅張積層板、内部に内層回路を備える多層銅張積層板の全てを含む概念として記載している。

【0073】
前記絶縁層構成材料が骨格材を含有するものであれば、リジッド銅張積層板となる。従来のリジッド銅張積層板で用いられていた骨格材は、ガラス織布又はガラス不織布が大半を占めてきた。一方、近年では、前述の様に従来無かったレベルのファインパターンを有する配線板を用いてＢＧＡやＣＳＰを作成するために、銅張積層板用の骨格材として、ガラス繊維よりも細いアラミド繊維を不織布で用いるなどして、表面の平坦化を図っている。その結果として、表面処理電解銅箔の接着面粗さが大きい場合には、エッチング後の表面の凹凸が電気特性等に与える影響がクローズアップされてしまう。従って、本件発明に係るリジッド銅張積層板は、特に電気特性の制御が重要なプリント配線板の作成用途に好適である。そして、前記絶縁層構成材料が可撓性を有するフレキシブル素材であれば、フレキシブル銅張積層板となる。
【0074】
前記銅張積層板は、全面の銅を溶解除去後の絶縁層構成材料表面のうねりの高低差（Ｗｍａｘ）が０．０５μｍ～０．７μｍとなる。前記表面処理電解銅箔には銅粒の付着などの粗化処理は施しておらず、接着面のうねりの高低差（Ｗｍａｘ）を０．０５μｍ～０．７μｍとしている。この時、全面の銅を溶解除去した後の絶縁層構成材料の表面は、表面処理電解銅箔の接着面のレプリカであり、そのうねりの高低差（Ｗｍａｘ）も０．０５μｍ～０．７μｍの一致した範囲を示す。
【0075】
プラスチックフィルムを用いたフレキシブル銅張積層板では、プラスチックフィルム自体の表面が平滑であるため、用いた表面処理電解銅箔の接着面のうねりの高低差（Ｗｍａｘ）と、全面の銅を溶解除去した後の絶縁層構成材料の表面のうねりの高低差（Ｗｍａｘ）との一致性が最も得られやすい。しかし、リジッド銅張積層板では、骨格材を用いているため、骨格材の凹凸が表面形状に影響を与える場合がある。しかしながら、前述のように銅張積層板用の骨格材として、ガラス繊維よりも細いアラミド繊維の不織布を用いるなどして表面の平坦化を図ったり、樹脂付銅箔を用いた場合には、骨格材の影響を考える必要が無くなり、用いた表面処理電解銅箔の接着面のうねりの高低差（Ｗｍａｘ）と、全面の銅を溶解除去した後の絶縁層構成材料の表面のうねりの高低差（Ｗｍａｘ）との良好な一致性が得られやすい。
【0076】
これら銅張積層板の製造方法に関しては、従来技術を用いることが可能である。具体的には、リジッド銅張積層板又はフレキシブル銅張積層板を製造する場合には、ホットプレス方式や連続ラミネート方式を用いて製造することが可能であり、本件発明に係る表面処理電解銅箔、ＦＲ－４クラスのプリプレグ等のリジッド絶縁層形成材又はポリイミド樹脂フィルム等のフレキシブル絶縁層形成材、鏡板を用いて、所望のレイアップ状態としたブックを形成し、当該ブックを１７０℃～２００℃に加熱した熱板に挟んで加圧し成形する。
【0077】
一方、フレキシブル銅張積層板の製造には、ロールラミネート方式やキャスティング方式が採用可能である。このロールラミネート方式とは、本件発明に係る表面処理銅箔のロールと、ポリイミド樹脂フィルムやＰＥＴフィルム等の樹脂フィルムロールとを用いて、Ｒｏｌｌ　ｔｏ　Ｒｏｌｌ方式で圧力をかけた加熱ロールの間を重ねて通し、熱圧着させる方法である。そして、キャスティング方式とは、本件発明に係る表面処理銅箔の表面に、ポリアミック酸等の加熱することによりポリイミド樹脂化する樹脂組成膜を形成し、加熱して縮合反応を起こさせることで表面処理銅箔の表面にポリイミド樹脂皮膜を直接形成する方法である。
【0078】
本件発明に係る、前記リジッド銅張積層板を用いて得られたリジッドプリント配線板、又は前記フレキシブル銅張積層板を用いて得られたフレキシブルプリント配線板は、上記から明らかなように、ファインパターンが狙い通りに形成され、且つ、配線端部の波打ち

が少なく、配線の直線性が良いという点から、特に、電気特性の安定したプリント配線板である。また、本件発明に係る表面処理電解銅箔の接着面に存在する表面凹凸は、析出面のうねりに沿って存在している微細なもののみであるため、薄い絶縁層構成材料を用いることの多い高多層プリント配線板の製造用途にも好適である。

【0079】

ここで、上記リジッド銅張積層板又はフレキシブル銅張積層板（以下、単に「銅張積層板」と称する。）のいずれかを用いてプリント配線板に加工する場合の、一般的加工方法の一例を念のために述べておく。最初に、銅張積層板表面へエッチングレジスト層を形成し、エッチング配線パターンを露光し、現像し、エッチングレジストパターンを形成する。このときのエッチングレジスト層は、ドライフィルム、液体レジスト等の感光性樹脂が用いられる。その他、露光はＵＶ露光が一般的であり、定法に基づいたエッチングレジストパターンの形成方法が採用できる。

【0080】

そして、銅エッチング液を用いて電解銅箔を配線形状にエッチング加工し、エッチングレジスト剥離を行うことで、リジッド基材又はフレキシブル基材の表面に所望の配線形状を形成する。このときのエッチング液に関しても、酸性銅エッチング液、アルカリ性銅エッチング液等の全ての銅エッチング液の使用が可能である。

【0081】

従って、両面銅張積層板及び多層銅張積層板を用いる場合には、エッチングなどによる配線形成途中で、その層間での導通を確保することが必要な場合がある。係る場合には、定法によるスルーホール、ビアホール等の形状形成を行い、その後層間導通を得るための導通めっき処理が施される。一般的に、この導通めっき処理には、パラジウム触媒による活性化処理を行い銅無電解めっきが施され、その後電解銅めっきで膜厚成長を行うものである。

【0082】

そして、銅エッチングによる配線形成が終了すると十分に水洗を行い、乾燥、その他必要に応じて防錆処理等が施されて、リジッドプリント配線板又はフレキシブルプリント配線板となる。

【実施例】

【0083】

＜電解銅箔の製造＞

この実施例では、各種添加剤濃度を表１に記載の濃度に調整した電解液７種類を用い、電解銅箔を作成した。具体的には、硫酸系銅電解液として、硫酸銅（試薬）と硫酸（試薬）とを純水に溶解し、銅濃度８０ｇ／Ｌ、フリー硫酸濃度１４０ｇ／Ｌに調製し、基本溶液とした。そして、この基本溶液に、活性硫黄化合物のスルフォン酸塩としてＭＰＳ－Ｎａ又はＳＰＳ－Ｎａ、環状構造を持つ４級アンモニウム塩重合体としてＤＤＡＣ重合体３種（センカ（株）製ユニセンス：ＦＰＡ１００Ｌ、ＦＰＡ１０１Ｌ、ＦＰＡ１０２Ｌ）及び塩酸を添加した。なお、用いたＤＤＡＣ重合体の分子量はＦＰＡ１００Ｌ＜ＦＰＡ１０１Ｌ＜ＦＰＡ１０２Ｌである。

【0084】

【表1】

実施例	添加剤濃度(ppm)			
	活性硫黄化合物のスルフォン酸塩		DDAC重合体／(商品名)	塩素
	MPS-Na	SPS-Na		
実施例1	5	-	30／(FPA100L)	25
実施例2	5	-	5／(FPA100L)	10
実施例3	5	-	30／(FPA100L)	25
実施例4	-	5	35／(FPA100L)	30
実施例5	-	6	37／(FPA100L)	29
実施例6	-	30	71／(FPA101L)	40
実施例7	-	200	71／(FPA102L)	40

【0085】
電解銅箔の作成に当たっては、表面を＃２０００の研磨紙を用いて研磨し表面粗さ（Ｒａ）を０．２０μｍに調整したチタン板電極を回転陰極に用い、陽極にはＤＳＡを用いて、液温を５０℃とし、第１ステップ電解の陽極電流密度（ＤＡ）を７４Ａ／ｄｍ^2、第２ステップ電解の陽極電流密度（ＤＡ）を５２Ａ／ｄｍ^{2}として電解した。実施例１では、１５μｍ厚さの電解銅箔を得、実施例２では、厚さ１２μｍ厚さの電解銅箔を得た。実施例３では、実施例１と同一の液を用いて電解時間を調節し厚さ７０μｍの電解銅箔を得た。そして、実施例４及び実施例５では、ＭＰＳ－Ｎａを用いずＳＰＳ－Ｎａを用いた以外は実施例１及び実施例３とほぼ同等の電解液を用い、厚さ１５μｍの電解銅箔を得た。ＳＰＳ－Ｎａを用いた実施例６及び実施例７では、分子量が大きいＤＤＡＣ重合体を使用し、その他の添加剤濃度が最適になるよう調整して厚さ１２μｍの電解銅箔を得た。以上の実施例１～実施例７から得られた電解銅箔の評価結果等を、表２に示す。そして実施例１の電解銅箔について断面観察を実施した。図４に示す観察像から明らかなように、２層構造となっていることが確認された。

【0086】
【表2】

対　象	銅箔厚さ(μm)	電解銅箔析出面						
		三次元表面構造解析			触針式粗さ計		光沢度Gs(60°)	
		Wmax	PV	Wmax/PV	Rzjis	RSm		
		(μm)	(μm)	(-)	(μm)	(mm)	TD	MD
実施例1	15	0.37	0.39	0.949	0.32	0.19	659	665
実施例2	12	0.45	0.48	0.938	0.31	0.16	664	671
実施例3	70	0.065	0.079	0.823	0.17	0.39	691	686
実施例4	15	0.27	0.30	0.904	0.29	0.18	790	790
実施例5	15	0.36	0.39	0.943	0.31	0.16	775	773
実施例6	12	0.42	0.44	0.959	0.47	0.22	654	687
実施例7	12	0.58	0.66	0.869	0.71	0.14	608	640
比較例	12	0.82	1.87	0.439	1.00	0.07	324	383

【0087】
次に、実施例８～実施例１１として、全面の銅を溶解除去後の絶縁層構成材料表面を評価することを目的とし、前述の実施例１～実施例７と同じ基本溶液を用いて表３に示す電解液４種類を調製した。この電解液を用い、電解条件は実施例１～実施例７と共通とした条件で、厚さ１５μｍの電解銅箔を４種類作成した。

【0088】
【表3】

	添加剤濃度（ppm）				表面処理箔接着面		銅を溶解除去後の絶縁層構成材料表面	
	DDAC重合体	MPS-Na	SPS-Na	塩素	Wmax(μm)	Rzjis(μm)	Wmax(μm)	Rzjis(μm)
実施例8	18	1.6	-	25	0.34	0.29	0.39	0.31
実施例9	25	1.3	-	29	0.36	0.37	0.37	0.37
実施例10	26	-	1.9	29	0.29	0.42	0.28	0.27
実施例11	29	-	3.1	29	0.27	0.23	0.28	0.25

【0089】
＜表面処理電解銅箔の製造＞
そして、実施例１～実施例１１で得られたそれぞれの電解銅箔の両面に防錆処理を施した。ここでは以下に述べる条件の無機防錆を採用した。硫酸亜鉛浴を用い、フリー硫酸濃度７０ｇ／Ｌ、亜鉛濃度２０ｇ／Ｌとし、液温４０℃、電流密度１５Ａ／ｄｍ^{2}とした亜鉛防錆処理を施した。更に、前記亜鉛防錆を施した後に、電解でクロメート防錆処理を施した。このときの電解条件は、クロム酸濃度５．０ｇ／Ｌ、ｐＨ　１１．５、液温３５℃、電流密度８Ａ／ｄｍ^2、電解時間５秒とした。
【0090】
以上の防錆処理及び水洗後、直ちに析出面側にシランカップリング剤の吸着を行った。このときの溶液組成は、純水を溶媒として、γ－グリシドキシプロピルトリメトキシシランを５ｇ／Ｌの濃度となるよう加えたものとした。そして、この溶液をシャワーリングにて吹き付けることにより吸着処理し、水分を気散させて１１種類の表面処理電解銅箔を得た。
【0091】
実施例１～実施例７では表面処理電解銅箔に関する評価を実施した。評価結果を表４に示す。そして、うねり成分と粗さ成分との分離を実施例１で得られた表面処理電解銅箔の析出面に対して実施した。具体的には、三次元表面構造解析顕微鏡（ｚｙｇｏ　Ｎｅｗ　Ｖｉｅｗ　５０３２）の観察データから、面内において任意に選択された直線データを用いて解析した。結果を図５に示す。
【0092】
また、実施例８～実施例１１では表面処理電解銅箔の他、該表面処理電解銅箔を用いて作成した銅張積層板の銅を全面溶解して、その後の絶縁層構成材料表面を評価した。具体的には、各実施例から得られた表面処理電解銅箔の析出面側に、ポリイミド樹脂前駆体を塗布し、３５０℃で加熱することにより、厚さ３８μｍのポリイミドフィルム層を表面処理電解銅箔上に積層させた。このようにして得られたフレキシブル銅張積層板を、塩化第二銅エッチング液を用いて銅箔を全面エッチングした。銅エッチング後の絶縁層構成材料表面は、三次元表面構造解析顕微鏡（ｚｙｇｏ　Ｎｅｗ　Ｖｉｅｗ　５０３２）を使用して、張合わせた表面処理電解銅箔と同じ設定で評価した。以上の実施例８～実施例１１から得られた評価結果等を、表３に示す。
【0093】

【表4】

対　象	表面処理後析出面						
	三次元表面構造解析			触針式粗さ計		光沢度Gs（60°）	
	Wmax	PV	Wmax/PV	Rzjis	RSm		
	（μm）	（μm）	(-)	（μm）	(mm)	TD	MD
実施例1	0.23	0.27	0.852	0.28	0.17	540	514
実施例2	0.50	0.55	0.909	0.44	0.16	507	479
実施例3	0.063	0.07	0.851	0.15	0.34	570	570
実施例4	0.32	0.34	0.930	0.29	0.21	581	584
実施例5	0.32	0.34	0.918	0.30	0.18	629	622
実施例6	0.28	0.32	0.869	0.55	0.16	595	627
実施例7	0.57	0.64	0.886	0.70	0.14	509	560
比較例	0.75	1.80	0.417	0.98	0.06	272	322

【比較例】

【0094】

比較例は、特許文献１に記載された実施例４のトレース実験である。陰極には本願実施例と同様のチタン板を用いた。具体的には、硫酸銅（試薬）と硫酸（試薬）とを純水に溶解して銅濃度９０ｇ／Ｌ、フリー硫酸濃度１１０ｇ／Ｌとし、特許文献１に記載の硫酸系銅電解液の基本溶液を調製した。これに、３－メルカプト１－プロパンスルホン酸ナトリウム濃度４ｐｐｍ、ヒドロキシエチルセルロース濃度５ｐｐｍ、低分子量膠（平均分子量１０００）濃度５ｐｐｍとなるように添加し、更に塩化ナトリウムを用いて塩素濃度を３０ｐｐｍになるように調整し、硫酸系銅電解液を得た。電解条件は特許文献１に準じ、厚さ１２μｍの電解銅箔を得た。得られた電解銅箔の評価結果を表２に示す。そして得られた電解銅箔の両面に実施例と同様に防錆処理を施した。得られた表面処理電解銅箔の評価結果を表４に示す。更に、得られた表面処理電解銅箔の析出面について、実施例１で得られた表面処理電解銅箔と同様にしてうねり成分と粗さ成分とを分離した。結果を図６に示す。

【0095】

＜電解銅箔及び表面処理電解銅箔の対比＞

以降、表２、表３及び表４に記載の電解銅箔及び表面処理電解銅箔から得られたデータを用い、本件実施例と比較例に係る電解銅箔、表面処理電解銅箔を対比して説明する。

【0096】

実施例１と実施例３との対比：　表２に見られるように、電解銅箔の析出面の評価特性比較においては、実施例１の厚さ１５μｍ電解銅箔に対し、実施例３の厚さ７０μｍ電解銅箔の方が、Ｗｍａｘは０．３７μｍに対して０．０６５μｍ、表面粗さ（Ｒｚｊｉｓ）が０．３２μｍに対して０．１７μｍ、光沢度は（ＴＤ／ＭＤ）で（６５９／６６５）に対して（６９１／６８６）といずれも優れており、本件発明に係る電解銅箔では、厚みを増すに従って優れた平滑性を有する析出面が得られる傾向がある。

【0097】

実施例１～実施例７（除：実施例３）の対比：　表２に見られるように、厚さ７０μｍである実施例３を除き実施例１～実施例７で得られた電解銅箔では、析出面のうねりの最大高低差（Ｗｍａｘ）が０．２７μｍ～０．５８μｍ、凹凸の最大高低差（ＰＶ）は０．３０μｍ～０．６６μｍ、（Ｗｍａｘ／ＰＶ）比は０．８６９～０．９５９、表面粗さ（Ｒｚｊｉｓ）は０．２９μｍ～０．７１μｍ、ＲＳｍは０．１４μｍ～０．２２μｍ、光沢度［Ｇｓ（６０°）］は（ＴＤ／ＭＤ）で（６０８～７９０／６４０～７９０）であり、全ての項目において若干のレベル差はあるものの、優れた平滑性と小さなうねりを両立した析出面を有する電解銅箔となっている。また、ＴＤ／ＭＤの方向差は見られておらず、均質である。

【0098】
実施例１と実施例４の対比：　ここでは、活性硫黄化合物のスルフォン酸塩としてのＭＰＳ－ＮａとＳＰＳ－Ｎａの比較を電解銅箔で実施する。表２を見ると、実施例１で得られた電解銅箔と実施例４で得られた電解銅箔では、析出面のうねりの最大高低差（Ｗｍａｘ）は０．３７μｍと０．２７μｍ、凹凸の最大高低差（ＰＶ）は０．３９と０．３０、（Ｗｍａｘ／ＰＶ）比は０．９４９と０，９０４、表面粗さ（Ｒｚｊｉｓ）は０．３２μｍと０．２９μｍ、ＲＳｍは０．１９μｍと０．１８μｍ、光沢度［Ｇｓ（６０°）］は（ＴＤ／ＭＤ）で（６５９／６６５）と（７９０／７９０）であり、実施例４のようにＳＰＳ－Ｎａを用いると光沢度に若干の優位性が見られるものの、実施例１と実施例４で得られた電解銅箔は、ともに優れた平滑性と小さなうねりを両立した析出面を有する電解銅箔となっている。
【0099】
そして、表４に示す表面処理電解銅箔においても、実施例３で得られた厚さ７０μｍ銅箔を例外とすると、実施例１～実施例７で得られた表面処理電解銅箔では、析出面のうねりの最大高低差（Ｗｍａｘ）は０．２３μｍ～０．５７μｍ、凹凸の最大高低差（ＰＶ）は０．２７μｍ～０．６４μｍ、（Ｗｍａｘ／ＰＶ）比は０．８５２～０．９３０、表面粗さ（Ｒｚｊｉｓ）は０．２８μｍ～０．７０μｍ、ＲＳｍは０．１４μｍ～０．２１μｍ、光沢度［Ｇｓ（６０°）］は（ＴＤ／ＭＤ）で（５０７～６２９／４７９～６２７）であり、全ての項目において若干のレベル差はあるものの、接着面に優れた平滑性と小さなうねりを両立した表面処理電解銅箔となっている。また、ＴＤ／ＭＤの方向差は見られておらず、均質である。
【0100】
全面の銅を溶解除去後の絶縁層構成材料表面の評価：　表３を見ると、実施例８～実施例１１で得られた表面処理電解銅箔と、該表面処理電解銅箔を張合わせた後に銅を全面エッチングした絶縁層構成材料との表面形状の比較において、うねりの高低差（Ｗｍａｘ）は（表面処理箔接着面／絶縁層構成材料表面）が（０．２７μｍ～０．３６μｍ／０．２８μｍ～０．３９μｍ）であり、表面粗さ（Ｒｚｊｉｓ）は（表面処理箔接着面／絶縁層構成材料表面）が（０．２３μｍ～０．４２μｍ／０．２５μｍ～０．３７μｍ）と、ほぼ同等であった。
【0101】
実施例と比較例との対比：　比較例で得られた電解銅箔は、表２に示すとおり、特許文献１の再現はほぼ出来ているものの、明らかに本願実施例に係る電解銅箔には劣るものとなっている。そして、光沢度［Ｇｓ（６０°）］はＴＤで３２４、ＭＤでも３８３と、測定方向による違いが見られる。
【0102】
そして、比較例で得られた表面処理電解銅箔でも、表４に示すとおり、配線端面の直線性に大きく影響を与える接着面のうねりの最大高低差（Ｗｍａｘ）の値が、本件実施例で得られた同じ厚さの表面処理電解銅箔よりも大きな値を示すものとなっている。従って、電解銅箔同様、比較例の表面処理電解銅箔は明らかに本願実施例に係る表面処理電解銅箔には劣るものとなっている。そして、光沢度［Ｇｓ（６０°）］はＴＤで２７２、ＭＤでは３２２と測定方向による違いが見られる。更に、図５と図６の比較からも明らかであるが、本願実施例で得られた表面処理電解銅箔の析出面では、うねり成分の変位に対して、粗さ成分の変位が明らかに小さくなっている。これに対し、比較例で得られた表面処理電解銅箔では、うねり成分の変位そのものが、本願実施例で得られた表面処理電解銅箔のうねり成分の変位よりも大きくなっている。また、それ以上に粗さ成分の変位が大きく、うねり成分と同レベルの変位を示している。そして、触針式粗さ計を用いて得られるＲＳｍの値からも、本件発明に係る表面処理電解銅箔の方が、比較例で得られた表面処理電解銅箔よりもうねりのピッチが狭いことが明らかである。この点からも、触針式粗さ計を用いた測定は指標となり得ることがわかる。この比較から、本件発明に係る表面処理電解銅箔が、２０μｍピッチレベルの微細配線形成用途に好適であることの理由が、一層明らかと

なっている。そして、基本的には、良好な特性を有する表面処理電解銅箔を得るためには、良好な電解銅箔が必要であることが伺える。

【0103】

なお、上記実施例では、本件発明に係る電解銅箔の製造に際して、硫酸系銅電解液の銅濃度を５０ｇ／Ｌ～１２０ｇ／Ｌ、フリー硫酸濃度を６０ｇ／Ｌ～２５０ｇ／Ｌ程度とした電解液組成により良好な結果を得ている。しかし、実操業に当たっては、第１ステップ電解の電流密度と第２ステップ電解以降の電流密度はもとより、液組成の範囲や液温等も含め、その設備仕様に合った、好適な範囲に変更をしてもかまわないのである。そして、上記実施例及び比較例に記載の、ＭＰＳ、ＳＰＳやＤＤＡＣ重合体等の添加方法又は添加形態にはこだわらず、例えばＭＰＳを添加する場合には、ＭＰＳ－Ｎａの代わりに他のアルカリ金属又はアルカリ土類金属塩を用いてもかまわない。この時、ＳＰＳ－Ｃｕ塩を用いることは、Ｎａの蓄積を防ぐことが出来るために好ましい。そして、本件発明に係る硫酸系銅電解液は、その他の添加剤類の存在を否定しているものでもなく、上記添加剤類の効果を更に際だたせたり、連続生産時の品質安定化に寄与できること等が確認されているものであれば任意に添加してかまわない。

【産業上の利用可能性】

【0104】

本件発明に係る表面処理電解銅箔は、従来市場に供給されてきた低プロファイル表面処理電解銅箔と同レベル以上の低プロファイルを有しており、且つ、接着面のうねりが小さいものである。よって、テープ　オートメーティド　ボンディング（ＴＡＢ）基板やチップ　オン　フィルム（ＣＯＦ）基板のファインピッチ配線、特に２０μｍピッチレベルの微細配線の形成に好適である。同様に、プラズマディスプレイパネルの電磁波シールドパターンの形成材料としても好適であり、また、キャパシタ内蔵プリント配線板の内蔵キャパシタの下部電極形成材料としても好適である。更に、リチウムイオン二次電池の負極集電体としても好適に用い得るものである。

【図面の簡単な説明】

【0105】

【図1】接着面のうねりが大きい銅箔を用いて作成したプリント配線板で得られる配線の鳥瞰模式図である。

【図2】図１に示すＡ－Ａ’部分における配線断面の模式図である。

【図3】接着面のうねりが小さい銅箔を用いて作成したプリント配線板で得られる配線の断面模式図である。

【図4】実施例１で得られた電解銅箔の断面結晶組織を観察した図である。

【図5】実施例１で得られた表面処理電解銅箔の析出面を三次元表面構造解析顕微鏡（ｚｙｇｏ　Ｎｅｗ　Ｖｉｅｗ　５０３２）で観察した面内において任意に選択された直線データからうねり成分と粗さ成分とを分離して併記した図である。

【図6】比較例で得られた表面処理電解銅箔の析出面を三次元表面構造解析顕微鏡（ｚｙｇｏ　Ｎｅｗ　Ｖｉｅｗ　５０３２）で観察した面内において任意に選択された直線データからうねり成分と粗さ成分とを分離して併記した図である。

【符号の説明】

【0106】

Ｆ　　絶縁層構成材料

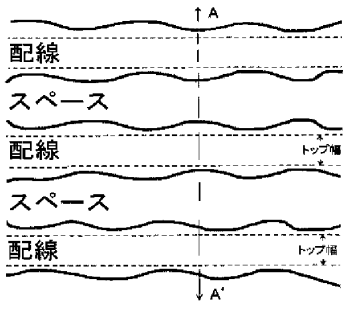
Ｉ　　接着面

SW_T　　うねりの頂点側を向いて形成されたサイドウォール

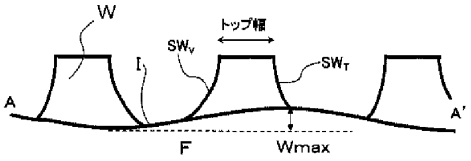
SW_V　　うねりの谷側を向いて形成されたサイドウォール

Ｗ　　配線

【図1】



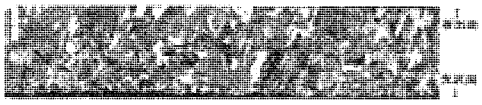
【図2】



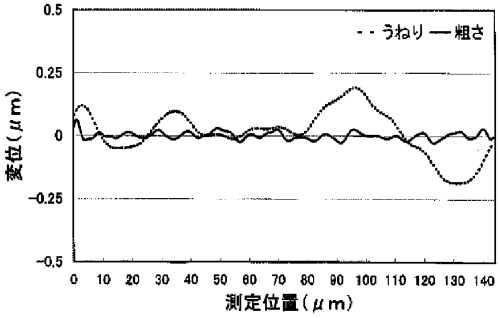
【図3】



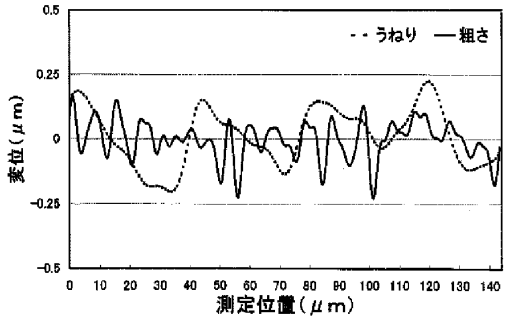
【図4】



【図5】



【図6】



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/054681

A. CLASSIFICATION OF SUBJECT MATTER
C25D1/04(2006.01)i, *B32B15/08*(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, B32B15/08, 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 1996-2007
Kokai Jitsuyo Shinan Koho 1971-2007 Toroku Jitsuyo Shinan Koho 1994-2007

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 Y	WO 2003/096776 A1 (Mitsui Mining & Smelting Co., Ltd.), 20 November, 2003 (20.11.03), Claims & US 2004/163842 A1 & CN 1533686 A	6,7 1-5,8,19-24
Y A	JP 2004-263296 A (Furukawa Techno-Research Co., Ltd.), 24 September, 2004 (24.09.04), Par. Nos. [0021] to [0024]; Fig. 6 & US 2004/157080 A1 & EP 1448036 A1 & JP 2004-263300 A	1-5,8,19-24 6,7

☒ 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
05 June, 2007 (05.06.07)	19 June, 2007 (19.06.07)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/054681

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2004-263289 A (Fukuda Metal Foil & Powder Co., Ltd.), 24 September, 2004 (24.09.04), Full text & WO 2004/090197 A1 & US 2006/191897 A1	2-5,8 9-18
E,X	JP 3910623 B1 (Mitsui Mining & Smelting Co., Ltd.), 25 April, 2007 (25.04.07), Full text (Family: none)	6-8
A	JP 50-2378 B1 (Mishima Kosan Kabushiki Kaisha), 25 January, 1975 (25.01.75), (Family: none)	9-18
A	JP 2005-15861 A (Nikko Materials Co., Ltd.), 20 January, 2005 (20.01.05), Par. Nos. [0010], [0023] (Family: none)	1-24

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

国際調査報告	国際出願番号　ＰＣＴ／ＪＰ２００７／０５４６８１

Ａ．　発明の属する分野の分類（国際特許分類（ＩＰＣ））

Int.Cl.　C25D1/04(2006.01)i, B32B15/08(2006.01)i, C25D7/06(2006.01)i, H05K1/09(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.　C25D1/04, B32B15/08, C25D7/06, H05K1/09

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	１９７１－２００７年
日本国実用新案登録公報	１９９６－２００７年
日本国登録実用新案公報	１９９４－２００７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	関連する請求の範囲の番号
X Y	WO 2003/096776 A1（三井金属鉱業株式会社）2003.11.20, 請求の範囲 & US 2004/163842 A1　& CN 1533686 A	6,7 1-5,8,19-24
Y A	JP 2004-263296 A（古河テクノリサーチ株式会社）2004.09.24, 【００２１】－【００２４】,【図６】 & US 2004/157080 A1　& EP 1448036 A1　& JP 2004-263300 A	1-5,8,19-24 6,7

☑　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
０５．０６．２００７	１９．０６．２００７
国際調査機関の名称及びあて先 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	特許庁審査官（権限のある職員）　４Ｅ　３０３２ 瀧口　博史 電話番号　０３－３５８１－１１０１　内線　３４２５

様式ＰＣＴ／ＩＳＡ／２１０（第２ページ）（２００５年４月）

国際調査報告	国際出願番号　ＰＣＴ／ＪＰ２００７／０５４６８１

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	関連する請求の範囲の番号
Y	JP 2004-263289 A (福田金属箔粉工業株式会社) 2004.09.24, 全文	2-5,8
A	& WO 2004/090197 A1 & US 2006/191897 A1	9-18
E,X	JP 3910623 B1 (三井金属鉱業株式会社) 2007.04.25, 全文 (ファミリーなし)	6-8
A	JP 50-2378 B1 (三島光産株式会社) 1975.01.25 (ファミリーなし)	9-18
A	JP 2005-15861 A (株式会社日鉱マテリアルズ) 2005.01.20, 【００１０】,【００２３】 (ファミリーなし)	1-24

様式ＰＣＴ／ＩＳＡ／２１０（第２ページの続き）（２００５年４月）

(81)指定国　　AP(BW,GH,GM,KE,LS,MW,MZ,NA,SD,SL,SZ,TZ,UG,ZM,ZW),EA(AM,AZ,BY,KG,KZ,MD,RU,TJ,TM),EP(AT,BE,BG,CH,CY,CZ,DE,DK,EE,ES,FI,FR,GB,GR,HU,IE,IS,IT,LT,LU,LV,MC,MT,NL,PL,PT,RO,SE,SI,SK,TR),OA(BF,BJ,CF,CG,CI,CM,GA,GN,GQ,GW,ML,MR,NE,SN,TD,TG),AE,AG,AL,AM,AT,AU,AZ,BA,BB,BG,BR,BW,BY,BZ,CA,CH,CN,CO,CR,CU,CZ,DE,DK,DM,DZ,EC,EE,EG,ES,FI,GB,GD,GE,GH,GM,GT,HN,HR,HU,ID,IL,IN,IS,JP,KE,KG,KM,KN,KP,KR,KZ,LA,LC,LK,LR,LS,LT,LU,LY,MA,MD,MG,MK,MN,MW,MX,MY,MZ,NA,NG,NI,NO,NZ,OM,PG,PH,PL,PT,RO,RS,RU,SC,SD,SE,SG,SK,SL,SM,SV,SY,TJ,TM,TN,TR,TT,TZ,UA,UG,US,UZ,VC,VN,ZA,ZM,ZW

(72)発明者　酒井　久雄
埼玉県上尾市原市１３３３－２　三井金属鉱業株式会社　総合研究所内
(72)発明者　坂田　智浩
埼玉県上尾市原市１３３３－２　三井金属鉱業株式会社　総合研究所内
(72)発明者　吉岡　淳志
埼玉県上尾市原市１３３３－２　三井金属鉱業株式会社　総合研究所内
(72)発明者　西川　丞
埼玉県上尾市原市１３３３－２　三井金属鉱業株式会社　総合研究所内
(72)発明者　田口　丈雄
埼玉県上尾市原市１３３３－２　三井金属鉱業株式会社　総合研究所内
Ｆターム(参考) 4E351 AA02　AA16　BB01　BB30　BB38　DD04　DD55　GG20

（注）この公表は、国際事務局（ＷＩＰＯ）により国際公開された公報を基に作成したものである。なおこの公表に係る日本語特許出願（日本語実用新案登録出願）の国際公開の効果は、特許法第１８４条の１０第１項(実用新案法第４８条の１３第２項）により生ずるものであり、本掲載とは関係ありません。

Electronic Acknowledgement Receipt

EFS ID:	34623799
Application Number:	15307069
International Application Number:	
Confirmation Number:	9113
Title of Invention:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Dae Young KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/Samantha Lingo
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313221.00005
Receipt Date:	18-DEC-2018
Filing Date:	27-OCT-2016
Time Stamp:	16:29:43
Application Type:	U.S. National Stage under 35 USC 371

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	00005_IDS_Trans.pdf	25187 74d910ff9f2f35740d1e6ca122eea9a374b5d0e7	no	3

Warnings:

Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	00005_PTOsb08.pdf	1035203 ac7c0b21026935b1d59f44e9a6ba05d9d6b9a4eb	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.					
3	Other Reference-Patent/App/Search documents	JP_OA.pdf	557906 fcdadff7eb7f4cc06c7ce70e32bbfc5286229de8	no	3
Warnings:					
Information:					
4	Foreign Reference	JP2012022939.pdf	337339 27c4d6e3851ae9d6454138764e49dab468da3ae5	no	9
Warnings:					
Information:					
5	Foreign Reference	JP2012151106.pdf	1331380 f3cd11afa2e8aa39e7faa4e2d03ee5ecf9001693	no	19
Warnings:					
Information:					
6	Foreign Reference	WO2007105635.pdf	2993809 0191f2ab81088f1a4d9962e90090b6132458cb81	no	27
Warnings:					
Information:					
		Total Files Size (in bytes):	6280824		

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:	Dae Young KIM
Appl. No.:	15/307,069
Conf. No.:	9113
Filed:	October 27, 2016
Title:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1727
Examiner:	USYATINSKY, ALEXANDER
Docket No.:	0313221.00005

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

[ ] 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.

[X] 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)

[X] 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 $ 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: December 18, 2018

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 15/307,069	Filing Date 10/27/2016	☐ To be Mailed

ENTITY: ☑ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED - PART I

	(Column 1)	(Column 2)			
FOR	NUMBER FILED	NUMBER EXTRA		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A		N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A		N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*		x $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	12/17/2018	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 16	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 2	Minus	*** 3	= 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".	/VENESSA JONES/
*** 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.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Dae Young KIM
Appl. No.:	15/307,069
Conf. No.:	9113
Filed:	October 27, 2016
Title:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1727
Examiner:	USYATINSKY, ALEXANDER
Docket No.:	0313221.00005

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 October 30, 2018.

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

Remarks begin on page 7 of this paper.

Electronic Acknowledgement Receipt	
EFS ID:	34607747
Application Number:	15307069
International Application Number:	
Confirmation Number:	9113
Title of Invention:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Dae Young KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/Elias Santiago
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313221.00005
Receipt Date:	17-DEC-2018
Filing Date:	27-OCT-2016
Time Stamp:	16:55:20
Application Type:	U.S. National Stage under 35 USC 371

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		00005_RespRestriction.pdf	32117 047bc6406f3456328aa17fa7737b98dfd5bf0029	yes	7

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Applicant Arguments/Remarks Made in an Amendment	7	7
	Claims	2	6
	Response to Election / Restriction Filed	1	1
Warnings:			
Information:			
	Total Files Size (in bytes):	32117	

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.

REMARKS

This Response is submitted in reply to the Restriction Requirement dated October 30, 2018 The Examiner is requiring the Applicant to elect one of the following inventions:

I. Claims 1-11, drawn to an electrolytic foil; or

II. Claims 12-16 drawn to a method for producing of the electrolytic foil.

Applicant hereby elects Group I, including claims 1 to 11, without traverse for examination on the merits. No new matter is added by these amendments. 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: December 17, 2018

IN THE CLAIMS

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

1. (Original) An electrolytic copper foil for a secondary battery, the electrolytic copper foil comprising:

a first surface; and

a second surface opposite to the first surface,

wherein each of the first and second surfaces has a peak count roughness R_{pc} of 10 to 100,

wherein the peak count roughness R_{pc} of each of the first and second surfaces is an average of peak count roughness R_{pc} values measured at randomly-selected three points,

the peak count roughness R_{pc} of each point is the number of effective peaks which rise above an upper criteria line of 0.5 μm per unit sampling length of 4 mm in a surface roughness profile obtained according to steel-iron test schedule (SEP 1940), and

there is at least one valley deeper than a lower criteria line of -0.5 μm between adjacent ones of the effective peaks.

2. (Original) The electrolytic copper foil according to claim 1, wherein a difference in peak count roughness R_{pc} between the first and second surfaces is 60 or less.

3. (Original) The electrolytic copper foil according to claim 1, wherein each of the first and second surfaces has a ten-point mean roughness R_{pc} of 2 μm or less.

4. (Original) The electrolytic copper foil according to claim 1, wherein the electrolytic copper foil has a thickness of 3 to 20 μm and tensile strength of 30 to 60 kgf/mm^2.

5. (Previously Presented) A current collector for a secondary battery the current collector comprising:

the electrolytic copper foil according to claim 1; and

a protective layer disposed on the electrolytic copper foil,

wherein the protective layer comprises at least one of chromate, benzotriazole and a silane compound.

6. (Original) The current collector according to claim 5, wherein the protective layer is formed on the first and second surfaces of the electrolytic copper foil.

7. (Previously Presented) An electrode for a secondary battery, the electrode comprising:

a current collector comprising the electrolytic copper foil according to claim 1; and

an active material layer disposed on the current collector;

wherein the active material layer comprises at least one active material selected from the group consisting of: carbon; a metal (Me) of Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni or Fe; an alloy containing the metal; an oxide of the metal (MeO_x); and a complex of the metal and carbon.

8. (Original) The electrode according to claim 7, wherein the active material layer comprises Si.

9. (Original) the electrode according to claim 7, wherein the current collector further comprises a protective layer comprising at least one lf chromate, benzotriazole and a silane compound, and

wherein the protective layer is interposed between the electrolytic copper foil and the active material layer.

10. (Previously Presented) A secondary battery comprising:

a cathode;

an anode;

an electrolyte for providing an environment enabling lithium ions to move between the cathode and the anode; and

a separator for electrically insulating the cathode from the anode,

wherein the anode comprises:

a current collector comprising the electrolytic copper foil according to claim 1; and

an active material layer disposed on the current collector.

11. (Original) The secondary battery according to claim 10, further comprising a protective layer comprising at least one of chromate, benzotriazole and a silane compound,

wherein the protective layer is interposed between the electrolytic copper foil and the active material layer.

12. (Withdrawn) A method of producing an electrolytic copper foil by allowing a current to flow between a cathode plate and a rotational anode drum spaced from each other in an electrolytic solution so as to electrodeposit a copper of the rotational anode drum, the method comprising:

heat-treating a copper wire;

acid-cleaning the heat-treated copper wire;

dipping the acid-cleaned copper wire in the electrolytic solution;

conducting electroplating, while the copper wire is dipped in the electrolytic solution, by allowing a current to flow between the cathode plate and the rotational anode drum; and

conducting continuous filtration to remove solid impurities from the electrolytic solution during the electroplating.

13. (Withdrawn) The method according to claim 12, wherein concentrations of organic impurities and metal impurities in the electrolytic solution during the electroplating are maintained at 1g/L or less and 10 g/L or less, respectively.

14. (Withdrawn) The method according to claim 12, wherein the heat-treatment of the copper wire is carried out at 600 to 800°C.

15. (Withdrawn) The method according to claim 12, wherein the electrolytic solution comprises 50 to 100 g/L of a copper ion, 50 to 150 g/L of sulfuric acid, 50 ppm or less of a chlorine ion and an organic additive.

16. (Withdrawn) The method according to claim 15, wherein the organic additive is hydroxyethyl cellulose (HEC), organic sulfide, organic nitride, a thiourea compound, or a mixture of two or more thereof.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/307,069	10/27/2016	Dae Young KIM	0313221.00005	9113

24573 7590 10/30/2018

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

EXAMINER	
USYATINSKY, ALEXANDER	

ART UNIT	PAPER NUMBER
1727	

NOTIFICATION DATE	DELIVERY MODE
10/30/2018	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. 15/307,069	Applicant(s) KIM et al.	
	Examiner ALEXANDER USYATINSKY	Art Unit 1727	AIA 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 10/27/2016.

☐ 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) 1-16 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) 1-16 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

Election/Restriction

REQUIREMENT FOR UNITY OF INVENTION

As provided in 37 CFR 1.475(a), a national stage application shall relate to one invention only or to a group of inventions so linked as to form a single general inventive concept ("requirement of unity of invention"). Where a group of inventions is claimed in a national stage application, the requirement of unity of invention shall be fulfilled only when there is a technical relationship among those inventions involving one or more of the same or corresponding special technical features. The expression "special technical features" shall mean those technical features that define a contribution which each of the claimed inventions, considered as a whole, makes over the prior art.

The determination whether a group of inventions is so linked as to form a single general inventive concept shall be made without regard to whether the inventions are claimed in separate claims or as alternatives within a single claim. See 37 CFR 1.475(e).

When Claims Are Directed to Multiple Categories of Inventions:

As provided in 37 CFR 1.475 (b), a national stage application containing claims to different categories of invention will be considered to have unity of invention if the claims are drawn only to one of the following combinations of categories:

(1) A product and a process specially adapted for the manufacture of said product; or

(2) A product and a process of use of said product; or

(3) A product, a process specially adapted for the manufacture of the said product, and a use of the said product; or

(4) A process and an apparatus or means specifically designed for carrying out the said process; or

(5) A product, a process specially adapted for the manufacture of the said product, and an apparatus or means specifically designed for carrying out the said process.

Otherwise, unity of invention might not be present. See 37 CFR 1.475 (c).

Restriction is required under 35 U.S.C. 121 and 372.

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

In accordance with 37 CFR 1.499, applicant is required, in reply to this action, to elect a single invention to which the claims must be restricted.

Group I, claims 1-11 drawn to an electrolytic foil

Group II, claims 12-16 drawn to a method for producing of the electrolytic foil

The groups of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

The lack unity of invention because even though the inventions of these groups require the technical feature of the electrolytic foil , this technical feature is not a special technical feature as it does not make a contribution over the prior art in view of CN 1480563 (claims 1-11) and JP 3850155B2 (claims 12-16).

Applicant is advised that the reply to this requirement to be complete must include (i) an election of a species or 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 or species may be made with or without traverse. To preserve 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 on the elected invention or species.

Should applicant traverse on the ground that the inventions have unity of invention (37 CFR 1.475(a)), applicant must provide reasons in support thereof. Applicant may 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. Where such evidence or admission is provided by applicant, 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(a) of the other invention.

Applicant is reminded that upon the cancellation of claims to a non-elected invention, the inventorship must be corrected in compliance with 37 CFR 1.48(a) if one or more of the currently named inventors is no longer an inventor of at least one claim remaining in the application. A request to correct inventorship under 37 CFR 1.48(a)

must be accompanied by an application data sheet in accordance with 37 CFR 1.76 that identifies each inventor by his or her legal name and by the processing fee required under 37 CFR 1.17(i).

Any inquiry concerning this communication or earlier communications from the examiner should be directed to ALEXANDER USYATINSKY whose telephone number is (571)270-7703. The examiner can normally be reached on IFP.

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, Barbara Gilliam can be reached on 5712721330. 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.

/Alexander Usyatinsky/
Primary Examiner, Art Unit 1727

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	15307069
Filing Date	2016-10-27
First Named Inventor	Dae Young KIM
Art Unit	1727
Examiner Name	USYATINSKY, ALEXANDER
Attorney Docket Number	0313221.00005

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
	1	5431803		1995-07-11	DIFRANCO, ET AL.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

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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	3067199	EP	A1	2016-09-14	IIJIN MATERIALS CO., LTD		
	2	2660359	EP	A1	2013-11-06	FURUKAWA ELECTRIC CO., LTD		
	3	1876266	EP	A1	2008-01-09	MITSUI MINING & SMELTING CO., LTD		

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15307069
	Filing Date	2016-10-27
	First Named Inventor	Dae Young KIM
	Art Unit	1727
	Examiner Name	USYATINSKY, ALEXANDER
	Attorney Docket Number	0313221.00005

	4	20001011684	JP	A	2001-01-16	UNKNOWN		
	5	3850155	JP	A	2006-11-29	NIPPON DENKAI KK	Also published as JP2000-182623	
	6	1480563	CN	A	2004-03-10	FURUKAWA CIRCUIT FOIL		

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	Chinese Office Action for related Chinese Application No. 201680000680.4; action dated August 1, 2018; (8 pages)	
	2	European Search Report for related European Application No. 16814576.1; report dated October 17, 2018; (9 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	15307069
	Filing Date	2016-10-27
	First Named Inventor	Dae Young KIM
	Art Unit	1727
	Examiner Name	USYATINSKY, ALEXANDER
	Attorney Docket Number	0313221.00005

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)	2018-10-26
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.

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Electrolytic copper foil and electrolytic copper foil for secondary cell collector

Inventor(s): HIDEO OTSUKA [JP]; AKITOSHI SUZUKI [JP] ± (利)

Applicant(s): FURUKAWA CIRCUIT FOIL [JP] ± (古河电路铜箔株式会社)

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An electrodeposited copper foil having an extremely smooth surface roughness at the deposition surface, having an extremely fine crystal structure, and yet not having too high an ordinary temperature tensile strength, superior in elongation, maintaining a stable strength without softening by heat even after heat treatment, and having a high elongation rate even in a high temperature atmosphere. The electrodeposited copper foil has a surface roughness Rz at a deposition surface at ordinary temperature smaller than 2.5 mum in terms of 10-point average roughness Rz, has a minimum distance between peaks of a base foil peak of at least 5 mum, has an ordinary temperature tensile strength of not more than 40 kg/mm<2>, and has a drop in ordinary temperature tensile strength after heat treatment at 130 DEG C. for 15 hours of less than 15%. Also, copper foil for a secondary battery collector using that foil.

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[71] 申请人 古河电路铜箔株式会社
地址 日本东京
[72] 发明人 大塚英雄 铃木昭利
[74] 专利代理机构 上海专利商标事务所
代理人 胡 烨
权利要求书 1 页 说明书 11 页

[54] 发明名称 电解铜箔及二次电池集电体用电解铜箔

[57] 摘要

本发明涉及电解铜箔和采用该电解铜箔所制成的充放电循环寿命长、过充电时很难产生断裂的二次电池集电体用电解铜箔；该电解铜箔的析出面表面非常平滑、并且晶体组织非常细微，同时常温抗拉强度不过高，延伸率良好，经热处理后也无热软化现象并保持恒定的强度，高温气氛中的延伸率也高。电解铜箔析出面的表面粗糙度，即常温下晶体组织的十点平均粗糙度 Rz 小于 2.5μm，且底层表面突起的最小峰间距在 5μm以上。另外，所述电解铜箔的常温抗拉强度在 40kg/mm^2 以下，于 130℃进行 15 小时热处理后的常温抗拉强度的减少率在 15%以内。此外，所述二次电池集电体用电解铜箔是将上述电解铜箔用作二次电池集电体用铜箔。

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1.电解铜箔，其特征在于，电解铜箔析出面的表面粗糙度，即常温下的晶体组织的十点平均粗糙度 Rz 小于 2.5μm，且底层表面突起的最小峰间距在 5μm 以上，常温抗拉强度在 40kg/mm² 以下，于 130℃进行 15 小时热处理后的常温抗拉强度的减少率在 15%以内。

2.根据权利要求 1 所述的电解铜箔，其特征在于，经上述热处理后不发生热软化。

3.根据权利要求 2 所述的电解铜箔，其特征在于，厚度为 35μm 时的常温延伸率在 14%以上，常温－200℃的气氛中，随着温度的上升，延伸率增大。

4.二次电池集电体用电解铜箔，其特征在于，将权利要求 1－3 中任一项所述电解铜箔用作二次电池集电体用铜箔。

5. 根据权利要求 4 所述的二次电池集电体用电解铜箔，其特征在于，所述二次电池为锂离子二次电池。

电解铜箔及二次电池集电体用电解铜箔

技术领域

本发明涉及电解铜箔和由该电解铜箔构成的二次电池集电体用电解铜箔，该电解铜箔的析出面表面非常平滑、且晶体组织非常细小，同时常温抗拉强度不过高，延伸率良好，经热处理后也无热软化现象并保持恒定强度，即使在高温气氛中，延伸率也高。

本发明还涉及充放电循环寿命长，过充电时也很难断裂的二次电池集电体用电解铜箔。

背景技术

近年来，随着移动电话、摄像机等电子仪器的小型化，就需要有高能量密度的二次电池。尤其是锂离子二次电池，因其具有较高的能量密度、良好的充放电循环特性，并且量轻的优异特性，它被广泛应用。作为锂离子二次电池负极集电体的制成方法为：通常使用铜箔，在该铜箔的表面上，涂布有加工成膏状的碳粉等负极活性物质，干燥后，进行轧辊压延等，进行压平。然后，和隔层材料和涂布有正极活性物质的铝箔一起进行卷绕，制得锂离子二次电池。

用作负极集电体的铜箔有压延铜箔和电解铜箔二类；压延铜箔由压延加工而制成箔状；而电解铜箔是由将以硫酸铜为主要成分的溶液电解，铜在由钛或 SUS 制的旋转阴极上析出，并将铜连续剥离而制成。

迄今为止，用作锂离子二次电池的负极集电体电极用铜箔多为压延铜箔。但由于用作锂离子二次电池负极集电体电极用铜箔的厚度为 10μm 左右的压延铜箔的高价，且由于重结晶抗拉强度变得极小的原因，涂布碳等负极活性物质、干燥后进行轧辊压延等压涂制造工序中的操作性较差，易产生皱纹，有时，还会发生断裂。再者，压延制成的铜箔宽度通常为 60cm 左右，还存在制造时效率较低的缺点。

对此，最近，人们越来越多试着采用电解铜箔以代替压延铜箔，该电解铜箔的抗拉强度大于因重结晶而使抗拉强度极度降低的压延铜箔，由此操作性较强，还能将铜箔制成 100cm 以上宽度的铜箔，使生产率提高，所以和压延铜箔比较，

该电解铜箔的价格较为便宜。

但以往所用的电解铜箔的析出面为柱状晶体组织，电解铜箔析出面的表面较为粗糙，所以和碳粉等负极活性物质的接触部分较少，接触电阻较大，充放电循环寿命较短，为此，人们开发出晶体组织细微化、使电解铜箔析出面表面的粗糙度和压延铜箔一样小的电解铜箔，用于锂离子二次电池。

日本特许公开公报平 7-188969、日本特许公开公报平 8-53789、日本特许公开公报 2000-182623 号公开了晶体组织细微化、析出面表面粗糙度小的电解铜箔。所公开的电解铜箔的特性是通过对各种添加剂、电解液的组成、电解液温度、电解液流速、电流密度等的控制来达到的，使电解铜箔析出面表面的粗糙度变小。

然而，人们要求进一步提高二次电池的重要特性，即充放电循环寿命和过充电特性。所谓充放电循环寿命指的是重复进行充放电，膨胀收缩所产生的应力等使集电体（铜箔）和活性物质的接触变差，一部分活性物质变成不能用于充放电，引起容量降低。过充电特性指的是：在进行过充电时，要求不发生由集电体（铜箔）的经时劣化而引起的龟裂和断裂。

上述日本特许公开公报平 7-188969、日本特许公开公报平 8-53789、日本特许公开公报平 2000-182623 各公报所公开的晶体组织微化、表面粗糙度小的电解铜箔虽然比以往所用的压延铜箔优异，但要满足市场对充放电循环寿命、过充电特性的要求，还是很不够的。

即，关于用作锂离子二次电池用负极电极集电体的电解铜箔，有以下值得研究的条件：

1.关于表面平滑性：虽然上述 3 个公报中所公开的电解铜箔表面的十点平均粗糙度 Rz 小于 2.5μm，但在用电子显微镜对其表面进行观察时却发现：有平均粒径为零点几微米的细小晶体粒子在电解铜箔的析出面上均匀析出、密集、平滑性不够。而且，由于平均粒径为零点几微米的晶体粒子在表面上显露，密集，所以若将其视为底层表面突起的话，其峰间距和粒径相同，为零点几微米。这样，具有凹凸的电解铜箔的表面和碳粉等负极活性物质的接触较差，导致容量降低、充放电循环寿命缩短。另外，十点平均粗糙度是根据 JIS-B-0601，利用表面光洁测量仪所测得的值。

2.关于常温抗拉强度：上述 3 个公报所公开的电解铜箔的常温抗拉强度都在 50kg/mm^2 以上，这些铜箔非常硬。一般来说，当晶体组织为平均粒径为零点几微米的细小晶体，十点平均粗糙度 Rz 在 2.5μm 以下时，铜箔的常温抗拉强度非常

高，为硬铜箔。而铜箔较硬时，在将涂有活性物质的铜箔进行轧辊压延等的压平工序中，铜箔无足够变形以适应活性物质表面，导致和活性物质的接触较差，容量降低，充放电循环寿命缩短。另外，通常，人们公知抗拉强度和硬度存在比例关系。

3.关于常温延伸率：上述 3 个公报所公开的电解铜箔的延伸率都在 11%以下，由于这样低的延伸率，在将涂布有活性物质的电解铜箔进行轧辊压延等的压平工序中，对铜箔产生应力，出现龟裂，导致容量降低，充放电循环降低。

4.关于非重结晶性：日本特许公开公报 2000-182623 所公开的电解铜箔在 130℃左右发生重结晶。因此，和压延铜箔一样，抗拉强度会因热软化而极度降低，在涂布活性物质、加热干燥时，箔产生延伸皱纹和断裂。另外，因沿着重结晶组织界面上存在龟裂，所以容量降低，充放电循环寿命缩短。

5.关于 180℃高温气氛中的延伸率：因日本特许公开公报平 8-53789 实施例 2 所公开的电解铜箔的厚度为 35μm 时在 180℃高温气氛中延伸率为 9.5%，比通常的电解铜箔低，也比在常温下的延伸率低。为此，在进行过充电特性试验中，承受不住过充电时的发热所引起的膨胀应力，铜箔会产生龟裂。另一方面，日本特许公开公报平 7-188969 及日本特许公开公报 2000-182623 所公开的电解铜箔，即使在过充电特性试验中无龟裂，但也存在在高温气氛中的延伸率比常温下的延伸率更加高的趋势。

发明内容

本发明的目的是提供一种表面粗糙度小的电解铜箔及适合作为二次电池负极集电体的电解铜箔。

本发明权利要求 1 中的电解铜箔具有如下特征：所述电解铜箔的析出面的表面粗糙度，即常温下的晶体组织的十点平均粗糙度 Rz 小于 2.5μm，且底层表面突起的最小峰间距在 5μm 以上，常温抗拉强度在 40kg/mm^2 以下，于 130℃进行 15 小时热处理后的常温抗拉强度的减少率在 15%以内。

较好的电解铜箔在进行上述热处理后，最好不发生热软化。

更好的电解铜箔还具有在厚度为 35μm 时，其常温延伸率在 14%以上，常温－200℃的氛围中，随着温度上升，延伸率增大的特征。

本发明权利要求 3 中的二次电池集电体用电解铜箔具有将上述权利要求 1－3 中任一项的电解铜箔用作二次电池集电体用铜箔的特征。

本发明权利要求 4 中的二次电池集电体用电解铜箔具有上述二次电池为锂离子二次电池的特征。

具体实施方式

本发明者为实现提供一种表面粗糙度小的电解铜箔的目的，就怎样改良上述各公报中所公开的电解铜箔的缺陷等进行了深入研究，结果发现：影响充放电循环寿命及过充电特性的铜箔的重要特性是：十点平均粗糙度 Rz 无法表示的表面平滑性、常温抗拉强度、延伸率、非重结晶性、高温气氛中的延伸率；并成功得到能赋予二次电池最高效果的铜箔。

将本发明电解铜箔的析出面表面粗糙度定为十点平均粗糙度 Rz，电解铜箔的表面粗糙度小于 2.5μm。尽管如此，像其他表面粗糙度小的电解铜箔一样，电解铜箔的析出面应无平均粒径为零点几微米的细小晶体粒子显露，底层表面突起的峰间距在 5μm 以上，析出面非常平滑。因此，活性物质和集电体的接触性良好，导电率变大，成为充放电循环寿命优异的铜箔。

即使十点平均粗糙度 Rz 很小，表面上还有平均粒径在 0.1μm 以上的晶体粒子显露，集电体表面上有凹凸的情况下，活性物质碳粉和集电体的接触点变少，接触电阻增大。若将用了这样的铜箔制成的二次电池进行重复充放电的话，由于膨胀收缩所产生的应力等会使集电体和活性物质的距离慢慢拉大，一部分的活性物质变为不能用于充放电，使容量降低。

因此，除了将电解铜箔析出面的表面粗糙度定为十点平均粗糙度 Rz，比 2.5μm 小以外，还必须在析出面上无平均粒径为零点几微米的晶体粒子显露，底层表面突起的峰间距在 5μm 以上。这是因为，若底层表面突起的峰间距小于 5μm 时，如上所述，和负极活性物质的接触点较少，不能得到充分的接触电阻。

另外，由于本发明的电解铜箔晶体组织非常细小，同时常温抗拉强度在 40kg/mm^2 以下，所以铜箔自身是柔软的。

通常，平面状集电体表面上形成有电极构成物质层的电极采用如下方法：将含有活性物质和粘合剂的电极构成物质层涂布在集电体的表面后，进行轧辊压延等压平操作而制成。该压平工序具有按规定密度将电极进行压缩的作用；使活性物质粒子间距离接近而使其具有适当导电性的作用。经过压平工序处理后的电极，其活性物质粒子间以及活性物质和集电体的接触性都变好，导电率变大。另外，为得到充分的电池特性，除了将活性物质粒子间的距离及活性物质和集电体的距

离变小十分重要以外，集电体形状和活性物质表面形状适应也很重要。若集电体随活性物质表面而发生变形的话，活性物质和集电体的接触性会变得更好，导电率变得更大，充放电循环特性便提高。

为此，常温抗拉强度必须在 40kg/mm^2 以下。这是因为，若超过 40kg/mm^2，因铜箔自身柔软性不够，涂布活性物质后进行轧辊压延等压平处理时，铜箔适应活性物质表面的变形不够，导致和活性物质的接触较差，容量降低，充放电循环寿命缩短，是不理想的。

本发明电解铜箔的常温延伸率在 35μm 厚度时，最好在 14%以上。

本发明的电解铜箔还具有如下特征：130℃、15 小时热处理后的状态 St 时的常温抗拉强度的减少率在 15%以内，因不发生重结晶，充放电循环特性和生产率优异。

下面，显示本发明的一实施方式和比较例。但本发明不受这些实施方式的限制。

实施例 1

添加平均分子量 3000 的低分子量明胶 7ppm，羟乙基纤维素 3ppm、3－氢硫基 1－丙磺酸钠 1ppm 到含有 280g/l 硫酸铜五水合物、100 g/l 硫酸、35ppm 氯离子的硫酸酸性硫酸铜电解液中，在电解液温度为 55℃、流速为 0.3m/分、电流密度为 50A/dm^2 的条件下，制成箔。对于此时的电解液，在其进入电解槽之前，将其通过活性碳处理塔，使电解结束后从电解槽中出来的电解液进行沸腾处理，然后将其铜浓度、游离的硫酸浓度、氯离子浓度调整到所希望的浓度，供再次电解进行循环用。由此，制得箔特性测定用的厚度为 35μm 和二次电池电极用的厚度为 12μm 的电解铜箔。

利用所得的厚度为 35μm 的电解铜箔进行表 1 项目下的箔特性试验。将其结果表示在表 1 中。表面粗糙度 Rz 是根据 JIS-B-0601，利用（株式会社）小坂研究所制造的 SE-3C 型表面光洁度测量仪进行测定。另外，利用电子显微镜以倍率 2000 倍进行拍摄，从所得照片来测定底层表面突起的最小峰间距 Ds。在常温以及 180℃和 200℃的高温氛围中及 150℃15 小时的热处理后，将其恢复到常温时的抗拉强度、延伸率是根据 IPC-TM-650 来进行测定的。表 1 中，将 150℃15 小时热处理后再恢复到常温时的状态记述为状态 St。另外，若制得箔后直接进行常温抗拉强度和延伸率的测定的话，因电解时有应变存在，二个指数有增高的趋势，所以

较好在常温下放置3天后再进行测定。

将厚度为12μm的方法电解铜箔在1g/l浓度的CrO_3水溶液中浸渍5秒钟，进行铬酸盐光泽处理，水洗干燥。另外，在这里虽然进行了铬酸盐光泽处理，也可以进行苯三唑类处理、或者有机硅烷偶合剂处理。

利用这样所得的12μm厚度的电解铜箔，如下所述制成二次电池的负极。负极活性物质的调制方式是：将石油沥青烧结，再使粗粒状的沥青焦炭形成平均粒径为20μm的粉末，在惰性气体中，进行1000℃的烧结，将杂质除去，得到焦炭材料粉末，将90重量%的该焦炭粉末和10重量%的聚偏氟乙烯的粘合剂进行混合，制得负极合剂。下面，将该负极合剂分散到溶剂N-甲基2－吡咯烷酮中，制成浆液，将该浆液涂布在该电解铜箔的两面上，干燥后，利用轧辊压延机将其压缩成形，制成带状，制得负极。该带状负极成形后，负极合剂两面的膜厚都为90μm，是相同的，该负极的宽度为55.6mm，长度为551.5mm。下面是正极的制造方法：将$LiCoO_2$作为正极活性物质，将石墨作为导电材料，将聚偏氟乙烯作为粘合剂，以91重量%的正极活性物质、6重量%的导电材料和3重量%的粘合剂进行混合，制得正极合剂，将其分散到N-甲基－2－吡咯烷酮中，制成浆液。

均匀将该浆液涂布在由厚度为20μm的带状铝构成的正极集电体的两面上，干燥后，利用轧辊压延机进行压缩成形，得到厚度为160μm的带状正极。该带状正极成形后的正极合剂的两面的膜厚都为70μm，该正极的宽度为53.6mm，长度为523.5mm。将这样制得的带状正极、带状负极和厚度为25μm、宽度为58.1mm的微多孔性聚丙烯薄膜隔层进行层压，制得积层集电体。沿长度方向，以负极为内侧将该积层集电体进行多次卷绕，成为螺旋状，用胶带将最外周面的隔层的最端部进行固定，制成螺旋式集电体。

该螺旋式集电体的中空部分内径为3.5mm，外径为17mm。将上下配置有绝缘板的上述所制得的螺旋式集电体放入镀镍的铁制电池外壳中，引出各种引线后，注入在碳酸亚丙酯和碳酸二乙酯等容量混合的溶剂中溶解有1摩尔/L的$LiPF_6$的非水电解液5.0g，进行封口，就制得圆筒形的锂离子的二次电池。对该锂离子的二次电池进行100次循环后，测定其容量维持率R_B，并用直流电2A进行40分钟的过充电后，将电池解体，确认铜箔有无断裂。以N_B来表示过充电后的该铜箔的断裂数目，将结果表示在表1中。

实施例2

添加 10ppm 的羟乙基纤维素、3－氢硫基 1－丙磺酸钠 1ppm 到含有 280g/l 硫酸铜五水合物、100 g/l 硫酸、50ppm 氯离子的硫酸酸性硫酸铜电解液中，在电解液温度为 55℃、流速为 0.5m/分、电流密度为 50A/dm^2 的条件下，制成箔。此时的电解液，在进入电解槽之前，让其通过活性碳处理塔，将电解结束后从电解槽中出来的电解液进行沸腾处理，再将其调整到所希望的浓度，供给电解循环用。由此，制得厚度为 35μm 和厚度为 12μm 的电解铜箔。进行和实施例 1 一样的特性试验。将结果表示在表 1 中。另外，用厚度为 12μm 的铜箔制造和实施例 1 一样的锂离子二次电池，和实施例 1 一样进行 100 次循环，测定容量维持率 R_B，并用直流电 2A 进行 40 分钟的过充电后，将电池解体，确认铜箔有无断裂，将结果表示在表 1 中。

实施例 3

添加平均分子量 3000 的低分子量明胶 10ppm，羟乙基纤维素 3ppm、3－氢硫基 1－丙磺酸钠 1ppm 到含有 280g/l 硫酸铜五水合物、100 g/l 硫酸、50ppm 氯离子的硫酸酸性硫酸铜电解液中，在电解液温度为 55℃、流速为 0.3m/分、电流密度为 50A/dm^2 的条件下，制成箔。此时的电解液，在进入电解槽之前，让其通过活性碳处理塔，将电解结束后从电解槽中出来的电解液进行沸腾处理后，再将其调整到所希望的浓度，供给电解循环用。再对该电解铜箔的电解析出面进行如下的镀铜光泽处理：在 200g/l 硫酸铜五水合物、60 g/l 硫酸、40ppm 氯离子、液温为 55℃的电解液中，随时补充添加日本シエーリング（株式会社）制造的カパラシド 210 メイキヤツブ剂 10cc/l、光泽剂（A）0.5cc/l、光泽剂（B）。由此，制得厚度为 35μm 和厚度为 12μm 的电解铜箔。进行和实施例 1 一样的特性试验。将结果表示在表 1 中。另外，用厚度为 12μm 的铜箔制造和实施例 1 一样的锂离子二次电池，和实施例 1 一样进行 100 次循环，此后，测定容量维持率 R_B，并用直流电 2A 进行 40 分钟的过充电后，将电池解体，确认铜箔有无断裂，将结果表示在表 1 中。

比较例 1

利用日本特许公开公报平 7-188969 所公开的实施例 1－A 的条件来制得厚度为 35μm 和 12μm 的电解铜箔，进行和实施例 1 一样的特性试验。将结果表示在表 1 中。另外，用厚度为 12μm 的铜箔和实施例 1 一样的制造锂离子二次电池，和实

施例 1 一样进行 100 次循环，此后，测定容量维持率 R_B，用直流电 2A 进行 40 分钟的过充电后，将电池解体，确认铜箔有无断裂，将该结果表示在表 1 中。

比较例 2

利用日本特许公开公报平 8-53789 所公开的实施例 2 的条件来制得厚度为 35μm 和 12μm 的电解铜箔，进行和实施例 1 一样的特性试验。将该结果表示在表 1 中。另外，用厚度为 12μm 的铜箔和实施例 1 一样的制造锂离子二次电池，和实施例 1 一样进行 100 次循环，此后，测定容量维持率 R_B，并用直流电 2A 进行 40 分钟的过充电后，将电池解体，确认铜箔有无断裂，将该结果表示在表 1 中。

比较例 3

利用日本特许公开公报 2000-182623 所公开的实施例 1 的条件来制得厚度为 35μm 和 12μm 的电解铜箔，进行和实施例 1 一样的特性试验。将该结果表示在表 1 中。另外，用厚度为 12μm 的铜箔和实施例 1 一样的制造锂离子二次电池，和实施例 1 一样进行 100 次循环，此后，测定容量维持率 R_B，用直流电 2A 进行 40 分钟的过充电后，将电池解体，确认铜箔有无断裂，将结果表示在表 1 中。

表 1

	粗糙度 Rz	最小峰间距 Ds	常温		180℃	200℃	状态 St		减少率	维持率	断裂数目
			抗拉强度 (A)	延伸率	延伸率	延伸率	抗拉强度 (B)	延伸率	(1－B/A)	R_B	N_B
	(μm)	(μm)	(kg/mm^2)	(%)	(%)	(%)	(kg/mm^2)	(%)	(%)	(%)	(个)
实施例 1	1.3	5.2	32	18	24	26	31	19	3.1	95	0
实施例 2	2.1	5.0	38	14	18	21	37	15	2.6	91	0
实施例 3	1.2	5.4	36	17	22	25	35	18	2.8	95	0
比较例 1	2.0	0.8	67	8	23	24	65	8	3.0	71	0
比较例 2	2.4	1.2	51	11	9	6	50	11	2.0	62	21
比较例 3	1.6	0.5	56	7	26	23	23	26	59.0	78	0

在实施例1—实施例3中，本发明的电解铜箔的十点平均粗糙度Rz都在2.5μm以下，同时底层表面突起的最小峰间距Ds都在5μm以上，常温下晶体组织为细小晶体，同时常温抗拉强度在40kg/mm²以下，35μm厚度的常温延伸率在14%以上。另外，在130℃15小时热处理后的状态St下，常温抗拉强度的减少率在15%以内，无热软化现象，常温—200℃的高温气氛中，随着温度的上升，延伸率有增大的趋势，并且35μm厚度时的180℃气氛中的延伸率在18%以上。因有这些特性，根据以下的理由，充放电循环寿命和过充电特性能使人满足。

对于本发明电解铜箔，在电解铜箔析出面上无平均粒径为零点几微米的细小晶体粒子显露，析出面非常平滑，所以和活性物质的接触良好。另外，晶体组织非常细小，同时常温抗拉强度不过高，集电体会适应活性物质进行足够的变形，保持活性物质和集电体良好的接触。加之，由于常温下的延伸率高，就可以防止铜箔在活性物质涂布后进行的轧辊压延等压平工序中发生龟裂。另外，因无重结晶，充放电循环寿命特性优异，同时高温气氛中的延伸率高，随着温度的上升而增大。由此，采用该电解铜箔的话，就可以提供过充电特性优异的二次电池集电体用的电解铜箔。

以往，用于二次电池集电体的铜箔的压延铜箔和一部分的电解铜箔由于在一百多度的高温下重结晶，在作为集电体时，抗拉强度会经时降低，随着充放电的进行，活性物质会产生膨胀收缩，由此在集电体用铜箔上有龟裂和断裂发生，导致容量降低、充放电循环寿命缩短，尤其是沿着重结晶的组织界面上易产生龟裂。

另外，由于重结晶后会使抗拉强度极度变小，在涂布负极活性物质、干燥后进行压涂的制造工序中，操作性较差，易产生皱纹，有时还会断裂，所以人们要求用作二次电池集电体的铜箔不发生重结晶。本发明电解铜箔由于不发生重结晶，就不会发生龟裂和断裂，充放电循环寿命变长，操作性也变得优异。之所以将电解铜箔在130℃15小时热处理后的状态St下的常温抗拉强度的减少率规定在15%以内，就是因为要满足这些条件。

若上述延伸率低的话，在活性物质涂布后进行轧辊压延等压平工序中会产生应力，铜箔龟裂，会导致容量降低、充放电循环降低。由此，电解铜箔的常温延伸率最好在14%以上。

本发明的电解铜箔由于在常温—200℃高温气氛中，存在延伸率增大的趋势，并且厚度为35μm时的180℃气氛中的延伸率在18%以上，二次电池的过充电特性优异。

另一方面，比较例 1 的十点平均粗糙度 Rz 虽为 2.0μm，平滑，为细小晶体，但是，底层表面突起的最小峰间距只有 0.8μm，所以，和活性物质碳粉的接触点较少，接触电阻变大，由于充放电循环时伴随活性物质的膨胀收缩所产生的应力等会使集电体和活性物质的距离慢慢变大，所以一部分活性物质不能用于充放电，引起容量降低。另外，和实施例 1－实施例 3 的电解铜箔比较，常温抗拉强度高，为非常硬的箔，常温延伸率低。由此，在活性物质涂布后进行轧辊压延等压平的工序中，铜箔不会沿着活性物质的表面进行足够的变形，和活性物质的接触较差，铜箔的一部分发生龟裂，导致容量降低，充放电循环寿命缩短。

比较例 2 虽和比较例 1 相同，但高温气氛中的延伸率更低，比常温值也有低下的倾向，由此，在进行过充电特性试验时，不能承受过充电时发热所产生的膨胀应力，铜箔会发生断裂。

比较例 3 和比较例 1 一样，但是，进行过 130℃×15 小时的热处理后的常温抗拉强度降低，变为 23kg/mm^2，发生重结晶。由此，因为伴随着充放电所产生的活性物质的膨胀收缩，集电体用铜箔发生龟裂和断裂，导致容量降低，充放电循环寿命缩短。

本发明的电解铜箔的电解铜箔析出面的表面非常平滑，且晶体组织非常细小，同时常温抗拉强度不过高，延伸率优良，即使热处理后，无热软化现象，维持了恒定的强度，高温气氛中延伸率也优异，适合作为二次电池集电体用铜箔，发挥了二次电池充放电循环寿命长、过充电特性优异的特性，具有良好的工业应用效果。

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(71) Applicant: **MITSUI MINING & SMELTING CO., LTD.**
Tokyo 141-8584 (JP)

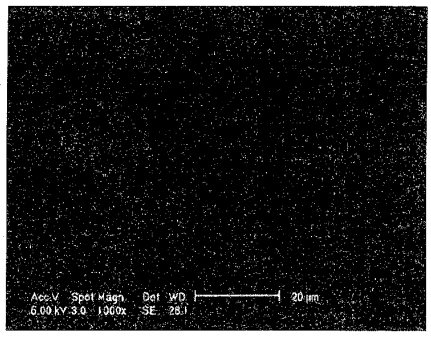
(72) Inventors:
- **MATSUDA, Mitsuyoshi, MITSUI MINING&SMELT.CO., LTD**
Ageo-shi, Saitama 362-0021 (JP)
- **SAKAI, Hisao, MITSUI MINING & SMELTING CO., LTD**
Ageo-shi, Saitama 362-0021 (JP)
- **TOMONAGA, Sakiko, MITSUI MINING & SMELTING CO.,LTD**
Ageo-shi, Saitama 362-0021 (JP)
- **DOBASHI, Makoto, MITSUI MINING & SMELTING CO., LTD**
Ageo-shi Saitama 362-0021 (JP)

(74) Representative: **Bohmann, Armin K.**
Bohmann & Loosen
Anwaltssozietät
Nymphenburger Strasse 1
80335 München (DE)

(54) ELECTROLYTIC COPPER FOIL AND PROCESS FOR PRODUCING ELECTROLYTIC COPPER FOIL, SURFACE TREATED ELCTROLYTIC COPPER FOIL USING SAID ELECTROLYTIC COPPER FOIL, AND COPPER-CLAD LAMINATE PLATE AND PRINTED WIRING BOARD USING SAID SURFACE TREATED ELECTROLYTIC COPPER FOIL

(57) It is an object of the present invention to provide an electrodeposited copper foil which has a lower profile and a higher gloss than low-profile electrodeposited copper foil conventionally supplied in markets. For achieving this object, the present invention employs an electrodeposited copper foil which has a super lowprofile, the surface roughness (Rzjis) of the deposit side of lower than 1.0-micron meter, and the gloss [Gs(60-deg.)] thereof of not lower than 400 irrespective to its thickness. The present invention also provides a manufacturing method of an electrodeposited copper foil obtained by electrodeposition using a sulfuric acid base copper electrolytic solution obtained by adding 3-mercapto-1-propanesulfonic acid and/or bis(3-sulfopropyl)disulfide, a quaternary ammonium salt polymer having a cyclic structure, and chlorine.

Fig. 1



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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to an electrodeposited copper foil, a surface-treated electrodeposited copper foil, a manufacturing method of an electrodeposited copper foil, and a copper-clad laminate and a printed wiring board using the surface-treated electrodeposited copper foil. Particularly, the present invention relates to an electrodeposited copper foil of which the bonding surface to an insulating layer-forming material has a low profile and a high gloss.

Description of the Related Art

[0002] Since metal copper is a good electric conductor, relatively inexpensive, and easy to handling, electrodeposited copper foils are widely used as a basic material of printed wiring boards. For electronic and electric devices which use printed wiring boards so much, the so-called down sizing such as smaller size with lighter weight is demanded. Conventionally, for achieving the down sizing of such electronic and electric devices, the wiring of signal circuits is needed to be made of a finest possible pitch, and the manufacturers have handled it by shortening the set time of over-etching and improving the etching factor of the formed wiring when employing thin copper foils and forming the wiring by etching.

[0003] Further, for electronic and electric devices reduced in size and weight, the high-performance is also simultaneously demanded. Therefore, for securing a largest possible component mounting area in a limited board area accompanying the spread of the surface mount system, keeping up with the favorable etching factor of wiring of printed wiring boards has been necessary. For the purpose, an electrodeposited copper foil having a lower profile than for ordinary printed wiring board applications has been demanded especially for tape automated bonding (TAB) boards and chip on film (COF) boards as so-called interposer boards on which IC chips, etc. are directly mounted. Here, "profile" is specified by a value obtained by measuring a surface roughness Rzj is of a bonding surface, which is the laminating interface with an insulating layer-forming material in the specification for copper foil for a printed wiring boards (hereinafter in the present application, "laminating interface" is not used, and unified into and referred to as "bonding surface"), in the TD according to JIS B 0601-2001, and "low-profile" means having a low surface roughness Rzjis of a bonding surface.

[0004] For solving such problems, Japanese Patent Laid-Open No. 9-143785 discloses a surface- treated electrodeposited copper foil characterized in that the deposit side of an untreated electrodeposited copper foil having a surface roughness Rz of equal to or lower than that of the shiny side of the untreated electrodeposited copper foil is roughened, and made to be the bonding surface. In manufacturing the untreated electrodeposited copper foil, an electrolytic solution added with a compound having a mercapto group, a chloride ion, a low molecular weight glue having a molecular weight of not more than 10, 000 and a macromolecular polysaccharide is used. Specifically, the compound having a mercapto group is 3-mercapto-1-propanesulfonate; the molecular weight of the low molecular weight glue is not more than 3,000; and the macromolecular polysaccharide is a hydroxyethylcellulose.

[0005] Japanese Patent Laid-Open No. 2004-35918 discloses a manufacturing method of an electrodeposited copper foil characterized in that, in the manufacturing method of the electrodeposited copper foil by the electrolysis of a sulfuric acid base copper electrolytic solution, the sulfuric acid base copper electrolytic solution containing a copolymer of diallyldialkylammonium salt and sulfur dioxide is used. It is contended that the sulfuric acid base copper electrolytic solution preferably contains a polyethylene glycol, chlorine and 3-mercapto-1-sulfonic acid, and that the deposit side to be bonded to an insulating base material has a low surface roughness, and provides a low profile of 1.0-micron meter $\pm$ 0.5-micron meter in ten-point average roughness Rz for an electrodeposited copper foil of 10-micron meter in thickness.

[0006] If an electrodeposited copper foil is manufactured using these manufacturing methods, a deposit side having a low profile is surely formed, and the foil has favorable characteristics for a conventional low-profile electrodeposited copper foil.

[0007] In addition, the clock frequency of personal computers representing electronic and electric devices rises, and the operation speed becomes remarkably fast. Computers do not only have simply a conventional intrinsic role of data processing but also have functions of using the computers themselves similarly to AV devices. Specifically, not only the music playing, but DVD pictures recording with playing, TV pictures receiving/recording/playing, TV phone, etc. are being added one after another.

[0008] That monitors of personal computers only simply satisfy a data monitoring function is insufficient, and the picture quality enough endurable to a long time viewing even if pictures like movie pictures are displayed is demanded. Inexpensive and much supply of monitors of such a quality are required. As such current monitors, liquid crystal monitors are much used. For mounting driver elements of the liquid crystal panels, the above-mentioned tape automated bonding (TAB) boards and chip on film (COF) boards are commonly used. For achieving the high-definition of monitors, formationof a finer circuit also on the driver boards comes to be required so as to correspond to the increase in the number of

scanning lines. With upsizing panels, attempts are made to suppress the product dimension by narrowest possible widths of the outer periphery. Since for arranging drivers on a rear surface, a TAB board or COF board must be folded and installed, the board is demanded to have a favorable flexibility from the first. COF, different from TAB, has fined lead parts for bonding lined with a film. Therefore, it has a disadvantage in the flexibility in comparison with TAB, which has no film, so use of a more flexible material than conventional ones is effective for preventing wire breaking.

[0009] In addition, in electronic circuits for automotive use, accompanying the spreading of hybridization and the development of fuel cell cars, the circuit has no choice but to respond to big electric currents. Despite that the necessitated thickness of conductors for automotive use is presumed to exceed 200-micron meter even in future, they are used as flexible wiring boards from the viewpoint of space saving. For applying such a thick copper foil to flexible boards, the bonding surface roughness of the copper foil is essentially low, and even a rolled copper foil is being studied in view that conventional electrodeposited copper foils cannot respond. This is because in the case of conventional electrodepositedcopperfoils, the thicker foil has the rougher bonding surface.

[0010] In the case of using copper foils as negative electrode current collectors for lithium ion batteries, the copper foils having the smooth surface are preferably used. Specifically, for applying a slurry containing an active substance on a copper foil in a uniform coating thickness when the active substance is applied on the copper foil, use of a copper foil having the smooth surface as the current collector is advantageous. Since the negative electrode active substance repeats expansion and contraction at the time of charge and discharge, the dimensional change of the copper foil as the current collecting material is large, and the copper foil expansion/contraction behavior cannot follow the current collector expansion/contraction, whereby a phenomenon of the breakage thereof occurs. Therefore, mechanical properties of copper foil as current collecting material, for bearing the repeated expansion/contraction behavior, are required to have a favorable balance between the tensile strength and elongation. Further, also when a dielectric layer for a capacitor is formed on a copper foil by the sol-gel method, use of a copper foil having the smooth surface is similarly advantageous.

[0011] As described above, the market of the electrodeposited copper foils have been spread out from printed wiring board applications. Consequently, it has been clear that there exists the request for an electrodeposited copper foil which has a lowerprofile in the thickness of not more than 450-micron meter, andalsoabetterflexibility, comparedwithlow-profile electrodeposited copper foils for printed wiring board applications conventionally supplied in the market.

SUMMARY OF THE INVENTION

[0012] As a result of extensive studies from the above-mentioned background, the present inventors have acquired an idea of a low-profile electrodeposited copper foil which is as productive as electrodeposited copper foils by conventional production methods, and shows good performance at a maximum thickness exceeding 450-micron meter.

[0013] The electrodeposited copper foil according to the present invention: the present invention is to provide an electrodeposited copper foil characterized in that the surface roughness (Rzjis) of the deposit side is lower than 1.0-micron meter, and the gloss [Gs(60-deg.)] thereof is not lower than 400.

[0014] In the electrodeposited copper foil according to the present invention, the above-mentioned gloss [Gs(60-deg.)] of the deposit side has a ratio of the TD gloss measured in the transverse direction to the MD gloss measured in the machine direction [TD gloss/MD gloss] of preferably 0.9 to 1.1.

[0015] In the electrodeposited copper foil according to the present invention, the deposit side preferably has a relationship of gloss [Gs(20-deg.)] > gloss [Gs(60-deg.)].

[0016] Further, in the electrodeposited copper foil according to the present invention, the shiny side preferably has a surface roughness (Rzjis) of lower than 2.0-micron meter, and gloss *[Gs(60-deg.)] of not lower than 70.

[0017] From the viewpoint of mechanical properties of the electrodeposited copper foil according to the present invention, the electrodeposited copper foil exhibits the mechanical properties of a tensile strength of not less than 33 kgf/mm^2 and an elongation of not less than 5% for as received.

[0018] The electrodeposited copper foil according to the present invention exhibits the mechanical properties of a tensile strength after heating (180°C×60 min, in the air) of not less than 30 kgf/mm^2 and an elongation after heating (180°C×60 min, in the air) of not less than 8%.

[0019] The surface-treated electrodeposited copper foil according to the present invention: the surface-treated electrodeposited copper foil according to the present invention is obtained by subjecting at least one selected from rustproofing treatment and silane coupling agent treatment on a surface of the electrodeposited copper foil.

[0020] The bonding surface to an insulating layer-forming material of the surface-treated electrodeposited copper foil according to the present invention preferably has a surface roughness (Rzjis) of not more than 1.5-micron meter.

[0021] The bonding surface to an insulating layer-forming material of the surface-treated electrodeposited copper foil according to the present invention preferably has a gloss [Gs(60-deg.)] of not lower than 250.

[0022] Further, in the surface-treated electrodeposited copper foil according to the present invention, the bonding surface to aninsulatinglayer-forming materialofthesurface-treated electrodeposited copper foil is also preferably rough-

ened.

[0023] As the bonding surface to an insulating layer-forming material of the surface-treated electrodeposited copper foil according to the present invention, the deposit side of the electrodeposited copper foil is preferably used.

[0024] The manufacturing method of the electrodeposited copper foil according to the present invention: the manufacturing method of the electrodeposited copper foil according to the present invention is a method for manufacturing an electrodeposited copper foil in which the copper deposited on a cathode surface by the electrolysis method using a sulfuric acid base copper electrolytic solution is peeled off, and is characterized in that the sulfuric acid copper electrolytic solution contains, at least one selected from 3-mercapto-1-propanesulfonic acid (hereinafter in the present application, referred to as "MPS") or bis(3-sulfopropyl)disulfide (hereinafter in the present application, referred to as "SPS"), a quaternary ammonium salt polymer having a cyclic structure, and chlorine.

[0025] The total concentration of MPS and/or SPS in the sulfuric acid base copper electrolytic solution is preferably 0.5 ppm to 100 ppm.

[0026] The concentration of the quaternary ammonium salt polymer having a cyclic structure in the sulfuric acid base copper electrolytic solution is preferably 1 ppm to 150 ppm.

[0027] . As the quaternary ammonium salt polymer having a cyclic structure, a diallyldimethylammonium chloride (hereinafter in the present application, referred to as "DDAC") polymer is especially preferably used.

[0028] Further, the chloride concentration in the sulfuric acid base copper electrolytic solution is preferably 5 ppm to 120 ppm.

[0029] The present invention provides an electrodeposited copper foil manufactured by the above-mentioned manufacturing method.

[0030] The copper-clad laminate according to the present invention: The copper-clad laminate according to the present invention is obtained by laminating the above-mentioned surface-treated electrodeposited copper foil and an insulating layer-forming material. When the insulating layer-forming material constituting the copper-clad laminate according to the present invention contains a skeletal material, the copper-clad laminate becomes a rigid copper-clad laminate. By contrast, when the insulating layer-forming material constituting the copper-clad laminate according to the present invention is a flexible material, the copper-clad laminate becomes a flexible copper-clad laminate.

[0031] The printed wiring board according to the present invention: by using the surface-treated electrodeposited copper foil according to the present invention, a copper-clad laminate is obtained. By subjecting the copper-clad laminate to an etching process, the printed wiring board according to the present invention is obtained. Namely, by using the above-mentioned rigid copper-clad laminate, a rigid printed wiring board is obtained. By using the above-mentioned flexible copper-clad laminate, a flexible printed wiring board is obtained.

[0032] The electrodeposited copper foil according to the present invention has a better low profile property in comparison with low-profile electrodeposited copper foils conventionally supplied in the market. Consequently, the electrodeposited copper foil according to the present invention has an excellent gloss exceeding conventional low-profile electrodeposited copper foils. Moreover, the electrodeposited copper foil according to the present invention shows excellent performance in low profile when the thickness of the electrodeposited copper foil goes up. Such a tendency that thicker (copper) foil shows higher surface roughness is a contrary property in conventional electrodeposited copper foils.

[0033] When the electrodeposited copper foil is actually supplied to the market, various surface treatments are performed to prevent the oxidization in the air and improve the adhesion with a base material, and the electrodeposited copper foil is generally supplied as a surface-treated electrodeposited copper foil. Use of the electrodeposited copper foil according to the present invention allows low profiling exceeding commercially available low-profile electrodeposited copper foils having been subjected to a surface treatment even if the surface treatment is performed, as long as the surface treatment is appropriately performed.

[0034] Accordingly, use of the surface-treated electrodeposited copper foil according to the present invention for a copper-clad laminate provides an excellent thickness uniformity of an insulating layer located between conductor layers formed of the surface-treated electrodeposited copper foils according to the present invention, and remarkably improves the interlayer insulation reliability causing no short-circuit even if a thin insulating layer is used. Especially when a uniform roughening treatment is performed, the copper foil becomes suitable for a copper-clad laminate for high frequencies applications.

[0035] Further, a printed wiring board obtained by using the copper-clad laminate according to the present invention and subj ecting it to an etching process, since the surface-treated electrodeposited copper foil according to the present invention used for the copper-clad laminate can be low-profile, is suitable for forming a fine-pitch circuit.

BRIEF DESCRIPTION OF THE DRAWINGS

[0036]

FIG. 1 is a SEM photograph of a deposit side of 12-micron meter thick electrodeposited copper foil obtained in Example 11; and

FIG. 2 is a SEM photograph of a deposit side of 12-micron meter thick electrodeposited copper foil obtained in Comparative Example 5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[Embodiments of the electrodeposited copper foil according to the present invention]

[0037] Before describing the electrodeposited copper foil according to the present invention, manufacturing methods of general electrodeposited copper foils will be described for the sake of easy understanding of the description. "An electrodeposited copper foil" according to the present invention is one which has not been subjected to any surface treatment, and is sometimes referred to as "an untreated copper foil", "a drum foil", etc. In the present specification, it is simply referred to as "an electrodeposited copper foil". Manufacture of the electrodeposited copper foil generally employs the continuous production method, wherein a sulfuric acid base copper electrolytic solution is made to flow between a rotating cathode in a drum-shape and a lead-based anode or dimensionally stable anode (DSA) which is arranged along and faces on the shape of the rotating cathode; copper is deposited on the surface of the rotating cathode by utilizing the electrolysis reaction; and the deposited copper is continuously peeled off in a foil state from the rotating cathode and wound up. Since the electrodeposited copper foil thus obtained assumes a roll shape wound up in a certain width, for denoting the direction in measuring physical properties and the like, the direction of the foil same with the cathode rotation is referred to as MD (Machine Direction), and the transverse direction, which is the perpendicular direction to MD, is referred to as TD (Transverse Direction).

[0038] The surface shape of the electrodeposited copper foil on the side thereof peeled off from the contact state with the rotating cathode assumes a shape formed by transfer of the shape of the rotating cathode surface which has been subjected to a polishing treatment, and has a gloss, so this surface is referred to as "shiny side". On the other hand, the surface shape on the deposited side generally assumes an angular and irregular shape because crystal growth rates of deposited copper are generally different for every crystalline plane, so this side is referred to as " deposit side". The roughness of the deposit side is generally higher than that of the shiny side, and in subj ecting an electrodeposited copper foil to a surface treatment, the deposit side is more often roughened. This deposit side performs the bonding surface to an insulating layer-forming material in manufacturing a copper-clad laminate. Therefore, the lower surface roughness of this bonding surface provides a more excellent low-profile surface-treated electrodeposited copper foil.

[0039] Although electrodeposited copper foils delivered to the market are finished by performing surface treatment, a roughening treatment to reinforce bonding to insulating layer-forming materials by a mechanical anchor effect and a rustproofing. But they are sometimes used without the roughening treatment depending on applications. Hereinafter, the electrodeposited copper foil according to the present invention will be described.

[0040] The electrodeposited copper foil according to the present invention has a surface roughness (Rzjis) of the deposit side of lower than 1.0-micron meter and a gloss [Gs(60-deg.)] thereof of not lower than 400. More preferably, the surface roughness (Rzj is) is lower than 0.6-micron meter, and the gloss [Gs(60-deg.)] is not lower than 600. First, gloss will be described. The gloss [Gs(60-deg.)] is obtained by irradiating the surface of an electrodeposited copper foil with a measuring light at an incidence angle of 60-deg. and measuring the light intensity reflected at a reflection angle of 60-deg. The incidence angle as it is here referred to as, sets the perpendicular direction to the light irradiation surface to be 0-deg. JIS Z 8741-1997 describes five mirror-gloss measurement methods having different incidence angles, and provides to select an optimum incidence angle corresponding to the gloss of a sample. It describes that setting the incidence angle to be 60-deg. out of incidence angles allows the measurement in a wide range from samples of low gloss to samples of high gloss. Therefore, for the gloss measurement of the electrodeposited copper foil, etc. according to the present invention, 60-deg. ismainlyemployed.

[0041] For the evaluation of smoothness of the deposit side of an electrodeposited copper foil, the surface roughness Rzjis has generally been used as a parameter. However, Rzjis only provide information only in the height direction of irregularities, and cannot provide the information such as pitch in irregularities and undulation. Since the gloss is a parameter reflecting the information of the both, use of the gloss together with Rzjis allows collectively estimating various parameters such as the surface roughness pitch, undulation and uniformity in the plane.

[0042] The electrodeposited copper foil according to the present invention satisfies the conditions that the surface roughness (Rzjis) of the deposit side is lower than 1.0-micron meter, and the gloss [Gs(60-deg.)] thereof is not lower than 400. Namely, the electrodeposited copper foil whose quality can be guaranteed in such ranges and which can be supplied to markets have not conventionally been available. The appropriate use of a manufacturing method described later can even provide an electrodeposited copper foil having a surface roughness (Rzjis) of lower than 0.6-micron meter and a gloss [Gs(60-deg.)] of not lower than 700. The upper limit of gloss is not set up here, but judging from experience, the upper limit of the gloss [Gs(60-deg.)] is about 780. The gloss in the present invention is measured using a gloss

meter VG-2000 manufactured by Nippon Denshoku Kogyo KK according to a measurement method of the gloss, JIS Z 8741-1997.

[0043] With respect to the electrodeposited copper foil as it is here referred to as, the thickness in not limited. This is because there is a favorable tendency of the deposit side having a lower roughness and a higher gloss as the foil becomes thicker. If the upper limit is positively set up, an electrodeposited copper foil having a thickness of not more than 450-micron meter, which is a commercially viable limit even when the electrodeposited copper foil is industrially manufactured, is aimed at.

[0044] Here, the lower limit of the surface roughness (Rzjis) of the deposit side is not set up. Depending on the sensitivity of a measuring instrument, the lower limit of the surface roughness is about 0.1-micron meter from experience. However, since there are variations in actual measurement, the lower limit as a reliable measurement is believed to be about 0.2-micron meter.

[0045] The gloss [Gs(60-deg.)] of the deposit side of the electrodeposited copper foil according to the present invention is divided into the TD gloss measured in the transverse direction and the MD gloss measured in the machine direction, and the ratio [TD gloss / MD gloss] is in the range of 0.9 to 1.1. This means a very small difference between in the transverse direction and in the machine direction.

[0046] Specifically, the generally accepted idea is that electrodeposited copper foils have mechanical properties different between in the transverse direction (TD) and in the machine direction (MD) under the influenceofpolishingstreaks, etc. on the surface of a rotating drum as the cathode; however, the electrodeposited copper foil according to the present invention has a uniform smooth deposit side irrespective of its thickness, and a value of [(TD gloss) / (MD gloss)] of the gloss [Gs(60-deg.)] as its visual property is 0.9 to 1.1, whose variation range is less than 10%, thereby meaning very small variations of the surface shapes in the TD and MD of the electrodeposited copper foil according to the present invention.

[0047] Additionally, no difference in appearances in the TD and MD implies a uniformly formed electrolysis and uniformity in terms of crystalline structure. Specifically, this also means small differences in mechanical properties including tensile strengths and elongations between in the TD and MD. If the differences in mechanical properties between in the TD and MD are small in such a manner, effects on the dimensional change rates of boards and the straightness of circuits depending on directions of copper foils when printed wiring boards are manufactured become preferably small. In this connection, rolled copper foils, which can be said to be a representative of smooth-surface copper foils, are well known to have different mechanical properties between in the TD and MD due to their working method. Consequently, they receive an almost established valuation of being unsuitable for fine pattern applications because of a large dimensional change rate in film carrier tapes, thin rigid printed wiring boards, etc. which are applications the present invention expects.

[0048] By using [Gs(20-deg.)] and [Gs(60-deg.)] as the gloss, the difference from the conventional low-profile electrodeposited copper foils can be understood more clearly. Specifically, the electrodeposited copper foil according to the present invention can provide a relationship of the gloss [Gs(20-deg.)] > the gloss [Gs(60-deg.)] for the deposit side. For the same substance, evaluation of the gloss by selecting one incident angle is predicted to be a sufficient one, but even if the substance is the same, since the reflection is different depending on the incident angles, the distribution of the reflected light in the space varies depending on the surface irregularities in the sampling area with varied incident angles, thus causing differences in gloss. As a result of studies based on such a fact, the present inventors have found the following tendency from experience. Specifically, in the case of an electrodeposited copper foil of a high gloss and a low surface roughness, a relationship of the gloss [Gs(20-deg.)] > the gloss [Gs(60-deg.)] > the gloss [Gs(85 deg.)] is satisfied. In contrast, in the case of an electrodeposited copper foil of a low gloss and a low surface roughness, a relationship of the gloss [Gs(60-deg.)] > the gloss [Gs(20-deg.)] > the gloss [Gs(85-deg.)] is satisfied. In addition, in the case of an electrodeposited copper foil of matte and a low surface roughness, a relationship of the gloss [Gs(85-deg.)] > the gloss [Gs(60-deg.)] > the gloss [Gs(20-deg.)] is satisfied. As is clear from above, the valuation of the smoothness by a relationship of an absolute value of a gloss at a certain incident angle and an additional gloss measurement at a different incident angle, is significant.

[0049] For the electrodeposited copper foil according to the present invention, the surface condition of the shiny side is also important. The shiny side is required to have a surface roughness (Rzjis) and a gloss [Gs(60-deg.)] which are close to a level of the deposit side of the electrodeposited copper foil according to the present invention. Specifically, the electrodeposited copper foil according to the present invention preferably has a surface roughness (Rzj is) of lower than 2.0-micron meter and a gloss [Gs(60-deg.)] of not lower than 70 for its shiny side. More preferably, it is desirable that it has a surface roughness (Rzj is) of lower than 1.7-micron meter and a gloss [Gs(60-deg.)] of not lower than 100. The upper limit of the gloss [Gs(60-deg.)] of the shiny side is not specified, but speaking from experience, it is about 500. Namely, for obtaining the surface condition of the deposit side as described heretofore, formation of the surface condition as described here of the shiny side is preferable. Out of this condition, a difference in the surface conditions between in the TD and in the MD is liable to be increased, and differences in mechanical properties including tensile strengths, elongations and the like in the TD and in the MD are also liable to be increased. The surface condition of the

shiny side is a transferred surface condition of a cathode as the electrodeposit surface, and is established by the surface condition of the cathode. Therefore, when an especially thin electrodeposited copper foil is manufactured, the cathode surface is required to have a property of a surface roughness (Rzjis) of lower than 2.0-micron meter.

[0050] As the mechanical properties of the electrodeposited copper foil according to the present invention, the tensile strength is not less than 33 kgf/mm^2 and the elongation thereof is not less than 5% for as received. After heating (180°C × 60 min, in the atmosphere), preferably, the tensile strength is not less than 30 kgf/mm^2, and the elongation is not less than 8%.

[0051] In the present invention, by optimizing the manufacturing condition, the electrodeposited copper foil can be provided with a more excellent mechanical properties of a tensile strength as received of not less than 38 kgf/mm^2 and that after heating (180°C × 60 min, in the air) of not less than 33 kgf/mm^2. Therefore, this favorable mechanical properties can not only fully bear bending usage of flexible printed wiring boards, but also are suitable for an application to current collecting materials constituting cathodes of lithium ion secondary batteries, which are subjected to the expansion/contraction behavior.

[Embodiments of the surface-treated electrodeposited copper foil according to the present invention]

[0052] The surface-treated electrodeposited copper foil according to the present invention is obtained by subjecting at least one selected from rustproofing and silane coupling agent treatment on a surface of the above-mentioned electrodeposited copper foil. The rustproofing layer is to prevent oxidation corrosion of the electrodeposited copper foil surface so as not to bring about troubles in manufacturing processes of copper-clad laminates and printed wiring boards. It is further recommended to have a constitution of not inhibiting the adhesion with an insulating layer-forming material and if possible, improving that. A method used for rustproofing can be selected from one or combination of an organic rustproofing using benzotriazole,imidazole, etc. and an inorganic rustproofing using zinc, a chromate, a zinc alloy, etc. as long as suitable for their purposes and applications without problem.

[0053] The silane coupling agent treatment is a treatment to chemically improve the adhesion with an insulating layer-forming material after the rustproofing.

[0054] Now, a method for forming a rustproofing layer will be described. In the case of organic rustproofing, the layer can be formed by a method such as the immersion coating, showering coating or electrodeposition of an organic rust-preventive agent. In the case of inorganic rustproofing, a method of electroplating elements for rustproofing on the surface of an electrodeposited copper foil, the so-called substitute precipitation method, etc. are applicable. For example, when the zinc rustproofing is performed, a zinc pyrophosphate plating bath, zinc cyanide plating bath, zinc sulfate plating bath, etc. are applicable. For example, in the case of a zinc pyrophosphate plating bath, the conditions are a concentration of zinc of 5 g/l to 30 g/l, that of potassium pyrophosphate of 50 g/l to 500 g/l, a solution temperature of 20-deg. C. to 50-deg. C. , pH of 9 to 12 and a current density of 0.3 A/dm^2 to 10 A/dm^2, etc.

[0055] The silane coupling agent used in the above-mentioned silane coupling agent treatment is not required to be especially limited. In consideration of properties of both an insulating layer-forming material to be used and a plating solution used in the printed wiring board manufacturing process and the like, an epoxy-functional silane coupling agent, amino-functional silane coupling agent, mercapto-functional silane coupling agent, etc. are optionally selectively applicable. The silane coupling can be performed by employing a method such as the immersion coating, showering coating or electrodeposition of a silane coupling agent solution.

[0056] More specifically, centered on coupling agents similar to those used in prepreg glass cloth for printed wiring boards, vinyltrimethoxysilane, vinylphenyltrimethoxysilane, gamma-methacryloxypropyltrimethoxysilane, gamma-glycidoxypropyltrimethoxysilane, 4-glycidylbutyltrimethoxysilane, gamma-aminopropyltriethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyltrimethoxysilane, N-3-(4-(3-aminopropoxy)butoxy)propyl-3-aminopropyltrimeth oxysilane, imidazolesilane, triazinesilane, gamma-mercaptopropyltrimethoxysilane, etc. are applicable.

[0057] The surface roughness (Rzjis) of the bonding surface to an insulating layer-forming material of the above-mentioned surface-treated electrodeposited copper foil preferably has a low profile of not more than 1.5-micron meter. By adjusting the surface roughness in this range, the surface-treated electrodeposited copper foil becomes one suitable for forming fine-pitch circuits.

[0058] The gloss [Gs(60-deg.)] of the bonding surface to an insulating layer-forming material of the surface-treated electrodeposited copper foil is also preferably not lower than 250. Since a rustproofing layer and a silane coupling agent layer are formed by the surface treatment, even if the change in the surface roughness is below a detectable level, the light reflectance, etc. may vary between before and after the surface treatment. Therefore, although the absolute value of the gloss sometimes varies after the surface treatment, if the gloss [Gs(60-deg.)] on the bonding surface of the surface-treated electrodeposited copper foil keeps not lower than 250, the surface-treated layer can be judged to be formed in a suitable thickness.

[0059] The bonding surface to an insulating layer-forming material of the surface-treated electrodeposited copper foil is preferably roughened. Well-known methods are applicable to the roughening treatment, and performing of a minimum

roughening treatment required including a combination with the rustproofing is sufficient. However, in forming a fine-pitch wiring below a pitch of 25-micron meter preferably used for the surface-treated electrodeposited copper foil according to the present invention, not being subjected to the roughening treatment is preferable to raise the set precision required of the over-etching time.

[0060] As a method of the roughening treatment, either a method involving adhering to form fine metal particles on the surface of an electrodeposited copper foil or a method involving forming a roughened surface by an etching method is employed. Now, as the former method of deposition for putting fine metal particles, a method of deposition for putting fine copper particles on the surface will be exemplified. This roughening treatment process is formed of a step of deposition for putting fine copper particles on the surface of the electrodeposited copper foil and a seal plating step to prevent dropping-off of the fine copper particles.

[0061] In the step of deposition for putting fine copper particles on the surface of an electrodeposited copper foil, the electrolysis condition employs the condition for burning plating. Therefore, the solution concentration used in the step of deposition for putting fine copper particles is generally a low concentration so as to easily make the burning plating condition. This burning plating condition is not especially limited, and is decided in consideration of qualities of production lines. For example, in the case of using a copper sulfate-based solution, the conditions are copper of 5 g/l to 20 g/l in concentration, free sulfuric acid of 50 g/l to 200 g/l in concentration, other additives as required (alpha-naphthoquinoline, dextrin, glue, thiourea, etc.), a solution temperature of 15-deg. C. to 40-deg. C., a current density of 10 A/dm^2 to 50 A/dm^2, etc.

[0062] The seal plating step to prevent dropping-off of fine copper particles is a step of uniformly depositing copper as is the case to coat fine copper particles by the level plating condition. Therefore, a copper electrolytic solution similar to that used in the afore-mentioned manufacturing process of an electrodeposited copper foil can be used as a supply source of copper ions. This level plating condition is not especially limited, and is decided in consideration of qualities of production lines. For example, in the case of using a copper sulfate-based solution, the conditions are copper of 50 g/l to 80 g/l in concentration, free sulfuric acid of 50 g/l to 150 g/l in concentration, a solution temperature of 40-deg. C. to 50-deg. C., a current density of 10 A/dm^2 to 50 A/dm^2, etc.

[0063] The bonding surface to an insulating layer-forming material of the surface-treated electrodeposited copper foil is preferably the deposit side. As described before, since the shiny side has a transferred shape of the surface shape of a cathode drum, making no difference at all between in the TD and in the MD is difficult. Therefore, formakingvariations in straightness of wiring edges, as are caused in the case of the shape of the bonding surface having directionality in TD/MD, to be little, the deposit side is preferred to be the bonding surface.

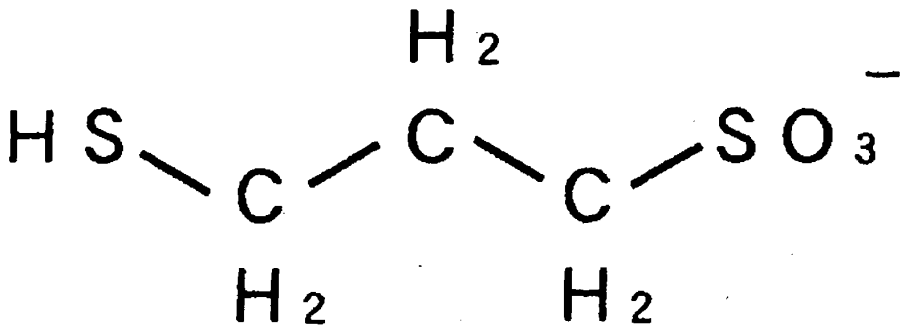
[Embodiments of the manufacturing method of the electrodeposited copper foil according to the present invention]

[0064] The present invention provides a method for manufacturing the above-mentioned electrodeposited copper foil by peeling off copper deposited on the cathode surface by the electrolysis methodusing a sulfuric acid base copper electrolytic solution, characterized in that the sulfuric acid base copper electrolytic solution contains at least one selected from MPS or SPS, a quaternary ammonium salt polymer having a cyclic structure, and chlorine. Use of the sulfuric acid base copper electrolytic solution of this composition allows stable manufacturing of the low-profile electrodeposited copper foil according to the present invention. Further, by optimizing the electrolysis condition, the gloss [Gs(60-deg.)] exceeding 700 can be obtained. The copper concentration in this sulfuric acid base copper electrolytic solution is 40 g/l to 120 g/l, more preferably 50 g/l to 80 g/l; and the free sulfuric acid concentration is 60 g/l to 220 g/l, more preferably 80 g/l to 150 g/l.

[0065] The total concentration of MPS and/or SPS in the sulfuric acid base copper electrolytic solution according to the present invention is preferably 0.5 ppm to 100 ppm, more preferably 0.5 ppm to 50 ppm, further preferably 1 ppm to 30 ppm. With the concentration of MPS and/or SPS of less than 0.5 ppm, the deposit side of the electrodeposited copper foil tends to be rough, and it becomes difficult to obtain a low-profile electrodeposited copper foil. By contrast, with the concentration of MPS and/or SPS exceeding 100 ppm, the effect for making the deposit side of the obtained electrodeposited copper foil smooth is not improved, and only an increase in treating cost of the waste liquid is brought about. Now, MPS and/or SPS as they are referred to as in the present invention, involves their salts in their meaning, and a described value of the concentration is a converted one in terms of sodium 3-mercapto-1-propanesulfonate (hereinafter in the present application, referred to as "MPS-Na") as a sodium salt. MPS assumes the SPS structure through dimerization in the sulfuric acid base copper electrolytic solution according to the present invention; therefore, the concentration of MPS or SPS is a concentration including a single substance of 3-mercapto-1-propanesulfonic acid and salts such as MPS-Na, and additionally a substance added as SPS and modified substances polymerized into SPS, etc. after added as MPS in the electrolytic solution. The structural formula of MPS is shown below as Chemical Formula 1; and that of SPS is as Chemical Formula 2. From comparison of these structural formulas, the SPS structure is known to be a dimer of MPS.

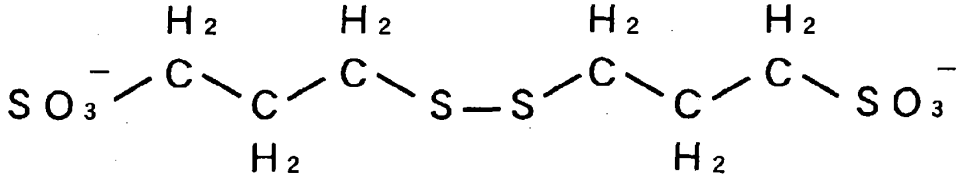
[0066]

Chemical Formula 1



[0067]

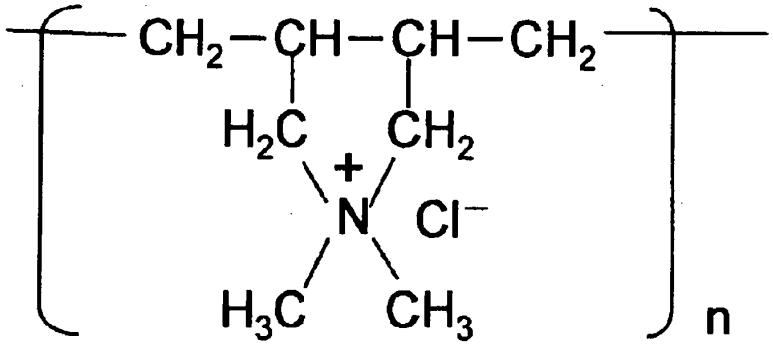
Chemical Formula 2



[0068] The concentration of the quaternary ammonium salt polymer having a cyclic structure in the sulfuric acid base copper electrolytic solution according to the present invention is preferably 1 ppm to 150 ppm, more preferably 10 ppm to 120 ppm, further preferably 15 ppm to 40 ppm. As the quaternary ammonium salt polymer having a cyclic structure, various kinds thereof are applicable, but in consideration of the effect of forming a low profile deposit side, a DDAC polymer is most preferably used. DDAC assumes a cyclic structure when making a polymerized structure and a part of the cyclic structure is formed of a nitrogen atom of the quaternary ammonium. Since the cyclic structure of the DDAC polymer is considered to be any of a four-membered ring to seven-membered ring or a mixture thereof, a compound having a five-membered ring out of these polymers is made to represent them, and is shown below as Chemical Formula 3. As is clear from Chemical Formula 3, this DDAC polymer has a polymer structure of dimer or more multimer.

[0069]

Chemical Formula 3



[0070] The concentration of the DDAC polymer in the sulfuric acid base copper electrolytic solution is preferably 1 ppm to 150 ppm, more preferably 10 ppm to 120 ppm, further preferably 15 ppm to 40 ppm. When the concentration of the DDAC polymer in the sulfuric acid base copper electrolytic solution is less than 1 ppm, the deposit side of an electrodeposited copper tends to be rough even though much the concentration of MPS or SPS may be raised, and obtaining a low-profile electrodeposited copper foil becomes difficult. When the concentration of the DDAC polymer in the sulfuric acid base copper electrolytic solution exceeds 150 ppm, the deposition of copper becomes unstable, and a low-profile electrodeposited copper foil is hardly obtained.

[0071] Further, the chlorine concentration in the sulfuric acid base copper electrolytic solution is preferably 5 ppm to 120 ppm, further preferably 10 ppm to 60 ppm. With the chlorine concentration of less than 5 ppm, the deposit side of the electrodeposited copper foil tends to be rough, and lowprofile cannot be maintained. By contrast, with the chlorine concentration exceeding 120 ppm, the deposit side of the electrodeposited copper foil tends to be rough; the electrodeposition cannot be stable; and a low profile deposit side cannot be formed.

[0072] As described above, the composition balance of MPS or SPS, the DDAC polymer, and chlorine in the sulfuric acid base copper electrolytic solution is most important. Deviation of their quantitative balance from the above range results a rough deposit side of the electrodeposited copper foil, and low profile cannot be maintained.

[0073] When an electrodeposited copper foil is manufactured by using the sulfuric acid base copper electrolytic solution, the electrolysis is performed using a cathode whose surface roughness is adjusted in a prescribed range and an insoluble anode. The electrolysis is recommended to be performed in a solution temperature of 20-deg. C. to 60-deg. C., more preferably 40-deg. C. to 55-deg. C. , and at a current density of 15 A/dm^2 to 90 A/dm^2, more preferably 50 A/dm^2 to 70 A/dm^2.

[0074] In the manufacturing method of the electrodeposited copper foil according to the present invention, for stably obtaining properties the electrodeposited copper foil is required to have, the cathode surface state in manufacture must be managed. Referring to JIS C 6515, the specification of electrodeposited copper foil for a printed wiring board, the surface roughness (Rzjis) of a shiny side of an electrodeposited copper foil is required to have is provided to be a maximum of 2.4-micron meter. A cathode used for manufacturing the electrodeposited copper foil is a rotating cathode drum made of titanium (Ti) material, and cause changes in its appearance and its metal phase due to the surface oxidation during a continuous use. Therefore, periodic surface polishing, and/or machining such as polishing with a whetstone or lathing depends on its situations are required. Such machining of the cathode surface inevitably causes a streak-shaped working pattern in the circumferential direction because the cathode is worked while rotating. Hence, there is a difficulty in maintaining a low surface roughness (Rzjis) as it is in a steady state, and the above-mentioned specified value is allowed for from the viewpoint of cost and on condition of not cause obstacles on manufacturing printed wiring boards.

[0075] With respect to conventional electrodeposited copper foils, that the foils exhibit a tendency of having a rougher deposit side as the thickness goes up, and that electrodeposited copper foils obtained using a cathode drum having a roughness at an upper-limit level of the above-mentioned generally specified value or more has a tendency of having a high surface roughness of the deposit side under the influence of the surface shape of the cathode, are known from

experience. By contrast, with respect to manufacturing the electrodeposited copper foil according to the present invention, use of the above-mentioned sulfuric acid base copper electrolytic solution allows forming a smooth deposit side by reducing the influence of the cathode shape in the process of becoming thicker while filling in the irregularities of the cathode surface. Therefore, even if a cathode whose surface is rough to some degree is used, the deposit side is hardly affected by the cathode surface shape as is the case with conventional electrodeposited copper foils. As long as the manufacturing method described here is employed, the thicker an electrodeposited copper foil is, the electrodeposited copper foil provided with the smoother deposit side is obtained.

[0076] However, when in an electrodeposited copper foil of less than 20-micron meter in thickness, the deposit side roughness (Rzjis) of lower than 1.0-micron meter is intended, use of a cathode having such a surface condition that the surface roughness (Rzjis) of the shiny side of the obtained electrodeposited copper foil is lower than 2.0-micron meter, preferably lower than 1.2-micron meter, and the gloss [Gs(60-deg.)] is not lower than 70, preferably not lower than 120 is preferable from the viewpoint of reducing the differences in the mechanical properties and surface properties in the TD and in the MD.

[0077] The present invention provides an electrodeposited copper foil manufactured by the above-mentioned manufacturing method.

[Embodiments of the copper-clad laminate according to the present invention]

[0078] The present invention provides a copper-clad laminate obtained by laminating the above-mentioned surface-treated electrodeposited copper foil and an insulating layer-forming material. With respect to manufacturing methods of the copper-clad laminates, the roll lamination system and the casting systemof conventional methods are useable for flexible copper-clad laminates; and the hot press system and the continuous lamination system are applicable for manufacturing rigid copper-clad laminates. Now, the flexible copper-clad laminates and rigid copper-clad laminates as they are referred to as in the present invention, are a concept involving all of single-sided copper-clad laminates, double-sided copper-clad laminates and multi-layered copper-clad laminates. The multi-layered copper-clad laminate is formed of the surface-treated copper foil according to the present invention for its outer layer and an inner layer core provided with an inner layer circuit for its inner layer. On description of copper-clad laminates hereinafter, these are not differentiated because they overlap.

[0079] The present invention provides a rigid copper-clad laminate, in which the above-mentioned insulating layer-forming material contains a skeletal material. Most of the skeletal material used in conventional rigid copper-clad laminates is a glass woven fabric or a glass paper, and it has been reported that such problems possibly arise that the roughness of the copper foil bonding surface affects the interlayer insulation in the case of a level exceeding 10-micron meter and affects the migration resistance by direct contact of the glass fiber of the skeletal material and a circuit even in the case of not more than 10-micron meter. It has been said that if the roughness is around 5-micron meter, those problems would not arise. However, in recent years, finer patterns than ever are required in, for example, BGA and CSP of package boards on which electronic components are directly mounted, and making the surface smooth has been tried, for example, by using as the skeletal material a paper of a finer aramid fiber than a glass fiber. In the case of mounting components, etc. whose clock frequency is high, if the straightness and cross-sectional shape of circuits are far apart from the ideal state, the transmission characteristic of signals especially in a high frequency range is not satisfied. Accordingly, the copper-clad laminate according to the present invention is suitable for manufacturing applications of printed wiring boards having of fine patterns and especially high-frequency signal transmission circuits.

[0080] Further, the present invention provides a flexible copper-clad laminate in which the above-mentioned insulating layer-forming material is formed of a flexible material having flexibility. The flexible copper-clad laminate segregates its applications from the above-mentioned rigid copper-clad laminate due to its flexibility and lightweight, and the insulating layer-forming material is tried to reduce its thickness to accomplish the lightweight and a high flexibility. At the same time, conductor layers as well are required to reduce the thickness, and electrodeposited copper foils have become a major material. Since securing of the insulation reliability is required for thin films, and a low profile of not more than 1/10 of the insulating layer thickness is required for the bonding surface especially in multi-layered flexible board applications, the above-mentioned surface roughness (Rzj is) of about 5-micron meter is an applicable upper limit if the copper-clad laminate is a conventional one. However, in the flexible copper-clad laminates using the electrodeposited copper foil of the present invention, even if the film thickness is further reduced, the insulation reliability is secured. Further, the flexible copper-clad laminates are more flexible than flexible copper-clad laminates using conventional low-profile electrodeposited copper foils, thus providing a more reliable copper-clad laminate also in this respect.

[0081] Now, manufacturing methods of a rigid copper-clad laminate and a flexible copper-clad laminate will be specifically exemplified. When a rigid copper-clad laminate or a flexible copper-clad laminate is manufactured, a desired lay-up state is formed using the surface-treated electrodeposited copper foil according to the present invention, a rigid insulating layer forming material such as a prepreg of FR-4 class or a flexible insulating layer forming material such as a polyimide resin film, and a flat plate, and molded by hot press at 170°C to 200°C.

[0082] On the other hand, for the flexible copper-clad laminate, the above-mentioned roll lamination system and casting system are employable. The roll lamination system is a method in which a web of the surface-treated copper foil according to the present invention and a resin film web such as polyimide resin film or PET film are heat-pressed by the pressure of a heating roller in the Roll to Roll system. The casting system involves directly forming a polyimide resin film on the surface of the surface-treated copper foil according to the present invention by forming a resin composition film, such as a polyamic acid, which is converted into a polyimide resin by heating, on the surface-treated copper foil, and heat to cause the condensation reaction.

[Embodiments of the printed wiring board according to the present invention]

[0083] The present invention provides a rigid printed wiring board characterized by being obtained using the above-mentioned rigid copper-clad laminate. For manufacturing a printed wiring board using the copper-clad laminate with an electrodeposited copper foil, whose bonding surface is smooth, according to the present invention as described before, of course, the subtractive method and also the pattern plating/flash etching method are applicable. Since the over-etching time can be set to be short in either method, the edge of the obtained circuit becomes more linear, and its cross-section becomes more rectangular. Therefore, the printed wiring board is excellent in overall reliability, which is excellent in the inter-circuit insulation reliability in fine patterns, is simultaneously excellent especially in the signal transmission characteristic in a high-frequency region flowing in the vicinity of the circuit surface by the skin effect, and hardly causes noises such as crosstalk.

[0084] The present invention further provides a flexible printed wiring board characterized by being obtained using the above-mentioned flexible copper-clad laminate. For manufacturing the printed wiring board, of course the subtractive method and also the pattern plating/flash etching method are applicable. Since the over-etching time can be set to be short in either method, the edge of the obtained circuit becomes more linear, and its cross-section becomes more rectangular. Therefore, the printed wiring board is excellent in reliability, which is excellent in the signal transmission characteristic in a high frequency region, and hardly causes noises such as crosstalk; and simultaneously, it is excellent in the insulation reliability and flexibility, and exhibits the most superiority especially when the board is made to be a film carrier on which devices are directly mounted.

[0085] Now, one example of common processing methods in the case of processing into printed wiring boards by using either of the rigid copper-clad laminate or a flexible copper-clad laminate (hereinafter, simply referred to as "copper-clad laminate") will be described to make sure of it. First, an etching resist layer is formed on a copper-clad laminate surface, exposed with an etching circuit pattern, and developed to form an etching resist pattern. For the etching resist layer, a photosensitive resin such as a dry film or a liquid resist is used. Besides, the exposure is generallyUV exposure, and forming methods of an etching resistpatternbasedon common methods are employable.

[0086] Then, the electrodeposited copper foil is subjected to the etching processing into a circuit shape by using a copper etching solution; and stripping of the etching resist is performed to form a desired circuit shape on the surface of the rigid board or the flexible board. For the etching solution, all copper etching solutions of an acidic copper etching solution, an alkali copper etching solution, etc. are applicable.

[0087] The copper-clad laminate as it is referred to as above in the present invention, is described as a concept containing all of single-sided copper-clad laminates, double-sided copper-clad laminates and multi-layered copper-clad laminates internally provided with inner layer circuits. Therefore, in the case of double-sided copper-clad laminates and multi-layered copper-clad laminates, there are cases necessary to secure the interlayer connection, in which cases the shape formation by common methods such as through-hole and via hole is performed, and thereafter the conductive plating treatment is performed to obtain the interlayer connection. Generally, the conductive plating treatment involves performing the activation treatment by a palladium catalyst, performing the electroless copper plating, and thereafter performing the film thickness growing by the electrolytic copper plating.

[0088] After the copper etching finishes, the resultant is fully washed with water, dried, and as required, subjected to the rustproofing, etc. to make a rigid printed wiring board or a flexible printed wiring board.

[Examples]

[0089] Examples and Comparative Examples used titanium plate electrodes whose surface roughness (Rzjis) was adjusted to 0.85-micron meter by polishing their surface with a polishing paper of No. 2,000, with consideration paid so as not to be affected by the surface shape of the cathodes.

[First example group]

[0090] In a first example group, Example 1 to Example 8 was practiced. Example 1 to Example 8 each used a solution as the sulfuric acid base copper electrolytic solution, in which the copper concentration and the free sulfuric acid con-

centration of a copper sulfate solution were adjusted to 80 g/l and 140 g/l, respectively, and the concentrations of MPS, a DDAC polymer (Unisence FPA100L, manufactured by Senka Corp.) and chlorine were adjusted to the concentrations described in Table 1. In Example 9, SPS, which is a dimer of MPS, was used in place of MPS.

[0091]

Table 1

Object	Additive concentration (ppm)		
	MPS-Na	DDAC polymer	Chlorine
Example 1	5	3	10
Example 2	5	3	10
Example 3	7	5	10
Example 4	7	5	10
Example 5	4	3	10
Example 6	4	3	10
Example 7	21	20	10
Example 8	21	20	10
Example 9	7*	5	10
* : the MPS-Na concentration in Example 9 is a converted value of the case where SPS is converted to a Na salt.			

[0092] Preparation of electrodeposited copper foils was performed by using DSA as an anode, and electrolyzing at a solution temperature of 50-deg. C. in a current density of 60 A/dm^2 to obtain nine kinds of electrodeposited copper foils of 12-micron meter and 210-micron meter in thickness. The mechanical properties of the copper foils specifically of 12-micron meter among them were evaluated. The results are shown in Table 2.

[0093]

Table 2

	Copper foil thickness (micron meter)	Electrodeposited copper foil property			
		As received		After heating (180°C×60 min.)	
		Tensile strength (kgf/mm^2)	Elongation (%)	Tensile strength (kgf/mm^2)	Elongation (%)
Example 1	12	38.2	6.2	34.6	9.8
Example 3	12	36.6	8.2	32.9	10.3
Example 5	12	39.3	8.1	34.3	11.0
Example 7	12	35.3	7.7	31.7	10.5
Example 9	12	36.7	7.9	32.2	11.0
Comparative Example 1	12	36.2	4.0	32.4	5.6
Comparative Example 2	12	31.4	3.5	26.8	5.8
Comparative Example 3	12	40.5	3.6	39.5	4.4
Comparative Example 4	12	38.6	4.0	37.4	4.8

[0094] Then, a rustproofing was performed on both surfaces of the electrodeposited copper foils. An inorganic rustproofing under the following conditions was employed. A zinc rustproofing was performed, using a zinc sulfate bath of

a free sulfuric acid concentration of 70 g/l and a zinc concentration of 20 g/l, at a solution temperature of 40-deg. C. in a current density of 15 A/dm^2.

[0095] Further, in the Examples, a chromate layer was formed by electrolysis on the zinc rustproofing layers. The electrolysis conditions were a chromic acid concentration of 5.0 g/l, pH of 11.5, a solution temperature of 35-deg. C., a current density of 8 A/dm^2 and an electrolysis time of 5 sec.

[0096] After the rustproofing was finished as described above, the rustproofing layer was rinsed with water, and immediately a silane coupling agent was adsorbed on the rustproofing layer of the deposit side in a silane coupling agent bath. The solution composition was pure water as a solvent, and gamma-glycidoxypropyltrimethoxysilane of 5 g/l in concentration. Then, the adsorption treatment was performed by spraying the solution by showering.

[0097] After the silane coupling agent treatment was finished, the moisture was finally volatilized by an electric heater to obtain nine kinds of surface-treated electrodeposited copper foils. According to the crystalline structure analysis of the obtained electrodeposited copper foils, the average crystal grain size was larger than that of electrodeposited copper foils which are used for conventional film carrier tapes and made to be of a low profile by micro-crystallization, and the presence of twin crystals was confirmed. The surface roughness (Rzjis) and the gloss [Gs(20-deg.)], [Gs(60-deg.)] and [Gs(85-deg.)] of a deposit side of the electrodeposited copper foils, and the surface roughnesses (Rzjis) and the gloss [Gs(60-deg.)] of the deposit side of the surface-treated electrodeposited copper foils, obtained as described above, are shown in Table 3.

Table 3

	Copper foil thickness (micron meter)	Electrodeposited copper foil								Surface-treated copper foil copper foil		
		deposit side								deposit side		
		Rzjis (micron meter)	Gloss							Rzjis (micron meter)	Gloss Gs(60 deg.)	
			Gs(20-deg.)		Gs(60-deg.)			Gs(85 deg.)				
			TD	MD	TD	MD	TD/MD	TD	MD		TD	MD
Example 1	12	0.30	844	988	652	675	0.97	129	138	0.32	621	647
Example 2	210	0.27	1169	1263	624	661	0.94	124	129	0.33	592	602
Example 3	12	0.33	910	970	647	673	0.96	129	140	0.29	597	613
Example 4	210	0.29	1074	1144	656	670	0.98	115	128	0.36	546	547
Example 5	12	0.35	718	838	643	660	0.97	123	138	0.33	581	602
Example 6	210	0.34	1147	1182	631	662	0.95	112	119	0.36	587	582
Example 7	12	0.33	941	1043	650	677	0.96	132	142	0.30	606	611
Example 8	210	0.30	1223	1271	661	692	0.96	118	124	0.32	576	576
Example 9	12	0.34	800	824	650	674	0.96	117	133	0.32	618	623
Comparative Example 1	12	0.85	-	-	-	283	-	-	-	-	-	-
	210	0.70	-	-	-	221	-	-	-	-	-	-
Comparative Example 2	12	0.83	-	-	-	374	-	-	-	-	-	-
	210	1.22	-	-	-	386	-	-	-	-	-	-
Comparative Example 3	12	3.60	-	-	-	0.7 7	-	-	-	-	-	-
Comparative Example 4	12	3.59	-	-	-	1.0	-	-	-	-	-	-

[Second example group]

[0098] A second example group includes Example 10 to Example 14, which each used a solution as the sulfuric acid base copper electrolytic solution, in which the copper concentration and the free sulfuric acid concentration were adjusted to 80 g/l and 140 g/l, respectively, and the concentrations of SPS, a DDAC polymer (Unisence FPA100L, manufactured by Senka Corp.) and chlorine were adjusted to the concentrations described in Table 4.

[0099]

Table 4

	Additive concentration (ppm)		
	SPS-Na	DDAC polymer	Chlorine
Example 10	5	30	25
Example 11	10	20	22
Example 12	100	100	100
Example 13	50	70	100
Example 14	50	100	50

[0100] Preparation of electrodeposited copper foils was performed by using DSA as an anode, and electrolyzing at a solution temperature of 50-deg. C. in a current density of 60 A/dm^2 to obtain two kinds of electrodeposited copper foils of 12-micron meter and 70-micron meter in thickness in Example 10, and four kinds of electrodeposited copper foils of 12-micron meter in thickness in Example 11 to Example 14.

[0101] The tensile strengths and the elongations as received and after 180°C×60 min-heating of the 12-micron meter and 70-micron meter electrodeposited copper foils obtained in Example 10, are shown in Table 5. The tensile strength as received of the 12-micron meter electrodeposited copper foil is 35.5 kgf/mm^2; the elongation thereof is 11.5%; and the tensile strength after 180°Cx60 min-heating is 33.2 kgf/mm^2; and the elongation thereof is 11.2%. These favorable mechanical properties are at a level of sufficiently applicable for bending usage of flexible printed wiring boards.

[0102]

Table 5

	Copper thickness (micron meter)	As received		After heating After heating	
		Tensile strength	Elongation	Tensile strength	Elongation
		Kgf/mm^2	%	Kgf/mm^2	%
Example 10	12	35.5	11.5	33.2	11.2
	70	34.4	28.0	32.3	31.8
Comparative Example 5	12	37.9	8.0	31.6	7.5

[0103] According to the evaluation of the 12-micron meter electrodeposited copper foil as itself for folding endurance test by the MIT method, it exhibited to be able to bear a bending test of 1,200 to 1,350 times for as received, and that of 800 to 900 times for after heating. The test by the MIT method is conducted using a film folding endurance tester (model No.: 549) with furnace manufactured by Toyo Seiki Seisaku-sho; Ltd. as a MIT folding endurance test apparatus, and with a bending radius of 0.8 mm, a load of 0.5 kgf and a sample size of 15 mm × 150 mm. The obtained values exhibit that the evaluated electrodeposited copper foil has the double folding endurance with those of conventional general-purpose electrodeposited copper foils because when the general-purpose electrodeposited copper foils having been used conventionally for flexible printed wiring boards are evaluated in the same conditions, they show about 600 times for as received and about 500 times for after heating. This difference is presumed to be due to the effect that cracks, which triggers a break, are hard to be formed due to their smooth surface.

[0104] The electrodeposited copper foils obtained above were immersed in a dilute sulfuric acid solution of 150 g/l in concentration and of a solution temperature of 30-deg. C. for 30 seconds to remove foreign materials and surface oxides, and washed with water. For the 12-micron meter electrodeposited copper foil and the 70-micron meter electrodeposited copper foil obtained in Example 10, two kinds of the surface-treated electrodeposited copper foil which was roughened

and the surface-treated electrodeposited copper foil which was not roughened were prepared, respectively, to prepare four kinds in total of surface-treated electrodeposited copper foils.

[0105] After the pickling treatment of the 12-micron meter electrodeposited copper foil and the 70-micron meter electrodeposited copper foil among the above which were objects of a roughening treatment was finished, the foils were subjected to, as a process to form fine copper particles on the deposit side of the electrodeposited copper foil, a step of deposition for putting fine copper particles on the deposit side of the electrodeposited copper foils and a seal plating step to prevent the dropping-off of the fine copper particles. The former step of deposition for putting fine copper particles was performed by electrolysis for 5 seconds under the conditions of a copper concentration of 15 g/l and a free sulfuric acid concentration of 100 g/l of a copper sulfate solution, a solution temperature of 25-deg. C., and a current density of 30 A/dm^2.

[0106] After the fine copper particles were deposited and put on a deposit side, copper was uniformly deposited so as to seal the fine copper particles under the level plating condition as a seal plating step to prevent dropping-off of the fine copper particles. The level plating was performed by electrolysis for 5 seconds under the conditions of a copper concentration of 60 g/l and a free sulfuric acid concentration of 100 g/l of a copper sulfate solution, a solution temperature of 45-deg. C., and a current density of 45 A/dm^2.

[0107] Both surfaces of all the electrodeposited copper foils obtained in the Examples were subjected to a rustproofing. The inorganic rustproofing under the following conditions was employed. The zinc rustproofing was performed using a zinc sulfate bath of a free sulfuric acid concentration of 70 g/l and a zinc concentration of 20 g/l, at a solution temperature of 40-deg. C. in a current density of 15 A/dm^2.

[0108] A chromate layer was further formed on the zinc rustproofing layers by electrolysis. The electrolysis conditions were a chromic acid concentration of 5.0 g/l, pH of 11.5, a solution temperature of 35-deg. C., a current density of 8 A/dm^2, and an electrolysis time of 5 sec.

[0109] After the rustproofing was finished as above and rinsed with water, immediately a silane coupling agent was adsorbed on the rustproofing layers of a deposit side. The solution composition for this was pure water as a solvent and gamma-glycidoxypropyltrimethoxysilane of 5 g/l in concentration. The adsorption treatment was performed by spraying the solution by showering. After the silane coupling agent treatment was finished, the moisture was finally volatized by an electric heater to obtain six kinds of surface-treated electrodeposited copper foils including one kind of the roughened foil.

[0110] The surface roughness (Rzjis) and the gloss [Gs(60-deg.)] of the shiny side of the electrodeposited copper foils obtained in Example 10 to Example 14, and the surface roughness (Rzjis) and the gloss [Gs(20-deg.)], [Gs(60-deg.)] and [Gs(85-deg.)] of a deposit side thereof, and the surface roughness (Rzjis) and the gloss [Gs(60-deg.)] of a deposit side of the surface-treated foils obtained in Example 10, and the surface roughness (Rzjis) of the roughened surface of the roughened foil thereof, are shown in Table 6.

[0111]

Table 6

	Copper thickness (micron meter)	Electrodeposited copper foil												Surface-treated copper foil				
		Shiny side			deposit side									deposit side				Roughened surface
		Gloss Gs(-deg.) 60		Rjis (micron meter)	Gloss Gs(20-deg.)		Gloss Gs(60-deg.)			Gloss Gs(85-deg.)		Rzjis (micronmeter)	Gloss Gs(60-deg.)		Rzjis (micronmeter)	Rzjis (micron meter)
		TD	MD		TD	MD	TD	MD	TD/MD	TD	MD		TD	MD		
Example 10	12	165	311	0.87	1027	1058	659	665	0.99	142	139	0.32	540	514	0.28	0.97
Example 10	70	140	291	0.84	1510	1506	691	686	1.01	149	150	0.17	570	570	0.15	-
Example 11	12	157	294	1.14	925	1206	735	759	0.97	114	112	0.30	-	-	-	-
Example 12	12	158	279	0.91	823	976	613	651	0.94	98	118	0.39	-	-	-	-
Example 13	12	159	295	0.97	800	955	603	665	0.91	116	129	0.41	-	-	-	-
Example 14	12	158	295	1.02	867	968	627	649	0.97	114	129	0.32	-	-	-	-
Comparative Example 5	12	150	260	1.14	116	126	324	383	0.85	111	117	1.00	150	260	0.98	1.70

[Comparative Examples]

[Comparative Example 1]

[0112] This Comparative Example was a tracing experiment of example 1 described inJapanese Patent Laid-OpenNo. 2004-35918. A basis solution as the sulfuric acid base copper electrolytic solution was one in which copper sulfate (reagent) and sulfuric acid (reagent) were dissolved in pure water, where the copper sulfate concentration (in terms of pentahydrate) was 280 g/l, and the free sulfuric acid concentration was 90 g/l. A sulfuric acid base copper electrolytic solution was prepared by adjusting concentration of a copolymer (trade name: PAS-A-5, a weight-average molecular weight of 4,000, manufactured by Nitto Boseki Co., Ltd.) of a diallyldialkylammonium salt and sulfur dioxide to 4 ppm, a polyethylene glycol (an average molecular weight of 1, 000) to 10 ppm and MPS-Na to 1 ppm, and further adjusting chlorine concentration to 20 ppm by using sodium chloride.

[0113] The electrolysis was performed using a lead plate as an anode, at a temperature of the above electrolytic solution of 40-deg. C. in a current density of 50 A/dm^2 to obtain electrodeposited copper foils of 12-micron meter and 210-micron meter in thickness. The mechanical properties of the electrodeposited copper foils are shown in Table 2 together with Examples; and the surface roughness (Rzj is) and the gloss [Gs(60-deg.)] of a deposit side are shown in Table 3 together with Examples.

[Comparative Example 2]

[0114] In this Comparative Example, a solution as the sulfuric acid base copper electrolytic solution of a copper concentration of 90 g/l and a free sulfuric acid concentration of 110 g/l was subjected to a cleaning treatment through an activated carbon filter. A copper electrolytic solution was prepared by adding, to the cleaned solution, MPS-Na so as to be 1 ppm in concentration; a hydroxyethylcellulose as a macromolecular polysaccharide, 5 ppm; a low molecular glue (a number-average molecular weight of 1,560), 4 ppm; and chlorine, 30 ppm. The electrolysis was performed using the copper electrolytic solution thus prepared and using a DSA electrode as the anode, at a solution temperature of 58-deg. C. in a current density of 50 A/dm^2 to obtain electrodeposited copper foils of 12-micron meter and 210-micron meter in thickness. The mechanical properties of the electrode posited copper foils are shown in Table 2 together with Examples; and the surface roughness (Rzjis), the gloss; etc. of a deposit side, in Table 3.

[Comparative Example 3]

[0115] In this Comparative Example, a solution as the sulfuric acid base copper electrolytic solution of a copper concentration of 80 g/l, a free sulfuric acid concentration of 140 g/l, a DDAC polymer (Unisence FPA100L, manufactured by Senka Corp.) concentration of 4 ppm and a chlorine concentration of 15 ppm, was used. The electrolysis was performed using a DSA electrode as the anode, at a solution temperature of 50-deg. C. in a current density of 60 A/dm^2 to obtain an electrodeposited copper foil of 12-micron meter in thickness. The mechanical properties of the electrodeposited copper foil are shown in Table 2 together with Examples; and the surface roughness (Rzjis), the gloss, etc. of the deposit side, in Table 3.

[Comparative Example 4]

[0116] In this Comparative Example, a solution as the sulfuric acid base copper electrolytic solution of a copper concentration of 80 g/l, a free sulfuric acid concentration of 140 g/l, a DDAC polymer (Unisence FPA100L, manufactured by Senka Corp.) concentration of 4 ppm, a low molecular weight glue (a number-average molecular weight of 1,560) concentration of 6 ppm and a chlorine concentration of 15 ppm, was used. The electrolysis was performed using a DSA electrode as the anode, at a solution temperature of 50-deg. C. in a current density of 60A/dm^2 to obtain an electrodeposited copper foil of 12-micron meter in thickness. The mechanical properties of the electrodeposited copper foil are shown in Table 2 together with Examples; and the surface roughness (Rzjis) and the gloss [Gs(60-deg.)] of the deposit side, in Table 3.

[Comparative Example 5]

[0117] This Comparative Example was a tracing experiment of example 4 described in Japanese Patent Laid-Open No . 2004 -35918. A basis solution as the sulfuric acid base copper electrolytic solution was one in which copper sulfate (reagent) and sulfuric acid (reagent) were dissolved in pure water, where the copper sulfate concentration (in terms of pentahydrate) was 280 g/l, and the free sulfuric acid concentration was 90 g/l. The electrolytic solution was prepared by adjusting a copolymer (trade name: PAS-A-5, a weight-average molecular weight of 4,000, manufactured by Nitto Boseki

Co., Ltd.) of a diallyldialkylammonium salt and sulfur dioxide to 4 ppm in concentration, a polyethylene glycol (an average molecular weight of 1,000) to 10 ppm in concentration and MPS-Na to 1 ppm in concentration, and further adjusting chlorine to 20 ppm in concentration using sodium chloride.

[0118] The electrolysis was performed using a lead plate as the anode, at a temperature of the above electrolytic solution of 40-deg. C. in a current density of 50 A/dm^2 to obtain electrodeposited copper foils of 12-micron meter and 70-micron meter in thickness. Thereafter, two kinds of electrodeposited copper foils were obtained as in Example 10. The mechanical properties of the electrodeposited copper foils as received and after 180°C×60 min-heating are shown in Table 5; and the surface roughness (Rzjis) and the gloss [Gs(20-deg.)], [Gs(60-deg.)] and [Gs(85-deg.)] of the deposit side of the electrodeposited copper foil, the surface roughness (Rzjis) and the gloss [Gs(60-deg.)] of the deposited side after the surface treatment, and the surface roughness (Rzjis) of the roughened surface of the roughened foil, are shown in Table 6.

[Comparison of Examples and Comparative Examples]

[0119] Hereinafter, the results of comparing Comparative Examples and Examples will be described. Any deposit side of the electrodeposited copper foils obtained in Examples satisfies whole specifications of the present invention of the surface roughness (Rzjis) < 1.0-micron meter, the gloss [Gs(60-deg.)] ≥ 400, the TD/MD ratio of 0.9 to 1.1, and [Gs(20-deg.)] > [Gs(60-deg.)] > [Gs(85-deg.)]. The mechanical properties are also satisfied in whole specifications of the present invention of not less than 33 kgf/mm^2 in tensile strength and of not less than 5% in elongation for as received, and of not less than 30 kgf/mm^2 in tensile strength and of not less than 8% in elongation for after heating.

[0120] Comparison of Examples and Comparative Example 1: Comparing the surface roughness (Rzjis) of a deposit side of the electrodeposited copper foils, the electrodeposited copper foil of Comparative Example 1 is also made to have a favorable low profile. However, while any surface roughness (Rzjis) of a deposit side of the 12-micron meter electrodeposited copper foils of the present invention is 0.30-micron meter to 0.41-micron meter, the surface roughness (Rzjis) of the deposit side of the 12-micron meter electrodeposited copper foil of Comparative Example 1 is 0.85-micron meter; and while any surface roughness (Rzjis) of a deposit side of the 210-micron meter electrodeposited copper foils of the present invention is 0.27-micron meter to 0.34-micron meter, the surface roughness (Rzjis) of the deposit side of the 210-micron meter electrodeposited copper foil of Comparative Example 1 is 0.70-micron meter. Therefore, a tendency that a smoother deposit side is obtained when the thickness of the copper foil goes up is common, but the electrodeposited copper foil according to the present invention is superior in the value itself of smoothness. Comparing the gloss [Gs(60-deg.)], while the gloss [Gs(60-deg.)] of Comparative Example 1 is in the range of 221 to 283, the gloss [Gs(60-deg.)] of Examples exhibit the range of 603 to 759, which are far different. Consequently, the electrodeposited copper foils of Examples can be said to have a deposit side which is smoother and closer to a mirror surface than the electrodeposited copper foil of Comparative Example 1. With respect to the mechanical properties, the 12-micron meter electrodeposited copper foil of Comparative Example 1 has a tensile strength of 36.2 kgf/mm^2 and an elongation of 4.0% for as received, and a tensile strength of 32.4 kgf/mm^2 and an elongation of 5.6% for after heating. The tensile strength as received only can be said to be the same as that of the electrodeposited copper foils of Examples.

[0121] Comparison of Examples and Comparative Example 2: Comparing a surface roughness (Rzjis) of a deposit side of the electrodeposited copper foils, the electrodeposited copper foil of Comparative Example 2 is also made to have a favorable low profile. However, while any surface roughness (Rzjis) of the deposit side of the 12-micron meter electrodeposited copper foils of the present invention is 0.30-micron meter to 0.41-micron meter, the surface roughness (Rzjis) of the deposit side of the 012-micron meter electrodeposited copper foil of Comparative Example 2 is 0.83-micron meter; and while any surface roughness (Rzjis) of a deposit side of the 210-micron meter electrodeposited copper foils of the present invention is 0.27-micron meter to 0.34-micron meter, the surface roughness (Rzjis) of the deposit side of the 210-micron meter electrodeposited copper foil of Comparative Example 2 is 1.22-micron meter. Therefore, in Comparative Example 2, since the smoothness of the deposit side is worsened when the thickness of the copper foil goes up, a stably smooth electrodeposited copper foil is considered to be hard to obtain. With respect to the mechanical properties, the 12-micron meter electrodeposited copper foil of Comparative Example 2 has a tensile strength of 31.4 kgf/mm^2 and an elongation of 3.5% for as received, and a tensile strength of 26.8 kgf/mm^2 and an elongation of 5.8% for after heating; therefore, the electrodeposited copper foils of Examples are superior.

[0122] Comparison of Examples and Comparative Example 3: Comparative Example 3 is to examine the effects in the case where MPS and SPS are not present in the copper electrolytic solution. As can be seen from Table 3, the surface roughness (Rzjis) of the deposit side of the electrodeposited copper foil obtained in Comparative Example 3 in which MPS, etc. are not contained in the copper electrolytic solution exhibits 3.60-micron meter, thus a low profile is not achieved. As for the gloss [Gs(60-deg.)], since the gloss turns to matte, it exhibits a remarkably low value of 0.7. Then, although the mechanical properties of the 12-micron meter copper foil exhibits a large value of 40.5 kgf/mm^2 in tensile strength, the elongation is as small as 3.6%, and its change by heating is small. Consequently, the electrodeposited copper foils according to the present invention can be said to be superior in the surface roughness and the elongation.

[0123] Comparison of Examples and Comparative Example 4: Comparative Example 4 is to examine the effects in the case of adding a low molecular glue in the copper electrolytic solution in place of MPS. As a result, as can be seen from Table 3, even if a low molecular glue is contained in the copper electrolytic solution in place of MPS, the surface roughness (Rzjis) of the deposit side of the electrodeposited copper foil exhibits 3.59-micron meter, thus a low profile is not achieved. As for the gloss [Gs(60-deg.)], since the gloss turns to matte, it exhibits a remarkably low value of 1.0. Although the mechanical properties exhibit 38.6 kgf/mm^2 in tensile strength for as received, the nearly same value as that of Examples, the elongation is as small as 4.0%, and the change by heating is small as in Comparative Example 3. Consequently, the electrodeposited copper foils according to the present invention can be said to be superior in the surface roughness and the elongation.

[0124] Comparison of Examples and Comparative Example 5: Hereinafter, 12-micron meter electrodeposited copper foils will be compared between Examples and Comparative Example 5 referring to the data described in Table 5 and Table 6.

[0125] In comparing of the surface roughness (Rzj is) of a deposit side, the electrodeposited copper foils obtained in Examples show 0.30-micron meter to 0.41-micron meter, and the electrodeposited copper foil obtained in Comparative Example 5 shows 1.00-micron meter, whereby the difference is clear. While the gloss [Gs(60-deg.)] of the deposit side of the electrodeposited copper foil obtained in Comparative Example 5 is in the range of 324 to 383, if it is examined on [Gs(60-deg.] only, those of the electrodeposited copper foils obtained in Examples are in the absolutely different range of 603 to 759. Namely, the electrodeposited copper foils in Examples have deposit side which is smoother and closer to a mirror surface compared to the electrodeposited copper foil of Comparative Example 5. In comparison on the mechanical properties as received, electrodeposited copper foil of Comparative Example 5 shows 37.9 kgf/mm^2 in tensile strength and 8.0% in elongation, and the electrodeposited copper foil of Example 10 shows 35.5 kgf/mm^2 in tensile strength and 11.5% in elongation, which is slightly better in flexibility. In comparison on the mechanical properties, electrodeposited copper foil of Comparative Example 5 after 180°Cx60 min-heating shows 31.6 kgf/mm^2 in tensile strength and 7.5% in elongation, and the electrodeposited copper foil of Example 10 shows 33.2 kgf/mm^2 in tensile strength and 11.2% in elongation, whereby the electrodeposited copper foil according to the present invention is superior. From this result, in consideration of the thermal history when the electrodeposited copper foil is processed into a copper-clad laminate, for example, a flexible printed wiring board using the electrodeposited copper foil according to the present invention is anticipated to have an excellent flexibility, etc.

[0126] Then, the advantage in using three kinds of gloss as an index to measure the uniformity of surfaces is confirmed. When the difference of the gloss in common direction, for the MD of a deposit side of the 12-micron meter electrodeposited copper foil obtained in Examples are examined, [Gs(20-deg.)] is 824 to 1, 206; [Gs(60-deg.)] is 649 to 759; and [Gs(85-deg.)] is 112 to 142, showing a higher value as the incident angle of the measuring light approaches perpendicular. By contrast, the evaluation result measured in the MD of the deposit side of the 12-micron meter electrodeposited copper foil obtained in Comparative Example 5 is examined, [Gs(20-deg.)] is 126; [Gs(60-deg.)] is 383; and [Gs(85-deg.)] is 117, showing the nearly same values at [Gs(20-deg.)] and [Gs(85-deg.)]. Therefore, the deposit side of the 12-micron meter electrodeposited copper foil obtained in Comparative Example 5 has some characteristic shape.

[0127] Then, a SEM photograph of the deposit side of the 12-micron meter electrodeposited copper foil obtained in Example 11 is shown in FIG. 1; and a SEM photograph of the deposit side of the 12-micron meter electrodeposited copper foil obtained in Comparative Example 5 is shown in FIG. 2. As is clear from FIG. 2, the deposit side of the electrodeposited copper foil obtained in Comparative Example 5 shows irregularities, though small, and moreover, irregular depositing parts, which could not be found without the large magnification observation, are found here and there. Namely, the diffused reflection of this irregular part makes the value of the gloss [Gs(20-deg.)] low and the surface roughness (Rzjis) high. In FIG. 1 which is a SEM photograph for the electrode posited copper foil according to the present invention, no evident irregularities nor irregular depositing parts are not observed. Accordingly, the electrodeposited copper foil according to the present invention is superior in surface roughness and gloss.

[0128] When the surface-treated electrodeposited copper foils subjected to the roughening treatment are compared between Example 10 and Comparative Example 5, the increases in surface roughness (Rzj is) by the roughening treatment performed under the same condition are nearly equal, about 0.7-micron meter. As is clear from FIG. 2, this is presumed to be because since the irregularities observed in the deposit side shape of the electrodeposited copper foil obtained in Comparative Example 5 has a pitch of about 3-micron meter but is smooth, fine particles obtained by the roughening treatment put along their corresponding irregular shape. However, since the electrodeposited copper foil of Comparative Example 5 has a high surface roughness (Rzjis) of the deposit side to be the base, the surface roughness (Rzjis), which is a requirement of the present invention, of the bonding surface to an insulating layer-forming material cannot be made to be not more than 1.5-micron meter, thus clarifying the superiority of the electrodeposited copper foil according to the present invention.

[0129] Comparison of MPS and SPS: Although SPS was used in place of MPS in Example 9 to Example 14, the surface roughness (Rzj is) of a deposit side of the obtained 12-micron meter electrodeposited copper foils is 0.30-micron meter to 0.41-micron meter; and the gloss [Gs(60-deg.)] is 603 to 759, whereby use of SPS also is confirmed to have

the same effect as MPS.

[0130] Now, although when the electrodeposited copper foils in above Examples according to the present invention were manufactured, favorable results were obtained in solution constitutions of sulfuric acid base copper electrolytic solutions in which the copper concentrations were about 40 g/l to 120 g/l, and the free sulfuric acid concentrations were about 60 g/l to 220 g/l, there is no trouble in shifting the concentration range according to applications of purposes. Further, the presence of additives other than the additives described in above Examples is not excluded, and they can rather be optionally added as long as they are confirmed to further enhance their effect and contribute to the quality stability in continuous production.

[0131] The deposit side of the electrodeposited copper foil according to the present invention has a lower profile than low-profile electrodeposited copper foils conventionally supplied in markets; the roughness of the deposit side is lower than that of the shiny side of the electrodeposited copper foil; and both the surfaces are together glossy smooth surfaces. The copper electrolytic solution used in manufacture of the electrodeposited copper foil has a large durability to deviations in manufacturing conditions and variations in thickness, and is superior in productivity. Accordingly, it is suitable for forming fine pitch circuits of tape automated bonding (TAB) boards and chip on film (COF) boards and further electromagnetic wave-shielding circuits of plasma display panels. Moreover, since the electrodeposited copper foil has excellent mechanical properties, it is suitable for use as current collecting materials constituting anodes of lithium ion secondary batteries, etc.

Claims

1. An electrodeposited copper foil, wherein a deposit side thereof has a surface roughness (Rzjis) lower than 1.0-micron meter, and a gloss [Gs(60-deg.)] not lower than 400.

2. The electrodeposited copper foil according to claim 1, wherein the gloss [Gs(60-deg.)] of the deposit side has a ratio of a TD gloss measured in the transverse direction to an MD gloss measured in the machine direction [TD gloss/MD gloss] is 0.9 to 1.1.

3. The electrodeposited copper foil according to claim 1 or claim 2, wherein the deposit side has a relationship of a gloss [Gs(20-deg.)] > a gloss [Gs(60-deg.)].

4. The electrodeposited copper foil according to any one of claims 1 to 3, wherein a shiny side thereof has a surface roughness (Rzj is) of lower than 2.0-micron meter, and a gloss [Gs(60-deg.)] of not lower than 70.

5. The electrodeposited copper foil according to any one of claims 1 to 4, wherein the copper foil as received has a tensile strength of not less than 33 kgf/mm^2, and an elongation of not less than 5%.

6. The electrodeposited copper foil according to any one of claims 1 to 5, wherein the copper foil after heating [180°C×60 min, in the air) has a tensile strength of not less than 30 kgf/mm^2, and an elongation of not less than 8%.

7. A surface-treated electrodeposited copperfoil,obtained by subjecting a surface of the electrodeposited copper foil according to any of claims 1 to 6 to at least one selected from rustproofing treatment and silane coupling agent treatment.

8. The surface-treated electrodeposited copper foil according to claim 7, wherein a surface roughness (Rzjis) of a bonding surface to an insulating layer-forming material of the surface-treated electrodeposited copper foil is not more than 1.5-micron meter.

9. The surface-treated electrodeposited copper foil according to claim 7 or claim 8, wherein a gloss [Gs(60-deg.)] of the bonding surface to the insulating layer-formingmaterial of the surface-treated electrodeposited copper foil is not lower than 250.

10. The surface-treated electrodeposited copper foil according to claim 7, wherein the bonding surface to the insulating layer-forming material of the surface-treated electrodeposited copper foil is roughened.

11. The surface-treated electrodeposited copper foil according to any one of claims 7 to 10, wherein the bonding surface to the insulating layer-forming material of the surface-treated electrodeposited copper foil is a deposit side thereof.

12. A method for manufacturing an electrodeposited copper foil, comprising peeling off copper deposited on a cathode surface by an electrolysis method using a sulfuric acid base copper electrolytic solution, wherein the sulfuric acid base copper electrolytic solution contains at least one selected from 3-mercapto-1-propanesulfonic acid or bis(3-sulfopropyl)disulfide, a quaternary ammonium salt polymer having a cyclic structure, and chlorine.

13. The method for manufacturing an electrodeposited copper foil according to claim 12, wherein a total concentration of 3-mercapto-1-propanesulfonic acid and/or bis (3-sulfopropyl) disulfide in the sulfuric acid base copper electrolytic solution is 0.5 ppm to 100 ppm.

14. The method for manufacturing an electrodeposited copper foil according to claim 12 or claim 13, wherein a concentration of the quaternary ammonium salt polymer having a cyclic structure in the sulfuric acid base copper electrolytic solution is 1 ppm to 150 ppm.

15. The method for manufacturing an electrodeposited copper foil according to any one of claims 12 to 14, wherein the quaternary ammonium salt polymer having a cyclic structure in the sulfuric acid base copper electrolytic solution is a diallyldimethylammonium chloride polymer.

16. The method for manufacturing an electrodeposited copper foil according to any one of claims 12 to 15, wherein a concentration of chlorine in the sulfuric acid base copper electrolytic solution is 5 ppm to 120 ppm.

17. An electrodeposited copper foil, manufactured by the manufacturing method according to claim 12.

18. A copper-clad laminate, obtained by laminating the surface-treated electrodeposited copper foil according to any one of claims 7 to 11 to an insulating layer-forming material.

19. The rigid copper-clad laminate according to claim 18, wherein the insulating layer-forming material contains a skeletal material.

20. A rigid printed wiring board, obtain by using the rigid copper-clad laminate according to claim 19.

21. The flexible copper-clad laminate according to claim 18, wherein the insulating layer-forming material is formed of a flexible material having a flexibility.

22. A flexible printed wiring board, obtained by using the flexible copper-clad laminate according to claim 21.

Fig. 1

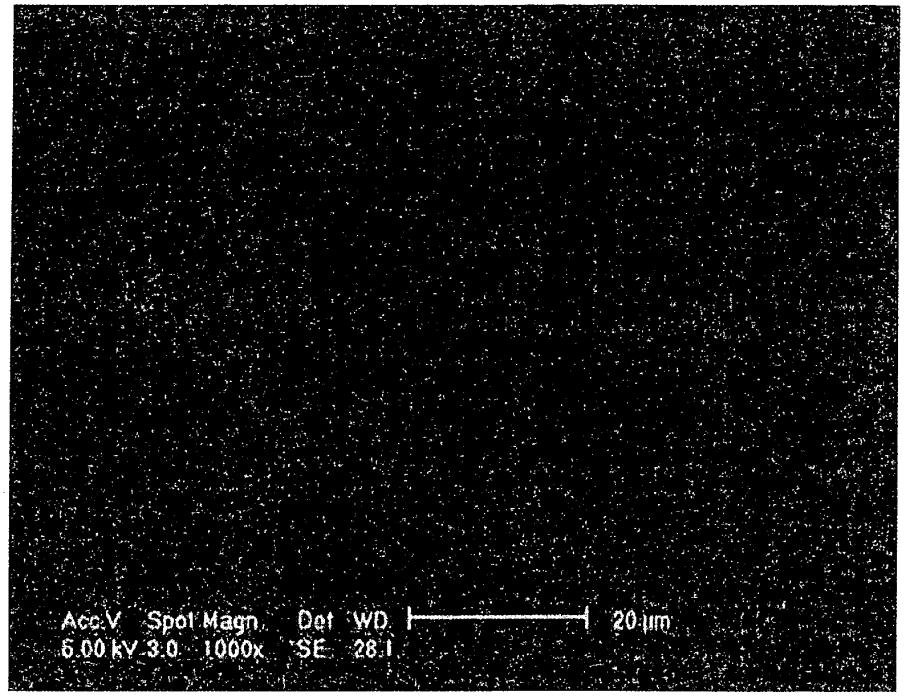
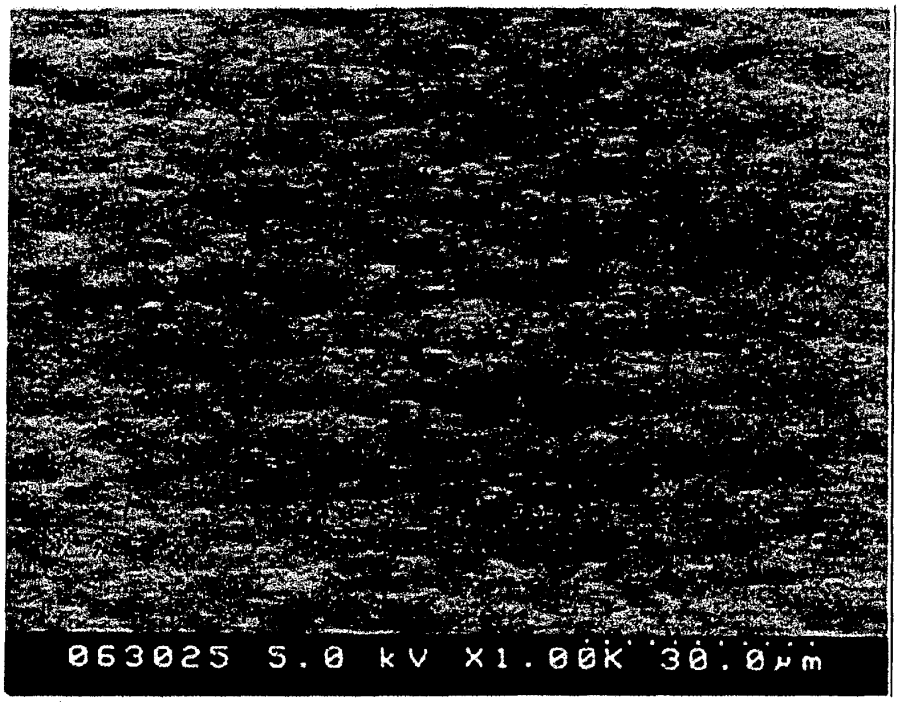


Fig. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/306920

A. CLASSIFICATION OF SUBJECT MATTER
C25D1/04(2006.01), ***C25D1/00***(2006.01), ***H05K1/09***(2006.01)

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(2006.01), ***C25D1/00***(2006.01), ***H05K1/09***(2006.01), ***C25D3/38***(2006.01)

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 1996-2006
Kokai Jitsuyo Shinan Koho 1971-2006 Toroku Jitsuyo Shinan Koho 1994-2006

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 2004-162172 A (Nisshin Sozai Sangyo Kabushiki Kaisha), 10 June, 2004 (10.06.04), Example 6; Par. Nos. [0034] to [0036] & KR 2003/36415 A & US 2004/104117 A1	1-22
A	JP 2001-329390 A (Mitsui Mining & Smelting Co., Ltd.), 27 November, 2001 (27.11.01), Par. No. [0048] & WO 2001/088228 A1 & US 2001/42686 A1 & EP 1221498 A1 & CN 2001/380915 A	1-11,18-22
X	JP 2004-35918 A (Nippon Denkai Ltd.), 05 February, 2004 (05.02.04), Full text (Family: none)	12-17

☒ 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
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"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
21 June, 2006 (21.06.06)	27 June, 2006 (27.06.06)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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(71) Applicant: **Furukawa Electric Co., Ltd.**
Chiyoda-ku
Tokyo 100-8322 (JP)

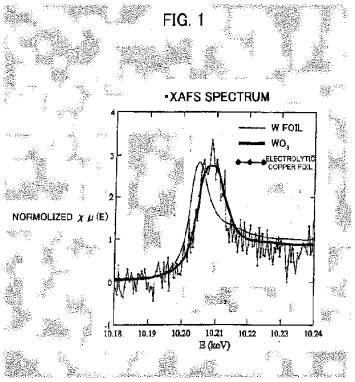
(72) Inventors:
- **SUZUKI, Akitoshi**
  Tokyo 100-8322 (JP)
- **SHINOZAKI, Kensaku**
  Tokyo 100-8322 (JP)
- **FUJISAWA, Kimiko**
  Tokyo 100-8322 (JP)
- **TSURUTA, Takahiro**
  Tokyo 100-8322 (JP)
- **EZURA, Takeshi**
  Tokyo 100-8322 (JP)
- **SHINOZAKI, Jun**
  Tokyo 100-8322 (JP)
- **EBISUGI, Masato**
  Tokyo 100-8322 (JP)
- **SASAKI, Hirokazu**
  Tokyo 100-8322 (JP)
- **YAMAZAKI, Satoshi**
  Tokyo 100-8322 (JP)

(74) Representative: **Horn Kleimann Waitzhofer**
Elsenheimerstraße 65
DE-80687 München (DE)

(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



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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.

>N-C(=S)-N<

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	0.0353	0.0132	650	530	3.5	4.3	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	800	601	4.2	3.9	80	No wrinkles or other changes
	1-8		70	50	30	7.0	80	40	0.0208	0.0230	788	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	30	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	0.0060	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	60	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	0.0162	600	445	4.8	6.3	81	Some

		methyl														wrinkles
	1-25	thiourea	70	50	5	21.0	1010	40	0.0592	0.0055	560	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	62	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)	Wconcentration 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 1 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	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
						9				
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	%
	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
Ex.	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.

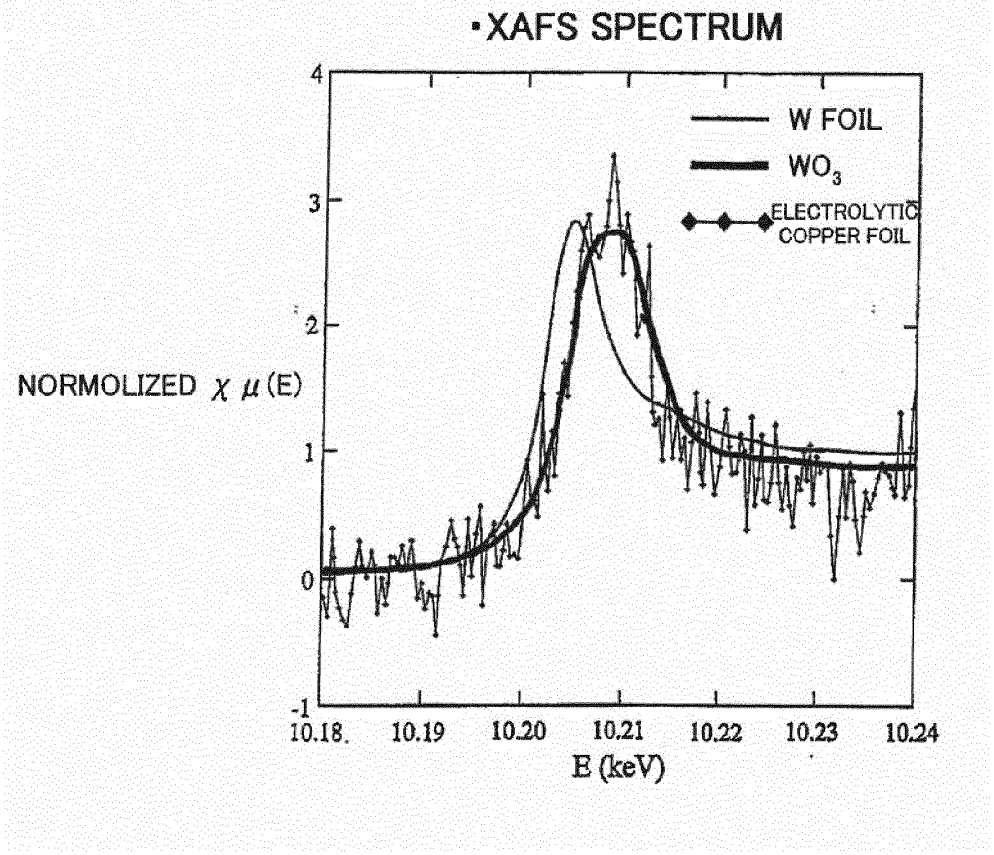
17. The electrolyte for forming an electrolytic copper foil as set forth in claim 16, wherein the electrolyte has 10 to 1,000 ppm of tungsten or a tungsten compound as tungsten, 1 to 20 ppm of a thiourea compound, and 1 to 100 ppm of chlorine ions added to it.

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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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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- JP 4273309 B **[0018] [0032]**
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- JP 9067693 A **[0025] [0032]**

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(71) Applicant: **Iljin Materials Co., Ltd.**
Iksan-si, Jeollabuk-do 570-998 (KR)

(72) Inventors:
- **LEE, Sun Hyoung**
  Iksan-si
  Jeollabuk-do 570-775 (KR)
- **JO, Tae Jin**
  Seongnam-si
  Gyeonggi-do 462-813 (KR)
- **PARK, Seul Ki**
  Jindo-gun
  Jeollanam-do 539-814 (KR)
- **SONG, Ki Deok**
  Suwon-si
  Gyeonggi-do 441-862 (KR)

(74) Representative: **Zech, Stefan Markus**
Meissner Bolte Patentanwälte
Rechtsanwälte Partnerschaft mbB
Postfach 86 06 24
81633 München (DE)

(54) **ELECTRODEPOSITED COPPER, AND ELECTRICAL COMPONENT AND BATTERY COMPRISING SAME**

(57) Disclosed is an electrodeposited copper foil, in which a center line roughness average Ra (μm), a maximum height Rmax (μm), and a ten-point height average Rz (μm) of a matte side satisfy an Equation below, $1.5 \leq (Rmax - Rz)/Ra \leq 6.5$. The electrodeposited copper foil according to the present invention maintains low roughness and high strength, and exhibits a high elongation rate, and particularly, has excellent glossiness, so that the electrodeposited copper foil may be used in a current collector of a medium and large lithigum ion secondary battery and a semiconductor packaging substrate for Tape Automated Bonding (TAB) used in a Tape Carrier Package (TCP).

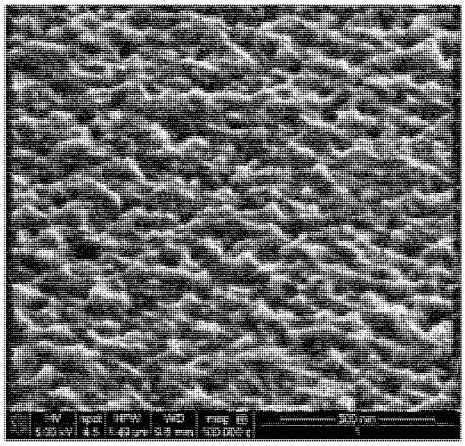


FIG.5

EP 3 067 199 A1

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Description

[Technical Field]

[0001] The present invention relates to an electrodeposited copper foil, and an electrical component and a battery including the electrodeposited copper foil, and more particularly, to low rough, highly strong, and highly elongated electrodeposited copper foil, which has both high tensile strength and a high elongation rate even after a high-temperature heat treatment.

[Background Art]

[0002] A copper foil is generally used as a current collector of a secondary battery. As the copper foil, a rolled copper foil obtained by rolling processing is mainly used, but fabricating cost of the rolled copper is high and it is difficult to fabricate a copper foil having a wide width. Further, since the rolled copper foil uses lubricating oil during the rolling processing, adhesion with an active material may be degraded by a contamination of the lubricating oil, so that a charging and discharging cycle characteristic of the battery may be degraded.

[0003] A lithium battery accompanies a change in volume during charging and discharging and a heating phenomenon according to overcharging. Further, in order to improve adhesion with an electrode active material and, in relation to expansion and contraction of an active material layer according to the charging and discharging cycle, in order to prevent wrinkle, fracture, and the like from being generated in the copper foil, which serves as a current collector, with little influence from a copper foil base material, surface roughness of the copper foil needs to be low. Accordingly, a highly elongated, highly strong, and low rough copper foil, which is capable of resisting to a change in volume and a heating phenomenon of the lithium battery and has excellent adhesion with an active material, is required.

[0004] Further, according to a demand for a light, thin, short, and small electronic device, in order to increase a degree of integration of a circuit within a small area according to high performance, compactness, and lightness, a demand for fine wiring of a semiconductor mounted substrate or a main board substrate is increased. When a thick copper foil is used for fabricating a printed wiring board having a fine pattern, an etching time for forming a wiring circuit is increased and lateral wall verticality of a wiring pattern is degraded. Particularly, when a line width of the wiring pattern formed by etching is small, the wiring may be disconnected. Accordingly, in order to obtain a fine pitch circuit, a thinner copper foil is demanded. However, a thickness of a thin copper foil is limited, so that mechanical strength of the thin copper foil is weak, so that a frequency of the generation of a failure, such as wrinkle and bending, is increased during fabricating the wiring substrate.

[0005] Further, a plurality of terminals of an Integrated Circuit (IC) chip is directly bonded to an inner lead disposed in a device hall positioned at a center portion of a product in a semiconductor packaging substrate for Tape Automated Bonding (TAB) used in a Tape Carrier Package (TCP) and the like, and in this case, a current is made to momentarily flow in the inner lead by using a bonding device to heat the inner lead and apply a predetermined pressure to the inner lead. Accordingly, the inner lead formed by etching the electrodeposited copper foil is elongated and stretched by a bonding pressure.

[0006] Accordingly, a copper foil having a small thickness, high mechanical strength, a high elongation property, and low roughness is required.

[Disclosure]

[Technical Problem]

[0007] The present invention has been made in an effort to provide a new electrodeposited copper foil.

[0008] The present invention has also been made in an effort to provide an electrical component including an electrodeposited copper foil.

[0009] The present invention has also been made in an effort to provide a battery including an electrodeposited copper foil.

[Technical Solution]

[0010] An exemplary embodiment of the present invention provides an in which a center line roughness average Ra (μm), a maximum height Rmax (μm), and a ten-point height average Rz (μm) of a matte side satisfy an Equation below.

$$1.5 \leq (Rmax - Rz)/Ra \leq 6.5.$$

[0011] Tensile strength of the electrodeposited copper foil before a heat treatment may be 40 kgf/mm^2 to 70 kgf/mm^2, and tensile strength of the electrodeposited copper foil after a heat treatment for one hour at 180°C may be 40 kgf/mm^2 to 70 kgf/mm^2. The heat treatment may be performed for one hour at 180°C. Tensile strength of the electrodeposited copper foil after the heat treatment may be 85% to 99% of tensile strength of the electrodeposited copper foil before the heat treatment.

[0012] An elongation rate before a heat treatment may be 2% to 15%, and an elongation rate after a heat treatment may be 4% to 15%. The heat treatment may be performed for one hour at 180°C. An elongation rate after a heat treatment may be one time to 4.5 times of an elongation rate before the heat treatment.

[0013] A corner curl angle of the electrodeposited copper foil may be 0° to 45°, a corner curl height of the electrodeposited copper foil may be 0 mm to 40 mm, and the electrodeposited copper foil may have a thickness of 2 μm to 10 μm.

[0014] Another exemplary embodiment of the present invention provides a battery including the electrodeposited copper foil.

[0015] Yet another exemplary embodiment of the present invention provides an electrical component, including: an insulating base material; and the electrodeposited copper foil attached onto one surface of the insulating base material.

[Advantageous Effects]

[0016] According to the exemplary embodiment of the present invention, a difference between a maximum vertical distance and an average of vertical distances of surface factors protruding to the outside on a matte side is small, so that the electrodeposited copper foil of the present invention exhibits high glossiness even before a post-treatment process, thereby improving a quality of a product. Further, the electrodeposited copper foil of the present invention exhibits high strength and a high elongation rate, and stress inside the electrodeposited copper foil is small, thereby preventing a corner curling phenomenon. Accordingly, the electrodeposited copper foil of the present invention exhibits low roughness, high strength, and a high elongation rate, thereby being advantageous to perform a process and decreasing a product defective, and when the electrodeposited copper foil of the present invention is used in a product, such as a PCB or a negative electrode current collector of a secondary battery, it is possible to improve product reliability.

[Description of Drawings]

[0017]

FIG. 1 is an image of a Field Emission Scanning Electron Microscopy (FESEM) of an electrodeposited copper foil magnified by 2,000 times according to an exemplary embodiment of the present disclosure.

FIG. 2 is an image of an FESEM of an electrodeposited copper foil magnified by 10,000 times according to an exemplary embodiment of the present disclosure.

FIG. 3 is an image of an FESEM of an electrodeposited copper foil magnified by 50,000 times according to an exemplary embodiment of the present disclosure.

FIG. 4 is an image of an FESEM of an electrodeposited copper foil magnified by 100,000 times according to an exemplary embodiment of the present disclosure.

FIG. 5 is an image of an FESEM of an electrodeposited copper foil magnified by 100,000 times according to an exemplary embodiment of the present disclosure.

FIG. 6 is an X-ray diffraction (XRD) spectrum of a matte side of an electrodeposited copper foil fabricated in Example 1.

FIG. 7 is an image of a Scanning Electron Microscopy (SEM) of a surface of the electrodeposited copper foil fabricated in Example 1.

FIG. 8 is an image of an SEM for a surface of an electrodeposited copper foil fabricated in Example 2.

FIG. 9 is an image of an SEM for a surface of an electrodeposited copper foil fabricated in Example 3.

FIG. 10 is an image of an SEM for a surface of an electrodeposited copper foil fabricated in Example 4.

FIG. 11 is an image of an SEM for a surface of an electrodeposited copper foil fabricated in Comparative Example 1.

FIG. 12 is an image of an SEM for a surface of an electrodeposited copper foil fabricated in Comparative Example 2.

FIG. 13 is an image of an SEM for a surface of an electrodeposited copper foil fabricated in Comparative Example 3.

FIG. 14 is an image of an SEM for a surface of an electrodeposited copper foil fabricated in Comparative Example 4.

[Best Mode]

[0018] In an electrodeposited copper foil according to an aspect of the present invention, a center line roughness average (Ra) of a matte side, a maximum height (Rmax), and a 10-point height average (Rz) satisfy the Equation below.

$$1.5 \leq (Rmax - Rz)/Ra \leq 6.5$$

[Mode for Carrying out the Invention]

[0019] Hereinafter, an electrodeposited copper foil according to the present invention, an electrical component and a battery including the electrodeposited copper foil, and a method of fabricating the electrodeposited copper foil will be described in more detail.

[0020] An electrodeposited copper foil according to an exemplary embodiment of the present invention satisfies the Equation below.

[Equation 1]

$$1.5 \leq (Rmax - Rz)/Ra \leq 6.5$$

[0021] In Equation 1, Ra means a center line roughness average (μm) of a matte side, Rmax means a maximum height (μm), and Rz means a 10-point height average (μm).

[0022] Ra (roughness average) is a roughness average of a matte side, and represents a sum of an absolute value of an area between an actual surface and a center line, that is, a height of a contour of a measured section surface. Rmax means a vertical distance from a most highly protruding surface factor, that is, the highest peak, to the most deeply dug point, that is, the deepest valley. That is, Rmax means a maximum vertical distance of a surface factor. Rz is an average of values obtained by adding depths of five deepest valleys to heights of five highest peaks measured in an entire measurement section.

[0023] The "surface factor" in the present specification is a bright portion on a matte side and means a portion protruding from a surface of the electrodeposited copper foil, and a high surface factor among the surface factors is referred to as a peak, and a region dug between the surface factors is referred to as a valley.

[0024] Glossiness of the matte side of the electrodeposited copper foil according to the present invention is very high. The electrodeposited copper foil is obtained by extracting a copper foil on a surface of a negative electrode drum by supplying a current between a rotated negative electrode drum immersed in a bathtub of a copper electrolyte and a positive electrode, and a surface of the electrodeposited copper foil, which is in contact with the negative electrode drum, is referred to as a shiny side (S surface), and an opposite surface of the shiny side is referred to as a matte side. The matte side is a side on which an electrodeposited copper foil is extracted as it is unlike the shiny side which is in contact with the drum, so that the matte side originally has low glossiness and high surface roughness. Accordingly, a process of decreasing surface roughness and applying glossiness as necessary through a post-treatment is performed on the matte side.

[0025] However, a glossiness degree of the matte side of the electrodeposited copper foil according to the present invention is high even before the post-treatment processing. FIG. 1 is an image of a Field Emission Scanning Electron Microscopy (FESEM) of the electrodeposited copper foil magnified by 2,000 times according to the exemplary embodiment of the present disclosure.

[0026] When the matte side is generally 2,000 times FESEM analyzed according to a characteristic of the process, concave-convex portions are shown on the surface and glossiness is not high. By contrast, in FIG. 1, the matte side of the electrodeposited copper foil according to the present invention exhibits glossiness, such as a mirror, similar to the shiny side.

[0027] When a 10,000 times FESEM image of FIG. 2, a 50,000 times FESEM image of FIG. 3, and a 100,000 times FESEM image of FIG. 4 are analyzed by increasing resolution of the FESEM analysis, when the resolution is high, it is possible to confirm concave-convex portions, that is, surface factors, on the surface. However, it is difficult to confirm the concave-convex portions even in the 10,000 times FESEM image, and the concave-convex portions are confirmed at ultra-high resolution, such as the 50,000 times FESEM analysis and the 100,000 times FESEM analysis.

[0028] In FIG. 4, a size and a height of the surface factor of the matte side of the electrodeposited copper foil according to the present invention are uniform. A result of the 100,000 times FESEM analysis obtained by tilting the same sample at 52° is represented in FIG. 5. In FIG. 5, a valley between the protruding surface factors is more clearly shown.

[0029] Even when the surface of the electrodeposited copper foil has the same surface roughness, and when an area of the valley exposed to the outside is small or the number of valleys is small, surface glossiness is improved. When the roughness is determined based on a volume of the surface factors, and when a height of the peak is large at the same surface roughness, it may be considered that the peak and the valley are sharply formed. That is, when it is assumed that the surface roughness is an entire region, in which the surface factors protrude or are inserted from the surface, and when a height of the peak is large and a depth of the valley at the same surface roughness is large, it may be considered that the surface factor is sharply formed. This may means that when a height of the peak is small and a depth of the valley at the same surface roughness is small, it may be considered that the surface factor is bluntly formed.

[0030] In this case, when a depth of the valley in the matte side is small and an average diameter of a dark portion shown to the outside is large, the valley, which is the dark region represented on the surface, may further influence glossiness. That is, this means that when a depth of the valley is small and an average diameter of a dark portion is small, the dark region shown to the outside is small, so that glossiness may be improved even without an additional treatment.

[0031] Accordingly, the valley in the matte side of the electrodeposited copper foil according to the present invention having a relatively large depth and small average diameter is preferable in an aspect of glossiness. For the large depth and a small average diameter of the valley, the surface factor needs to have a large height and to be sharply formed.

[0032] To this end, the electrodeposited copper foil according to the exemplary embodiment of the present invention satisfies the Equation below.

[Equation 1]

$$1.5 \leq (Rmax - Rz)/Ra \leq 6.5$$

[0033] In Equation 1, Ra means a center line roughness average (μm) of the matte side, Rmax means a maximum height (μm), and Rz means a 10-point height average (μm).

[0034] In the Equation, when a value of (Rmax - Rz)/Ra is 6.5 or less, it is possible to obtain a high glossiness value without a post-treatment process. By contrast, when a value of (Rmax - Rz)/Ra is 1.5 or less, a difference between Rmax and Rz is too small, a value from the peak to the valley of the surface factor is generally increased, so that entire surface roughness is increased.

[0035] A value obtained by subtracting Rz from Rmax is a value obtained by subtracting Rz, which is an average value of values obtained by adding heights of the five highest peaks and depths of the five deepest valleys among the surface factors, from Rmax, which is a value obtained by adding a height from a center line of the highest peak and a depth from a center line of the deepest valley among the surface factors. That is, the value obtained by subtracting Rz from Rmax means a difference between a maximum vertical length based on the center line of the surface factor and an average value of the five peaks and the five valleys including the highest peak and the deepest valley. The large difference means that a difference in height between the highest peak and the four remaining peaks is large, and this means that the surface factors are generally formed so as to have a height or depth deviation. The small difference means that the large number of high peaks and deep valleys is formed, and a height deviation of the surface factors is not large. However, Rz represents the average value of the values of the five peaks and five valleys, so that it is possible to obtain an average deviation by reflecting Ra to the Equation.

[0036] When a value of (Rmax - Rz)/Ra is large at the same surface roughness, a height deviation of the surface factors of the matte side is large, and the surface factors are bluntly formed. When a value of (Rmax - Rz)/Ra is small, a height deviation of the surface factors of the matte side is small, and the surface factors are sharply formed, thereby improving glossiness. A maximum value and a minimum value of (Rmax - Rz)/Ra will be further described below with reference to the exemplary embodiment.

[0037] In the electrodeposited copper foil according to the exemplary embodiment of the present invention, surface roughness Rz of the matte side is 1.4 μm or less, tensile strength after a heat treatment is 40 kgf/mm^2, and an elongation rate is 4% or more.

[0038] The electrodeposited copper foil is a low-rough copper foil having surface roughness Rz of 1.4 μm or less and has high tensile strength of 40 kgf/mm^2 or more, so that mechanical strength thereof is high. Further, the electrodeposited copper foil has a high elongation rate of 4% or more even after a high-temperature heat treatment.

[0039] Further, a corner curl angle of the electrodeposited copper foil according to the present invention is 0° to 45°. The corner curl angle means an angle, at which an end portion, that is, a corner or an edge, of the electrodeposited copper foil is bent when the electrodeposited copper foil is laid on a flat floor. It is known that the corner curling phenomenon of the electrodeposited copper foil is generated when internal energy of the electrodeposited copper foil is not uniform, and when the corner curling phenomenon is generated, a plurality of defects, such as a torn corner, may be generated during a process, such as deposition, in a PCB process, and in a process of the lithium secondary battery, a corner may

be torn or folded, or wrinkles may be generated during a coating of an active material. When a corner curl angle of the electrodeposited copper foil is large, it is difficult to use the electrodeposited copper foil in a subsequent process, so that the corner curl angle may be 0° to 45°. Further, the electrodeposited copper foil is laid out on a flat floor and is cut in an X-shape, and a height of a rolled-up cut portion of the electrodeposited copper foil is referred to as a corner curl height, and the corner curl height may be 0 mm to 40 mm. In the case of the electrodeposited copper foil according to the present invention, impurities exist within a copper crystal, so that strength of the electrodeposited copper foil is high, and thus it is expected that a degree of corner curling is large, but impurities do not exist in a copper grain boundary, so that internal stress is decreased and thus a degree of corner curl is decreased.

[0040] Accordingly, the electrodeposited copper foil may be used for both a Printed Circuit Board (PCB)/Flexible PCB (FPC) and a current collector of a battery.

[0041] In the electrodeposited copper foil, when the surface roughness Rz of the matte side is larger than 1.4 μm, a contact surface between the surface of the electrodeposited copper foil for the negative electrode current collector and the active material is decreased, so that a life of a charging and discharging cycle and an electricity capacity at an initial stage of the charging may be decreased. Further, when the surface roughness Rz of the matte side is larger than 1.4 μm, it may not be easy to form a high-density circuit having a fine pitch on a printed wiring board.

[0042] The electrodeposited copper foil has a high strength characteristic having tensile strength of 40 kgf/mm^2 to 70 kgf/mm^2 Further, tensile strength of the electrodeposited copper foil is 40 kgf/mm^2 to 70 kgf/mm^2 even after a heat treatment. The heat treatment may be performed, for example, at 150°C to 220°C, and more particularly, 180°C. The heat treatment may be performed for 30 minutes, one hour, two hours, and several hours. The heat treatment is performed for measuring tensile strength of the electrodeposited copper foil, and is a treatment for obtaining tensile strength or an elongation rate having a value which has a predetermined level and is not changed when the electrodeposited copper foil is stored or enters a subsequent process.

[0043] When tensile strength of the electrodeposited copper foil is less than 40 kgf/mm^2 after the heat treatment, mechanical strength of the electrodeposited copper foil is weak, so that it may be difficult to handle the electrodeposited copper foil.

[0044] It is preferable that the tensile strength of the electrodeposited copper foil after the heat treatment is similar to the tensile strength of the electrodeposited copper foil before the heat treatment. The tensile strength of the electrodeposited copper foil after the heat treatment may be 85% to 99% of the tensile strength of the electrodeposited copper foil before the heat treatment, and when the strength is maintained even after the heat treatment, it is easy to handle the electrodeposited copper foil in a subsequent process and a yield is increased.

[0045] An elongation rate of the electrodeposited copper foil before the heat treatment may be 2% to 15%. Further, an elongation rate of the electrodeposited copper foil after the heat treatment may be 4% to 15%, and the heat treatment may be performed for one hour at 180°C. Otherwise, the elongation rate of the electrodeposited copper foil after the heat treatment may be 1 time to 4.5 times of the elongation rate of the electrodeposited copper foil before the heat treatment.

[0046] When the elongation rate of the electrodeposited copper foil after the heat treatment is less than 4%, a crack may be generated when a subsequent process is a high-temperature process. For example, when the electrodeposited copper foil is used as the negative electrode current collector of the secondary battery, a process of fabricating the negative electrode current collector is a high-temperature process and a volume change of the active material layer is accompanied during charging/discharging, so that a crack may be generated and a defect may be caused. Accordingly, the electrodeposited copper foil needs to maintain a predetermined elongation rate after the heat treatment.

[0047] In an XRD spectrum for the matte side of the electrodeposited copper foil, it can be recognized that a ratio I(200)/I(111) of strength (I(200)) of a diffraction peak for a (200) crystalline surface to strength (I(111)) of a diffraction peak for a (111) crystalline surface is 0.5 to 1.0.

[0048] For example, as illustrated in FIG. 6, the XRD spectrum for the matte side represents a diffraction peak for the (111) crystalline surface at a diffraction angle (2θ) 43.0° ± 1.0° and a diffraction peak for the (200) crystalline surface at a diffraction angle (2θ) 50.5° ± 1.0°, and a strength ratio I(200)/I(111) thereof may be 0.5 to 1.5 or more.

[0049] For example, a strength ratio I(200)/I(111) of the electrodeposited copper foil may be 0.5 to 0.8. In the XRD spectrum for the matte side of the electrodeposited copper foil, M(200)/M(111) that is a ratio of an orientation index (M(200)) for the (200) crystalline surface to an orientation index (M(111)) for the (111) crystalline surface may be 1.1 to 1.5. The orientation index is a value obtained by dividing relative peak strength of a specific crystalline surface for a predetermined sample by relative peak strength of a specific crystalline surface obtained from a standard sample non-oriented to all of the crystalline surfaces. For example, a strength ratio M(200)/M(111) in the electrodeposited copper foil may be 1.2 to 1.4.

[0050] An elongation rate of the electrodeposited copper foil may be 10% or more after the heat treatment for one hour at 180°C. That is, the electrodeposited copper foil may have a high elongation rate, which is 10% or more, after a high-temperature heat treatment. For example, an elongation rate of the electrodeposited copper foil may be 10% to 20% after the high-temperature heat treatment. For example, an elongation rate of the electrodeposited copper foil may

be 10% to 15% after the high-temperature heat treatment. For example, an elongation rate of the electrodeposited copper foil may be 10% to 13% after the high-temperature heat treatment. An elongation rate of the electrodeposited copper foil before the heat treatment may be 2% or more. For example, an elongation rate of the electrodeposited copper foil before the heat treatment may be 2% to 20%. For example, an elongation rate of the electrodeposited copper foil before the heat treatment may be 5% to 20%. For example, an elongation rate of the electrodeposited copper foil before the heat treatment may be 5% to 15%. For example, an elongation rate of the electrodeposited copper foil before the heat treatment may be 5% to 10%. The term "before the heat treatment" means 25°C to 130°C which are temperatures before a heat treatment to a high-temperature state. The elongation rate is a value obtained by dividing a distance elongated just before the electrodeposited copper foil is fractured by an initial length of the electrodeposited copper foil.

[0051] The surface roughness Rz of the matte side of the electrodeposited copper foil may be 0.7 μm or less. The electrodeposited copper foil has the surface roughness Rz of 0.7 μm or less, so that the electrodeposited copper foil may be used for both a copper foil for a PCB/FPC and a copper foil for a negative electrode current collector for a secondary battery. For example, the surface roughness Rz of the matte side of the electrodeposited copper foil may be 0.5 μm or less. For example, the surface roughness Rz of the matte side of the electrodeposited copper foil may be 0.45 μm or less.

[0052] The surface roughness Ra of the matte side of the electrodeposited copper foil may be 0.15 μm or less. The electrodeposited copper foil has the surface roughness Ra of 0.15 μm or less, so that the electrodeposited copper foil may be used for both a copper foil for a PCB/FPC and a copper foil for a negative electrode current collector for a secondary battery. For example, the surface roughness Ra of the matte side of the electrodeposited copper foil may be 0.12 μm or less. For example, the surface roughness of the matte side of the electrodeposited copper foil may be 0.11 μm or less.

[0053] The tensile strength of the electrodeposited copper foil after the heat treatment may be 85% or more of the tensile strength of the electrodeposited copper foil before the heat treatment. For example, the tensile strength of the electrodeposited copper foil after the heat treatment for one hour at 180°C may be 90% or more of the tensile strength of the electrodeposited copper foil before the heat treatment. The tensile strength of the electrodeposited copper foil before the heat treatment is the tensile strength of the electrodeposited copper foil obtained without a high-temperature heat treatment. The tensile strength of the electrodeposited copper foil before the heat treatment may be 40 kgf/mm^2 to 70 kgf/mm^2.

[0054] Glossiness (Gs(60°)) in a width direction of the matte side of the electrodeposited copper foil may be 500 or more. For example, glossiness (Gs(60°)) in a width direction of the matte side of the electrodeposited copper foil may be 500 to 1,000. The glossiness is a value measured according to JIS Z 871-1997.

[0055] A thickness of the electrodeposited copper foil may be 35 μm or less. For example, a thickness of the electrodeposited copper foil may be 6 μm to 35 μm. For example, a thickness of the electrodeposited copper foil may be 6 μm to 18 μm. Further, for example, a thickness of the electrodeposited copper foil may be 2 μm to 10 μm.

[0056] When the electrodeposited copper foil needs to be bonded with an insulating resin and the like, a surface treatment may be additionally performed in order to obtain adhesion of a practical level or more. An example of the surface treatment on the copper foil includes any one of a heat resistant and chemically resistant treatment, a chromate treatment, and a silane coupling treatment, or a combination thereof, and the kind of surface treatment to be performed may be selected by those skilled in the art according to a resin used as an insulating resin or a process condition.

[0057] An electrical component according to an exemplary embodiment includes an insulating base material, and the electrodeposited copper foil attached onto one surface of the insulating base material, and includes a circuit formed by etching the electrodeposited copper foil.

[0058] An example of the electrical component includes a TAB tape, a PCB, and a FPC, but the electrical component is not essentially limited thereto, and any product, in which the electrodeposited copper foil is attached onto an insulating base material, and which may be used in the art, may be accepted.

[0059] A battery according to an exemplary embodiment includes the electrodeposited copper foil. The electrodeposited copper foil may be used as a negative electrode current collector of the battery, but is not essentially limited thereto, and may be used as another constituent element used in the battery. The battery is not particularly limited, and includes both a primary battery and a secondary battery, and is a battery, such as a lithium ion battery, a lithium polymer battery, and a lithium air battery, in which an electrodeposited copper foil is used as a current collector, and which may be used in the art, may be accepted.

[0060] A method of fabricating an electrodeposited copper foil according to an exemplary embodiment includes electrolyzing a copper electrolyte including an additive A, an additive B, an additive C, and an additive D, and the additive A is one or more selected from the group consisting of a thiourea-based compound and a compound, in which a thiol group is connected to a heterocycle including nitrogen, the additive B is a sulfone acid of a compound including a sulfur atom or metallic salt thereof, the additive C is a nonionic water soluble polymer, and the additive D is a phenazinium-based compound.

[0061] The method of fabricating the electrodeposited copper foil includes the additives of the new compositions, so

that it is possible to fabricate a thin, highly mechanically strong, highly elongated, and low rough copper foil. The cooper electrolyte may include chlorine (chlorine ion) of a concentration of 1 to 40 ppm. When a small amount of chlorine ions exists in the copper electrolyte, initial nucleation sites are increased during the electroplating, so that crystal grains become fine, and the extracted materials of $CuCl_2$ formed on an interface of a grain boundary suppress the crystal from being grown during the heating at a high temperature, thereby improving thermal stability at a high temperature. When a concentration of chlorine ions is less than 1 ppm, a concentration of chlorine ions required in a sulfuric acid-copper sulphate electrolyte is short, so that tensile strength of the electrodeposited copper foil before a heat treatment may be degraded and thermal stability at a high temperature may be degraded. When a concentration of chlorine ions is larger than 40 ppm, the surface roughness of the matte side is increased, so that it is difficult to fabricate a low rough electrodeposited copper foil, tensile strength of the electrodeposited copper foil before a heat treatment may be degraded, and thermal stability at a high temperature may be degraded.

[0062] In the cooper electrolyte, a content of additive A is 1 to 10 ppm, a content of additive B is 10 to 200 ppm, a content of additive C is 5 to 40 ppm, and a content of additive D is 1 to 10 ppm.

[0063] The additive A in the copper electrolyte may improve fabricating stability of the electrodeposited copper foil and improve strength of the electrodeposited copper foil. When the content of additive A is less than 1 ppm, tensile strength of the electrodeposited copper foil may be degraded, and when the content of additive A is larger than 10 ppm, surface roughness of the matte side is increased, so that it may be difficult to fabricate a low rough electrodeposited copper foil and tensile strength of the electrodeposited copper foil may be degraded.

[0064] The additive B in the copper electrolyte may improve surface glossiness of the electrodeposited copper foil. When the content of additive B is less than 10 ppm, glossiness of the electrodeposited copper foil may be degraded, and when the content of additive B is larger than 200 ppm, surface roughness of the matte side is increased, so that it may be difficult to fabricate a low rough electrodeposited copper foil and tensile strength of the electrodeposited copper foil may be degraded.

[0065] The additive C in the copper electrolyte may decrease surface roughness of the electrodeposited copper foil and improve surface glossiness. When the content of additive C is less than 5 ppm, surface roughness of the matte side is increased, so that it may be difficult to fabricate a low rough electrodeposited copper foil and glossiness of the electrodeposited copper foil may be degraded, and when the content of additive C is larger than 40 ppm, there is no difference in a physical property or an appearance of the electrodeposited copper foil, and the method of fabricating the electrodeposited copper foil may not be economical.

[0066] The additive D in the copper electrolyte may serve to improve flatness of a surface of the electrodeposited copper foil. When the content of additive D is less than 1 ppm, surface roughness of the matte side is increased, so that it may be difficult to fabricate a low rough electrodeposited copper foil and glossiness of the electrodeposited copper foil may be degraded, and when the content of additive D is larger than 40 ppm, an extraction state of the electrodeposited copper foil is unstable and tensile strength of the electrodeposited copper foil may be degraded.

[0067] The thiourea-based compound may be one or more selected from the group consisting of diethyl thiourea, ethylene thiourea, acetylene thiourea, diprophyl thiourea, dibutyl thiourea, N-trifluoroacetylthiourea, N-ethylthiourea, N-cyanoacetylthiourea, N-allylthiourea, o-tolylthiourea, N,N'-butylene thiourea, thiazolidinethiol, 4-thiazolinethiol, 4-methyl-2-pyrimidinethiol, and 2-thiouracil, but is not essentially limited thereto, and any kind of thiourea compound usable as an additive in the art may be accepted. The compound, in which a thiol group is connected to a heterocycle including nitrogen, may be, for example, 2-mercapto-5-benzoimidazole sulfonic acid sodium salt, sodium 3-(5-mercapto-1-tetrazolyl)benzene sulfonate, and 2-mercapto benzothiazole.

[0068] The sulfone acid of the compound including a sulfur atom or the metallic salt thereof may be one or more selected from the group consisting of, for example, bis-(3-sulfopropyl)-disulfide disodium salt (SPS), 3-macapto-1-propane sulfonic acid (MPS), 3-(N,N-dimethyl thiocarbamoyl)-thiopropane sulfonate sodium salt (DPS), 3-[(amino-iminomethyl)thio]1-propane sulfonate sodium salt (UPS), o-ethyldithio carbonate-S-(e-sulfopropyl)-ester sodium salt (OPX), 3-(benzothiazolyl-2-macapto)-propyl-sulfonic acid sodium salt (ZPS), Ethylenedithiodipropylsulfonic acid sodium salt, thioglycolic acid, Thiophosphoric acid-o-ethyl-bis-(ω-sulfopropyl)ester disodium salt, and Thiophosphoric acid-tris-(ω-sulfopropyl)ester trisodium salt, but is not essentially limited thereto, and any kind of sulfonic acid of a compound including a sulfur atom usable as an additive in the related art or metallic salt thereof may be acceptable.

[0069] The nonionic water soluble polymer may be one or more selected from the group consisting of polyethylene glycol, polyglycerine, hydroxyethyl cellulose, carboxymethylcellulose, Nonylphenol polyglycol ether, Octane diol-bis-(polyalkylene glycol ether, ocatanol polyalkylene glycol ether, Oleic acid polyglycol ether, polyethylene propylene glycol, polyethylene glycol dimethyl ether, polyoxypropylene glycol, polyvinyl alcohol, β-naphthol polyglycol ether, stearic acid polyglycol eter, andStearyl alcohol polyglycol ether, but is not essentially limited thereto, and any kind of water soluble polymer usable as an additive in the related art may be acceptable. For example, molecular weight of the polyethylene glycol may be 2,000 to 20,000.

[0070] The phenazinium-based compound may be one or more selected from the group consisting of safranine-O, Janus Green B, and the like.

[0071] A temperature of the cooper electrolyte used in the fabricating method may be 30 to 60°C, but is not essentially limited to the range, and may be appropriately adjusted within a range, in which the object of the present invention may be achieved. For example, a temperature of the copper electrolyte may be 40°C to 50°C.

[0072] A current density used in the fabricating method may be 20 to 500 A/dm^2, but is not essentially limited to the range, and may be appropriately adjusted within a range, in which the object of the present invention may be achieved. For example, the current density may be 30 to 40 A/dm^2. The copper electrolyte may be a sulfuric acid-copper sulphate electrolyte. A concentration of Cu^{2+} ions in the sulfuric acid-copper sulphate electrolyte may be 60 g/L to 180 g/L, but is not essentially limited to the range, and may be appropriately adjusted within a range, in which the object of the present invention may be achieved. For example, the concentration of Cu^{2+} ions may be 65 g/L to 175 g/L.

[0073] The copper electrolyte may be fabricated by a publicly known method. For example, the concentration of Cu^{2+} ions may be obtained by adjusting the amount of copper ions or copper sulfonate added, and the concentration of SO_4^{2+} ions may be obtained by adjusting the amount of sulfuric acid or copper sulfonate added.

[0074] A concentration of the additives included in the copper electrolyte may be obtained from the input amount and molecular weight of additives input into the copper electrolyte, or by analyzing the additives included in the copper electrolyte by a publicly known method, such as column chromatography.

[0075] The electrodeposited copper foil may be fabricated by a publicly known method except for the use of the copper electrolyte.

[0076] For example, the electrodeposited copper foil may be fabricated by supplying the copper electrolyte between a negative electrode surface on a curved surface of titanium of a rotating titanium drum and a positive electrode surface and electrolyzing the copper electrolyte, extracting the electrodeposited copper foil on the negative electrode surface, and continuously winding the extracted electrodeposited copper.

[0077] Hereinafter, the present invention will be described in detail with reference to Examples, but the present invention is not limited thereto.

(Fabricate the electrodeposited copper foil)

Example 1

[0078] In order to fabricate the electrodeposited copper foil by electrolysis, a 3 L electrolytic bath system which is capable of being circulated at 20 L/min was used, and a temperature of the copper electrolyte was uniformly maintained at 45°C. A dimensionally Stable Electrode (DSE) plate having a thickness of 5 mm and a size of 10 x 10 cm^2 was used as a positive electrode, and a titanium electrode plate having the same size and thickness as those of the positive electrode was used as a negative electrode.

[0079] For a smooth movement of Cu^{2+} ions, plating was performed with a current density of 35 A/dm^2, and the electrodeposited copper foil having a thickness of 18 μm was fabricated.

[0080] A basic composition of the copper electrolyte is as follows.

$CuSO_4 \cdot 5H_2O$: 250 to 400 g/L

H_2SO_4: 80 to 150 g/L

[0081] Chlorine ions and additives were added to the copper electrolyte, and the compositions of the added additives and chlorine ions are represented in Table 1 below. In Table 1 below, ppm means the same concentration as mg/L.

[0082] An SEM picture of a surface of a matte side (M side) of the fabricated electrodeposited copper foil is represented in FIG. 7.

Examples 2 to 4 and Comparative Examples 1 to 4

[0083] An electrodeposited copper foil was fabricated by the same method as that of Example 1, except for the change in the composition of the copper electrolyte as represented in Table 1 below. The SEM pictures of surfaces of matte sides of the electrodeposited copper foils fabricated in Examples 2 to 4 and Comparative Examples 1 to 4 are represented in FIGs. 8 to 14, respectively.

[Table 1]

	Example 1	Example 2	Example3	Example 4	Comparative Example 1	Comparative Example2	Comparative Example 3	Comparative Example 4
Concentrati	20	20	20	20	40	40	35	40

(continued)

	Example 1	Example 2	Example3	Example 4	Comparative Example 1	Comparative Example2	Comparative Example 3	Comparative Example 4
on of chlorine [ppm]								
DET [ppm]	3	2	3	3			1.5	7
SPS [ppm]	60	45		45	55	55		
MPS [ppm]			60				5	20
PEG [ppm]	20	20	20	20				
ZPS [ppm]	40	10	40	30				
JGB [ppm]		3						
SAO [ppm]	3		3	3				
2M-SS[ppm]					30	40		
DDAC [ppm]					70	70		
PGL [ppm]							30	10

Abbreviations in Table 1 mean compounds below.
DET: Diethyl thiourea
SPS: Bis-(3-sulfopropyl)-disulfide
MPS: 3-macapto-1-propane sulfonic acid
PEG: Polyethylene glycol (Kanto Chemical Cas No. 25322-68-3)
ZPS: 3-(benzothiazolyl-2-macapto)-propyl-sulfonic acid sodium salt
JGB: Janus Green B
2M-SS: 2-mercapto-5-benzoimidazole sulfonic acid sodium salt
DDAC: Diallyl dimethyl ammonium chloride
PGL: Polygylcerine (KCI, PGL 104 KC)

Evaluative Example 1: SEM test

[0084] The surfaces of the matte sides of the electrodeposited copper foils obtained in Examples 1 to 4, and Comparative Examples 1 to 4 were measured with the SEM, and results of the measurement are represented in FIGs. 7 to 14, respectively.

[0085] As illustrated in FIGs. 7 to 14, the electrodeposited copper foils obtained in Examples 1 to 4 had lower surface roughness than those of the electrodeposited copper foils of Comparative Examples 1 to 4.

Evaluative Example 2: Evaluation of glossiness

[0086] Glossiness of the surfaces of the matte sides of the electrodeposited copper foils obtained in Examples 1 to 4, and Comparative Examples 1 to 4 were measured. The glossiness is a value measured according to JIS Z 871-1997.

[0087] The glossiness was measured by radiating measurement light to the surface of the cooper foil at an incident angle of 60° according to a flow direction (an MD direction) of the electrodeposited copper foil, and measuring intensity of light reflected an a reflection angle of 60° under the glossiness measuring method JIS Z 8741-1997.

[0088] The measurement results are represented in Table 2 below.

[Table 2]

	Glossiness [Gs(60°)]
Example 1	700
Example 2	699

(continued)

	Glossiness [Gs(60°)]
Example 3	630
Example 4	680
Comparative Example 1	438
Comparative Example 2	472
Comparative Example 3	353
Comparative Example 4	451

[0089] As represented in Table 2, the electrodeposited copper foil of Examples 1 to 4 exhibit improved glossiness compared to the electrodeposited copper foils of Comparative Examples 1 to 4.

Evaluative Example 3: XRD test

[0090] XRD spectrums of the surfaces of the electrodeposited copper foils obtained in Examples 1 to 4, and Comparative Examples 1 to 4 were measured. The XRD spectrum of Example 1 is illustrated in FIG. 6.

[0091] As illustrated in FIG. 6, peak strength of the (111) crystalline surface is largest, and the peak strength of the (200) crystalline surface is the next.

[0092] A ratio I(200)/I(111) of strength (I(200)) of a diffraction peak for the (200) crystalline surface to strength (I(111)) of a diffraction peak for the (111) crystalline surface is 0.605.

[0093] Further, in the XRD spectrum for the matte side, orientation indexes M for the (111), (200), (220), (311), and (222) crystalline surfaces were measured, and the measurement results are represented in Table 3 below.

[0094] The orientation index was measured by using the orientation index M suggested by S.Yoshimura, S. Yoshihara, T.Shirakashi, E.Sato, Electrochim. Acta 39, 589(1994).

[0095] For example, in a specimen having the (111) surface, the orientation index M is calculated by a method below.

$$IFR(111)=IF(111)/\{IF(111)+IF(200)+IF(220)+IF(311)\}$$

$$IR(111)=I(111)/\{I(111)+I(200)+I(220)+I(311)\}$$

$$M(111)=IR(111)/IFR(111)$$

[0096] IF(111) is XRD strength in a JCPDS card, and I(111) is an experiment value. When M(111) is larger than 1, preferred orientation is parallel to the (111) surface, and when M(111) is smaller than 1, it means preferred orientation is decreased.

[Table 3]

Crystalline surface	(111)	(200)	(220)	(311)	(222)
Orientation index	1.02	1.34	0.80	0.25	0.97

[0097] Referring to Table 3, in the XRD spectrum for the matte side, M(200)/M(111) that is a ratio of an orientation index (M(200)) for the (200) crystalline surface to an orientation index (M(111)) for the (111) crystalline surface is 1.31.

Evaluative Example 4: Measurement of surface roughness (Rz, Ra, and Rmax)

[0098] Surface roughness Rz, Ra, and Rmax of the matte sides of the electrodeposited copper foils obtained in Examples 1 to 4, and Comparative Examples 1 to 4 was measured under the standard JISB 0601-1994. The surface

roughness Rz, Ra, and Rmax obtained by the measurement method is represented in Table 4 below. A small value means low roughness.

[0099] Evaluative Example 5: Measurement of room-temperature tensile strength, room-temperature elongation rate, high-temperature tensile strength, and high-temperature elongation rate

[0100] A maximum load of the tensile strength measured by extracting tension specimens having a width of 12.7 mm x and a gauge length of 50 mm from the electrodeposited copper foils obtained in Examples 1 to 4 and Comparative Examples 1 to 4, and then performing a tension test at a crosshead speed of 50.8 mm/min under the standard IPC-TM-650 2.4.18B was referred to as room-temperature tensile strength, and an elongation rate at the fracture in this case was referred to as a room-temperature elongation rate. Here, the normal temperature is 25°C.

[0101] The same electrodeposited copper foil as the electrodeposited copper foil used for measuring the tensile strength and the elongation rate at the room temperature was heat treated for one hour at 180°C and then taken out, and tensile strength and an elongation rate of the electrodeposited copper foil were measured by the same method, and the measured tensile strength and the measured elongation rate of the electrodeposited copper foil were referred to as high-temperature tensile strength and a high-temperature elongation rate, respectively.

[0102] The room-temperature tensile strength, the room-temperature elongation rate, the high-temperature tensile strength, the high-temperature elongation rate obtained by the measurement method are represented in Table 4 below.

[Table 4]

	Rmax [μm]	Rz [μm]	Ra [μm]	(Rmax - Rz) /Ra	Room-temperature tensile strength [kgf/mm^2]	Room-temperature elongation rate [%]	High-temperature tensile strength [kgf/mm^2]	High-temperature elongation rate [%]
Example 1	0.81	0.30	0.08	6.37	46.15	7.21	43.30	11.63
Example 2	0.73	0.28	0.07	6.42	42.28	5.00	40.16	12.06
Example 3	0.89	0.38	0.10	5.10	45.41	6.16	41.55	9.38
Example 4	0.91	0.44	0.11	4.27	44.74	6.62	40.78	10.53
Comparative Example 1	2.02	0.67	0.16	8.43	86.65	2.18	77.91	3.30
Comparative Example 2	1.81	0.48	0.10	13.30	98.76	1.30	92.30	1.74
Comparative Example 3	3.84	0.46	0.24	14.08	52.81	1.64	49.53	1.87
Comparative Example 4	3.63	0.38	0.25	13.00	70.73	1.71	64.30	1.47

[0103] As represented in Table 4, surface roughness Rz of the electrodeposited copper foils of Examples 1 to 4 is less than 0.5 μm, which is low, tensile strength after a high-temperature heat treatment of the electrodeposited copper foils of Examples 1 to 4 is 40 kgf/mm^2 or more, and most of the elongation rates of the electrodeposited copper foils of Examples 1 to 4 are 10% or more, which is high.

[0104] By contrast, the electrodeposited copper foils of Comparative Examples 1 to 4 have higher surface roughness and lower elongation rates after the high-temperature heat treatment compared to of the electrodeposited copper foils of Examples 1 to 4, so that the electrodeposited copper foils of Comparative Examples 1 to 4 are not appropriate to be used as a negative electrode current collector for a secondary battery and/or a low rough copper foil for a PDB/FPC.

[0105] Further, it is represented that values of (Rmax - Rz)/Ra of Examples 1 to 4 are 6.5 or less, which is low, but values of (Rmax - Rz)/Ra of Comparative Examples 1 to 4 are 6.5 or more, which is high. Accordingly, as can be seen in Table 2, glossiness of the electrodeposited copper foils of Examples 1 to 4 is 600 or more, so that the electrodeposited copper foils of Examples 1 to 4 exhibit high glossiness even without a post-treatment process, but the electrodeposited copper foils of Comparative Examples 1 to 4 exhibit glossiness of 500 or less.

Evaluative Example 6: Measurement of a degree of corner curling

[0106] Specimens having a width 10 cm x a length 10 cm were extracted from the electrodeposited copper foils obtained in Examples 1 to 4 and Comparative Examples 1 to 4, the extracted specimens were laid on a flat floor and were cut at an angle (corner curl angle), at which corner portions were bent and in a shape of "X", and then heights (corner curl height), by which the cut portions were rolled up, were measured, and the measurement results are represented in Table 5 below.

[Table 5]

	Corner curl angle (°)	Corner curl height (mm)
Example 1	5	4
Example 2	15	12
Example 3	8	6
Example 4	30	26
Comparative Example 1	52	48
Comparative Example 2	48	44
Comparative Example 3	46	43
Comparative Example 4	50	46

[0107] As represented in Table 5, the corner curl angles of the electrodeposited copper foils of Examples 1 to 4 are 5° to 30°, which are equal to or less than 45°. However, the corner curl angles of the electrodeposited copper foils of Comparative Examples 1 to 4 are 46° to 52°, which are larger than 45°, so that it is represented that the electrodeposited copper foils of Comparative Examples 1 to 4 are difficult to be treated during a subsequent process. Further, the corner curl heights of the electrodeposited copper foils of Comparative Examples 1 to 4 exceed 40 mm, so that the electrodeposited copper foils of Comparative Examples 1 to 4 exhibit poor quality states. Accordingly, the electrodeposited copper foil according to the present invention has high strength and low internal stress, thereby exhibiting a little corner curl phenomenon and excellent performance.

[0108] The present invention is not limited to the exemplary embodiments and the accompanying drawings, and shall be construed by the accompanying claims. Further, it is apparent to those skilled in the art that the present invention may be substituted, modified, and changed into various forms within the scope without departing from the technical spirit of the present invention described in the claims.

Claims

1. An electrodeposited copper foil, in which a center line roughness average Ra (μm), a maximum height Rmax (μm), and a ten-point height average Rz (μm) of a matte side satisfy an Equation below, $1.5 \leq (Rmax - Rz)/Ra \leq 6.5$.

2. The electrodeposited copper foil of claim 1, wherein tensile strength of the electrodeposited copper foil before a

heat treatment is 40 kgf/mm^2 to 70 kgf/mm^2.

3. The electrodeposited copper foil of claim 1, wherein tensile strength of the electrodeposited copper foil after a heat treatment for one hour at 180°C is 40 kgf/mm^2 to 70 kgf/mm^2.

4. The electrodeposited copper foil of claim 1, wherein tensile strength of the electrodeposited copper foil after a heat treatment for one hour at 180°C is 40 kgf/mm^2 to 70 kgf/mm^2.

5. The electrodeposited copper foil of claim 3, wherein tensile strength of the electrodeposited copper foil after the heat treatment is 85% to 99% of tensile strength of the electrodeposited copper foil before the heat treatment.

6. The electrodeposited copper foil of claim 1, wherein an elongation rate before a heat treatment is 2% to 15%.

7. The electrodeposited copper foil of claim 1, wherein an elongation rate after a heat treatment is 4% to 15%.

8. The electrodeposited copper foil of claim 1, wherein an elongation rate after a heat treatment for one hour at 180 °C is 4% to 15%.

9. The electrodeposited copper foil of claim 3, wherein an elongation rate after a heat treatment is one time to 4.5 times of an elongation rate before the heat treatment.

10. The electrodeposited copper foil of claim 1, wherein a corner curl angle of the electrodeposited copper foil is 0° to 45°.

11. The electrodeposited copper foil of claim 1, wherein a corner curl height of the electrodeposited copper foil is 0 mm to 40 mm.

12. The electrodeposited copper foil of claim 1, wherein the electrodeposited copper foil has a thickness of 2 μm to 10 μm.

13. A battery including the electrodeposited copper foil of any one of claims 1 to 12.

14. An electrical component, comprising:

an insulating base material; and
the electrodeposited copper foil of any one of claims 1 to 12 attached onto one surface of the insulating base material.

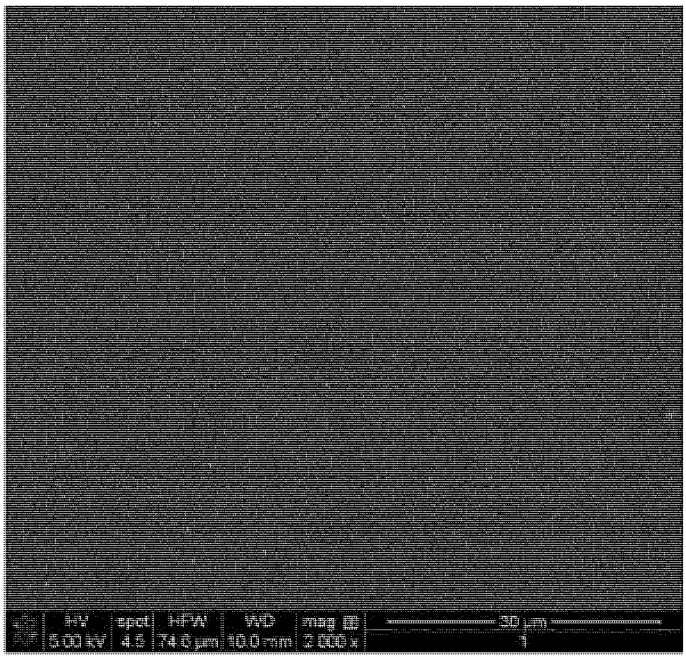


FIG.1

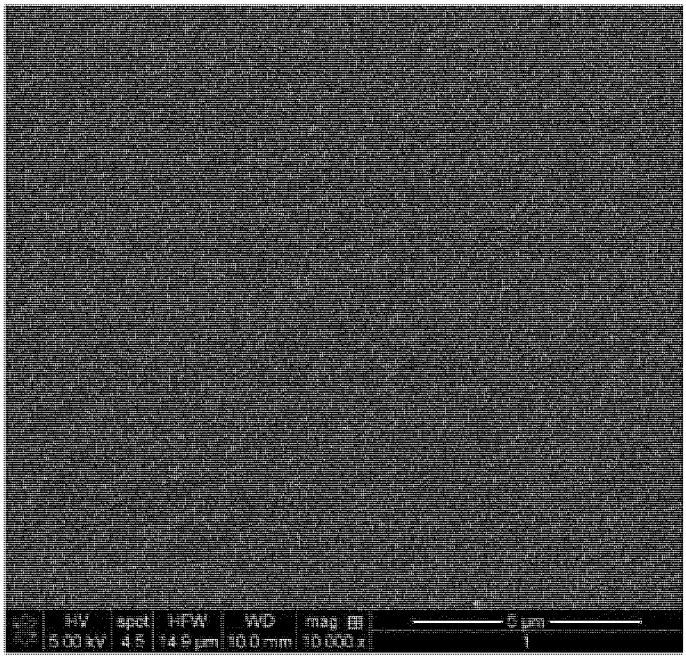


FIG.2

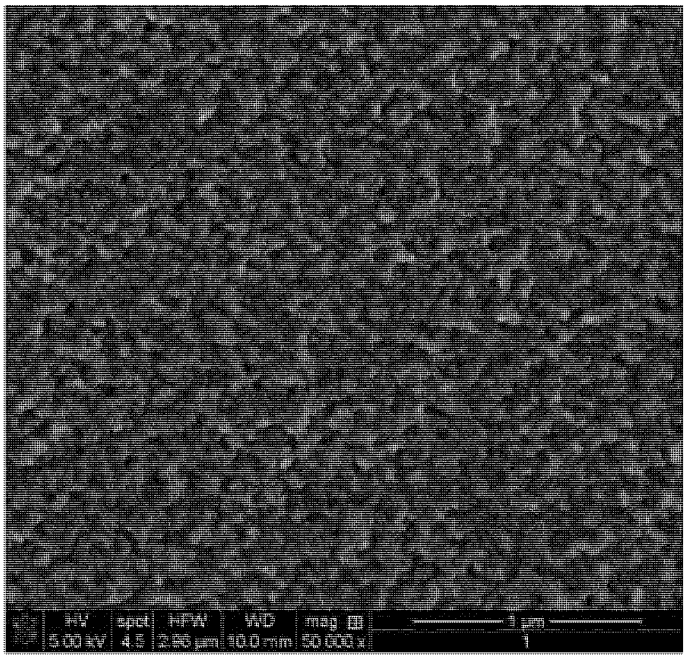


FIG.3

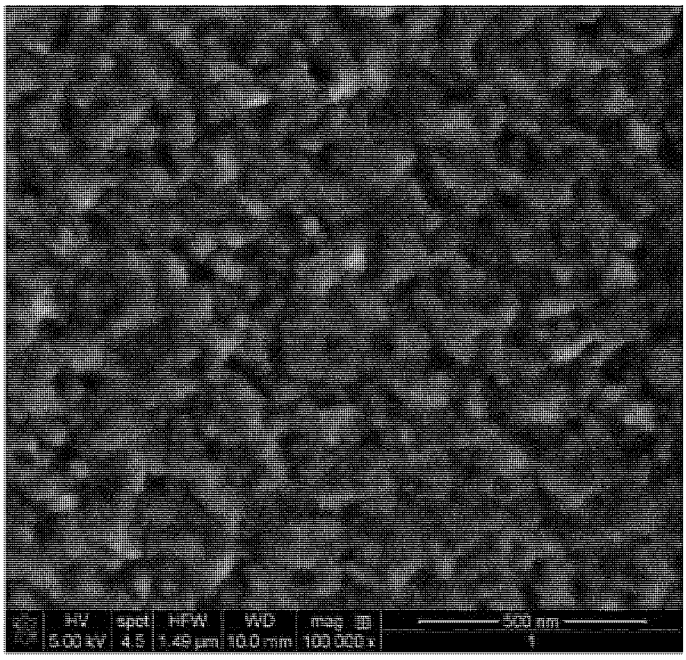


FIG.4

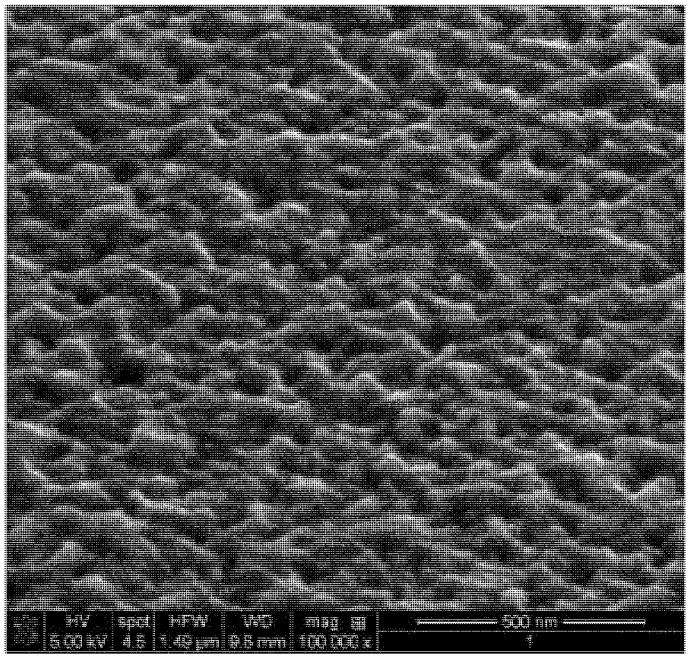

HV
spot
HFW
WD
mag
5.00 kV
4.5
1.49 µm
9.5 mm
100 000 x
500 nm

FIG.5

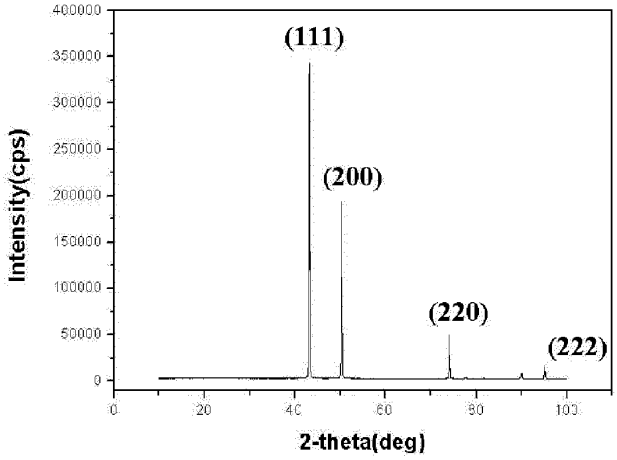

(111)
(200)
(220)
(222)
Intensity(cps)
2-theta(deg)
400000
350000
300000
250000
200000
150000
100000
50000
0
0
20
40
60
80
100

FIG.6

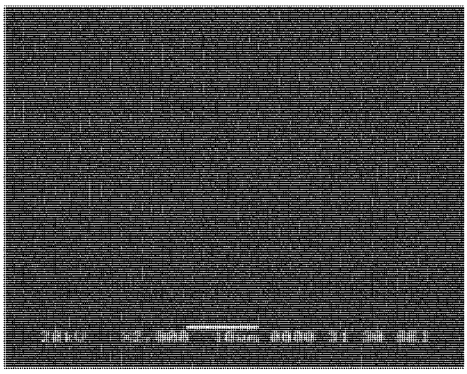


FIG.7



FIG.8

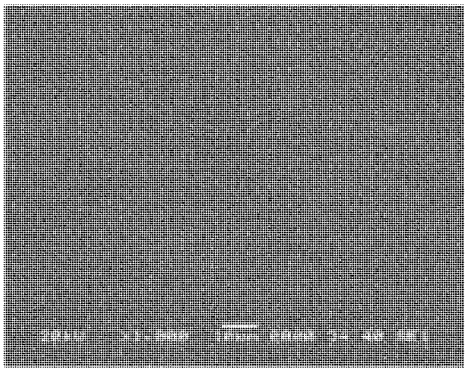


FIG.9

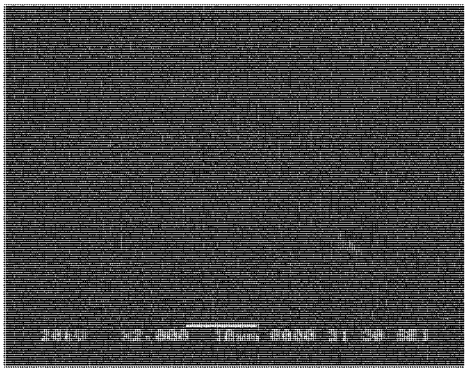


FIG.10

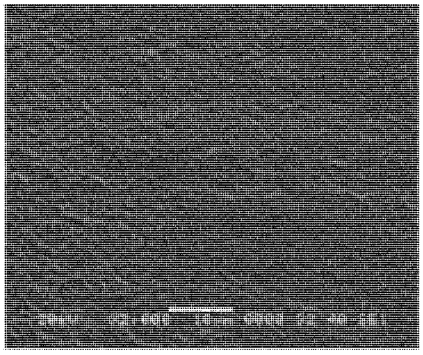


FIG.11

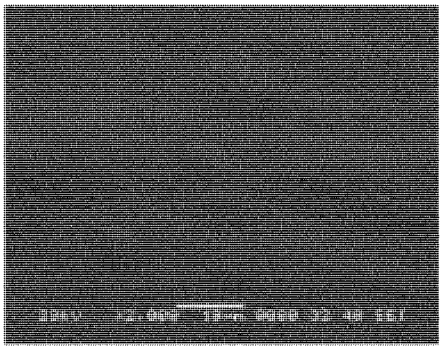


FIG.12

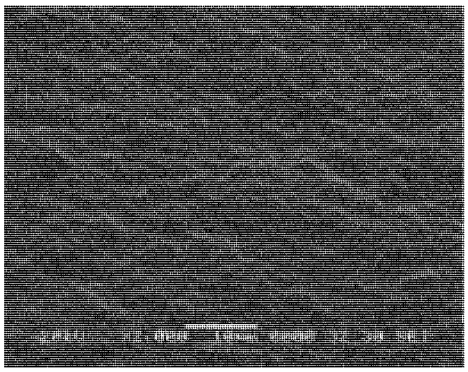


FIG.13



FIG.14

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2014/010737

A. CLASSIFICATION OF SUBJECT MATTER

B32B 15/20(2006.01)i, H05K 1/05(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)

B32B 15/20; C25D 3/38; C25C 1/12; H05K 3/00; C25D 1/04; C25D 1/00; B29C 65/02; H05K 1/05

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility models and applications for Utility models: IPC as above
Japanese Utility models and applications for Utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS (KIPO internal) & Keywords: Ra, Rz, Rmax, Rmax, Rz, Rz, electrolytic copper foil, tensile strength, elongation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2007-0107803 A (MITSUI MINING & SMELTING CO., LTD.) 07 November 2007 See paragraphs [0010]-[0027] and [0085]-[0088].	1-14
A	KR 10-0195603 B1 (MITSUI MINING & SMELTING CO., LTD.) 15 June 1999 See page 4, lines 14-48.	1-14
A	JP 2002-052614 A (KANEGAFUCHI CHEM IND CO., LTD.) 19 February 2002 See paragraphs [0014]-[0019].	1-14
A	KR 10-2011-0114971 A (ILJIN MATERIALS CO., LTD.) 20 October 2011 See paragraphs [0029]-[0031].	1-14

☐ 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
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"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
13 FEBRUARY 2015 (13.02.2015)	**16 FEBRUARY 2015 (16.02.2015)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 189 Seonsa-ro, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2014/010737

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Form PCT/ISA/210 (patent family annex) (July 2009)

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Information on patent family members

International application No.
PCT/KR2014/010737

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		WO 2011-129633 A3	01/03/2012

Form PCT/ISA/210 (patent family annex) (July 2009)

Espacenet

Bibliographic data: JP3850155 (B2) — 2006-11-29

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

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

Applicant(s): NIPPON DENKAI KK

Classification: **- international:** ***C25D1/04; H01M10/28; H01M4/64; H01M4/66***
- cooperative:

Application number: JP19980353213 19981211

Priority number (s): JP19980353213 19981211

Also published as: JP2000182623 (A)

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.

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H01M	4/64	(2006.01)	H01M	4/64	A
H01M	4/66	(2006.01)	H01M	4/66	A
H01M	10/40	(2006.01)	H01M	10/40	Z

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(73)特許権者　000232014
日本電解株式会社
茨城県筑西市下江連１２２６番地
(74)代理人　100086494
弁理士　穂高　哲夫
(72)発明者　張ヶ谷　浩一
茨城県下館市下江連１２２６番地　日本電解株式会社下館工場内
(72)発明者　野口　英男
茨城県下館市下江連１２２６番地　日本電解株式会社下館工場内
(72)発明者　小林　勝己
茨城県下館市下江連１２２６番地　日本電解株式会社下館工場内

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)【特許請求の範囲】
【請求項1】
銅箔中の炭素含有量が５ｐｐｍ以下、硫黄含有量が３ｐｐｍ以下、酸素含有量が５ｐｐｍ以下、窒素含有量が０．５ｐｐｍ以下であり、かつ炭素、硫黄、酸素、窒素及び水素の合計含有量が１５ｐｐｍ以下であることを特徴とする電解銅箔。
【請求項2】
請求項１記載の電解銅箔からなることを特徴とするリチウムイオン二次電池の集電体用銅箔。
【請求項3】
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リチウムイオン二次電池において、負極の平面状集電体が請求項１記載の電解銅箔であることを特徴とするリチウムイオン二次電池。

【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Ｖ

ＴＲ、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、硫黄含有量が３ｐｐｍ以下、酸素含有量が５ｐｐｍ以下、窒素含有量が０．５ｐｐｍ以下であり、かつ炭素、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リチウムイオン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リチウムイオン二次電池において、負極の平面状集電体が上記の電解銅箔であることを特徴とするリチウムイオン二次電池に関する。
【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／mm²）		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／ｍｍ²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。

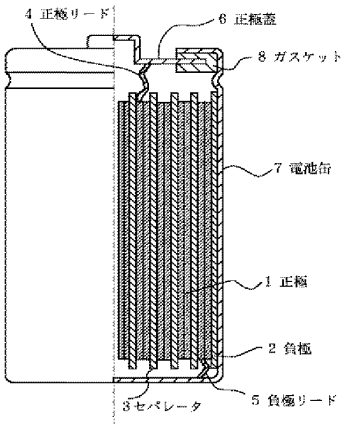
【図面の簡単な説明】

【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】



(72)発明者　阿曽　和義
茨城県下館市下江連１２２６番地　日本電解株式会社下館工場内

審査官　青木　千歌子

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特開平１０－１０６６２９（ＪＰ，Ａ）

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JP2001011684A - PRODUCTION OF ELECTROLYTIC COPPER FOIL

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Abstract

PROBLEM TO BE SOLVED: To provide a method for manufacturing electrolytic copper foil by which the electrolytic copper foil which is thin, has large tensile strength and high rigidity and thereby is excellent in handling easiness, both surfaces of which are smooth and have equal surface roughness and which is excellent in extension percentage, can be manufactured by using an electrolytic solution obtained from inexpensive copper scrap. SOLUTION: Copper scrap is subjected to sintering treatment and then to pickling treatment. Obtained processed copper is dissolved in a sulfuric acid aqueous solution to produce an electrolytic solution. Obtained electrolytic solution is subjected to electrolysis to deposit copper.; The sintering treatment is desirably executed by blowing hot air of 500 to 800 deg.C to the copper scrap for 1 to 30 minutes and the pickling treatment is desirably executed by oscillating the sintering-treated copper scrap in the sulfuric acid aqueous solution of 0.1 to 2.0 mol/l.

Description

[0001] BACKGROUND OF THE INVENTION 1. Field of the Invention The present invention relates to a method of manufacturing an electrolytic copper foil suitably used as a circuit of an electronic part or a negative electrode of a lithium secondary battery.

[0002] 2. Description of the Related Art The process for producing electrodeposited copper foil comprises a dissolving step of dissolving a copper raw material in an electrolytic solution and a copper depositing step of depositing copper by electrolysis using an electrolytic solution containing a copper raw material dissolved therein It is a composite process and it is necessary to dissolve copper raw material in the electrolyte corresponding to the deposited copper.Copper raw materials are inexpensive and copper scraps with large surface area are used.As the copper scraps, it is common to use scrap copper wire which is chopped, but others such as those obtained by chopping molten extruded products are also used.These copper scraps are contaminated by wire drawing oil at the time of extrusion processing, impurities derived from the

coating material, impurities attached at the time of scraping and shredding.

[0003] In recent years, in order to realize a high-density electronic circuit, a thin electrolytic copper foil suitable for forming a fine circuit is desired.There is known a method of producing a thin electrodeposited copper foil by electrolysis using an electrolytic solution prepared by adding organic substances or chlorides such as gelatin to a copper sulfate aqueous solution in which a copper raw material is dissolved in an aqueous solution of sulfuric acid but this method The electrodeposited copper foil thus obtained had a low tensile strength and poor rigidity, which made handling difficult.In addition, the electrolytic copper foil obtained by this manufacturing method had a relatively large surface roughness on the copper foil precipitation surface side and had a nonuniform thickness, so that there was a tendency for the thin copper foil to cause wrinkles etc. .Furthermore, the large surface roughness causes overetching and has a problem of hindering the formation of microcircuits.

[0004] SUMMARY OF THE INVENTION An object of the present invention is to provide an electrolytic solution obtained from conventionally used inexpensive copper scrap, which is thin, has high tensile strength and high rigidity, Which can produce an electrodeposited copper foil having excellent smoothness, smooth surface on both sides and equivalent surface roughness, and excellent in elongation percentage.

[0005] As a result of diligent research aimed at achieving the above object, the present inventors have found that when copper scrap is used as a copper raw material to be dissolved in an electrolytic solution and copper scrap is calcined By using pickled copper waste obtained by pickling treatment, it is thin, has high tensile strength and high rigidity, it is excellent in handleability, has smooth surface on both sides and has the same surface roughness, elongation The present inventors have found that an electrolytic copper foil having an excellent rate can be produced, and based on this finding, the present invention has been completed.

[0006] [0006] That is, the present invention relates to a method for producing an electrolytic solution, which comprises the steps of calcining copper waste and then pickling the treated copper scrap, dissolving the treated copper scrap in an aqueous sulfuric acid solution to prepare an electrolyte solution, Wherein copper is precipitated by decomposition of the electrolytic copper foil.

[0007] Since the electrolytic copper foil obtained by the present invention is thin and has high tensile strength and is suitable for formation of a fine circuit and excellent in elongation percentage, for example, it is based on thermal

expansion when used as an inner layer circuit It is possible to prevent a disconnection failure and has extremely excellent characteristics as a copper foil for an electronic circuit.Furthermore, since both surfaces are smooth and have the same surface roughness and high rigidity, it is easy to coat both sides of the active material mixture for a secondary battery, and since the elongation ratio is excellent, lithium secondary secondary It is a very useful copper foil as a copper foil for a negative electrode plate of a battery.

[0008] DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS As the copper scrap used in the present invention, those having a copper content of not less than 99% not contaminating foreign matter or dissimilar materials are preferably used.More preferably, No. 1 nugget copper defined in JIS H 2109 is used.This is inexpensively available copper scrap, a copper wire or copper wire with a nugget processed (short cut line), which is pure and has a copper content of 99.9% or more.Also, it is one in which foreign materials such as copper-clad steel wire and foreign matter are not mixed.In addition, No. 1 copper wire scrap specified in JIS H 2109 can be used.In the present invention, an electrolytic solution is prepared by dissolving treated copper scrap obtained by burning and pickling copper waste in sulfuric acid.

[0009] By performing the firing treatment, oxidized and burned surface deposits of copper scrap are oxidized and the oxidized surface is easily eroded with acid, so pickling efficiency improves, and deposits such as oils and the like So that it can be easily removed.Conditions for the calcination treatment are such that a thin copper oxide layer is formed on the surface of the copper scrap, and it is preferable to subject the copper scrap to an oxidizing atmosphere at 500 ° C. to 800 ° C., preferably for 1 minute to 30 minutes .This operation may be repeated.Specifically, it is performed by blowing hot air of 500 to 800 ° C. for 1 minute to 30 minutes to the object to be treated.Although there is no limitation on the type of firing treatment apparatus used in the firing treatment, oxidation proceeds by flowing copper scrap inside, so that one having an appropriate swinging mechanism and stirring mechanism is preferably used.

[0010] After the firing treatment, pickling treatment is performed on the burned copper scraps.In the pickling treatment, an aqueous solution of sulfuric acid of 0.1 to 2.0 mol / l is preferably used as the pickling solution.In addition to an aqueous sulfuric acid solution, an electrolytic solution used for electrolysis can be used.Other aqueous solutions of inorganic acids or organic acids are not preferable because they cause contamination of the electrolytic solution.Although the type of the water washing machine is not limited, it is preferable to have a mechanism for sufficient contact with the copper scrap.Such a device can be realized by providing a circulation mechanism of

the pickling solution and swinging the object to be processed, or the like.The pickling treatment is carried out by rocking the object to be treated in a sulfuric acid aqueous solution preferably at a temperature of 10 ° C. to 60 ° C. for 1 minute to 30 minutes.After the pickling treatment, the treated copper scrap is thoroughly washed with pure water to remove deposits.

[0011] Next, the treated copper scrap obtained in the above is dissolved in an aqueous sulfuric acid solution.As this sulfuric acid aqueous solution, a concentration of 0.1 to 5 mol / l is preferable, and a concentration of 0.5 to 3 mol / l is more preferable.It is preferable to dissolve the copper scrap while feeding air into the sulfuric acid aqueous solution.Then, electrolysis is carried out using the obtained electrolytic solution, and copper is precipitated on the cathode.Conditions for electrolysis are not particularly limited, and are carried out under electrolysis conditions for ordinary electrolytic copper foil production.Preferably, electrolytic copper foil having a thickness of 2 μm or more can be obtained under the conditions of a current density of 5 to 150 A / dm 2 and an electrolysis time of 1 to 30 minutes.In order to obtain an electrolytic copper foil having a small thickness, that is, 2 to 10 .mu.m, current and electrolysis time are appropriately controlled.If necessary, roughening treatment and rust prevention treatment can be performed on the copper foil surface.

[0012] EXAMPLES Hereinafter, the present invention will be described more specifically with reference to examples of the present invention and comparative examples, but the present invention is not limited to these examples.

[0013] Example 1 500 g of No. 1 nugget copper (average weight 0.2 g / piece) prescribed in JIS H 2109 was placed in a platinum metal gauze and hot air of 700 ° C. was blown from the bottom for 1 minute.Nugget copper was thoroughly mixed, and hot air of 700 ° C. was again blown for 1 minute.By repeating this blowing operation 10 times, firing treatment was carried out.

[0014] Reagent Nugget copper baked to 1 mol / l sulfuric acid aqueous solution prepared from sulfuric acid was charged and rocked in an aqueous sulfuric acid solution for 3 minutes.Next, nugget copper was transferred into pure water and rocked for 3 minutes.These two operations were repeated three times.

[0015] Reagent Nugget copper which was subjected to pickling treatment was added to a 2 mol / l sulfuric acid aqueous solution prepared from sulfuric acid, and nugget copper was completely dissolved while feeding air.Note that air was passed through a sulfuric acid aqueous solution, an aqueous solution of

sodium hydroxide and silica gel, and then mixed with dust and impurities via a 0.5 μm filter was used.

[0016] Next, the concentration was adjusted to 280 g / l of copper sulfate and 80 g / l of sulfuric acid with sulfuric acid and pure water to prepare an electrolytic solution.

[0017] A titanium cylindrical electrode having a diameter of 5 cm was used as a cathode, and the surface thereof was polished using polishing paper No. 2.The surface roughness was 0.20 μm in Ra.A cylindrical lead plate was used for the anode plate, and electrolytic decomposition was carried out for 5 minutes at a liquid temperature of 40 ° C. and a current density of 10 A / dm 2 using the above electrolytic solution to precipitate a copper foil.However, the rotational speed of the cylindrical electrode was 300 rpm.The copper foil had gloss on both sides, and the thickness determined by gravimetric method was 12 μm.Measurement results of mechanical properties are shown in Table 1.

[0018] COMPARATIVE EXAMPLE 1 A copper foil was prepared in the same manner as in Example 1 except that the calcination treatment was not carried out, and mechanical properties were evaluated.The results are shown in Table 1.

[0019] Comparative Example 2 A copper foil was prepared in the same manner as in Example 1 except that the pickling treatment was not carried out, and mechanical properties were evaluated.The results are shown in Table 1.

[0020] COMPARATIVE EXAMPLE 3 Copper foils were prepared in the same manner as in Example 1 except that the calcination treatment and pickling treatment were not carried out, and the mechanical properties were evaluated.The results are shown in Table 1.

[0021] Surface roughness was measured according to JIS B 0651.Tensile strength was measured under normal conditions (23 ° C) and tensile strength after heating at 180 ° C for 1 hour based on JIS C 6515.The elongation was measured under normal conditions (23 ° C.) and tensile strength after heating at 180 ° C. for 1 hour based on JIS C 6515.

[0022] Since the electrodeposited copper foil obtained by the production method of the present invention is thin, has high tensile strength and high rigidity, it is excellent in handleability, has smooth surface on both sides and has the same surface roughness , And is extremely useful as a copper foil for an electronic circuit having a fine circuit with excellent elongation rate and a copper foil for a negative electrode plate of a lithium ion secondary battery.

Claims

[0001] Characterized in that after treatment of burning copper scraps, pickling treatment is treated to prepare an electrolytic solution by dissolving the treated copper in an aqueous sulfuric acid solution, and copper is precipitated by electrolysis using the obtained electrolytic solution Thereby forming an electrolytic copper foil.

[0002] 2. The method for producing an electrolytic copper foil according to claim 1, wherein the calcination treatment is carried out by blowing hot air of 500 to 800 ° C. to copper scrap for 1 to 30 minutes.

[0003] 3. The method for producing an electrolytic copper foil according to claim 1 or 2, wherein the pickling treatment is carried out by rocking the burned copper scrap in an aqueous sulfuric acid solution of 0.1 to 2.0 mol / l.

[0004] 4. The method for producing an electrolytic copper foil according to claim 1, 2 or 3, wherein the copper scrap is No. 1 nugget copper defined in JIS H 2109.

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APPLICANT : NIPPON DENKAI KK;

INVENTOR : ASO KAZUYOSHI;

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TITLE : PRODUCTION OF ELECTROLYTIC COPPER FOIL

ABSTRACT : PROBLEM TO BE SOLVED: To provide a method for manufacturing electrolytic copper foil by which the electrolytic copper foil which is thin, has large tensile strength and high rigidity and thereby is excellent in handling easiness, both surfaces of which are smooth and have equal surface roughness and which is excellent in extension percentage, can be manufactured by using an electrolytic solution obtained from inexpensive copper scrap.

SOLUTION: Copper scrap is subjected to sintering treatment and then to pickling treatment. Obtained processed copper is dissolved in a sulfuric acid aqueous solution to produce an electrolytic solution. Obtained electrolytic solution is subjected to electrolysis to deposit copper. The sintering treatment is desirably executed by blowing hot air of 500 to 800°C to the copper scrap for 1 to 30 minutes and the pickling treatment is desirably executed by oscillating the sintering-treated copper scrap in the sulfuric acid aqueous solution of 0.1 to 2.0 mol/l.

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(71)出願人　000232014
日本電解株式会社
東京都文京区本郷四丁目９番25号
(72)発明者　張ヶ谷　浩一
茨城県下館市下江連1226番地　日本電解株式会社下館工場内
(72)発明者　野口　英男
茨城県下館市下江連1226番地　日本電解株式会社下館工場内
(74)代理人　100086494
弁理士　穂高　哲夫

最終頁に続く

(54)【発明の名称】　電解銅箔の製造方法

(57)【要約】
【課題】　安価な銅くずから得られる電解液を用いて、薄くて引張強度が大きく、剛性が高いことから取扱性に優れ、両面が平滑で同等の表面粗さを有し、伸び率に優れた電解銅箔を製造することができる電解銅箔の製造方法を提供する。
【解決手段】　銅くずを焼成処理した後、酸洗処理して得られた処理銅を硫酸水溶液に溶解して電解液を作製し、得られた電解液を用いて電気分解により銅析出を行う電解銅箔の製造方法。

【特許請求の範囲】
【請求項１】　銅くずを焼成処理した後、酸洗処理して得られた処理銅を硫酸水溶液に溶解して電解液を作製し、得られた電解液を用いて電気分解により銅析出を行うことを特徴とする電解銅箔の製造方法。
【請求項２】　焼成処理が、銅くずに５００～８００℃の熱風を１～３０分間送風することにより行われる請求項１記載の電解銅箔の製造方法。
【請求項３】　酸洗処理が、焼成処理した銅くずを０．１～２．０ｍｏｌ／ｌの硫酸水溶液中で揺動させることにより行われる請求項１又は２記載の電解銅箔の製造方法。
【請求項４】　銅くずがＪＩＳ　Ｈ　２１０９に規定される１号ナゲット銅である請求項１、２又は３記載の電解銅箔の製造方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、電子部品の回路やリチウム二次電池の負極に好適に用いられる電解銅箔の製造方法に関する。
【０００２】
【従来の技術】電解銅箔の製造工程は、銅原料を電解液に溶解させる溶解工程と銅原料を溶解した電解液を用いて電気分解により銅を析出させる銅析出工程とからなる複合工程であり、析出する銅に見合うだけの銅原料を電解液に溶解させる必要がある。銅原料としては安価であり、表面積の大きな銅くずが使用されている。銅くずとしては、スクラップ銅線を細断したものを用いるのが一般的であるが、その他、溶融押出品を細断したものなども用いられている。これらの銅くずは、押出加工時の伸線油や被覆材料由来の不純物、スクラップ化及び細断時に付着した不純物により汚染されている。
【０００３】近年、高密度電子回路を実現するため、微細回路形成に適した薄い電解銅箔が望まれている。銅原料を硫酸水溶液に溶解させた硫酸銅水溶液にゼラチンなど有機物や塩化物などを添加した電解液を用い、電気分解により薄い電解銅箔を製造する方法が知られているが、この方法により得られた電解銅箔は引張強度が小さく、剛性に乏しいため取扱が難しいという難点があった。また、この製造方法で得られた電解銅箔は銅箔析出面側の表面粗さが比較的大きく、厚さが不均一であるため、薄銅箔ではしわなどの原因となる傾向があった。さらに、表面粗さが大きいことはオーバーエッチングの原因となり、微細回路の形成に支障をきたすという問題があった。
【０００４】
【発明が解決しようとする課題】本発明の目的は、従来から使用されている安価な銅くずから得られる電解液を用いて、薄くて引張強度が大きく、剛性が高いことから取扱性に優れ、両面が平滑で同等の表面粗さを有し、伸び率に優れた電解銅箔を製造することができる電解銅箔の製造方法を提供することにある。
【０００５】
【課題を解決するための手段】本発明者らは、前記目的を達成するために鋭意研究を重ねた結果、電解液に溶解する銅原料として銅くずを用い、銅くずを焼成処理した後、酸洗処理して得られた処理銅くずを用いることにより、薄くて引張強度が大きく、剛性が高いことから取扱性に優れ、両面が平滑で同等の表面粗さを有し、伸び率に優れた電解銅箔を製造することができることを見出し、この知見に基づいて本発明を完成するに至った。
【０００６】すなわち、本発明は、銅くずを焼成処理した後、酸洗処理して得られた処理銅くずを硫酸水溶液に溶解して電解液を作製し、得られた電解液を用いて電気分解により銅析出を行うことを特徴とする電解銅箔の製造方法を提供するものである。
【０００７】本発明により得られた電解銅箔は、薄くて引張強度が大きく、微細回路の形成に適し、伸び率に優れていることから、例えば、内層回路として用いた場合に熱膨張に基づく断線不良を防止することができ、電子回路用銅箔として極めて優れた特性を有している。さらに、両面が平滑で同等の表面粗さを有し、剛性が高いことから二次電池用活物質合剤の両面塗工が容易であり、また、伸び率に優れることから、リチウムイオン二次電池の負極板用銅箔としても極めて有用な銅箔である。
【０００８】
【発明の実施の形態】本発明において用いられる銅くずとしては、好ましくは、異物、異材を混入しない銅分が９９％以上のものが用いられる。より好ましくは、ＪＩＳ　Ｈ　２１０９に規定される１号ナゲット銅が用いられる。これは、安価に入手できる銅くずで、銅線又は銅より線をナゲット加工した（短切線）純良なもので、銅分が９９．９％以上のものである。また、銅覆鋼線など異材及び異物が混入していないものである。また、ＪＩＳ　Ｈ　２１０９に規定される１号銅線くずも使用可能である。本発明においては、この銅くずに焼成処理と酸洗処理を行って得られた処理銅くずを硫酸に溶解して電解液を作製する。
【０００９】焼成処理を行うことにより、銅くずの表面付着物が酸化・燃焼するとともに、酸化された表面が酸で容易に浸食されるため、酸洗効率が向上し、油分などの付着物が容易に除去できるようになる。焼成処理の条件は銅くずの表面に薄い酸化銅層が形成される条件が適切であり、好ましくは銅くずを５００℃～８００℃の酸化雰囲気に、好ましくは１分～３０分間さらすことにより行われる。この操作を繰り返し行ってもよい。具体的には被処理物に５００～８００℃の熱風を１分～３０分送風することにより行われる。焼成処理に用いられる焼成処理装置の形式は問わないが、内部で銅くずを流動させることで酸化が進むため、適切な揺動機構や撹拌機構

を有するものが好ましく用いられる。

【００１０】焼成処理を行った後、焼成処理された銅くずに酸洗処理を行う。酸洗処理において、酸洗液としては０．１～２．０ｍｏｌ／ｌの硫酸水溶液が好ましく用いられる。硫酸水溶液のほか、電気分解に用いる電解液を用いることもできる。その他の無機酸や有機酸の水溶液は、電解液の汚染原因となることから好ましくない。水洗装置も形式を問わないが、銅くずと十分に接触するための機構を有することが好ましい。このような装置は、酸洗液の循環機構を設けて被処理物を撹動させるなどによって実現可能である。酸洗処理は硫酸水溶液中で被処理物を好ましくは１０℃～６０℃の温度で、１分～３０分間撹動させることにより行われる。酸洗処理後に純水を用いて処理銅くずを十分に洗浄し、付着物を除去する。

【００１１】次に、上記で得られた処理銅くずを硫酸水溶液に溶解する。この硫酸水溶液としては、濃度が０．１～５ｍｏｌ／ｌのものが好ましく、０．５～３ｍｏｌ／ｌのものがより好ましい。銅くずの溶解は硫酸水溶液に空気を送り込みながら行うことが好ましい。次いで得られた電解液を用いて電気分解を行い、陰極に銅を析出させる。電気分解の条件は特に限定されず、通常の電解銅箔製造の電解条件で行われる。好ましくは、電流密度５～１５０Ａ／ｄｍ^2、電解時間１～３０分間の条件で行われ、厚さ２μｍ以上の電解銅箔が得られる。薄い、すなわち、２～１０μｍの電解銅箔を得るためには、電流と電解時間適宜制御して行う。更に必要ならば、銅箔面に粗化処理や防錆処理を行うことができる。

【００１２】

【実施例】以下、本発明の実施例及びその比較例によって本発明を更に具体的に説明するが、本発明はこれらの実施例に限定されるものではない。

【００１３】実施例１

ＪＩＳ　Ｈ　２１０９に規定される１号ナゲット銅（平均重量０．２ｇ／個）５００ｇを白金製金網に入れ、下から７００℃の熱風を１分間送風した。ナゲット銅を十分に混合した後、再度７００℃の熱風を１分間送風した。この送風操作を１０回繰り返して行うことで、焼成処理を行った。

【００１４】試薬硫酸から調製した１ｍｏｌ／ｌの硫酸水溶液に焼成処理されたナゲット銅を投入し、硫酸水溶液中で３分間撹動させた。次いでナゲット銅を純水中に移して３分間撹動させた。この二つの操作を三回繰り返した。

【００１５】試薬硫酸から調製した２ｍｏｌ／ｌの硫酸水溶液に酸洗処理したナゲット銅を投入し、空気を送り込みながらナゲット銅を完全に溶解させた。なお、空気は硫酸水溶液、水酸化ナトリウム水溶液とシリカゲルとを通気させた後、０．５μｍフィルタを介してゴミや不純物の混入を防止したものを用いた。

【００１６】次いで硫酸と純水とで硫酸銅２８０ｇ／ｌ、硫酸８０ｇ／ｌに濃度を調節し、電解液とした。

【００１７】陰極として、径５ｃｍのチタン製円筒状電極を用い、表面を２０００番の研磨紙を用いて研磨を行った。表面粗さはＲａで０．２０μｍであった。陽極板には円筒状の鉛板を用い、上記の電解液を用いて液温４０℃、電流密度１０Ａ／ｄｍ^{2}で５分間電気分解を行い、銅箔を析出させた。ただし円筒状電極の回転数は３００ｒｐｍとした。銅箔は両面ともに光沢を有し、重量法により求めた厚さは１２μｍであった。機械特性の測定結果を表１に示す。

【００１８】比較例１

焼成処理を行わないほかは実施例１と同様に銅箔を調製し、機械特性を評価した。結果を表１に示した。

【００１９】比較例２

酸洗処理を行わないほかは実施例１と同様に銅箔を調製し、機械特性を評価した。結果を表１に示した。

【００２０】比較例３

焼成処理と酸洗処理を行わないほかは実施例１と同様に銅箔を調製し、機械特性を評価した。結果を表１に示した。

【００２１】

【表１】

		実施例１	比較例１	比較例２	比較例３
表面粗さ（μｍ、Ｒａ）	電極面側	0.20	0.20	0.20	0.20
	析出面側	0.21	0.55	0.58	0.60
引張強度（Ｎ／ｍｍ^2）	常態	580	350	340	330
	加熱後（180℃／1h）	250	340	330	320
伸び率（％）	常態	4	7	7	6
	加熱後（180℃／1h）	20	8	8	7

表面粗さはＪＩＳ　Ｂ　０６５１に基づいて測定した。引張強度は常態（２３℃）及び１８０℃で１時間加熱後の引張強度をＪＩＳ　Ｃ６５１５に基づいて測定した。伸び率は常態（２３℃）及び１８０℃で１時間加熱後の引張強度をＪＩＳ　Ｃ６５１５に基づいて測定した。

【００２２】

【発明の効果】本発明の製造方法により得られた電解銅箔は、薄くて引張強度が大きく、剛性が高いことから取

扱性に優れ、両面が平滑で同等の表面粗さを有し、伸び率に優れた、微細回路を有する電子回路用銅箔やリチウムイオン二次電池の負極板用銅箔として極めて有用である。

フロントページの続き

(72)発明者　小林　勝己
茨城県下館市下江連1226番地　日本電解株式会社下館工場内
(72)発明者　成島　良一
茨城県下館市下江連1226番地　日本電解株式会社下館工場内
(72)発明者　阿曽　和義
茨城県下館市下江連1226番地　日本電解株式会社下館工場内

Fターム(参考)　4K001 AA09 BA22 CA07 CA09 DB03 DB17
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4K058 AA23 BA21 BA38 CA04 CA11 CA13 CA25 CA28 EB04 EB16 ED04 FA01 FA06

Electronic Acknowledgement Receipt

EFS ID:	34127177
Application Number:	15307069
International Application Number:	
Confirmation Number:	9113
Title of Invention:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Dae Young KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/Samantha Lingo
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313221.00005
Receipt Date:	26-OCT-2018
Filing Date:	27-OCT-2016
Time Stamp:	15:55:47
Application Type:	U.S. National Stage under 35 USC 371

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	00005_IDS_Trans.pdf	24788 76a79d47c3af5e86037117c5c91977236cd608ec	no	3

Warnings:

Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	00005_PTOsb08.pdf	1035604 a95e882e54ae4a6fe49385ee1ba8ee04d6054a7c	no	4
Warnings:					
Information:					
3	Foreign Reference	CN1480563.pdf	2043499 fef8c10ef89f098602357e595344904be812336f	no	14
Warnings:					
Information:					
4	Foreign Reference	EP1876266.pdf	1767688 e683604b09d0c240ff0a13299617bd8c89e6a257	no	28
Warnings:					
Information:					
5	Foreign Reference	EP2660359.pdf	1670443 c15fe91f2ab3057f8cbaad65f940735b3892c1f1	no	33
Warnings:					
Information:					
6	Foreign Reference	EP3067199.pdf	4841202 a5814679978a9cf75f907654d38cde08ccf798b3	no	27
Warnings:					
Information:					
7	Foreign Reference	JP3850155B2.pdf	425405 5998a414f24af45a7b4134dc65e4d3d78917fc41	no	10
Warnings:					
Information:					
8	Foreign Reference	JP20001011684.pdf	461679 bab029114b26cbbbb56d3710b7bb5a93251ecf11	no	11
Warnings:					
Information:					

9	Other Reference-Patent/App/Search documents	OP16-KF-007-US-00_CN-OA.pdf	451285 adcc9341a24528dae7b574d2d66800f255bd2a21	no	8
Warnings:					
Information:					
10	Other Reference-Patent/App/Search documents	OP16-KF-007-US-00_EPEESR.pdf	282652 f0eea78135f16c5187e481d384ef0e9f0f45f51a	no	9
Warnings:					
Information:					
		Total Files Size (in bytes):	13004245		

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<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
<u>New International Application Filed with the USPTO as a Receiving Office</u>
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Dae Young KIM
Appl. No.:	15/307,069
Conf. No.:	9113
Filed:	October 27, 2016
Title:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1727
Examiner:	USYATINSKY, ALEXANDER
Docket No.:	0313221.00005

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 $ 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: October 26, 2018

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	15307069
	Filing Date	2016-10-27
	First Named Inventor	Dae Young KIM
	Art Unit	1727
	Examiner Name	USYATINSKY, ALEXANDER
	Attorney Docket Number	0313221.00005

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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	2011129633	WO	A2	2011-10-20	ILJIN MATERIALS CO., LTD.		
	2	2014033917	WO	A1	2014-03-06	JX NIPPON MINING & METALS CORPORATION		
	3	2006299320	JP	A	2006-02-11	LS CABLE LTD.		

EFS Web 2.1.17

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15307069
	Filing Date	2016-10-27
	First Named Inventor	Dae Young KIM
	Art Unit	1727
	Examiner Name	USYATINSKY, ALEXANDER
	Attorney Docket Number	0313221.00005

	4	104846407	CN	A	2015-08-19	LINGBAO WASON COPPER FOIL CO		

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

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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	Taiwanese Notice of Allowance for related Taiwanese Application No. 105119183; action dated February 8, 2018; (8 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	15307069
	Filing Date	2016-10-27
	First Named Inventor	Dae Young KIM
	Art Unit	1727
	Examiner Name	USYATINSKY, ALEXANDER
	Attorney Docket Number	0313221.00005

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)	2018-05-08
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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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: CN104846407 (A) — 2015-08-19

Additive and process for producing 6mu.m high-tensile-strength electrolytic copper foil by using same

Inventor(s): FAN BINFENG; WANG JIANZHI; CHAI YUN; ZHANG XIN; HE TIESHUAI ± (FAN BINFENG, ; WANG JIANZHI, ; CHAI YUN, ; ZHANG XIN, ; HE TIESHUAI)

Applicant(s): LINGBAO WASON COPPER FOIL CO ± (LINGBAO WASON COPPER FOIL CO., LTD)

Classification: **- international:** ***C25D1/04; C25D3/38***
- cooperative:

Application number: CN20151238827 20150512 Global Dossier

Priority number(s): CN20151238827 20150512

Abstract of CN104846407 (A)

The invention relates to an additive; the additive is an aqueous solution which contains brightening agent SPS and HEC, wherein the concentration of the SPS in the additive is 5-15g/L, and the concentration of the HEC is 2-10g/L. The invention also discloses a process for producing a 6mu.m high-tensile-strength electrolytic copper foil by using the additive. The tensile strength of the 6mu.m electrolytic copper foil obtained By adopting the additive and the process thereof is more than or equal to 430Mpa, the coefficient of elongation is more than or equal to 4%, and the technical added value is remarkably improved.

(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 104846407 A
(43)申请公布日 2015.08.19

(21)申请号 201510238827.0

(22)申请日 2015.05.12

(71)申请人 灵宝华鑫铜箔有限责任公司
地址 472500 河南省三门峡市灵宝市黄河路131号

(72)发明人 樊斌锋 王建智 柴云 张欣 何铁帅

(74)专利代理机构 郑州联科专利事务所(普通合伙) 41104
代理人 时立新 杨海霞

(51)Int.Cl.
C25D 1/04(2006.01)
C25D 3/38(2006.01)

权利要求书1页 说明书3页 附图2页

(54)发明名称

一种添加剂及使用该添加剂生产6μm高抗拉强度电解铜箔的工艺

(57)摘要

本发明涉及一种添加剂，该添加剂为含有光亮剂SPS和HEC的水溶液，添加剂中SPS的浓度为5－15g/l，HEC的浓度为2－10g/l。本发明还公开了一种采用该添加剂生产6μm高抗拉强度电解铜箔的工艺。采用本发明所述添加剂及其工艺生产所得6μm电解铜箔抗拉强度在430Mpa以上，延伸率在4%以上，技术附加值显著提高。

CN 104846407 A

1. 一种添加剂，其特征在于，该添加剂为含有光亮剂 SPS 和 HEC 的水溶液，添加剂中 SPS 的浓度为 5 — 15g/l，HEC 的浓度为 2 — 10g/l。

2. 一种采用权利要求 1 所述添加剂生产 6μm 高抗拉强度电解铜箔的工艺，其特征在于，包括如下步骤：

1）溶铜制液：将原材料铜杆在硫酸溶液中溶解生成硫酸铜电解液，调节硫酸铜电解液中的铜离子含量、硫酸浓度、氯离子含量及温度指标达到规定范围；

2）电解制箔：将步骤 1）所得硫酸铜电解液过滤后送至净液槽，在净液槽中按比例添加权利要求 1 所述的添加剂，然后将添加有添加剂的硫酸铜电解液送至电解槽内进行电解制箔；

3）防氧化处理：将电解所得毛箔经防氧化处理后获得成品电解铜箔试样。

3. 如权利要求 2 所述生产 6μm 高抗拉强度电解铜箔的工艺，其特征在于，步骤 1）中调节硫酸铜电解液中的铜离子含量为 60 — 110g/L，H_2SO_4 浓度 75 — 125g/L，氯离子含量 10 — 20ppm，温度 40 — 50℃。

4. 如权利要求 2 所述生产 6μm 高抗拉强度电解铜箔的工艺，其特征在于，步骤 2）中向净液槽内添加添加剂时，分别加入 SPS 溶液和 HEC 溶液，控制 SPS 溶液的流量为 90 — 110ml/min，HEC 溶液的流量为 105 — 135ml/min；电解制箔时电流密度为 35 — 90A/dm^2。

5. 如权利要求 2 所述生产 6μm 高抗拉强度电解铜箔的工艺，其特征在于，步骤 3）中防氧化处理时防氧化电镀槽内的溶液组成如下：Cr^{6+} 含量 0.6 — 0.9g/l，pH 值为 1.0 — 3.0；温度 20 — 35℃。

一种添加剂及使用该添加剂生产6μm高抗拉强度电解铜箔的工艺

技术领域

[0001] 本发明属于电解铜箔生产技术领域，具体涉及一种添加剂及使用该添加剂生产6μm高抗拉强度电解铜箔的工艺。

背景技术

[0002] 目前，政府政策的刺激引领市场快速发展，带动新能源产业进一步升级和爆发式增长。高精端电解铜箔可广泛应用于锂离子动力电池等生产行业，对于当前国家极力倡导的“低碳环保”能源的开发与利用具有深远的意义。

[0003] 由于6μm铜箔较传统的铜箔更薄，同样容量下，可以使得锂电池的体积比容量大幅提升。而电解铜箔在常温下的加工处理性和刚性的提高以及高温下避免PCB变形，均需优异的抗拉强度及延伸率。因此，研发高抗拉强度的6μm锂电池铜箔，将为锂电池的发展注入了新的动力，其有着更广阔的市场前景。

发明内容

[0004] 本发明目的在于针对现有技术的不足，提供一种电解铜箔用添加剂，该添加剂成本较低，生产出来的电解铜箔性能指标满足市场要求。

[0005] 本发明另一目的在于提供一种采用上述添加剂生产6μm高抗拉强度电解铜箔的工艺。

[0006] 为实现上述目的，本发明采用如下技术方案：

一种添加剂，该添加剂为含有光亮剂SPS和HEC的水溶液，添加剂中SPS的浓度为5－15g/l，HEC的浓度为2－10g/l。

[0007] 一种采用上述添加剂生产6μm高抗拉强度电解铜箔的工艺，其包括如下步骤：

1）溶铜制液：将原材料铜杆在硫酸溶液中溶解生成硫酸铜电解液，调节硫酸铜电解液中的铜离子含量、硫酸浓度、氯离子含量及温度指标达到规定范围；

2）电解制箔：将步骤1）所得硫酸铜电解液过滤后送至净液槽，在净液槽中按比例添加权利要求1所述的添加剂，然后将添加有添加剂的硫酸铜电解液送至电解槽内进行电解制箔；

3）防氧化处理：将电解所得毛箔经防氧化处理后获得成品电解铜箔试样。

[0008] 具体的，步骤1）中调节硫酸铜电解液中的铜离子含量为60－110g/L，H_2SO_4浓度75－125g/L，氯离子含量10－20ppm，温度40－50℃。

[0009] 步骤2）中向净液槽内添加添加剂时，分别加入SPS溶液和HEC溶液，控制SPS溶液的流量为90－110ml/min，HEC溶液的流量为105－135ml/min；电解制箔时电流密度为35－90A/dm^2。

[0010] 步骤3）中防氧化处理时防氧化电镀槽内的溶液组成如下：Cr^{6+}含量0.6－0.9g/l，pH值为1.0－3.0；温度20－35℃。

[0011] 光亮剂SPS的化学名称：聚二硫二丙烷磺酸钠(分子式$C_6H_{12}O_6S_4Na_2$)；选用的HEC的化学名称：羟乙基纤维素(分子式$C_2H_6O_2 \cdot x$)。本发明的添加剂配方中，光亮剂SPS 用作晶粒细化剂、整平剂，能提高铜箔抗拉强度和延伸率；HEC的主要作用在于细化晶粒，阻碍晶粒长大，改变抗拉强度和延伸率。通过控制两者的合适比例，使得生产所得的6μm电解铜箔具有极高的抗拉强度和延伸率。和现有技术相比，本发明产生的有益效果是：采用本发明所述添加剂及其工艺生产所得6μm电解铜箔抗拉强度在430MPa以上，延伸率在4%以上，技术附加值显著提高。该技术成果达到了国内外先进水平，提升了企业在电解铜箔行业的地位，有效提高了我国电子工业加工的整体水平。

附图说明

[0012] 图1为采用实施例1工艺制备的6μm电解铜箔毛面×1000倍SEM照片；

图2为采用实施例2工艺制备的6μm电解铜箔毛面×1000倍SEM照片；

图3为采用实施例3工艺制备的6μm电解铜箔毛面×1000倍SEM照片。

具体实施方式

[0013] 以下通过具体实施例来说明本发明的技术方案，但本发明的保护范围并不局限于此。

[0014] 实施例1

一种添加剂，该添加剂为含有光亮剂SPS和HEC的水溶液，添加剂中SPS的浓度为9g/l，HEC的浓度为6g/l。

[0015] 一种采用上述添加剂生产6μm高抗拉强度电解铜箔的工艺，其包括如下步骤：

1)溶铜制液：将原材料铜杆在硫酸溶液中溶解生成硫酸铜电解液，调节硫酸铜电解液中的铜离子含量为85g/L，H_2SO_4浓度93g/L，氯离子含量14ppm，温度42℃；

2)电解制箔：将步骤1)所得硫酸铜电解液过滤后送至净液槽，在净液槽中按比例添加权利要求1所述的添加剂(即分别加入SPS溶液和HEC溶液，控制SPS溶液的流量为100ml/min，HEC溶液的流量为130ml/min)，然后将添加有添加剂的硫酸铜电解液送至电解槽内进行电解制箔：电解制箔时电流密度为55A/dm^2；

3)防氧化处理：将电解所得毛箔经防氧化处理后获得成品电解铜箔试样；防氧化处理时防氧化电镀槽内的溶液组成如下：Cr^{6+}含量0.8g/l，pH值为2.1；温度26℃。

[0016] 实施例2

一种添加剂，该添加剂为含有光亮剂SPS和HEC的水溶液，添加剂中SPS的浓度为7g/l，HEC的浓度为8.5g/l。

[0017] 一种采用上述添加剂生产6μm高抗拉强度电解铜箔的工艺，其包括如下步骤：

1)溶铜制液：将原材料铜杆在硫酸溶液中溶解生成硫酸铜电解液，调节硫酸铜电解液中的铜离子含量为90g/L，H_2SO_4浓度105g/L，氯离子含量16ppm，温度47℃；

2)电解制箔：将步骤1)所得硫酸铜电解液过滤后送至净液槽，在净液槽中按比例添加权利要求1所述的添加剂(即分别加入SPS溶液和HEC溶液，控制SPS溶液的流量为95ml/min，HEC溶液的流量为125ml/min)，然后将添加有添加剂的硫酸铜电解液送至电解槽内进行电解制箔：电解制箔时电流密度为55A/dm^2；

3）防氧化处理：将电解所得毛箔经防氧化处理后获得成品电解铜箔试样；防氧化处理时防氧化电镀槽内的溶液组成如下：Cr^{6+}含量 0.8g/l，pH 值为 2.1；温度 26℃。

[0018] 实施例 3

一种添加剂，该添加剂为含有光亮剂 SPS 和 HEC 的水溶液，添加剂中 SPS 的浓度为 12.5g/l，HEC 的浓度为 9g/l。

[0019] 一种采用上述添加剂生产 6μm 高抗拉强度电解铜箔的工艺，其包括如下步骤：

1）溶铜制液：将原材料铜杆在硫酸溶液中溶解生成硫酸铜电解液，调节硫酸铜电解液中的铜离子含量为 100g/L，H_2SO_4浓度 100g/L，氯离子含量 17ppm，温度 45℃；

2）电解制箔：将步骤 1）所得硫酸铜电解液过滤后送至净液槽，在净液槽中按比例添加权利要求 1 所述的添加剂（即分别加入 SPS 溶液和 HEC 溶液，控制 SPS 溶液的流量为 105ml/min，HEC 溶液的流量为 110ml/min），然后将添加有添加剂的硫酸铜电解液送至电解槽内进行电解制箔；电解制箔时电流密度为 55A/dm^2；

3）防氧化处理：将电解所得毛箔经防氧化处理后获得成品电解铜箔试样；防氧化处理时防氧化电镀槽内的溶液组成如下：Cr^{6+}含量 0.8g/l，pH 值为 2.1；温度 26℃。

[0020] 取上述实施例 1 至 3 所得电解铜箔试样，测试毛面亮度，常温、高温抗拉强度及延伸率，结果见下表 1。由表 1 可看出：所得铜箔成品的性能达到高抗拉强度电解铜箔的生产要求，该类铜箔可作为锂电池专用铜箔。

[0021] 本发明研发的 6μm 电解铜箔生产工艺的抗拉强度及延伸率等主要性能指标均达到下游客户要求。同时，由于本发明从添加剂的最优配比角度进行开发，易于实现工业化、批量化生产，对提高我国在高档电解铜箔的市场占有率方面有着重要意义。

表 1 实施例 1-3 所得电解铜箔试样的主要性能

性能指标		实施例 1	实施例 2	实施例 3
毛面粗糙度（μm）		1.13	1.37	1.22
毛面亮度	光泽单位	62	83	76
抗拉强度（MPa）	常温	449.2	454.5	464.9
	180℃	436.9	439.7	439.4
延伸率（%）	常温	4.57	4.35	4.09
	180℃	4.96	5.02	4.18

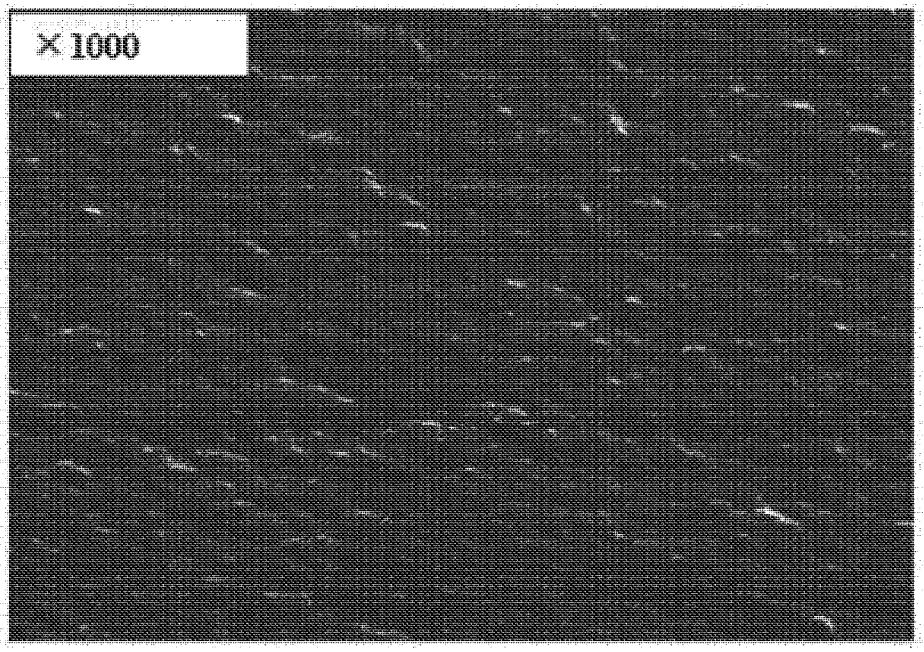


图 1

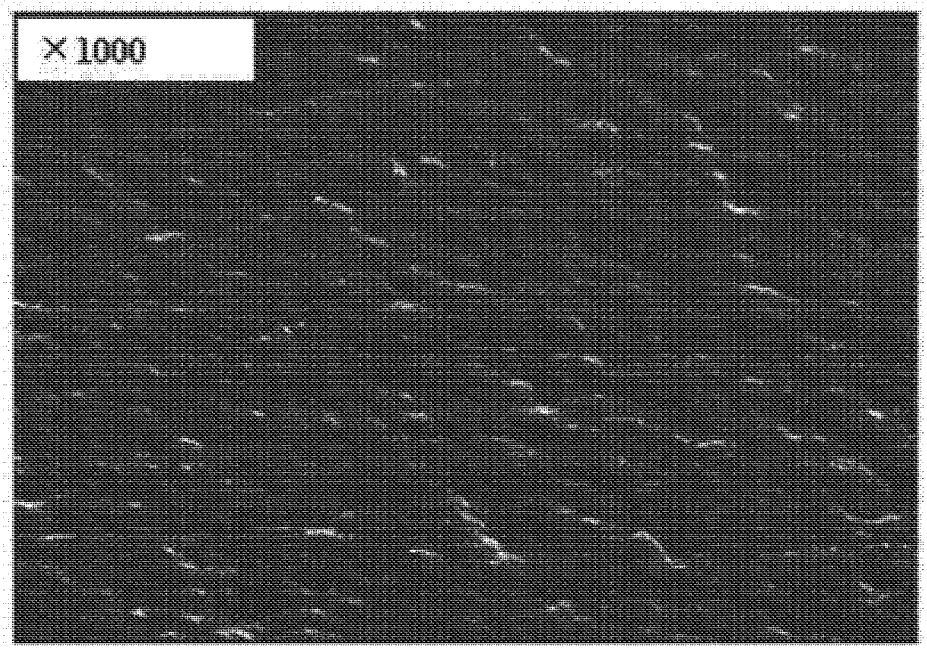


图 2

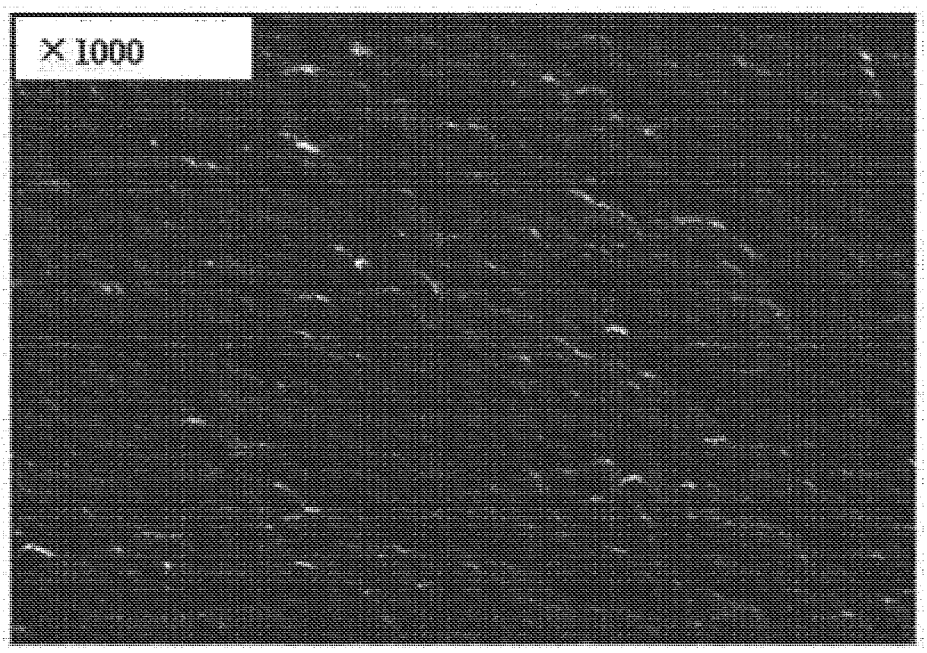


图 3

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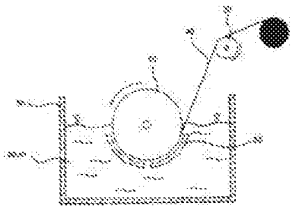
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(71)Applicant	LS CABLE LTD
(72)Inventor	KIM JEONG IK KIM SANG YUM JO CHA JEA



(54)HIGH STRENGTH LOW ROUGHNESS COPPER FOIL AND METHOD OF MANUFACTURING THE SAME

(57)Abstract

PROBLEM TO BE SOLVED: To provide high strength low roughness copper foil obtained by adding the most suitable additive using a raw material such as low cost waste electric cables which are now conventionally used dispensing with the change or the modification of the design of a conventionally used foil making machine and without adding equipment or processes for mechanical polishing in the manufacture of the copper foil.

SOLUTION: The copper foil 40 is obtained by carrying out a step (S1000) for supplying an electrolyte 60 to an electrolytic cell so as to house the rotary drum 10 and an anode plate 20 in the electrolytic cell 50 and a step (S2000) for adding the additive 61 comprising the prescribed quantity of gelatin, hydroxy ethyl cellulose (HEC), bis(sodium sulfopropyl)disulfide (SPS) and ethylene thiourea (EU) into the electrolyte and applying current between the rotary drum and the anode plate to be deposited on the rotary drum. As a result, the roughness of the contact surface of the electrolytic copper foil which is stuck on an insulation substrate for a printed circuit board is lowered, remaining copper is not produced even in the formation of a fine printed circuit and the deformation of a fine circuit in the welding process for mounting an electronic components in the fine printed circuit is prevented by improving the tensile strength.

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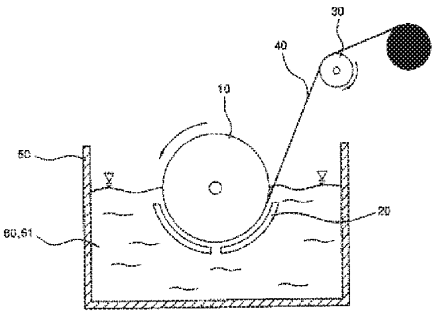
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(71)出願人　502297933
エルエス　ケーブル　リミテッド
大韓民国　１３５－０９０　ソウル，　ガンナムーグ，サムスン－ドン　アセム　タワー　１５９１９－２０Ｆ
(74)代理人　100081318
弁理士　羽切　正治
(74)代理人　100007983
弁理士　笹川　拓
(74)代理人　100122541
弁理士　小野　友彰
(74)代理人　100132458
弁理士　仲村　圭代

最終頁に続く

(54)【発明の名称】高強度を有する低粗度銅箔及びその製造方法

(57)【要約】
【課題】　銅溶製造時、既存で使用している製箔機の設計変更や改造が不要であり、また、機械的な研磨のための設備や工程を追加せずに、既存で使用している低価の廃電線類の原材料を使用しながら最適の添加剤を添加して得られる高強度を有する低粗度銅箔及びその製造方法を提供する。
【解決手段】　電解槽５０内に回転ドラム１０及び陽極板２０が収蔵されるように電解液６０を供給するステップ（Ｓ１０００）と、電解液に所定量のゼラチンとＨＥＣとＳＰＳとＥＵとから構成される添加剤６１を添加するステップ（Ｓ２０００）とにより、回転ドラム及び陽極板に電流を印加して回転ドラムに電着された銅箔４５を収得する。これにより、印刷回路基板用絶縁基板に接着される電解銅箔の接着面の粗度を低めて微細印刷回路形成時にも残銅が生じず、引張り強度を高めて微細印刷回路に電子部品を実装する溶接工程時、微細回路の変形を防止できる。
【選択図】　図１



【特許請求の範囲】
【請求項1】
電解槽５０内に、回転ドラム１０と前記ドラム１０に対して所定の間隔を置いて位置する陽極板２０とが設けられた製箔機を用いて銅箔を製造する方法において、
前記電解槽５０内に回転ドラム１０及び陽極板２０が収蔵されるように電解液６０を供給するステップＳ１０００；
前記電解槽５０内に供給された電解液６０に０．１～１００ｐｐｍのゼラチンと、０．０５～５０ｐｐｍのＨＥＣと、０．０５～２０ｐｐｍのＳＰＳと、０．０５～３０ｐｐｍのＥＵとから構成される添加剤６１を添加するステップＳ２０００；及び
前記回転ドラム１０及び陽極板２０に極性電流を印加して回転ドラム１０に電解電着された銅箔４５を取得するステップＳ３０００；を含むことを特徴とする高強度を有する低粗度銅箔の製造方法。
【請求項2】
前記Ｓ２０００のステップにおいて、前記ゼラチンの分子量は１０，０００以上であることを特徴とする請求項１に記載の高強度を有する低粗度銅箔の製造方法。
【請求項3】
前記Ｓ２０００のステップにおいて、前記ゼラチンの添加量は２～５ｐｐｍであることを特徴とする請求項１に記載の高強度を有する低粗度銅箔の製造方法。
【請求項4】
前記Ｓ２０００のステップにおいて、前記ＨＥＣの添加量は１～３ｐｐｍであることを特徴とする請求項１に記載の高強度を有する低粗度銅箔の製造方法。
【請求項5】
前記Ｓ２０００のステップにおいて、前記ＳＰＳの添加量は０．５～３ｐｐｍであることを特徴とする請求項１に記載の高強度を有する低粗度銅箔の製造方法。
【請求項6】
前記Ｓ２０００のステップにおいて、前記ＥＵの添加量は０．１～１ｐｐｍであることを特徴とする請求項１に記載の高強度を有する低粗度銅箔の製造方法。
【請求項7】
前記Ｓ３０００のステップ以後、
前記銅箔４０の接着力を増大させるためにノジュールを形成するステップＳ３１００；と、銅箔４０が拡散されることを防ぐためにバリヤーするステップＳ３２００；と、銅箔４０の酸化を防止するために防錆処理するステップＳ３３００；及び銅箔４０の接着力を向上させるためにシランカップリング剤により表面処理するステップＳ３４００；が更に含まれることを特徴とする請求項１に記載の高強度を有する低粗度銅箔の製造方法。
【請求項8】
前記銅箔４０は銅張積層板、印刷回路基板、リチウムイオン電池、または軟性回路基板に使用されることを特徴とする請求項７に記載の高強度を有する低粗度銅箔の製造方法。
【請求項9】
請求項１乃至請求項７に記載のうち、いずれか１に記載の高強度を有する低粗度銅箔の製造方法により製造される銅箔であって、前記電解液６０内に０．１～１００ｐｐｍのゼラチンと、０．０５～５０ｐｐｍのＨＥＣと、０．０５～２０ｐｐｍのＳＰＳと、０．０５～３０ｐｐｍのＥＵとから構成される添加剤６１；を添加し、前記回転ドラム１０及び陽極板２０に極性電流を印加して前記ドラム１０に電着させて得られることを特徴とする高強度を有する低粗度銅箔。

【発明の詳細な説明】
【技術分野】
【0001】
本発明は、銅箔製造時、既存で使用している製箔機の設計変更や改造が不要であり、また、機械的な研磨のための設備や工程を追加することなく、既存で使用している低価の廃電線類の原材料をそのまま使用しながら、最適の添加剤を添加して得られる高強度を有す

る低粗度銅箔及びその製造方法であって、より詳しくは、印刷回路基板（ＰＣＢ）用の絶縁基板（Ｐｒｅｐｒｅｇ）に接着される電解銅箔に対して銅箔の接着面（Ｍａｔｔｅ　Ｓｉｄｅ）の粗度を低めて微細印刷回路パターン形成時にも残銅が生じないようにし、銅箔の引張り強度を高めて微細パターンに電子部品を実装する溶接工程中、微細回路の変形を防止できる高強度を有する低粗度銅箔及びその製造方法に関するものである。

【背景技術】

【0002】

一般的に、印刷回路基板は、ラジオ、テレビジョン、洗濯機などの民生用電気／電子製品及びコンピュータ、無線通信機器、各種制御機器などの産業用電気／電子機器の精密制御に広範囲に使用されている。

【0003】

この時、産業用印刷回路の絶縁基板としては、主に、ガラス繊維をエポキシ樹脂に含浸させた難燃性の絶縁基板が使用されており、印刷回路基板は、絶縁基板に印刷回路用電解銅箔を高温高圧下で接着し、回路設計に従ってエッチングして得る。

【0004】

絶縁基板に接着される電解銅箔は、一般的に硫酸銅溶液を用いて連続的に電解電着法により銅生箔（Ｒａｗ　Ｆｏｉｌ）を作り、これを絶縁基板との接着力向上のために銅生箔面にノジュール（Ｎｏｄｕｌｅ）を形成する粗化処理をしたり、粗化処理された表面にバリヤー（Ｂａｒｒｉｅｒ）層を形成させた後、電解クロメート（Ｃｈｒｏｍａｔｅ）防錆処理して電解銅箔を得ている。

【0005】

最近では、電気／電子機器の軽薄短小化が加速化されることにより、基板用印刷回路が微細化、高集積小型化されており、これにより、基板及び印刷回路の製造方法を強化するため、精密印刷回路基板に適合する極低粗度銅箔が開発されている。

【0006】

米国特許第５，２１５，６４６号（特許文献１）では、電解される区間を二つに分け、一つ目の区間より二つ目の区間の電流密度を高めることにより、低粗度銅箔を得る方法が開示されているが、この方法は製造設備の改造により相当な費用が必要とされて望ましくない。

【0007】

米国特許第５，４３１，８０３号（特許文献２）では、電解液のうち、塩素イオンの濃度を１ｐｐｍ以下に低めて低粗度銅箔を得る方法が開示されているが、電解銅箔の製造の場合、ほとんど原材料として銅スクラップを使用しており、塩素イオンの濃度を１ｐｐｍ以下に低めることは事実上不可能であり、例え、可能であるとしても莫大な別途設備の投資が必要な方法である。

【0008】

米国特許第５，８９７，７６１号（特許文献３）、同第５，８５８，５１７号（特許文献４）及び同第６，２９１，０８１　Ｂ１号（特許文献５）では、一般的に製造された電解銅箔をバフィング（Ｂｕｆｆｉｎｇ）を介して機械的に研磨し、低粗度銅箔を得る方法が開示されているが、この方法は別途の生産設備を備えなければならず、また、バフィング工程時に発生した銅分が残っていれば、印刷回路基板の製造時、残銅が生じる恐れがあるなど、望ましくない方法である。

【0009】

米国特許第５，８６３，４１０号（特許文献６）では、低分子量収容性セルロースエテル、低分子量収容性ポリアルキレングリコールエテル、低分子収容性ポリエチレンイミン、収容性サルファネーティッド有機硫黄化合物を適正量添加して低粗度銅箔を得る方法が開示されているが、この方法で製造された銅箔の場合、接着面の粗度（Ｒｚ）値が３．８１μｍ水準であって、最近の低粗度銅箔の要求に応ずることができない。

【0010】

米国特許第５，９５８，２０９号（特許文献７）及び同第６，１９４，０５６　Ｂ１号

（特許文献８）では、少ない量のポリエチレングリコール、錫イオン、鉄イオン及び０．１ｐｐｍ以下の塩素イオンを含む電解液で低粗度の銅箔を製造する方法が開示されているが、この方法も前記の通り、事実上塩素イオンの濃度を０．１ｐｐｍ以下に維持するのが不可能であるため、望ましくない方法である。

【0011】

以上のように、従来の技術は大きく四つの方法で低粗度銅箔を製造しようとした。

【0012】

一つ目は、米国特許第５，２１５，６４６号（特許文献１）のように、製造設備である製箔機の構造を変更させて通常スーパーアノード（Ｓｕｐｅｒ　Ａｎｏｄｅ）という装置を取り付けることである。このようなスーパーアノード装置を適用すれば、スーパーアノードと本アノードとにかける電流量を調節することにより初期核生成時、核のサイズを変えることができる。初期核のサイズを微細に調節することにより低粗度銅箔を製造することができるが、この方法のみでは現在の微細回路パターンに対応する低粗度の銅箔を得ることができない。

【0013】

二つ目は、塩素イオンの量を１ｐｐｍまたは０．１ｐｐｍ以下の極めて少ない量に調節し、電解塗金時の分極を変化させて一つ目の例と同様に初期核のサイズを微細に調整する方法などが米国特許第５，４３１，８０３号（特許文献２）、同第５，９５８，２０９号（特許文献７）及び同第６，１９４，０５６　Ｂ１号（特許文献８）などに開示されている。前述したように、大量生産体制で銅スクラップを使用することになると、銅スクラップのほとんどを占めている廃電線からの塩素イオンを防ぐことができる経済的な方法は現在明らかにされておらず、この方法の実用性はない。

【0014】

三つ目は、既存の方法の通りに、電解銅箔を製造した後、機械的な研磨を通じて粗度値を低める方法であり、米国特許第５，８５８，５１７号（特許文献４）、同第５，８９７，７６１号（特許文献３）及び同第６，２９１，０８１　Ｂ１号（特許文献５）などに詳しく開示されている。この方法は機械的な研磨方法により銅箔の粗度を低めるため、バフィングの程度によって極めて低い低粗度銅箔の製造も可能である。この方法で製造する場合には、バフィング設備を追加するための投資が必要であり、新たな工程の適用による生産性低下の原因となって経済的な方法であるといえない。

【0015】

最後に、米国特許第５，８６３，４１０号（特許文献６）のように、電解液に添加する添加剤を変えて銅箔の表面形状（Ｍｏｒｐｈｏｌｏｇｙ）を調節する方法がある。このような方法は、既存の製箔機の変更及び改造無しに電解液の添加剤のみを変更することにより所望の低粗度の銅箔を得ることができ、バフィングのような機械的な研磨工程も必要でなく、塩素イオンを極度に低く管理する必要もなく、最も経済的で、望ましい方法であるといえる。米国特許第５，８６３，４１０号（特許文献６）によると、低分子量収容性セルロースエテルはピークカウント（Ｐｅａｋ　Ｃｏｕｎｔ：Ｎｕｍｂｅｒ　Ｏｆ　Ｐｅａｋｓ　Ｐｅｒ　Ｓｕｒｆａｃｅ　Ａｒｅａ）を顕著に低める役割をするといい、低分子量収容性ポリアルキレングリコールエテルは銅箔の微細組織の均一性を改善させる役割をするとされている。

【0016】

一方、低分子収容性ポリエチレンイミンはピークの模様を鋭くして後工程での樹脂と接着の際、接着力増大に多くの寄与をし、収容性サルファネーティッド有機硫黄化合物はピークの数は増やし、高さは低める機能を担当するとされている。しかしながら、これらの方法で製造された銅箔では接着面の粗度（Ｒｚ）値が３．８１μｍ水準であって、最近の低粗度銅箔の要求に応ずることができない。

【0017】

【特許文献1】米国特許第５，２１５，６４６号明細書

【特許文献2】米国特許第５，４３１，８０３号明細書

【特許文献3】

米国特許第５，８９７，７６１号明細書
【特許文献4】米国特許第５，８５８，５１７号明細書
【特許文献5】米国特許第６，２９１，０８１　Ｂ１号明細書
【特許文献6】米国特許第５，８６３，４１０号明細書
【特許文献7】米国特許第５，９５８，２０９号明細書
【特許文献8】米国特許第６，１９４，０５６　Ｂ１号明細書
【発明の開示】
【発明が解決しようとする課題】
【0018】
従って、本発明は上記のような従来の問題点に鑑みてなされたものであって、本発明の第１の目的は、印刷回路基板用絶縁基板に接着される電解銅箔に対して銅箔の接着面の粗度を低め、微細印刷回路形成時にも残銅が生じないようにし、銅箔の引張り強度を高めて微細パターンに電子部品を実装する溶接工程時、微細回路の変形を防止できる高強度を有する低粗度銅箔及びその製造方法を提供することである。
【0019】
そして、本発明の第２の目的は、銅箔製造時、既存で使用している製箔機の設計変更や改造が不要であり、機械的な研磨のための設備や工程を追加することなく、既存で使用している低価の廃電線類の原材料をそのまま使用しながら、最適の添加剤を添加して得られる高強度を有する低粗度銅箔及びその製造方法を提供することである。
【課題を解決するための手段】
【0020】
このような本発明の目的は、電解槽５０内に、回転ドラム１０と前記ドラム１０に対して所定の間隔を置いて位置する陽極板２０とが設けられた製箔機を用いて銅箔を製造する方法において、前記電解槽５０内に回転ドラム１０及び陽極板２０が収蔵されるように電解液６０を供給するステップＳ１０００；前記電解槽５０内に供給された電解液６０に０．１～１００ｐｐｍのゼラチンと、０．０５～５０ｐｐｍのＨＥＣと、０．０５～２０ｐｐｍのＳＰＳと、０．０５～３０ｐｐｍのＥＵとから構成される添加剤６１を添加するステップＳ２０００；及び前記回転ドラム１０及び陽極板２０に極性電流を印加してドラム１０に電解電着された銅箔４５を収得するステップＳ３０００；を含むことを特徴とする高強度を有する低粗度銅箔の製造方法によって達成される。
【0021】
前記Ｓ２０００ステップにおいて、前記ゼラチンの分子量は１０，０００以上であることが望ましい。
【0022】
前記Ｓ２０００ステップにおいて、前記ゼラチンの添加量は２～５ｐｐｍであることが望ましい。
【0023】
前記Ｓ２０００ステップにおいて、前記ＨＥＣの添加量は１～３ｐｐｍであることが望ましい。
【0024】
前記Ｓ２０００ステップにおいて、前記ＳＰＳの添加量は０．５～３ｐｐｍであることが望ましい。
【0025】
前記Ｓ２０００ステップにおいて、前記ＥＵの添加量は０．１～１ｐｐｍであることが望ましい。
【0026】
前記Ｓ３０００ステップ以後、前記銅箔４０の接着力を増大させるためにノジュールするステップＳ３１００と、銅箔４０が拡散されることを防ぐためのバリヤーするステップＳ３２００と、銅箔４０の酸化処理を防止するために防錆するステップＳ３３００及び銅箔４０の接着力を信頼させるためにシランカップリング剤として処理するステップＳ３４

００とが更に含まれるのが望ましい。

【0027】

前記銅箔４０は銅張積層板、印刷回路基板、リチウムイオン電池、または軟性回路基板に使用されるのが望ましい。

【0028】

合わせて、本発明の目的などは、第１項乃至第７項のうち、いずれか１に記載の方法で製造される銅箔において、前記電解液６０内に０．１～１００ｐｐｍのゼラチンと、０．０５～５０ｐｐｍのＨＥＣと、０．０５～２０ｐｐｍのＳＰＳと、０．０５～３０ｐｐｍのＥＵとから構成される添加剤６１；を添加し、前記回転ドラム１０及び陽極板２０に当該極性電流を印加して前記ドラム１０に電解電着された銅箔４０が収得されることを特徴とする高強度を有する低粗度銅箔によって達成される。

【0029】

本発明のその他の目的、特定した長所など及び新規な特徴は、図面を参照して以下に詳細に説明する。

【発明の効果】

【0030】

以上のような高強度を有する低粗度銅箔の製造方法によれば、機械的な研磨のための設備や工程を追加することなく、既存で使用している低価の廃電線類の原材料をそのまま使用しながら、最適の添加剤を添加して高強度で低粗度の銅箔を製造できる。

【0031】

また、印刷回路基板用絶縁基板に接着される電解銅箔に対して銅箔の接着面の粗度を低めて微細印刷回路パターン形成時にも残銅が生じないようにし、銅箔の引張り強度を高めて微細パターンに電子部品を実装する溶接工程中、微細回路の変形を防止できる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】

【0032】

次に、本発明による高強度を有する低粗度銅箔の製造方法に関して添付した図面を参照して詳しく説明する。

【0033】

図１は、本発明によるドラム構造の電解製箔機の構成図、図２は、本発明による高強度を有する低粗度銅箔の製造方法のフローチャートである。図１及び図２に示すように、製箔機は機械的な圧延と共に銅箔４０を製造する代表的な成型装置である。

【0034】

ここで、電解槽５０には電解液６０が入れられており、０．１～１００ｐｐｍのゼラチンと、０．０５～５０ｐｐｍのＨＥＣ（Ｈｙｄｒｏｘｙｅｔｈｙｌ　Ｃｅｌｌｕｌｏｓｅ）と、０．０５～２０ｐｐｍのＳＰＳ（ｂｉｓ（ｓｏｄｉｕｍｓｕｌｆｏｐｒｏｐｙｌ）ｄｉｓｕｌｆｉｄｅ）と、０．０５～３０ｐｐｍのＥＵ（Ｅｔｈｙｌｅｎｅｔｈｉｏｕｒｅａ）とからなされた添加剤６１が添加される。

【0035】

この時、電解液６０の基本組成はH_2SO_4：５０～２００ｇ／１、Cu^{2+}：３０～１５０ｇ／１、Cl^-：２００ｍｇ／１以下であり、電解液６０の温度は常温８０℃であり、電流密度は２０～１５０Ａ／dm^2である。

【0036】

このような電解液６０には分割された円弧状の陽極板２０及び陽極板２０の窪んだ部位に対応して陰極電極として機能するドラム１０が収蔵されている。この時、ドラム１０及び陽極板２０に、各極性に対応する電流が印加され、ドラム１０の回転方向であって電解液６０の外部にはローラー３０が位置している。

【0037】

これにより、（－）電流が印加され回転するドラム１０と、（＋）電流が印加された陽極板２０との間からは銅が析出され、ドラム１０の表面には銅箔４０が電着される。電着

される銅箔４０はローラー３０によって引かれて巻き取られることによりロール形態で収得される。

【0038】

このような銅箔４０は、所定の後処理過程を経ることにより、選択的に銅張積層板（Ｃｏｐｐｅｒ　Ｃｌａｄ　Ｌａｍｉｎａｔｅ）、印刷回路基板、リチウムイオン電池の電極材、軟性回路基板等に使用することができる。

【0039】

図２は、本発明による高強度を有する低粗度銅箔の製造方法のフローチャートである。図２に示すように、本発明による高強度を有する低粗度銅箔の製造方法は、後処理を行うことなく高強度を有する低粗度銅箔を作る方法である。

【0040】

まず、回転ドラム１０と陽極板２０とが設けられた電解槽５０内に電解液６０を供給する（Ｓ１０００）。この時、電解液６０の基本組成はH_2SO_4：５０～２００ｇ／ｌ、Cu^{2+}：３０～１５０ｇ／ｌ、Cl^-：２００ｍｇ／ｌ以下であり、電解液６０の温度は常温８０℃であり、電流密度は２０～１５０Ａ／dm^2である。

【0041】

そして、基本組成された電解液６０に０．１～１００ｐｐｍのゼラチンと、０．０５～５０ｐｐｍのＨＥＣと、０．０５～２０ｐｐｍのＳＰＳと、０．０５～３０ｐｐｍのＥＵとで構成される添加剤６１を添加する（Ｓ２０００）。

【0042】

その後、回転ドラム１０及び陽極板２０に当該極性電流を印加してドラム１０に電解電着された高強度を有する低粗度銅箔４０を収得する（Ｓ３０００）。

【0043】

以下、各添加剤６１の添加量による物性について説明する。

【0044】

ゼラチンは銅箔４０塗金層の機械的な強度を向上させるために使用される物質である。ゼラチンの添加量として０．１～１００ｐｐｍが好適な理由は、０．１ｐｐｍ以下の場合には、初期組織を得ることができるが、電解銅箔の成長を促進させて粗大な組織の電解銅箔が得られ、このように粗大な組織は高いピーク高さを有することになって、所望の低粗度の銅箔４０が得られない。

【0045】

また、１００ｐｐｍ以上添加された場合は、銅箔４０の粗大成長を抑制して低粗度の銅箔４０を得ることができるが、微細回路形成時の主要特性の一つである高温下での伸び率（ＨＴＥ；Ｈｉｇｈ　Ｔｅｍｐｅｒａｔｕｒｅ　Ｅｌｏｎｇａｔｉｏｎ、１８０℃で測定）特性が顕著に落ちるためである。

【0046】

また、ＨＥＣは、ＳＰＳ、ゼラチン及びＥＵと交互に作用して銅箔４０の安定した低粗度を実現する役割を果たす。ＨＥＣの添加量として０．０５～５０ｐｐｍが好適な理由は、０．０５ｐｐｍ以下の場合は、ＳＰＳ及びゼラチンとの交互作用能力が落ちて均一でない電解銅箔が製造され、５０ｐｐｍ以上の場合は、電解銅箔に銅分を析出させる役割をして印刷回路基板の製造時、残銅など不良の原因となるためである。

【0047】

ＳＰＳは、塗金時、光沢剤として使用される物質であって、ＨＥＣとゼラチンとの交互作用により塗金組織の粗度を低める主な役割を果たす。ＳＰＳの添加量として０．０５～２０ｐｐｍが好適な理由は、０．０５ｐｐｍ以下の場合、他の物質との交互作用能力が落ちて粗度の高い、均一でない電解銅箔が製造され、また、２０ｐｐｍ以上添加しても特別な効果も無く費用のみ増大させるためである。

【0048】

ＥＵは、塗金時、塗金層内に析出相を形成して機械的な強度を増加させる。ＥＵの添加量として０．０５～３０ｐｐｍが好適な理由は、０．０５ｐｐｍ以下の場合は、析出相の

形成程度が落ちて機械的な強度が向上される効果を表す電解銅箔４０の製造が難しく、３０ｐｐｍ以上添加すると、過度な析出像による銅箔４０の常温及び高温下での伸び率の急激な減少により銅箔が容易に砕ける現象が発生するなど、機械的な特性を悪化させ、他の物質との交互作用能力が落ちて粗度が急激に上昇させることになって望ましくない。

【0049】

図３は、本発明の実施例によって収得された銅箔の電子顕微鏡ＳＥＭ撮影写真図であり、図４は、下記比較例によって収得された銅箔の電子顕微鏡ＳＥＭ撮影写真図である。

【0050】

以下において、図３及び図４を参照して本発明の製造方法による実施例及び実施例を比較するための比較例に従って互いに相違した条件で銅箔４０を製造する方法を示す。

〔実施例〕

電解液の組成はH_2SO_4：１００ｇ／ｌ、Cu^{2+}：１００ｇ／ｌ、Cl^-：３０ｍｇ／ｌ以下であり、温度は常温６０℃であり、電流密度は１００Ａ／dm^2として製造した。この時、添加された添加剤の添加量は〔表１〕の通りである。

〔表１〕

	ゼラチン	ＨＥＣ	ＳＰＳ	ＥＵ
例１）	２．５	１	１．５	０．１
例２）	３．５	２	２．５	０．４
例３）	４．５	１．５	２	１

【0051】

〔比較例〕

電解液の組成はH_2SO_4：１００ｇ／ｌ、Cu^{2+}：１００ｇ／ｌ、Cl^-：３０ｍｇ／ｌ以下であり、温度は常温６０℃であり、電流密度は１００Ａ／dm^2として製造した。この時、添加された添加剤の添加量は〔表２〕の通りである。

〔表２〕

	ゼラチン	ＨＥＣ	ＳＰＳ	ＥＵ
比較例１）	２．５		１．５	
比較例２）	３．５			０．４
比較例３）	３．５	１．５	２	―

【0052】

上記において、実施例から製造された電解銅箔の表面形状は図３と同じであり、比較例から製造された電解銅箔の表面形状は図４の通りである。

【0053】

図３及び図４に示すように、実施例の銅箔よりも比較例の銅箔のほうが表面粗度が相対的に高いことがみてとれる。このように比較例に従って製造された銅箔は、表面粗度等の銅箔物性（粗度、引張り強度、伸び率、高温での引張り強度、高温での伸び率）が落ち、その結果は〔表３〕に示す通りである。

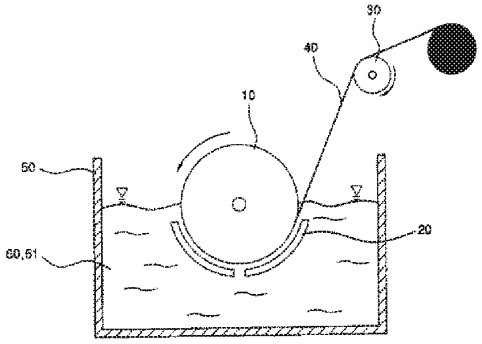
〔表３〕

	ＲＺ（μｍ）	引張り強度（kgf/mm²）	伸び率（％）	高温での引張り強度（kgf/mm²）	高温での伸び率（％）
実施例１）	2.1	47.5	6.7	24.2	13.7
実施例２）	1.8	52.5	6.4	24.3	16.4
実施例３）	1.9	62.7	5.4	23.4	11.4
比較例１）	2.5	34.1	5.8	20.1	8.5
比較例２）	3.5	33.8	8.3	20.3	2.1
比較例３）	2.0	32.5	6.9	20.4	5.7

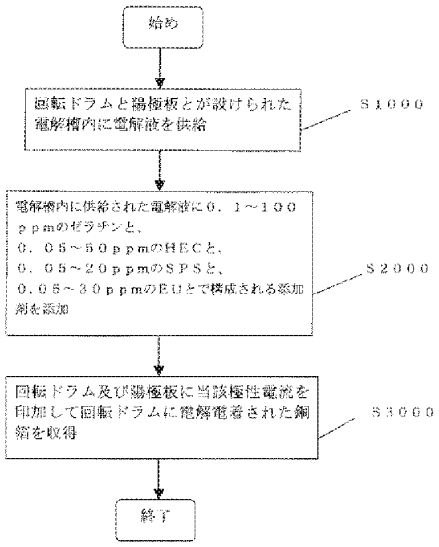
【0054】
〔表３〕に示すように、本発明による実施例が比較例よりも表面粗度は低いながら、銅箔の物性（粗度、引張り強度、伸び率、高温での引張り強度、高温での伸び率）は向上される。
【0055】
従って、本発明による実施例によれば、比較例により製造された電解銅箔よりも相対的に高強度を有する低粗度銅箔を製造することができる。
【0056】
図５は、図２に示す工程以降の後処理工程を示すフローチャートである。図２に示すように、実施例に従って製造した高強度を有する銅箔は、図５に示すような後処理工程を経て、選択的に銅張積層板、印刷回路基板、リチウムイオン電池の電極材、軟性回路基板に使うことができる。
【0057】
図５に示すように、後処理工程は、図２に示す工程に従って、銅箔４０を収得し（Ｓ３０００）、連続的に樹脂との接着力を増大させるためのノジュール形成処理（Ｓ３１００）と、樹脂に銅箔４０が拡散されることを防ぐためのバリヤー処理（Ｓ３２００）と、銅箔４０の酸化を防止するための防錆処理（Ｓ３３００）と、銅箔４０の接着力を向上させるためのシランカップリング剤（Ｓｉｌａｎｅ　Ｃｏｕｐｌｉｎｇ　Ａｇｅｎｔ）によるカップリング処理（Ｓ３４００）とを有する。
【0058】
以上のように、本発明による高強度を有する低粗度銅箔の製造方法は前記の実施例で言及された各条件に限らず、本発明で提示された範囲内で他の多様な実施例の施行が可能であり、これを通じて多様な特性の銅箔及びそれを用いた電子部品の製造が可能である。
【0059】
本発明は、前記の通り望ましい実施例と関連して説明したが、特許請求の範囲に記載された本発明の要旨に属する範囲で、適宜修正や変更が可能である。
【図面の簡単な説明】
【0060】
【図1】本発明によるドラム構造の電解製箔機の構成図である。
【図2】本発明による高強度を有する低粗度銅箔の製造方法のフローチャートである。
【図3】本発明の実施例に従って収得された銅箔の電子顕微鏡ＳＥＭ撮影写真図である。
【図4】比較例に従って収得された銅箔の電子顕微鏡ＳＥＭ撮影写真図である。
【図5】図２に示す工程以降の後処理工程を示すフローチャートである。
【符号の説明】
【0061】
１０：ドラム
２０：陽極板
３０：ローラー

４０：銅箔
５０：電解槽
６０：電解液
６１：添加剤

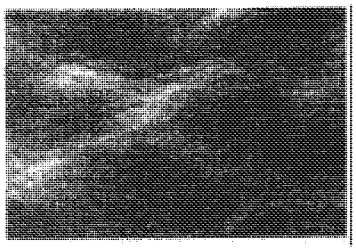
【図1】



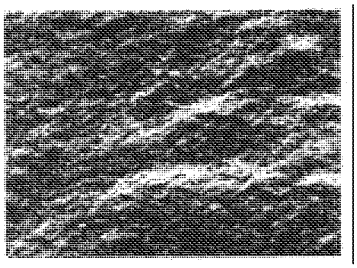
【図2】



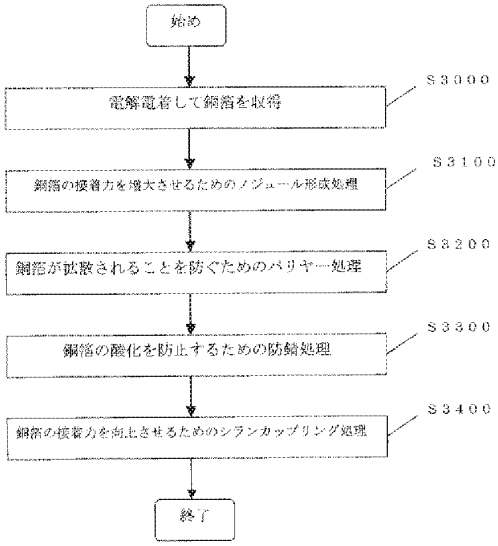
【図3】



【図4】



【図5】


始め
電解電着して銅箔を取得
S3000
銅箔の接着力を増大させるためのメジュール形成処理
S3100
銅箔が拡散されることを防ぐためのバリヤー処理
S3200
銅箔の酸化を防止するための防錆処理
S3300
銅箔の接着力を向上させるためのシランカップリング処理
S3400
終了

(72)発明者　金廷益
大韓民国ソウル特別市瑞草区蚕院洞東亜アパート１０５－４０４
(72)発明者　金尚謙
大韓民国京畿道安養市東安区富林洞１５８７－５孔雀アパート２０５－６０６
(72)発明者　趙次済
大韓民国京畿道安養市東安区虎渓洞９６８－１号保佑ビル５０２号
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(71) Applicant *(for all designated States except US)*: **ILJIN MATERIALS CO., LTD.** [KR/KR]; 827 Palbong-dong, Iksan-city, Jeollabuk-do 570-998 (KR).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **HWANG, Duck Young** [KR/KR]; 606-902, Banseok Maeul Apt., Banseok-dong, Yuseong-gu, Daejeon 305-750 (KR). **RYU, Jong Ho** [KR/KR]; 104-1302, Yeolmae Maeul 1-Danji, Jijok-dong, Yuseong-gu, Daejeon 305-769 (KR). **SONG, Ki Deok** [KR/KR]; 191-2 Seryu 1-dong, Gwonseon-gu, Suwon-si, Gyeonggi-do 441-862 (KR). **YANG, Chang Yol** [KR/KR]; 105-802, Chonggu Narae Apt., 462-4 Jeonmin-dong, Yuseong-gu, Daejeon 305-390 (KR). **KIM, Sang Beom** [KR/KR]; 503-103, Banseok Maeul Apt., Banseok-dong, Yuseong-gu, Daejeon 305-749 (KR).

(74) Agent: **Y.P.LEE, MOCK & PARTNERS**; 1575-1, Seocho-dong, Seocho-gu, Seoul 137-875 (KR).

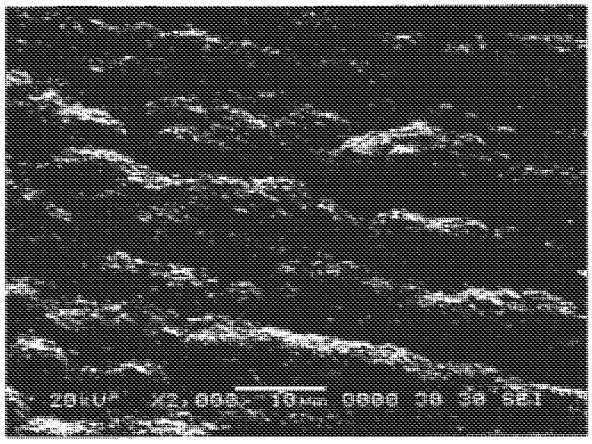
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[Continued on next page]

(54) Title: COPPER ELECTROLYSIS SOLUTION FOR PRODUCING ELECTROLYTIC COPPER FOIL, METHOD OF PRODUCING ELECTROLYTIC COPPER FOIL, AND ELECTROLYTIC COPPER FOIL

[Fig.1]



(57) Abstract: Provided is a copper electrolysis solution for producing an electrolytic copper foil, according to an embodiment of the present invention, includes a Cl- ion, and collagen peptide, wherein the collagen peptide has a number average molecular weight of 4,000 to 10,000 and a concentration of 0.5 to 20 ppm, and the Cl-ion has a concentration of 0.5 to 1.5 ppm. The copper electrolysis solution may provide an electrolytic copper foil having a relatively simple manufacturing process, high thermal stability, low roughness, and high strength. The electrolytic copper foil may be used as a current collector for middle or large-sized lithium ion secondary batteries for use in hybrid electric vehicles and as a semiconductor packing substrate for tape automated bonding (TAB) used in a tape carrier package (TCP).

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Description

Title of Invention: COPPER ELECTROLYSIS SOLUTION FOR PRODUCING ELECTROLYTIC COPPER FOIL, METHOD OF PRODUCING ELECTROLYTIC COPPER FOIL, AND ELECTROLYTIC COPPER FOIL

Technical Field

[1] The present invention relates to a copper electrolysis solution for producing an electrolytic copper foil, a method of producing an electrolytic copper foil, and an electrolytic copper foil, and more particularly, to a copper electrolysis solution including a protein having a predetermined number average molecular weight, and an electrolytic copper foil that is produced by using the copper electrolysis solution and has high thermal stability at high temperature, low roughness, high strength, and high heat resistance.

Background Art

[2] In general, a copper foil is used as a current collector for middle or large sized lithium batteries for use in hybrid electric vehicles (HEV). A pressed copper foil formed by pressing is often used as a copper foil. However, the pressed copper foil has high manufacturing costs, and is difficult to be made in a wide width.

[3] Also, during pressing, lubricant oil is used. Thus, an adhesion force between the pressed copper foil and an active material may be reduced due to contamination caused by the lubricant oil, thereby decreasing charge and discharge cycle characteristics.

[4] Lithium batteries undergo a volumetric change during charge and discharge and dissipate heat due to overcharge. Also, in order to improve an adhesive force with the active material, a surface roughness of the copper foil needs to be lowered. Accordingly, there is a need to develop a copper foil that endures the volumetric change and the heat dissipation of a lithium battery, and has a strong adhesion force with the active material, high heat resistance, high strength, and low roughness.

[5] Meanwhile, demand for fine wiring in a semiconductor mount substrate and/or a main board substrate to increase a degree of integration in a relatively small area in response to demand for small, lightweight, and high-performance electronic devices is increasing. If a thick copper foil is used in manufacturing a printed interconnection plate having a fine pattern, an etching time for forming an interconnection circuit may be long and vertical characteristics of a side wall may be degraded. In particular, if a wiring pattern formed by etching has a small line width, the formed wiring can be disconnected. Accordingly, a thinner copper foil is required to obtain a fine pitch circuit.

However, since a thin copper foil may have a limited thickness, it has a weak mechanical strength and thus, when a printed interconnection substrate is manufactured, crumpling or bending are likely to occur. Accordingly, a copper foil having a small thickness and high mechanical strength is required.

Disclosure of Invention

Technical Problem

[6] The present invention provides a copper electrolysis solution for producing an electrolytic copper foil.

[7] The present invention also provides a method of manufacturing an electrolytic copper foil by using the copper electrolysis solution.

[8] The present invention also provides an electrolytic copper foil produced by using the method.

Solution to Problem

[9] According to an aspect of the present invention, there is provided a copper electrolysis solution for producing an electrolytic copper foil, including a Cl^- ion, and collagen peptide, wherein the collagen peptide has a number average molecular weight of 4,000 to 10,000 and a concentration of 0.5 to 20 ppm, and the Cl^- ion has a concentration of 0.5 to 1.5 ppm.

[10] According to another aspect of the present invention, there is provided a method of producing an electrolytic copper foil using the copper electrolysis solution described above.

[11] According to another aspect of the present invention, there is provided an electrolytic copper foil produced by using the method.

Advantageous Effects of Invention

[12] According to the one or more embodiments of the present invention, due to use of a copper electrolysis solution including a protein having a predetermined molecular weight and a predetermined concentration, an electrolytic copper foil having low surface roughness, high tensile strength, and high thermal stability may be obtained.

Brief Description of Drawings

[13] FIG. 1 is a scanning electron microscope (SEM) image of a surface of an electrolytic copper foil manufactured according to Example 1.

[14] FIG. 2 is a graph of tensile strength with respect to an annealing temperature of electrolytic copper foils manufactured according to Examples 1 and 5 and Comparative Examples 1, 6, and 9.

Best Mode for Carrying out the Invention

[15] Hereinafter, a copper electrolysis solution for producing an electrolytic copper foil, a method of producing an electrolytic copper foil by using the copper electrolysis

solution, and an electrolytic copper foil produced by using the method, according to one or more embodiments of the present invention, will be described in detail.

[16] A copper electrolysis solution for producing an electrolytic copper foil, according to an embodiment of the present invention, includes a Cl^- ion, and collagen peptide, wherein the collagen peptide has a number average molecular weight of 4,000 to 10,000 and a concentration of 0.5 to 20 ppm, and the Cl^- ion has a concentration of 0.5 to 1.5 ppm.

[17] The collagen peptide may be a polypeptide that is prepared by decomposing gelatin extracting from bovine bones and skins, swine bones and skins, etc. A source for the collagen peptide is not limited, and may be any one of collagen peptides that are obtained by decomposing all kinds of proteins. A number average molecular weight of the collagen peptide may be, for example, 4,000 to 10,000. For example, the number average molecular weight of the collagen peptide may be, 5,000 to 8,000.

[18] If the number average molecular weight of the collagen peptide is less than 4,000, tensile strength and elongation of an electrolytic copper foil at high temperature may be reduced and a shape of grooves formed on a matte side of the electrolytic copper foil may have non-uniformity and thus the electrolytic copper foil has high roughness. If the number average molecular weight of the collagen peptide is greater than 10,000, tensile strength and elongation of an electrolytic copper foil at room temperature may be reduced and a shape of grooves formed on a matte side of the electrolytic copper foil may have non-uniformity and thus the electrolytic copper foil has high roughness.

[19] A concentration of the collagen peptide may be, for example, 0.5 to 15 ppm. For example, a concentration of the collagen peptide may be 0.5 to 10 ppm.

[20] If the concentration of the collagen peptide is less than 0.5 ppm, the concentration of the collagen peptide in a sulfuric acid-copper sulfate electrolysis solution is low and thus an electrolytic copper foil formed using the electrolysis sotluion may have low tensile strength and low thermal stability at high temperature, and also, due to the low thermal stability at high temperature, the tensile strength of the electrolytic copper foil may be easily lowered. On the other hand, if the concentration of the collagen peptide is higher than 20 ppm, much copper powder may be generated and viscosity of the sulfuric acid-copper sulfate electrolysis solution may be too high, thereby generating bubbles in an electrolysis solution and pores in an electrolytic copper foil and thus tensile strength of the electrolytic copper foil may be lowered.

[21] Regarding an electrolytic copper foil that is produced by reduction precipitation at a cathode drum that continuously rotates due to an electrochemical reaction in an electrolysis solution, high-speed plating is performed using a direct current that is often used to improve productivity. However, if an electrolytic copper foil is produced by using such a method using high-speed plating, thermal stability of the electrolytic

copper foil may be substantially lowered at high temperature. To solve this problem, according to the present invention, a small concentration of the Cl^- ion is added to an electrolysis solution to improve thermal stability of an electrolytic copper foil.

[22] If a small concentration of the Cl^- ion is included in an electrolysis solution, many initial nucleus generation sites are generated during electrolysis plating and thus, fine crystal grains are generated and precipitates of $CuCl_2$ formed at an intergranular boundary may hinder crystal growth during heated at high temperature, thereby increasing thermal stability at high temperature.

[23] If the concentration of the Cl^- ion is less than 0.5 ppm, the concentration of the Cl^- ion in the sulfuric acid-copper sulfate electrolysis solution is low, an electrolytic copper foil formed by using the copper electrolysis solution may have low room-temperature tensile strength and thermal stability at high temperature may be lowered. On the other hand, if the concentration of the Cl^- ion is higher than 1.5 ppm, a surface roughness of a matte side of the electrolytic copper foil may be increased and thus it is difficult to produce an electrolytic copper foil having low roughness, and the formed electrolytic copper foil may have low room-temperature tensile strength and low thermal stability at high temperature.

[24] That is, an electrolytic copper foil produced from a copper electrolysis solution including collagen peptide having the number average molecular weight range and the concentration range may have high mechanical strength and a matte side having low surface roughness and mechanical strength.

[25] A copper electrolysis solution for producing an electrolytic copper foil, according to another embodiment of the present invention, includes a solvent, a Cu^{2+} ion, a SO_4^{2-} ion, a Cl^- ion, and a collagen peptide, wherein the collagen peptide has a number average molecular weight of 4,000 to 10,000 and a concentration of 0.5 to 20 ppm, and the Cl^- ion has a concentraton of 0.5 to 1.5 ppm.

[26] In general, a copper foil that is generated by electro-plating has two different sides: a shiny side (S side) contacting a cathode drum and a matte side (M side) contacting an electrolysis solution on which crystal granules grow by reduction deposition. Also, surface roughness of the matte side is affected by surface roughness of the shiny side. For example, the lower the surface roughness of the shiny side, the lower the surface roughness of the matte side. A surface roughness (Rz) of a shiny side of an electrolytic copper foil produced by using the copper electrolysis solution may be 1.5 ㎛ or less.

[27] A surface roughness (Rz) of a matte side (M side) of an electrolytic copper foil produced by using the copper electrolysis solution may be 1.5 ㎛ or less. For example, the surface roughness of the matte side of the electrolytic copper foil may be 0.5 to 1.5 ㎛. For example, the surface roughness of the matte side of the electrolytic copper foil may be 0.8 to 1.5 ㎛. If the surface roughness of the matte side is higher than 2.0 ㎛, a

contacting area between the electrolytic copper foil as a current collector for a cathode and an active material may be reduced, and thus, charge and discharge cycle lifetime may be reduced and high electric capacity at initial charging may be difficult to be maintained.

[28] A room-temperature tensile strength of the electrolytic copper foil may be 50 to 70 kg/mm^2. A tensile strength of the electrolytic copper foil after the electrolytic copper foil is annealed at a temperature of 250°C for 1 hour, that is, high-temperature tensile strength of the electrolytic copper foil, may be 70% or more of a room-temperature tensile strength of the electrolytic copper foil. The room-temperature tensile strength refers to a tensile strength of a copper foil obtained at room temperature without performing a high-temperature heat treatment.

[29] A concentration of Cu^{2+} ion in a sulfuric acid-copper sulfate copper electrolysis solution may be 70 g/L to 150 g/L, but is not limited thereto. The concentration of Cu^{2+} ion in the sulfuric acid-copper sulfate copper electrolysis solution may be appropriately controlled as long as the objectives of the present invention are achieved. For example, the concentration of Cu^{2+} may be 85 g/L to 100 g/L.

[30] A concentration of the free SO_4^{2-} refers to a concentration of the residual SO_4^{2-} formed by substracting the concentration of SO_4^{2-} calculated from conversion of the Cu^{2+} concentration in the copper electrolyte solution to $CuSO_4$ from the total SO_4^{2-} concentration in the copper electrolyte solution. The concentration of the free SO_4^{2-} may be 50 g/L to 200 g/L, but is not limited thereto, and may be appropriately controlled as long as the objectives of the present invention are achieved. For example, the concentration of SO_4^{2-} may be 80 g/L to 150 g/L.

[31] The copper electrolysis solution may be prepared by using any known method. For example, the concentration of the Cu^{2+} may be adjusted by controlling a concentration of a copper sulfate, and the concentration of SO_4^{2-} ion may be adjusted by controlling a concentration of a sulfuric acid and copper sulfate. The concentration and the number average molecular weight of the collagen polypeptide included in the copper electrolysis solution may be calculated from an amount and a number average molecular weight of collagen polypeptide added to the copper electrolysis solution, or may be obtained by analyzing the collagen polypeptide included in the copper electrolysis solution by any known method, such as column chromatography.

[32] A method of producing an electrolytic copper foil according to an embodiment of the present invention is performed by using the copper electrolysis solution for producing an electrolytic copper foil. The method of producing an electrolytic copper foil may be the same as a known method, except that the copper electrolysis solution as described above is used.

[33] An example of the method of producing the electrolytic copper foil will now be

described in detail.

[34] A copper electrolysis solution is supplied between the curved surface of a revolving drum-shaped titanium cathode and an anode to conduct electrolysis, thereby depositing in the form of a deposited foil on the surface of the cathode and continuously taking up the foil.

[35] A temperature of the copper electrolysis solution used in the method may be 45 to 65℃, but is not limited thereto, and may be appropriately controlled as long as the objectives of the present invention are achieved. For example, the temperature of the copper electrolysis solution may be 50 to 60℃.

[36] A current density used in the method may be 40 to 100 A/dm^2, but is not limited thereto, and may be appropriately controlled as long as the objectives of the present invention are achieved. For example, the current density may be 50 to 80 A/dm^2.

[37] An electrolytic copper foil according to an embodiment of the present invention may be produced by using the method described above.

[38] The electrolytic copper foil produced by using the method described above may have a matte side having a surface roughness (Rz) of 1.5 ㎛ or less. For example, the surface roughness of the electrolytic copper foil may be 0.5 to 1.5 ㎛. For example, the surface roughness of the electrolytic copper foil may be 0.8 to 1.5 ㎛. If the surface roughness of the electrolytic copper foil is 1.5 ㎛ or more, a contacting area between the electrolytic copper foil as a current collector for a cathode and an active material may be reduced, and thus, charge and discharge cycle lifetime may be reduced and high electric capacity at initial charging may be difficult to be maintained.

[39] A tensile strength of the electrolytic copper foil after the electrolytic copper foil is annealed at a temperature of 250℃ for 1 hour may be 70% or more of the room-temperature tensile strength. The room-temperature tensile strength refers to a tensile strength of a copper foil obtained at room temperature without performing a high-temperature heat treatment.

Mode for the Invention

[40] Hereinafter, examples of the present invention will be described in detail, but the present invention is not limited thereto.

[41] (Production of Electrolytic Copper Foil)

[42] Examples 1-6 and Comparative Examples 1-9

[43] In order to produce an electrolytic copper foil by an electrochemical system, a 3L-capacity electrolytic cell system that circulates at a rate of 20 L/min was used and a temperature of an electrolysis solution was maintained at 50℃. A dimensionally stable electrode (DSE) plate having a thickness of 5 mm and a size of 10×10 cm^2 was used as an anode, and a titanium electrode plate having the same size and thickness was used

as a cathode. A copper electrolysis solution used included 87.5 g/L of Cu^{2+} and 125 g/L of SO_4^{2-} . All examples used a Cl^- ion except for Comparative Example 7.

[44] All examples used a collagen peptide (C&A Biotech, Collagen peptide) except for Comparative Example 1.

[45] A distance between the cathode and the anode was maintained at 10 cm, and plating was performed with a current density of 60 A/dm^2 so as to allow Cu^{2+} ions to flow smoothly, and an electrolytic copper foil having a thickness of 18 ㎛ was produced. FIG. 1 shows a scanning electron microscope (SEM) image of a surface of the electrolytic copper foil.

[46] Table 1 shows compositions of electrolysis solutions used in Examples 1-6 and Comparative Examples 1-9.

[47] Table 1

[Table 1]

	Thickness(㎛)	Temperature(℃)	Current density(A/dm²)	Basic composition			Collagen peptide	
				Cu(g/L)	SO_4^{2-}(g/L)	Cl(ppm)	Molecular weight	Concentration(ppm)
Example 1	18	50	60	87.5	125	1	7,000	1
Example 2	18	50	60	87.5	125	1	4,000	1
Example 3	18	50	60	87.5	125	1	10,000	1
Example 4	18	50	60	87.5	125	1	7,000	0.5
Example 5	18	50	60	87.5	125	1	7,000	5
Example 6	18	50	60	87.5	125	1	7,000	10
Comparative Example 1	18	50	60	87.5	125	1	-	-
Comparative Example 2	18	50	60	87.5	125	1	3,000	1
Comparative Example 3	18	50	60	87.5	125	1	20,000	1
Comparative Example 4	18	50	60	87.5	125	1	7,000	0.05
Comparati	18	50	60	87.5	125	1	7,000	30

ve Example 5								
Comparative Example 6	18	50	60	87.5	125	1	7,000	50
Comparative Example 7	18	50	60	87.5	125	-	7,000	1
Comparative Example 8	18	50	60	87.5	125	2	7,000	1
Comparative Example 9	18	50	60	87.5	125	5	7,000	1

[48]

[49] Evaluation Example 1: Evaluation of Surface Roughness (Rz)

[50] Surface roughness (Rz) of a matte side and a shiny side of each of electrolytic copper foils produced according to Examples 1 to 6 and Comparative Examples 1 to 9 was evaluated according to JISB 0601-1994 criteria. The evaluated surface roughness (Rz) values are shown in Table 2 below. The lower the Rz value, the lower a degree of roughness.

[51] Evaluation Example 2: Evaluation of Room-Temperature Tensile Strength and Room-Temperature Elongation

[52] A tensile sample having a width of 12.7 mm and a gage length of 50 mm was collected from each of electrolytic copper foils produced according to Examples 1 to 5 and Comparative Examples 1 to 8, and then a tensile strength test was performed thereon at a crosshead speed of 50.8 mm/min according to IPC-TM-650 2.4.18B criteria. A maximum weight of a tensile strength was referred to as a room-temperature tensile strength, and an elongation when the electrolytic copper foils were broken was referred to as a room-temperature elongation. The room-temperature tensile strengths and the room-temperature elongations evaluated as described above are shown in

Table 2 below.

[53] Table 2

[Table 2]

	Surface roughness		Room-temperature tensile strength[kgf/mm^2]	Room-temperature elongation[%]
	Matte side (M side)(Rz)[㎛]	Shiny side(S side)(Rz)[㎛]		
Example 1	1.03	1.04	62.43	6.16
Example 2	1.07	1.19	59.97	4.02
Example 3	1.12	1.44	59.74	4.78
Example 4	1.09	1.34	60.15	4.77
Example 5	1.17	1.28	61.07	4.26
Example 6	1.12	1.27	61.17	4.85
Comparative Example 1	1.85	1.79	50.83	2.59
Comparative Example 2	1.78	1.71	51.55	2.61
Comparative Example 3	1.76	1.74	52.51	3.28
Comparative Example 4	1.89	1.75	51.91	2.59
Comparative Example 5	1.98	1.82	47.15	2.01
Comparative Example 6	2.37	1.83	42.18	1.77
Comparative Example 7	1.15	1.81	50.38	1.77
Comparative Example 8	2.63	1.85	48.42	2.25
Comparative Example 9	3.55	1.93	38.29	1.95

[54]

[55] As shown in Table 2, the electrolytic copper foils of Examples 1 to 6 have lower

surface roughness and higher room-temperature tensile strength and elongation than the electrolytic copper foils of Comparative Examples 1 to 9.

[56] Evaluation Example 3: Evaluation of Tensile Strength according to Heat Treatment Temperature

[57] In order to evaluate thermal stability of an electrolytic copper foil, each of electrolytic copper foils produced according to Examples 1 to 6 and Comparative Example s1 to 9 was not heat treated, or annealed at temperatures of 100℃, 150℃, 200℃, and 250℃, each for 1 hour. Then, a tensile test was performed thereon with a crosshead speed of 50.8 mm/min according to IPC-TM-650 2.4.18B criteria, and then, tensile strength was measured at room temperature. The room temperature was 25℃.

[58] A tensile strength according to a heat treatment temperature obtained by using the evaluation method is shown in Table 3 and FIG. 2.

[59] Table 3

[Table 3]

	Tensile strength according to heat treatment temperature (kgf/mm^2)				
	No heat treatment	100℃	150℃	200℃	250℃
Example 1	62.43	56.61	53.52	49.57	48.58
Example 2	59.97	55.41	52.78	48.98	46.77
Example 3	59.74	57.01	53.97	48.87	45.14
Example 4	60.15	55.97	52.41	47.57	46.01
Example 5	61.07	56.44	54.35	55.84	51.59
Example 6	61.17	55.74	53.14	49.75	48.98
Comparative Example 1	50.83	48.53	31.78	27.28	26.29
Comparative Example 2	51.55	44.42	39.52	36.14	29.97
Comparative Example 3	50.54	45.99	43.73	30.14	26.71
Comparative Example 4	51.91	50.11	30.05	25.38	22.94
Comparative Example 5	47.15	46.52	38.24	33.14	29.85
Comparative Example 6	42.18	38.45	30.57	28.74	23.04
Comparative Example 7	50.38	49.49	29.95	26.28	24.01
Comparative Example 8	48.42	47.58	41.31	35.76	31.41
Comparative Example 9	38.29	34.51	36.29	32.21	30.85

[60]

[61] As shown in Table 2 and FIG. 2, the tensile test on the electrolytic copper foils of Examples 1-6 that had been annealed at a temperature of 100 to 250℃ for 1 hour has the flowing results. A tensile strength after the annealing was performed at a tem-

perature of 250℃ was 70% or more of a room-temperature tensile strength of an electrolytic copper foil that had not been annealed. However, regarding Comparative Examples 1-9, a tensile strength after the annealing was performed at a temperature of 250℃ was 60% or less of a room-temperature tensile strength of an electrolytic copper foil that had not been annealed. Accordingly, a decrease in tensile strength of each of the electrolytic copper foils of Examples 1-6 according to increasing temperature was relatively low.

[62] Also, as shown in FIG. 2, regarding the electrolytic copper foils of Comparative Examples 1, 6, and 9, a tensile strength after the annealing was performed at a temperature of 250℃ was 40% or less of a room-temperature tensile strength of an electrolytic copper foil that had not been annealed. In particular, the tensile strength of the electrolytic copper foil of Comparative Example 6 according to a heat treatment temperature increase was significantly decreased. Accordingly, it was confirmed that the electrolytic copper foils of the comparative examples have low thermal stability and thus are not suitable for use as a current collector for a lithium battery.

Industrial Applicability

[63] According to the one or more embodiments of the present invention, due to use of a copper electrolysis solution including a protein having a predetermined molecular weight and a predetermined concentration, an electrolytic copper foil having low surface roughness, high tensile strength, and high thermal stability may be obtained.

Claims

[Claim 1] A copper electrolysis solution for producing an electrolytic copper foil, comprising a Cl^- ion, and collagen peptide, wherein the collagen peptide has a number average molecular weight of 4,000 to 10,000 and a concentration of 0.5 to 20 ppm, and the Cl^- ion has a concentration of 0.5 to 1.5 ppm.

[Claim 2] The copper electrolysis solution of claim 1, wherein the electrolytic copper foil has a matte side having a surface roughness (Rz) is 1.5 ㎛ or less.

[Claim 3] The copper electrolysis solution of claim 1, wherein the electrolytic copper foil has a room-temperature tensile strength of 50 to 70 kg/mm^2.

[Claim 4] The copper electrolysis solution of claim 1, wherein a tensile strength of the electrolytic copper foil after the electrolytic copper foil is annealed at a temperature of 250℃ for 1 hour is 70% or more of a room-temperature tensile strength of the electrolytic copper foil.

[Claim 5] A method of producing an electrolytic copper foil using the copper electrolysis solution of any one of claims 1-4.

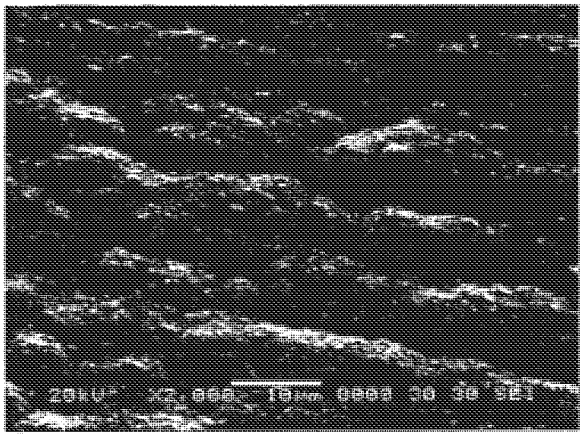
[Claim 6] An electrolytic copper foil produced by using the method of claim 5.

[Claim 7] The electrolytic copper foil of claim 6, wherein the electrolytic copper foil has a matte side (M side) and a shiny side (S side), wherein a surface roughness (Rz) of the M side is 1.5 ㎛ or lower and a surface roughness (Rz) of the shiny side (S side) is 1.5㎛ or lower.

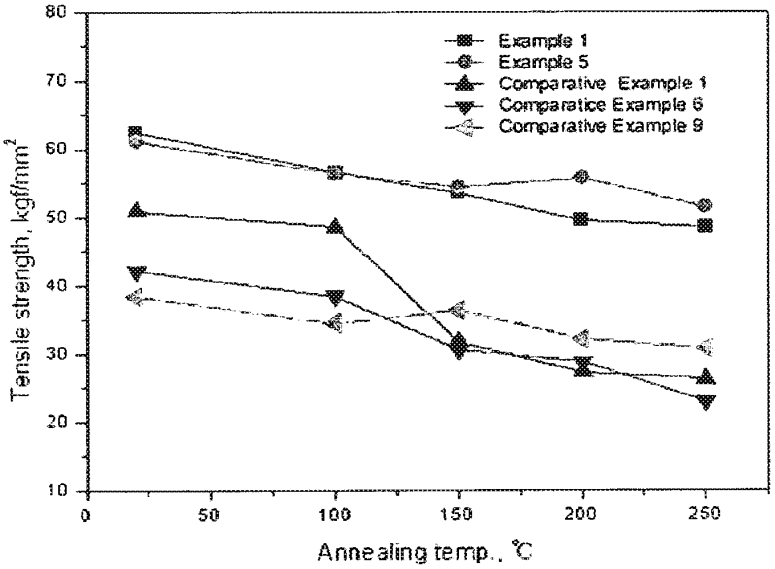
[Claim 8] The electrolytic copper foil of claim 6, wherein the electrolytic copper foil has a room-temperature tensile strength of 50 to 70 kg/mm^2.

[Claim 9] The electrolytic copper foil of claim 6, wherein a tensile strength of the electrolytic copper foil after the electrolytic copper foil is annealed at a temperature of 250℃ for 1 hour is 70% or more of a room-temperature tensile strength of the electrolytic copper foil.

[Fig.1]



[Fig.2]


Example 1
Example 5
Comparative Example 1
Comparatice Example 6
Comparative Example 9
Tensile strength, kgf/mm²
Annealing temp., ℃
80
70
60
50
40
30
20
10
0
50
100
150
200
250

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(71) 出願人 (米国を除く全ての指定国について): ＪＸ日鉱日石金属株式会社(JX Nippon Mining & Metals Corporation) [JP/JP]; 〒1008164 東京都千代田区大手町二丁目６番３号 Tokyo (JP).

(72) 発明者; および

(75) 発明者/出願人 (米国についてのみ): 古曳 倫也 (KOHIKI Michiya) [JP/JP]; 〒3170056 茨城県日立市白銀町３丁目３番１号 ＪＸ日鉱日石金属株式会社 日立事業所 銅箔製造部内 Ibaraki (JP).

(74) 代理人: 小越 勇(OGOSHI Isamu); 〒1050001 東京都港区虎ノ門２丁目９番１４号 発明会館５階 小越国際特許事務所 Tokyo (JP).

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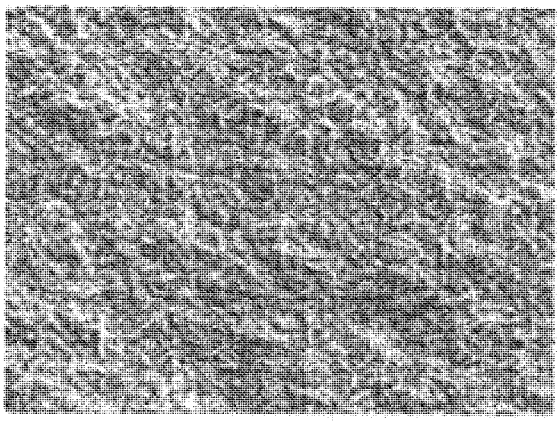
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(54) Title: ELECTROLYTIC COPPER FOIL AND PROCESS FOR PRODUCING SAME

(54) 発明の名称 : 電解銅箔及びその製造方法

[図3]



(57) Abstract: Provided is an electrolytic copper foil which has high normal-state tensile strength, is reduced in surface roughness, and has few protrusions due to abnormal electrodeposition, in particular, an electrolytic copper foil which is useful as a negative current collector for secondary batteries. This electrolytic copper foil is a copper foil which has a normal-state tensile strength of 45-70 kgf/mm^2, and in which the number of protrusions due to abnormal electrodeposition that have a height of 1.0 μm or more and a diameter of 4.0 μm or more is 20 or less per cm^2, and which has a surface roughness Rz of 2.0 μm or less.

(57) 要約: 常態引張り強さが高く、表面粗さが小さく、異常電着による突起の少ない電解銅箔、特に二次電池用負極集電体に有用である電解銅箔を提供する。 本発明の電解銅箔は、常態引張り強さが４５ｋｇｆ／ｍｍ^2～７０ｋｇｆ／ｍｍ^{2}であり、高さが１．０μｍ以上、直径が４．０μｍ以上である異常電着による突起の個数が２０個／ｃｍ^{2}以下であり、表面粗さＲｚが２．０μｍ以下である。

WO 2014/033917 A1

明 細 書

発明の名称 ： 電解銅箔及びその製造方法

技術分野

[0001] 本発明は、表面粗さが小さく、強度が高く、異常電着による突起形状が少ない電解銅箔及びその製造方法に関し、特に二次電池負極集電体に有用である電解銅箔に関する。

背景技術

[0002] 電気めっきによって製造される電解銅箔は、電気・電子関連産業の発展に大きく寄与しており、印刷回路材や二次電池負極集電体として不可欠の存在となっている。電解銅箔の製造の歴史は古い（特許文献１及び特許文献２参照）が、最近は二次電池負極集電体としてその有用性が再確認されている。

[0003] 電解銅箔の製造例を示すと、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する。

この電解槽の中に、銅、硫酸、にかわを導入して電解液とする。そして、線速、電解液温、電流密度を調節し、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、連続的に銅箔を製造している。

[0004] この電解銅箔製造方法は製造コストの低減化を図ることができ、数μｍ程度の極めて薄い層厚から７０μｍ程度の厚い銅箔まで製造することが可能であり、また電解銅箔の片面が適度な粗度を有するので、樹脂との接着強度が高いという、多くの利点を有している。

[0005] 近年、車載用電池負極材用銅箔として電解銅箔が使用されるが、その特性として電解銅箔の強度が高いことが要求されている。従来、製造されている電解銅箔は、この高強度の要求に応えられる特性を有している。しかしながら、銅層形成過程において異常電着により核成長が急速に進行した突起形状が５０個／ｃｍ^{2}の密度で発生するという問題がある。

[0006] なお、異常電着による突起形状は、高さが１．０μｍ以上、直径が４．０μｍ以上である円柱状の突起形状であるが、従来の電解銅箔では、高さは１．０～５．０μｍで平均としては２．７μｍ、径は４．０～２０．０μｍで平均としては９．８μｍの分布を有している。

代表的な異常電着による突起形状を図１に示す。また、異常電着による突起形状の数量は電子顕微鏡観察にて計測し、その高さ及びサイズは3次元表面形状測定装置（ＶＥＥＣＯ社製：ＮＴ１１００）にて計測したものである。

[0007] 異常電着による突起形状は、電解銅箔の製造工程で発生する電着工程に原因があると考えられる。異常電着による突起形状は、銅箔特性に直接的な影響を与えるものではないが、極力低減する必要がある。

先行技術文献

特許文献

[0008] 特許文献1：特開平７－１８８９６９号公報

特許文献2：特開２００４－１０７７８６号公報

発明の開示

発明が解決しようとする課題

[0009] 本発明は、表面粗さが小さく、強度が高く、異常電着による突起形状が少ない電解銅箔及びその製造方法に関し、特に二次電池負極集電体に有用である電解銅箔を提供することを課題とする。

課題を解決するための手段

[0010] 本願は、次の発明を提供するものである。

１）表面粗さＲｚ２．０μｍ以下であり、高さが１．０μｍ以上、直径が４．０μｍ以上である異常電着による突起形状の個数が２０個／ｃｍ^{2}以下であることを特徴とする電解銅箔。

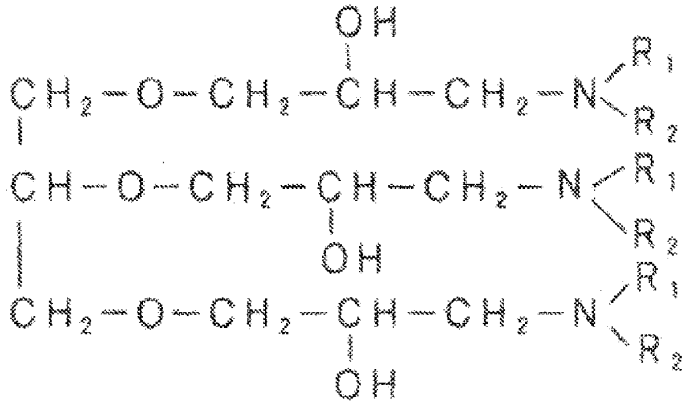
２）抗張力が４５～７０ｋｇｆ／ｍｍ^{2}であることを特徴とする前記１）記載の電解銅箔。

３）二次電池負極集電体用銅箔であることを特徴とする前記１）又は２）記

載の電解銅箔。

[0011] ４）硫酸系銅電解液を用いた電解法により電解銅箔を製造する方法であって、にかわ：２～５ｍａｓｓｐｐｍ、１分子中に１個以上のエポキシ基を有する化合物とアミン化合物とを付加反応させることにより得られる下記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３～１０ｍａｓｓｐｐｍを含む電解液を用いて、電解液温度を６０～６５°Ｃとし、電流密度を６０～１２０Ａ／ｄｍ²として電解することを特徴とする電解銅箔の製造方法。

[0012] [化1]

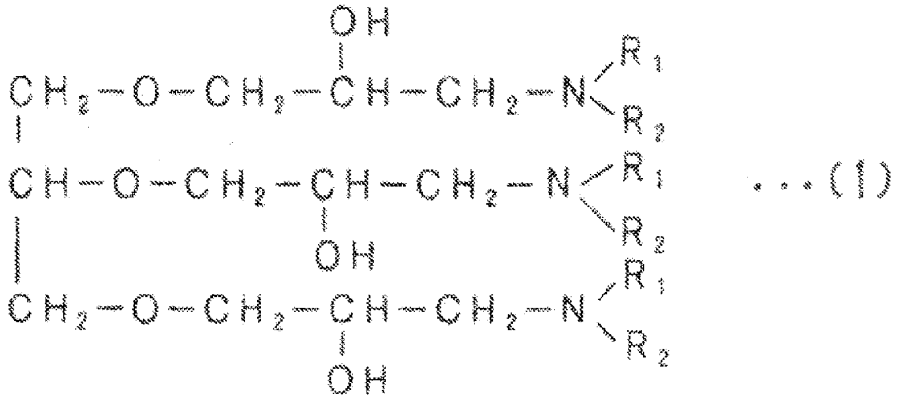


...(1)

（一般式（１）中、Ｒ１及びＲ２はヒドロキシアルキル基、エーテル基、アリール基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものである。）

５）硫酸系銅電解液を用いた電解法により電解銅箔を製造する方法であって、にかわ：２～５ｍａｓｓｐｐｍ、１分子中に１個以上のエポキシ基を有する化合物とアミン化合物とを付加反応させることにより得られる下記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３～１０ｍａｓｓｐｐｍを含む電解液を用いて、電解液温度を６０～６５°Ｃとし、電流密度を６０～１２０Ａ／ｄｍ²として電解することにより、１）又は２）に記載の電解銅箔を製造することを特徴とする電解銅箔の製造方法。

[0013] [化2]



...(1)

（一般式（１）中、Ｒ１及びＲ２はヒドロキシアルキル基、エーテル基、アリール基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものである。）

（６）上記４）又は５）による二次電池負極集電体用銅箔の製造方法。

発明の効果

[0014] 本発明は、強度が高く、かつ異常電着による突起形状が少ない電解銅箔及びその製造方法に関し、特に二次電池負極集電体に有用である電解銅箔を提供できる優れた効果を有している。

図面の簡単な説明

[0015] [図1]異常電着粒子の形状を示す顕微鏡写真である。

[図2]一般式（１）で示す特定骨格を有するアミン化合物の添加剤を有していない比較例の代表的な表面状態の電子顕微鏡写真を示す図である。

[図3]実施例の代表的な表面状態の電子顕微鏡写真を示す図である。

発明を実施するための形態

[0016] 本発明は、電解銅箔の中に、異常電着による突起形状が少なく、かつ高強度を発現できる電解銅箔を提供するものである。本願発明の電解銅箔は、二次電池負極集電体用銅箔として特に有用である。

具体的には、にかわ：２～５ｍａｓｓｐｐｍ、１分子中に１個以上のエポ

キシ基を有する化合物とアミン化合物とを付加反応させることにより得られる一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３～１０ｍａｓｓｐｐｍを含む電解液を用いることでメッキ過程での銅層成長を抑制する。

すなわち、これによって異常電着を抑制することができ、表面粗さがＲｚ：２．０μｍ以下であり、４５ｋｇｆ／ｍｍ²～７０ｋｇｆ／ｍｍ²の高強度でありかつ異常電着による突起形状を２０個／ｃｍ²の発生密度に低減した電解銅箔を提供するものである。

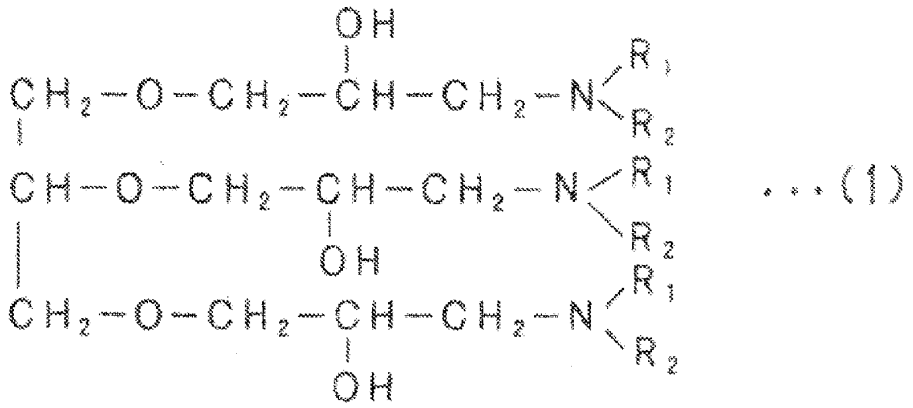
[0017] 一般的に銅層は粒界の核発生と核生成の進行により形成される。従来の製造方法は添加剤により、核生成より核発生の割合を多くすることで、微細粒界を形成させ、低粗度、高強度特性を発現する。しかしながら、従来の製造方法では、核発生の発生速度が核生成速度に合わず、一部核生成が進行することで異常電着による突起形状が発生する問題が生じている。

[0018] 本発明は添加剤として従来添加剤であるにかわの他に新たに分子中に１個以上のエポキシ基を有する化合物とアミン化合物とを付加反応させることにより得られる一般式（１）で示す特定骨格を有するアミン化合物の添加剤を加えることで、銅層の形成速度を全体的に抑制し、核発生の発生速度と核生成速度を調整し、異常電着による突起形状の個数を低減したものである。

[0019] 以上の硫酸系銅電解液を用いた電解法により電解銅箔を製造する方法において、平均粒径５～１５μｍサイズの異常電着粒子が２０個／ｃｍ²以下であり、強度が４５～７０ｋｇｆ/ｍｍ²であり、かつ表面粗さがＲｚ２．０μｍ以下の電解銅箔を製造するためには、にかわ：２～５ｍａｓｓｐｐｍ、１分子中に１個以上のエポキシ基を有する化合物とアミン化合物とを付加反応させることにより得られる一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３～１０ｍａｓｓｐｐｍを含む電解液を用いて、電解液温度を６０～６５°Ｃとし、電流密度を６０～１２０Ａ／ｄｍ²として電解することが、好適が条件である。

[0020]

[化3]



[0021] 前記一般式（１）中、Ｒ１及びＲ２はヒドロキシアルキル基、エーテル基、アリール基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものである。

[0022] 本願発明の電解銅箔は、硫酸系銅電解液を用いた電解法により電解銅箔を製造する。本願発明は、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従来の電解銅箔製造装置を用いて、製造することができる。この装置の例は一例であり、装置の仕様に特に制限はない。

[0023] この電解槽の中に、銅濃度：８０～１１０ｇ／Ｌ、硫酸濃度：７０～１１０ｇ／Ｌ、にかわ濃度：２．０～１０．０ｍａｓｓｐｐｍ、１分子中に１個以上のエポキシ基を有する化合物とアミン化合物とを付加反応させることにより得られる一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３～１０ｍａｓｓｐｐｍを導入して電解液とする。

[0024] そして、電解液温：６０°Ｃ～６５°Ｃ、電流密度：６０～１２０Ａ／ｄｍ²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、連続的に銅箔を製造する。

すなわち、上記の通り、電解液温度を６０～６５°Ｃとし、電流密度を６

０～１２０Ａ／ｄｍ²として電解することが、上記の特性を有する電解銅箔を得る好適な条件である。特に電解液温の調整は重要である。詳細は、実施例及び比較例で説明する。

なお、電解銅箔の厚みは、以下に制限されないが、例えば３５μｍ以下、好ましくは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。厚みの限界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。上述の厚みの電解銅箔は二次電池負極集電体用電解銅箔としても好適に用いることが出来る。

[0025] この電解の表面又は裏面、さらには両面に、次の防錆処理を行う。好ましい防錆処理は、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である。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。

[0026] 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、水溶性亜鉛塩、例えばＺｎＯ 、ＺｎSO_4・７H_2Oなど少なくとも一種と、水酸化アルカリとの混合水溶液が用いられる。代表的なめっき浴組成と電解条件例は次の通りである。こうして得られた銅箔は、優れた耐熱性剥離強度、耐酸化性及び耐塩酸性を有する。

[0027] （クロム防錆処理）

$K_2Cr_2O_7$（$Na_2Cr_2O_7$或いはCrO_3）：２～１０ｇ／リットル

ＮａＯＨ或いはＫＯＨ ：１０～５０ｇ／リットル

ＺｎＯ 或いはＺｎSO_4・７H_2O：０．０５～１０ｇ／リットル

ｐＨ：３～１３

浴温：２０～８０° Ｃ

電流密度D_k ：０．０５～５Ａ／ｄｍ²

時間：５～３０秒

アノード：Ｐｔ－Ｔｉ 板、ステンレス鋼板等

[0028] クロム酸化物はクロム量として１５μｇ／ｄｍ²以上、亜鉛は３０μｇ／ｄｍ²以上の被覆量が要求される。

また、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。例えば、平均の表面粗さＲａを０．０４～０．２０μｍとすることができる。この場合、平均の表面粗さＲａの下限を０．０４μｍとする理由は、微細な粒子を形成し、密着性を良好にするためである。

[0029] これによって、例えば二次電池の活物質を極力多く塗布することが可能となり、電池の電気容量を高めることができる。他方、上限を０．２０μｍとする理由は、重量厚みのばらつきを少なくするためである。これによって、例えば二次電池の充放電特性を向上させることができる。これらの表面粗さは一例を示すものであり、電解銅箔の用途に応じて適宜調節できる。

[0030] 二次電池用負極集電体用銅箔を例に挙げると、粗化処理面の粗化粒子の平均直径を０．１～０．４μｍとすることが望ましい。粗化粒子は、微細な粒子であると共に、その微細粒子がより均一であることが望まれる。これも、上記と同様に、電池活物質の密着性を向上させ、活物質を極力多く塗布して電池の電気容量を高めるために好ましい形態である。

[0031] 二次電池用負極集電体用銅箔は、粗化処理層の最大高さを０．２μｍ以下とすることが望ましい。これも粗化処理層の厚みばらつきを低減させ、電池活物質の密着性を向上させ、活物質を極力多く塗布して電池の電気容量を高めるために好ましい形態である。本願発明は、この粗化粒子の厚みを０．２μｍ以下とする指標を基に、管理し、これを達成することが可能である。

[0032] 二次電池用負極集電体用銅箔は、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、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形態の要素である。

[0033] 本発明の二次電池用負極集電体用銅箔上の粗化処理を、例えば銅の粗化処理又は銅－コバルト－ニッケル合金めっき処理を施すことができる。

例えば、銅の粗化処理は、次の通りである。

銅粗化処理

Ｃｕ： １０～２５ｇ／Ｌ

H_2SO_4： ２０～１００ｇ／Ｌ

温度： ２０～４０° Ｃ

Ｄｋ： ３０～７０Ａ／ｄｍ^2

時間： １～５秒

[0034] また、銅－コバルト－ニッケル合金めっき処理による粗化処理は、次の通りである。電解めっきにより、付着量が１５～４０ｍｇ／ｄｍ^{2}銅－１００～３０００μｇ／ｄｍ^{2}コバルト－１００～５００μｇ／ｄｍ^{2}ニッケルであるような３元系合金層を形成するように実施する。この３元系合金層は耐熱性も備えている。

[0035] こうした３元系銅－コバルト－ニッケル合金めっきを形成するための一般的浴及びめっき条件は次の通りである。

（銅－コバルト－ニッケル合金めっき）

Ｃｕ：１０～２０ｇ／リットル

Ｃｏ：１～１０ｇ／リットル

Ｎｉ：１～１０ｇ／リットル

ｐＨ：１～４

温度：３０～５０° Ｃ

電流密度D_k：２０～５０Ａ／ｄｍ^2

時間：１～５秒

[0036] 粗化処理後、粗化面上にコバルト－ニッケル合金めっき層を形成することができる。このコバルト－ニッケル合金めっき層は、コバルトの付着量が２

００～３０００μｇ／ｄｍ²であり、かつコバルトの比率が６０～７０質量％とする。この処理は広い意味で一種の防錆処理とみることができる。

[0037] コバルトーニッケル合金めっきの条件は次の通りである。

（コバルトーニッケル合金めっき）

Ｃｏ：１～２０ｇ／リットル

Ｎｉ：１～２０ｇ／リットル

ｐＨ：１．５～３．５

温度：３０～８０°Ｃ

電流密度D_k：１．０～２０．０Ａ／ｄｍ²

時間：０．５～４秒

[0038] コバルトーニッケル合金めっき上に更に、亜鉛ーニッケル合金めっき層を形成することができる。亜鉛ーニッケル合金めっき層の総量を１５０～５００μｇ／ｄｍ²とし、かつニッケルの比率を１６～４０質量％とする。これは、耐熱防錆層という役割を有する。

[0039] 亜鉛ーニッケル合金めっきの条件は、次の通りである。

（亜鉛ーニッケル合金めっき）

Ｚｎ：０～３０ｇ／リットル

Ｎｉ：０～２５ｇ／リットル

ｐＨ：３～４

温度：４０～５０°Ｃ

電流密度D_k：０．５～５Ａ／ｄｍ²

時間：１～３秒

[0040] 最後に、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される。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。

[0041] 上記については、主として二次電池用負極集電体に適用する本願発明の電解銅箔への付加的な表面処理層について説明したが、電解銅箔の用途に応じてこれらを任意に適用できることは言うまでもない。本発明はこれらを全て包含するものである。

実施例

[0042] 以下、実施例及び比較例に基づいて説明する。なお、本実施例はあくまで一例であり、この例のみに制限されるものではない。すなわち、本発明に含まれる他の態様または変形を包含するものである。

[0043] （実施例１）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６０°Ｃ、電流密度：８５Ａ／ｄｍ^{2}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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0044] この条件を表１に示す。このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：５４．１ｋｇｆ／ｍｍ^2、Ｒｚ表面粗さ：１．３μｍ、異常電着による突起形状数：１個／ｃｍ^{2}となった。

いずれも本願発明の条件を満足していた。また、代表的な表面状態の電子顕微鏡写真を図3に示す。図3より、明らかに異常電着による突起形状の発生が抑制されていることが確認できる。以下の実施例及び比較例の、結果も表１に示す。

[0045]

[表1]

	にかわの濃度 2～8 (mass ppm)	前記一般式(1)で表す特定構造を有するアミン化合物の添加剤 2～10 (mass ppm)	電解液温度 60～65 (℃)	電流密度 80～120 (A/dm2)	抗張力 45～70 (kgf/mm2)	Rz平均粗さ 2以下 (μm)	実施者間による実施形態数 2以下
実施例1	3	3	60	85	54.1	1.3	1
実施例2	3	5	60	85	58.3	1.4	1
実施例3	3	10	60	85	61.7	1.8	1
実施例4	3	3	60	61	58.3	1.5	1
実施例5	3	3	60	73	58.5	1.5	1
実施例6	3	3	60	85	57.7	1.4	1
実施例7	3	3	60	120	61.2	1.7	16
実施例8	3	3	64	68	52.1	1.2	2
比較例1	0	3	60	85	56.3	3.2	61
比較例2	3	0	60	85	55.9	1.5	53
比較例3	3	1	60	85	58.7	1.4	52
比較例4	2	3	57	85	59.3	1.6	26
比較例5	3	12	60	85	65.2	2.1	1
比較例6	3	3	60	46	44.3	1.5	36
比較例7	3	3	60	133	71.3	2.2	35
比較例8	2	3	57	85	62.3	1.4	43

[0046] （実施例２）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：５ｍａｓｓｐｐｍを導入して電解液とした。そして、電解液温：６０°Ｃ、電流密度：８５Ａ／ｄｍ^{2}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、連続的に銅箔を製造した。なお、銅箔の厚みは１２μｍとした。

[0047] このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：５９．３ｋｇｆ／ｍｍ^2、Ｒｚ表面粗さ：１．４μｍ、異常電着による突起形状数：１個/ｃｍ^{2}となった。

いずれも本願発明の条件を満足していた。

[0048] （実施例３）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：１０ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６０°Ｃ、電流密度：８５Ａ／ｄｍ^{2}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、連続的に銅箔を製造した。なお、銅箔の厚みは６μｍとした。

[0049] このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：６１．７ｋｇｆ／ｍｍ^2、Ｒｚ表面粗さ：１．８μｍ、異常電着による突起形状数：１個/ｃｍ^{2}となった。

いずれも本願発明の条件を満足していた。

[0050] （実施例４）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６０°Ｃ、電流密度：６１Ａ／ｄｍ²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、連続的に銅箔を製造した。なお、銅箔の厚みは２０μｍとした。

[0051] このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：５８．３ｋｇｆ／ｍｍ²、Ｒｚ表面粗さ：１．５μｍ、異常電着による突起形状数：１個/ｃｍ²となった。いずれも本願発明の条件を満足していた。

[0052] （実施例５）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物と有機硫黄化合物の添加剤：３ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６０°Ｃ、電流密度：７３Ａ／ｄｍ²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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0053] このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：５８．５ｋｇｆ／ｍｍ²、Ｒｚ表面粗さ：１．８μｍ、異常電着による突起形状数：１個/ｃｍ²となった。いずれも本願発明の条件を満足していた。

[0054] （実施例６）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６０°Ｃ、電流密度：８５Ａ／ｄｍ²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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0055] このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：５７．７ｋｇｆ／ｍｍ²、Ｒｚ表面粗さ：１．４μｍ、異常電着による突起形状数：１個/ｃｍ²となった。いずれも本願発明の条件を満足していた。

[0056] （実施例７）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６０°Ｃ、電流密度：１２０Ａ／ｄｍ²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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0057] このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：６１．２ｋｇｆ／ｍｍ²、Ｒｚ表面粗さ：１．７μｍ、異常電着による突起形状数：１０個/ｃｍ²となった。いずれも本願発明の条件を満足していた。

[0058] （実施例８）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６４°Ｃ、電流密度：８５Ａ／ｄｍ^{2}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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0059] このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：５２．１ｋｇｆ／ｍｍ^2、Ｒｚ表面粗さ：１．２μｍ、異常電着による突起形状数：２個/ｃｍ^{2}となった。いずれも本願発明の条件を満足していた。

[0060] （比較例１）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：０ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６０°Ｃ、電流密度：８５Ａ／ｄｍ^{2}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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0061] この条件を表１に示す。このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：５６．３ｋｇｆ／ｍｍ^2、Ｒｚ表面粗さ：３．２μｍ、異常電着による突起形状数：０．１個／ｃｍ^{2}となった。表面粗さの要件を満足していないことがわかる。

[0062] （比較例２）

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する

。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：０ｍａｓｓｐｐｍを導入して電解液とした。（すなわち、比較例２においては、前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤を電解液に添加していない。）

そして、電解液温：６０°Ｃ、電流密度：８５Ａ／ｄｍ²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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0063] この条件を表１に示す。このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：５５．９ｋｇｆ／ｍｍ²、Ｒｚ表面粗さ：１．５μｍ、異常電着による突起形状数：５３個／ｃｍ²となった。

異常電着による突起形状の個数が本願発明の条件を満足していなかった。また、代表的な表面状態の電子顕微鏡写真を図２に示す。

図２より、前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤を含有していない状態では、異常電着による突起形状が発生しやすい状態であることが確認できる。

[0064]（比較例３）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：１ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６０°Ｃ、電流密度：８５Ａ／ｄｍ²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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0065] この条件を表１に示す。このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果

、強度（常態引張り強さ）：５８．７ｋｇｆ／ｍｍ²、Ｒｚ表面粗さ：１．４μｍ、異常電着による突起形状数：５２個／ｃｍ²となった。

異常電着による突起形状の個数が本願発明の条件を満足していなかった。

[0066] （比較例４）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：５７°Ｃ、電流密度：８５Ａ／ｄｍ²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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0067] この条件を表１に示す。このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：５９．３ｋｇｆ／ｍｍ²、Ｒｚ表面粗さ：１．６μｍ、異常電着による突起形状数：２５個／ｃｍ²となった。

異常電着による突起形状の個数が本願発明の条件を満足していなかった。

[0068] （比較例５）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：１２ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６０°Ｃ、電流密度：８５Ａ／ｄｍ²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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0069] この条件を表１に示す。このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果

、強度（常態引張り強さ）：６５．２ｋｇｆ／ｍｍ²、Ｒｚ表面粗さ：２．１μｍ、異常電着による突起形状数：１個／ｃｍ²となった。

表面粗さＲｚが本願発明の条件を満足していなかった。

[0070]（比較例６）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６０°Ｃ、電流密度：４８Ａ／ｄｍ²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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0071] この条件を表１に示す。このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：４４．３ｋｇｆ／ｍｍ²、Ｒｚ表面粗さ：１．５μｍ、異常電着による突起形状数：３０個／ｃｍ²となった。

異常電着による突起形状の個数が本願発明の条件を満足していなかった。

[0072]（比較例７）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：３ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：６０°Ｃ、電流密度：１３３Ａ／ｄｍ²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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0073] この条件を表１に示す。このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果

、強度（常態引張り強さ）：７１．３ｋｇｆ／ｍｍ^2、Ｒｚ表面粗さ：２．２μｍ、異常電着による突起形状数：３５個／ｃｍ^{2}となった。

いずれも本願発明の条件を満足していなかった。

[0074] （比較例８）

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する。この電解槽の中に、銅濃度：９０ｇ／Ｌ、硫酸濃度：８０ｇ／Ｌ、にかわ濃度：７ｍａｓｓｐｐｍ、さらに前記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３ｍａｓｓｐｐｍを導入して電解液とした。

そして、電解液温：５７°Ｃ、電流密度：８５Ａ／ｄｍ^{2}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、連続的に銅箔を製造した。なお、銅箔の厚みは１０μｍとした。

[0075] この条件を表１に示す。このようにして製造した電解銅箔の強度（常態引張り強さ）、Ｒｚ表面粗さ、異常電着による突起形状数を調べた。その結果、強度（常態引張り強さ）：６２．３ｋｇｆ／ｍｍ^2、Ｒｚ表面粗さ：１．４μｍ、異常電着による突起形状数：５３個／ｃｍ^{2}となった。

異常電着による突起形状の個数が本願発明の条件を満足していなかった。

産業上の利用可能性

[0076] 本発明は、常態引張り強さが高く、かつ表面粗さＲｚ2.0μｍ以下である電解銅箔を提供でき、さらに異常電着による突起形状数の少ない電解銅箔を提供できるので、特に二次電池用負極集電体用電解銅箔に有用である。

請求の範囲

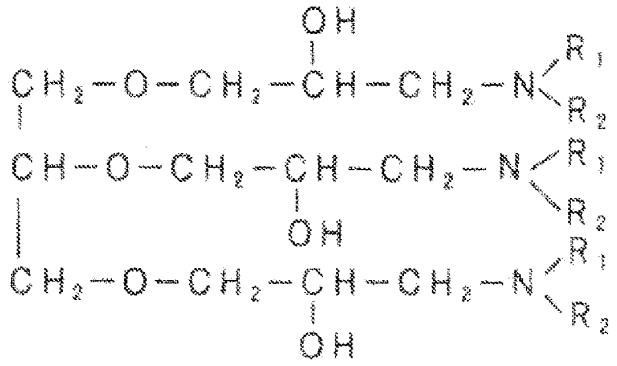
[請求項1] 表面粗さＲｚ２．０μｍ以下であり、高さは１．０μｍ以上、径は４．０μｍ以上である異常電着による突起形状の個数が２０個／ｃｍ^{2}以下である、ことを特徴とする電解銅箔。

[請求項2] 抗張力が４５～７０ｋｇｆ／ｍｍ^{2}であることを特徴とする請求項１記載の電解銅箔。

[請求項3] 二次電池負極集電体用銅箔であることを特徴とする請求項１又は２記載の電解銅箔。

[請求項4] 硫酸系銅電解液を用いた電解法により電解銅箔を製造する方法であって、にかわ：２～５ｍａｓｓｐｐｍ、１分子中に１個以上のエポキシ基を有する化合物とアミン化合物とを付加反応させることにより得られる下記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３～１０ｍａｓｓｐｐｍを含む電解液を用いて、電解液温度を６０～６５°Ｃとし、電流密度を６０～１２０Ａ／ｄｍ^{2}として電解することを特徴とする電解銅箔の製造方法。

[化4]

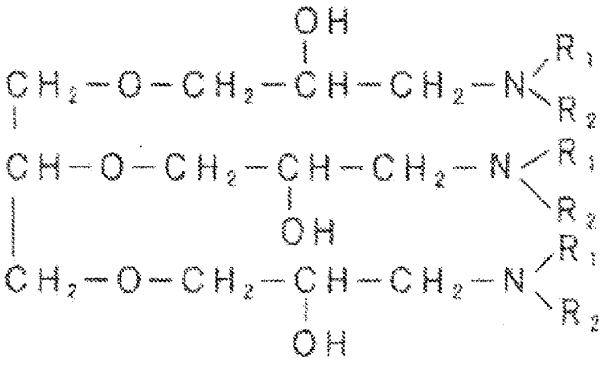


...(1)

（一般式（１）中、Ｒ１及びＲ２はヒドロキシアルキル基、エーテル基、アリール基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものである。）

[請求項5] 硫酸系銅電解液を用いた電解法により電解銅箔を製造する方法であって、にかわ：２～５ｍａｓｓｐｐｍ、１分子中に１個以上のエポキシ基を有する化合物とアミン化合物とを付加反応させることにより得られる下記一般式（１）で示す特定骨格を有するアミン化合物の添加剤：３～１０ｍａｓｓｐｐｍを含む電解液を用いて、電解液温度を６０～６５°Ｃとし、電流密度を６０～１２０Ａ／ｄｍ²として電解することにより、請求項１又は２記載の電解銅箔を製造することを特徴とする電解銅箔の製造方法。

[化5]

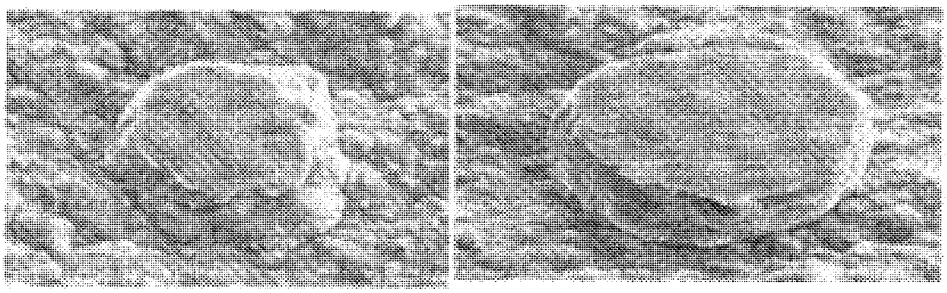


...(1)

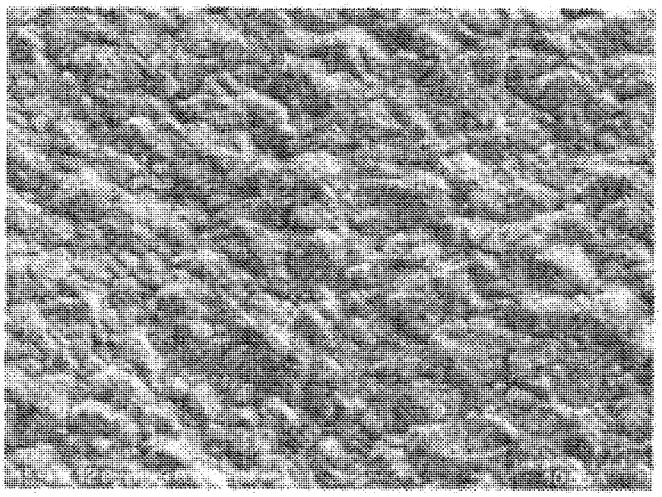
（一般式（１）中、Ｒ１及びＲ２はヒドロキシアルキル基、エーテル基、アリール基、芳香族置換アルキル基、不飽和炭化水素基、アルキル基からなる一群から選ばれるものである。）

[請求項6] 上記請求項４又は５による二次電池負極集電体用銅箔の製造方法。

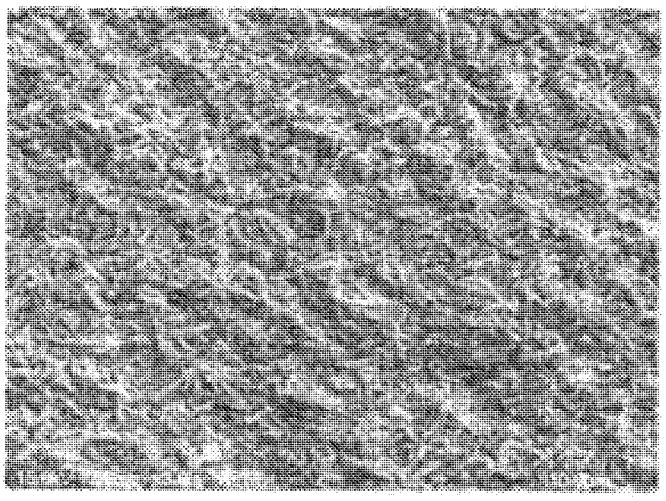
[図1]



[図2]



[図3]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/072183

A. CLASSIFICATION OF SUBJECT MATTER
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)
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	1996-2012
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.
X Y A	JP 2004-263289 A (Fukuda Metal Foil & Powder Co., Ltd.), 24 September 2004 (24.09.2004), claim 1; paragraphs [0005], [0057], [0062], [0064]; fig. 1, 7	1-3 6 4,5
X	JP 2007-217791 A (Mitsui Mining & Smelting Co., Ltd.), 30 August 2007 (30.08.2007), claim 1; paragraphs [0089] to [0102], [0118]; fig. 1	1
X	JP 2009-293103 A (Nippon Denkai Ltd.), 17 December 2009 (17.12.2009), claims 1, 2; paragraph [0013]	1

☒ 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 13 September, 2012 (13.09.12)	Date of mailing of the international search report 25 September, 2012 (25.09.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/072183

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2004-107786 A (Nikko Materials Co., Ltd.), 08 April 2004 (08.04.2004), claims	4,6 5
Y A	WO 2009/116432 A1 (Nippon Mining & Metals Co., Ltd.), 24 September 2009 (24.09.2009), paragraphs [0032], [0038], [0052]	4,6 5

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

JP 2004-263289 A	2004.09.24	US 2006/0191798 A1 WO 2004/090197 A1 KR 10-2005-0114701 A CN 1764744 A
JP 2007-217791 A	2007.08.30	JP 2007-217787 A JP 2007-217788 A US 2010/0038115 A1 EP 1876266 A1 WO 2006/106956 A1 KR 10-2007-0107803 A CN 101146933 A TW 285686 B CN 101851769 A KR 10-0941219 B
JP 2009-293103 A	2009.12.17	(Family: none)
JP 2004-107786 A	2004.04.08	US 2004/0149583 A1 US 2005/0252778 A1 EP 1524335 A1 WO 2004/009876 A1 TW 250225 B HK 1064713 A CN 1522316 A
WO 2009/116432 A1	2009.09.24	CN 101978100 A KR 10-2010-0122519 A TW 200946719 A

国際調査報告

国際出願番号　ＰＣＴ／ＪＰ２０１２／０７２１８３

Ａ．　発明の属する分野の分類（国際特許分類（ＩＰＣ））

Int.Cl.　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.　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	１９７１－２０１２年
日本国実用新案登録公報	１９９６－２０１２年
日本国登録実用新案公報	１９９４－２０１２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 Y A	JP 2004-263289 A（福田金属箔粉工業株式会社）2004.09.24,　【請求項１】、【0005】、【0057】、【0062】、【0064】、【図１】、【図７】	1-3 6 4,5
X	JP 2007-217791 A（三井金属鉱業株式会社）2007.08.30,　【請求項１】、【0089】－【0102】、【0118】、【図１】	1
X	JP 2009-293103 A（日本電解株式会社）2009.12.17,　【請求項１】、【請求項２】、【0013】	1

☑　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

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「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
１３．０９．２０１２	２５．０９．２０１２

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	9625
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	川村　健一		
	電話番号　０３－３５８１－１１０１　内線　３４２５		

様式ＰＣＴ／ＩＳＡ／２１０（第２ページ）（２００９年７月）

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
Y A	JP 2004-107786 A（株式会社日鉱マテリアルズ）2004.04.08,　【特許請求の範囲】	4,6 5
Y A	WO 2009/116432 A1（日鉱金属株式会社）2009.09.24,　[0032]、[0038]、[0052]	4,6 5

JP 2004-263289 A	2004.09.24	US 2006/0191798 A1 WO 2004/090197 A1 KR 10-2005-0114701 A CN 1764744 A
JP 2007-217791 A	2007.08.30	JP 2007-217787 A JP 2007-217788 A US 2010/0038115 A1 EP 1876266 A1 WO 2006/106956 A1 KR 10-2007-0107803 A CN 101146933 A TW 285686 B CN 101851769 A KR 10-0941219 B
JP 2009-293103 A	2009.12.17	ファミリーなし
JP 2004-107786 A	2004.04.08	US 2004/0149583 A1 US 2005/0252778 A1 EP 1524335 A1 WO 2004/009876 A1 TW 250225 B HK 1064713 A CN 1522316 A
WO 2009/116432 A1	2009.09.24	CN 101978100 A KR 10-2010-0122519 A TW 200946719 A

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Application Number:	15307069
International Application Number:	
Confirmation Number:	9113
Title of Invention:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Dae Young KIM
Customer Number:	24573
Filer:	Matthew S. Dicke/Samantha Lingo
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	0313070.00007
Receipt Date:	08-MAY-2018
Filing Date:	27-OCT-2016
Time Stamp:	15:27:35
Application Type:	U.S. National Stage under 35 USC 371

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	00005_IDS_Trans.pdf	24804 25c64f742e96b283aaee8761d713e62441e21ad0	no	3

Warnings:

Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	00005_PTOsb08.pdf	1035478 26ce36b1c0e1a2c433bef2afb0de9e7e50556a61	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.					
3	Other Reference-Patent/App/Search documents	TW_NOA.pdf	1190476 150b0ca4bcc76482f0e81d2dffebae2e51c6c3e6	no	8
Warnings:					
Information:					
4	Foreign Reference	CN104846407A.pdf	620162 dd7d9b5d375652d8cf25b2bc39fc9f6c5d7af835	no	8
Warnings:					
Information:					
5	Foreign Reference	JP2006299320A.pdf	1035077 9b0bf5cf9a9ed15ef0defbcdaa45205ad44cb108	no	13
Warnings:					
Information:					
6	Foreign Reference	WO2011-129633.pdf	1920781 508564c535a75b8200c98f06a2f4059165da8241	no	17
Warnings:					
Information:					
7	Foreign Reference	WO2014-033917.pdf	2297494 d73a2f70ea200f867fa8112cc7e08e7a819892de	no	31
Warnings:					
Information:					
		Total Files Size (in bytes):	8124272		

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:	Dae Young KIM
Appl. No.:	15/307,069
Conf. No.:	9113
Filed:	October 27, 2016
Title:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit:	1727
Examiner:	USYATINSKY, ALEXANDER
Docket No.:	0313070.00007 (0313221.00005)

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 $ 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: May 8, 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
15/307,069	10/27/2016	Dae Young KIM	0313070.00007

CONFIRMATION NO. 9113

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

PUBLICATION NOTICE

OC000000099273150

Title:ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

Publication No.US-2018-0119301-A1
Publication Date:05/03/2018

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Public Records Division. The Public Records Division can be reached by telephone at (571) 272-3150 or (800) 972-6382, by facsimile at (571) 273-3250, by mail addressed to the United States Patent and Trademark Office, Public Records Division, Alexandria, VA 22313-1450 or via the Internet.

In addition, information on the status of the application, including the mailing date of Office actions and the dates of receipt of correspondence filed in the Office, may also be accessed via the Internet through the Patent Electronic Business Center at www.uspto.gov using the public side of the Patent Application Information and Retrieval (PAIR) system. The direct link to access this status information is currently https://portal.uspto.gov/pair/PublicPair. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

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

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UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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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
15/307,069	10/27/2016	1726	1480	0313070.00007	16	2

CONFIRMATION NO. 9113

CORRECTED FILING RECEIPT

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



Date Mailed: 03/13/2018

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

Dae Young KIM, Yongin-si, KOREA, REPUBLIC OF;
Seung Min KIM, Osan-si, KOREA, REPUBLIC OF;

Applicant(s)

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

Power of Attorney: The patent practitioners associated with Customer Number 24573

Domestic Priority data as claimed by applicant

This application is a 371 of PCT/KR2016/004449 04/28/2016

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 10-2015-0090000 06/24/2015

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.

If Required, Foreign Filing License Granted: 01/22/2018
The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 15/307,069**
Projected Publication Date: 05/03/2018

Non-Publication Request: No

Early Publication Request: No

Title

ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, 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

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific 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 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
15/307,069	10/27/2016	Dae Young KIM	0313070.00007

CONFIRMATION NO. 9113

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

POA ACCEPTANCE LETTER

OC000000097412024

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**.

/snguyen/

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Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
15/307,069	10/27/2016	Dae Young KIM	P11304US

CONFIRMATION NO. 9113

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

POWER OF ATTORNEY NOTICE

OC000000097411994

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**.

/snguyen/

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

PTO/AIA/82A (07-13)
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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	15307069
Filing Date	10/27/2016
First Named Inventor	Dae Young KIM
Title	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit	1726
Examiner Name	USYATINSKY, ALEXANDER
Attorney Docket Number	0313070.00007

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.**

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

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POWER OF ATTORNEY BY APPLICANT

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

Application Number	Filing Date

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

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

OR

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

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

☐ The address associated with the above-mentioned Customer Number

OR

☑ The address associated with Customer Number: 24573

OR

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

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

LS MTRON LTD.

☐ Inventor or Joint Inventor (title not required below)

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

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

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

SIGNATURE of Applicant for Patent

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

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

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

☐ Total of forms are submitted.

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

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

PTO/AIA/96 (08-12)
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STATEMENT UNDER 37 CFR 3.73(c)

Applicant/Patent Owner: LS MTRON LTD.

Application No./Patent No.: 15/307,069 Filed/Issue Date: 10/27/2016

Titled: ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

LS MTRON LTD., a CORPORATION

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

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

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

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

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

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

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

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

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

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

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

A. ☑ An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in the United States Patent and Trademark Office at Reel 040147, Frame 0977, or for which a copy thereof is attached.

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

1. From: _____ To: _____

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

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

2. From: _____ To: _____

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

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

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

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

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

STATEMENT UNDER 37 CFR 3.73(c)

3. From: _____ To: _____

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

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

4. From: _____ To: _____

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

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

5. From: _____ To: _____

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

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

6. From: _____ To: _____

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

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

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

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

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

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

/Matthew S. Dicke/	2018-02-12
Signature	Date
Matthew S. Dicke	58,819
Printed or Typed Name	Title or Registration 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.

Electronic Acknowledgement Receipt

EFS ID:	31765820
Application Number:	15307069
International Application Number:	
Confirmation Number:	9113
Title of Invention:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Dae Young KIM
Customer Number:	86144
Filer:	Matthew S. Dicke/Elias Santiago
Filer Authorized By:	Matthew S. Dicke
Attorney Docket Number:	P11304US
Receipt Date:	12-FEB-2018
Filing Date:	27-OCT-2016
Time Stamp:	17:09:51
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Power of Attorney	07_LS_MTRON_POA.pdf	288506 2b4c1fc401f7bce5457eef58ebaa8a5e851c64ff	no	2

Warnings:

Information:					
2	Assignee showing of ownership per 37 CFR 3.73	07_373.pdf	119379 c216939d27f39db4e613da98fa9e46aa473689e6	no	3
Warnings:					
Information:					
			Total Files Size (in bytes):	407885	

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.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 15/307,069

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	300
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	520
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	760
TOTAL CLAIMS (37 CFR 1.16(i))	16 minus 20 =	*			OR	x 100 =	0.00
INDEPENDENT CLAIMS (37 CFR 1.16(h))	2 minus 3 =	*				x 460 =	0.00
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	1580

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	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
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	

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

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

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

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

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	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
15/307,069	10/27/2016		1480	P11304US	16	2

CONFIRMATION NO. 9113

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

FILING RECEIPT



Date Mailed: 01/24/2018

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

Dae Young KIM, Yongin-si, KOREA, REPUBLIC OF;
Seung Min KIM, Osan-si, KOREA, REPUBLIC OF;

Applicant(s)

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

Power of Attorney: The patent practitioners associated with Customer Number 86144

Domestic Priority data as claimed by applicant

This application is a 371 of PCT/KR2016/004449 04/28/2016

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 10-2015-0090000 06/24/2015

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.

If Required, Foreign Filing License Granted: 01/22/2018
The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 15/307,069**
Projected Publication Date: 05/03/2018

Non-Publication Request: No

Early Publication Request: No

Title

ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

Preliminary Class

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific 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).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

SelectUSA

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 U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

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

U.S. APPLICATION NUMBER NO.	FIRST NAMED INVENTOR	ATTY. DOCKET NO.
15/307,069	Dae Young KIM	P11304US

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

INTERNATIONAL APPLICATION NO.	
PCT/KR2016/004449	
I.A. FILING DATE	PRIORITY DATE
04/28/2016	06/24/2015

CONFIRMATION NO. 9113
371 ACCEPTANCE LETTER

OC000000096840787

Date Mailed: 01/24/2018

NOTICE OF ACCEPTANCE OF APPLICATION UNDER 35 U.S.C 371 AND 37 CFR 1.495

The applicant is hereby advised that the United States Patent and Trademark Office, in its capacity as a Designated / Elected Office (37 CFR 1.495), has ACCEPTED the above identified international application for national patentability examination in the United States Patent and Trademark Office.

The United States Application Number assigned to the application is shown above. A Filing Receipt will be issued for the present application in due course. **THE DATE APPEARING ON THE FILING RECEIPT AS THE "FILING DATE or 371(c) DATE" IS THE DATE ON WHICH THE LAST OF THE 35 U.S.C. 371 (c)(1) and (c)(2) REQUIREMENTS HAS BEEN RECEIVED IN THE OFFICE. THIS DATE IS SHOWN BELOW.** The filing date of the above identified application is the international filing date of the international application (Article 11(3) and 35 U.S.C. 363)

10/27/2016
DATE OF RECEIPT OF 35 U.S.C.
371(c)(1) and (c)(2) REQUIREMENTS

The following items have been received:

- Copy of the International Application filed on 10/27/2016
- Copy of the International Search Report filed on 10/27/2016
- Preliminary Amendments filed on 10/27/2016
- Information Disclosure Statements filed on 10/27/2016
- Inventor's Oath or Declaration filed on 10/27/2016
- U.S. Basic National Fees filed on 10/27/2016
- Authorize Access to Search Results filed on 10/27/2016
- Priority Documents filed on 10/27/2016
- Power of Attorney filed on 10/27/2016
- Authorization to Permit Access filed on 10/27/2016
- Application Data Sheet (37 CFR 1.76) filed on 10/27/2016

FORM PCT/DO/EO/903 (371 Acceptance Notice)

Applicant is reminded that any communications to the United States Patent and Trademark Office must be mailed to the address given in the heading and include the U.S. application no. shown above (37 CFR 1.5)

JAMILAH Z HARRIS

Telephone: (703) 756-1124

FORM PCT/DO/EO/903 (371 Acceptance Notice)

MULTIPLE DEPENDENT CLAIM FEE CALCULATION SHEET Substitute for Form PTO-1360 (For use with Form PTO/SB/06)	Application Number 15307069	Filing Date
	Applicant(s) Dae Young KIM	
	* May be used for additional claims or amendments	

CLAIMS	AS FILED		AFTER FIRST AMENDMENT		AFTER SECOND AMENDMENT	
	Indep	Depend	Indep	Depend	Indep	Depend
1	1		1			
2		1		1		
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6		4		1		
7		(1)		1		
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Total Indep	2		2		0	
Total Depend	20	↵	14	↵	0	↵
Total Claims	22		16		0	

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	LS MTRON LTD.	Confirmation No.:	N/A
Int'l Appl. No.:	PCT/KR2016/004449	Group Art Unit:	N/A
Int'l Filing Date:	April 28, 2016	Examiner:	N/A

Title: ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

PRELIMINARY AMENDMENT

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

Sir:

Prior to an examination on the merits, entry of the present Preliminary Amendment for the above-referenced application is respectfully requested, in accordance with the following:

Amendments to the Specification begin on page 2 of this paper.

Amendments to the Claims are reflected in the listing of claims which begins on page 3 of this paper.

Remarks begin on page 8 of this paper.

IN THE SPECIFICATION

Please replace the paragraph beginning at page 15, line 20, which starts with "A capacity per weight", with the following amended paragraph:

-- A capacity per weight (g) of the cathode was measured at a charge operating voltage of 4.3V and a discharge operating voltage of 3.4V, charge/discharge test was conducted 50 cycles at 50℃ and at a ~~current density~~ charge/discharge rate of 0.2C to evaluate high temperature lifespan, and discharge capacity maintenance was calculated in accordance with the following Equation 1:

--

IN THE CLAIMS

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

LISTING OF CLAIMS

1. (Original) An electrolytic copper foil for a secondary battery, the electrolytic copper foil comprising:

a first surface; and

a second surface opposite to the first surface,

wherein each of the first and second surfaces has a peak count roughness R_{pc} of 10 to 100,

wherein the peak count roughness R_{pc} of each of the first and second surfaces is an average of peak count roughness R_{pc} values measured at randomly-selected three points,

the peak count roughness R_{pc} of each point is the number of effective peaks which rise above an upper criteria line of 0.5 μm per unit sampling length of 4 mm in a surface roughness profile obtained according to steel-iron test schedule (SEP 1940), and

there is at least one valley deeper than a lower criteria line of -0.5 μm between adjacent ones of the effective peaks.

2. (Original) The electrolytic copper foil according to claim 1, wherein a difference in peak count roughness R_{pc} between the first and second surfaces is 60 or less.

3. (Original) The electrolytic copper foil according to claim 1, wherein each of the first

and second surfaces has a ten-point mean roughness R_{zJIS} of 2 μm or less.

4. (Original) The electrolytic copper foil according to claim 1, wherein the electrolytic copper foil has a thickness of 3 to 20 μm and tensile strength of 30 to 60 kgf/mm^2.

5. (Currently Amended) A current collector for a secondary battery, the current collector comprising:

the electrolytic copper foil according to claim 1 ~~any one of claims 1 to 4~~; and

a protective layer disposed on the electrolytic copper foil,

wherein the protective layer comprises at least one of chromate, benzotriazole and a silane compound.

6. (Original) The current collector according to claim 5, wherein the protective layer is formed on the first and second surfaces of the electrolytic copper foil.

7. (Currently Amended) An electrode for a secondary battery, the electrode comprising:

a current collector comprising the electrolytic copper foil according to claim 1 ~~any one of claims 1 to 4~~; and

an active material layer disposed on the current collector,

wherein the active material layer comprises at least one active material selected from the group consisting of: carbon; a metal (Me) of Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni or Fe; an alloy containing the metal; an oxide of the metal (MeO_x); and a complex of the metal and carbon.

8. (Original) The electrode according to claim 7, wherein the active material layer comprises Si.

9. (Original) The electrode according to claim 7, wherein the current collector further comprises a protective layer comprising at least one of chromate, benzotriazole and a silane compound, and

wherein the protective layer is interposed between the electrolytic copper foil and the active material layer.

10. (Currently Amended) A secondary battery comprising:

a cathode;

an anode;

an electrolyte for providing an environment enabling lithium ions to move between the cathode and the anode; and

a separator for electrically insulating the cathode from the anode,

wherein the anode comprises:

a current collector comprising the electrolytic copper foil according to claim 1 ~~any one of claims 1 to 4~~; and

an active material layer disposed on the current collector.

11. (Original) The secondary battery according to claim 10, further comprising a

protective layer comprising at least one of chromate, benzotriazole and a silane compound,

wherein the protective layer is interposed between the electrolytic copper foil and the active material layer.

12. (Original) A method of producing an electrolytic copper foil by allowing a current to flow between a cathode plate and a rotational anode drum spaced from each other in an electrolytic solution so as to electrodeposit a copper on the rotational anode drum, the method comprising:

heat-treating a copper wire;

acid-cleaning the heat-treated copper wire;

dipping the acid-cleaned copper wire in the electrolytic solution;

conducting electroplating, while the copper wire is dipped in the electrolytic solution, by allowing a current to flow between the cathode plate and the rotational anode drum; and

conducting continuous filtration to remove solid impurities from the electrolytic solution during the electroplating.

13. (Original) The method according to claim 12, wherein concentrations of organic impurities and metal impurities in the electrolytic solution during the electroplating are maintained at 1g/L or less and 10 g/L or less, respectively.

14. (Original) The method according to claim 12, wherein the heat-treatment of the copper wire is carried out at 600 to 800°C.

15. (Original) The method according to claim 12, wherein the electrolytic solution comprises 50 to 100 g/L of a copper ion, 50 to 150 g/L of sulfuric acid, 50 ppm or less of a chlorine ion and an organic additive.

16. (Original) The method according to claim 15, wherein the organic additive is hydroxyethyl cellulose (HEC), organic sulfide, organic nitride, a thiourea compound, or a mixture of two or more thereof.

REMARKS

Prior to an examination on the merits, entry and consideration of the present Preliminary Amendment is respectfully requested.

Specifically, in the Specification of the instant application, the paragraph beginning at page 15, line 20, which starts with "A capacity per weight", has been replaced with the following amended paragraph:

-- A capacity per weight (g) of the cathode was measured at a charge operating voltage of 4.3V and a discharge operating voltage of 3.4V, charge/discharge test was conducted 50 cycles at 50℃ and at a ~~current density~~ charge/discharge rate of 0.2C to evaluate high temperature lifespan, and discharge capacity maintenance was calculated in accordance with the following Equation 1: --

This paragraph is related to a test method conducted to prove the effects of the invention, where the unit 'C' means 'C-rate' which is widely used for charge/discharge rate. No new matter is believed to be introduced by this amendment.

In addition, claims 5, 7 and 10 have been amended to be not multiple dependent claims. No new matter is believed to be introduced by this amendment.

Accordingly, entry of the present Preliminary Amendment and a speedy examination on the merits of this application, as amended, is earnestly solicited. If there should be any questions or comments regarding the present application, the Examiner is respectfully invited to contact Applicant's representative at the below-listed telephone number.

Respectfully submitted,

/Taeksoo Lee/

Taeksoo Lee
Reg. No. 61,976

LRK Patent Law Firm
1952 Gallows Road, Suite 200
Vienna, VA 22182-3823
Phone: +1-703-854-1331

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Application Number	
Filing Date	
First Named Inventor	Dae Young KIM
Title	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
Art Unit	
Examiner Name	
Attorney Docket Number	P11304US

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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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	[signature]	Date (Optional)	Feb. 10, 2015
Name	Kim, YoungHwan		
Title	IP Team Leader		

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ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an electrolytic copper foil, a current collector including the same, an electrode including the same, a secondary battery including the same, and a method for manufacturing the same.

2. Description of Related Art

Secondary batteries are energy conversion devices which are capable of storing electrical energy in chemical form and of converting into electrical energy to generate electricity when needed. They are also called "rechargeable batteries" because they can be charged repeatedly.

Secondary batteries are more economically and environmentally advantageous than single-use primary batteries and include lead storage batteries, nickel cadmium secondary batteries, nickel hydride secondary batteries, lithium secondary batteries and the like.

Lithium secondary batteries can store greater energy relative to size and weight, as compared to other secondary batteries. Accordingly, lithium secondary batteries are preferred in the field of information communicative apparatuses which require portability and mobility as essential factors and have an extended applicability as energy storage devices for hybrid cars and electric cars.

Lithium secondary batteries are repeatedly used in each cycle including charge

and discharge. When a certain device is operated with a completely charged lithium secondary battery, the lithium ion secondary battery should have a high charge/discharge capacity in order to increase an operation time of the device. Accordingly, there is a continuous demand for research to satisfy users' increasing needs for charge/discharge capacity of lithium secondary batteries.

Meanwhile, although secondary batteries have a sufficiently high charge/discharge capacity, when charge/discharge capacity of the secondary batteries is rapidly decreased (that is, when capacity maintenance is low or lifespan is short) with repeated charge/discharge cycles, users frequently need to change secondary batteries, causing users' discomfort and energy waste.

SUMMARY OF THE INVENTION

Therefore, the present invention is directed to an electrolytic copper foil, a current collector including the same, an electrode including the same, a secondary battery including the same and a method of producing the same capable of preventing these limitations and drawbacks of the related art.

An aspect of the present invention is to provide an electrolytic copper foil which is capable of securing a secondary battery with high capacity maintenance.

Another aspect of the present invention is to provide a current collector which is capable of securing a secondary battery with high capacity maintenance.

Further another aspect of the present invention is to provide an electrode which is capable of securing a secondary battery with high capacity maintenance.

Further another aspect of the present invention is to provide a secondary battery with high capacity maintenance.

Yet another aspect of the present invention is to provide a method of producing

an electrolytic copper foil which is capable of securing a secondary battery with high capacity maintenance.

Additional aspects and features of the present invention will be set forth in part in the description which follows and in part will become apparent to those having ordinary skill in the art upon examination of the following or may be learned from practice of the invention. The objectives and other advantages of the invention may be realized and attained by the structure particularly pointed out in the written description and claims.

In accordance with the one aspect of the present invention, there is provided an electrolytic copper foil for a secondary battery, the electrolytic copper foil comprising a first surface and a second surface opposite to the first surface, wherein each of the first and second surfaces has a peak count roughness R_{pc} of 10 to 100, wherein the peak count roughness R_{pc} of each of the first and second surfaces is an average of peak count roughness R_{pc} values measured at randomly-selected three points, the peak count roughness R_{pc} of each point is the number of effective peaks which rise above an upper criteria line of 0.5 μm per unit sampling length of 4 mm in a surface roughness profile obtained according to steel-iron test schedule (SEP 1940), and there is at least one valley deeper than a lower criteria line of -0.5 μm between adjacent ones of the effective peaks.

In accordance with another aspect of the present invention, there is provided a current collector for a secondary battery, the current collector comprising an electrolytic copper foil having a first surface and a second surface, each having a peak count roughness R_{pc} of 10 to 100 and a protective layer disposed on the electrolytic copper foil, wherein the protective layer includes at least one of chromate, benzotriazole and a silane compound.

In accordance with further another aspect of the present invention, there is provided an electrode for a secondary battery, the electrode comprising a current

collector having a first surface and a second surface, each having a peak count roughness R_{pc} of 10 to 100, and an active material layer disposed on the current collector, wherein the active material layer includes at least one active material selected from the group consisting of: carbon; metal (Me) of Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni or Fe; an alloy containing the metal; an oxide of the metal (MeO_x); and a complex of the metal and carbon.

In accordance with further another aspect of the present invention, there is provided a secondary battery including a cathode, an anode, an electrolyte for providing an environment enabling the lithium ions to move between the cathode and the anode, and a separator for electrically insulating the cathode from the anode, wherein the anode includes a current collector a current collector having a first surface and a second surface, each having a peak count roughness R_{pc} of 10 to 100, and an active material layer disposed on the current collector.

In accordance with yet another aspect of the present invention, there is provided a method of producing an electrolytic copper foil by allowing a current to flow between a cathode plate and a rotational anode drum spaced from each other in an electrolytic solution so as to electrodeposit a copper on the rotational anode drum, the method comprising heat-treating a copper wire, acid-cleaning the heat-treated copper wire, dipping the acid-cleaned copper wire in the electrolytic solution, conducting electroplating, while the copper wire is dipped in the electrolytic solution, by allowing a current to flow between the cathode plate and the rotational anode drum, and conducting continuous filtration to remove solid impurities from the electrolytic solution during the electroplating.

General description related to the present invention given above serves to illustrate or disclose the present invention and should not be construed as limiting the

scope of the present invention.

ADVANTAGEOUS EFFECTS

According to the present invention, long-lifespan secondary batteries which are capable of maintaining high charge/discharge capacity for a long time in spite of repetition of charge/discharge cycles can be produced. Accordingly, electronic product consumers' discomfort and energy waste resulting from frequent change of secondary batteries can be minimized.

BRIEF DESCRIPTION OF DRAWINGS

The accompanying drawings, which are included to provide a further understanding of the invention and are incorporated in and constitute a part of this application, illustrate embodiment(s) of the invention and together with the description serve to explain the principle of the invention. In the drawings:

FIG. 1 is a sectional view of an electrode for a secondary battery according to an embodiment of the present invention; and

FIG. 2 illustrates a surface roughness profile obtained according to steel-iron test schedule (SEP 1940) specification.

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, embodiments according to the present invention will be described in detail with reference to the annexed drawings.

Those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims. Accordingly, the present invention includes

modifications and alterations which fall within the scope of inventions as claimed and equivalents thereto.

A lithium ion secondary battery includes a cathode, an anode, an electrolyte for providing an environment enabling the lithium ions to move between the cathode and the anode, and a separator for electrically insulating the cathode from the anode to prevent unnecessary consumption of electrons because of movement of electrons generated in one electrode to the other electrode.

FIG. 1 is a sectional view of an electrode for secondary batteries according to an embodiment of the present invention.

As shown in FIG. 1, the electrode for secondary batteries 100 according to an embodiment of the present invention includes a current collector 110 and an active material layer 120. FIG. 1 illustrates the active material layer 120 which is formed on both of the upper and lower surfaces of the current collector 110, but the present invention is not limited thereto and the active material layer 120 may be formed only on one surface of the current collector 110.

In general, in a lithium secondary battery, an aluminum foil is used as a cathode current collector coupled to a cathode active material and a copper foil is used as an anode current collector coupled to an anode active material.

According to an embodiment of the present invention, the electrode for secondary batteries 100 is an anode, the current collector 110 is an anode current collector and the active material layer 120 includes an anode active material.

The current collector 110 of the present invention which is an anode current collector, includes an electrolytic copper foil 111 having a thickness of 3 to 20 μm and a tensile strength of 30 to 60 kgf/mm^2. In addition, as shown in FIG. 1, the current collector 110 may further include a protective layer 112 disposed on the electrolytic

copper foil 111. FIG. 1 illustrates the protective layer 112 which is formed on both of the upper and lower surfaces of electrolytic copper foil 111, but the present invention is not limited thereto and the protective layer 112 may be formed only on one surface of the electrolytic copper foil 111.

The electrolytic copper foil 111 of the present invention may be formed on a rotational anode drum by electroplating, thereby having a first surface (also called a "shiny surface") 111a which contacts the rotational anode drum in the process of electroplating and a second surface (also called a "matte surface") 111b opposite to the first surface.

In general, the shiny surface 111a has a lower roughness than the matte surface 111b, but the present invention is not limited thereto and the shiny surface 111a may have a roughness equal to or higher than the matte surface 111b. Here, roughness of the shiny surface 111a and the matte surface 111b means a ten-point mean roughness (R_{zJIS}).

The active material layer 120 contains, as an anode active material, at least one active material selected from the group consisting of: carbon; metal (Me) of Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni or Fe; an alloy containing the metal; an oxide of the metal (MeO_x); and a complex of the metal and carbon.

In order to increase charge/discharge capacity of secondary batteries, the active material layer 120 may be formed using a mixture of anode active materials containing a predetermined amount of Si.

Meanwhile, as a result of repeated charge/discharge of secondary batteries, the active material layer 120 alternately contracts and expands, which induces separation of the active material layer 120 from the current collector 110, causing deterioration in charge/discharge efficiency of secondary batteries. Accordingly, in order for the secondary electrodes to secure predetermined levels of capacity maintenance and lifespan

(that is, in order to prevent deterioration in charge/discharge efficiency of secondary batteries), the current collector 110 should have excellent coatability to the active material so that adhesion strength between the current collector 110 and the active material layer 120 can be increased.

In a broad sense, as the ten-point mean roughness R_{zJIS} of the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 decreases, deterioration in charge/discharge efficiency of the secondary battery including the current collector 110 decreases.

Accordingly, each of the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 according to an embodiment of the present invention has a ten-point mean roughness R_{zJIS} of 2 μm or less. When the shiny surface 111a or the matte surface 111b has a ten-point mean roughness R_{zJIS} exceeding 2 μm, contact uniformity between the current collector 110 and the active material layer 120 does not reach a desired level and the secondary battery thus cannot satisfy a capacity maintenance of 90% or higher required in the art.

However, the present applicant found that an electrolytic copper foil 111 the shiny surface 111a and the matte surface 111b of which have a ten-point mean roughness R_{zJIS} of 2 μm or less does not always secure capacity maintenance of the secondary battery, of 90% or higher. That is, a low ten-point mean roughness R_{zJIS} (for example, 2 μm or less) of the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 cannot be a sufficient condition for capacity maintenance of the secondary battery of 90% or higher.

In particular, it was found that there is less correlation between the ten-point mean roughness R_{zJIS} of the electrolytic copper foil 111 and capacity maintenance of the secondary battery when the active material layer 120 contains Si for high capacity of the

secondary battery.

As a result of repeated research, the present applicant found that a peak count roughness R_{pc} of the electrolytic copper foil 111 is an important factor in stably securing capacity maintenance of 90% or higher.

Hereinafter, the peak count roughness R_{pc} of the electrolytic copper foil 111 will be described with reference to FIG. 2.

As used herein, the peak count roughness R_{pc} of each of the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 means an average of peak count roughness R_{pc} values obtained at three randomly-selected points, and the peak count roughness R_{pc} of each point is the number of effective peaks P_1, P_2, P_3 and P_4 which rise above an upper criteria line C1 of 0.5 μm per unit sampling length of 4 mm in the surface roughness profile obtained according to steel-iron test schedule (SEP 1940). In this case, there is at least one valley deeper than a lower criteria line C2 of -0.5 μm between adjacent ones of the effective peaks. If there is no valley deeper than the lower criteria line C2 of -0.5 μm between adjacent peaks rising above the upper criteria line C1, all of the adjacent peaks cannot be "effective peaks" used for measurement of the peak count roughness R_{pc} and relatively lower one is excluded in determining the number of "effective peaks".

According to the present invention, the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 have a peak count roughness R_{pc} of 10 to 100, respectively.

When the peak count roughness R_{pc} is less than 10, capacity maintenance of the secondary battery is deteriorated. This is because the stress caused during the charge/discharge of the secondary battery is concentrated on mountains which locally protrude.

Furthermore, when the peak count roughness R_{pc} exceeds 100, capacity maintenance of the secondary battery is also deteriorated. This is because the active material cannot be uniformly coated on the electrolytic copper foil 111 due to the excessive number of mountains.

The difference in peak count roughness R_{pc} between the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 is preferably 60 or less because, according to an embodiment of the present invention, both surfaces of the current collector 110 are coated with the active material. When the difference in the peak count roughness R_{pc} exceeds 60, capacity maintenance of the secondary battery is deteriorated due to difference in surface appearance between both surfaces 111a and 111b.

As described above, the current collector 110 for secondary batteries of the present invention may further include a protective layer 112 on the electrolytic copper foil 111. The protective layer 112 may be formed by anticorrosion treatment of the electrolytic copper foil 111. That is, the electrolytic copper foil 111 of the present invention may be used as the current collector, but is preferably subjected to anticorrosion treatment using chromate, benzotriazole and/or a silane compound. The anticorrosion treatment prevents corrosion of the electrolytic copper foil 111, improves heat resistance and enhances adhesive strength to the active material layer 120, thus inhibiting deterioration in charge/discharge efficiency of secondary batteries.

Hereinafter, a method of producing an electrolytic copper foil according to an embodiment of the present invention will be described in detail.

A deposition machine used for producing the electrolytic copper foil 111 includes an electrolytic bath containing an electrolytic solution, and a rotational anode drum and a cathode plate spaced from each other in the electrolytic solution.

The electrolytic copper foil 111 is produced by adding a small amount of organic

additive such as hydroxyethyl cellulose (HEC), organic sulfide, organic nitride, and/or thiourea-based compound to an electrolytic solution containing 50 to 100 g/L of a copper ion, 50 to 150 g/L of sulfuric acid and 50 ppm or less of chlorine ions, and then depositing copper on the surface of the rotational anode drum at a current density of 10 to 80 A/dm^2 at 40 to 60 ℃.

The ten-point mean roughness R_{zJIS} and the peak count roughness R_{pc} of the shiny surface 111a of the electrolytic copper foil 111 depend on a polishing level of the surface of the rotational anode drum (the surface on which copper is deposited by electroplating).

According to the present invention, in order for the shiny surface 111a to have a peak count roughness R_{pc} of 10 to 100 and a ten-point mean roughness R_{zJIS} of 2 μm or less, the surface of the rotational anode drum is polished with a #800 to #1500 grit polishing brush.

The ten-point mean roughness R_{zJIS} and the peak count roughness R_{pc} of the matte surface 111b of the electrolytic copper foil 111 depend on the composition of the electrolytic solution (particularly, concentrations of organic impurities and metal impurities), used for electroplating, the current density of electroplating and the like.

According to the present invention, in order for the matte surface 111b to have a peak count roughness R_{pc} of 10 to 100 and a ten-point mean roughness R_{zJIS} of 2 μm or less, the concentrations of organic impurities and metal impurities in the electrolytic solution are controlled to 1 g/L or less and 10 g/L or less, respectively, and the electroplating is conducted at a current density of 10 to 80 A/dm^2.

In addition, according to the present invention, in order to control concentrations of organic impurities and metal impurities in the electrolytic solution controlled to 1 g/L or less and 10 g/L or less, respectively, organic substances are burned by thermal treatment at a high temperature of 600 to 800 ℃ (for example, about 700 ℃) and then

cleaned with an acid before addition of a highly pure copper wire to the electrolytic solution. In addition, continuous filtration is performed to remove solid impurities including organic impurities and metal impurities from the electrolytic solution during electroplating, thereby maintaining concentrations of organic impurities and metal impurities in the electrolytic solution at 1 g/L or less and at 10 g/L or less, respectively.

Subsequently, a protective layer 112 is formed on the shiny surface 111a and/or the matte surface 111b of the electrolytic copper foil 111 by anticorrosion treatment using chromate, benzotriazole (BTA) and/or a silane compound, thereby producing the current collector 110 of the present invention.

For example, the protective layer 112 can be formed by dipping the electrolytic copper foil 111 in 1 to 10 g/L of a potassium dichromate solution at room temperature for 2 to 20 seconds.

Subsequently, the current collector 110 is coated with at least one active material selected from the group consisting of: carbon; metal (Me) of Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni or Fe; an alloy containing the metal (Me); oxides of the metal (Me) (MeO_x); and a complex of the metal (Me), to produce an electrode (that is, anode) for secondary batteries of the present invention.

For example, 100 parts by weight of carbon as an anode active material, 1 to 3 parts by weight of styrene butadiene rubber (SBR) and 1 to 3 parts by weight of carboxymethyl cellulose (CMC) are mixed and produced into a slurry using distilled water as a solvent. Subsequently, the slurry is applied to a thickness of 20 to 60 μm onto the current collector 110 using a doctor blade and pressed at 110 to 130℃ and at a pressure of 0.5 to 1.5 ton/cm^2.

A lithium secondary battery can be produced using the electrode (anode) for secondary batteries of the present invention produced by the method as described above,

in combination with an ordinary cathode, electrolyte and separator.

Hereinafter, the present invention will be described in more detail with reference to the following examples and comparative Examples. The following examples are only given for better understanding of the present invention and should not be construed as limiting the scope of the present invention.

* Production of Electrolytic copper foil

Examples 1 to 4 and Comparative Examples 1 to 4

Electrolytic copper foils were produced under the same conditions except that i) whether or not a copper wire was subjected to heat treatment and what the heat treatment temperature was, ii) whether or not continuous filtration is conducted during electroplating, and/or iii) the grit of polishing brush used for surface polishing of the rotational anode drum are changed as shown in the following Table 1.

Subsequently, the peak count roughness R_{pc} of the shiny surface and matte surface of the electrolytic copper foils was measured using a MahrSurf M300 roughness tester available from Mahr company and results are shown in the following Table 1.

As described above, the peak count roughness R_{pc} of the shiny surface 111a and the matte surface 111b of the electrolytic copper foil 111 means an average of peak count roughness R_{pc} values obtained at three randomly-selected points, the peak count roughness R_{pc} of each point is the number of effective peaks which rise above an upper criteria line C1 of 0.5 μm per unit sampling length of 4 mm in the surface roughness profile obtained according to the steel-iron test schedule (SEP 1940).

If there is no valley deeper than a lower criteria line C2 of -0.5 μm between adjacent peaks rising above the upper criteria line C1, relatively lower one is excluded in

determining the number of "effective peaks".

TABLE 1

	Heat treatment temperature of copper wire (℃)	Whether continuous filtration is conducted	Grit of polishing brush (#)	R_{pc} of matte surface (count)	R_{pc} of shiny surface (count)	Difference in R_{pc} (count)
Ex. 1	720	○	1200	13	42	29
Ex. 2	700	○	1400	20	24	4
Ex. 3	680	○	800	39	98	59
Ex. 4	660	○	1000	98	89	9
Comp. Ex. 1	810	○	1600	8	9	1
Comp. Ex. 2	-	○	700	112	128	16
Comp. Ex. 3	-	×	1200	181	47	134
Comp. Ex. 4	670	○	600	47	139	92

* Production of secondary battery

Examples 5 to 8 and Comparative Examples 5 to 8

The electrolytic copper foils of Examples 1 to 4 and Comparative Examples 1 to 4 were dipped in 10 g/L of a potassium dichromate solution for 10 seconds to obtain current collectors including a protective layer formed on an electrolytic copper foil. Subsequently, 100 parts by weight of commercially available carbon as an anode active material was mixed with 2 parts by weight of SBR and 2 parts by weight of CMC, and a slurry was produced using distilled water as a solvent. The slurry was applied to a thickness of 50 μm on the current collectors having a width of 10 cm using a doctor blade, dried at 120℃ and pressed at a pressure of 1 ton/cm^2 to produce 8 anodes for secondary batteries.

8 secondary batteries were produced using the anodes for secondary batteries thus

produced in combination with an electrolytic solution and a cathode for secondary batteries. The electrolytic solution and the cathode were prepared as follows.

$LiPF_6$ as a solute was dissolved in a non-aqueous organic solvent containing a mixture of ethylene carbonate (EC) and ethylene methyl carbonate (EMC) in a ratio of 1:2 to prepare a 1M basic electrolytic solution, and 99.5% by weight of the basic electrolytic solution was mixed with 0.5% by weight of succinic anhydride, to prepare the electrolytic solution.

In addition, lithium manganese oxide ($Li_{1.1}Mn_{1.85}Al_{0.05}O_4$) was mixed with an orthorhombic crystal structure of lithium manganese oxide (o-$LiMnO_2$) in a weight ratio of 90:10 to produce a cathode active material. The cathode active material, carbon black and polyvinylidene fluoride (PVDF) as a binder were mixed in a weight ratio of 85:10:5 and was further mixed with NMP as an organic solvent to prepare a slurry. The slurry was applied onto opposite surfaces of an aluminum foil with a thickness of 20 μm, followed by drying to produce the cathode.

Capacity maintenance was measured for 8 secondary batteries of Examples 5 to 8 and Comparative Example 5 to 8 thus produced according to the following method and results are shown in Table 2.

* Discharge capacity maintenance of secondary battery

A capacity per weight (g) of the cathode was measured at a charge operating voltage of 4.3V and a discharge operating voltage of 3.4V, charge/discharge test was conducted 50 cycles at 50℃ and at a current density of 0.2C to evaluate high temperature lifespan, and discharge capacity maintenance was calculated in accordance with the following Equation 1:

Equation 1

Discharge capacity maintenance (%) = (50th discharge capacity/1st discharge capacity) × 100

For reference, the discharge capacity maintenance of secondary batteries required in the art is 90% or higher.

TABLE 2

	R_{pc} of matte surface of electrolytic copper foil (count)	R_{pc} of shiny surface of electrolytic copper foil (count)	Difference in R_{pc} between two surfaces of electrolytic copper foil (count)	Discharge capacity maintenance of secondary battery (%)
Ex. 5	13	42	29	95
Ex. 6	20	24	4	97
Ex. 7	39	98	59	93
Ex. 8	98	89	9	94
Comp. Ex. 5	8	9	1	84
Comp. Ex. 6	112	128	16	85
Comp. Ex. 7	181	47	134	85
Comp. Ex. 8	47	139	92	87

From Table 2, it can be seen that, when at least one of the shiny surface and the matte surface of the electrolytic copper foil has a peak count roughness R_{pc} exceeding 100 (count), discharge capacity maintenance of the secondary battery produced using such electrolytic copper foil cannot satisfy 90% or higher required in the art (Comparative Examples 6-8). This is considered because the active material is not uniformly coated on the electrolytic copper foil due to excessively many mountains.

In addition, it can be seen that, when at least one of the shiny surface and the matte surface of the electrolytic copper foil has a peak count roughness R_{pc} less than 100

(count), discharge capacity maintenance of the secondary battery produced using such electrolytic copper foil cannot satisfy 90% or higher required in the art (Comparative Example 5). This is considered because stress is concentrated on mountains which locally protrude upon charge/discharge of the secondary battery.

Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

CLAIMS

1. An electrolytic copper foil for a secondary battery, the electrolytic copper foil comprising:

a first surface; and

a second surface opposite to the first surface,

wherein each of the first and second surfaces has a peak count roughness R_{pc} of 10 to 100,

wherein the peak count roughness R_{pc} of each of the first and second surfaces is an average of peak count roughness R_{pc} values measured at randomly-selected three points,

the peak count roughness R_{pc} of each point is the number of effective peaks which rise above an upper criteria line of 0.5 μm per unit sampling length of 4 mm in a surface roughness profile obtained according to steel-iron test schedule (SEP 1940), and

there is at least one valley deeper than a lower criteria line of -0.5 μm between adjacent ones of the effective peaks.

2. The electrolytic copper foil according to claim 1, wherein a difference in peak count roughness R_{pc} between the first and second surfaces is 60 or less.

3. The electrolytic copper foil according to claim 1, wherein each of the first and second surfaces has a ten-point mean roughness R_{zJIS} of 2 μm or less.

4. The electrolytic copper foil according to claim 1, wherein the electrolytic copper foil has a thickness of 3 to 20 μm and tensile strength of 30 to 60 kgf/mm^2.

5. A current collector for a secondary battery, the current collector comprising:

the electrolytic copper foil according to any one of claims 1 to 4; and

a protective layer disposed on the electrolytic copper foil,

wherein the protective layer comprises at least one of chromate, benzotriazole and a silane compound.

6. The current collector according to claim 5, wherein the protective layer is formed on the first and second surfaces of the electrolytic copper foil.

7. An electrode for a secondary battery, the electrode comprising:

a current collector comprising the electrolytic copper foil according to any one of claims 1 to 4; and

an active material layer disposed on the current collector,

wherein the active material layer comprises at least one active material selected from the group consisting of: carbon; a metal (Me) of Si, Ge, Sn, Li, Zn, Mg, Cd, Ce, Ni or Fe; an alloy containing the metal; an oxide of the metal (MeO_x); and a complex of the metal and carbon.

8. The electrode according to claim 7, wherein the active material layer comprises Si.

9. The electrode according to claim 7, wherein the current collector further comprises a protective layer comprising at least one of chromate, benzotriazole and a silane compound, and

wherein the protective layer is interposed between the electrolytic copper foil and the active material layer.

10. A secondary battery comprising:

a cathode;

an anode;

an electrolyte for providing an environment enabling lithium ions to move between the cathode and the anode; and

a separator for electrically insulating the cathode from the anode,

wherein the anode comprises:

a current collector comprising the electrolytic copper foil according to any one of claims 1 to 4; and

an active material layer disposed on the current collector.

11. The secondary battery according to claim 10, further comprising a protective layer comprising at least one of chromate, benzotriazole and a silane compound,

wherein the protective layer is interposed between the electrolytic copper foil and the active material layer.

12. A method of producing an electrolytic copper foil by allowing a current to flow between a cathode plate and a rotational anode drum spaced from each other in an electrolytic solution so as to electrodeposit a copper on the rotational anode drum, the method comprising:

heat-treating a copper wire;

acid-cleaning the heat-treated copper wire;

dipping the acid-cleaned copper wire in the electrolytic solution;

conducting electroplating, while the copper wire is dipped in the electrolytic solution, by allowing a current to flow between the cathode plate and the rotational anode drum; and

conducting continuous filtration to remove solid impurities from the electrolytic solution during the electroplating.

13. The method according to claim 12, wherein concentrations of organic impurities and metal impurities in the electrolytic solution during the electroplating are maintained at 1g/L or less and 10 g/L or less, respectively.

14. The method according to claim 12, wherein the heat-treatment of the copper wire is carried out at 600 to 800℃.

15. The method according to claim 12, wherein the electrolytic solution comprises 50 to 100 g/L of a copper ion, 50 to 150 g/L of sulfuric acid, 50 ppm or less of a chlorine ion and an organic additive.

16. The method according to claim 15, wherein the organic additive is hydroxyethyl cellulose (HEC), organic sulfide, organic nitride, a thiourea compound, or a mixture of two or more thereof.

ABSTRACT

An electrolytic copper foil, a current collector including the same, an electrode including the same, a secondary battery including the same and a method for manufacturing the same which can secure secondary batteries with high capacity maintenance. The electrolytic copper foil includes a first surface and a second surface opposite to the first surface, wherein each of the first and second surfaces has a peak count roughness R_{pc} of 10 to 100.

FIG. 1

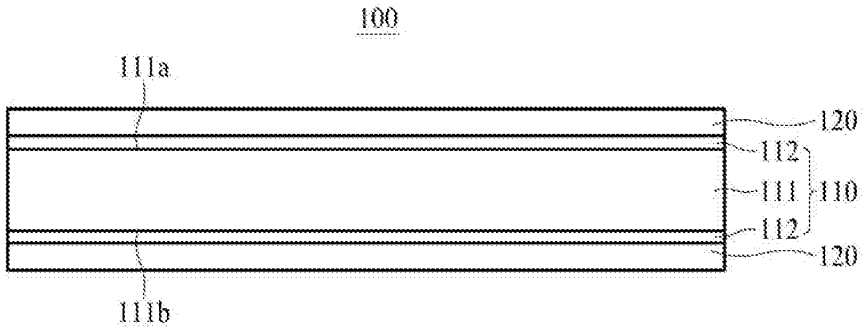
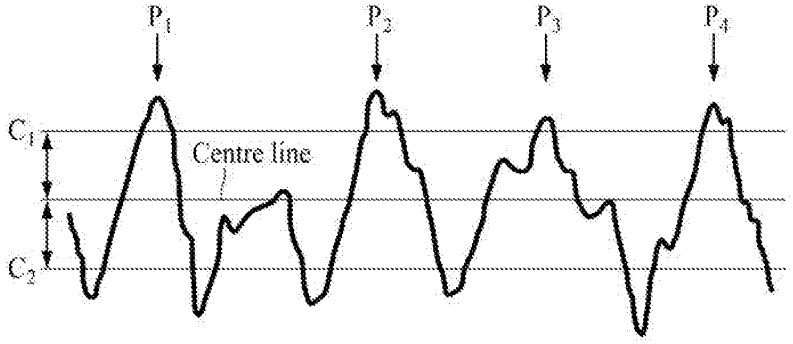

100
111a
120
112
111
110
112
120
111b

FIG. 2


P1
P2
P3
P4
C1
Centre line
C2

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RÉPUBLIQUE DE CORÉE

Date of mailing *(day/month/year)*	IMPORTANT NOTIFICATION
04 May 2016 (04.05.2016)	
Applicant's or agent's file reference	International application No.
2015F0127Pc	PCT/KR2016/004449

The applicant is hereby **notified** that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

LS MTRON LTD. (all designated States)

International filing date: 28 April 2016 (28.04.2016)
Priority date(s) claimed: 24 June 2015 (24.06.2015)
Date of receipt of the record copy by the International Bureau: 04 May 2016 (04.05.2016)
List of designated Offices:

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The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 70 90

Authorized officer
Cruz Juan
e-mail pt01.pct@wipo.int
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Date of mailing *(day/month/year)* 11 May 2016 (11.05.2016)	
Applicant's or agent's file reference 2015F0127Pc	**IMPORTANT NOTIFICATION**
International application No. PCT/KR2016/004449	International filing date *(day/month/year)* 28 April 2016 (28.04.2016)
International publication date *(day/month/year)* **Not yet published**	Priority date *(day/month/year)* 24 June 2015 (24.06.2015)
Applicant LS MTRON LTD.	

The applicant is hereby notified of the date of receipt (or of obtaining by the International Bureau) of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to the date of receipt, **the priority document concerned was submitted or transmitted to or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-*bis*)**. This Form replaces any previously issued notification concerning submission, transmittal or obtaining of priority documents.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
24 June 2015 (24.06.2015)	10-2015-0090000	KR	09 May 2016 (09.05.2016)

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1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 70 90

Authorized officer
Kihwan Moon
e-mail pt01.pct@wipo.int
Telephone No. +41 22 338 74 01

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II-2	우측 지정국에 관한 출원인	**모든 지정국 (all designated States)**
II-4ko	성명	**엘에스엠트론 주식회사**
II-4en	Name:	**LS MTRON LTD.**
II-5ko	주소	**대한민국** **14119** **경기도 안양시 동안구 엘에스로 127**
II-5en	Address:	**127, LS-ro, Dongan-gu,** **Anyang-si, Gyeonggi-do 14119** **Republic of Korea**
II-6	국적	**대한민국 KR**
II-7	거주국	**대한민국 KR**
II-11	출원인 코드	**1-2008-029030-3**

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III-1	출원인 및/또는 발명자	
III-1-1	이 사람은	오직 발명자 **(inventor only)**
III-1-3	우측 지정국에 관한 발명자	모든 지정국 **(all designated States)**
III-1-4ko	성명	김대영
III-1-4en	Name (LAST, First):	**KIM, Dae Young**
III-1-5ko	주소	대한민국 **16826** 경기도 용인시 수지구 신수로**783**번길 **22** (동천동, 영풍아파트) **101**동 **1205**호
III-1-5en	Address:	**101-1205, (Youngpung Apt., Dongcheon-dong)** **22, Sinsu-ro 783beon-gil, Suji-gu,** **Yongin-si Gyeonggi-do 16826** **Republic of Korea**
III-2	출원인 및/또는 발명자	
III-2-1	이 사람은	오직 발명자 **(inventor only)**
III-2-3	우측 지정국에 관한 발명자	모든 지정국 **(all designated States)**
III-2-4ko	성명	김승민
III-2-4en	Name (LAST, First):	**KIM, Seung Min**
III-2-5ko	주소	대한민국 **18105** 경기도 오산시 양산로 **460** (양산동, 세마이편한세상아파트) **105**동 **1902**호
III-2-5en	Address:	**105-1902, (Sema e-Pyeonhansesang Apt., Yangsan-dong)** **460, Yangsan-ro,** **Osan-si, Gyeonggi-do 18105** **Republic of Korea**

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IV-1-2ko	주소	대한민국 **06225** 서울시 강남구 역삼로 **233, 5**층 (역삼동, 신성빌딩)
IV-1-2en	Address:	**(ShinSung Building, Yeoksam-dong)** **5th Floor, 233, Yeoksam-ro,** **Gangnam-gu, Seoul 06225** **Republic of Korea**
IV-1-3	전화번호	**+82-2-3453-0635**
IV-1-4	팩스번호	**+82-2-3453-0645**
IV-1-5	이메일 주소	**info@cheonmoon.com**
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IV-1-6	대리인 코드	**9-2009-100001-0**
V	**지정국**	
V-1	**본 출원서의 제출로, 규칙 4.9(a)에 따라, 부여될 수 있는 모든 종류의 권리 보호를 위하여, 그리고 해당하는 경우 지역특허 및 국내특허 모두를 위하여 당해 국제출원일에 PCT에 기속되는 모든 체약국이 지정된다.**	
V-2	**V-2란은 출원서 제출시 또는 규칙 26의2.1에 의해 그 이후 출원서 제6기재란에 위 특정 관련 체약국의 국내 선출원에 대한 우선권주장이 포함되어 있을 경우 당해 체약국의 국내법에 의해 해당 국내 선출원의 효력이 상실되는 것을 방지하기 위한 목적으로 당해 체약국의 지정을 제외하는 데에만 사용될 수 있다 (지정 제외시 이의 취소 불가능).**	**KR**
VI-1	**선국내출원에 대한 우선권 주장**	
VI-1-1	출원일	**2015년 06월 24일 (24.06.2015)**
VI-1-2	출원번호	**10-2015-0090000**
VI-1-3	파리협약 당사국명 또는 WTO 회원국명	**KR**
VI-2	**우선권서류 신청** 주관관청에 대하여 위에 명시된 선출원의 인증등본을 준비하여 국제사무국에 송부하여 줄 것을 신청한다.	**VI-1**
VI-3	**인용에 의한 보완** 조약 제11조(1)(iii)(d) 또는 (e)에서 규정하는 국제출원의 요소, 또는 규칙 20.5(a)에서 규정하는 명세서, 청구 범위 또는 도면의 일부가 본 국제출원에는 포함되어 있지 않지만 조약 제11조(1)(iii) 규정의 요소 중 하나 이상이 주관관청에 최초로 접수된 날에 우선권주장의 기초가 된 선출원에 완전히 포함되어 있는 경우, 그 요소 또는 부분은 규칙 20.6 규정에 의한 확인을 조건으로, 규칙 20.6의 규정과 관련하여 본 국제출원에 있어서 인용에 의해 보완된다.	

PCT 국제서

VIII-1	국제조사기관(ISA)의 명칭	대한민국 특허청 (ISA/KR)	
VIII	견해서	청구항 제1	
VIII-2	신규성, 진보성 및 산업상 이용가능성에 대한 견해	-	
VIII-3	신규성에 대한 견해	-	
VIII-4	진보성에 대한 견해	-	
VIII-5	산업상 이용가능성에 대한 견해	-	
IX	서열 목록	청구항	서열 목록 첨부
IX-1	국제출원에 포함된 서열	5	✓
IX-2	서열	10	✓
IX-3	뉴클레오타이드	3	✓
IX-4	아미노산	1	✓
IX-5	기타	1	✓
IX-6	서열 목록 스크리	20	
IX-7	추가 자료	제출 필요	제출 필요 없음
IX-8	전자 형태로 제출	-	✓
IX-9	서면으로 제출	-	✓
IX-10	추가 서열 목록 스크리 제출	1	
IX-11	국제출원 언어	한국어	
X-1	청구인, 제3자 또는 대표자 성명		
X-1-1	성	특허법인 친구	
X-1-2	이름	특허법인 친구	
X-1-3	청구인 또는 제3자 또는 대표자 주소		

PCT 출원서

출력(전자적 형태가 원본)

수리관청 전용

10-1	국제출원으로 제출된 서류의 실제 접수일	
10-2	도면	
10-2-1	접수	
10-2-2	미접수	
10-3	국제출원으로 제출된 서류를 완성하는 서류 또는 도면의 추후 기간내 제출에 따른 정정된 실제 접수일	
10-4	**PCT** 제11조(2)에 따라 제출이 요구된 보완서로서 기간내 제출된 보완서의 접수일	
10-5	국제조사기관(**ISA**)	**ISA/KR**
10-6	조사료 납부시까지 지연된 조사용 사본의 송부	

국제 사무국 전용

11-1	국제 사무국의 기록원본 접수일	

명세서

발명의 명칭: 전해 동박, 그것을 포함하는 집전체, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법

기술분야

[1] 본 발명은 전해 동박, 그것을 포함하는 집전체, 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 분야의 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] 한편, 이차전지가 충분히 높은 충전/방전 용량을 갖고 있다고 하더라도 충전/방전 사이클이 반복됨에 따라 이차전지의 충전/방전 용량이 급격히 감소한다면(즉, 용량 유지율이 낮다면 또는 수명이 짧다면), 소비자는 이차전지를 빈번하게 교체할 필요가 있을 것이고, 그로 인해 소비자 불편 및 자원 낭비가 초래될 것이다.

발명의 상세한 설명

기술적 과제

[7] 따라서, 본 발명은 위와 같은 관련 기술의 제한 및 단점들에 기인한 문제점들을 방지할 수 있는 전해 동박, 그것을 포함하는 집전체, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법에 관한 것이다.

[8] 본 발명의 일 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전해 동박을 제공하는 것이다.

[9] 본 발명의 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는

집전체를 제공하는 것이다.

[10] 본 발명의 또 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전극을 제공하는 것이다.

[11] 본 발명의 또 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 제공하는 것이다.

[12] 본 발명의 또 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전해 동박을 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.

과제 해결 수단

[14] 위와 같은 본 발명의 일 관점에 따라, 제1 면; 및 상기 제1 면의 반대 편의 제2 면을 포함하되, 상기 제1 및 제2 면들 각각은 10 내지 100 개의 피크 수 조도(peak count roughness: R_{pc})를 갖는 - 상기 제1 및 제2 면들 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값이고, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스텔-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 4mm의 단위 샘플링 길이당 0.5㎛의 상위 기준선(upper criteria line: C1) 위로 솟아 있는 유효 피크들의 개수이고, 상기 유효 피크들 중 이웃하는 유효 피크들 사이에는 -0.5㎛의 하위 기준선(lower criteria line: C2)보다 깊은 적어도 하나의 골(valley)이 존재함 -, 이차전지용 전해동박이 제공된다.

[15] 본 발명의 다른 관점에 따라, 10 내지 100 개의 피크 수 조도(R_{pc})를 각각 갖는 제1 및 제2 면들을 포함하는 전해동박; 및 상기 전해동박 상의 보호층을 포함하되, 상기 보호층은 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는, 이차전지용 집전체가 제공된다.

[16] 본 발명의 또 다른 관점에 따라, 10 내지 100 개의 피크 수 조도(R_{pc})를 각각 갖는 제1 및 제2 면들을 포함하는 전해동박을 포함하는 집전체; 및 상기 집전체 상의 활물질층을 포함하되, 상기 활물질층은, 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 선택되는 하나 이상의 활물질을 포함하는, 이차전지용 전극이 제공된다.

[17] 본 발명의 또 다른 관점에 따라, 양극(cathode); 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 포함하되, 상기 음극은, 10 내지 100 개의 피크 수 조도(R_{pc})를 각각 갖는 제1 및 제2 면들을 포함하는 전해동박을 포함하는 집전체; 및 상기 집전체 상의 활물질층을 포함하는, 이차전지가 제공된다.

[18] 본 발명의 또 다른 관점에 따라, 전해액 내에 서로 이격되게 배치된 양극판 및

회전 음극드럼을 통전시킴으로써 상기 회전 음극드럼 상에 구리를 석출시키는 전해동박 제조방법으로서, 구리 와이어를 열처리하는 단계; 상기 열처리된 구리 와이어를 산세하는 단계; 상기 산세된 구리 와이어를 상기 전해액에 투입하는 단계; 상기 구리 와이어가 상기 전해액에 투입된 상태에서 상기 양극판 및 회전 음극드럼을 통전시킴으로써 전기 도금을 수행하는 단계; 및 상기 전기 도금 중에 상기 전해액으로부터 고형 불순물을 제거하기 위한 연속 여과를 수행하는 단계를 포함하는, 전해동박 제조방법이 제공된다.

[19] 위와 같은 본 발명에 대한 일반적 서술은 본 발명을 예시하거나 설명하기 위한 것일 뿐으로서, 본 발명의 권리범위를 제한하지 않는다.

발명의 효과

[20] 본 발명에 의하면, 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

[21] 첨부된 도면은 본 발명의 이해를 돕고 본 명세서의 일부를 구성하기 위한 것으로서, 본 발명의 실시예들을 예시하며, 발명의 상세한 설명과 함께 본 발명의 원리들을 설명한다.

[22] 도 1은 본 발명의 일 실시예에 따른 이차전지용 전극의 단면도이고,

[23] 도 2는 스텐-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일을 예시한다.

발명의 실시를 위한 형태

[24] 이하에서는 첨부된 도면을 참조하여 본 발명의 실시예들을 상세하게 설명한다.

[25] 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.

[26] 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 절연시켜 주는 분리막(separator)을 포함한다.

[27] 도 1은 본 발명의 일 실시예에 따른 이차전지용 전극의 단면도이다.

[28] 도 1에 예시된 바와 같이, 본 발명의 일 실시예에 따른 이차전지용 전극(100)은 집전체(110) 및 활물질층(120)을 포함한다. 도 1은 상기 집전체(110)의 상하면 모두 위에 형성된 활물질층(120)을 예시하고 있으나, 본 발명이 이에 국한되는 것은 아니며, 상기 활물질층(120)은 상기 집전체(110)의 일 면 상에만 형성될

수도 있다.

[29] 리튬 이차전지에 있어서, 양극 활물질과 결합되는 양극 집전체로서는 알루미늄 호일(foil)이 사용되고 음극 활물질과 결합되는 음극 집전체로서는 동박이 사용되는 것이 일반적이다.

[30] 본 발명의 일 실시예에 의하면, 상기 이차전지용 전극(100)은 음극이고, 상기 집전체(110)는 음극 집전체이며, 상기 활물질층(120)은 음극 활물질을 포함한다.

[31] 음극 집전체인 본 발명의 집전체(110)는 3 내지 20 ㎛의 두께 및 30 내지 60 kgf/mm²의 인장강도를 갖는 전해 동박(111)을 포함한다. 또한, 도 1에 예시된 바와 같이, 상기 집전체(110)는 상기 전해 동박(111) 상의 보호층(112)을 더 포함할 수 있다. 도 1은 상기 전해 동박(111)의 상하면 모두 위에 형성된 보호층(112)을 예시하고 있으나, 본 발명이 이에 국한되는 것은 아니며, 상기 보호층(112)은 상기 전해 동박(111)의 일 면 상에만 형성될 수도 있다.

[32] 본 발명의 전해 동박(111)은 전기도금을 통해 회전 음극드럼 상에 형성될 수 있으며, 전기도금 과정에서 상기 회전 음극드럼과 접촉하였던 제1 면[일명 "샤이니 면(Shiny surface)"](111a) 및 상기 제1 면의 반대 편의 제2 면[일명 "매트 면(Matte surface)"](111b)을 갖는다.

[33] 샤이니 면(111a)이 매트 면(111b)에 비해 더 낮은 조도를 갖는 것이 일반적이기는 하지만 본 발명이 이에 국한되는 것은 아니며 샤이니 면(111a)의 조도가 매트 면(111b)의 조도와 동일하거나 더 높을 수도 있다. 여기서, 샤이니 면(111a)과 매트 면(111b)의 조도는 10점 평균조도(ten-point mean roughness: R_{zJIS})를 의미한다.

[34] 상기 활물질층(120)은, 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 선택되는 하나 이상의 활물질을 음극 활물질로서 포함한다.

[35] 이차전지의 충방전 용량을 증가시키기 위하여, Si를 소정량 포함한 음극 활물질들의 혼합물로 상기 활물질층(120)이 형성될 수 있다.

[36] 한편, 이차전지의 충방전이 반복됨에 따라 활물질층(120)의 수축 및 팽창이 번갈아 발생하고, 이것은 상기 활물질층(120)과 상기 집전체(110)의 분리를 유발하여 이차전지의 충방전 효율을 저하시킨다. 따라서, 이차전극이 일정 수준 이상의 용량 유지율 및 수명을 확보하기 위해서는(즉, 이차전지의 충방전 효율 저하를 억제하기 위해서는), 상기 집전체(110)가 상기 활물질에 대하여 우수한 코팅성을 가짐으로써 상기 집전체(110)와 활물질층(120)의 접착 강도가 높아야 한다.

[37] 거시적 관점에서 볼 때, 상기 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)의 10점 평균조도(R_{zJIS})가 작을수록, 상기 집전체(110)를 포함하는 이차전지의 충방전 효율이 대체로 덜 저하되는 경향이 있다.

[38] 따라서, 본 발명의 일 실시예에 따른 전해 동박(111)의 샤이니 면(111a)과 매트

면(111b) 각각은 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖는다. 상기 샤이니 면(111a) 또는 매트 면(111b)이 2㎛를 초과하는 10점 평균조도(R_{zJIS})를 갖는다면 상기 집전체(110)와 활물질층(120) 사이의 접촉 균일성이 일정 수준에 미치지 못할 것이고, 따라서 이차전지가 업계에서 요구되는 90% 이상의 용량 유지율을 만족하지 못할 것이다.

[39] 그러나, 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)이 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖는다고 하더라도, 그러한 전해 동박(111)이 반드시 90% 이상의 이차전지 용량 유지율을 담보할 수 있는 것이 아님이 본 출원인에 의해 밝혀졌다. 즉, 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)의 낮은 10점 평균조도(R_{zJIS})(예를 들어, 2㎛ 이하)가 90% 이상의 이차전지 용량 유지율에 대한 충분 조건이 될 수 없다.

[40] 특히, 이차전지의 고용량화를 위하여 상기 활물질층(120)이 Si를 포함할 경우 전해 동박(111)의 10점 평균조도(R_{zJIS})와 이차전지의 용량 유지율 사이의 연관성이 더욱 낮은 것으로 드러났다.

[41] 본 출원인은, 연구를 거듭한 결과, 90% 이상의 용량 유지율을 안정적으로 확보함에 있어서 전해 동박(111)의 피크 수 조도(peak count roughness: R_{pc})가 중요한 인자임을 밝혀내었다.

[42] 이하에서는, 도 2를 참조하여 전해 동박(111)의 피크 수 조도(R_{pc})를 설명한다.

[43] 본 명세서에서 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b) 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값을 지칭하며, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스텐-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 4mm의 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 피크 수 조도(R_{pc})의 측정에 이용되는 "유효 피크"가 될 수는 없으며, "유효 피크" 개수를 구함에 있어서 상기 피크들 중 상대적으로 더 낮은 피크는 무시된다.

[44] 본 발명에 의하면, 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)은 10 내지 100 개(count)의 피크 수 조도(R_{pc})를 각각 갖는다.

[45] 상기 피크 수 조도(R_{pc})가 10개 미만인 경우 이차전지의 용량 유지율의 열화가 발생하는데, 이것은 이차전지의 충방전시 국부적으로 돌출된 산(mountain)에 응력이 집중되기 때문인 것으로 파악된다.

[46] 반면, 피크 수 조도(R_{pc})가 100개를 초과하는 경우에도 이차전지의 용량 유지율의 열화가 마찬가지로 발생하는데, 이것은 너무 많은 산들로 인해 상기 전해 동박(111) 상에 활물질이 균일하게 코팅되지 못하기 때문인 것으로

판단된다.

[47] 본 발명의 일 실시예에 의하면 상기 집전체(110)의 양 면들 모두에 활물질이 코팅되기 때문에, 상기 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)의 피크 수 조도(R_{pc}) 차이는 60개 이하인 것이 바람직하다. 상기 피크 수 조도(R_{pc}) 차이가 60개를 초과하면 양 면들(111a, 111b)의 표면 형상의 차이로 인해 이차전지의 용량 유지율 열화가 발생한다.

[48] 전술한 바와 같이, 본 발명의 이차전지용 집전체(110)는 상기 전해 동박(111) 상의 보호층(112)을 더 포함할 수 있다. 상기 보호층(112)은 상기 전해 동박(111)의 방청 처리를 통해 형성될 수 있다. 즉, 본 발명의 전해 동박(111)은 그대로 집전체로서 사용될 수도 있지만, 크롬산염, 벤조트리아졸, 및/또는 실란계 화합물로 방청 처리(anticorrosion treatment)되는 것이 바람직하다. 이와 같은 방청 처리는 전해 동박(111)의 부식을 방지하고, 내열성을 향상시키며, 활물질층(120)과의 접착 강도를 높여 이차 전지의 충방전 효율 저하를 억제시킬 수 있다.

[49] 이하에서는, 본 발명의 일 실시예에 따른 전해 동박의 제조방법을 구체적으로 설명한다.

[50] 상기 전해 동박(111)의 제조에 이용되는 제박기는 전해액이 담겨진 전해조, 상기 전해액 내에서 서로 이격되어 있는 회전 음극드럼 및 양극판을 포함한다.

[51] 50 내지 100 g/L의 구리 이온, 50 내지 150 g/L의 황산 및 50 ppm 이하의 염소 이온을 포함하는 전해액에 하이드록시에틸 셀룰로오스(HEC), 유기 황화물, 유기 질화물, 및/또는 티오요소(thiourea)계 화합물과 같은 유기 첨가제를 소량 첨가한 후, 10 내지 80 A/dm^{2}의 전류밀도로 40 내지 60 ℃에서 상기 회전 음극드럼 표면에 구리를 전착함으로써 전해 동박(111)을 제조한다.

[52] 상기 전해 동박(111)의 샤이니 면(111a)의 10점 평균조도(R_{zJIS}) 및 피크 수 조도(R_{pc})는 회전 음극드럼 표면(전기도금에 의해 구리가 석출되는 면)의 연마 정도에 의존한다.

[53] 본 발명에 의하면, 상기 샤이니 면(111a)이 10 내지 100 개의 피크 수 조도(R_{pc}) 및 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖도록 하기 위하여, #800 내지 #1500의 입도(Grit)를 갖는 연마 브러시로 상기 회전 음극드럼의 표면이 연마된다.

[54] 상기 전해 동박(111)의 매트 면(111b)의 10점 평균조도(R_{zJIS}) 및 피크 수 조도(R_{pc})는 전기도금에 이용되는 전해액의 조성(특히, 유기 불순물 및 금속 불순물의 농도), 전기도금의 전류 밀도 등에 의존한다.

[55] 본 발명에 의하면, 상기 매트 면(111b)이 10 내지 100 개의 피크 수 조도(R_{pc}) 및 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖도록 하기 위하여, 상기 전해액 내 유기 불순물 및 금속 불순물의 농도가 각각 1g/L 이하 및 10g/L 이하로 제어되며, 10 내지 80 A/dm^{2}의 전류밀도로 상기 전기도금이 수행된다.

[56] 또한, 본 발명에 의하면, 상기 전해액 내 유기 불순물 및 금속 불순물의 농도를 각각 1g/L 이하 및 10g/L 이하로 제어하기 위하여, 고순도 구리 와이어를

전해액에 투입하기 전에 600 내지 800℃(예를 들어, 약 700℃)의 고온에서 열처리하여 유기물을 태운 후 황산 등의 산으로 산세(acid cleaning) 한다. 또한, 전기도금 중에 상기 전해액으로부터 유기 불순물 및 금속 불순물을 포함하는 고형 불순물을 제거하기 위한 연속 여과를 수행함으로써 상기 전해액 내의 유기 불순물 및 금속 불순물의 농도를 각각 1g/L 이하 및 10g/L 이하로 유지시킨다.

[57] 이어서, 크롬산염(chromate), 벤조트리아졸(benzotriazole: BTA), 및/또는 실란계 화합물(silane compound)을 이용한 방청 처리(anticorrosion treatment)를 통해 상기 전해 동박(111)의 샤이니 면(111a) 및/또는 매트 면(111b) 상에 보호층(112)을 형성함으로써 본 발명의 집전체(110)를 제조할 수 있다.

[58] 예를 들어, 1 내지 10 g/L의 중크롬산 칼륨 용액에 상기 전해 동박(111)을 상온에서 2 내지 20초 침지시킴으로써 상기 보호층(112)을 형성할 수 있다.

[59] 이어서, 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 선택되는 하나 이상의 음극 활물질을 상기 집전체(110) 상에 코팅함으로써 본 발명의 이차전지용 전극(즉, 음극)을 제조한다.

[60] 예를 들어, 탄소 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 집전체(110) 상에 20 내지 60㎛ 두께로 상기 슬러리를 도포하고, 110 내지 130℃에서 0.5 내지 1.5 ,ton/cm^2의 압력으로 프레스한다.

[61] 이상의 방법으로 제조된 본 발명의 이차전지용 전극(음극)과 함께 통상의 양극, 전해질, 및 분리막을 이용하여 리튬 이차전지를 제조할 수 있다.

[62]

[63] 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.

[64]

[65] *** 전해 동박의 제조**

[66] 실시예 1 내지 4 및 비교예 1 내지 4

[67] i) 구리 와이어 열처리 여부/온도, ii) 전기 도금 수행시 연속 여과 수행 여부, 및/또는 iii) 회전 음극 드럼의 표면 연마에 이용된 연마 브러시의 입도를 아래의 표 1과 같이 변경한 것을 제외하고는 동일한 조건 하에서 전해 동박들을 각각 제조하였다.

[68] 이어서, 상기 전해 동박들의 샤이니 면 및 매트 면의 피크 수 조도(R_{pc})를 Mahr社의 Mahrsurf M300 조도계를 이용하여 각각 측정하였고, 그 결과를 아래의 표 1에 나타내었다.

[69] 전술한 바와 같이, 샤이니 면과 매트 면 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값이며, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스텐-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 4mm의 단위 샘플링 길이당 0.5㎛의 상위 기준선(C1) 위로 솟아 있는 유효 피크들의 개수이다.

[70] 상위 기준선(C1) 위로 솟아 있는 이웃하는 피크들 사이에 -0.5㎛의 하위 기준선(C2)보다 깊은 골이 하나도 존재하지 않는 경우에는, "유효 피크" 개수를 구함에 있어서 상기 피크들 중 상대적으로 더 낮은 피크는 무시되었다.

[71] [표1]

	구리 와이어 열처리 온도(℃)	연속 어과 수행 여부	연마 브러시 입도(#)	매트 면의 R_{pc}(count)	샤이니 면의R_{pc}(count)	R_{pc} 차이 (count)
실시예1	720	○	1200	13	42	29
실시예2	700	○	1400	20	24	4
실시예3	680	○	800	39	98	59
실시예4	660	○	1000	98	89	9
비교예1	810	○	1600	8	9	1
비교예2	-	○	700	112	128	16
비교예3	-	×	1200	181	47	134
비교예4	670	○	600	47	139	92

[72]

[73] * 이차전지의 제조

[74] 실시예 5 내지 8 및 비교예 5 내지 8

[75] 실시예 1 내지 4 및 비교예 1 내지 4의 전해 동박들을 10g/L의 중크롬산 칼륨 용액에 10초 동안 각각 침지시킴으로써 전해 동박 상에 보호층이 형성된 집전체들을 얻었다. 이어서, 음극 활물질용으로 시판되는 탄소 100 중량부에 SBR 2 중량부 및 CMC 2 중량부를 혼합한 후 증류수를 용제로 이용하여 슬러리를 제조하였다. 10cm의 폭을 갖는 상기 집전체들 상에 상기 슬러리를 닥터 블레이드를 이용하여 50㎛의 두께로 각각 도포하고 120℃에서 건조시킨 후 1 ton/cm^2의 압력으로 프레스함으로써 총8개의 이차전지용 음극들을 제조하였다.

[76] 이와 같이 제조된 이차전지용 음극들 각각과 함께 전해액 및 이차전지용 양극을 이용하여 총8개의 이차전지들을 제조하였다. 상기 전해액과 양극은 아래와 같이 준비되었다.

[77] 에틸렌카보네이트(EC) 및 에틸렌메틸카보네이트(EMC)를 1:2의 비율로 혼합한 비수성 유기용매에 용질로서 $LiPF_6$를 1M 용해시킨 것을 기본 전해액으로 하고, 이 기본 전해액 99.5 중량%와 숙신산 무수물(succinic anhydride) 0.5 중량%를 혼합하여 상기 전해액을 제조하였다.

[78] 또한, 리튬망간산화물($Li_{1.1}Mn_{1.85}Al_{0.05}O_4$)과 orthorhombic 결정구조의 리튬망간산화물(o-$LiMnO_2$)을 90:10(중량비)로 혼합하여 양극 활물질을 제조하였다. 상기 양극 활물질과 카본블랙을 결착제인 폴리비닐리덴플루오라이드(PVDF)와 85:10:5(중량비)로 유기용매인 NMP와 혼합하여 슬러리를 제조하였다. 상기 슬러리를 두께 20㎛의 알라미늄 호일의 양면에 도포한 후 건조시킴으로써 상기 양극을 제조하였다.

[79]

[80] 위와 같이 제조된 실시예 5 내지 8 및 비교예 5 내지 8의 이차전지들의 용량 유지율을 아래의 방법으로 측정하였고, 그 결과를 표 2에 나타내었다.

[81] * 이차전지의 방전용량 유지율

[82] 4.3V의 충전작동전압 및 3.4V의 방전작동전압으로 양극의 g당 용량을 측정하였고, 고온 수명을 평가하기 위하여 50℃에서 0.2 C의 전류밀도로 50회으 충/방전 실험을 수행하였으며, 방전용량 유지율을 아래의 식 1에 따라 산출하였다.

[83] 식 1: 방전용량 유지율(%) = (50회차의 방전용량/1회차의 방전용량)×100

[84] 참고로, 업계에서 요구되는 이차전지의 방전용량 유지율은 90% 이상이다.

[85] [표2]

	전해 동박 매트 면의 R_{pc}(count)	전해 동박 샤이니 면의 R_{pc}(count)	전해 동박 양면들의 R_{pc} 차이 (count)	이차전지의 방전용량 유지율(%)
실시예5	13	42	29	95
실시예6	20	24	4	97
실시예7	39	98	59	93
실시예8	98	89	9	94
비교예5	8	9	1	84
비교예6	112	128	16	85
비교예7	181	47	134	85
비교예8	47	139	92	87

[86] 위 표 2로부터, 전해 동박의 샤이니 면과 매트 면 중 어느 하나라도 100개(count)를 초과하는 피크 수 조도(R_{pc})를 가질 경우 그러한 전해 동박을 이용하여 제조된 이차전지의 방전용량 유지율은 업계에서 요구되는 90% 이상을

만족시키지 못함을 알 수 있다(비교예 6-8). 너무 많은 산들로 인해 전해 동박 상에 활물질이 균일하게 코팅되지 못하였기 때문인 것으로 판단된다.

[87] 또한, 전해 동박의 샤이니 면과 매트 면이 10개 미만의 피크 수 조도(R_{pc})를 가질 경우 그러한 전해 동박을 이용하여 제조된 이차전지의 방전용량 유지율은 업계에서 요구되는 90% 이상을 만족시키지 못함을 알 수 있는데(비교예 5), 이것은 이차전지의 충방전시 국부적으로 돌출된 산에 응력이 집중되었기 때문인 것으로 파악된다.

청구범위

[청구항 1] 제1 면(111a); 및
상기 제1 면(111a)의 반대 편의 제2 면(111b)을 포함하되,
상기 제1 및 제2 면들(111a, 111b) 각각은 10 내지 100 개의 피크 수 조도(peak count roughness: R_{pc})를 갖는 - 상기 제1 및 제2 면들(111a, 111b) 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값이고, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스텁-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 4mm의 단위 샘플링 길이당 0.5㎛의 상위 기준선(upper criteria line: C1) 위로 솟아 있는 유효 피크들의 개수이고, 상기 유효 피크들 중 이웃하는 유효 피크들 사이에는 -0.5㎛의 하위 기준선(lower criteria line: C2)보다 깊은 적어도 하나의 골(valley)이 존재함 -,
이차전지용 전해동박.

[청구항 2] 제1항에 있어서,
상기 제1 및 제2 면들(111a, 111b)의 피크 수 조도(R_{pc}) 차이는 60개 이하인,
이차전지용 전해동박.

[청구항 3] 제1항에 있어서,
상기 제1 및 제2 면들(111a, 111b) 각각은 2㎛ 이하의 10점 평균조도(ten-point mean roughness: R_{zJIS})를 갖는,
이차전지용 전해동박.

[청구항 4] 제1항에 있어서,
3 내지 20 ㎛의 두께 및 30 내지 60 kgf/mm^{2}의 인장강도를 갖는,
이차전지용 전해동박.

[청구항 5] 제1항 내지 제4항 중 어느 한 항의 전해동박(111); 및
상기 전해동박 상의 보호층(112)을 포함하되,
상기 보호층(112)은 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는,
이차전지용 집전체.

[청구항 6] 제5항에 있어서,
상기 보호층(112)은 상기 전해동박(111)의 상기 제1 및 제2 면들(111a, 111b) 위에 형성된,
이차전지용 집전체.

[청구항 7] 제1항 내지 제4항 중 어느 한 항의 전해동박(111)을 포함하는 집전체(110); 및
상기 집전체 상의 활물질층(120)을 포함하되,
상기 활물질층(120)은, 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 선택되는 하나 이상의 활물질을 포함하는,
이차전지용 전극.

[청구항 8] 제7항에 있어서,
상기 활물질층(120)은 Si를 포함하는,
이차전지용 전극.

[청구항 9] 제7항에 있어서,
상기 집전체(110)는 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는 보호층(112)을 더 포함하고,
상기 보호층(112)은 상기 전해동박(111)과 상기 활물질층(120) 사이에 배치된,
이차전지용 전극.

[청구항 10] 양극(cathode);
음극(anode)(100);
상기 양극과 음극 사이에서 리튬 이온이 이동할 수 있는 환경을 제공하는 전해질(electrolyte); 및
상기 양극과 상기 음극(100)을 전기적으로 절연시켜 주는
분리막(separator)을 포함하되,
상기 음극(100)은,
제1항 내지 제4항 중 어느 한 항의 전해동박(111)을 포함하는 집전체(110); 및
상기 집전체(110) 상의 활물질층(120)을 포함하는,
이차전지.

[청구항 11] 제10항에 있어서,
상기 집전체(110)는 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는 보호층(112)을 더 포함하고,
상기 보호층(112)은 상기 전해동박(111)과 상기 활물질층(120) 사이에 배치된,
이차전지.

[청구항 12] 전해액 내에 서로 이격되게 배치된 양극판 및 회전 음극드럼을 통전시킴으로써 상기 회전 음극드럼 상에 구리를 석출시키는
전해동박(111) 제조방법에 있어서,
구리 와이어를 열처리하는 단계;
상기 열처리된 구리 와이어를 산세하는 단계;
상기 산세된 구리 와이어를 상기 전해액에 투입하는 단계;
상기 구리 와이어가 상기 전해액에 투입된 상태에서 상기 양극판 및 회전 음극드럼을 통전시킴으로써 전기 도금을 수행하는 단계; 및
상기 전기 도금 중에 상기 전해액으로부터 고형 불순물을 제거하기 위한

연속 여과를 수행하는 단계를 포함하는,
전해동박 제조방법.

[청구항 13] 제12항에 있어서,
상기 전기 도금 중에 상기 전해액 내의 유기 불순물 및 금속 불순물의 농도가 1g/L 이하 및 10g/L 이하로 각각 유지되는,
전해동박 제조방법.

[청구항 14] 제12항에 있어서,
상기 구리 와이어의 열처리 단계는 600 내지 800℃에서 수행되는,
전해동박 제조방법.

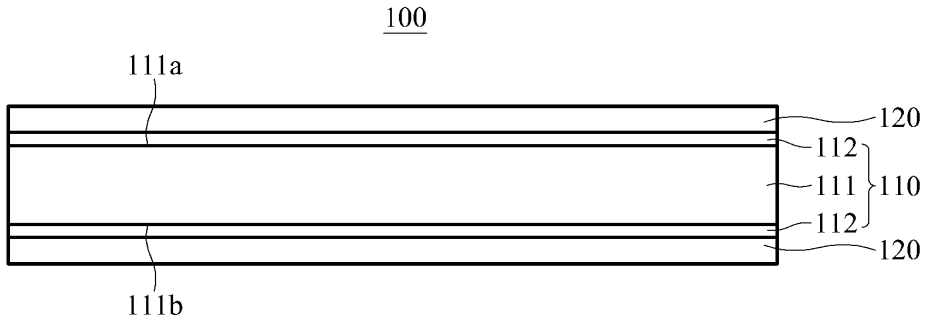
[청구항 15] 제12항에 있어서,
상기 전해액은 50 내지 100 g/L의 구리 이온, 50 내지 150 g/L의 황산, 50 ppm 이하의 염소 이온, 및 유기 첨가제를 포함하는,
전해동박 제조방법.

[청구항 16] 제15항에 있어서,
상기 유기 첨가제는 하이드록시에틸 셀룰로오스(HEC), 유기 황화물, 유기 질화물, 티오요소(thiourea)계 화합물, 또는 이들 중 2 이상의 혼합물인,
전해동박 제조방법.

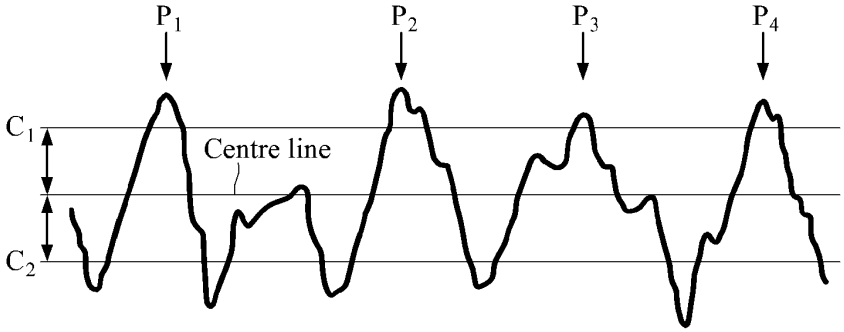
요약서

높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전해 동박, 그것을 포함하는 집전체, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법이 개시된다. 본 발명의 전해 동박은 제1 면; 및 상기 제1 면의 반대 편의 제2 면을 포함하되, 상기 제1 및 제2 면들 각각은 10 내지 100 개의 피크 수 조도(peak count roughness: R_{pc})를 갖는다.

[도1]


100
111a
120
112
111
110
112
120
111b

[도2]


P1
P2
P3
P4
C1
Centre line
C2

특허협력조약

PCT

국제조사보고서
(PCT 제 18 조 및 PCT규칙 43 및 44)

출원인 또는 대리인의 서류참조기호 2015F0127Pc	**추가적인 조치**	서식 PCT/ISA/220 및 아래 5.(해당하는경우) 참조
국제출원번호 **PCT/KR2016/004449**	국제출원일 *(일/월/년)* 28 April 2016 (28.04.2016)	(최) 우선일 *(일/월/년)* 24 June 2015 (24.06.2015)
출원인 엘에스엠트론 주식회사		

본 국제조사보고서는 본 국제조사기관에 의하여 작성되었으며 PCT 제18조의 규정에 따라 출원인에게 송부됩니다. 이 국제조사보고서의 사본은 국제사무국에 송부됩니다.

본 국제조사보고서는 총 **4** 매로 구성되어 있습니다.

☒ 본 보고서에서 인용된 각 선행기술 문헌의 사본도 첨부되어 있습니다.

1. **보고서의 기초**
   a. **언어**와 관련하여, 국제조사는 아래에 기초하여 수행되었습니다.
      ☒ 출원시의 언어로 된 국제출원
      ☐ 국제조사를 위해 _____ 로 번역되어 제출된 국제출원의 번역문(PCT규칙 12.3(a) 및 23.1(b))
   b. ☐ 본 국제조사보고서는 PCT규칙 91의 규정에 따라 당해 기관이 허가하였거나 또는 당해 기관에 통보된 **명백한 잘못의 정정**을 고려하여 작성되었습니다(PCT규칙 43.6의2(a)).
   c. ☐ 국제출원에 개시된 **핵산염기 및/또는 아미노산 서열**에 관하여는 제1기재란을 참조하십시오.
2. ☐ **일부 청구항은 조사할 수 없습니다**(제2기재란 참조).
3. ☐ **발명의 단일성이 결여되어 있습니다**(제3기재란 참조).
4. **발명의 명칭**과 관련하여,
   ☐ 출원인이 제출한 대로 승인합니다.
   ☒ 본 국제조사기관이 다음과 같이 발명의 명칭을 작성하였습니다:
   전해 동박, 그 전해 동박을 포함하는 집전체, 그 집전체를 포함하는 전극, 그 전극을 포함하는 이차전지 및 이의 제조방법
5. **요약서**와 관련하여,
   ☐ 출원인이 제출한 대로 승인합니다.
   ☒ PCT규칙 38.2의 규정에 따라 본 기관이 제4기재란에 표시된 대로 요약서를 작성하였습니다. 출원인은 본 국제조사보고서의 발송일부터 1월 이내에 본 기관에 의견을 제출할 수 있습니다.
6. **도면**과 관련하여,
   a. 요약서와 함께 공개될 도면은 제 1 도이며
      ☒ 출원인이 제안하였습니다.
      ☐ 출원인이 도면의 번호를 제안하지 않았기 때문에 본 기관이 선택하였습니다.
      ☐ 본 도면이 발명의 특징을 더 잘 나타내고 있기 때문에 본 기관이 선택하였습니다.
   b. ☐ 요약서와 함께 공개될 도면이 없습니다.

제4기재란 요약서의 내용(첫 번째 용지의 5의 계속)

높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전해 동박, 그 전해 동박을 포함하는 집전체, 그 집전체를 포함하는 전극, 그 전극을 포함하는 이차전지 및 이의 제조방법이 개시된다. 본 발명의 전해 동박은 제1면; 및 상기 제1면의 반대편의 제2면을 포함하되, 상기 제1 및 제2면들 각각은 10 내지 100 개의 피크 수 조도(peak count roughness: Rpc)를 갖는다.

국제조사보고서

국제출원번호
PCT/KR2016/004449

A. 발명이 속하는 기술분류(국제특허분류(IPC))

H01M 4/66(2006.01)i, H01M 10/052(2010.01)i, C25D 1/04(2006.01)i

B. 조사된 분야

조사된 최소문헌(국제특허분류를 기재)

H01M 4/66; H05K 1/05; B32B 15/20; C25D 7/06; H01M 4/64; H05B 33/26; H05B 33/02; C25D 1/04; B32B 15/08; H01M 2/02; H01M 10/052

조사된 기술분야에 속하는 최소문헌 이외의 문헌

한국등록실용신안공보 및 한국공개실용신안공보: 조사된 최소문헌란에 기재된 IPC
일본등록실용신안공보 및 일본공개실용신안공보: 조사된 최소문헌란에 기재된 IPC

국제조사에 이용된 전산 데이터베이스(데이터베이스의 명칭 및 검색어(해당하는 경우))

eKOMPASS(특허청 내부 검색시스템) & 키워드: 이차전지, 전해동박, 피크 수 조도, 인장강도, 평균조도, 집전체, 이차전지용 전극

C. 관련 문헌

카테고리*	인용문헌명 및 관련 구절(해당하는 경우)의 기재	관련 청구항
X	JP 2000-182623 A (NIPPON DENKAI KK) 2000.06.30 단락 [0018]-[0044]; 및 청구항 1-5 참조.	12-16
A		1-11
A	JP 2014-135175 A (MITSUI MINING & SMELTING CO., LTD.) 2014.07.24 단락 [0021]; 및 청구항 1-14 참조.	1-16
A	KR 10-1449342 B1 (일진머티리얼즈 주식회사) 2014.10.13 청구항 1-3, 12 및 13 참조.	1-16
A	KR 10-2014-0090069 A (창춘 페트로케미칼 컴퍼니 리미티드) 2014.07.16 청구항 1-11 참조.	1-16
A	US 2001-0051282 A1 (YATES, C. B. 등) 2001.12.13 청구항 1-12 참조.	1-16

☐ 추가 문헌이 C(계속)에 기재되어 있습니다.

☒ 대응특허에 관한 별지를 참조하십시오.

* 인용된 문헌의 특별 카테고리:

"A" 특별히 관련이 없는 것으로 보이는 일반적인 기술수준을 정의한 문헌

"E" 국제출원일보다 빠른 출원일 또는 우선일을 가지나 국제출원일 이후에 공개된 선출원 또는 특허 문헌

"L" 우선권 주장에 의문을 제기하는 문헌 또는 다른 인용문헌의 공개일 또는 다른 특별한 이유(이유를 명시)를 밝히기 위하여 인용된 문헌

"O" 구두 개시, 사용, 전시 또는 기타 수단을 언급하고 있는 문헌

"P" 우선일 이후에 공개되었으나 국제출원일 이전에 공개된 문헌

"T" 국제출원일 또는 우선일 후에 공개된 문헌으로, 출원과 상충하지 않으며 발명의 기초가 되는 원리나 이론을 이해하기 위해 인용된 문헌

"X" 특별한 관련이 있는 문헌. 해당 문헌 하나만으로 청구된 발명의 신규성 또는 진보성이 없는 것으로 본다.

"Y" 특별한 관련이 있는 문헌. 해당 문헌이 하나 이상의 다른 문헌과 조합하는 경우로 그 조합이 당업자에게 자명한 경우 청구된 발명은 진보성이 없는 것으로 본다.

"&" 동일한 대응특허문헌에 속하는 문헌

국제조사의 실제 완료일	국제조사보고서 발송일
2016년 07월 29일 (29.07.2016)	2016년 07월 29일 (29.07.2016)

ISA/KR의 명칭 및 우편주소
대한민국 특허청
(35208) 대전광역시 서구 청사로 189, 4동 (둔산동, 정부대전청사)
팩스 번호 +82-42-481-8578

심사관
김동석
전화번호 +82-42-481-5405

서식 PCT/ISA/210 (두 번째 용지) (2015년 1월)

국제조사보고서
대응특허에 관한 정보

국제출원번호
PCT/KR2016/004449

국제조사보고서에서 인용된 특허문헌	공개일	대응특허문헌	공개일
JP 2000-182623 A	2000/06/30	JP 3850155 B2	2006/11/29
JP 2014-135175 A	2014/07/24	EP 2945467 A1	2015/11/18
		US 2015-0340639 A1	2015/11/26
		WO 2014-109081 A1	2014/07/17
KR 10-1449342 B1	2014/10/13	TW 201523992 A	2015/06/16
		WO 2015-069075 A1	2015/05/14
KR 10-2014-0090069 A	2014/07/16	CN 103911633 A	2014/07/09
		JP 2014-132106 A	2014/07/17
		JP 5696179 B2	2015/04/08
		US 2014-0193660 A1	2014/07/10
		US 9365942 B2	2016/06/14
US 2001-0051282 A1	2001/12/13	US 6372113 B2	2002/04/16

(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
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(43)公開日　平成12年6月30日(2000.6.30)

(51)Int.Cl.'		識別記号	Ｆ Ｉ			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）

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(71)出願人　000232014
日本電解株式会社
東京都文京区本郷３丁目９番25号
(72)発明者　張ヶ谷　浩一
茨城県下館市下江連1220番地　日本電解株式会社下館工場内
(72)発明者　野口　真男
茨城県下館市下江連1220番地　日本電解株式会社下館工場内
(74)代理人　100096484
弁理士　蔭山　栄夫

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）の破断状態をみる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、電解液を活性炭る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】

	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	8.3	2.3	10.6	1.5	0.9	24.6
比較例３	46.4	13.0	86.5	19.0	9.0	177.9
比較例４	…	…	…	…	…	…

	引張り強さ (kgf/mm²)		伸び率 (%)		引き裂き伝播時間 (秒)	過充電試験 割れ数 (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	25.6	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	19.8	0.2	15	16
比較例２	37.8	37.0	8.7	8.9	0.2	82	83
比較例３	56.1	53.2	5.2	3.9	0.1	48	82
比較例４	42.0	15.8	1.4	19.8	7.6	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。

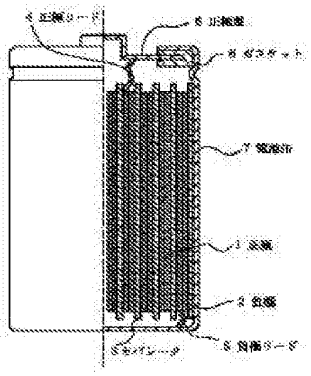
【図面の簡単な説明】

【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

(72)発明者　小林　勝己
茨城県下館市下江連1226番地　日本電解株式会社下館工場内
(72)発明者　阿曽　和義
茨城県下館市下江連1226番地　日本電解株式会社下館工場内

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(71)Applicant NIPPON DENKAI KK
(72)Inventor HARIGAYA KOICHI
NOGUCHI HIDEO
KOBAYASHI KATSUMI
ASO KAZUYOSHI

(54)ELECTROLYTIC COPPER FOIL, COPPER FOIL FOR CURRENT COLLECTOR OF SECONDARY BATTERY, AND SECONDARY BATTERY

(57)Abstract
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 overdharging 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.

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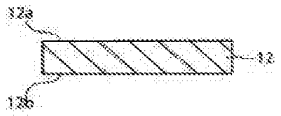
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(71)出願人　000006183
三井金属鉱業株式会社
東京都品川区大崎１丁目１１番１号
(74)代理人　100113365
弁理士　高村　雅晟
(74)代理人　100131842
弁理士　加島　広基
(72)発明者　松浦　宣範
埼玉県上尾市原市１３３３－２　三井金属鉱業株式会社総合研究所内

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(54)【発明の名称】電解銅箔及び電子デバイス



[0001]　本発明は、電解銅箔及びそれを用いた電子デバイスに関するものである。

[0002]　近年、有機ＥＬ照明等の発光素子が、環境に配慮したグリーンデバイスとして注目されている。有機ＥＬ照明の特徴としては、１）白熱灯に対して低消費電力であること、２）薄型かつ軽量であること、３）フレキシブルであることが挙げられる。現在、有機ＥＬ照明は、上記２）及び３）の特徴を実現すべく開発が進められている。この点、フラットパネルディスプレイ（ＦＰＤ）等で従来使用されてきたガラス基板では、上記２）及び３）の特徴を実現することは不可能である。

[0003]　そこで、有機ＥＬ照明のための支持体としての基板（以下、支持基材という）に対する研究が進められており、その候補として、極薄ガラス、樹脂フィルム、金属箔等が提案されている。極薄ガラスは、耐熱性、バリア性、及び光透過性に優れ、フレキシブル性も良好であるが、ハンドリング性がやや劣り、熱伝導性が低く、材料コストも高い。また、樹脂フィルムは、ハンドリング性及びフレキシブル性に優れ、材料コストも低く、光透過性も良好であるが、耐熱性及びバリア性に乏しく、熱伝導性が低い。

[0004]　これに対し、金属箔は、光透過性が無いことを除けば、耐熱性、バリア性、ハンドリング性、熱伝導性に優れ、

フレキシブル性も良好であり、材料コストも低いといった優れた特徴を有する。特に、熱伝導性については、典型的なフレキシブルガラスやフィルムが１Ｗ／ｍ℃以下と極めて低いのに対し、銅箔の場合、４００Ｗ／ｍ℃程度と極めて高い。

[0005] 金属基板を用いた発光素子を実現するために、特許文献１（特開２００９－１５２１１３号公報）では金属基板の表面を研磨処理やメッキ処理により平滑化して、その上に有機層を形成することが提案されている。また、特許文献２（特開２００８－２４３７７２号公報）では金属基板上にニッケルめっき層を設けることで研磨等をすることなく平滑面を形成し、その上に有機ＥＬ素子を形成することが提案されている。一方、金属基板を用いた光電素子も提案されており、例えば、特許文献３（特開２０１１－２２２８１９号公報）には平滑化処理された金属基材上に有機薄膜起電力層を設けた太陽電池が開示されている。これらの技術においては、電極間の短絡防止のため、金属基板表面の平滑化が重要な課題となっている。この課題に対処した技術として、特許文献４（国際出願第２０１１／１５２０９１号）及び特許文献５（国際出願第２０１１／１５２０９２号）では、算術平均粗さＲａが１０．０ｎｍ以下と極めて低い超平坦面を備えた金属箔を支持基材兼電極として用いることが提案されている。

[0006] 一方、リチウムイオン二次電池用電解銅箔として、両面ともに表面粗さＲｚが０．８～２．８μｍであり、２００～４００℃で加熱処理後の０．２%耐力が２５０Ｎ／ｍｍ^{2}以上の電解銅箔が知られている（特許文献６（特開２０１２－１５１１０６号公報）参照）。

[0007] 【特許文献 1】 特開２００９－１５２１１３号公報

【特許文献 2】 特開２００８－２４３７７２号公報

【特許文献 3】 特開２０１１－２２２８１９号公報

【特許文献 4】 国際出願第２０１１／１５２０９１号

【特許文献 5】 国際出願第２０１１／１５２０９２号

【特許文献 6】 特開２０１２－１５１１０６号公報

[0008] 本発明者らは、今般、電解銅箔において、加熱後０．２%耐力を高くし、かつ、凹部優位な表面プロファイルを付与することにより、電子デバイス用電極として極めて有用な電解銅箔を提供できるとの知見を得た。

[0009] したがって、本発明の目的は、電子デバイス用電極として極めて有用な電解銅箔を提供することにある。

[0010] 本発明の一態様によれば、電子デバイス用電極として用いられる、銅又は銅合金からなる電解銅箔であって、

窒素雰囲気中、２００℃で６０分間の熱処理を施した後における前記電解銅箔の０．２%耐力が２５０Ｎ／ｍｍ^{2}以上であり、かつ、

前記電解銅箔の少なくとも一方の最表面に、ＪＩＳ　Ｂ　０６０１－２００１に準拠して１８１μｍ×１３６μｍの矩形領域に対して測定される、断面曲線の最大山高さＰｐに対する断面曲線の最大谷深さＰｖのＰｖ／Ｐｐ比が１．２以上の凹部優位面を備えてなる、電解銅箔が提供される。

[0011] 本発明の他の一態様によれば、前記電極箔と、

前記電極箔の前記超平坦面上に設けられる、半導体特性を有する半導体機能層と、

を備えた、電子デバイスが提供される。

[0013] 定義

本明細書において使用される用語の定義を以下に示す。

[0014] 「０．２%耐力」は、応力－ひずみ線図において、除荷時の永久ひずみが０．２%になる応力を意味し、降伏現象を示さない材料における降伏応力の代替指標として一般的に使用されているものである。本明細書における０．２%耐力は、電解銅箔から１２．５ｍｍ×９０ｍｍのサイズの矩形状試験片を採取し、得られた矩形状試験片を市

販の引張試験機にセットして、ＪＩＳ　Ｚ　２２４１（２０１１）に準拠して測定することができる。このとき、引張試験機に固定するための片側２０ｍｍのつかみ部を試験片の両端に確保することで、実質的な測定箇所の長さを５０ｍｍとするのが望ましい。なお、ロール状電解銅箔から矩形状試験片を採取する場合、矩形状試験片の長辺及び短辺がロール状電解銅箔の長尺方向（ＭＤ方向）及び短尺方向（ＴＤ方向）とそれぞれ一致するように矩形状試験片が採取され、長尺方向（ＭＤ方向）に引っ張られるように引張試験機にセットされる。

[0015] 「Ｐｖ／Ｐｐ比」は、試料表面に対して、ＪＩＳ　Ｂ　０６０１－２００１に準拠して１８１μｍ×１３６μｍの矩形領域に対して測定される、断面曲線の最大山高さＰｐに対する断面曲線の最大谷深さＰｖの比である。最大山高さＰｐは凸部の高さを表す一方、最大谷深さＰｖは凹部の深さを表すことから、Ｐｖ／Ｐｐ比が高いほど凹部優位の表面であることを意味する。なお、最大山高さＰｐ及び最大谷深さＰｖは、市販の非接触表面形状測定機を用いてＪＩＳ　Ｂ　０６０１－２００１に準拠して測定することができる。

[0016] 電解銅箔

本発明による電解銅箔は電子デバイス用電極として用いられるものである。図１に本発明による電解銅箔の模式断面図を示す。図１に示される電解銅箔１２は、銅又は銅合金からなり、表面１２ａ及び裏面１２ｂを有する。電解銅箔は比較的安価でありながら、強度、フレキシブル性、電気的特性等に優れる。電解銅箔１２は、窒素雰囲気中、２００℃で６０分間の熱処理を施した後における０．２％耐力（以下、加熱後０．２％耐力ともいう）が２５０Ｎ／ｍｍ^{2}以上のものである。そして、電解銅箔１２の少なくとも一方の最表面（すなわち表面１２ａ及び／又は裏面１２ｂ）は、ＪＩＳ　Ｂ　０６０１－２００１に準拠して１８１μｍ×１３６μｍの矩形領域に対して測定される、断面曲線の最大山高さＰｐに対する断面曲線の最大谷深さＰｖのＰｖ／Ｐｐ比が１．２以上の凹部優位面となっている。すなわち、最大山高さＰｐは凸部の高さを表す一方、最大谷深さＰｖは凹部の深さを表す。したがって、１．２以上のＰｖ／Ｐｐ比は、凹部を凸部よりも優先的に備えた特異的な表面プロファイルを意味する。このように加熱後０．２％耐力を高くし、かつ、凹部優位な表面プロファイルを付与することにより、電子デバイス用電極として極めて有用な電解銅箔を提供することができる。

[0017] すなわち、加熱後０．２％耐力を２５０Ｎ／ｍｍ^{2}以上とすることによって、電解銅箔を電極として用いて電子デバイスを製造するに際し、加熱を伴う工程で起こりうる箔のうねりを効果的に抑制することができる。例えば、有機ＥＬ照明や有機薄膜太陽電池のように、電解銅箔上に有機半導体材料を連続的に塗布していく場合、一連のロール・トゥ・ロール・プロセスで併せて焼成を連続して行うことが望まれる。この焼成は、有機半導体材料の種類にもよるが、１５０～３００℃の温度域で行われるのが一般的である。しかしながら、現在使用されている平滑銅箔では、１５０℃以上の温度で焼成されると、結晶粒の再結晶化によって箔が軟化する現象が起こる。特に、電極機能以外に基板としての機能を平滑銅箔に持たようとした場合、平滑銅箔の軟化はその箔自身のうねりをもたらしうるため、積層させる有機半導体の膜厚の不均一化など、箔上に設けられる電子デバイスの不具合（発光斑等）を引き起こす可能性がある。例えば、張力がかかった状態で電解銅箔に熱処理を行うと、局所的に再結晶化により塑性変形を起こし、大きなうねりを伴うアンジュレーションという現象を起こすことがある。また、銅箔端部の波模様のうねりが発生するフレアという現象も起こることがある。これらの現象が発生すると、銅箔上に有機高分子材料を塗布した際、塗膜の膜厚に悪影響を与える可能性があり、上述した不具合を電子デバイスにもたらしうる。また、フレアが大きくなると、塗布用のスリットコータ部に接触してキズを与えることがある。これらの問題はロール形態の電解銅箔に限らず、所定サイズに切断されたシート状の電解銅箔についても同様に当てはまる。もっとも、ロール・トゥ・ロール・プロセスにおいては、平滑銅箔の軟化は正確な搬送を阻害して巻ズレや巻皺の誘発しうるため、歩留りを下げる原因にもなりうる。これらの種々の問題が加熱後０．２％耐力を２５０Ｎ／ｍｍ^{2}以上とすることによって解決又は軽減され、そのような電解銅箔を用いた電子デバイスの信頼性を格段に向上することができる。好ましい加熱後０．２％耐力は２８０Ｎ／ｍｍ^{2}以上であり、より好ましくは３００Ｎ／ｍｍ^{2}以上であり、さらに好ましくは３５０Ｎ／ｍｍ^{2}以上である。なお、加熱後０．２％耐力の上限値は特に限定されないが、より好ましくは１０００Ｎ／ｍｍ^{2}以下であり、さらに好ましくは９００Ｎ／ｍｍ^{2}以下である。

[0018] また、電解銅箔１２の少なくとも一方の最表面（すなわち表面１２ａ及び／又は裏面１２ｂ）をＰｖ／Ｐｐ比が１．２以上の凹部優位面とすることによっても、そのような電解銅箔を用いた電子デバイスの信頼性を格段に向上することができる。これは凸部の形成が抑制されることで電極間の短絡（具体的には対向電極との短絡や半導体機能層間における短絡）が防止されることによるものと考えられる。好ましいＰｖ／Ｐｐ比は１．５以上であり、より好ましくは２．０以上、さらに好ましくは３．０以上、特に好ましくは４．０以上であり、最も好ましくは５．０以上である。Ｐｖ／Ｐｐ比は高ければ高い程望ましいため特に限定されないが、費用対効果の観点からその上限値は１０．０辺りが現実的である。

[0019] 特に、凹部優位面のＰｖ／Ｐｐ比を２．０以上とすれば電解銅箔に優れた光散乱性を持たせることができ、この目的のためには、好ましくは２．３以上であり、より好ましくは２．５以上、さらに好ましくは２．８以上、特に好ましくは３．０以上である。すなわち、本発明者らの知見によれば、このような凹部優位の特異的な表面プロファイルを電解銅箔に付与することにより、優れた光散乱性を電極箔自体に発揮させることができ、それにより電極箔自体で発光効率や発電効率を向上することができる。これは、優先的に形成される凹部に起因して光が散乱されるとともに、上述したように凸部の形成が抑制されることで電極間の短絡（具体的には対向電極との短絡や半導体機能層間における短絡）が防止されることによるものと考えられる。特に、本発明の電極箔にあっては、金属箔ないし電極箔の表面プロファイル自体で光散乱効果が得られるため、マイクロレンズ形成及びそれに伴う微細加工を不要として生産性やコスト効率の低下を回避することができ、それ故、大面積化にも適している。

[0020] さらに、本発明者らは、１．２以上のＰｖ／Ｐｐ比を有する凹部優位面が、何らかの要因によって、ロール状態で準備又は保管された電解銅箔の酸化を抑制する効果をも与えうることを知見している。この酸化抑制効果は、電解銅箔の電子デバイス用電極としての適性を向上しうるものである。すなわち、銅箔は錆びやすいため、有機防錆、無機防錆、カップリング処理等の表面処理が従来から行われてきた。しかしながら、銅箔を電極基板として使用する場合、有機防錆剤等が存在すると、素子特性等への悪影響が懸念される。一方で、防錆処理を行わないと表面の酸化が進行してしまい、反射膜の剥離や素子抵抗の増加といった問題が懸念される。特に、ロール・トゥ・ロール・プロセス用に銅箔をロール状にした場合、酸化の進行が顕著となることから、特に電子デバイス用の電極基板として量産化する際に問題となる。このような問題が電解銅箔１２の少なくとも一方の最表面におけるＰｖ／Ｐｐ比を１．２以上とすることで解決又は軽減され、そのような銅箔を用いた電子デバイスの信頼性を向上することができる。好ましいＰｖ／Ｐｐ比は１．５以上であり、より好ましくは２．０以上、さらに好ましくは３．０以上、特に好ましくは４．０以上であり、最も好ましくは５．０以上である。

[0021] 凹部優位面は、ＪＩＳ　Ｂ　０６０１－２００１に準拠して測定される、１０ｎｍ以下の算術平均粗さＲａを有する超平坦面でもあるのが好ましく、より好ましくは７．０ｎｍ以下であり、さらに好ましくは５．０ｎｍ以下であり、特に好ましくは３．０ｎｍ以下である。電解銅箔に求められる用途や性能等に応じて粗さを適宜決定すればよい。算術平均粗さＲａの下限は特に限定されずゼロであってもよいが、平坦化処理の効率を考慮すると０．５ｎｍが下限値の目安として挙げられる。この算術平均粗さＲａは、ＪＩＳ　Ｂ　０６０１－２００１に準拠して市販の粗さ測定装置を用いて測定することができる。凹部優位面の算術平均粗さＲａが上述のごとく極めて小さいことで、発光素子、光電素子等の電子デバイスに使用した際の電極間の短絡をより一層効果的に防止できる。このような超平坦面は、ＣＭＰ（Chemical Mechanical Polishing）処理により電解銅箔を研磨することにより実現することができる。ＣＭＰ処理は、公知の研磨液及び公知の研磨パッドを用いて、公知の条件に従って行うことができる。好ましい研磨液としては、セリア、シリカ、アルミナ、ジルコニア等から選択される１種以上の研磨砥粒約０．１～１０重量％程度を含んでなり、かつ、ベンゾトリアゾール（ＢＴＡ）等の防錆剤と、更に／又は、キナルジン酸、キノリン酸、ニコチン酸、リンゴ酸、アミノ酸、クエン酸、カルボン酸、ポリアクリル酸等の有機錯体形成剤と、カチオン性界面活性剤、アニオン性界面活性剤等の界面活性剤と、所望により防食剤とをさらに含むものが挙げられる。好ましい研磨パッドとしては、ウレタン製のパッドが挙げられる。研磨条件は、パッド回転速度、ワーク荷重、研磨液塗布流量等を適宜調整すればよく特に限定されないが、回転速度を２０～１０００ｒｐｍの範囲内に、ワーク荷重を１００～５００ｇｆ／ｃｍ^{2}の範囲内に、研磨液塗布流量を２０～２００ｃｃ／ｍｉｎ範囲内に調整するのが好ましい。

[0022] あるいは、電解銅箔の片面が凹部優位面を構成し、電解銅箔の他方の面が１０ｎｍ以下の算術平均粗さＲａを有する超平坦面になるようにしてもよい。好ましくは、電解銅箔の表面１２ａがＲａ：１０ｎｍ以下の超平坦な表面プロファイルを有し、かつ、裏面１２ｂがＰｖ／Ｐｐ比：１．２以上の凹部優位な表面プロファイルを有する。このように両面処理された箔とすることにより、上述した電極間の短絡防止効果に加えて、ロール状態とされた際に、巻き傷を防止しながら、超平坦面の酸化をより効果的に抑制することができる。特に、素子形成されるための超平坦面の酸化を、素子特性等への悪影響が懸念される有機防錆剤を用いることなく効果的に抑制できる点で、本発明の電解銅箔は電子デバイス用の電極基板として特に適する。この酸化抑制効果の詳細なメカニズムについては定かではないが、以下のように幾つかの要因によるものではないかと推察される。第一に、電解銅箔表面の平坦性をＲａ：１０ｎｍ以下と極度に向上させ、表面に形成される酸化膜が極薄（例えば厚さ数ｎｍ）で均一かつ緻密に形成されることで、その後の酸化の進行が抑制されるものと考えられる。なお、この酸化抑制状態は電解銅箔の表面をＸ線光電子分光装置（ＸＰＳ）で分析することにより確認することができるが、表層から深さ１０ｎｍ未満の情報を取得することになるため、電解銅箔の表面にその測定深さ未満の極薄の酸化膜しか形成されていないのであれば、測定深さ内に存在する未酸化の金属銅に起因するピークが検出されることになる。第二に、上記のように酸化の進行が抑制されることで、ロール状態とされた際に互いに接触する表面と裏面の間で未酸化の金属銅が酸化物と接触する頻度や程度が低下し、それによっても酸化物の成長が更に抑制されるものと考えられる。これは、酸化物との接触があると本来未酸化の金属部分も酸化環境に曝され、酸化されやすくなるためである。第三に、ロール状態

とされた際に電解銅箔の超平坦面及び凹部優位面の特有の表面プロファイルに起因して表面と裏面の間に入り込みにくくなり、それによる酸化抑制効果もありうるものと推察される。いずれにしても、このように両面処理された電解銅箔において実現される酸化抑制効果は予想外なものであり、従来から実施されていた防錆処理を不要とすることが可能であり、それにより素子特性等への悪影響が懸念される有機防錆剤を箔表面から無くすことができる。また、銅箔がロール状態とされると巻き傷が箔表面に発生しやすいという問題に対して、両面（特に粗度が高くなりがちな裏面）の表面プロファイルを制御したことで、ロール品とした際の巻き傷を低減することもできる。この効果は裏面のＰｖ／Ｐｐ比を１．５以上とすることでより効果的に実現される。

[0023] 電解銅箔１２の両面が凹部優位面を構成するのも好ましい。すなわち表面１２ａのみならず裏面１２ｂも上述したＰｖ／Ｐｐ比を有する凹部優位面とすることでロール品とした際の巻き傷をより一層効果的に防止することができる。この効果は裏面のＰｖ／Ｐｐ比を１．５以上とすることでより効果的に実現される。

[0024] 算術平均粗さＲａが１０ｎｍ以下の超平坦面は、電解研磨法、バフ研磨法、薬液研磨法、及びこれらの組み合わせ等を用いて電解銅箔を研磨することによっても実現することができる。薬液研磨法は、薬液、薬液温度、薬液浸漬時間等を適宜調整して行えばよく特に限定されないが、例えば、銅箔の薬液研磨は、２－アミノエタノールと塩化アンモニウムとの混合物を使用することにより行うことができる。薬液温度は室温が好ましく、浸漬法（Ｄｉｐ法）を用いるのが好ましい。また、薬液浸漬時間は、長くなると平坦性が悪化する傾向があるため、１０～１２０秒間が好ましく、３０～９０秒間がより好ましい。薬液研磨後の電解銅箔は流水により洗浄されるのが好ましい。このような平坦化処理によれば、Ｒａ算術平均粗さＲａ１２ｎｍ程度の表面をＲａ１０．０ｎｍ以下、例えば３．０ｎｍ程度にまで平坦化することができる。

[0025] 超平坦面は、電解銅箔の表面をブラストにより研磨する方法や、電解銅箔１２の表面をレーザー、抵抗加熱、ランプ加熱等の手法により溶融させた後に急冷させる方法等によっても実現することもできる。

[0026] しかしながら、単に超平坦面と同様にして超平坦化したとしても、凹部及び凸部が概ね同程度に形成されるため、１．２以上のＰｖ／Ｐｐ比になることは通常あり得ない。そこで、１．２以上のＰｖ／Ｐｐ比を付与するための処理が行われるのが好ましい。そのような表面処理の好ましい例としては、超音波洗浄、化学研磨液を用いた化学研磨、及び／又はドライアイスブラスト法等が挙げられる。超音波洗浄は、例えば、市販の流水式超音波洗浄機を用い、所定の高周波出力（例えば６０Ｗ）で電解銅箔表面を所定時間（例えば１０分間）処理することによって行うことができる。化学研磨は、例えば、化学研磨液（例えば三菱ガス化学社製のＣＰＢ－１０等の純銅用の研磨液）を用い、研磨液と水を所定の割合（例えば１：２の重量割合）で混合して室温下で１分間浸漬させ、純水洗浄、希硫酸（例えば０．１Ｎ希硫酸）での洗浄、再度の純水洗浄、及び乾燥を経ることにより行うことができる。あるいは、電解銅箔を１質量％の過酸化水素水に浸漬させ、その後超純水にて洗浄してもよい。ドライアイスブラスト法は、例えばドライアイススノーシステム（エアウォーター社製）等の市販の装置を用いて、高圧に圧縮した炭酸ガスを細いノズルから噴射させることにより、低温固化した炭酸を裏面１２ｂに吹き付けることにより行うことができる。なお、電解銅箔を電積させる際に、有機物、塩素等添加の有無や量を適宜調整することにより、電解銅箔の表面形状を制御することも可能である。この場合、得られた電解銅箔の表面平坦度に応じて後処理（例えば超音波洗浄、化学研磨、ドライアイスブラスト処理、ＣＭＰ処理等）を適宜選択すればよい。

[0027] 電解銅箔の厚さは、フレキシブル性を損なうことなく、箔として単独でハンドリングが可能な厚さである限り特に限定されないが、１～２５０μｍであり、好ましくは５～２００μｍ、より好ましくは１０～１５０μｍ、さらに好ましくは１５～１００μｍであるが、電極箔に求められる用途や性能等に応じて厚さを適宜決定すればよい。したがって、金属の使用量の低減や軽量化がより望まれる場合には厚さの上限は５０μｍ、３５μｍ又は２５μｍとするのが特に好ましい一方、強度がより望まれる場合には厚さの下限を２５μｍ、３５μｍ又は５０μｍとするのが特に好ましい。このような厚さであれば、市販の裁断機を用いて簡単に切断することが可能である。また、電解銅箔は、ガラス基板と異なり、割れ、欠け等の問題が無く、また、切断時のパーティクルが発生しづらい等の利点も有する。電解銅箔は、四角形以外の形状、例えば、円形、三角形、多角形といった様々な形状とすることができ、しかも切断及び溶接も可能なことから、切り貼りによりキュービック状やボール状といった立体的な形状の電子デバイスを作製することも可能である。この場合、電解銅箔の切断部や溶接部には、半導体機能層を形成しないことが好ましい。

[0028] 電解銅箔の長さは特に限定されずが、ロール・トゥ・ロール・プロセスに適用させるためにはある程度の長さを有するのが好ましい。電解銅箔の好ましい長さは、装置の仕様等に応じて異なってくるが、概ね２ｍ以上であり、生産性向上の観点から、より好ましくは２０ｍ以上、さらに好ましくは５０ｍ以上、特に好ましくは１００ｍ以上、最も好ましくは１０００ｍ以上である。もっとも、電解銅箔は所定サイズに切断されたシート状であってもよい。また、電解銅箔の好ましい幅は、装置の仕様等に応じて異なってくるが、概ね１５０ｍｍ以上であり、生産性向上の観点から、好ましくは３５０ｍｍ以上、より好ましくは６００ｍｍ以上、特に好ましくは１０００ｍｍ以上である。なお、前述したとおり、本発明の特定の態様による電解銅箔にあっては、巻きによって発生しうる傷を効果

的に抑制できることから、フィルム、エンボスフィルム等、電極箔よりも弾力性の高い材料を表面と裏面の間に挟むといった巻き傷防止対策が不要となり、ロール品としての取り扱いが簡素化する。

[0029] 超平坦面及び凹部優位面はアルカリ溶液で洗浄することが好ましい。そのようなアルカリ溶液としては、アンモニアを含有した溶液、水酸化ナトリウム溶液、水酸化カリウム溶液等の公知のアルカリ溶液が使用可能である。好ましいアルカリ溶液はアンモニアを含有した溶液であり、より好ましくはアンモニアを含有した有機系アルカリ溶液、さらに好ましくはテトラメチルアンモニウムハイドロオキサイド（ＴＭＡＨ）溶液である。ＴＭＡＨ溶液の好ましい濃度は０．１～３．０ｗｔ％である。そのような洗浄の一例としては、０．４％ＴＭＡＨ溶液を用いて２３℃で１分間の洗浄を行うことが挙げられる。このようなアルカリ溶液による洗浄と併せて、又は、アルカリ溶液による洗浄の代わりに、ＵＶ（Ultra Violet）処理を行っても同様の洗浄効果を得ることができる。さらに、銅箔等の場合、希硫酸等の酸性洗浄液を用いて、銅表面に形成されうる酸化物を除去することも可能である。酸洗浄の一例としては、希硫酸を用いて３０秒間の洗浄を行うことが挙げられる。

[0030] 超平坦面及び凹部優位面上に存在するパーティクルを除去することが好ましい。有効なパーティクル除去の手法としては、超純水によるソニック洗浄法やドライアイスブラスト法等が挙げられるが、ドライアイスブラスト法がより効果的である。ドライアイスブラスト法は、高圧に圧縮した炭酸ガスを細いノズルから噴射させることにより、低温固化した炭酸を超平坦面１２ａに吹き付けてパーティクルを除去する方法である。このドライアイスブラスト法は、ウェット工程とは異なり、乾燥工程を省くことができ、また有機物の除去ができる等の利点を有する。ドライアイスブラスト法は、例えばドライアイススノーシステム（エアウォーター社製）等の市販の装置を用いて行うことができる。もっとも、１．５以上のＰｖ／Ｐｐ比を付与するための処理（例えばドライアイスブラスト法）によって既にパーティクルが除去されている場合には、このパーティクル除去工程は省略可能である。

[0031] 電極箔

本発明の電解銅箔は、箔単独の形態で、又は他の機能層を積層させた形態で、電極箔として使用されるのが好ましい。図２に電極箔１０の一例の模式断面図を示す。図２に示される電極箔１０は電解銅箔１２を備えてなる。電極箔１０は、所望により電解銅箔１２の表面１２ａに直接、又は拡散防止層を介して設けられる反射層１３を備えていてもよい。また、電極箔１０は、所望により少なくとも電解銅箔１２の超平坦面１２ａ又は（存在する場合には）反射層１３の表面１３ａ上に直接設けられるバッファ層１４を備えていてもよい。図２に示される電極箔１０は電解銅箔１２、反射層１３及びバッファ層１４を備えた３層構成であるが、本発明の電極箔はこれに限定されず、電解銅箔１２の１層構成であってもよいし、電解銅箔１２及び反射層１３の２層構成であってもよい。あるいは、電解銅箔１２の両面に反射層１３及びバッファ層１４を備えた５層構成であってもよい。

[0032] このように電解銅箔１２を支持基材のみならず電極として用いることで、支持基材と電極の機能を兼ね備えた電極箔を提供することができる。特に、電解銅箔１２の厚さを適切な範囲（好ましくは１～２５０μｍ）とすれば、フレキシブル電子デバイス用の支持基材を兼ねた電極として用いることができる。このようなフレキシブル電子デバイスの製造に関して、電極箔１２は、電解銅箔をベースとしているため、支持基材を特に必要とすることなく、例えばロール・トゥ・ロール（roll-to-roll）プロセスによって効率的に製造することができる。ロール・トゥ・ロール・プロセスは、ロール状に巻いた長尺状の箔を引き出して所定のプロセスを施したのち再び巻き取るという電子デバイスを効率的に量産する上で極めて有利なプロセスであり、本願発明の用途である発光素子及び光電素子等の電子デバイスの量産化を実現する上で鍵になるプロセスである。このように、本発明の電極箔は、支持基材及び反射層を不要にすることができる。このため、本発明の電極箔は、少なくとも電子デバイスが構築される部分に絶縁層を有しないのが好ましく、より好ましくはいかなる部位にも絶縁層を有しない。

[0033] 所望により電解銅箔１２の表面１２ａ上には反射層１３が直接、又は後述する反射防止層を介して設けられてもよい。反射層１３は、アルミニウム、アルミニウム系合金、銀、及び銀系合金からなる群から選択される少なくとも一種で構成されるのが好ましい。これらの材料は、光の反射率が高いため反射層に適しており、しかも薄膜化した際の平坦性にも優れる。特に、アルミニウム又はアルミニウム系合金は安価な材料であることから好ましい。アルミニウム系合金及び銀系合金としては、発光素子や光電素子においてアノード又はカソードとして使用される一般的な合金組成を有するものが幅広く採用可能である。好ましいアルミニウム系合金組成の例としては、Ａｌ－Ｎｉ、Ａｌ－Ｃｕ、Ａｌ－Ａｇ、Ａｌ－Ｃｅ、Ａｌ－Ｚｎ、Ａｌ－Ｂ、Ａｌ－Ｔａ、Ａｌ－Ｎｄ、Ａｌ－Ｓｉ、Ａｌ－Ｌａ、Ａｌ－Ｃｏ、Ａｌ－Ｇｅ、Ａｌ－Ｆｅ、Ａｌ－Ｌｉ、Ａｌ－Ｍｇ、Ａｌ－Ｍｎ、Ａｌ－Ｔｉ合金が挙げられる。これらの合金を構成する元素であれば、必要な特性に合わせて任意に組み合わせることが可能である。また、好ましい銀合金組成の例としては、Ａｇ－Ｐｄ、Ａｇ－Ｃｕ、Ａｇ－Ａｌ、Ａｇ－Ｚｎ、Ａｇ－Ｍｇ、Ａｇ－Ｍｎ、Ａｇ－Ｃｒ、Ａｇ－Ｔｉ、Ａｇ－Ｔａ、Ａｇ－Ｃｏ、Ａｇ－Ｓｉ、Ａｇ－Ｇｅ、Ａｇ－Ｌｉ、Ａｇ－Ｂ、Ａｇ－Ｐｔ、Ａｇ－Ｆｅ、Ａｇ－Ｎｄ、Ａｇ－Ｌａ、Ａｇ－Ｃｅ合金が挙げられる。これらの合金を構成する元素であれば、必要な特性に合わせて任意に組み合わせることが可能である。反射層１３の膜厚は特に限定されるものではないが、３０～５００ｎｍの厚さを有するのが好ましく、より好ましくは５０～３００ｎｍであり、さらに好ましく

は１００～２５０ｎｍである。

[0034] 反射層１３がアルミニウム膜又はアルミニウム系合金膜で構成される場合、反射層を少なくとも２つの層からなる積層構造で構成してもよい。この態様にあっては、反射層１３が界面によって仕切られた２つの層の積層構造を有し、この界面を境に下層及び上層が互いに異なる結晶方位を有する。これにより、電極箔がかなりの高温に曝される場合であっても、銅箔とアルミニウム含有反射層の間の界面から起こりうるサーマルマイグレーションを効果的に抑制して、サーマルマイグレーションに起因する表面平坦性や反射率の低下を抑制することができる。すなわち、電極箔の耐熱性を向上することができる。したがって、この態様は、２００℃以上、好ましくは２３０℃以上、より好ましくは２５０℃以上の温度で行われる、正孔注入層塗布後の熱処理において特に有効であるといえる。このような耐熱性の向上は、結晶粒界を優先して進行するサーマルマイグレーションが、結晶粒界が不連続となる界面によって阻止されることにより実現されるものと考えられる。なお、反射層１３中の界面の数は２つ以上であってもよく、この場合、反射層は3層以上の積層構造となる。

[0035] 所望により電解銅箔１２と反射層１３との間に設けられる拡散防止層は、電解銅箔に由来する金属の拡散を防止する機能を有するものであればよく、公知のあらゆる組成および構造の膜が採用可能である。これにより、電極箔がかなりの高温に曝される場合であっても、銅箔とアルミニウム含有反射層の間の界面から起こりうるサーマルマイグレーションを効果的に抑制して、サーマルマイグレーションに起因する表面平坦性や反射率の低下を抑制することができる。すなわち、電極箔の耐熱性を向上することができる。したがって、この態様は、２００℃以上、好ましくは２３０℃以上、より好ましくは２５０℃以上の温度で行われる、正孔注入層塗布後の熱処理において特に有効であるといえる。なお、拡散防止層は2層以上の積層構造としてもよい。

[0036] 電解銅箔１２又は存在する場合には反射層１３の少なくとも一方の最表面にはバッファ層１４が直接設けられ、このバッファ層の表面が光散乱面を構成するのが好ましい。発光素子又は光電素子の場合、バッファ層１４は、半導体機能層と接触して所望の仕事関数を与えるものであれば特に限定されない。本発明におけるバッファ層は、光散乱効果を十分に確保するため、透明又は半透明であるのが好ましい。

[0037] バッファ層１４は、導電性非晶質炭素膜、導電性酸化物膜、マグネシウム系合金膜、及びフッ化物膜から選択される少なくとも一種であるのが好ましく、電子デバイスのアノード又はカソードといった適用用途及び要求される特性に応じて適宜選択すればよい。

[0038] 本発明による電解銅箔又は電極箔は、各種電子デバイス用の電極（すなわちアノード又はカソード）として好ましく用いることができる。本発明の電極箔は、概して低応力で屈曲が容易なことからフレキシブル電子デバイス用の電極として用いるのが特に好ましいが、フレキシブル性に劣る又は剛性のある電子デバイスに用いるものであってもよい。そのような電子デバイス（主としてフレキシブル電子デバイス）の例としては、（ｉ）発光素子、例えば有機ＥＬ素子、有機ＥＬ照明、有機ＥＬディスプレイ、電子ペーパー、液晶ディスプレイ、無機ＥＬ素子、無機ＥＬディスプレイ、ＬＥＤ照明、ＬＥＤディスプレイ、（ｉｉ）光電素子、例えば薄膜太陽電池が挙げられるが、好ましくは有機ＥＬ素子、有機ＥＬ照明、有機ＥＬディスプレイ、有機太陽電池、色素増感太陽電池であり、より好ましくは極薄で高輝度の発光が得られる点で有機ＥＬ照明である。また、有機太陽電池の場合、電極材料に求められる特性の多くが有機ＥＬ素子の場合に求められる特性と共通するため、本発明による電極箔は有機太陽電池のアノード又はカソードとして好ましく用いることができる。すなわち、本発明による電極箔上に積層させる有機半導体機能層の種類を公知の技術に従い適宜選択することにより、有機デバイスを有機ＥＬ素子及び有機太陽電池のいずれにも構成することが可能となる。

[0039] 本発明の電解銅箔又は電極箔はその両面を超平坦にしてもよく、その場合には電極箔の両側に電子デバイスを設けるのに有利となり、これにより電子デバイスを両面に備えた両面機能素子又は両面機能素子箔を提供することができる。また、同一電極の一方の面に発光素子を、他方の面に発電素子を形成することも可能となり、それによって有機ＥＬ素子の機能と有機太陽電池の機能を併せ持った従来に無い複合電子デバイスを作製することもできる。さらに、本発明による電極箔は、有機ＥＬ素子の電極のみならず、ＬＥＤの実装基板にも使用することができる。特に、本発明による電極箔は、ＬＥＤ素子を密に実装することができる点でＬＥＤ照明用のアノード又はカソードとして好ましく用いることができる。

[0040] 電子デバイス

本発明による電解銅箔又はそれを用いた電極箔を用いることで、半導体特性を有する半導体機能層を電極箔の光散乱面上に備えた電子デバイスを提供することができる。半導体機能層は光散乱面に直接形成されるのが好ましい。半導体機能層は、電極上又は電極間で所望の機能を発現しうる半導体特性を有する層であればいかなる構成や材質のものであってもよいが、有機半導体、無機半導体又はそれらの混合物又は組合せを含むものであるのが好ましい。例えば、半導体機能層は、励起発光又は光励起発電の機能を有し、それにより電子デバイスが発光素子又は光電素子として機能するのが好ましい。また、発光素子や光電素子にあっては、半導体機能層上に透明又は半透明の対

向電極が設けられるのが好ましい。本発明の電極箔は、半導体機能層の形成に際して、高分子材料や低分子材料をクロロベンゼン等の溶剤に溶解させて塗布するプロセスが好ましく適用可能であり、また、インライン式の真空プロセスも適用可能であり、生産性の向上に適する。前述したとおり、半導体機能層は電極箔の両面に設けられてもよい。

[0041] （1）有機ＥＬ素子及び有機ＥＬ照明

本発明による電極箔を反射電極として用いて、その光散乱面にトップエミッション型有機ＥＬ素子を備えた発光素子及び有機ＥＬ照明を構築することができる。

[0042] 図3に、本発明の電極箔をアノードとして用いたトップエミッション型有機ＥＬ素子の層構成の一例を示す。図3に示される有機ＥＬ素子は、電解銅箔２２、反射層２３及び所望によりバッファ層２４を備えたアノードとしての電極箔２０と、バッファ層２４の表面に直接設けられる有機ＥＬ層２６と、有機ＥＬ層２６の表面に直接設けられる透光電極としてのカソード２８とを備えてなる。バッファ層２４は、アノードとして適するように導電性非晶質炭素膜又は導電性酸化物膜で構成されるのが好ましい。

[0043] 有機ＥＬ層２６としては、有機ＥＬ素子に使用される公知の種々のＥＬ層構成が使用可能であり、所望により正孔注入層及び／又は正孔輸送層、発光層、ならびに所望により電子輸送層及び／又は電子注入層を、アノード電極箔２０からカソード２８に向かって順次備えてなることができる。正孔注入層、正孔輸送層、発光層、電子輸送層、及び電子注入層としては、それぞれ公知の種々の構成ないし組成の層が適宜使用可能であり特に限定されるものではない。

[0044] 図4に、図3に示される有機ＥＬ素子が組み込まれたトップエミッション型有機ＥＬ照明の層構成の一例が示される。図4に示される有機ＥＬ照明において、有機ＥＬ素子はアノード電極箔２０の電解銅箔２２を介して電源３０に電気的に接続可能とされる。バッファ層２４表面の、有機ＥＬ層２６と非接触の領域は層間絶縁膜２９で被覆される。層間絶縁膜２９としては、ＣＶＤ成膜したＳｉ系絶縁膜が、有機層を劣化させる原因となる水分及び酸素に対するバリア性が高いことから好ましく、より好ましくはＳｉＮ系絶縁膜である。さらに好ましい層間絶縁膜は、膜の内部応力が小さく、屈曲性に優れる点で、ＳｉＮＯ系絶縁膜である。

[0045] カソード２８の上方には有機ＥＬ素子と対向して封止材３２が設けられ、封止材３２とカソード２８との間には封止用樹脂が充填されて封止膜３４が形成される。封止材３２としては、ガラスやフィルムを用いることができる。ガラスの場合は、封止膜３４上に疎水性粘着テープを用いて直接接着することができる。フィルムの場合は、両面及び端面をＳｉ系絶縁膜で被覆して用いることが可能である。将来的にバリア性の高いフィルムが開発された場合には、被覆処理を行うことなく封止することが可能となり、量産性に優れたものになることが予想される。封止材３２としては、フレキシブル性を付与する観点からはフィルムの方が望ましいが、厚さ２０～１００μｍの非常に薄いガラスにフィルムを接着させた封止材を使用して所望の性能を得ることも可能である。

[0046] カソード２８としてはトップエミッション型有機ＥＬ素子に使用される公知の種々のカソードが使用可能であり、光を透過する必要があるため透明又は半透明のものであれば特に限定されないが、仕事関数の低いものが好ましい。好ましいカソードとしては、導電性酸化物膜、マグネシウム系合金膜及びフッ化物膜が挙げられ、これらを２層以上に組み合わせるのがより好ましい。これらの膜は、電極箔のバッファ層で述べたものと同様のものが使用可能である。

[0047] 特に好ましいカソードは、導電性酸化物膜からなるカソード層としての透明酸化物層に、マグネシウム系合金膜及び／又はフッ化物膜からなるバッファ層としての半透過金属層を積層させた２層構造であり、抵抗の観点からも実用性が高い。この場合、カソード２８の半透過金属層（バッファ層）側を有機ＥＬ層２６と接触させて用いることにより、高い光透過性と低い仕事関数がもたらされ、有機ＥＬ素子の輝度及び電力効率を向上することができる。最も好ましい例としては、ＩＺＯ（インジウム亜鉛酸化物）からなる透明酸化物層（カソード層）とＭｇ－Ａｇからなる半透過金属層（バッファ層）が積層されてなるカソード構造体が挙げられる。また、カソード構造体は、２層以上の透明酸化物層及び／又は２層以上の半透過金属層を備えるものであってもよい。こうして、有機ＥＬ層２６で発生した光はカソード２８及び封止膜３４及び封止材３２を通過して外部に放出される。

[0048] なお、電極箔２０の裏面には、使用形態に応じて補助的な基材を適宜設置してもよい。この部分は、発光特性に影響を与えないため、材料選択の自由度は高い。例えば、ポリエチレンテレフタレート（ＰＥＴ）、ポリイミド（ＰＩ）、ポリカーボネート（ＰＣ）、ポリエーテルサルフォン（ＰＥＳ）、ポリエーテルニトリル（ＰＥＮ）等の樹脂フィルムを使用すればフレキシブル性を損なうことが無いので最適といえる。

[0049] 図5に、本発明の電極箔をカソードとして用いたトップエミッション型有機ＥＬ素子の層構成の一例を示す。図5に示される有機ＥＬ素子は、電解銅箔４２、反射層４３及びバッファ層４４を備えたカソード電極箔４０と、

バッファ層４４の表面に直接設けられる有機ＥＬ層４６と、有機ＥＬ層４６の表面に直接設けられる対向電極としてのアノード４８とを備えてなる。有機ＥＬ層４６は、図３に示される有機ＥＬ層２６と同様に構成可能であり、バッファ層４４は、図３に示されるカソード２８と同様に構成可能であり、導電性酸化物膜、マグネシウム系合金膜、フッ化物膜、又はそれらの２層以上の組み合わせで構成されるのが好ましい。より好ましいバッファ層４４は、マグネシウム系合金膜及び／又はフッ化物膜からなる半透過金属層である。

[0050] すなわち、図５に示される力ソード電極箔４０を用いた有機ＥＬ素子は、図３に示されるアノード電極箔２０を用いた有機ＥＬ素子において、バッファ層２４と力ソード２８を入れ替え、かつ、有機ＥＬ層２６内部のアノード側から力ソード側への積層順等を逆転させた構成に相当する。例えば、力ソード電極箔４０のバッファ層４４としてマグネシウム系合金膜又はフッ化物膜をスパッタリング又は蒸着により形成する一方、アノード４８として導電性非晶質炭素、MoO_3又はV_2O_5の膜を蒸着法により形成するのが好ましい。特に、導電性非晶質炭素膜を有機ＥＬ層上に成膜する場合には、スパッタ時のプラズマダメージを避けるため真空蒸着法を用いるのが好ましい。

[0051] （２）光電素子

本発明による電極箔を反射電極として用いて、その光散乱面に光電素子を構築することができる。本発明の好ましい態様による光電素子は、電極箔と、電極箔の表面に直接設けられる半導体機能層としての光励起層と、光励起層の表面に直接設けられる対向電極としての透光電極とを備えてなる。光励起層としては、光電素子の半導体機能層として知られる種々の構成及び材料が使用可能である。

[0052] 例えば、図３に示される有機ＥＬ層２６を公知の有機太陽電池活性層で置き換えることにより、有機太陽電池を構成することができる。本発明の電極箔をアノードとして用いる有機太陽電池の場合、バッファ層（例えば力ーボンバッファ層）上に、正孔輸送層（ＰＥＤＯＴ：ＰＳＳ（３０ｎｍ））、ｐ型有機半導体機能層（例えばＢＰ（ベンゾポルフィリン））、ｎ型有機半導体とｐ型有機半導体のｉ型ミキシング層（例えばＢＰ：ＰＣＢＮＢ（フラーレン誘導体））、ｎ型有機半導体機能層（例えばＰＣＢＭ（フラーレン誘導体））、低い仕事関数を有するバッファ層（例えばＭｇ－Ａｇ）及び透明電極層（例えばＩＺＯ）を順次積層させて太陽電池を構成することが可能である。また、別の例としては、電解銅箔（例えば銅箔）が反射層（例えばアルミニウム膜）及びｎ型半導体バッファ層（例えばＺｎＯ、SnO_2、TiO_2、ＮｂＯ、In_2O_3、Ga_2O_3、及びこれらの組合せ等のｎ型酸化物半導体）を備え、このｎ型半導体バッファ層上に、ｐ型有機半導体とｎ型有機半導体のブレンド層（例えばＰ３ＨＴ：ＰＣＢＭ）、正孔輸送層（例えばＰＥＤＯＴ：ＰＳＳ）、並びに電極を順次積層させて太陽電池を構成してもよい。これらの各層を構成する材料としては公知の材料を適宜使用することができ、特に限定されない。有機太陽電池に使用される電極は、有機ＥＬ素子に使用される電極と同じ材料及び構造を有するものであってよい。本発明の電極箔は反射層を備えることで、キャビティー効果に起因する光の閉じ込めによる発電効率の向上が期待される。

[0053] このように光励起層は公知の複数の機能層を有して構成されるが、その積層は電極箔から対向電極に向かって各相を順に積層させることによって行ってもよいし、あるいは、電極箔側の第一の積層部分と対向電極側の第二の積層部分とを別個に作製した後、第一及び第二の積層部分を互いに貼り合わせて所望の光励起層を備えた光電素子を得てもよい。

[0054] 本発明を以下の例によってさらに具体的に説明する。

[0055] 例Ａ１：各種表面処理銅箔の作製及び評価

（１）試料の作製及び評価

種々の加熱後耐力及びＰｖ／Ｐｐ比を有する電極箔試料Ａ１～Ａ３の作製を行った。その際、各試料の表面性状の測定方法は以下のとおりとした。

[0056] （算術平均粗さＲａ）

走査型プローブ顕微鏡（Ｖｅｅｃｏ社製、Ｎａｎｏ　Ｓｃｏｐｅ　Ⅴ）を用いてＪＩＳ　Ｂ　０６０１－２００１に準拠して各試料表面の算術平均粗さＲａを測定した。この測定は、１０μｍ平方の範囲について、Ｔａｐｐｉｎｇ　Ｍｏｄｅ　ＡＦＭにて行った。

[0057] （Ｐｖ／Ｐｐ比）

非接触表面形状測定機（ＮｅｗＶｉｅｗ５０３２、Ｚｙｇｏ社製）を用いてＪＩＳ　Ｂ　０６０１－２００１に準拠して、１８１μｍ×１３６μｍの矩形領域に対して、断面曲線の最大山高さＰｐに対する断面曲線の最大谷深さＰｖを測定し、Ｐｖ／Ｐｐ比を算出した。その際の測定条件及びフィルタリング条件は以下とした。

・レンズ：５０×

・ＩｍａｇｅＺｏｏｍ：０．８Ｘ

・測定エリア：１８１×１３６μｍ

・Ｆｉｌｔｅｒ　Ｈｉｇｈ：Ａｕｔｏ

・Ｆｉｌｔｅｒ　Ｌｏｗ：Ｆｉｘｅｄ（１５０μｍ）

[0058]　〈０．２％耐力〉

ロール状電解銅箔から１２．５ｍｍ×９０ｍｍのサイズの矩形状試験片を、その長辺及び短辺がロール状電解銅箔の長尺方向（ＭＤ方向）及び短尺方向（ＴＤ方向）とそれぞれ一致するように採取した。得られた矩形状試験片を用いて、引張試験機（インストロン社製、１１２２型）に長尺方向（ＭＤ方向）に引っ張られるようにセットして、ＪＩＳ　Ｚ　２２４１（２０１１）に準拠して０．２％耐力を測定した。このとき、引張試験機に固定するための片側２０ｍｍのつかみ部を試験片の両端に確保することで、実質的な測定箇所の長さを５０ｍｍとした。

[0059]　〈試料Ａ１－加熱後低耐力箔（比較）〉

本発明の比較態様としての加熱後低耐力箔を次のようにして作製した。まず、硫酸濃度を１４０ｇ／Ｌ及び銅濃度８０ｇ／Ｌの硫酸系硫酸銅水溶液を調製した。この硫酸銅水溶液を用いて、３－メルカプト－１－プロパンスルホン酸ナトリウム２０ｐｐｍ、膠１０ｐｐｍ及び塩素３０ｐｐｍを含む電解液を調製した。この電解液の液温を６０℃とし、電解電流密度４０Ａ／ｄｍ^{2}で電解し、厚さ３５μｍ、幅３００ｍｍ及び長さ１００ｍの電解銅箔を作製した。この電解銅箔の作製は、ドラム形状をしたチタン製の陰極と、その回転陰極の形状に沿って対向して配置される陽極電極との間に、上記硫酸系電解液を液ポンプで循環させながら電解電流を印加させることで、チタン製の回転ドラムに銅を析出させ、所定の厚さに達した銅箔を引き剥がして連続的に巻き取ることにより行った。この電解銅箔のメッキ面のＲａは８２ｎｍであった。そして常態での０．２％耐力を測定したところ、３９６Ｎ／ｍｍ^{2}であった。次に、この銅箔の表面を、エムエーティー社製研磨機を用いたＣＭＰ処理に付した。このＣＭＰ処理は、ＸＹ溝付き研磨パット及びコロイダルシリカ系研磨液を用いて、パッド回転数：５０ｒｐｍ、荷重：１７０ｇｆ／ｃｍ^2、液供給量：３０ｃｃ／ｍｉｎの条件で６０秒間行った。こうして銅箔表面を超平坦面とした。ＣＭＰ処理後の試料Ａ１のＰｖ／Ｐｐ比は１．５、Ｒａは３．１ｎｍであった。試料Ａ１を２００℃で６０分間、窒素雰囲気中で焼成した後の０．２％耐力を３回にわたって測定したところ、２３３、２２０及び２０４Ｎ／ｃｍ^{2}であった。また、ロール・トゥ・ロール・プロセスで行われたＣＭＰ処理工程から搬出された電解銅箔を観察したところ、図６に示されるように箔中央部分にアンジュレーションが発生し、図７に示されるように箔の端部にフレアが発生していた。

[0060]　〈試料Ａ２－加熱後高耐力箔〉

本発明の加熱後高耐力箔を次のようにして作製した。まず、硫酸濃度１４０ｇ／Ｌ及び銅濃度８０ｇ／Ｌの硫酸系硫酸銅水溶液を調製した。この硫酸銅水溶液を用いて、３－メルカプト－１－プロパンスルホン酸ナトリウム２０ｐｐｍ、ジアリルジメチルアンモニウムクロライド１５ｐｐｍ及び塩素３０ｐｐｍを含む電解液を調製した。この電解液の液温を６０℃とし、電解電流密度６０Ａ／ｄｍ^{2}で電解し、厚さ３５μｍ、幅３００ｍｍ及び長さ１００ｍの電解銅箔を試料Ａ１と同様の手順で作製した。この電解銅箔のメッキ面のＲａは４４ｎｍであった。そして常態での０．２％耐力を測定したところ、３４７Ｎ／ｍｍ^{2}であった。次に、この銅箔の表面を、エムエーティー社製研磨機を用いたＣＭＰ処理に付した。このＣＭＰ処理は、ＸＹ溝付き研磨パット及びコロイダルシリカ系研磨液を用いて、パッド回転数：８０ｒｐｍ、荷重：１７０ｇｆ／ｃｍ^2、液供給量：３０ｃｃ／ｍｉｎの条件で６０秒間行った。こうして銅箔表面を超平坦面とした。ＣＭＰ処理後のサンプルのＰｖ／Ｐｐ比は１．３、Ｒａは２．４ｎｍ、２００℃で６０分間、窒素雰囲気中で焼成した後の０．２％耐力を３回にわたって測定したところ、３０１、２８９及び２６１Ｎ／ｃｍ^{2}であり、試料Ａ１よりも加熱後０．２％耐力が高い箔が得られた。また、ロール・トゥ・ロール・プロセスで行われたＣＭＰ処理工程から搬出された電解銅箔を観察したところ、図８及び９に示されるとおり、アンジュレーション及びフレアはいずれも発生しなかった。

[0061]　〈試料Ａ３－加熱後高耐力箔〉

硫酸濃度を１４０ｇ／Ｌ及び銅濃度８０ｇ／Ｌの硫酸系硫酸銅水溶液を用いて調製した、ビス（３－スルホプロピル）ジスルフィド６０ｐｐｍ、ジアリルジメチルアンモニウムクロライド９０ｐｐｍ、２－メルカプト－５－ベ

ンズイミダゾールスルホン酸３０ｐｐｍ及び塩素４５ｐｐｍを含む電解液を使用したこと以外は試料Ａ２と同様にして電解銅箔を作製した。２００℃で６０分間、窒素雰囲気中で焼成した後の０．２%耐力は９３８Ｎ／ｍｍ^{2}であった。この電解銅箔でも試料Ａ２と同様の効果が得られることを確認した。すなわち、ロール・トゥ・ロール・プロセスで行われたＣＭＰ処理工程から搬出された電解銅箔を観察したところ、アンジュレーション及びフレアはいずれも発生しなかった。

[0062] 例Ｂ

以下に示す例Ｂ１～Ｂ４は、表面及び／又は裏面を処理した電解銅箔について評価を行った参考例である。なお、以下の例において、参考例と称しているのは、０．２%耐力の評価を行っていないためである。

[0063] 例Ｂ１：両面処理銅箔の作製及び評価

本発明の両面処理銅箔の作製を以下のとおり行った。まず、厚さ３５μｍの市販の電解銅箔（三井金属鉱業社製ＤＦＦ（Ｄｕａｌ　Ｆｌａｔ　Ｆｏｉｌ）を用意した。なお、以下の説明において、この電解銅箔のめっき面（Ｒａ：５７ｎｍ）を「表面」と称し、ドラム面（Ｒａ：１６４ｎｍ）を「裏面」と称する。この銅箔の表面を、エムエーティー社製研磨機を用いたＣＭＰ処理に付した。このＣＭＰ処理は、ＸＹ溝付き研磨パット及びコロイダルシリカ系研磨液を用いて、パッド回転数：５０ｒｐｍ、荷重：１７０ｇｆ／ｃｍ^2、液供給量：３０ｃｃ／ｍｉｎの条件で１８０秒間行った。こうして銅箔表面を超平坦面とした。

[0064] 一方、銅箔の裏面に対しても、エムエーティー社製研磨機を用いて、ＸＹ溝付き研磨パット及びコロイダルシリカ系研磨液を用いて、パッド回転数：１００ｒｐｍ、荷重：１００ｇｆ／ｃｍ^2、液供給量：５０ｃｃ／ｍｉｎの条件で１８０秒間の条件でＣＭＰ処理を行った。次いで、銅箔を１質量%の過酸化水素水に浸漬させ、その後超純水にて洗浄して、銅箔裏面を凹部優位面とした。こうして得られた本発明の両面処理銅箔に対して以下の評価１～３を行った。

[0065] 評価１：Ｒａ及びＰｖ／Ｐｐ比の測定

得られた両面処理銅箔の両面について、非接触表面形状測定機（ＮｅｗＶｉｅｗ５０３２、Ｚｙｇｏ社製）を用いてＪＩＳ　Ｂ　０６０１－２００１に準拠して、１８１μｍ×１３６μｍの矩形領域に対して、断面曲線の最大山高さＰｐに対する断面曲線の最大谷深さＰｖを測定し、Ｐｖ／Ｐｐ比を算出した。同時に、ＪＩＳ　Ｂ　０６０１－２００１に準拠して算術平均粗さＲａをも測定した。具体的な測定条件及びフィルタリング条件は以下のとおりとした。

・レンズ：５０×

・ＩｍａｇｅＺｏｏｍ：０．８Ｘ

・測定エリア：１８１×１３６μｍ

・Ｆｉｌｔｅｒ　Ｈｉｇｈ：Ａｕｔｏ

・Ｆｉｌｔｅｒ　Ｌｏｗ：Ｆｉｘｅｄ（１５０μｍ）

[0066] その結果、両面処理銅箔の表面（超平坦面）のＲａは１．６９８ｎｍ、Ｐｖ／Ｐｐ比は０．７１２７である一方、その裏面（凹部優位面）のＲａは１１．４０７ｎｍ、Ｐｖ／Ｐｐ比は５．４０５３であった。非接触表面形状測定機で得られた表面の三次元プロファイルは図１０に示されるとおりであり、裏面の三次元プロファイルは図１１に示されるとおりであった。

[0067] 評価２：耐酸化性の評価

両面処理銅箔をロール状態で大気中に２週間放置した。両面処理銅箔をロールから引き出し、その表面を観察したところ、図１２に示されるとおりメタリックな光沢を有する外観を有していた。２週間放置後の銅箔表面の酸化状態の分析を、Ｃｕ－ＫＬＬオージェ電子スペクトルを測定することにより行った。この測定は、Ｘ線光電子分光装置（ＸＰＳ）（Ｑｕａｎｔｕｍ２０００、アルバック・ファイ（株）製）を用いて以下の条件で行った。

・Ｘ線源：Ａｌ線

・出力４０Ｗ

・測定ビーム径２００ｕｍΦ

・測定エリア：３００×９００ｕｍ（上記ビームをこの範囲でラスター）

・サーベイ測定（定性用）：測定範囲０～１４００ｅＶ、パスエネルギー５８．７ｅＶ、ステップ１．０ｅＶ、積算時間２０分

・ナロー測定（状態用）：

・Ｃｕ２ｐの場合：測定範囲９２５～９７５ｅＶ、パスエネルギー２３．５ｅＶ、ステップ０．１ｅＶ、積算回数３回

・ＣｕＬＬの場合：測定範囲５６０～５８０ｅＶ、パスエネルギー２３．５ｅＶ、ステップ０．１ｅＶ、積算回数３回

[0068] 得られた結果は図１３に示されるとおりであり、本発明の両面処理銅箔はロール状態で２週間大気放置しても、０価のＣｕ（すなわち金属Ｃｕ）に起因するピークが観察された。このように、両面処理銅箔においては酸化の進行が抑制されることが確認された。

[0069] また、両面処理銅箔の作製後２日、４日及び７日経過後におけるＣｕ－ＫＬＬオージェ電子スペクトルを上記同様にして測定したところ、図１４に示される結果が得られ、いずれの日数においても０価のＣｕ（すなわち金属Ｃｕ）に起因するピークが明確に観察された。図１４に示されるピーク高さに基づいて１価Ｃｕに対する０価Ｃｕの比率を算出したところ下記の表１に示されるとおり、いずれの放置時間においても０価のＣｕである金属Ｃｕ成分の割合が高く、本発明の両面処理銅箔は耐酸化性に優れることが分かる。

表　１

作製後の放置時間	０価	１価	０価／１価
２日	8081	6267	1．29
４日	6962	6035	1．15
７日	8453	7438	1．14

[0070] 評価３：巻き傷の有無の評価

ロールから引き出した両面処理銅箔の表面における巻き傷の有無を確認すべくレーザー顕微鏡（オリンパス社製、ＯＬＳ３０００）にて観察をおこなったところ、図１５に示される写真が得られた。同図において右下に存在するスケールバーの長さは２００μｍである。図１５から明らかなように、本発明の両面処理銅箔の表面には目立った巻き傷は見られなかった。

[0071] 例Ｂ２：両面処理銅箔の作製及び評価

銅箔裏面に対するＣＭＰ処理時間を６０秒にしたこと以外は、例Ｂ１と同様にして両面処理銅箔の作製及び評価を行った。その結果、得られた両面処理銅箔の表面（超平坦面）のＲａは１．６９８ｎｍ、Ｐｖ／Ｐｐ比は０．７１２７である一方、その裏面（凹部優位面）のＲａは５６．０７２ｎｍ、Ｐｖ／Ｐｐ比は２．３８５２であった。また、非接触表面形状測定機で得られた表面の三次元プロファイルは図１０と同様であり、裏面の三次元プロファイルは図１６に示される通りであった。ロール状態で２週間大気放置された両面処理銅箔の表面を観察したところ、例Ｂ１に関する図１２と同様の外観を有していた。

[0072] 例Ｂ３：片面処理銅箔の作製及び評価

銅箔裏面に対して何ら処理を行わなかったこと以外は例Ｂ１及びＢ２と同様にして、片面処理銅箔の作製及び評価を行った。得られた片面処理銅箔の表面（超平坦面）のＲａは１．３１３ｎｍ、Ｐｖ／Ｐｐ比は１．３０６９である一方、その裏面のＲａは１６４．３８７ｎｍ、Ｐｖ／Ｐｐ比は１．０７１１であった。また、非接触表面形状測定機で得られた表面の三次元プロファイルは図１７に示されるとおりである一方、裏面の三次元プロファイルは図１８に示される通りであった。ロール状態で２週間大気放置された片面処理銅箔の表面を観察したところ、図１９に示されるとおりであり、酸化に起因する褐色の度合いが薄く、酸化抑制効果が確認された。ロールから引き出した片面処理銅箔の表面における巻き傷の有無を確認すべくレーザー顕微鏡（オリンパス社製、ＯＬＳ３０００）にて観察を行ったところ、図２０に示される写真が得られた。同図において右下に存在するスケールバーの長

さは２００μｍである。図２０から明らかなように、本発明の片面処理銅箔の表面には巻き傷が散見された。

[0073] 例Ｂ４（比較）：両面未処理銅箔の作製及び評価

銅箔両面に対して何ら表面処理を行わなかったこと以外は例Ｂ１～Ｂ３と同様にして、両面未処理銅箔の作製及び評価を行った。得られた両面未処理銅箔の表面のＲａは５７．２１３ｎｍ、Ｐｖ／Ｐｐ比は０．９８５６である一方、その裏面のＲａは１６４．３８７ｎｍ、Ｐｖ／Ｐｐ比は１．０７１１であった。また、非接触表面形状測定機で得られた表面の三次元プロファイルは図２１に示されるとおりである一方、裏面の三次元プロファイルは例Ｂ３に関する図１８と同様であった。ロール状態で２週間大気放置された両面未処理銅箔の表面を観察したところ、図２２に示されるとおりであり、酸化に起因する褐色系の変色が例Ｂ３の片面未処理銅箔よりも顕著であった。従って、両面未処理銅箔はロール状態でも極めて酸化し易いことが分かる。Ｃｕ－ＫＬＬオージェ電子スペクトルの結果は図１３に示されるとおりであり、両面未処理銅箔はロール状態で２週間大気放置後、０価のＣｕ（すなわち金属Ｃｕ）に起因するピークが観察されなかった。このように、両面未処理銅箔は酸化しやすいことが確認された。

[0074] また、両面未処理銅箔を希硫酸で処理して酸化膜の除去を試みたが、２価のＣｕに相当するＣｕＯの高抵抗膜は除去できたものの、酸洗後２日目にして既に１価のＣｕに相当するＣｕ$_2$Ｏの酸化膜で箔表面が覆われてしまうことが分かった。ロール状態で２週間大気放置した後に酸洗処理を行った両面未処理銅箔のＣｕ－ＫＬＬオージェ電子スペクトルが図１３に示されるが、同図から明らかなように酸洗処理によって酸化膜の除去を試みたとしても箔表面には１価のＣｕ（すなわちＣｕ$_2$Ｏ）の酸化膜で覆われていることが分かる。この結果から、本発明の両面処理銅箔により実現される耐酸化性表面は単なる酸洗処理では実現できないことが分かる。

[0075] 例Ｃ

以下に示す例Ｃ１～Ｃ４は、Ｐｖ／Ｐｐ比が２．０以上であることの優位性を実証するための参考例である。なお、以下の例において、参考例と称しているのは、０．２%耐力の評価を行っていないためである。

[0076] 例Ｃ１：各種Ｐｖ／Ｐｐ比の電極箔における光散乱効果の測定

（１）試料の作製

各種Ｐｖ／Ｐｐ比の電極箔試料Ｃ１～Ｃ５の作製を行った。その際、各試料の表面性状の測定方法は以下のとおりとした。

[0077] （算術平均粗さＲａ）

走査型プローブ顕微鏡（Ｖｅｅｃｏ社製、Ｎａｎｏ　Ｓｃｏｐｅ　Ⅴ）を用いてＪＩＳ　Ｂ　０６０１－２００１に準拠して各試料表面の算術平均粗さＲａを測定した。この測定は、１０μｍ平方の範囲について、Ｔａｐｐｉｎｇ　Ｍｏｄｅ　ＡＦＭにて行った。

[0078] （Ｐｖ／Ｐｐ比）

非接触表面形状測定機（ＮｅｗＶｉｅｗ５０３２、Ｚｙｇｏ社製）を用いてＪＩＳ　Ｂ　０６０１－２００１に準拠して、１８１μｍ×１３６μｍの矩形領域に対して、断面曲線の最大山高さＰｐに対する断面曲線の最大谷深さＰｖを測定し、Ｐｖ／Ｐｐ比を算出した。その際の測定条件及びフィルタリング条件は以下とした。

・レンズ：５０×

・ＩｍａｇｅＺｏｏｍ：０．８Ｘ

・測定エリア：１８１×１３６μｍ

・Ｆｉｌｔｅｒ　Ｈｉｇｈ：Ａｕｔｏ

・Ｆｉｌｔｅｒ　Ｌｏｗ：Ｆｉｘｅｄ（１５０μｍ）

[0079] （試料Ｃ１－比較）

比較のための標準反射膜を備えた試料Ｃ１を得るために、算術平均粗さＲａが０．２ｎｍの石英基板の表面上に、反射層として厚さ２００ｎｍのアルミニウム膜をスパッタリング法により形成した。このスパッタリングは、純度９９．９９%のＡｌターゲットをクライオ（Ｃｒｙｏ）ポンプが接続されたマグネトロンスパッタ装置（ＭＳＬ

－４６４、トッキ株式会社製）に装着した後、投入パワー（ＤＣ）：１０００Ｗ（３．１Ｗ／cm^2）、到達真空度：＜５×10^{-6}Ｐａ、スパッタ圧力：０．５Ｐａ、Ａｒ流量：１００ｓｃｃｍ、基板温度：室温の条件で行った。こうして得られた試料Ｃ１の表面性状を測定したところ、算術平均粗さＲａは０．８ｎｍであり、Ｐｖ／Ｐｐ比は１．０２であった。

[0080] （試料Ｃ２）

Ｐｖ／Ｐｐ比が１．２以上２．０未満のＰｖ／Ｐｐ比の試料Ｃ２の作製を以下のとおり行った。まず、金属箔として、厚さ３５μｍの市販の電解銅箔（三井金属鉱業社製ＤＦＦ（Ｄｕａｌ　Ｆｌａｔ　Ｆｏｉｌ）を用意した。この銅箔表面の算術平均粗さＲａは１６．５ｎｍであった。この銅箔基板の表面を、化学研磨剤（三菱ガス化学社製、ＣＰＢ－１０）を用いて化学研磨した。この化学研磨は、化学研磨剤と水を１：２の重量割合で混合して希釈した溶液に、銅箔基板を室温で１分間浸漬させることにより行った。こうして処理された銅箔基板を純水で洗浄した後、０．１Ｎの希硫酸で洗浄を行い、純水で再度洗浄して、乾燥を行った。こうして研磨処理された表面上に、試料Ｃ１と同様の条件でアルミニウム反射層の形成を行った。得られた試料Ｃ２の表面の性状を試料Ｃ１と同様にして測定したところ、算術平均粗さＲａは１９．３ｎｍ、Ｐｖ／Ｐｐ比は１．８６であった。

[0081] （試料Ｃ３）

Ｐｖ／Ｐｐ比が２．０以上の試料Ｃ３の作製を以下のとおり行った。まず、金属箔として、厚さ３５μｍの市販の電解銅箔（三井金属鉱業社製ＤＦＦ（Ｄｕａｌ　Ｆｌａｔ　Ｆｏｉｌ）を用意した。この銅箔の表面を、エムエーティー社製研磨機を用いたＣＭＰ処理に付した。このＣＭＰ処理は、ＸＹ溝付き研磨パット及びコロイダルシリカ系研磨液を用いて、パッド回転数：３０ｒｐｍ、荷重：２００ｇｆ／cm^2、液供給量：１００ｃｃ／ｍｉｎの条件で４０秒間行った。こうしてＣＭＰ処理された銅箔表面の算術平均粗さＲａは６．２ｎｍであった。流水式超音波洗浄機（本多電子社製）を用いて、高周波出力６０Ｗで銅箔表面を２０分間処理した。こうして研磨及び表面改質された表面上に、試料Ｃ１と同様の条件でアルミニウム反射層の形成を行った。得られた試料Ｃ３の表面の性状を測定したところ、算術平均粗さＲａは１６．２ｎｍ、Ｐｖ／Ｐｐ比は２．１４であった。

[0082] （試料Ｃ４）

Ｐｖ／Ｐｐ比が２．０以上の試料Ｃ４の作製を以下のとおり行った。まず、金属箔として、厚さ３５μｍの市販の電解銅箔（三井金属鉱業社製ＤＦＦ（Ｄｕａｌ　Ｆｌａｔ　Ｆｏｉｌ）を用意した。この銅箔の表面を、エムエーティー社製研磨機を用いたＣＭＰ処理に付した。このＣＭＰ処理は、ＸＹ溝付き研磨パット及びコロイダルシリカ系研磨液を用いて、パッド回転数：３０ｒｐｍ、荷重：２００ｇｆ／cm^2、液供給量：１００ｃｃ／ｍｉｎの条件で６０秒間行った。こうしてＣＭＰ処理された銅箔表面の算術平均粗さＲａは３．１ｎｍであった。流水式超音波洗浄機（本多電子社製）を用いて、高周波出力６０Ｗで銅箔表面を１０分間処理した。こうして研磨及び表面改質された表面上に、試料Ｃ１と同様の条件でアルミニウム反射層の形成を行った。得られた試料Ｃ４の表面の性状を測定したところ、算術平均粗さＲａは６．１ｎｍ、Ｐｖ／Ｐｐ比は２．５４であった。

[0083] （試料Ｃ５）

Ｐｖ／Ｐｐ比が２．０以上の試料Ｃ５の作製を以下のとおり行った。まず、金属箔として、厚さ３５μｍの市販の電解銅箔（三井金属鉱業社製ＤＦＦ（Ｄｕａｌ　Ｆｌａｔ　Ｆｏｉｌ）を用意した。この銅箔の表面を、エムエーティー社製研磨機を用いたＣＭＰ処理に付した。このＣＭＰ処理は、ＸＹ溝付き研磨パット及びコロイダルシリカ系研磨液を用いて、パッド回転数：３０ｒｐｍ、荷重：２００ｇｆ／cm^2、液供給量：１００ｃｃ／ｍｉｎの条件で４０秒間行った。こうしてＣＭＰ処理された銅箔表面の算術平均粗さＲａは６．８ｎｍであった。流水式超音波洗浄機（本多電子社製）を用いて、高周波出力６０Ｗで銅箔表面を１０分間処理した。こうして研磨及び表面改質された表面上に、試料Ｃ１と同様の条件でアルミニウム反射層の形成を行った。得られた試料Ｃ５の表面の性状を測定したところ、算術平均粗さＲａは１３．７ｎｍ、Ｐｖ／Ｐｐ比は４．９であった。

[0084] （２）光散乱特性の測定

試料Ｃ１～Ｃ５について光散乱特性の測定を、分光光度計（日立ハイテクノロジーズ社製、Ｕ４１００）を用いて行った。この測定は、図２３に示されるように、各試料Ｓに対して所定の角度θで光を入射及び反射させて積分球７４に導くように複数のミラー７２ａ，７２ｂ，７２ｃ，７２ｄを配置させてなる光学測定系７０を用意して、測定波長域：２５０ｎｍ～８００ｎｍ（可視光域全域）、スキャン速度：３００ｎｍ／ｍｉｎの条件で行った。この測定系７０においては、試料Ｓによる光散乱が大きいほど、積分球７４に取り込まれる光量が減少する。

[0085] 光散乱効果の評価は、１０°、３０°及び６０°の各反射角について、標準反射膜としての試料Ｃ１の正絶対反

射率を１として、試料Ｃ２～５の正絶対反射率を相対的に評価することにより行った。すなわち、試料Ｃ２～５の正絶対反射率の値を測定し、これを標準反射膜（試料Ｃ１）の正絶対反射率の値で割った値を光散乱相対値として算出した。したがって、光散乱相対値が大きいほど光散乱効果が改善したことを意味する。なお、上述のとおり、各試料の反射層はいずれも同一の材質（純度９９．９９％のアルミニウム被膜）及び実質的に同一の膜厚（２００ｎｍ（±５％））として、反射膜の材質や厚さに起因する光吸収条件等が一致するようにした。また、試料のサイズは８０ｍｍ×８０ｍｍ平方とした。

[0086] 各試料について得られた光散乱相対値は以下の表２～４に示されるとおりであった。

表２：反射角10°における光散乱相対値

試料番号		試料C1（比較）	試料C2	試料C3	試料C4	試料C5
Pv/Pp 比		1.02	1.86	2.14	2.54	4.90
測定波長（nm）	700	1.00	1.03	1.08	1.14	1.14
	600	1.00	0.97	1.06	1.11	1.13
	500	1.00	1.03	1.10	1.15	1.17
	400	1.00	1.03	1.12	1.16	1.20
	380	1.00	1.04	1.14	1.16	1.24

表３：反射角30°における光散乱相対値

試料番号		試料C1（比較）	試料C2	試料C3	試料C4	試料C5
Pv/Pp 比		1.02	1.86	2.14	2.54	4.90
測定波長（nm）	700	1.00	1.00	1.07	1.14	1.13
	600	1.00	1.00	1.08	1.11	1.14
	500	1.00	1.00	1.10	1.15	1.15
	400	1.00	1.00	1.10	1.16	1.20
	380	1.00	1.00	1.11	1.16	1.24

表４：反射角60°における光散乱相対値

試料番号		試料C1（比較）	試料C2	試料C3	試料C4	試料C5
Pv/Pp 比		1.02	1.86	2.14	2.54	4.90
測定波長（nm）	700	1.00	1.00	1.02	1.09	1.11
	600	1.00	1.00	1.02	1.07	1.12
	500	1.00	1.00	1.03	1.08	1.13
	400	1.00	1.01	1.07	1.10	1.17
	380	1.00	1.01	1.08	1.10	1.18

[0089] その結果、各測定反射角及び、各測定波長領域において、Ｐｖ／Ｐｐが２．０以上の時、０．１以上の散乱効果がえられた。

[0090] 例Ｃ２：各種表面性状の電極箔の作製及び評価

例Ｃ１の試料Ｃ２～Ｃ５に示される各種の条件を適宜変更して、図２４に示される算術平均粗さＲａ及びＰｖ／Ｐｐ比を有する各種の電極箔を作製した。これらの電極箔について例Ｃ１と同様にして光散乱特性を評価したところ、図２４に示されるように、Ｐｖ／Ｐｐ比が２．０以上の試料はいずれも光散乱特性が１．２倍向上する一方、Ｐｖ／Ｐｐ比が２．０未満の試料はそのような高い光散乱性が得られなかった。また、これらの電極箔を用いて発光素子又は発電素子を作製したところ、図２４に示されるように、Ｒａが６０ｎｍ以下の場合には対向電極との短絡を回避して初期の素子特性が得られた。したがって、Ｐｖ／Ｐｐ比が２．０以上で、かつ、Ｒａが６０ｎｍ以下の表面プロファイルが好ましいことが分かる。

[0091] 図２４に矢印で特定される試料Ｃ６の光散乱面をＳＥＭ（１０００倍）で観察したところ、図２５に示されるように凹凸形状の判別が困難であった。そこで、図２４に矢印で特定される試料Ｃ６及びＣ７について表面プロファイルを非接触表面形状測定機（ＮｅｗＶｉｅｗ５０３２、Ｚｙｇｏ社製）で測定したところ、図２６～図２９に示されるプロファイル画像が得られた。図２６及び２７に示される表面プロファイルは本発明による光散乱効果の改善がみられた試料Ｃ６に関するものであり、凸部の形成が抑制され凹部が優先的に形成された望ましい表面プロファイルである。一方、図２８及び２９に示される表面プロファイルは光散乱効果の改善に乏しかった試料Ｃ７に関するものである。

[0092] 例Ｃ３：光電特性の評価

（１）光電素子の作製

図３０に示されるように、電極箔として例Ｃ２で得られた、銅箔８２上にアルミニウム反射層８３を備えた試料Ｃ６及びＣ７を用いて光電素子を作製した。まず、このアルミニウム反射層８３に、スパッタリングによってＺｎＯからなる厚さ２０ｎｍのｎ型半導体バッファ層８４を形成した。このバッファ層８４上に、プラズマＣＶＤ装置（サムコ社製、ＰＤ－２２０２Ｌ）を用いて、窒化ケイ素からなる層間絶縁膜を形成した。その際、厚さ０．１ｍｍ、幅2mm、長さ１０mmの複数枚の薄ガラスを２mm幅で電極箔上に並べることにより、受光部となるべき個所を覆った。窒化ケイ素成膜後、薄ガラスを除去した。その後、電極箔８０を、４０～５０℃に加熱したイソプロピルアルコール溶液で洗浄し、窒素ガスを用いて乾燥させた。次に、クロロベンゼン溶液中にＰ３ＨＴ（ポリ－３－ヘキシルチオフェン）とＰＣＢＭ（（６，６）－フェニル－Ｃ６１－ブチル酸メチルエステル）を各々１０ｍｇ／ｍｌ浸漬させ、２４時間で２５℃前後の環境下で放置させ、完全に溶解させた。Ｐ３ＨＴとＰＣＢＭが溶解した混合クロロベンゼン溶液を１５００ｒｐｍで電極箔８０にスピンコートし、Ｐ３ＨＴ：ＰＣＢＭ層８６ａが１００ｎｍの厚さになるように調整した。次に、ＰＥＤＯＴ：ＰＳＳ（ポリ（３，４－エチレンジオキシチオフェン／ポリ（４－スチレンスルホネート））分散溶液（１．３重量%）を５０００ｒｐｍで電極箔にスピンコートした。コーティングを１８０℃で３０分間、ホットプレート上で乾燥させて、ＰＥＤＯＴ：ＰＳＳ層８６ｂを得た。金を真空蒸着装置にて約１００ｎｍの厚さになるように成膜して対向電極８８ａを得た。その際、受光部となるべき箇所は、櫛形のメタルマスクを用いて光を遮蔽しないようにした。その後、１５０℃で３０分間、不活性雰囲気（窒素）下で焼成を行った。こうして図３０に示される光電素子を得た。

[0093] （２）光電特性の評価

得られた光電素子について、シミュレータ（三永電機製、ＸＥＳ－４０Ｓ１）、ＩＶ測定器（ＡＤＣＭＴ製、６２４１Ａ）及びソフトウェア（サンライズ社製）を用いて太陽電池発電効率を、ＡＭ（エアマス）：１．５（規準光）以下及び入射光強度：１００ｍＷ／ｃｍ^{2}の計測条件で測定した。測定結果は以下の表５及び図３１に示されるとおりであった。

表　５

	Pv／Pp比	短絡電流 Jsc(mA/cm^2)	開放電圧 Voc(V)	曲線因子 FF	変換効率 η(%)
試料C6	4.9	10.0	0.5	0.6	3.0
試料C7	1.9	8.5	0.6	0.5	2.5

[0095] 表４及び図３１に示されるように、Ｐｖ／Ｐｐ比が高い試料Ｃ６においては、Ｐｖ／Ｐｐ比が低い試料Ｃ７と比べて、曲線因子ＦＦ及び変換効率ηが有意に高いことから、発電効率が格段に優れていることが分かる。

[0096] 例Ｃ４：凹部のみ電極箔の作製及び評価

金属箔として厚さ３５μmの市販の電解銅箔（三井金属鉱業社製、３ＥＣ－ＩＩＩ）を用い、ＣＭＰ処理を２分間行ったこと以外は、試料Ｃ２と同様にして電極箔の作製を行い、試料Ｃ８とした。この試料Ｃ８の光散乱面をＳＥＭ（１０００倍）で観察したところ、図３２に示されるように実質的に凹部のみを有する表面性状が観察された。また、試料Ｃ８について表面プロファイルを非接触表面形状測定機（ＮｅｗＶｉｅｗ５０３２、Ｚｙｇｏ社製）で測定したところ、図３３及び３４に示されるプロファイル画像が得られた。これらの結果から明らかなように、試料Ｃ８の光散乱面は凸部が実質的に除去され、実質的に凹部のみが形成された極めて望ましい表面プロファイルを有していた。観察した凹部の殆どが深さ１μm以下、長手方向長さ１００μm以下のものであった。凹部の個数を、ＳＥＭ１０００倍視野（１００００μm^2）の視野においてカウントしたところ約１７０個であった。このような実質的に凹部のみが形成された電極箔にあっては、電極間の短絡をより一層確実に防止しながら、より優れた光散乱性を発揮することができ、それにより発光効率や発電効率が更に向上することが可能である。

[0097] 例Ｄ１：各種Ｒａ及びＰｖ／Ｐｐ比の電極箔の作製及び評価

例Ａ１の試料Ｄ２の作製条件を適宜変更させて、表６に示されるＲａ及びＰｖ／Ｐｐ比を表面に有する電解銅箔試料Ｄ１～Ｄ３を作製し、有機ＥＬ発光素子を作製した。発光素子としての評価を行ったところ表６に示されるとおりであった。表６に示される結果から、Ｒａが低く、かつ、Ｐｖ／Ｐｐが１．２以上であると信頼性のある発光素子を得る上で好ましいといえる。試料Ｄ１、Ｄ２及びＤ３の表面プロファイルを非接触表面形状測定機（ＮｅｗＶｉｅｗ５０３２、Ｚｙｇｏ社製）で測定したところ、図３５、３６及び３７に示されるプロファイル画像がそれぞれ得られた。

表　６

	Ra	Pv／Pp比	発光素子における評価		
			発光輝点発生の有無	発光可能性	発光素子としての総合評価
試料D1（比較）	18.3	0.99	あり	ショート発生のため発光不可	信頼性低い
試料D2	9.2	1.80	なし	発光可能	信頼性あり
試料D3	2.8	1.26	なし	より好ましく発光可能	信頼性高い

[0098]

【請求項１】
電子デバイス用電極として用いられる、銅又は銅合金からなる電解銅箔であって、

窒素雰囲気中、２００℃で６０分間の熱処理を施した後における前記電解銅箔の０．２%耐力が２５０Ｎ／mm^2以上であり、かつ、

前記電解銅箔の少なくとも一方の最表面に、ＪＩＳ　Ｂ　０６０１－２００１に準拠して１８１μm×１３６μmの矩形領域に対して測定される、断面曲線の最大山高さＰｐに対する断面曲線の最大谷深さＰｖのＰｖ／Ｐｐ比が１．２以上の凹部優位面を備えてなる、電解銅箔。

【請求項２】
前記凹部優位面のＰｖ／Ｐｐ比が１．５以上である、請求項１に記載の電解銅箔。

【請求項３】
前記凹部優位面のＰｖ／Ｐｐ比が２．０以上である、請求項１又は２に記載の電解銅箔。

【請求項４】
前記凹部優位面が、ＪＩＳ　Ｂ　０６０１－２００１に準拠して測定される、１０ｎm以下の算術平均粗さＲａを

有する、請求項１～３のいずれか一項に記載の電解銅箔。

【請求項５】
前記電解銅箔の片面が前記凹部優位面を構成し、前記電解銅箔の他方の面がＪＩＳ　Ｂ　０６０１－２００１に準拠して測定される、１０ｎｍ以下の算術平均粗さＲａを有する、請求項１～４のいずれか一項に記載の電解銅箔。

【請求項６】
前記電解銅箔の両面が前記凹部優位面を構成する、請求項１～４のいずれか一項に記載の電解銅箔。

【請求項７】
ロール・トゥ・ロール・プロセスによって製造される、請求項１～６のいずれか一項に記載の電解銅箔。

【請求項８】
前記電子デバイスがフレキシブル電子デバイスであり、該フレキシブル電子デバイスの支持基材を兼ねた電極として用いられる、請求項１～７のいずれか一項に記載の電解銅箔。

【請求項９】
前記電子デバイスが、発光素子又は光電素子である、請求項１～８のいずれか一項に記載の電解銅箔。

【請求項１０】
前記電解銅箔上に反射層及び／又はバッファ層を更に備えた、請求項１～９のいずれか一項に記載の電解銅箔。

【請求項１１】
請求項１～９のいずれか一項に記載の電解銅箔で構成される電極箔と、

前記電極箔の前記超平坦面上に設けられる、半導体特性を有する半導体機能層と、

を備えた、電子デバイス。

【請求項１２】
前記電極箔と前記半導体機能層の間に反射層及び／又はバッファ層を更に備えた、請求項１１に記載の電子デバイス。

【請求項１３】
前記半導体機能層が励起発光又は光励起発電の機能を有し、それにより前記電子デバイスが発光素子又は光電素子として機能する、請求項１１又は１２に記載の電子デバイス。

【請求項１４】
前記半導体機能層上に透明又は半透明の対向電極を備えた、請求項１１～１３のいずれか一項に記載の電子デバイス。

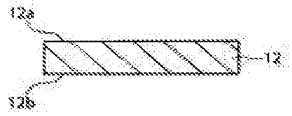
(57)【要約】
【課題】電子デバイス用電極として極めて有用な電解銅箔を提供する。
【解決手段】電子デバイス用電極として用いられる、銅又は銅合金からなる電解銅箔であって、窒素雰囲気中、２

34-18

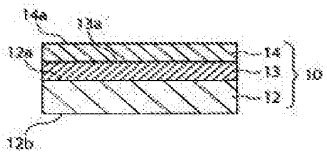
００℃で６０分間の熱処理を施した後における前記電解銅箔の０．２％耐力が２５０Ｎ／ｍｍ^{2}以上であり、かつ、電解銅箔の少なくとも一方の最表面に、ＪＩＳ　Ｂ　０６０１－２００１に準拠して１８１μｍ×１３６μｍの矩形領域に対して測定される、断面曲線の最大山高さＰｐに対する断面曲線の最大谷深さＰｖのＰｖ／Ｐｐ比が１．２以上の凹部優位面を備えてなる、電解銅箔。

【選択図】図１

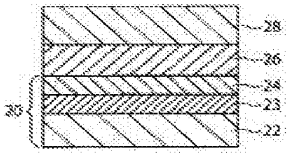
【図１】



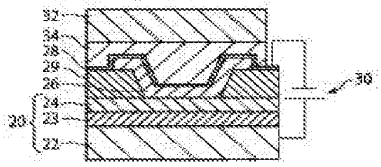
【図２】



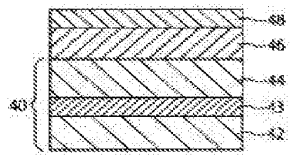
【図３】



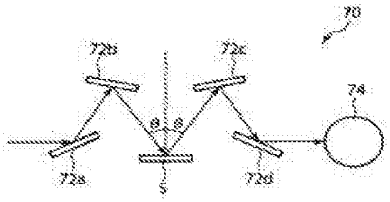
【図４】



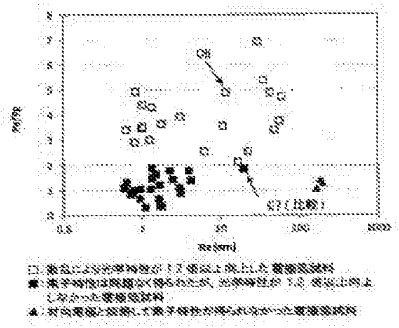
【図５】



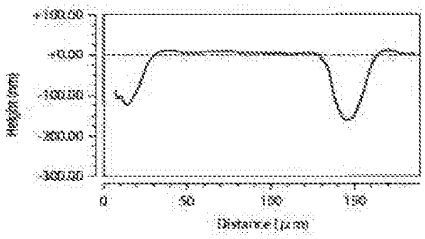
【圖 23】



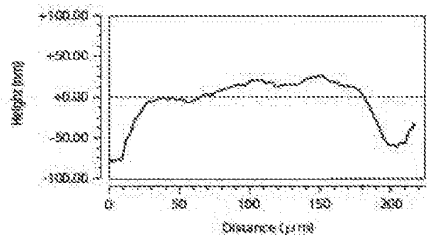
【圖 24】



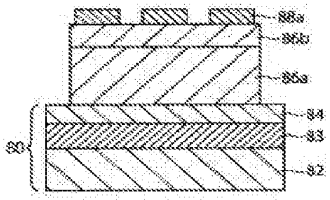
【圖 27】



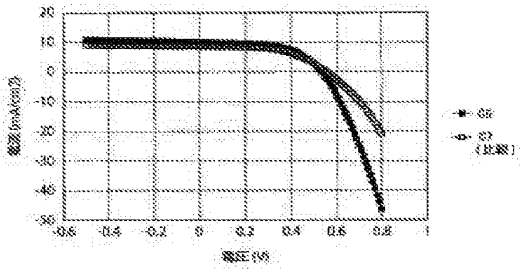
【圖 29】



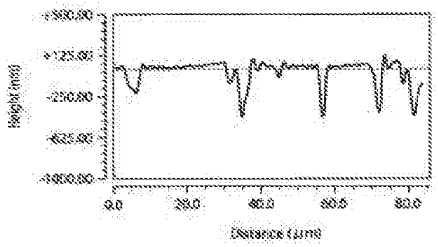
【圖 30】



【圖 31】

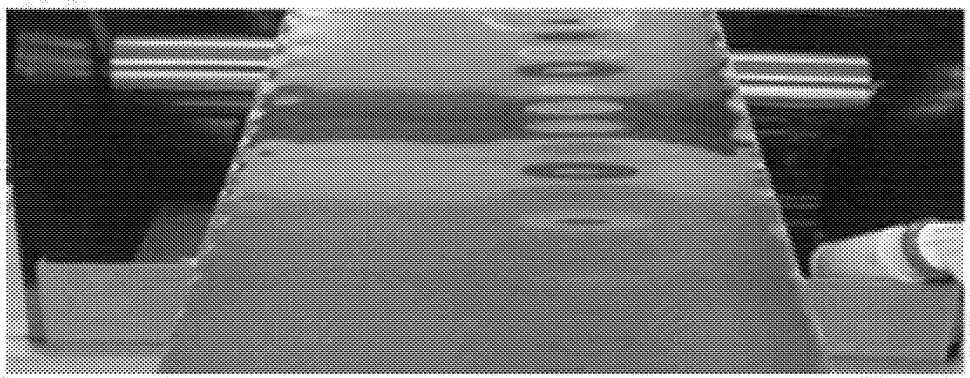


【圖 34】

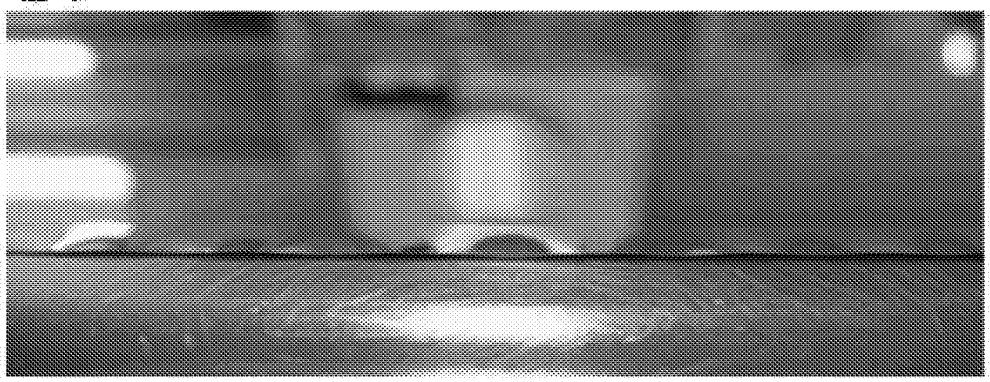


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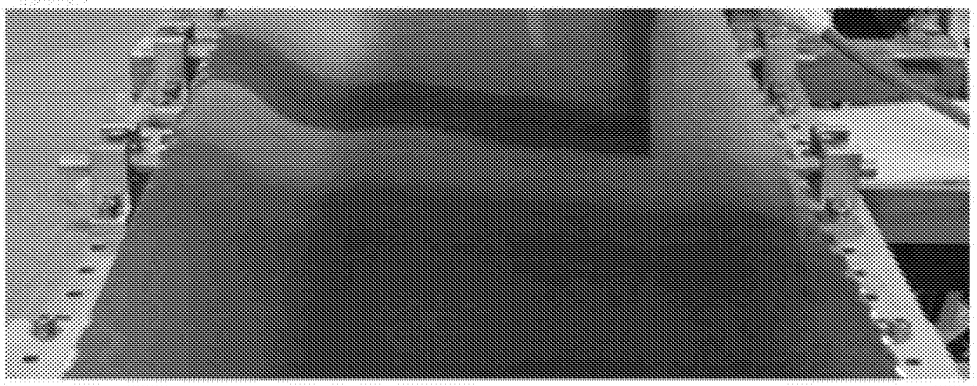
【圖 6】



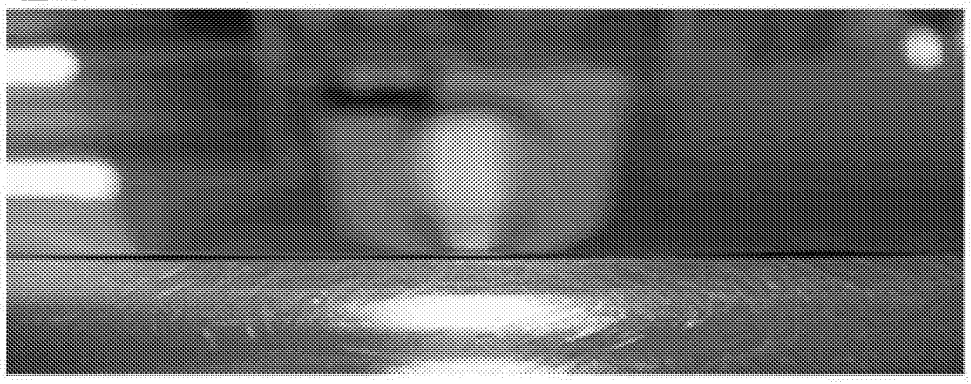
【圖 7】



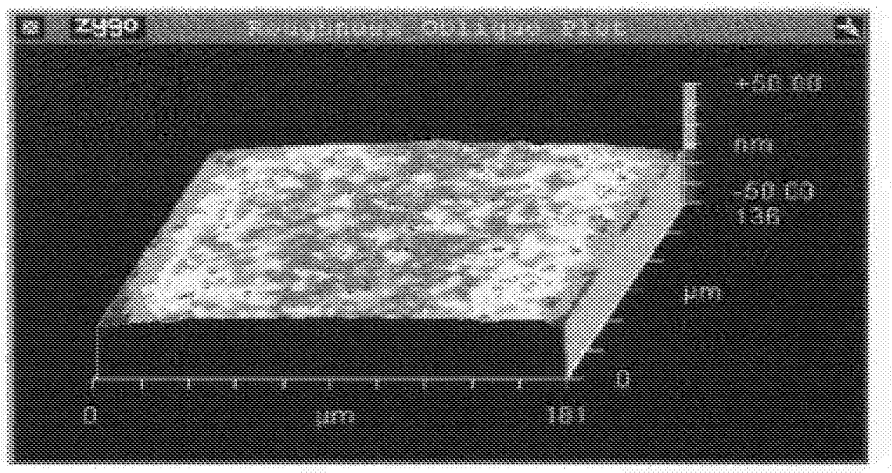
【圖 8】



【圖 9】

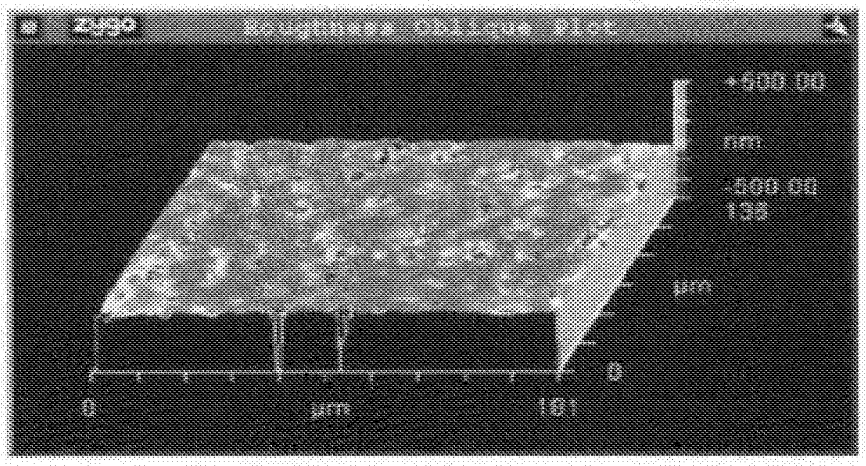


【圖 10】

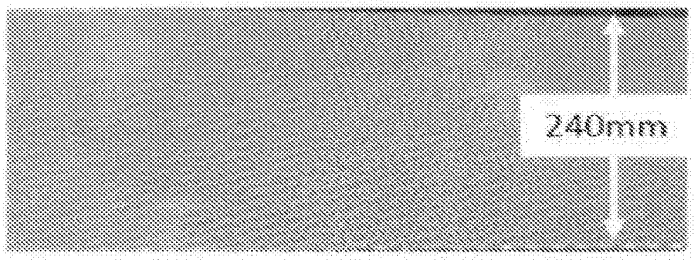


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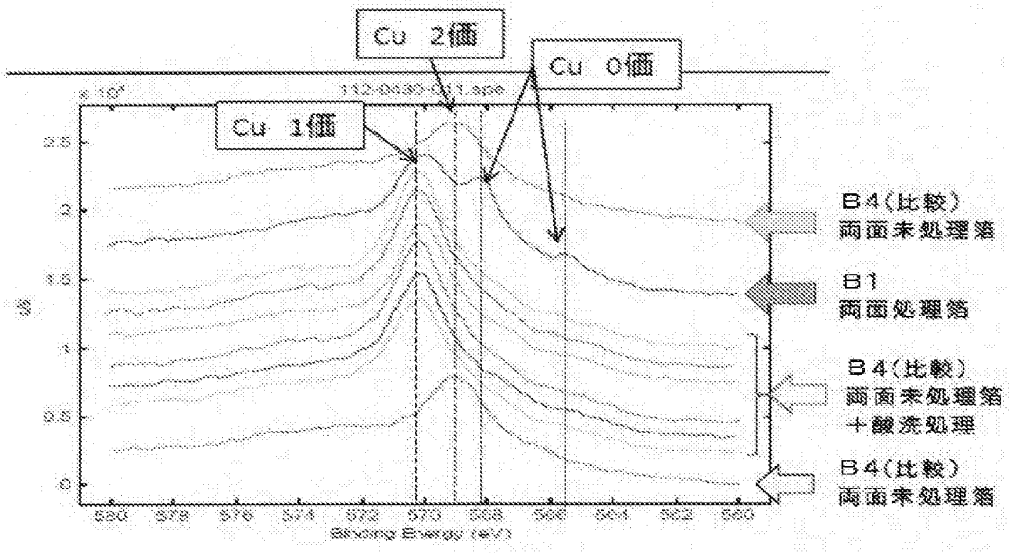
【圖 11】



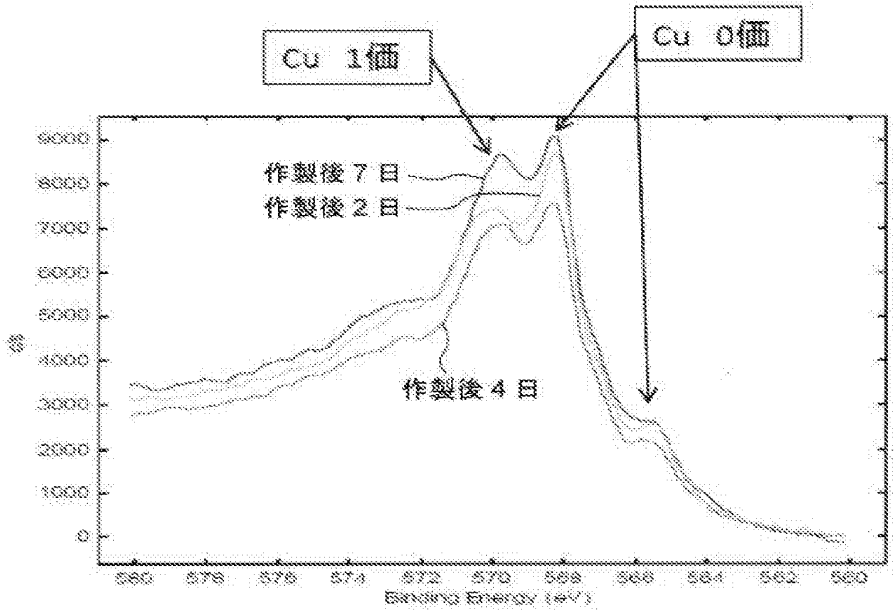
【圖 12】



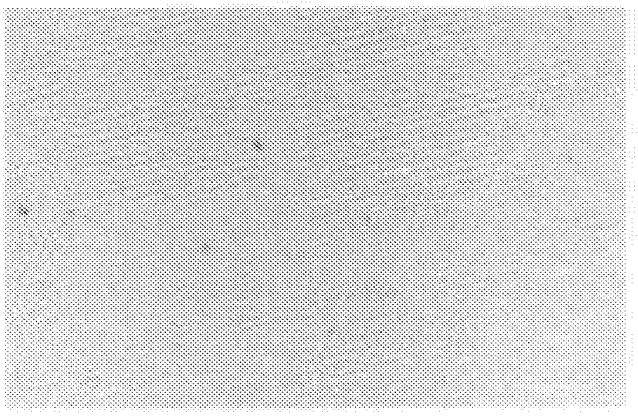
【圖 13】


Cu 2価
Cu 0価
Cu 1価
B4(比較)
両面未処理箔
B1
両面処理箔
B4(比較)
両面未処理箔
＋酸洗処理
B4(比較)
両面未処理箔
Binding Energy (eV)

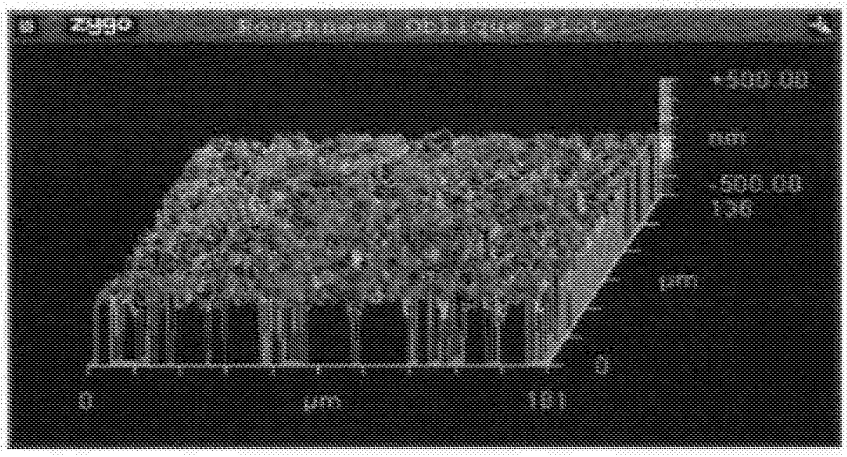
【圖 14】


Cu 1価
Cu 0価
作製後７日
作製後２日
作製後４日
Binding Energy (eV)

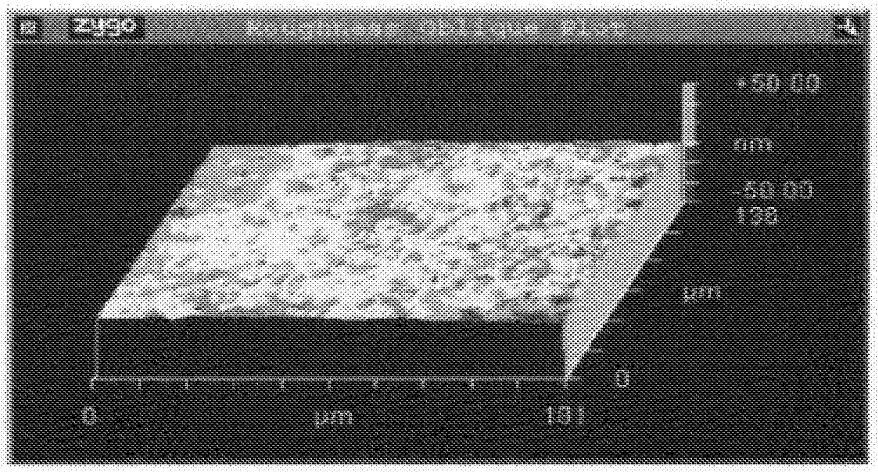
【圖 15】



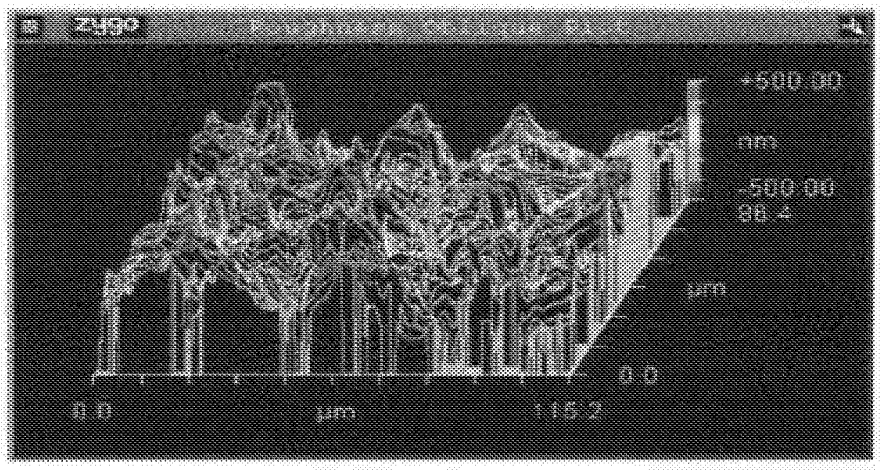
【圖 16】



[圖 17]

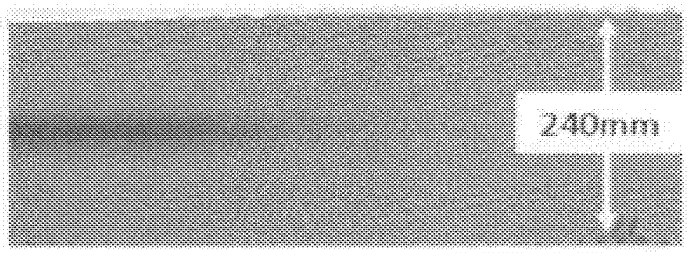

Zygo
+50.00
nm
-50.00
138
µm
0
0
µm
181

[圖 18]

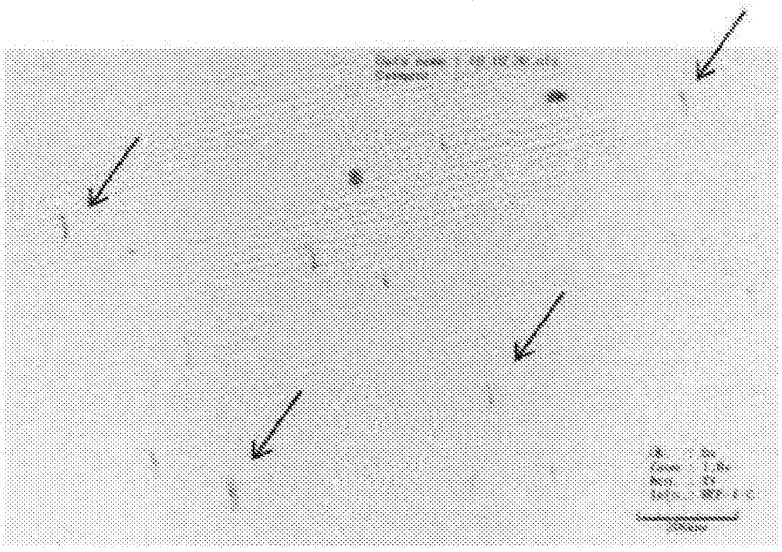

Zygo
+500.00
nm
-500.00
98.4
µm
0.0
0.0
µm
115.2

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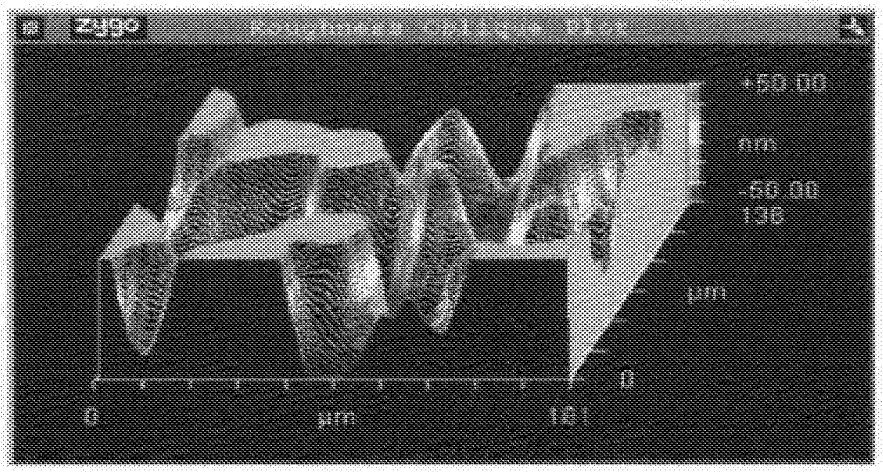
【圖 19】



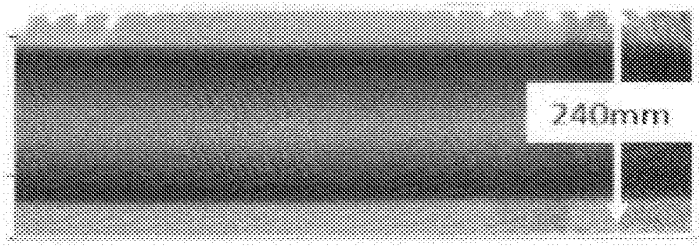
【圖 20】



【圖 21】

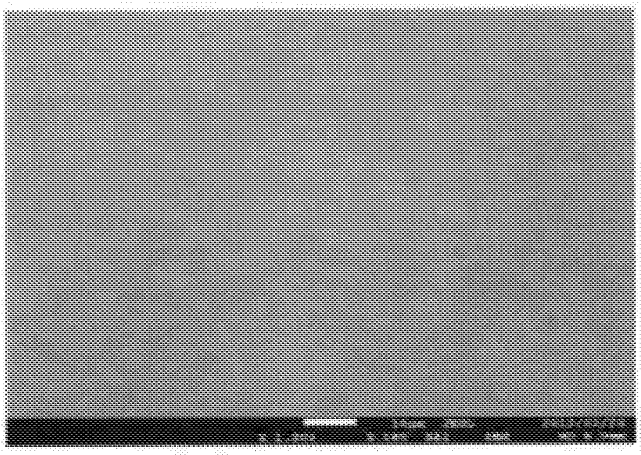


【圖 22】

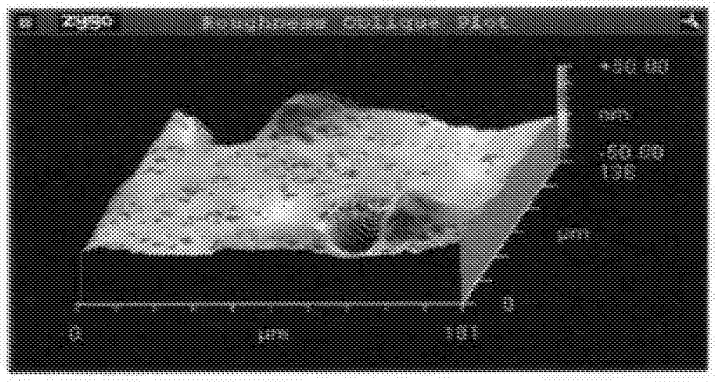


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【圖 25】

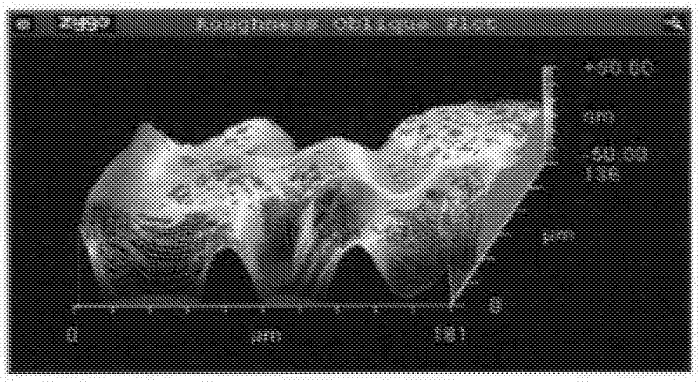


【圖 26】

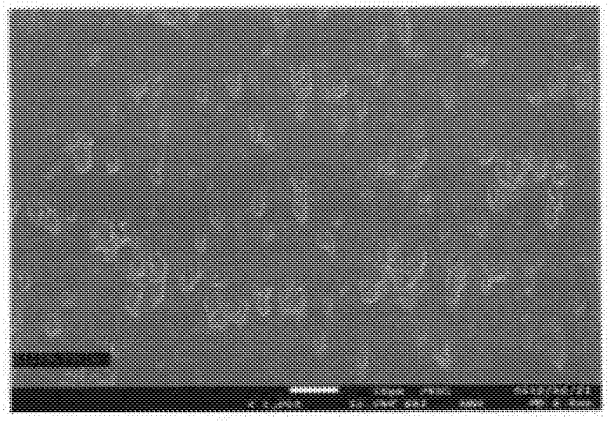


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【圖 28】

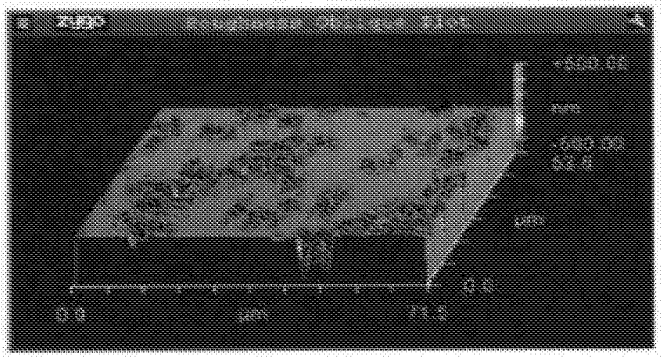


【圖 32】

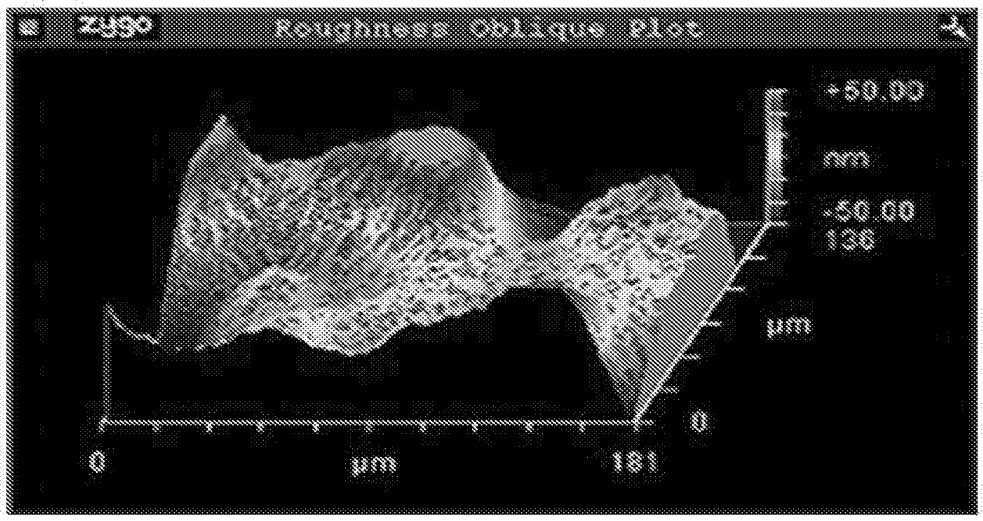


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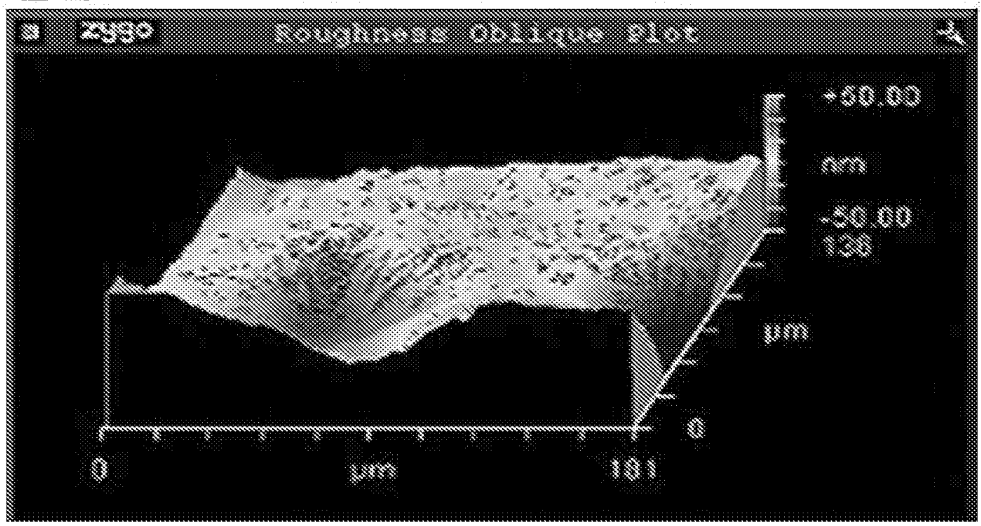
【圖 34】


zygo
0.0
µm

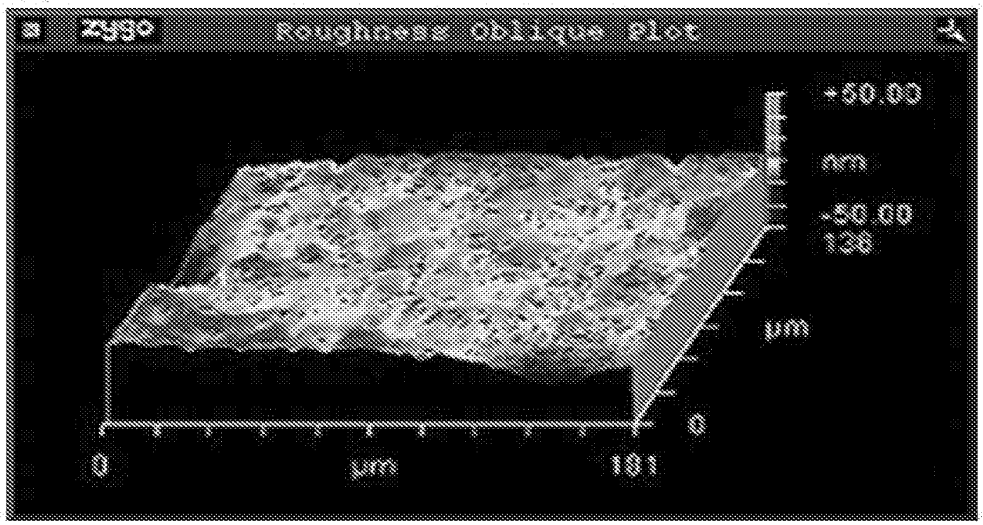
【圖 35】


zygo
Roughness Oblique Plot
+50.00
nm
-50.00
µm
0
0
µm
181

【図 36】



【図 37】



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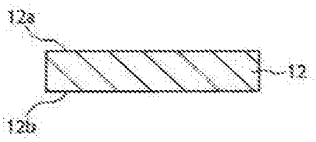
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(21)Application number	2013-001895
(22)Date of filing	09.01.2013
(71)Applicant	MITSUI MINING & SMELTING CO LTD
(72)Inventor	MATSUURA YOSHINORI



(54)ELECTROLYTIC COPPER FOIL AND ELECTRONIC DEVICE

(57)Abstract
PROBLEM TO BE SOLVED: To provide an electrolytic copper foil extremely useful as the electrode for an electronic device.
SOLUTION: An electrolytic copper foil composed of copper or a copper alloy and used as the electrode for an electronic device has a 0.2% proof stress of 250 N/mm2 or more after heat treatment at 200°C for 60 min in nitrogen atmosphere, and comprises a recessed dominant surface, where the Pv/Pp of the maximum valley depth to the maximum peak height Pp of a profile, measured for a rectangular region of 181 μm×136 μm in accordance with JIS B 0601-2001 is 1.2 or more, on the at least one outer most surface of the electrolytic copper foil.

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(12) 등록특허공보(B1)

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(73) 특허권자
일진머티리얼즈 주식회사
전라북도 익산시 석암로3길 63-25 (팔봉동)
(72) 발명자
이선형
전북 익산시 무왕로26길 11-5, 103동 903호 (부송동, 우남콤비타운아파트)
조대진
경기 성남시 중원구 박석로5번길 46, 401호 (상대원동, 영원골든빌)
(공동에 계속)
(74) 대리인
특허법인 아이피에스

전체 청구항 수 : 총 10 항 심사관 : 이인철

(54) 발명의 명칭 **전해동박, 이를 포함하는 전기부품 및 전지**

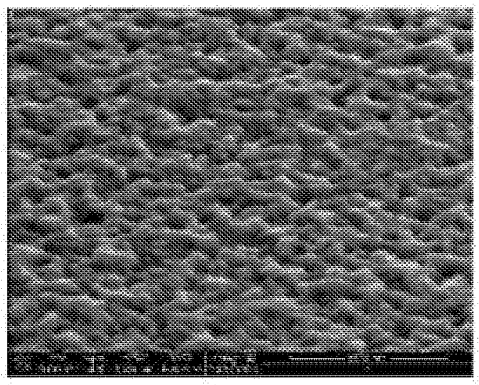
(57) 요 약

석출면의 중심선평균거칠기(Ra), 최대높이(Rmax) 및 10점평균높이(Rz)가 하기 식을 만족시키는 전해동박이 제시된다.

$1.5 \leq (Rmax - Rz)/Ra \leq 6.5$.

본 발명에 따른 전해동박은 저조도 및 고강도를 유지하면서 높은 연신율을 나타내고, 특히 광택도가 높아, 중대형 리튬이온 2차 전지의 집전체 및 TCP(Tape Carrier Package)에 사용되는 TAB(Tape Automated Bonding)용 반도체 패키징(Packaging) 기판 등에 사용될 수 있다.

대 표 도 - 도5



(72) 발명자
박슬기
전남 진도군 고군면 오산리 1525번지

송기덕
경기 수원시 권선구 세류로40번길 28, (세류동)

특허청구의 범위

청구항 1

석출면의 표면요소들의 높이 편차 및 형상을 조절하기 위한

석출면의 중심선평균거칠기 Ra(㎛), 최대높이 Rmax(㎛) 및 10점 평균높이 Rz(㎛)가 하기 식을 만족시키는 전해동박:

$1.5 \leq (Rmax - Rz)/Ra \leq 6.5$.

청구항 2

청구항 1에 있어서,

열처리 전 상온에서의 인장강도가 40~50 kgf/㎟ 및 연신율이 6~15 %인 것을 특징으로 하는 전해동박.

청구항 3

청구항 1에 있어서,

180℃에서 1시간 열처리 후 인장강도가 40~50 kgf/㎟ 및 연신율이 7~15 % 인 것을 특징으로 하는 전해동박.

청구항 4

삭제

청구항 5

청구항 3에 있어서,

열처리 후 인장강도는 열처리 전 인장강도의 85 % 내지 99 %인 것을 특징으로 하는 전해동박.

청구항 6

삭제

청구항 7

삭제

청구항 8

삭제

청구항 9

청구항 3에 있어서,

열처리 후 연신율은 열처리 전 연신율의 1배 내지 4.5배인 것을 특징으로 하는 전해동박.

청구항 10

청구항 1에 있어서,

모서리 말림각도는 0 ° 내지 45° 인 것을 특징으로 하는 전해동박.

청구항 11

청구항 1에 있어서,

모서리 말림높이는 0㎜ 내지 40 ㎜인 것을 특징으로 하는 전해동박.

청구항 12

청구항 1에 있어서,

두께가 2㎛ 내지 10㎛인 전해동박.

청구항 13

청구항 1~3, 5, 9~12 항 중 어느 한 항에 따른 전해동박을 포함하는 전지.

청구항 14

절연성 기재; 및

상기 절연성 기재의 일 표면에 부착된, 청구항 1~3, 5, 9~12 항 중 어느 한 항에 따른 전해동박;을 포함하는 전기부품.

발 명 의

기 술 분 야

[0001] 본 발명은 전해동박, 전해동박을 포함하는 전기부품 및 전지에 관한 것으로, 보다 상세하게는 고온 열처리 후에도 높은 인장강도와 연신율을 동시에 구비한 저조도, 고강도 및 고연신 전해동박에 관한 것이다.

배 경 기 술

[0002] 이차전지의 집전체로는 일반적으로 동박이 사용된다. 상기 동박은 압연가공에 의한 압연동박이 주로 사용되나, 제조비용이 고가이고 광폭의 동박 제조가 어렵다. 또한, 압연동박은 압연 가공시 윤활유를 사용해야 하기 때문에 윤활유의 오염에 의해 활물질과의 밀착성이 저하되어 전지의 충방전 사이클 특성이 저하될 수 있다.

[0003] 리튬전지는 충방전시 체적변화 및 과충전에 따른 발열현상을 수반한다. 또한, 전극활물질과의 밀착성을 향상시키고 충방전 사이클에 따른 활물질층의 팽창 수축과 관련하여 동박 기재에 영향을 덜 받아 집전체로서의 동박에 주름, 파단 등의 발생을 방지하는 효과가 있도록 동박의 표면 조도가 낮아야 한다. 따라서, 리튬전지의 체적변화 및 발열현상을 견딜 수 있고 활물질과의 밀착성이 우수한 고연신, 고강도 및 저조도 동박이 요구된다.

[0004] 또한, 전자기기의 경박단소 요구로 인하여 고기능화, 소형화, 경량화에 따른 적은 면적 내에 회로의 집적도를 높이고자 반도체실장기판이나 메인보드 기판의 미세 배선화에 대한 요구가 증가하고 있다. 이러한 미세 패턴을 가지는 프린트 배선판의 제조에 두꺼운 동박이 이용되면 배선 회로 형성을 위한 에칭 시간이 길어지고 배선 패턴의 측벽 수직성이 저하된다. 특히, 에칭에 의해 형성되는 배선패턴의 배선 선폭이 좁은 경우에는 배선이 단선될 수 있다. 따라서, 미세 피치 회로를 얻기 위해서는, 보다 두께가 얇은 동박이 요구된다. 그러나, 얇은 동박은 동박의 두께가 제한되므로 기계적 강도가 약해 프린트 배선 기판의 제조시에 구김이나 찍임 등의 불량 발생 빈도가 높아진다.

[0005] 그리고, TCP(Tape Carrier Package)에 사용되는 TAB(Tape Automated Bonding)용 반도체 패키징(packaging) 기판 등에서 제품의 중앙부에 위치하는 디바이스홀(device hall)에 배치되는 이너리드(inner lead)에 대해 IC 칩의 복수의 단자를 직접 본딩하게 되며, 이 때 본딩장치를 이용하여 순간적으로 전류를 흘려 가열하며 일정한 압력을 가한다. 따라서, 전해동박의 에칭에 의하여 형성된 이너리드가 본딩압에 의하여 당겨져 늘어나게 된다.

[0006] 따라서, 두께가 얇고, 기계적 강도가 높으면서도 고연신이 가능한 저조도 동박이 요구된다.

발명의 내용

해결하려는 과제

[0007] 본 발명의 한 측면은 새로운 전해동박을 제공하는 것이다.

[0008] 본 발명의 다른 한 측면은 전해동박을 포함하는 전기부품을 제공하는 것이다.

[0009] 본 발명의 또 다른 한 측면은 전해동박을 포함하는 전지를 제공하는 것이다.

발명의 해결 수단

[0010] 이상과 같은 목적을 달성하기 위한 본 발명의 일 측면에 따른 전해동박은, 석출면의 중심선평균거칠기(Ra), 최대높이(Rmax) 및 10점평균높이(Rz)가 하기 식을 만족시킨다.

[0011] $1.5 \leq (Rmax - Rz)/Ra \leq 6.5$

[0012] 전해동박은 열처리 전 인장강도가 40 kgf/mm^2 내지 70 kgf/mm^{2}일 수 있고, 열처리 후 인장강도 또한, 40 kgf/mm^2 내지 70 kgf/mm^{2}일 수 있다. 열처리는 180℃에서 1시간동안 수행될 수 있다. 나아가, 열처리 후 인장강도는 열처리 전 인장강도의 85 % 내지 99 %인 것이 바람직하다.

[0013] 전해동박은 열처리 전 연신율이 2 % 내지 15 %일 수 있고, 열처리 후 연신율은 4 % 내지 15 %일 수 있다. 열처리는 180℃에서 1시간동안 수행될 수 있다. 나아가, 열처리 후 연신율은 열처리 전 연신율의 1배 내지 4.5배일 수 있다.

[0014] 전해동박의 모서리 말림각도는 0 ° 내지 45° 일 수 있고, 모서리 말림높이는 0mm 내지 40 mm일 수 있으며, 전해동박의 두께는 2㎛ 내지 10㎛일 수 있다.

[0015] 본 발명의 다른 측면에 따르면, 상기와 같은 전해동박을 포함하는 전지가 제안된다.

[0016] 본 발명의 또다른 측면에 따르면, 절연성 기재; 및 절연성 기재의 일 표면에 부착된 상기의 전해동박;을 포함하는 전기부품이 제안된다.

발명의 효과

[0017] 본 발명의 전해동박은 석출면에서 외부로 돌출된 표면요소의 최대수직거리와 수직거리의 평균의 차가 작아 후처리 공정 이전에도 고광택도를 나타내어 제품품질을 향상시키는 효과가 있다. 또한, 본 발명에 따른 전해동박은 고강도를 나타내면서도 이와 함께 고연신율을 나타내고, 전해동박 내부의 스트레스가 작아 모서리 말림 현상을 방지할 수 있다. 따라서, 본 발명에 따른 전해동박은 저조도, 고강도 및 고연신율을 나타내어 공정 수행이 유리하고 제품불량률을 감소시키며, PCB 또는 이차전지의 음극집전체 등과 같은 제품에 사용되는 경우, 제품신뢰성을 향상시킬 수 있다.

도면의 간단한 설명

[0018] 도 1은 본 발명의 일실시예에 따른 전해동박의 2,000배 전계방출주사전자현미경(Field emission scanning electron microscopy, FESEM) 이미지이다.

도 2는 본 발명의 일실시예에 따른 전해동박의 10,000배 FESEM 이미지이다.

도 3은 본 발명의 일실시예에 따른 전해동박의 50,000배 FESEM 이미지이다.

도 4는 본 발명의 일실시예에 따른 전해동박의 100,000배 FESEM 이미지이다.

도 5는 본 발명의 일실시예에 따른 전해동박의 100,000배 FESEM 이미지이다.

도 6은 실시예 1에서 제조된 전해동박의 석출면에 대한 XRD(X-ray diffraction) 스펙트럼이다.

도 7은 실시예 1에서 제조된 전해동박의 표면에 대한 주사전자현미경(scanning electron microscopy, SEM) 이미지이다.

도 8은 실시예 2의 전해동박의 표면에 대한 SEM 이미지이다.

도 9는 실시예 3의 전해동박의 표면에 대한 SEM 이미지이다.

도 10은 실시예 4의 전해동박의 표면에 대한 SEM 이미지이다.

도 11은 비교예 1의 전해동박의 표면에 대한 SEM 이미지이다.

도 12는 비교예 2의 전해동박의 표면에 대한 SEM 이미지이다.

도 13은 비교예 3의 전해동박의 표면에 대한 SEM 이미지이다.

도 14는 비교예 4의 전해동박의 표면에 대한 SEM 이미지이다.

발명을 실시하기 위한 구체적인 내용

[0018] 이하에서는 본 발명에 따른 전해동박, 상기 전해동박을 포함하는 전기부품 및 전지, 및 전해동박 제조방법에 관하여 더욱 상세히 설명한다.

[0020] 본 발명의 일실시예에 따른 전해동박은 다음 식을 만족시킨다.

[0021] [수학식 1]

[0022] $1.5 \leq (Rmax - Rz)/Ra \leq 6.5$.

[0023] 식 중, Ra는 석출면의 중심선평균거칠기이고(㎛), Rmax는 최대높이(㎛)이며, Rz는 10점평균높이(㎛)를 의미한다.

[0024] Ra(Roughness Average)는 석출면에서의 평균거칠기로서, 실제 표면과 중심선 사이 면적, 즉 측정구간표면 윤곽의 높이의 절대값의 합을 나타낸다. Rmax는 가장 높이 돌출된 표면요소, 즉 가장 높은 피크(peak)로부터 가장 깊게 파인 곳, 즉 가장 깊은 밸리(valley)까지의 수직거리를 의미한다. 즉 Rmax는 표면요소의 최대수직거리를 의미한다. Rz는 전체 측정구간에서 측정한 5개의 가장 높은 피크의 높이에 5개의 가장 깊은 밸리의 깊이를 더한 값의 평균값이다.

[0025] 본 명세서에서 '표면요소'는 석출면에 보이는 밝은 부분으로서 전해동박의 표면에 돌출된 부분을 의미하는데, 표면요소 중 높은 것을 피크라 하고, 표면요소 사이에 파인 영역을 밸리라 한다.

[0026] 본 발명에 따른 전해동박은 석출면의 광택도가 매우 높다. 전해동박은 구리전해액 욕조에 침지된 회전하는 음극드럼과 양극사이에서 전류를 공급하여 음극드럼 표면에 동박을 석출시켜 얻는데, 전해동박 중 음극드럼과 접촉하는 면은 광택면(Shiny side, S면)이고, 그 반대면을 석출면이라고 한다. 석출면은 드럼과 접촉하는 광택면과 달리 전해된 구리 동박이 그대로 석출되는 면이므로 원칙적으로 광택이 적고 표면조도가 높다. 따라서, 석출면은 후처리를 통해 표면조도를 낮추고 필요에 따라 광택을 부여하는 처리를 수행한다.

[0027] 그러나, 본 발명에 따른 전해동박의 석출면의 광택도는 후처리공정 이전에도 높다. 도 1은 본 발명의 일실시예에 따른 전해동박의 2,000배 전계방출주사전자현미경(Field emission scanning electron microscopy, FESEM) 이미지이다.

[0028] 석출면은 공정의 특성상 일반적으로 2,000배 FESEM 분석하는 경우, 표면에 요철이 나타나면서 광택도가 높지 않다. 반면, 도 1에서 본 발명에 따른 전해동박의 석출면은 광택면과 유사하게 거울상(mirror)과 같은 광택을 나타내고 있다.

[0029] FESEM 분석의 해상도를 높여서 도 2의 10,000배 FESEM 이미지, 도 3의 50,000배 FESEM 이미지 및 도 4의 100,000배 FESEM 이미지를 분석해보면, 해상도를 높일수록 표면에 요철, 즉 표면요소를 확인할 수 있다. 그러나, 10,000배 FESEM 이미지에서도 요철을 확인하기 어렵고, 50,000배 FESEM 및 100,000배 FESEM 분석과 같은 초고해상도에서 요철이 확인되고 있다.

[0030] 도 4에서 본 발명에 따른 전해동박은 석출면의 표면요소의 크기 및 높이가 균일하다. 동일한 샘플에 대하여 52도 틸트(tilt)시켜 100,000배 FESEM 분석한 결과가 도 5에 나타나 있다. 도 5에서는 돌출된 표면요소 사이의 밸리가 더욱 명확히 나타난다.

[0031] 전해동박의 표면이 동일한 표면조도를 갖는 경우에도 밸리가 외부로 드러나는 영역이 작거나 밸리의 개수가 작은 경우, 표면광택도는 향상된다. 조도를 표면요소의 부피로 판단한다면 동일한 표면조도에서 피크의 높이가 높다면 피크와 밸리가 예리하게 형성되어 있다고 볼 수 있다. 즉 표면조도를 표면에서의 표면요소가 돌출되거나 인입된 전체 영역이라고 한다면, 동일한 표면조도에서 피크의 높이가 높고 밸리의 깊이가 깊으면 표면요소가 예리하게 형성되어 있다고 할 수 있다. 이는 동일한 표면조도에서 피크의 높이가 낮고 밸리의 깊이가 얕다면 표면요소는 뭉툭하게 형성되어 있다고 할 수 있다.

[0032] 이 경우, 석출면에서의 밸리의 깊이가 얕고, 외부로 보이는 어두운 부분의 평균직경이 크다면 표면에 나타난 어

두운 영역인 밸리가 더 크게 광택도에 영향을 미칠 수 있다. 즉, 밸리의 깊이가 깊고, 평균직경이 작다면 외부에 어두운 영역이 적게 나타나 추가적인 처리없이도 광택도가 향상될 수 있는 것이다.

[0033] 따라서, 본 발명에 따른 전해동박의 석출면에서의 밸리는 상대적으로 깊이는 깊고 평균직경은 작은 것이 광택도면에서 바람직하다. 밸리의 깊이가 깊고 평균직경이 작기 위해서는 표면요소의 높이가 높고, 예리하게 형성되어 있어야 한다.

[0034] 이를 위하여, 본 발명의 일실시예에 따른 전해동박은 다음 식을 만족시킨다.

[0035] [수학식 1]

[0036] $1.5 \leq (Rmax - Rz)/Ra \leq 6.5$

[0037] 식 중, Ra는 석출면의 중심선평균거칠기이고(㎛), Rmax는 최대높이(㎛)이며, Rz는 10점평균높이(㎛)이다.

[0038] 상기 식에서, (Rmax - Rz)/Ra 값은 6.5 이하이면 후처리 공정없이 우수한 광택도값을 얻을 수 있다. 반면, (Rmax - Rz)/Ra 값이 1.5 이하인 경우, Rmax와 Rz의 차이가 너무 작아, 표면요소의 피크부터 밸리까지의 값이 전체적으로 높아지게 되어 전체적인 표면조도가 높아지게 된다.

[0039] Rmax에서 Rz를 뺀 값은, 표면요소중 최대 높은 피크의 중심선으로부터의 높이와 최대 깊은 밸리의 중심선으로부터의 깊이를 더한 값인 Rmax에서 표면요소 중 가장 높은 피크 5개의 높이와 가장 깊은 밸리 5개의 깊이를 더한 값의 평균값인 Rz를 뺀 값이다. 즉, 표면요소의 중심선을 기준으로 한 최대수직길이와 가장 높은 피크 및 밸리를 포함한 높은 피크 및 밸리 각 5개의 평균값의 차이를 의미한다. 그 차이가 크다면, 가장 높은 피크와 나머지 4개의 높이 차이가 크다는 것을 의미하는데 이는 곧 전체적으로 표면요소가 높이나 깊이의 편차가 있도록 형성되어 있다는 것을 의미한다. 그 차이가 작다면, 높은 피크나 깊은 밸리가 많이 형성되어 있고, 표면요소의 높이의 편차가 많지 않다는 것을 의미한다. 다만, Rz가 5개의 피크 및 밸리값의 평균을 나타내므로 Ra를 식에 반영하여 평균적인 편차를 얻을 수 있다.

[0040] 표면조도가 동일한 경우, (Rmax - Rz)/Ra가 크다면, 석출면의 표면요소들의 높이 편차가 크게 되고 표면요소는 뭉툭하게 형성되게 된다. (Rmax - Rz)/Ra가 작다면, 석출면 표면요소들의 높이편차가 작아 표면요소는 예리하게 형성되고, 이는 광택도 향상효과를 나타낸다. (Rmax - Rz)/Ra의 최대값 및 최소값에 대하여는 이하, 실시예를 참조하여 더 설명하기로 한다.

[0041] 본 발명의 일실시예에 따른 전해동박은 석출면의 표면조도 Rz가 1.4㎛ 이하이며, 열처리 후 인장강도가 40kgf/㎟이상이며, 연신율이 4 % 이상이다.

[0042] 상기 전해동박은 표면조도가 Rz가 1.4㎛ 이하의 저조도 동박이면서도 40kgf/㎟이상의 높은 인장강도를 가지므로 기계적 강도가 높다. 이와 동시에, 상기 전해동박은 고온을 거친 후에도 4% 이상의 고연신율을 가진다.

[0043] 또한, 본 발명에 따른 전해동박은 모서리 말림(curl) 각도가 0 ° 내지 45° 이다. 모서리 말림 각도는 전해동박을 평평한 바닥 위에 놓을 경우 전해동박의 끝부분, 즉 모서리나 가장자리가 휘어지는 각도를 의미한다. 전해동박의 모서리 말림현상은 전해동박의 내부 에너지가 불균일할 때 발생하는 것으로 알려져 있는데 모서리 말림이 발생할 경우, PCB공정에서 적층 등의 공정에서 모서리가 찢어지는 것과 같이 불량이 다수 발생할 수 있고, 리튬이차전지 공정에서는 활물질 코팅 시 모서리가 찢어지거나 접히거나 또는 주름이 발생하는 등의 문제가 발생할 수 있다. 전해동박의 모서리 말림각도가 크면 후속공정에 사용하기 어려우므로 모서리 말림 각도는 0 ° 내지 45° 인 것이 바람직하다. 또한, 전해동박을 평평한 바닥위에 펼쳐놓고 X자로 갈라, 자른 부분이 올라오는 높이를 모서리 말림높이라 하는데, 모서리 말림높이는 0㎜ 내지 40 ㎜인 것이 바람직하다. 본 발명에 따른 전해동박의 경우, 구리 결정 내에 불순물이 존재하여 강도가 높으므로 모서리 말림정도가 클 것으로 예상되나 구리결정립계에 불순물이 존재하지 않아 내부 스트레스가 낮아져 모서리 말림정도가 낮아지게 된다.

[0044] 따라서, 상기 전해동박은 PCB(Printed Circuit Board)/FPC(Flexible PCB) 용도 및 전지의 집전체 용도로 동시에 사용될 수 있다.

[0045] 상기 전해동박에서 석출면의 표면조도 Rz가 1.4㎛를 초과이면 음극집전체용 전해동박의 표면과 활물질과의 접촉면이 작아져서 충방전 사이클의 수명 및 충전 초기의 전기 용량이 낮아질 수 있다. 또한, 상기 석출면의 표면조도 Rz가 1.4㎛를 초과이면 프린트배선판에서 미세 피치를 가지는 고밀도 회로를 형성하는 것이 용이하지 않다.

[0046] 상기 전해동박은 인장강도가 40kgf/㎟ 내지 70kgf/㎟로 고강도 특성을 갖는다. 또한, 상기 전해동박은 열처리

후에도 인장강도가 40kgf/㎟ 내지 70kgf/㎟이다. 열처리는 예를 들어 150℃ 내지 220℃에서 수행될 수 있고, 상세하게는 180℃에서 수행될 수 있다. 열처리는 30분, 1시간, 2시간 및 몇 시간에 걸쳐 수행될 수 있다. 열처리는 전해동박의 인장강도를 측정하기 위한 것으로서, 전해동박을 보관하거나 후속공정에 투입한 경우 일정 수준으로 변하지 않는 값으로 유지되는 인장강도나 연신율을 얻기 위한 처리이다.

[0047] 상기 전해동박은 열처리 후 인장강도가 40kgf/㎟미만이면 기계적 강도가 약해 취급이 어려울 수 있다.

[0048] 상기 전해동박은 열처리 후의 인장강도가 열처리 전의 인장강도와 유사한 것이 바람직하다. 상기 전해동박의 열처리 후의 인장강도는 열처리 전 인장강도의 85% 내지 99%인 것이 바람직한데, 열처리 후에도 강도를 유지하면 후속되는 공정에서의 취급이 용이하고 수율이 높아진다.

[0049] 상기 전해동박은 열처리 전 연신율이 2% 내지 15%일 수 있다. 또한, 상기 전해동박은 열처리 후 연신율이 4% 내지 15%일 수 있는데, 열처리는 180℃에서 1시간 수행될 수 있다. 또는, 열처리 후 연신율은 열처리 전 연신율의 1배 내지 4.5배일 수 있다.

[0050] 상기 전해동박에서 열처리 후 연신율이 4% 미만이면, 후속공정이 고온공정인 경우 크랙이 발생할 수 있다. 예를 들어, 상기 전해동박이 이차전지의 음극집전체로 사용되는 경우, 음극집전체 제조시의 공정이 고온공정이고, 충방전시에 활물질 층의 부피변화가 수반되므로 크랙이 발생하여 불량을 유발할 수 있으므로 열처리 후 소정 연신율을 유지하여야 한다.

[0051] 상기 전해동박은 석출면에 대한 XRD 스펙트럼에서 (200) 결정면에 대한 회절 피크의 강도(I(200))와 (111) 결정면에 대한 회절 피크의 강도(I(111))의 비인 I(200)/I(111)가 0.5 내지 1.0일 수 있다.

[0052] 예를 들어, 도 6에서 보여지는 바와 같이 석출면에 대한 XRD 스펙트럼에서 회절 각도(2θ) 43.0° ± 1.0° 에서 (111) 결정면에 대한 회절 피크를 나타내며, 회절 각도(2θ) 50.5° ± 1.0° 에서 (200) 결정면에 대한 회절 피크를 나타내며, 이들의 강도비 I(200)/I(111)가 0.5 내지 1.0이상일 수 있다.

[0053] 예를 들어, 상기 전해동박에서 I(200)/I(111)가 0.5 내지 0.8일 수 있다.상기 전해동박에서 상기 석출면에 대한 XRD 스펙트럼에서 (200) 결정면에 대한 배향지수(M(200))와 (111) 결정면에 대한 배향지수(M(111))로부터 얻어지는 배향지수의 비인 M(200)/M(111)가 1.1 내지 1.5일 수 있다. 상기 배향지수(orientation index)는 임의의 시료에 대한 특정 결정면의 상대적인 피크 강도를 모든 결정면에 대하여 무배향인 표준 시료에서 얻어지는 특정 결정면의 상대적인 피크 강도로 나누어준 값이다. 예를 들어, 상기 전해동박에서 M(200)/M(111)가 1.2 내지 1.4일 수 있다.

[0054] 상기 전해동박은 180℃에서 1시간 열처리 후 연신율이 10% 이상일 수 있다. 즉, 상기 전해동박은 고온열처리 후 연신율이 10% 이상인 고연신율을 가질 수 있다. 예를 들어, 상기 전해동박은 고온열처리 후 연신율이 10% 내지 20%일 수 있다. 예를 들어, 상기 전해동박은 고온열처리 후 연신율이 10% 내지 15%일 수 있다. 예를 들어, 상기 전해동박은 고온열처리 후 연신율이 10% 내지 13%일 수 있다. 상기 전해동박은 열처리 전 연신율이 2% 이상일 수 있다. 예를 들어, 상기 전해동박은 열처리 전 연신율이 2% 내지 20%일 수 있다. 예를 들어, 상기 전해동박은 열처리 전 연신율이 5% 내지 20%일 수 있다. 예를 들어, 상기 전해동박은 열처리 전 연신율이 5% 내지 15%일 수 있다. 예를 들어, 상기 전해동박은 열처리 전 연신율이 5% 내지 10%일 수 있다. 상기 "열처리 전"이라는 용어는 고온상태로 열처리하기 전의 온도인 25℃ 내지 130℃를 의미한다. 상기 연신율은 전해동박이 파단되기 직전까지 연신된 거리를 전해동박의 최초길이로 나눈 값이다.

[0055] 상기 전해동박은 석출면의 표면조도 Rz가 0.7㎛ 이하일 수 있다. 상기 전해동박은 Rz가 0.7㎛ 이하인 저조도를 가짐에 의하여 PCB/FPC 용 동박 및 이차전지용 음극집전체용 동박으로 모두 사용될 수 있다. 예를 들어, 상기 전해동박은 석출면의 표면조도 Rz가 0.5㎛ 이하일 수 있다. 예를 들어, 상기 전해동박은 석출면의 표면조도 Rz가 0.45㎛ 이하일 수 있다.

[0056] 상기 전해동박은 석출면의 표면조도 Ra가 0.15㎛ 이하일 수 있다. 상기 전해동박은 Ra가 0.15㎛ 이하인 저조도를 가짐에 의하여 PCB/FPC 용 동박 및 이차전지용 음극집전체용 동박으로 모두 사용될 수 있다. 예를 들어, 상기 전해동박은 석출면의 표면조도 Ra가 0.12㎛ 이하일 수 있다. 예를 들어, 상기 전해동박은 석출면의 표면조도 Ra가 0.11㎛ 이하일 수 있다.

[0057] 상기 전해동박의 열처리 후 인장강도가 열처리 전 인장강도의 85% 이상일 수 있다. 예를 들어, 상기 전해동박의 180℃에서 1시간 동안 열처리 후 인장강도가 열처리 전 인장강도의 90% 이상일 수 있다. 상기 열처리 전 인장강

도는 고온 열처리 없이 얻어진 동박의 인장강도이다. 상기 전해동박의 열처리 전 인장강도는 40kgf/㎟ 내지 70kgf/㎟일 수 있다.

[0058] 상기 전해동박에서 석출면의 폭 방향에 대한 광택도(Gs(60°))가 500 이상일 수 있다. 예를 들어, 상기 전해동박에서 석출면의 폭 방향에 대한 광택도(Gs(60°))가 500 내지 1000일 수 있다. 상기 광택도는 JIS Z 8741-1997에 따라 측정된 값이다.

[0059] 상기 전해동박의 두께는 35㎛ 이하일 수 있다. 예를 들어, 상기 전해동박의 두께는 6 내지 35㎛ 일 수 있다. 예를 들어, 상기 전해동박의 두께는 6내지 18㎛ 일 수 있다. 또한, 예를 들어 상기 전해동박의 두께는 2 내지 10㎛ 일 수 있다.

[0060] 상기 전해동박은 절연수지 등과 접착할 필요가 있는 경우, 밀착성을 실용 수준 또는 그 이상으로 만들기 위해서 표면 처리가 추가적으로 실시될 수 있다. 동박 상에서의 표면 처리로서는, 예를 들면 내열 및 내화학성 처리, 크로메이트 처리, 실란 커플링 처리 중 어느 하나 또는 이들의 조합 등을 들 수 있고, 어떤 표면 처리를 어떻게 실시하는가는 절연수지로 이용하는 수지나 공정조건에 따라서 본 발명이 속하는 기술분야에서 통상의 지식을 가진 자가 선택하여 수행된다.

[0061] 예시적인 일실시예에 따른 전기부품은 절연성 기재; 및 상기 절연성 기재의 일 표면에 부착된 상술한 전해동박;을 포함하며, 상기 전해동박을 에칭하여 형성된 회로를 포함한다.

[0062] 상기 전기부품은 예를 들어, TAB 테이프, 프린트배선판(PCB), 연성프린트배선판(FPC, Flexible PCB) 등이나 반드시 이들로 한정되지 않으며, 상기 전해동박을 절연성 기재상에 부착시켜 사용하는 것으로서 당해 기술분야에서 사용할 수 있는 것이라면 모두 가능하다.

[0063] 예시적인 일실시예에 따른 전지는 상기 전해동박을 포함한다. 상기 전해동박은 상기 전지의 음극집전체로 사용될 수 있으나 반드시 이들로 한정되지 않으며 전지에 사용되는 다른 구성요소로도 사용될 수 있다. 상기 전지는 특별히 한정되지 않으며 1차 전지, 2차 전지를 모두 포함하며, 리튬이온전지, 리튬폴리머 전지, 리튬공기전지 등 전해동박을 집전체로 사용하는 전지로서 당해기술분야에서 사용할 수 있는 전지라면 모두 가능하다.

[0064] 예시적인 일실시예에 따른 전해동박 제조방법은 첨가제 A; 첨가제 B; 첨가제 C 및 첨가제 D;를 포함하는 구리전해액을 전해하는 단계를 포함하며, 상기 첨가제 A가 티오우레아계 화합물 및 질소를 포함하는 헤테로고리에 티올기가 연결된 화합물로 이루어진 군에서 선택된 하나 이상이며, 상기 첨가제 B가 황원자를 포함하는 화합물의 술폰산 또는 그의 금속염이며, 상기 첨가제 C가 비이온성 수용성 고분자이며; 상기 첨가제 D가 페나지늄(phenazinium)계 화합물이다.

[0065] 상기 전해동박 제조방법은 새로운 조성의 첨가제들을 포함함에 의하여 두께가 얇고, 기계적 강도가 높으면서도 고연신이 가능한 저조도 동박을 제조할 수 있다. 상기 구리전해액은 농도 1 내지 40ppm의 염소(염소이온)를 포함할 수 있다. 구리전해액 중에 염소이온이 소량 존재하게 되면 전해도금시 초기 핵생성 사이트가 많아져서 결정립이 미세하게 되고 결정립계 계면에 형성되는 $CuCl_2$의 석출물들이 고온으로 가열시 결정 성장을 억제하여 고온에서의 열적 안정성을 향상시킬 수 있다. 상기 염소이온의 농도가 1 ppm 미만이면 황산-황산동 전해액 중에 필요한 염소이온의 농도가 부족하여 열처리 전 인장강도가 저하되고 고온에서의 열적 안정성이 저하될 수 있다. 염소이온의 농도가 40 ppm 초과이면 석출면의 표면조도가 상승하여 저조도의 전해동박 제조가 어렵고 열처리 전 인장강도가 저하되고 고온에서의 열적 안정성이 저하될 수 있다.

[0066] 상기 구리전해액에서 상기 첨가제 A의 함량이 1 내지 10ppm이며, 상기 첨가제 B의 함량이 10 내지 200ppm이며, 상기 첨가제 C의 함량이 5 내지 40ppm이며, 상기 첨가제 D의 함량이 1 내지 10ppm 일 수 있다.

[0067] 상기 구리전해액에서 첨가제 A는 전해동박의 제조 안정화를 향상시키고 전해동박의 강도를 향상시킬 수 있다. 상기 첨가제 A의 함량이 1ppm 미만이면 전해동박의 인장강도가 저하될 수 있으며, 상기 첨가제 A의 함량이 10ppm 초과이면 석출면의 표면조도가 상승하여 저조도의 전해동박 제조가 어렵고 인장강도가 저하될 수 있다.

[0068] 상기 구리전해액에서 첨가제 B는 전해동박의 표면광택을 향상시킬 수 있다. 상기 첨가제 B의 함량이 10ppm 미만이면 전해동박의 광택이 저하될 수 있으며, 상기 첨가제 B의 함량이 200ppm 초과이면 석출면의 표면조도가 상승하여 저조도의 전해동박 제조가 어렵고 전해동박의 인장강도가 저하될 수 있다.

[0069] 상기 구리전해액에서 첨가제 C는 전해동박의 표면 조도를 낮추고 표면광택을 향상시킬 수 있다. 상기 첨가제 C의 함량이 5ppm 미만이면 석출면의 표면조도가 상승하여 저도도의 전해동박 제조가 어렵고 전해동박의 광택이

저하될 수 있으며, 상기 첨가제 C의 함량이 40ppm 초과이면 전해동박의 물성이나 외관에 차이가 없으며 경제적이지 못할 수 있다.

[0070] 상기 구리전해액에서 첨가제 D는 전해동박의 표면을 평평함을 향상시키는 역할을 수행할 수 있다. 상기 첨가제 D의 함량이 1ppm 미만이면 석출면의 표면조도가 상승하여 저도도의 전해동박 제조가 어렵고 전해동박의 광택이 저하될 수 있으며, 상기 첨가제 D의 함량이 40ppm 초과이면 전해동박의 석출상태가 불안정해지고 전해동박의 인장강도가 저해될 수 있다.

[0071] 상기 티오우레아계 화합물은 디에틸티오우레아, 에틸렌티오우레아, 아세틸렌티오우레아, 디프로필티오우레아, 디부틸티오우레아, N-트리플루오로아세틸티오우레아(N-trifluoroacetylthiourea), N-에틸티오우레아(N-ethylthiourea), N-시아노아세틸티오우레아(N-cyanoacetylthiourea), N-알릴티오우레아(N-allylthiourea), o-톨릴티오우레아(o-tolylthiourea), N,N'-부틸렌 티오우레아(N,N'-butylene thiourea), 티오졸리딘티올(thiazolidinethiol), 4-티아졸리티올(4-thiazolinethiol), 4-메틸-2-피리미딘티올(4-methyl-2-pyrimidinethiol), 2-티오우라실(2-thiouracil)로 이루어진 군에서 선택된 하나 이상일 수 있으나 반드시 이를로 한정되지 않으며 당해 기술분야에서 첨가제로 사용가능한 티오우레아 화합물이라면 모두 가능하다. 상기 질소를 포함하는 헤테로고리에 티올기가 연결된 화합물은 예를 들어, 2-머캅토-5-벤조이미다졸 술폰산 소듐염(2-mercapto-5-benzoimidazole sulfonic acid sodium salt), 소듐 3-(5-머캅토-1-테트라졸릴)벤젠 술포네이트(Sodium 3-(5-mercapto-1-tetrazolyl)benzene sulfonate), 2-머캅토 벤조티아졸(2-mercapto benzothiazole)일 수 있다.

[0072] 상기 황원자를 포함하는 화합물의 술폰산 또는 그의 금속염은 예를 들어, 비스-(3-술포프로필)-디설파이드 디소듐염(SPS), 3-머캅토-1-프로판술폰산(MPS), 3-(N,N-디메틸티오카바모일)-티오프로판술포네이트 소듐염(DPS), 3-[(아미노-이미노메틸)티오]-1-프로판술포네이트 소듐염(UPS), o-에틸디티오카보네이토-S-(3-설포프로필)-에스테르 소듐염(OPX), 3-(벤조티아졸릴-2-머캅토)-프로필-술폰산 소듐염(ZPS), 에틸렌디티오디프로필술폰산 소듐염(Ethylenedithiodipropylsulfonic acid sodium salt), 티오글리콜산(Thioglycolic acid), 티오포스포릭산-o-에틸-비스-(ω-술포프로필)에스테르 디소듐염(Thiophosphoric acid-o-ethyl-bis-(ω-sulfopropyl)ester disodium salt), 티오포스포릭산-트리스-(ω-술포프로필)에스테르 트리소듐염(Thiophosphoric acid-tris-(ω-sulfopropyl)ester trisodium salt)으로 이루어진 군에서 선택된 하나 이상일 수 있으나 반드시 이를로 한정되지 않으며 당해 기술분야에서 첨가제로 사용할 수 있는 황원자를 포함하는 화합물의 술폰산 또는 그의 금속염이라면 모두 가능하다.

[0073] 상기 바이온성 수용성 고분자는 폴리에틸렌글리콜, 폴리글리세린, 하이드록시에틸셀룰로오스, 카르복시메틸셀룰로오스(Carboxymethylcellulose), 노닐페놀 폴리글리콜에테르(Nonylphenol polyglycol ether), 옥탄 디올-비스-(폴리알킬렌 글리콜 에테르(Octane diol-bis-(polyalkylene glycol ether), 옥탄올 폴리알킬렌 글리콜 에테르(Ocatanol polyalkylene glycol ether), 올레익산 폴리글리콜 에테르(Oleic acid polyglycol ether), 폴리에틸렌 프로필렌 글리콜(Polyethylene propylene glycol), 폴리에틸렌 글리콜 디메틸 에테르(Polyethylene glycol dimethyl ether), 폴리옥시프로필렌 글리콜(Polyoxypropylene glycol), 폴리비닐 알코올(Polyvinyl alcohol), β-나프톨 폴리글리콜 에테르(β-naphthol polyglycol ether), 스테아릭산 폴리글리콜 에테르(Stearic acid polyglycol eter), 스테아릴 알코올 폴리글리콜 에테르(Stearyl alcohol polyglycol ether)로 이루어진 군에서 선택된 하나 이상일 수 있으나 반드시 이들로 한정되지 않으며 당해 기술분야에서 첨가제로 사용될 수 있는 수용성 고분자라면 모두 가능하다. 예를 들어, 상기 폴리에틸렌글리콜은 분자량이 2000 내지 20000일 수 있다.

[0074] 상기 페나지늄계 화합물은 사프라닌-O(Safranine-O), 야누스 그린 B(Janus Green B) 등으로 이루어진 군에서 선택된 하나 이상일 수 있다.

[0075] 상기 제조방법에서 사용되는 구리전해액의 온도는 30 내지 60℃일 수 있으나, 반드시 이러한 범위로 한정되는 것은 아니며 본 발명의 목적을 달성할 수 있는 범위 내에서 적절히 조절될 수 있다. 예를 들어, 상기 구리전해액의 온도는 40 내지 50℃일 수 있다.

[0076] 상기 제조방법에서 사용되는 전류밀도는 20 내지 500A/dm^2일 수 있으나, 반드시 이러한 범위로 한정되는 것은 아니며 본 발명의 목적을 달성할 수 있는 범위 내에서 적절히 조절될 수 있다. 예를 들어, 상기 전류밀도는 30 내지 40 A/dm^2일 수 있다. 상기 구리전해액은 황산-황산등 구리전해액일 수 있다. 상기 황산-황산등 구리전해액에서 상기 Cu^{2+}이온의 농도는 60g/L 내지 180g/L일 수 있으나, 반드시 이러한 범위로 한정되는 것은 아니며 본

발명의 목적을 달성할 수 있는 범위 내에서 적절히 조절될 수 있다. 예를 들어, 상기 Cu^{2+}의 농도는 65g/L 내지 175g/L 일 수 있다.

[0077] 상기 구리전해액은 공지의 방법으로 제조될 수 있다. 예를 들어, Cu^{2+} 이온의 농도는 구리 이온 또는 황산구리의 첨가량을 조절하여 얻을 수 있으며, SO_4^{2-}이온의 농도는 황산 및 황산구리의 첨가량을 조절하여 얻을 수 있다.

[0078] 상기 구리전해액에 포함되는 첨가제들의 농도는 구리전해액에 투입되는 첨가제의 투입량 및 분자량에서 얻어지거나, 구리전해액에 포함된 첨가제들을 컬럼크로마토그래피와 같은 공지의 방법으로 분석하여 얻을 수 있다.

[0079] 상기 전해동박의 제조방법은 상술한 구리전해액을 사용한 것을 제외하고는 공지의 방법으로 제조될 수 있다.

[0080] 예를 들어, 상기 전해동박은 회전하는 티탄제 드럼상 티탄의 곡면상 음극 표면과 양극 사이에 상기 구리전해액을 공급하고 전해하여 음극 표면에 전해동박을 석출시키고 이를 연속적으로 권취하여 전해동박을 제조할 수 있다.

[0081] 이하 실시예를 들어 본 발명을 더욱 상세히 설명하나, 본 발명이 이에 한정되는 것은 아니다.

[0082] (전해동박의 제조)

[0083] 실시예 1

[0084] 전해에 의한 전해동박을 제조하기 위해 20L/min으로 순환 가능한 3L용량의 전해조 시스템을 이용하였고 구리전해액의 온도는 45℃로 일정하게 유지하였다. 양극은 두께가 5mm이고, 크기가 10×10cm^2의 DSE(Dimentionally Stable Electrode) 극판을 사용하였으며, 음극은 양극과 동일한 크기 및 두께를 가진 티타늄 극판을 사용하였다.

[0085] Cu^{2+}이온의 이동을 원활하게 하기 위하여 전류밀도는 35A/dm^2로 도금을 실시하였으며, 18㎛ 두께의 전해동박을 제조하였다.

[0086] 구리전해액의 기본조성은 다음과 같다:

[0087] $CuSO_4 \cdot 5H_2O$: 250~400g/L

[0088] H_2SO_4: 80~150g/L

[0089] 상기 구리전해액에 염소이온 및 첨가제가 추가되며, 첨가된 첨가제 및 염소이온의 조성은 하기 표 1에 나타내었다. 하기 표 1에서 ppm은 mg/L와 동일한 농도이다.

[0090] 제조된 전해동박 석출면(matte 면, M면)표면의 주사전자현미경 사진을 도 7에 나타내었다.

[0091] 실시예 2 내지 4 및 비교예 1 내지 4

[0092] 구리전해액의 조성을 하기 표 1에서와 같이 변경한 것을 제외하고는 실시예 1과 동일한 방법으로 전해동박을 제조하였다. 실시예 2 내지 4 및 비교예 1 내지 4에서 제조된 전해동박의 석출면 표면의 주사전자현미경 사진을 도 8 내지 14에 각각 나타내었다.

표 1

[0093]

	실시예 1	실시예 2	실시예 3	실시예 4	비교예 1	비교예 2	비교예 3	비교예 4
염소 농도 [ppm]	20	20	20	20	40	40	35	40
DET [ppm]	3	2	3	3			1.5	7
SPS [ppm]	60	45		45	55	55		
MPS [ppm]			60				5	20
PEG [ppm]	20	20	20	20				
ZPS [ppm]	40	10	40	30				
JGB [ppm]		3						
SA0 [ppm]	3		3	3				
2M-SS[ppm]					30	40		
DDAC [ppm]					70	70		

PGL [ppm]							30	10

[0094] 상기 표 1에서 약자들은 하기 화합물들을 의미한다.

[0095] DET: 디에틸 티오우레아

[0096] SPS: 비스-(3-술포프로필)-디설파이드

[0097] MPS: 3-머캅토-1-프로판술폰산

[0098] PEG: 폴리에틸렌글리콜(칸토 케미칼 Cas No. 25322-68-3)

[0099] ZPS: 3-(벤조티아졸릴-2-머캅토)-프로필-술폰산 소듐염

[0100] JGB: 야누스 그린 B

[0101] 2M-SS: 2-머캅토-5-벤조이미다졸 술폰산

[0102] DDAC: 디알릴디메틸암모늄클로라이드

[0103] PGL: 폴리글리세린(EC1, PGL 104EC)

[0104] 평가예 1: 주사전자현미경 실험

[0105] 실시예 1 내지 4 및 비교예 1 내지 4에서 얻어진 전해동박의 석출면의 표면에 대하여 주사전자현미경을 측정하여 그 결과를 도 7 내지 14에 각각 나타내었다.

[0106] 도 7 내지 14에서 보여지는 바와 같이 실시예 1 내지 4의 전해동박은 비교예 1 내지 4의 전해동박에 비하여 표면조도가 낮았다.

[0107] 평가예 2: 광택도 측정

[0108] 실시예 1 내지 4 및 비교예 1 내지 4에서 얻어진 전해동박의 석출면의 표면에 대하여 광택도를 측정하였다. 상기 광택도는 JIS Z 8741-1997에 따라 측정된 값이다.

[0109] 광택도의 측정은 전해동박의 흐름 방향(MD 방향)을 따라 당해 동박의 표면에 입사각 60° 로 측정광을 조사하고, 반사각 60° 로 반사된 빛의 강도를 측정한 것으로 광택도 측정 방법인 JIS Z 8741-1997에 준거하여 측정하였다.

[0110] 측정 결과를 하기 표 2에 나타내었다.

[0111] 표 2

	광택도 [Gs(60°)]
실시예 1	700
실시예 2	699
실시예 3	630
실시예 4	680
비교예 1	438
비교예 2	472
비교예 3	353
비교예 4	451

[0112] 상기 표 2에 기재된 바와 같이, 실시예 1 내지 4의 전해동박은 비교예 1 내지 4의 전해동박에 비하여 향상된 광택도를 나타내었다.

[0113] 평가예 3: XRD 실험

[0114] 실시예 1 내지 4 및 비교예 1 내지 4에서 얻어진 전해동박의 석출면에 대하여 XRD(X-ray diffraction) 스펙트럼을 측정하였다. 실시예 1에 대한 XRD 스펙트럼을 도 6에 나타내었다.

[0115] 도 6에서 보여지는 바와 같이 (111) 결정면의 피크 강도가 가장 높으며, 다음이 (200) 결정면이었다.

[0116] 상기 (200) 결정면에 대한 회절 피크의 강도(I(200))와 (111) 결정면에 대한 회절 피크의 강도(I(111))의 비인 I(200)/I(111)는 0.605이었다.

[0117] 또한, 상기 석출면에 대한 XRD 스펙트럼에서 (111), (200), (220), (311), (222) 결정면에 대한 배향지수(orientation index, M)를 측정하여 그 결과를 하기 표 3에 나타내었다.

[0118] 배향지수는 S.Yoshimura, S. Yoshihara, T.Shirakashi, E.Sato, Electrochim. Acta 39, 589(1994)에서 제안한 배향지수(M)를 사용하여 측정하였다.

[0119] 예를 들어, (111) 면을 갖는 시편의 경우 다음과 같은 방법으로 배향지수(orientation index)(M)을 계산한다.

[0120] IFR(111)=IF(111)/{IF(111)+IF(200)+IF(220)+IF(311)}

[0121] IR(111)=I(111)/{I(111)+I(200)+I(220)+I(311)}

[0122] M(111)=IR(111)/IFR(111)

[0123] IF(111)은 JCPDS 카드(Cards) 에서의 XRD 강도이며 I(111)은 실험값이다. M(111)이 1보다 크면 (111)면에 평행한 우선 방위를 가지며, M이 1보다 작으면 우선방위가 감소함을 의미한다.

표 3

[0124]

결정면	(111)	(200)	(220)	(311)	(222)
배향 지수	1.02	1.34	0.80	0.25	0.97

[0125] 상기 표 3을 참조하여, 상기 석출면에 대한 XRD 스펙트럼에서 (200)결정면에 대한 배향지수(M(200))와 (111) 결정면에 대한 배향지수(M(111))로부터 얻어지는 배향지수의 비인 M(200)/M(111)는 1.31이었다.

[0126] 평가예 4: 표면 조도(Rz, Ra 및 Rmax) 측정

[0127] 실시예 1 내지 4 및 비교예 1 내지 4에서 얻어진 전해동박의 석출면의 표면조도 Rz, Ra 및 Rmax를 JISB 0601-1994 규격에 따라 측정하였다. 상기 측정방법으로 얻어진 표면 조도 Rz, Ra 및 Rmax를 하기 표 4에 나타내었다. 값이 낮을수록 거칠기가 낮음을 의미한다.

[0128] 평가예 5: 상온 인장강도, 상온 연신율, 고온 인장강도 및 고온 연신율 측정

[0129] 실시예 1 내지 4 및 비교예 1 내지 4에서 얻어진 전해동박을 폭 12.7mm X 게이지 길이 50mm로 인장시편을 채취한 후 50.8 mm/min의 크로스헤드 속도로 인장시험을 IPC-TM-650 2.4.18B 규격에 따라 실시하여 측정되는 인장강도의 최대하중을 상온 인장강도라고 하고, 파단시의 연신율을 상온 연신율이라고 하였다. 여기서 상온은 25℃이다.

[0130] 상온에서의 인장강도 및 연신율 측정에 사용된 전해동박과 동일한 전해동박을 180℃에서 1시간 열처리 후 꺼내어 상기와 동일한 방법으로 인장강도 및 연신율을 측정하고 고온 인장강도 및 고온 연신율이라고 하였다.

[0131] 상기 측정방법으로 얻어진 상온 인장강도, 상온 연신율, 고온 인장강도, 고온 연신율을 하기 표 4에 나타내었다.

표 4

[0132]

	Rmax [㎛]	Rz [㎛]	Ra [㎛]	(Rmax - Rz) /Ra	상온 인장강도 [kgf/㎟]	상온 연신율 [%]	고온 인장강도 [kgf/㎟]	고온 연신율 [%]
실시예1	0.81	0.30	0.08	6.37	46.15	7.21	43.30	11.63
실시예2	0.73	0.28	0.07	6.42	42.26	5.00	40.16	12.06
실시예3	0.89	0.38	0.10	5.10	45.41	6.16	41.55	9.38
실시예4	0.91	0.44	0.11	4.27	44.74	6.62	40.78	10.53
비교예1	2.02	0.67	0.16	8.43	66.65	2.18	77.91	3.30
비교예2	1.81	0.48	0.10	13.30	98.76	1.30	92.30	1.74
비교예3	3.84	0.46	0.24	14.08	52.81	1.64	49.53	1.87

비교예4	3.63	0.38	0.25	13.00	70.73	1.71	64.30	1.47

[0133] 상기 표 4에서 보여지는 바와 같이 실시예 1 내지 4의 전해동박은 표면조도 Rz가 0.5㎛ 미만으로 낮고, 고온 열처리 후 인장강도가 40kgf/㎟이상이며, 고온 열처리 후 연신율이 대부분 10% 이상으로 높았다.

[0134] 이에 비해, 비교예 1 내지 4의 전해동박은 실시예 1 내지 4의 전해동박에 비하여 표면조도가 높고, 고온 열처리 후 연신율이 낮아 이차전지용 음극집전체 및/또는 PDB/FPC용 저저도 동박으로 사용하기에 부적합하였다.

[0135] 또한, 실시예 1 내지 실시예 4의 (Rmax - Rz)/Ra 값은 6.5 이하로 낮은 값을 나타내었으나, 비교예 1 내지 비교예 4의 (Rmax - Rz)/Ra 값은 6.5 이상으로 높은 값을 나타내었다. 이에 따라, 표 2에서 알 수 있듯, 실시예 1 내지 실시예 4의 전해동박의 광택도는 600이상으로 후처리 공정없이도 높은 광택도를 나타내었으나, 비교예 1 내지 비교예 4는 500 이하의 광택도를 나타내었다.

[0136] 평가예 6: 모서리 말림(curl) 정도 측정

[0137] 실시예 1 내지 4 및 비교예 1 내지 4에서 얻어진 전해동박을 폭 10cm X 길이 10 cm로 시편을 채취한 후 평평한 바닥 위에 놓고 모서리 부분이 휘어진 각도(모서리 말림 각도) 및 X자로 자른 뒤 자른 부분이 올라오는 높이(모서리 말림 높이)를 측정하여 하기 표 5에 나타내었다.

[0138] ※ 5

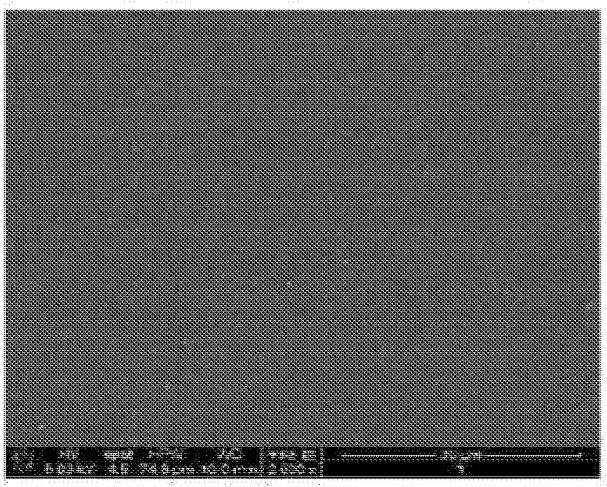
	모서리 말림 각도(°)	모서리 말림 높이(㎜)
실시예 1	5	4
실시예 2	15	12
실시예 3	8	6
실시예 4	30	26
비교예 1	52	48
비교예 2	48	44
비교예 3	46	43
비교예 4	50	46

[0139] 표 5에서 보여지는 바와 같이 실시예 1 내지 4의 전해동박은 모서리의 말림 각도가 5 내지 30° 로서 45° 이하였다. 그러나, 비교예 1 내지 비교예 4의 전해동박은 모서리의 말림 각도가 46° 내지 52° 로서 45° 를 초과하여 후속공정에서의 취급이 어려운 상태를 나타내었다. 아울러, 비교예 1 내지 비교예 4의 전해동박은 모서리 말림 높이가 40㎜를 초과하여 품질이 불량한 상태를 나타내었다. 따라서, 본 발명에 따른 전해동박은 고강도이면서도 내부 스트레스가 낮아 모서리 말림 현상이 적게 나타나 우수한 성능을 나타내었다.

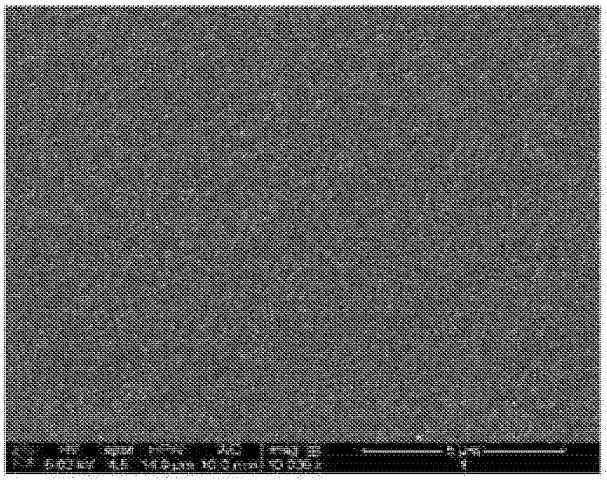
[0140] 본 발명은 상술한 실시형태 및 첨부된 도면에 의해 한정되는 것이 아니라, 첨부된 청구범위에 의해 해석되어야 한다. 또한, 본 발명에 대하여 청구범위에 기재된 본 발명의 기술적 사상을 벗어나지 않는 범위 내에서 다양한 형태의 치환, 변형 및 변경이 가능하다는 것은 당해 기술분야의 통상의 지식을 가진 자에게 자명할 것이다.

도면

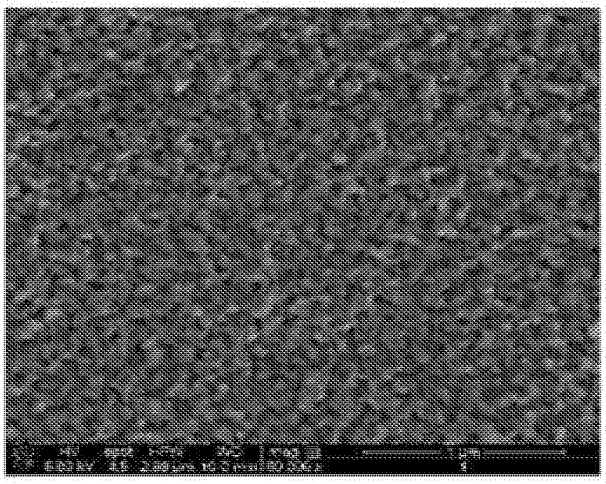
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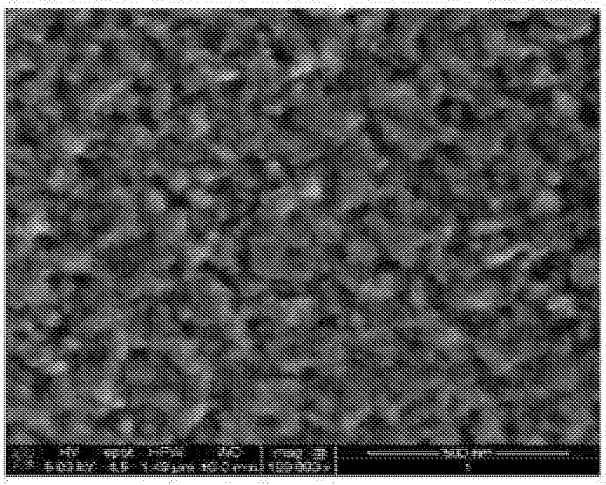
도면2



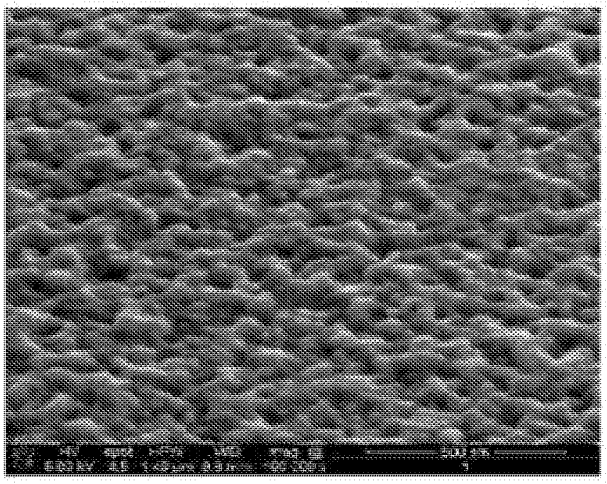
도면3



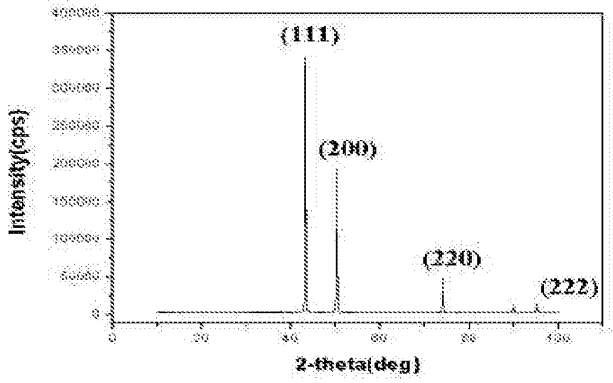
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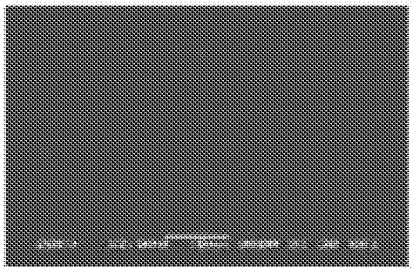
도면5



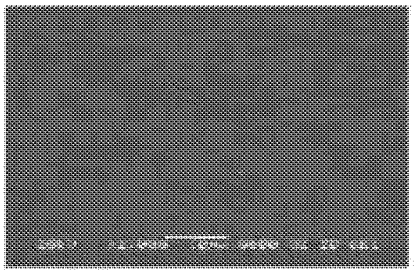
도면6



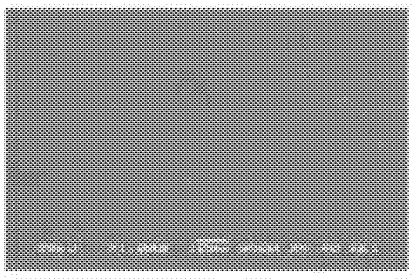
도면7



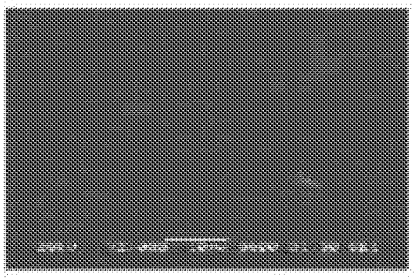
도면8



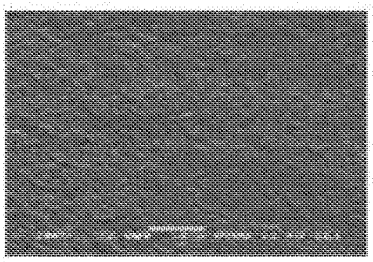
도면9



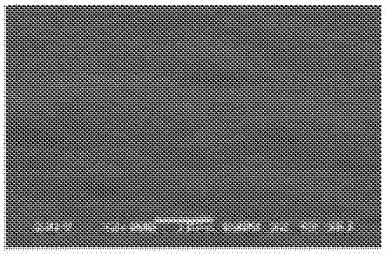
도면10



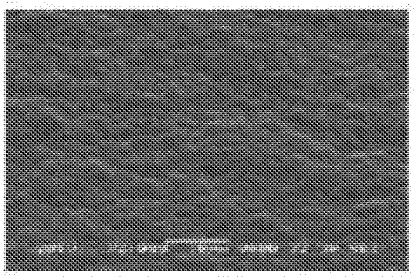
도면11



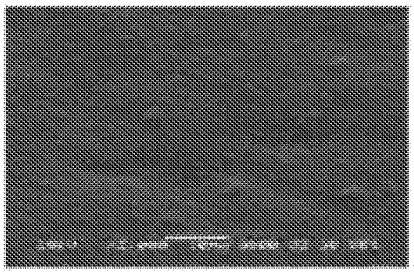
도면12



도면13



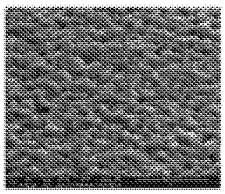
도면14



ELECTROLYTIC COPPER FOIL, ELECTRICAL PART AND BATTERY INCLUDING SAME FOIL

(11) Publication No.	101449342 B1
(43) Publication Date	13.10.2014
(21) Application No.	1020130136227
(22) Application Date	08.11.2013
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(51) Int. CL	B32B15/20(01.01.2006) H05K1/05(01.01.2006)
(52) CPC	
(73) Proprietor	ILJIN MATERIALS CO., LTD. (KR)
(72) Inventor	LEE, SUN HYOUNG (KR) JO, TAE JIN (KR) PARK, SEUL KI (KR) SONG, KI DEOK (KR)

Repr. Drawing



Zoom

Abstract Disclosed is an electrolytic copper foil that satisfies an equality of 1.5 003c#= (Rmax - Rz)/Ra 003c#=6.5. In the equality, Ra is an average roughness of the center line of the deposited surface; Rmax is the maximum height; and Rz is an average 10-point height. According to the present invention, the electrolyte copper foil has a high elongation rate while maintaining low roughness and high strength. Especially, the electrolyte copper foil is highly glossy and thus can be used for a semiconductor packaging substrate for tape automated bonding (TAB). The semiconductor packaging substrate is used for a current collector of a medium or large lithium-ion secondary battery, and for a tape carrier package (TCP).COPYRIGHT KIPO 2014

(19) 대한민국특허청(KR)
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대만 타이페이 송키앙로드 301호 7층
(72) 발명자
차이, 천-펑
대만, 타이페이, 송키앙 로드, 301번지, 7층
청, 췌이-샌
대만, 타이페이, 송키앙 로드, 301번지, 7층
린, 치앤-푸
대만, 타이페이, 송키앙 로드, 301번지, 7층
(74) 대리인
특허법인씨엔에스

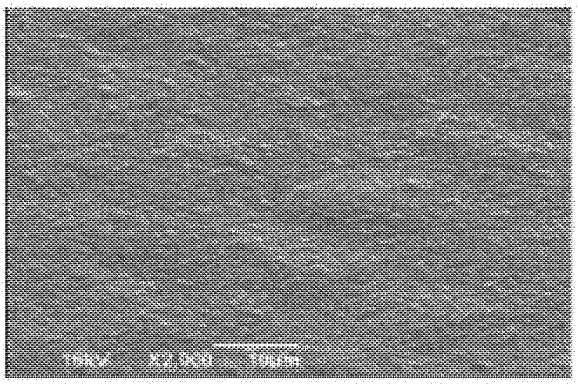
전체 청구항 수 : 총 11 항

(54) 발명의 명칭 **전해 동박 및 그 제조방법**

(57) 요 약

전해 동박이 제공된다. 상기 전해 동박은 샤이니면 및 상기 샤이니면에 대치하는 매트면을 가지며, 상기 샤이니면 및 상기 매트면 사이의 거칠기 차이는 0.5㎛이하이다. 상기 전해 동박은 45kg/㎟이상의 인장 강도를 가지며, 리튬 이온 2차 전지에 적용하기에 특히 적합하다.

대 표 도 - 도1



특허청구의 범위

청구항 1

샤이니면; 및

상기 샤이니면에 대치하는 매트면을 포함하며,

상기 샤이니면 및 상기 매트면은 0.5㎛이하의 거칠기 차이를 가지며, 그리고 전해 동박은 45kg/㎟이상의 인장강도를 갖는, 전해 동박.

청구항 2

제1항에 있어서,

상기 전해 동박은 상기 전해 동박 상에서 140℃에서 5시간 열처리를 수행한 후에 12%이상의 신장률을 갖는, 전해 동박.

청구항 3

제1항에 있어서,

상기 전해 동박의 샤이니면은 1.6㎛이하의 거칠기를 갖는, 전해 동박.

청구항 4

제1항에 있어서,

상기 전해 동박의 매트면은 1.6㎛이하의 거칠기를 갖는, 전해 동박.

청구항 5

제1항에 있어서,

상기 전해 동박의 매트면은 60° 의 광 입사각에서 60이상의 광택도를 갖는, 전해 동박.

청구항 6

황산구리 전해질에 과산화수소 용액을 첨가하는 단계; 및

과산화수소 용액이 첨가된 황산구리 전해질 상에서 전기화학 반응을 수행하여 전해 동박을 얻는 단계

를 포함하는, 전해 동박 제조방법.

청구항 7

제6항에 있어서,

상기 황산구리 전해질은 황산에 구리 원료 물질을 용해함으로써 제조되는, 전해 동박 제조방법.

청구항 8

제7항에 있어서,

상기 구리 원료 물질은 구리 폐기물인, 전해 동박 제조방법.

청구항 9

제6항에 있어서,

6-30mL의 과산화수소 용액이 시간당 상기 황산구리 전해질의 톤당 첨가되는, 전해 동박 제조방법.

청구항 10

제9항에 있어서,

상기 과산화수소 용액은 50중량%의 농도를 갖는 것인, 전해 동박 제조방법.

청구항 11

제6항에 있어서,

상기 과산화수소 용액이 첨가된 상기 황산구리 전해질 상에서 전기화학 반응을 수행하기 전에, 활성탄 필터를 사용하여 상기 황산구리 전해질을 여과하는 단계를 더 포함하는, 전해 동박 제조방법.

명 세 서

기 술 분 야

[0001] 본 발명은 전해 동박 및 그 제조방법에 관한 것으로, 보다 상세하게는, 리튬 이온 2차 전지에 사용하기에 적절한 양면 광택을 갖는 전해 동박 및 그 제조방법에 관한 것이다.

배 경 기 술

[0002] 전해 동박은 전해질로서 황산 및 황산구리로 구성된 수용액, 치수 안정성 애노드(DSA)로서 이리듐 또는 이의 산화물로 코팅된 티타늄 플레이트, 캐소드로서 티타늄 드럼을 이용하고, 두 전극 사이에 직류를 인가하여 티타늄 드럼 상에 전해액 내의 구리 이온을 전착시킨 다음, 티타늄 드럼의 표면으로부터 전해 동박을 스트리핑하고, 제조를 위해 연속적으로 권선하여 생성된다. 전해 동박이 티타늄 드럼의 표면과 접촉하는 면을 "샤이니면(S면)"이라 칭하고, 전해 동박의 뒷면을 "매트면(M면)"이라 칭한다. 통상적으로, 전해 동박의 S면의 거칠기는 티타늄 드럼의 표면의 거칠기에 따라 달라진다. 따라서, 전해 동박의 S면의 거칠기는 상대적으로 일정한 반면에, M면의 거칠기는 황산구리 전해질의 조건을 조정함으로써 조절될 수 있다.

[0003] 리튬 이온 2차 전지에 사용되는 전해 동박을 제조하기 위한 현재의 황산구리 전해질은 주로 두 카테고리로 분류될 수 있으며, 이중 하나는 소위 첨가제-함유 시스템, 즉, 황산구리 전해질에, 구리 이온의 전착을 억제할 수 있는 젤라틴, 히드록시에틸 셀룰로오즈(HEC) 또는 폴리에틸렌 글리콜(PEG), 및 결정질 입자를 정련(refining)할 수 있는 소듐 3-머캅토프로판 설포네이트(MPS) 및 비스-(3-소듐설포프로필 디설피드)(SPS)와 같은 유기 첨가제를 첨가하는 것이다. 이러한 전해 동박의 M면의 거칠기는 낮춰질 수 있으며, 이에 따라 양면 광택을 가지며, 미세한 결정 입자를 함유하는 구조를 갖는 전해 동박을 획득할 수 있다. 이러한 타입의 첨가제-함유 전해질 시스템에 의해 생성된 전해 동박은 전형적으로 40kg/㎟미만의 인장 강도를 갖는다. 다른 카테고리는 소위 첨가제-무함유 시스템, 즉, 황산구리 전해질에 어떠한 유기 첨가제를 첨가하지 않는 것이다. 이러한 타입의 첨가제-

무함유 시스템은 첨가제-함유 시스템과 상반된다. 황산구리 전해질 내의 유기물의 총 함량이 낮을수록, M면에서 낮은 거칠기를 가지며 그 표면 상에 비정상적인 돌출 입자가 없는 광택 전해 동박을 획득할 가능성이 높다. 첨가제-무함유 시스템으로부터 획득된 황산구리 전해질에 유기 첨가제가 첨가되지 않더라도, 황산구리 전해질에 사용된 구리 원료 물질은 주로 상업적으로 구입가능한 재생 구리선으로부터 얻어진다. 구리선의 표면은 기름이나 다른 유기 물질을 함유하며, 구리선이 황산에 용해될 경우에 전해 동박을 생성하기 위한 전해질이 기름이나 유기 불순물과 같은 불순물로 채워질 수 있다. 유기 불순물의 함량이 높을수록, M면 상에 수많은 비정상적인 돌출 입자를 갖는 전해 동박이 발생할 가능성이 높다. 이에 따라, 양면 광택을 갖는 전해 동박이 획득되지 않는다.

[0004] 더욱이, 전해 동박의 M면이 수많은 비정상적인 돌출 입자를 가질 경우에, 전해 동박의 제조시 후속적인 적용은 통상적으로 문제를 갖는다. 예를 들어, 구리 거칠기 처리 중에, M면 상의 비정상적 돌출 입자는 쉽게 첨단 방전(point discharging)을 유발하며, 이는 구리 거칠기 입자가 비정상적으로 집중되도록 한다. 후속적으로, 동클래드 적층판은 전해 동박을 프레스하여 형성되고, 불완전한 에칭에 기인하여 형성된 잔류 구리는 쉽게 합선을 일으킬 수 있다. 결과적으로, 그 하류 생성물의 수율은 저조하다.

[0005] M면 상에서 유기 불순물의 영향 및 첨가제-무함유 시스템에 의해 발생되는 전해 동박의 물리적 특성을 줄이기 위해, Nippon Denkai Ltd.의 일본 특허 제 3850155호 및 제 2850321호는 황산구리 전해질로부터 유기 불순물을 제거하는 방법을 개시하였다. 상기 방법에서, 동선은 600-900℃의 온도 하에서 30-60분간 동선의 표면을 태우고, 100g/L의 수성 황산 용액으로 동선의 표면을 세정하여 동선의 표면으로부터 유기 불순물을 제거하여 용해 전에 전처리된다. 다른 한편, 오존-발생 장치가 또한, 상기 전처리된 동선으로부터 획득된 황산구리 전해질 내의 기름 또는 유기 불순물을 분해하는데 사용되고, 활성탄 여과 장치를 사용하여 흡착에 의해 분해된 산물을 제거한다. 그러나, 상기 방법이 청결한 황산구리 전해질을 효과적으로 획득하는데 사용될 수 있음에도 불구하고, 동선을 고온에서 태우는 것은 다량의 에너지를 소모한다. 또한, 동선의 표면이 황산 수용액으로 세정되어 유기 불순물을 제거할 수 있음에도 불구하고, 소량의 구리가 유사하게 제거되어 구리 손실을 일으킬 수 있다. 또한, 오존은 가스이므로, 황산구리 전해질 내에 쉽게 유지되지 못한다. 또한, 고농도의 오존은 인체에 위험하고 안전성 문제를 초래한다.

발명의 내용

해결하려는 과제

[0006] 따라서, 높은 인장 강도, 열처리 후 높은 신장률, M면에서 낮은 거칠기, 및 S면과 M면 사이의 거칠기의 극히 작은 차이를 갖는 리튬 이온 2차 전지에 사용하기에 적절한 전해 동박을 개발할 필요가 산업적으로 시급히 요구된다. 그러나, 본 발명의 전해 동박의 제조공정은 단순하고, 전해질의 복잡성을 증가시키지 않고 안전성 문제로부터 벗어난다.

과제의 해결 수단

[0007] 본 발명은 서로 대치하는 샤이니면(S면) 및 매트면(M면)을 가지며, S면과 M면 사이의 거칠기(Rz)의 차이가 0.5㎛이하인 전해 동박을 제공한다. 본 발명의 전해 동박의 M면은, 60° 의 광 입사각에서 60이상의 광택도(gloss)를 갖는다. 본 발명의 전해 동박의 S면 및 M면의 거칠기는 1.6㎛이하이다.

[0008] 본 발명의 바람직한 구현으로, 본 발명의 S면 및 M면의 거칠기는 1.6㎛이하이다. 본 발명의 S면 및 M면 모두는 평활한 표면을 가져, 이들은 특히 리튬 이온 2차 전지에 사용하기에 적절하다.

[0009] 더욱이, 본 발명의 전해 동박은 45kg/㎟이상의 인장 강도를 가지며, 140℃에서 5시간 열처리 후에 12%이상의 신

장률을 갖는다. 본 발명의 전해 동박은 이와 동시에 높은 인장 강도 및 높은 신장률을 가지며, 그리고 양면에서 낮은 거칠기 및 양면 사이의 거칠기의 극히 작은 차이와 같이 우수한 특성을 달성할 수 있다. 이에 따라, 본 발명의 전해 동박은 광범위한 범위의 산업에 적용될 수 있다.

[0010] 또한, 본 발명은 황산구리 전해질에 과산화수소 용액을 제공하여 개선된 황산구리 전해질을 얻는 단계; 및 상기 개선된 황산구리 전해질로 전기화학 반응을 수행하여 본 발명의 전해 동박을 제조하는 단계를 포함하는, 전해 동박을 제조하는 방법을 제공한다. 또한, 바람직한 구현으로, 본 발명의 방법은 상기 개선된 황산구리 전해질로 전기화학 반응을 수행하기 전에, 활성탄을 사용하여 상기 개선된 황산구리 전해질을 여과하는 단계를 더 포함한다.

[0011] 본 발명에서, 황산구리 전해질의 제조는 황산에 구리 원료 물질을 용해하고, 과산화수소를 첨가하여 황산구리 전해질에 함유된 기름 또는 유기 불순물과 같은 불순물을 분해하여 황산구리 전해질을 얻는 것을 포함한다. 따라서, 본 발명의 방법에서, 버닝 또는 산 세척과 같은 동선의 전처리없이, 구리 폐기물의 재료(동선과 같은)가 황산에 직접 용해되어 청결한 황산구리 전해질을 얻을 수 있다.

도면의 간단한 설명

[0012] 도 1은 2000X 배율로 전자현미경 하에서 본 발명의 구현 1의 전해 동박의 M면의 사진이며;

도 2는 2000X 배율로 전자현미경 하에서 본 발명의 구현 2의 전해 동박의 M면의 사진이며;

도 3은 2000X 배율로 전자현미경 하에서 본 발명의 구현 3의 전해 동박의 M면의 사진이며;

도 4는 2000X 배율로 전자현미경 하에서 본 발명의 구현 4의 전해 동박의 M면의 사진이며;

도 5는 2000X 배율로 전자현미경 하에서 비교예 1의 전해 동박의 M면의 사진이며; 그리고

도 6은 2000X 배율로 전자현미경 하에서 비교예 2의 전해 동박의 M면의 사진이다.

발명을 실시하기 위한 구체적인 내용

[0013] 본 발명의 전해 동박은 서로 대치하는 S면 및 M면을 갖는다. 일 구현으로, S면 및 M면의 거칠기(Rz)의 차이는 0.5㎛이하이다.

[0014] 일 구현으로, 본 발명의 전해 동박의 S면은 평활한 표면이고, S면의 거칠기(Rz)는 1.6㎛이하이다.

[0015] 일 구현으로, 본 발명의 전해 동박의 M면의 거칠기(Rz)는 1.6㎛이다. 본 발명의 전해 동박의 M면은 60° 의 광입사각에서 60이상의 광택도를 갖는다.

[0016] 바람직한 구현으로, 본 발명의 전해 동박의 S면과 M면의 거칠기 차이는 0.5㎛이하이며, S면 및 M면의 거칠기(Rz)는 1.6㎛이하이다. S면 및 M면 모두는 평활한 표면을 갖는다. 이에 따라, 본 발명의 전해 동박은 리튬 이온 2차 전지에 사용하기에 적합하다.

[0017] 본 발명의 전해 동박의 양면의 평활한 표면은 크롬산에 침지된 후에 또는 전기도금에 의한 표면 녹 방지 처리된 후에, 리튬 이온 2차 전지의 음극 집전체용 동박으로 사용될 수 있다.

[0018] 더욱이, 본 발명의 전해 동박의 양면은 평활한 표면을 갖기 때문에, 전해 동박은 M면을 통상적인 구리 거칠기 처리, 합금층 처리 및 녹 방지 처리를 가하여 매우 낮은 프로파일(VLP) 동박을 형성할 수 있다. 본 발명의 전

해 동박의 M면은 비정상적인 돌출 입자를 갖지 않기 때문에, 광택이 나고 평활한 표면이다. 따라서, 구리 거칠기 처리 후에, M면의 표면 상에 구리 거칠기-입자는 균일하게 분포된다. 첨단 방전에 기인한 구리-거칠기 입자의 비정상적인 농축 현상이 일어나지 않을 것이다. 따라서, 동박은 보다 에칭에 접근 가능하여, 초미세 라인 인쇄 회로 기판에 적합하다.

[0019] 다른 구현으로, 본 발명의 전해 동박은 45kg/㎟이상, 바람직하게 45-60kg/㎟의 인장 강도를 갖는다. 본 발명의 전해 동박은 높은 인장 강도를 가져, 후속적인 제조공정에 사용시 우수한 조작성을 가지며 쉽게 주름을 발생시키지 않는다. 이는 열처리 후에 12%이상의 신장률을 갖는다.

[0020] 리튬 이온 2차 전지의 음극 집전체를 위한 동박의 표면은 탄소 물질로 코팅되고, 프레싱 및 슬리팅된다. 탄소 물질로 코팅되는 동안에, 동박의 인장 강도가 높을수록, 주름이 발생할 가능성은 낮아진다. 주름이 낮을수록, 탄소 물질을 이용한 코팅이 보다 균일해 진다. 본 발명의 전해 동박은 열처리 전에 우수한 인장 강도를 가져, 동박은 우수한 조작성을 가지며, 후속 공정에서 쉽게 주름지지 않는다.

[0021] 또한, 리튬 이온 2차 전지 내의 유기 전해질은 과도한 물을 함유하기 때문에, 충전 및 방전 중에 유기 전해질의 분해가 일어날 수 있다. 이는 리튬 이온 2차 전지의 내부 압력을 증가시켜, 위험을 발생시킨다. 따라서, 리튬 이온 2차 전지의 음극 집전체를 위한 동박은, 이의 표면이 탄소 물질로 코팅되고, 프레싱되고 슬리팅된 다음, 종종 140-150℃에서 수시간 동안 열처리하여 탄소 물질의 표면으로부터 물을 제거한 후에서야 전지 내로 조립된다. 열처리 중에, 물은 탄소 물질의 표면으로부터 제거되어, 동박 내에서 재결정화가 일어나 신장률을 증가시키고, 이에 따라 충전 및 방전 중에 리튬 이온 2차 전지의 팽창 및 수축에 기인한 동박의 파열을 예방하여, 리튬 이온 2차 전지의 효율성 및 장기 안정성을 유지할 수 있도록 한다.

[0022] 본 발명의 전해 동박은 열처리 후에 우수한 신장률을 가져, 상기 동박은 리튬 이온 2차 전지의 음극 집전체에 사용되거나 인쇄 회로 기판 상에 사용되든지 쉽게 파열되지 않는다.

[0023] 본 발명은 또한 활산구리 전해질에 과산화수소 용액을 제공하는 것을 포함하며, 여기서 6-30㎖/l의 과산화수소 용액이 시간당 활산구리 전해질 1톤당으로 첨가되며, 과산화수소 용액의 농도는 50중량%인, 전해 동박 제조방법을 개시한다.

[0024] 바람직한 구현으로, 상기 방법은 상기 개선된 활산구리 전해질로 전기화학 반응을 수행하기 전에 활성탄을 이용하여 상기 개선된 활산구리 전해질을 여과하는 것을 포함한다.

[0025] 본 발명의 방법에서, 과산화수소 용액은 활산구리 전해질에 첨가되어 활산구리 전해질 내의 기름 및 유기 불순물과 같은 불순물을 효과적으로 분해하고, 불순물 제거시 활성탄 필터의 효과를 증가시켜, 이에 따라 활산구리 전해질의 청결도를 증가시킨다.

[0026] 실시예

[0027] 이하, 특정 실시예를 사용하여 본 발명을 보다 상세히 설명한다. 당해 기술분야의 숙련자는 명세서의 상세한 설명에 기초하여 본 발명의 다른 장점 및 효과를 인식할 수 있을 것이다.

[0028] **실시예 1** 본 발명의 전해 동박의 제조

[0029] 전처리하지 않은 동선을 50중량%의 수성 황산 용액에 용해하여 270g/l의 황산구리($CuSO_4 \cdot 5H_2O$) 및 100g/l의 황산을 함유하는 황산구리 전해질을 제조하고, 6ml의 과산화수소(50중량%; Chang Chun Petrochemical Co., Ltd. 제조)를 시간당 황산구리 전해질 톤당 첨가하고, 그 혼합물을 활성탄 필터를 사용하여 여과하였다.

[0030] 8㎛ 두께의 전해 동박을 42℃의 액체 온도 및 50A/dm^2의 전류 밀도로 제조하였다. 본 발명의 전해 동박의 광택도, 거칠기, 인장 강도 및 신장률을 측정하고, 실시예 1에서 제조된 전해 동박의 M면의 외관을 도 1에 나타낸 바와 같이 2000X 배율로 주사 전자현미경(SEM)을 사용하여 관찰하였다. 실시예 1의 전해 동박을 탄소 물질을 이용하여 표면 코팅 시험하여 동박의 표면 상에서 주름이 발생하는지 관찰하였다. 최종적으로, 동박을 리튬 이온 2차 전지로 제조하였으며, 이를 동박의 표면 상에서 크랙이 발생하는지 관찰하기 위해 충전-방전 시험을 하였다.

[0031] **실시예 2** 본 발명의 전해 동박의 제조

[0032] 전처리하지 않은 동선을 50중량%의 수성 황산 용액에 용해하여 270g/l의 황산구리($CuSO_4 \cdot 5H_2O$) 및 100g/l의 황산을 함유하는 황산구리 전해질을 생성하고, 10ml의 과산화수소(50중량%; Chang Chun Petrochemical Co., Ltd. 제조)를 시간당 황산구리 전해질 톤당 첨가하고, 그 혼합물을 활성탄 필터를 사용하여 여과하였다.

[0033] 8㎛ 두께의 전해 동박을 42℃의 액체 온도 및 50A/dm^2의 전류 밀도로 제조하였다. 본 발명의 전해 동박의 광택도, 거칠기, 인장 강도 및 신장률을 측정하고, 실시예 2에서 제조된 전해 동박의 M면의 외관을 도 2에 나타낸 바와 같이 2000X 배율로 주사 전자현미경(SEM)을 사용하여 관찰하였다. 실시예 2의 전해 동박을 탄소 물질을 이용하여 표면 코팅 시험하여 동박의 표면 상에서 주름이 발생하는지 관찰하였다. 최종적으로, 동박을 리튬 이온 2차 전지로 제조하였으며, 이를 동박의 표면 상에서 크랙이 발생하는지 관찰하기 위해 충전-방전 시험을 하였다.

[0034] **실시예 3** 본 발명의 전해 동박의 제조

[0035] 전처리하지 않은 동선을 50중량%의 수성 황산 용액에 용해하여 270g/l의 황산구리($CuSO_4 \cdot 5H_2O$) 및 100g/l의 황산을 함유하는 황산구리 전해질을 생성하고, 20ml의 과산화수소(50중량%; Chang Chun Petrochemical Co., Ltd. 제조)를 시간당 황산구리 전해질 톤당 첨가하고, 그 혼합물을 활성탄 필터를 사용하여 여과하였다.

[0036] 8㎛ 두께의 전해 동박을 42℃의 액체 온도 및 50A/dm^2의 전류 밀도로 제조하였다. 본 발명의 전해 동박의 광택도, 거칠기, 인장 강도 및 신장률을 측정하고, 실시예 3에서 제조된 전해 동박의 M면의 외관을 도 3에 나타낸 바와 같이 2000X 배율로 주사 전자현미경(SEM)을 사용하여 관찰하였다. 실시예 3의 전해 동박을 탄소 물질을 이용하여 표면 코팅 시험하여 동박의 표면 상에서 주름이 발생하는지 관찰하였다. 최종적으로, 동박을 리튬 이온 2차 전지로 제조하였으며, 이를 동박의 표면 상에서 크랙이 발생하는지 관찰하기 위해 충전-방전 시험을 하였다.

[0037] **실시예 4** 본 발명의 전해 동박의 제조

[0038] 전처리하지 않은 동선을 50중량%의 수성 황산 용액에 용해하여 270g/l의 황산구리($CuSO_4 \cdot 5H_2O$) 및 100g/l의 황산을 함유하는 황산구리 전해질을 생성하고, 30ml의 과산화수소(50중량%; Chang Chun Petrochemical Co., Ltd. 제조)를 시간당 황산구리 전해질 톤당 첨가하고, 그 혼합물을 활성탄 필터를 사용하여 여과하였다.

[0039] 8㎛ 두께의 전해 동박을 42℃의 액체 온도 및 50A/dm^2의 전류 밀도로 제조하였다. 본 발명의 전해 동박의 광택도, 거칠기, 인장 강도 및 신장률을 측정하고, 실시예 4에서 제조된 전해 동박의 M면의 외관을 도 4에 나타낸

바와 같이 2000X 배율로 주사 전자현미경(SEM)을 사용하여 관찰하였다. 실시예 4의 전해 동박을 탄소 물질을 이용하여 표면 코팅 시험하여 동박의 표면 상에서 주름이 발생하는지 관찰하였다. 최종적으로, 동박을 리튬 이온 2차 전지로 제조하였으며, 이를 동박의 표면 상에서 크랙이 발생하는지 관찰하기 위해 충전-방전 시험을 하였다.

[0040] **비교예**

[0041] **비교예 1** 통상적인 전해 동박의 제조

[0042] 전처리하지 않은 동선을 50중량%의 수성 황산 용액에 용해하여 270g/l의 황산구리($CuSO_4 \cdot 5H_2O$) 및 100g/l의 황산(H_2SO_4)을 함유하는 황산구리 전해질을 생성하였다.

[0043] 그 다음, 상기 황산구리 전해질을 사용하였으며, 활성탄 필터를 사용하여 여과하였다.

[0044] 8㎛ 두께의 전해 동박을 42℃의 액체 온도 및 50A/dm^2의 전류 밀도로 제조하였다. 본 발명의 전해 동박의 광택도, 거칠기, 인장 강도 및 신장률을 측정하고, 비교예 1에서 제조된 전해 동박의 M면의 외관을 도 5에 나타낸 바와 같이 2000X 배율로 주사 전자현미경(SEM)을 사용하여 관찰하였다. 비교예 1의 전해 동박을 탄소 물질을 이용하여 표면 코팅 시험하여 동박의 표면 상에서 주름이 발생하는지 관찰하였다. 최종적으로, 동박을 리튬 이온 2차 전지로 제조하였으며, 이를 동박의 표면 상에서 크랙이 발생하는지 관찰하기 위해 충전-방전 시험을 하였다.

[0045] **비교예 2** (과산화수소의 불충분한 첨가를 이용한) 전해 동박의 제조

[0046] 전처리하지 않은 동선을 50중량%의 수성 황산 용액에 용해하여 270g/l의 황산구리($CuSO_4 \cdot 5H_2O$) 및 100g/l의 황산(H_2SO_4)을 함유하는 황산구리 전해질을 생성하고, 2ml의 과산화수소(50중량%; Chang Chun Petrochemical Co., Ltd. 제조)를 시간당 황산구리 전해질 톤당 첨가하고, 활성탄 필터를 사용하여 여과하였다.

[0047] 8㎛ 두께의 전해 동박을 42℃의 액체 온도 및 50A/dm^2의 전류 밀도로 제조하였다. 본 발명의 전해 동박의 열처리 후에, 광택도, 거칠기, 인장 강도 및 신장률을 측정하고, 비교예 2에서 제조된 전해 동박의 M면의 외관을 도 6에 나타낸 바와 같이 2000X 배율로 주사 전자현미경(SEM)을 사용하여 관찰하였다. 비교예 2의 전해 동박을 탄소 물질을 이용하여 코팅 시험하여 동박의 표면 상에서 주름이 발생하는지 관찰하였다. 최종적으로, 동박을 리튬 이온 2차 전지로 제조하였으며, 이를 동박의 표면 상에서 크랙이 발생하는지 관찰하기 위해 충전-방전 시험을 하였다.

[0048] 상기 실시예 1 내지 4, 및 비교예 1 및 2에서 제조된 전해 동박을 적절한 크기를 갖는 시편으로 잘라내었다. 시편을 광택의 유무에 대해 관찰하고, 이의 인장 강도, 신장률, 거칠기 및 광택도에 대해 측정하고, 탄소 물질로 코팅한 후에 전지 충전-방전 시험을 하였다. 시험 실시예에서 사용된 분석 방법을 하기에 상세히 나타내었다.

[0049] 광택도 시험:

[0050] 광택도계(BYK사; 모델 번호: micro-gloss 60° type)를 JIS Z8741 방법으로 사용하여, 즉, 60° 의 광 입사각에서 세로(기계) 방향(MD)으로 광택도를 측정하였다.

[0051] 거칠기(10 포인트의 평균 거칠기, Rz):

[0052] 측정은 α-타입 표면 거칠기 측정계(Kosaka Laboratory Ltd.; Model No. SE 1700) 및 IPC-TM-650 방법을 사용

하여 수행하였다.

[0053] 인장 강도 및 신장률:

[0054] 전해 동박을 100mm x 12.7mm(길이 x 폭) 크기의 시험 스트립으로 잘라내었다. IPC-TM-650 방법에 따라, AG-I 인장 강도 시험기(Shimadzu사 제조)를 사용하여 실온(약 25℃)에서 50mm의 척 거리(chuck distance) 및 50mm/min의 크로스헤드 속도의 조건 하에서 시험 스트립을 분석하였다.

[0055] 열 처리 후 신장률:

[0056] 전해 동박을 140℃에서 5시간 동안 구웠다. 전해 동박을 100mm x 12.7mm(길이 x 폭) 크기의 시험 스트립으로 잘라내었다. IPC-TM-650 방법에 따라, AG-I 인장 강도 시험기(Shimadzu사 제조)를 사용하여 실온(약 25℃)에서 50mm의 척 거리(chuck distance) 및 50mm/min의 크로스헤드 속도의 조건 하에서 시험 스트립을 분석하였다.

[0057] 탄소 물질을 이용한 코팅 시험:

[0058] 우선, 탄소 물질 슬러리를 네거티브 물질 배합물에 기초하여 제조하였다. 탄소 물질 슬러리의 총 중량에 기초하여, 네거티브 물질 배합물은 95중량%의 캐소드 활성 물질(Mesophase Graphite Powder Anode; MGPA), 1중량%의 도전제(즉, 전도성 탄소 분말, Super P), 1.6중량%의 하이드록시메틸 셀룰로오즈(CMC) 증점제 및 2.4중량%의 수성 스티렌-부타디엔 고무(SBR) 바인더를 포함한다. 네거티브 물질 배합물의 성분들을 혼합한 후, 탄소 물질 슬러리를 분당 5미터의 속도로 130㎛의 두께로 동박의 표면 상에 코팅하였다. 동박을 주름 발생에 대해 관찰하였다.

[0059] 전지 상에서 충전-방전 시험

[0060] 리튬 이온 2차 전지의 제조

[0061] N-메틸-2-피롤리돈(NMP)을 표 1에 나타낸 바와 같이 포지티브 물질(195중량%의 고체 대 액체 비율로(100g의 포지티브 물질: 195g의 NMP)을 위한 용매로 사용하여 포지티브 슬러리를 획득하였다. 물을 네거티브 물질을 위한 용매로 사용하여 네거티브 슬러리를 획득하였다.

[0062] 그 다음, 포지티브 슬러리를 알루미늄박 상에 코팅하고, 네거티브 슬러리를 실시예 1 내지 4 및 비교예 1 및 2에서 제조된 전해 동박 상에 코팅하였다. 용매가 증발된 후, 전해 동박을 프레싱하고, 특정 크기로 슬릿팅하여 포지티브 및 네거티브 전극을 형성하였다.

[0063] 포지티브 및 네거티브 전극을 전지 내로 조립하기 전에, 네거티브 전극을 140℃에서 5시간 구워 네거티브 물질의 표면으로부터 수분을 제거하고, 전해 동박에서 재결정화가 일어나도록 하여 전해 동박의 신장률을 증가시켰다. 그 후, 양극, 두 분리기(Celgard사 제조), 및 음극을 함께 권선하고, 용기에 두었다. 전해질로 용기를 채우고, 그 용기를 봉하여 전지를 형성하였다. 전지의 사양은 Battery Cylinder Type 18650이다.

[0064] 전해질은 에틸렌 카보네이트(EC)와 에틸 메틸 카보네이트의 1:2 부피비의 혼합 용액에 1M의 리튬 헥사플루오로 포스페이트($LiPF_6$) 및 2중량%의 비닐렌 카보네이트(VC)를 첨가하여 제조하였다. 실시예 1 내지 4 및 비교예 1 및 2의 전해 동박을 이용하여 제조된 리튬 이온 2차 전지를 충전-방전 시험하였다.

표 1

[0065]

포지티브 물질 배합물:	포지티브 물질의 총 중량 기준으로
포지티브 활성 물질($LiCoO_2$)	89중량%
도전제(플랭키드 그라파이트; KS6)	5중량%
도전제(전도성 탄소 분말, Super P)	1중량%
바인더(PVDF1300)	5중량%
네거티브 물질 배합물:	네거티브 물질의 총 중량 기준으로
네거티브 활성 물질(MGPA)	95중량%
도전제(전도성 탄소 분말, Super P)	1중량%
증점제(CMC)	1.6중량%
수성 바인더(SBR)	2.4중량%

[0066] 충전-방전 시험:

[0067] 실시예 1 내지 4 및 비교예 1 및 2의 전해 동박을 사용하여 제조된 리튬 이온 2차 전지를 300회 동안 반복적으로 충전 및 방전하였다. 그 다음, 리튬 이온 2차 전지를 분해하여 동박에서 크랙이 일어나는지 관찰하였다. 충전 모드는 정전류-정전압(CCCV) 모드이었고, 충전 전압은 4.2V이었으며, 충전 전류는 1C이었다. 방전 모드는 정전류(CC) 모드이었고, 방전 전압은 2.8V이었고, 방전 전류는 1C이었다. 전지에서의 충전-방전 시험은 실온(25℃)에서 수행하였다.

표 2

[0068] 전해 동박의 특성의 측정 결과

	실시예 1	실시예 2	실시예 3	실시예 4	비교예 1	비교예 2
인장 강도 (kg/mm^2)	48.5	53.2	57.6	56.9	39.8	40.2
신장률(%)	3.7	4.2	5.4	5.3	3.1	3.3
140℃에서 5시간 열처리 후, 신장률(%)	12.8	14.3	15.6	15.4	9.2	9.6
S면에서 거칠기(Rz)(㎛)	1.08	1.06	1.09	1.07	1.06	1.09
M면에서 거칠기(Rz)(㎛)	1.53	1.37	1.32	1.34	2.12	1.96
S면과 M면 사이의 거칠기(Rz) 차이(㎛)	0.45	0.31	0.23	0.27	1.06	0.87
MD 방향에서 M면의 광택도 (Gs60°)	68	72	82	80	35	43
M면의 시각적 관찰	○	○	○	○	×	×
탄소 물질로 코팅 시험한 후, 동박 상에 주름이 발생하였는지 여부	무	무	무	무	탄소 물질과 동박의 경계에서 주름이 발생하였음	탄소 물질과 동박의 경계에서 주름이 발생하였음
충전-방전 시험 후, 동박 상에 크랙이 발생하였는지 여부	무	무	무	무	크랙이 발생하였음	크랙이 발생하였음

[0069] ○: 외관에서 시각적으로 광택이 관찰됨

[0070] ×: 외관에서 시각적으로 광택이 관찰되지 않음

[0071] 도 1 내지 6에 나타낸 바와 같이, 황산구리 전해질에 과산화수소의 첨가는 전해 동박의 M면의 거칠기를 낮출 수 있으며, M면 상에서 비정상적 돌출 입자의 발생도 낮출 수 있었다. 과산화수소가 비교예 1의 황산구리 전해질에 첨가되지 않음에 따라, 비정상적 돌출 입자가 M면 상에서 발견되었으며, S면과 M면 사이의 거칠기 차이는 현저하였으며, 인장 강도는 더 낮았다. 네거티브 탄소 물질 슬러리로 코팅한 후에, 탄소 물질과 동박의 경계에서 주름이 발생하였다. 또한, 140℃에서 5시간 동안 열 처리한 후에, 신장률은 더 낮았으며, 이에 따라 동박은 전

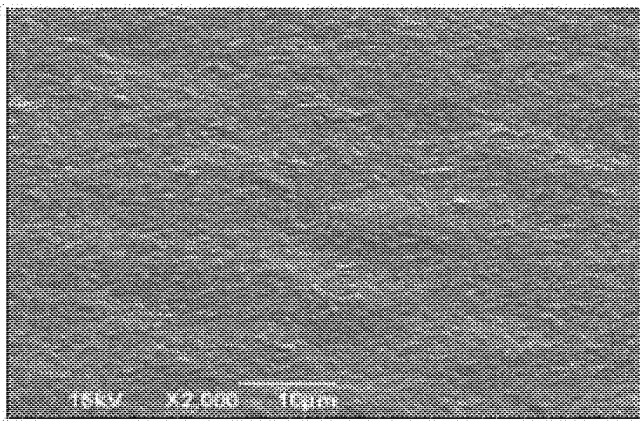
지를 충전-방전 시험한 후에 크랙이 발생하였다.

[0072] 또한, 표 2의 결과는 본 발명의 전해 동박을 제조하는 방법이 간단하고, 안전성 문제를 갖지 않음을 보여준다. 본 발명의 전해 동박은 높은 인장 강도를 가지며, 이의 S면과 M면의 거칠기 모두가 낮으며, 그리고 S면과 M면 사이의 거칠기 차이가 극히 작다. 또한, 네거티브 탄소 몰질 슬러리로 코팅한 후에, 전해 동박은 주름이 발생하지 않는다. 140℃에서 5시간 동안 열 처리한 후에, 전해 동박은 뛰어난 신장률을 갖는다. 리튬 이온 2차 전지를 충전-방전 시험한 후에, 전해 동박은 크랙을 발생하지 않으며, 리튬 이온 2차 전지의 수명을 유지할 수 있다.

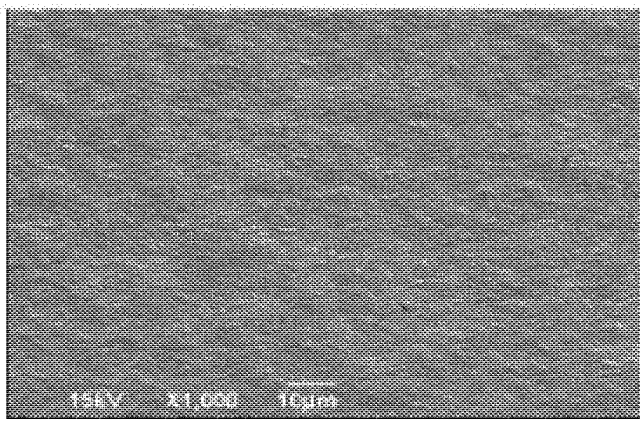
[0073] 상기 실시예는 본 발명의 원리를 설명하기 위해 사용된 것일 뿐이며, 본 발명을 한정하려는 것은 아니다. 상기 실시예는 하기 첨부된 청구범위에 기재된 본 발명의 정신 및 범위를 벗어나지 않고 당해 기술분야의 숙련자에 의해 모두 변형 및 변경될 수 있다.

도면

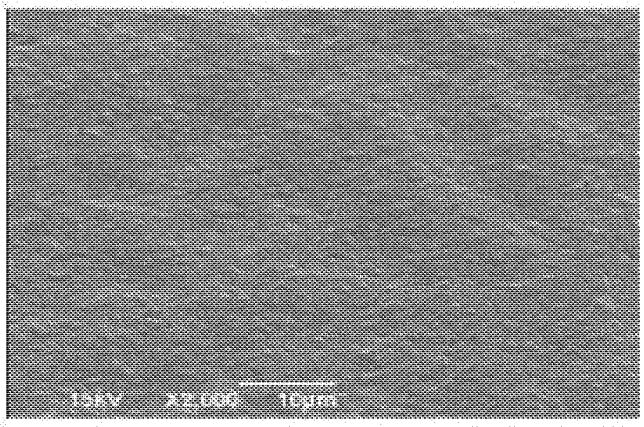
도면1



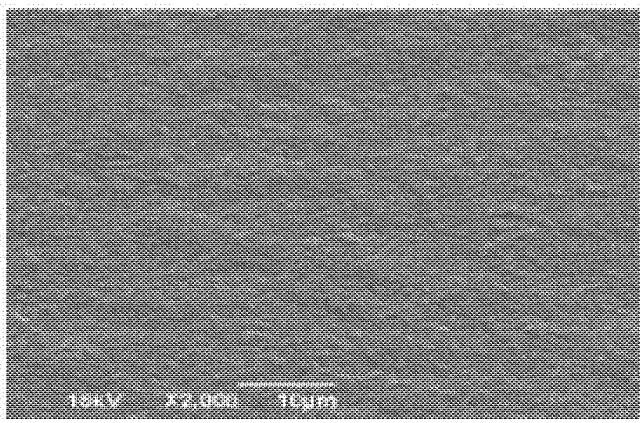
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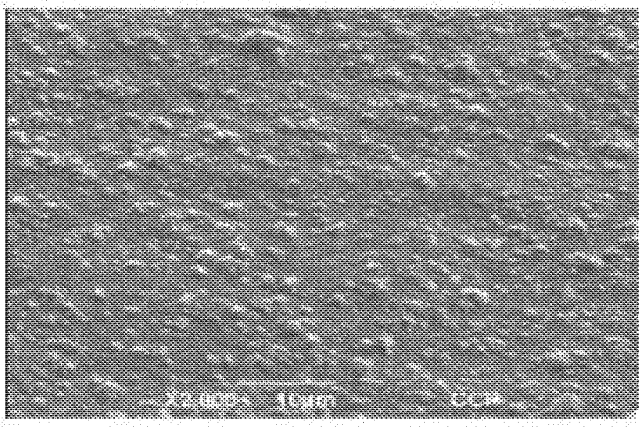
도면3



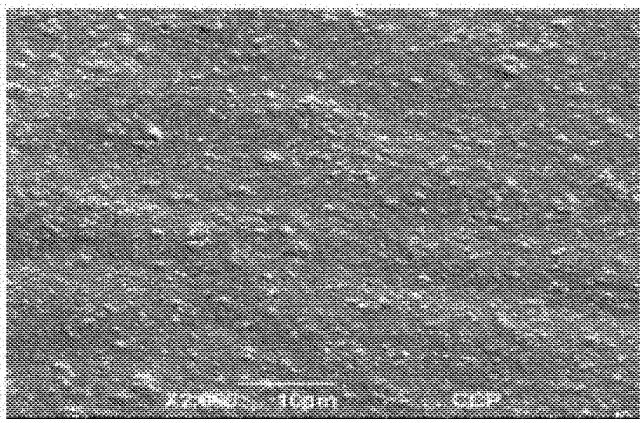
도면4



도면5



도면6

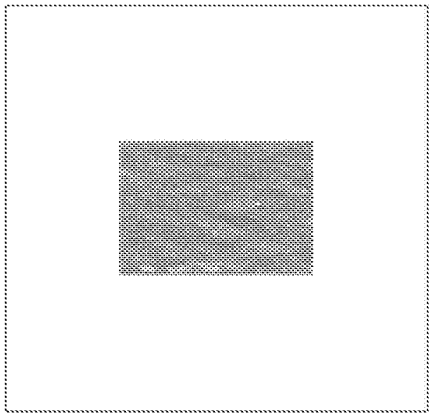


ELECTROLYTIC COPPER FOIL AND METHOD FOR PRODUCING SAME

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(52) CPC	

(71) Applicant	CHANG CHUN PETROCHEMICAL CORPORATION (TW)
(72) Inventor	TSAI CHEN PING (TW) CHENG KUEI SEN (TW) LIN CHYEN FU (TW)

Repr. Drawing



Zoom

Abstract An electrolytic copper foil is provided. The electrolytic copper foil has a shiny surface and a mat surface facing the shiny surface. A roughness difference between the shiny surface and the mat surface is 0.5 micrometer or less. The electrolytic copper foil has tensile strength of 45 kg/mm^2 or more and is applied to a lithium ion secondary battery.COPYRIGHT KIPO 2014

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME
First Named Inventor/Applicant Name:	Dae Young KIM
Filer:	Taeksoo Lee
Attorney Docket Number:	P11304US

Filed as Large Entity

Filing Fees for U.S. National Stage under 35 USC 371

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
NATIONAL STAGE FEE	1631	1	280	280
NATL STAGE SEARCH FEE - REPORT PROVIDED	1642	1	480	480
NATIONAL STAGE EXAM - ALL OTHER CASES	1633	1	720	720
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**1480**

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Authorized User	
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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Application Data Sheet	P11304_ads.pdf	1822759 b70365ae9737a9898279377183b336406d7d497a	no	8
Warnings:					
Information:					
2	Oath or Declaration filed	P11304_dec.pdf	650942 6ed18f5c14fdd57eafb189d24ab1ba7ac6d73a2a	no	3
Warnings:					
Information:					
3	Information Disclosure Statement (IDS) Form (SB08)	P11304_ids.pdf	1035328 8e164e565fc77c746f4e3a6313fb03c2541d6218	no	4
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4	Preliminary Amendment	P11304_pa.pdf	1549962 f1c0d63de8f2e9354a90ddb9e81c4b4998bd2464	no	9
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5	Power of Attorney	P11304_poa.pdf	1434136 8e6ca6b9bb26093ab91a0f0779347bbc1fffec48	no	3
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Information:					
6		P11304_spc.pdf	5459168 aa33d705ddbc484cbb8e80c2704f64879f40fd74	yes	22
	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	

	Specification		1	17	
	Claims		18	21	
	Abstract		22	22	
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7	Drawings-only black and white line drawings	FIGS.pdf	62083 0a273352545fa2e6ea9e1724eddf294b9e828586	no	1
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8	Documents submitted with 371 Applications	pct_IB301.pdf	51853 bdd230923ccda2909f53a68effd3cbb369605871	no	1
Warnings:					
Information:					
9	Documents submitted with 371 Applications	pct_IB304.pdf	60512 7b55def53434186af178db4be007a1aed9b2be7f	no	1
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10	Documents submitted with 371 Applications	pct_request.pdf	64188 a193a1646f289c76b72f5e729d10ca0d5516bf64	no	5
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11	Documents submitted with 371 Applications	pct_specification.pdf	297255 e0e481aa20ba37450aab52ba221b67aa21fbec3b	no	15
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12	Documents submitted with 371 Applications	Search_report.pdf	529678 b2c9932b9d0eb65c59f6c87a8676c0d5843ed732	no	4
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13	Foreign Reference	JP2000182623.pdf	984829 ba3cfed162065b1b043907abc24a25307d1455f5	no	6
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Warnings:					
Information:					
21	Fee Worksheet (SB06)	fee-info.pdf	35070 e8d0828ce6ace94e8ee908e624518fa2374f736e	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	26739206	

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.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	P11304US
	Application Number	
Title of Invention	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, 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
	Dae Young		KIM	

Residence Information (Select One) US Residency ● Non US Residency Active US Military Service

City	Yongin-si	Country of Residence [i]	KR

Mailing Address of Inventor:

Address 1	101-1205, (Youngpung Apt., Dongcheon-dong)
Address 2	22, Sinsu-ro 783beon-gil, Suji-gu
City	Yongin-si, Gyeonggi-do
State/Province	
Postal Code	16826
Country [i]	KR

Inventor 2 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	Osan-si	Country of Residence [i]	KR

Mailing Address of Inventor:

Address 1	105-1902, (Sema e-Pyeonhansesang Apt.,
Address 2	Yangsan-dong) 460, Yangsan-ro
City	Osan-si, Gyeonggi-do
State/Province	
Postal Code	18105
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:

PTO/AIA/14 (11-15)
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	P11304US
	Application Number	
Title of Invention	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME	

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	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME		
Attorney Docket Number	P11304US	**Small Entity Status Claimed**	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)		**Suggested Figure for Publication (if any)**	

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)

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Title of Invention	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME	

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	Pending	Remove	
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	a 371 of international	PCT/KR2016/004449	2016-04-28

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button. Add

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)
10-2015-0090000	KR	2015-06-24	

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.

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Title of Invention	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME	

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.

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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.

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	Application Number	
Title of Invention	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, 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)	2016-10-26
First Name	Taeksoo	Last Name	Lee	Registration Number	61976

Additional Signature may be generated within this form by selecting the Add button. Add

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	P11304US
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Title of Invention	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, ELECTRODE COMPRISING THE SAME, SECONDARY BATTERY COMPRISING THE SAME, AND METHOD FOR MANUFACTURING THE SAME	

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.

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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	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, 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: Dae Young KIM Date (Optional): 2016. 10. 11

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.

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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	ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR COMPRISING THE SAME, 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.

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LEGAL NAME OF INVENTOR

Inventor: Seung Min KIM Date (Optional): 2016. 10. 12

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.

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

Privacy Act Statement

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

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

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

Doc code: 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	Dae Young KIM
	Art Unit	
	Examiner Name	
	Attorney Docket Number	P11304US

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	1	20150340639	A1	2015-11-26	MITSUI MINING & SMELTING CO., LTD	
	2	20160260981	A1	2016-09-08	ILJIN MATERIALS CO., LTD	
	3	20140193660	A1	2014-07-10	CHANG CHUN PETROCHEMICAL CO., LTD.	
	4	20010051282	A1	2001-12-13	Charles B. YATES et al.	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Dae Young KIM
	Art Unit	
	Examiner Name	
	Attorney Docket Number	P11304US

	1	2000-182623	JP	A	2000-06-30	NIPPON DENKAI KK		☒
	2	2014-135175	JP	A	2014-07-24	MITSUI MINING & SMELTING CO LTD	Also published as US Patent Application Publication No. US 2015-0340639	☒
	3	10-1449342	KR	B1	2014-10-13	ILJIN M ATERIALS CO., LTD.	Also published as US Patent Application Publication No. US 2016-0260981	☒
	4	10-2014-0090069	KR	A	2014-07-16	CHANG CHUN PETROCHEM ICAL CORPORATION	Also published as US Patent Application Publication No. US 2014-0193660	☒

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	1	Search Report for International Application No. PCT/KR2016/004449	

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Dae Young KIM
	Art Unit	
	Examiner Name	
	Attorney Docket Number	P11304US

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)	2016-10-26
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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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)).

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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.

[redacted]

대한민국 특허청
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 : 10-2015-0090000
Application Number

출 원 년 월 일 : 2015년 06월 24일
Filing Date JUN 24, 2015

출 원 인 : 엘에스엠트론 주식회사
Applicant(s) LS Mtron Ltd.

2016 년 05 월 03 일

특 허 청
COMMISSIONER

[redacted]

2015-06-24

【서지사항】

【서류명】 특허출원서

【출원구분】 특허출원

【출원인】

【명칭】 엘에스엠트론 주식회사

【출원인코드】 1-2008-029030-3

【대리인】

【명칭】 특허법인 천문

【대리인코드】 9-2009-100001-0

【포괄위임등록번호】 2015-043650-5

【발명의 국문명칭】 전해 동박, 그것을 포함하는 집전체, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법

【발명의 영문명칭】 Electrolytic Copper Foil, Current Collector Comprising The Same, Electrode Comprising The Same, Secondary Battery Comprising The Same, and Method for Manufacturing The Same

【발명자】

【성명】 김대영

【성명의 영문표기】 KIM DAE YOUNG

【주민등록번호】 771110-1XXXXXX

【우편번호】 448-513

【주소】 경기도 용인시 수지구 동천동 911 영풍아파트 101동 1205호

【국적】 KR

【발명자】

【성명】 김승민

【성명의 영문표기】 KIM SEUNG MIN

2015-06-24

【주민등록번호】 770119-1XXXXXX

【우편번호】 447-768

【주소】 경기도 오산시 양산동 668-1 세마e-편한세상아파트 105동 1902호

【국적】 KR

【취지】 위와 같이 특허청장에게 제출합니다.

대리인 특허법인 천문 (서명 또는 인)

【수수료】

【출원료】	0	면	46,000 원
【가산출원료】	26	면	0 원
【우선권주장료】	0	건	0 원
【심사청구료】	0	항	0 원
【합계】	46,000 원		

【명세서】

【발명의 명칭】

전해 동박, 그것을 포함하는 집전체, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법{Electrolytic Copper Foil, Current Collector Comprising The Same, Electrode Comprising The Same, Secondary Battery Comprising The Same, and Method for Manufacturing The Same}

【기술분야】

<1> 본 발명은 전해 동박, 그것을 포함하는 집전체, 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> 한편, 이차전지가 충분히 높은 충전/방전 용량을 갖고 있다고 하더라도 충전/방전 사이클이 반복됨에 따라 이차전지의 충전/방전 용량이 급격히 감소한다면(즉, 용량 유지율이 낮다면 또는 수명이 짧다면), 소비자는 이차전지를 빈번하게 교체할 필요가 있을 것이고, 그로 인해 소비자 불편 및 자원 낭비가 초래될 것이다.

【발명의 내용】

【해결하려는 과제】

<7> 따라서, 본 발명은 위와 같은 관련 기술의 제한 및 단점들에 기인한 문제점들을 방지할 수 있는 전해 동박, 그것을 포함하는 집전체, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법에 관한 것이다.

<8> 본 발명의 일 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전해 동박을 제공하는 것이다.

<9> 본 발명의 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 집전체를 제공하는 것이다.

<10> 본 발명의 또 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전극을 제공하는 것이다.

<11> 본 발명의 또 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 제공하는 것이다.

<12> 본 발명의 또 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전해 동박을 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 면; 및 상기 제1 면의 반대 편의 제2 면을 포함하되, 상기 제1 및 제2 면들 각각은 10 내지 100 개의 피크 수 조도(peak count roughness: R_{pc})를 갖는 - 상기 제1 및 제2 면들 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값이고, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스틸-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 10㎜의 단위 샘플링 길이당 0.5㎛의 상위 기준선(upper criteria line: C1) 위로 솟아 있는 유효 피크들의 개수이고, 상기 유효 피크들 중

이웃하는 유효 피크들 사이에는 -0.5㎛의 하위 기준선(lower criteria line: C2)보다 깊은 적어도 하나의 골(valley)이 존재함 -, 이차전지용 전해동박이 제공된다.

<15> 본 발명의 다른 관점에 따라, 10 내지 100 개의 피크 수 조도(R_{pc})를 각각 갖는 제1 및 제2 면들을 포함하는 전해동박; 및 상기 전해동박 상의 보호층을 포함하되, 상기 보호층은 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는, 이차전지용 집전체가 제공된다.

<16> 본 발명의 또 다른 관점에 따라, 10 내지 100 개의 피크 수 조도(R_{pc})를 각각 갖는 제1 및 제2 면들을 포함하는 전해동박을 포함하는 집전체; 및 상기 집전체 상의 활물질층을 포함하되, 상기 활물질층은, 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 선택되는 하나 이상의 활물질을 포함하는, 이차전지용 전극이 제공된다.

<17> 본 발명의 또 다른 관점에 따라, 충전 시 리튬 이온을 제공하는 양극(cathode); 방전 시 전자 및 리튬 이온을 제공하는 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 포함하되, 상기 음극은, 10 내지 100 개의 피크 수 조도(R_{pc})를 각각 갖는 제1 및 제2 면들을 포함하는 전해동박을 포함하는 집전체; 및 상기 집전체 상의 활물질층

을 포함하는, 이차전지가 제공된다.

<18> 본 발명의 또 다른 관점에 따라, 전해액 내에 서로 이격되게 배치된 양극판 및 회전 음극드럼을 통전시킴으로써 상기 회전 음극드럼 상에 구리를 석출시키는 전해동박 제조방법으로서, 구리 와이어를 열처리하는 단계; 상기 열처리된 구리 와이어를 산세하는 단계; 상기 산세된 구리 와이어를 상기 전해액에 투입하는 단계; 상기 투입 단계 후에 상기 양극판 및 회전 음극드럼을 통전시킴으로써 전기 도금을 수행하는 단계; 및 상기 전기 도금 중에 상기 전해액으로부터 고형 불순물을 제거하기 위한 연속 여과를 수행하는 단계를 포함하는, 전해동박 제조방법이 제공된다.

<19> 위와 같은 본 발명에 대한 일반적 서술은 본 발명을 예시하거나 설명하기 위한 것일 뿐으로서, 본 발명의 권리범위를 제한하지 않는다.

【발명의 효과】

<20> 본 발명에 의하면, 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】

<21> 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 스틸-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일을 예시한다.

【발명을 실시하기 위한 구체적인 내용】

<22> 이하에서는 첨부된 도면을 참조하여 본 발명의 실시예들을 상세하게 설명한다.

<23> 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.

<24> 리튬 이온 이차전지는, 충전 시 전자 및 리튬 이온을 제공하는 양극(cathode), 방전 시 전자 및 리튬 이온을 제공하는 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 절연시켜 주는 분리막(separator)을 포함한다.

<25> 도 1은 본 발명의 일 실시예에 따른 이차전지용 전극의 단면도이다.

<26> 도 1에 예시된 바와 같이, 본 발명의 일 실시예에 따른 이차전지용 전극(100)은 집전체(110) 및 활물질층(120)을 포함한다. 도 1은 상기 집전체(110)의 상

하면 모두 위에 형성된 활물질층(120)을 예시하고 있으나, 본 발명이 이에 국한되는 것은 아니며, 상기 활물질층(120)은 상기 집전체(110)의 일 면 상에만 형성될 수도 있다.

<27> 리튬 이차전지에 있어서, 양극 활물질과 결합되는 양극 집전체로서는 알루미늄 호일(foil)이 사용되고 음극 활물질과 결합되는 음극 집전체로서는 동박이 사용되는 것이 일반적이다.

<28> 본 발명의 일 실시예에 의하면, 상기 이차전지용 전극(100)은 음극이고, 상기 집전체(110)는 음극 집전체이며, 상기 활물질층(120)은 음극 활물질을 포함한다.

<29> 음극 집전체인 본 발명의 집전체(110)는 3 내지 20 ㎛의 두께 및 30 내지 60 kgf/㎟의 인장강도를 갖는 전해 동박(111)을 포함한다. 또한, 도 1에 예시된 바와 같이, 상기 집전체(110)는 상기 전해 동박(111) 상의 보호층(112)을 더 포함할 수 있다. 도 1은 상기 전해 동박(111)의 상하면 모두 위에 형성된 보호층(112)을 예시하고 있으나, 본 발명이 이에 국한되는 것은 아니며, 상기 보호층(112)은 상기 전해 동박(111)의 일 면 상에만 형성될 수도 있다.

<30> 본 발명의 전해 동박(111)은 전기도금을 통해 회전 음극드럼 상에 형성될 수 있으며, 전기도금 과정에서 상기 회전 음극드럼과 접촉하였던 제1 면[일명 “샤이니 면(Shiny surface)”](111a) 및 상기 제1 면의 반대 편의 제2 면[일명 “매트 면(Matte surface)”](111b)을 갖는다.

<31> 샤이니 면(111a)이 매트 면(111b)에 비해 더 낮은 조도를 갖는 것이 일반적이기는 하지만 본 발명이 이에 국한되는 것은 아니며 샤이니 면(111a)의 조도가 매트 면(111b)의 조도와 동일하거나 더 높을 수도 있다. 여기서, 샤이니 면(111a)과 매트 면(111b)의 조도는 10점 평균조도(ten-point mean roughness: R_{zJIS})를 의미한다.

<32> 상기 활물질층(120)은, 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 선택되는 하나 이상의 활물질을 음극 활물질로서 포함한다.

<33> 이차전지의 충방전 용량을 증가시키기 위하여, Si를 소정량 포함한 음극 활물질들의 혼합물로 상기 활물질층(120)이 형성될 수 있다.

<34> 한편, 이차전지의 충방전이 반복됨에 따라 활물질층(120)의 수축 및 팽창이 번갈아 발생하고, 이것은 상기 활물질층(120)과 상기 집전체(110)의 분리를 유발하여 이차전지의 충방전 효율을 저하시킨다. 따라서, 이차전극이 일정 수준 이상의 용량 유지율 및 수명을 확보하기 위해서는(즉, 이차전지의 충방전 효율 저하를 억제하기 위해서는), 상기 집전체(110)가 상기 활물질에 대하여 우수한 코팅성을 가짐으로써 상기 집전체(110)와 활물질층(120)의 접착 강도가 높아야 한다.

<35> 거시적 관점에서 볼 때, 상기 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)의 10점 평균조도(R_{zJIS})가 작을수록, 상기 집전체(110)를 포함하는 이차전지

의 충방전 효율이 대체로 덜 저하되는 경향이 있다.

<36> 따라서, 본 발명의 일 실시예에 따른 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b) 각각은 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖는다. 상기 샤이니 면(111a) 또는 매트 면(111b)이 2㎛를 초과하는 10점 평균조도(R_{zJIS})를 갖는다면 상기 집전체(110)와 활물질층(120) 사이의 접촉 균일성이 일정 수준에 미치지 못할 것이고, 따라서 이차전지가 업계에서 요구되는 90% 이상의 용량 유지율을 만족하지 못할 것이다.

<37> 그러나, 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)이 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖는다고 하더라도, 그러한 전해 동박(111)이 반드시 90% 이상의 이차전지 용량 유지율을 담보할 수 있는 것이 아님이 본 출원인에 의해 밝혀졌다. 즉, 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)의 낮은 10점 평균조도(R_{zJIS})(예를 들어, 2㎛ 이하)가 90% 이상의 이차전지 용량 유지율에 대한 충분 조건이 될 수 없다.

<38> 특히, 이차전지의 고용량화를 위하여 상기 활물질층(120)이 Si를 포함할 경우 전해 동박(111)의 10점 평균조도(R_{zJIS})와 이차전지의 용량 유지율 사이의 연관성이 더욱 낮은 것으로 드러났다.

<39> 본 출원인은, 연구를 거듭한 결과, 90% 이상의 용량 유지율을 안정적으로 확보함에 있어서 전해 동박(111)의 피크 수 조도(peak count roughness: R_{pc})가 중요

한 인자임을 밝혀내었다.

<40> 이하에서는, 도 2를 참조하여 전해 동박(111)의 피크 수 조도(R_{pc})를 설명한다.

<41> 본 명세서에서 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b) 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값을 지칭하며, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스틸-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 10㎜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 피크 수 조도(R_{pc})의 측정에 이용되는 “유효 피크”가 될 수는 없으며, “유효 피크” 개수를 구함에 있어서 상기 피크들 중 상대적으로 더 낮은 피크는 무시된다.

<42> 본 발명에 의하면, 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)은 10 내지 100 개(count)의 피크 수 조도(R_{pc})를 갖는다.

<43> 상기 피크 수 조도(R_{pc})가 10개 미만인 경우 이차전지의 용량 유지율의 열화

가 발생하는데, 이것은 이차전지의 충방전시 국부적으로 돌출된 산(mountain)에 응력이 집중되기 때문인 것으로 파악된다.

<44> 반면, 피크 수 조도(R_{pc})가 100개를 초과하는 경우에도 이차전지의 용량 유지율의 열화가 마찬가지로 발생하는데, 이것은 너무 많은 산들로 인해 상기 전해 동박(111) 상에 활물질이 균일하게 코팅되지 못하기 때문인 것으로 판단된다.

<45> 본 발명의 일 실시예에 의하면 상기 집전체(110)의 양 면들 모두에 활물질이 코팅되기 때문에, 상기 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)의 피크 수 조도(R_{pc}) 차이는 60개 이하인 것이 바람직하다. 상기 피크 수 조도(R_{pc}) 차이가 60개를 초과하면 양 면들(111a, 111b)의 표면 형상의 차이로 인해 이차전지의 용량 유지율 열화가 발생한다.

<46> 전술한 바와 같이, 본 발명의 이차전지용 집전체(110)는 상기 전해 동박(111) 상의 보호층(112)을 더 포함할 수 있다. 상기 보호층(112)은 상기 전해 동박(111)의 방청 처리를 통해 형성될 수 있다. 즉, 본 발명의 전해 동박(111)은 그대로 집전체로서 사용될 수도 있지만, 크롬산염, 벤조트리아졸, 및/또는 실란계 화합물로 방청 처리(anticorrosion treatment)되는 것이 바람직하다. 이와 같은 방청 처리는 전해 동박(111)의 부식을 방지하고, 내열성을 향상시키며, 활물질층(120)과의 접착 강도를 높여 이차 전지의 충방전 효율 저하를 억제시킬 수 있다.

<47> 이하에서는, 본 발명의 일 실시예에 따른 전해 동박의 제조방법을 구체적으로 설명한다.

<48> 상기 전해 동박(111)의 제조에 이용되는 제박기는 전해액이 담겨진 전해조, 상기 전해액 내에서 서로 이격되어 있는 회전 음극드럼 및 양극판을 포함한다.

<49> 50 내지 100 g/L의 구리 이온, 50 내지 150 g/L의 황산 및 50 ppm 이하의 염소 이온을 포함하는 전해액에 하이드로에틸 셀룰로오스(HEC), 유기 황화물, 유기 질화물, 및/또는 티오요소(thiourea)계 화합물과 같은 유기 첨가제를 소량 첨가한 후, 10 내지 80 A/dm^2의 전류밀도로 40 내지 60 ℃에서 상기 회전 음극드럼 표면에 구리를 전착함으로써 전해 동박(111)을 제조한다.

<50> 상기 전해 동박(111)의 샤이니 면(111a)의 10점 평균조도(R_{zJIS}) 및 피크 수 조도(R_{pc})는 회전 음극드럼 표면(전기도금에 의해 구리가 석출되는 면)의 연마 정도에 의존한다.

<51> 본 발명에 의하면, 상기 샤이니 면(111a)이 10 내지 100 개의 피크 수 조도(R_{pc}) 및 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖도록 하기 위하여, #800 내지 #1500의 입도(Grit)를 갖는 연마 브러시로 상기 회전 음극드럼의 표면이 연마된다.

<52> 상기 전해 동박(111)의 매트 면(111b)의 10점 평균조도(R_{zJIS}) 및 피크 수 조도(R_{pc})는 전기도금에 이용되는 전해액의 조성(특히, 유기 불순물 및 금속 불순물의 농도), 전기도금의 전류 밀도 등에 의존한다.

<53> 본 발명에 의하면, 상기 매트 면(111b)이 10 내지 100 개의 피크 수 조도

(R_{pc}) 및 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖도록 하기 위하여, 상기 전해액 내 유기 불순물 및 금속 불순물의 농도가 각각 1g/L 이하 및 10g/L 이하로 제어되며, 10 내지 80 A/dm^2의 전류밀도로 상기 전기도금이 수행된다.

<54> 또한, 본 발명에 의하면, 상기 전해액 내 유기 불순물 및 금속 불순물의 농도를 각각 1g/L 이하 및 10g/L 이하로 제어하기 위하여, 고순도 구리 와이어를 전해액에 투입하기 전에 600 내지 800℃(예를 들어, 약 700℃)의 고온에서 열처리하여 유기물을 태운 후 황산 등의 산으로 산세(acid cleaning) 한다. 또한, 전기도금 중에 상기 전해액으로부터 유기 불순물 및 금속 불순물을 포함하는 고형 불순물을 제거하기 위한 연속 여과를 수행함으로써 상기 전해액 내의 유기 불순물 및 금속 불순물의 농도를 각각 1g/L 이하 및 10g/L 이하로 유지시킨다.

<55> 이어서, 크롬산염(chromate), 벤조트리아졸(benzotriazole: BTA), 및/또는 실란계 화합물(silane compound)을 이용한 방청 처리(anticorrosion treatment)를 통해 상기 전해 동박(111)의 샤이니 면(111a) 및/또는 매트 면(111b) 상에 보호층(112)을 형성함으로써 본 발명의 집전체(110)를 제조할 수 있다.

<56> 예를 들어, 1 내지 10 g/L의 중크롬산 칼륨 용액에 상기 전해 동박(111)을 상온에서 2 내지 20초 침지시킴으로써 상기 보호층(112)을 형성할 수 있다.

<57> 이어서, 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 선택되는 하나 이상의 음극 활물질을 상기

집전체(110) 상에 코팅함으로써 본 발명의 이차전지용 전극(즉, 음극)을 제조한다.

<58> 예를 들어, 탄소 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 집전체(110) 상에 20 내지 60㎛ 두께로 상기 슬러리를 도포하고, 110 내지 130℃에서 0.5 내지 1.5 ,ton/cm^2의 압력으로 프레스한다.

<59> 이상의 방법으로 제조된 본 발명의 이차전지용 전극(음극)과 함께 통상의 양극, 전해질, 및 분리막을 이용하여 리튬 이차전지를 제조할 수 있다.

<60> 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.

<61> * 전해 동박의 제조

<62> 실시예 1 내지 4 및 비교예 1 내지 4

<63> i) 구리 와이어 열처리 여부/온도, ii) 전기 도금 수행시 연속 여과 수행 여부, 및/또는 iii) 회전 음극 드럼의 표면 연마에 이용된 연마 브러시의 입도를 아래의 표 1과 같이 변경한 것을 제외하고는 동일한 조건 하에서 전해 동박들을 각각 제조하였다.

<64> 이어서, 상기 전해 동박들의 샤이니 면 및 매트 면의 피크 수 조도(R_{pc})를 Mahr社의 Mahrsurf M300 조도계를 이용하여 각각 측정하였고, 그 결과를 아래의 표

1에 나타내었다.

<65> 전술한 바와 같이, 샤이니 면과 매트 면 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값이며, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스틸-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 10㎜의 단위 샘플링 길이당 0.5㎛의 상위 기준선(C1) 위로 솟아 있는 유효 피크들의 개수이다.

<66> 상위 기준선(C1) 위로 솟아 있는 이웃하는 피크들 사이에 -0.5㎛의 하위 기준선(C2)보다 깊은 골이 하나도 존재하지 않는 경우에는, "유효 피크" 개수를 구함에 있어서 상기 피크들 중 상대적으로 더 낮은 피크는 무시되었다.

<67> 【표 1】

	구리 와이어 열처리 온도(℃)	연속 여과 수행 여부	연마 브러시 입도 (#)	매트 면의 R_{pc} (count)	샤이니 면의 R_{pc} (count)	R_{pc} 차이 (count)
실시예1	720	○	1200	13	42	29
실시예2	700	○	1400	20	24	4
실시예3	680	○	800	39	98	59
실시예4	660	○	1000	98	89	9
비교예1	810	○	1600	8	9	1
비교예2	-	○	700	112	128	16
비교예3	-	×	1200	181	47	134
비교예4	670	○	600	47	139	92

<68> * 이차전지의 제조

<69> 실시예 5 내지 8 및 비교예 5 내지 8

<70> 실시예 1 내지 4 및 비교예 1 내지 4의 전해 동박들을 10g/L의 중크롬산 칼

륨 용액에 10초 동안 각각 침지시킴으로써 전해 동박 상에 보호층이 형성된 집전체들을 얻었다. 이어서, 음극 활물질용으로 시판되는 탄소 100 중량부에 SBR 2 중량부 및 CMC 2 중량부를 혼합한 후 증류수를 용제로 이용하여 슬러리를 제조하였다. 10cm의 폭을 갖는 상기 집전체들 상에 상기 슬러리를 닥터 블레이드를 이용하여 50 ㎛의 두께로 각각 도포하고 120℃에서 건조시킨 후 1 ton/cm^2의 압력으로 프레스함으로써 총8개의 이차전지용 음극들을 제조하였다.

<71> 이와 같이 제조된 이차전지용 음극들 각각과 함께 전해액 및 이차전지용 양극을 이용하여 총8개의 이차전지들을 제조하였다. 상기 전해액과 양극은 아래와 같이 준비되었다.

<72> 에틸렌카보네이트(EC) 및 에틸렌메틸카보네이트(EMC)를 1:2의 비율로 혼합한 비수성 유기용매에 용질로서 $LiPF_6$를 1M 용해시킨 것을 기본 전해액으로 하고, 이 기본 전해액 99.5 중량%와 숙신산 무수물(succinic anhydride) 0.5 중량%를 혼합하여 상기 전해액을 제조하였다.

<73> 또한, 리튬망간산화물($Li_{1.1}Mn_{1.85}Al_{0.05}O_4$)과 orthorhombic 결정구조의 리튬망간산화물(o-$LiMnO_2$)을 90:10(중량비)로 혼합하여 양극 활물질을 제조하였다. 상기 양극 활물질과 카본블랙을 결착제인 폴리비닐리덴플루오라이드(PVDF)와 85:10:5(중량비)로 유기용매인 NMP와 혼합하여 슬러리를 제조하였다. 상기 슬러리를 두께 20 ㎛의 알라미늄 호일의 양면에 도포한 후 건조시킴으로써 상기 양극을 제조하였다.

<74> 위와 같이 제조된 실시예 5 내지 8 및 비교예 5 내지 8의 이차전지들의 용량 유지율을 아래의 방법으로 측정하였고, 그 결과를 표 2에 나타내었다.

<75> * 이차전지의 방전용량 유지율

<76> 4.3V의 충전작동전압 및 3.4V의 방전작동전압으로 양극의 g당 용량을 측정하였고, 고온 수명을 평가하기 위하여 50℃에서 0.2 C의 전류밀도로 50회으 충/방전 실험을 수행하였으며, 방전용량 유지율을 아래의 식 1에 따라 산출하였다.

<77> 식 1: 방전용량 유지율(%) = (50회차의 방전용량/1회차의 방전용량)×100

<78> 참고로, 업계에서 요구되는 이차전지의 방전용량 유지율은 90% 이상이다.

<79> 【표 2】

	전해 동박 매트 면의 R_{pc} (count)	전해 동박 샤이니 면의 R_{pc} (count)	전해 동박 양면들의 R_{pc} 차이 (count)	이차전지의 방전용량 유지율(%)
실시예5	13	42	29	95
실시예6	20	24	4	97
실시예7	39	98	59	93
실시예8	98	89	9	94
비교예5	8	9	1	84
비교예6	112	128	16	85
비교예7	181	47	134	85
비교예8	47	139	92	87

<80> 위 표 2로부터, 전해 동박의 샤이니 면과 매트 면 중 어느 하나라도 100개(count)를 초과하는 피크 수 조도(R_{pc})를 가질 경우 그러한 전해 동박을 이용하여 제조된 이차전지의 방전용량 유지율은 업계에서 요구되는 90% 이상을 만족시키지 못함을 알 수 있다(비교예 6-8). 너무 많은 산들로 인해 전해 동박 상에 활물질이

균일하게 코팅되지 못하였기 때문인 것으로 판단된다.

<81> 또한, 전해 동박의 샤이니 면과 매트 면이 10개 미만의 피크 수 조도(R_{pc})를 가질 경우 그러한 전해 동박을 이용하여 제조된 이차전지의 방전용량 유지율은 업계에서 요구되는 90% 이상을 만족시키지 못함을 알 수 있는데(비교예 5), 이것은 이차전지의 충방전시 국부적으로 돌출된 산에 응력이 집중되었기 때문인 것으로 파악된다.

【부호의 설명】

<82>

100: 이차전지 전극 110: 집전체

111: 전해 동박 111a: 제1 면(샤이니 면)

111b: 제2 면(매트 면) 112: 보호층

120: 활물질층

【특허청구범위】

【청구항 1】

제1 면(111a); 및

상기 제1 면(111a)의 반대 편의 제2 면(111b)을 포함하되,

상기 제1 및 제2 면들(111a, 111b) 각각은 10 내지 100 개의 피크 수 조도(peak count roughness: R_{pc})를 갖는 - 상기 제1 및 제2 면들(111a, 111b) 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값이고, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스틸-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 10㎜의 단위 샘플링 길이당 0.5㎛의 상위 기준선(upper criteria line: C1) 위로 솟아 있는 유효 피크들의 개수이고, 상기 유효 피크들 중 이웃하는 유효 피크들 사이에는 -0.5㎛의 하위 기준선(lower criteria line: C2)보다 깊은 적어도 하나의 골(valley)이 존재함 -,

이차전지용 전해동박.

【청구항 2】

제1항에 있어서,

상기 제1 및 제2 면들(111a, 111b)의 피크 수 조도(R_{pc}) 차이는 60개 이하인,

이차전지용 전해동박.

【청구항 3】

제1항에 있어서,

상기 제1 및 제2 면들(111a, 111b) 각각은 2㎛ 이하의 10점 평균조도(ten-point mean roughness: R_{zJIS})를 갖는,

이차전지용 전해동박.

【청구항 4】

제1항에 있어서,

3 내지 20 ㎛의 두께 및 30 내지 60 kgf/mm^2의 인장강도를 갖는,

이차전지용 전해동박.

【청구항 5】

제1항 내지 제4항 중 어느 한 항의 전해동박(111); 및

상기 전해동박 상의 보호층(112)을 포함하되,

상기 보호층(112)은 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는,

이차전지용 집전체.

【청구항 6】

제5항에 있어서,

상기 보호층(112)은 상기 전해동박(111)의 상기 제1 및 제2 면들(111a,

111b) 위에 형성된,

이차전지용 집전체.

【청구항 7】

제1항 내지 제4항 중 어느 한 항의 전해동박(111)을 포함하는 집전체(110); 및

상기 집전체 상의 활물질층(120)을 포함하되,

상기 활물질층(120)은, 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 선택되는 하나 이상의 활물질을 포함하는,

이차전지용 전극.

【청구항 8】

제7항에 있어서,

상기 활물질층(120)은 Si를 포함하는,

이차전지용 전극.

【청구항 9】

제7항에 있어서,

상기 집전체(110)는 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는 보호층(112)을 더 포함하고,

상기 보호층(112)은 상기 전해동박(111)과 상기 활물질층(120) 사이에 배치된,

이차전지용 전극.

【청구항 10】

충전 시 리튬 이온을 제공하는 양극(cathode);

방전 시 전자 및 리튬 이온을 제공하는 음극(anode)(100);

상기 양극과 음극 사이에서 리튬 이온이 이동할 수 있는 환경을 제공하는 전해질(electrolyte); 및

상기 양극과 상기 음극(100)을 전기적으로 절연시켜 주는 분리막(separator)을 포함하되,

상기 음극(100)은,

제1항 내지 제4항 중 어느 한 항의 전해동박(111)을 포함하는 집전체(110); 및

상기 집전체(110) 상의 활물질층(120)을 포함하는,

이차전지.

【청구항 11】

제10항에 있어서,

상기 집전체(110)는 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는 보호층(112)을 더 포함하고,

상기 보호층(112)은 상기 전해동박(111)과 상기 활물질층(120) 사이에 배치된,

이차전지.

【청구항 12】

전해액 내에 서로 이격되게 배치된 양극판 및 회전 음극드럼을 통전시킴으로써 상기 회전 음극드럼 상에 구리를 석출시키는 전해동박(111) 제조방법에 있어서,

구리 와이어를 열처리하는 단계;

상기 열처리된 구리 와이어를 산세하는 단계;

상기 산세된 구리 와이어를 상기 전해액에 투입하는 단계;

상기 투입 단계 후에 상기 양극판 및 회전 음극드럼을 통전시킴으로써 전기도금을 수행하는 단계; 및

상기 전기 도금 중에 상기 전해액으로부터 고형 불순물을 제거하기 위한 연속 여과를 수행하는 단계를 포함하는,

전해동박 제조방법.

【청구항 13】

제12항에 있어서,

상기 전기 도금 중에 상기 전해액 내의 유기 불순물 및 금속 불순물의 농도가 1g/L 이하 및 10g/L 이하로 각각 유지되는,

전해동박 제조방법.

【청구항 14】

제12항에 있어서,

상기 구리 와이어의 열처리 단계는 600 내지 800℃에서 수행되는,

전해동박 제조방법.

【청구항 15】

제12항에 있어서,

상기 전해액은 50 내지 100 g/L의 구리 이온, 50 내지 150 g/L의 황산, 50 ppm 이하의 염소 이온, 및 유기 첨가제를 포함하는,

전해동박 제조방법.

【청구항 16】

제15항에 있어서,

상기 유기 첨가제는 하이드로에틸 셀룰로오스(HEC), 유기 황화물, 유기 질화물, 티오요소(thiourea)계 화합물, 또는 이들 중 2 이상의 혼합물인,

전해동박 제조방법.

【요약서】

【요약】

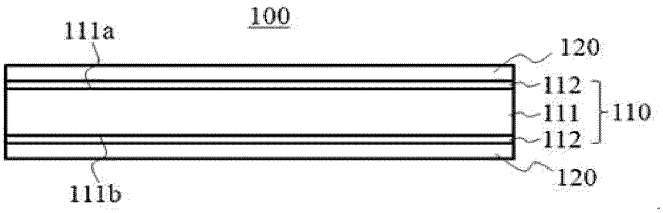
높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전해 동박, 그것을 포함하는 집전체, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조 방법이 개시된다. 본 발명의 전해 동박은 제1 면; 및 상기 제1 면의 반대 편의 제2 면을 포함하되, 상기 제1 및 제2 면들 각각은 10 내지 100 개의 피크 수 조도(peak count roughness: R_{pc})를 갖는다.

【대표도】

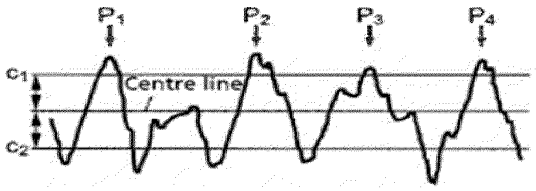
도 1

【도면】

【도 1】


100
111a
120
112
111
110
112
120
111b

【도 2】


P1
P2
P3
P4
c1
Centre line
c2

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DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

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34, chemin des Colombettes
1211 Geneva 20, Switzerland
www.wipo.int

PCT 출원서

출력(전자적 형태가 원본)

0	**수리관청 전용**	
0-1	국제출원번호	**PCT/KR2016/004449**
0-2	국제출원일자	**2016년 04월 28일 (28.04.2016)**
0-3	수리관청 명칭 및 "PCT 국제출원"	**RO/KR**

0-4	**서식 PCT/RO/101 - PCT 출원서**	
0-4-1	우측에 기재된 바와 같이 작성되었다.	**PCT-SAFE** **버전 3.51.073.249 MT/FOP 20160401/0.20.5.24**
0-5	**신청** 아래 서명인은 본 국제 출원서가 특허협력조약에 의해 처리될 것을 청구합니다.	
0-6	**출원인이 지정한 수리관청**	대한민국 특허청 (RO/KR)
0-7	**출원인 또는 대리인의 서류참조기호**	**2015F0127Pc**
I	**발명의 명칭**	전해 동박, 그것을 포함하는 집전체, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법
II	**출원인**	
II-1	이 사람은	오직 출원인 (applicant only)
II-2	우측 지정국에 관한 출원인	모든 지정국 (all designated States)
II-4ko	성명	엘에스엠트론 주식회사
II-4en	Name:	**LS MTRON LTD.**
II-5ko	주소	대한민국 **14119** 경기도 안양시 동안구 엘에스로 **127**
II-5en	Address:	**127, LS-ro, Dongan-gu,** **Anyang-si, Gyeonggi-do 14119** **Republic of Korea**
II-6	국적	대한민국 **KR**
II-7	거주국	대한민국 **KR**
II-11	출원인 코드	**1-2008-029030-3**

PCT 출원서

출력(전자적 형태가 원본)

III-1	**출원인 및/또는 발명자**	
III-1-1	이 사람은	**오직 발명자 (inventor only)**
III-1-3	우측 지정국에 관한 발명자	**모든 지정국 (all designated States)**
III-1-4ko	성명	**김대영**
III-1-4en	Name (LAST, First):	**KIM, Dae Young**
III-1-5ko	주소	**대한민국 16826 경기도 용인시 수지구 신수로783번길 22 (동천동, 영풍아파트) 101동 1205호**
III-1-5en	Address:	**101-1205, (Youngpung Apt., Dongcheon-dong) 22, Sinsu-ro 783beon-gil, Suji-gu, Yongin-si Gyeonggi-do 16826 Republic of Korea**
III-2	**출원인 및/또는 발명자**	
III-2-1	이 사람은	**오직 발명자 (inventor only)**
III-2-3	우측 지정국에 관한 발명자	**모든 지정국 (all designated States)**
III-2-4ko	성명	**김승민**
III-2-4en	Name (LAST, First):	**KIM, Seung Min**
III-2-5ko	주소	**대한민국 18105 경기도 오산시 양산로 460 (양산동, 세마이편한세상아파트) 105동 1902호**
III-2-5en	Address:	**105-1902, (Sema e-Pyeonhansesang Apt., Yangsan-dong) 460, Yangsan-ro, Osan-si, Gyeonggi-do 18105 Republic of Korea**

PCT 출원서

출력(전자적 형태가 원본)

IV-1	**대리인 또는 대표자** 아래에 기재된 자는 관할 국제기관에 대하여 우측에 표시된 자격으로 출원인을 대리하는 것으로 선임되었다.	대리인
IV-1-1ko	성명	특허법인 천문
IV-1-1en	Name:	**ASTRAN INT'L IP GROUP**
IV-1-2ko	주소	대한민국 **06225** 서울시 강남구 역삼로 **233, 5**층 (역삼동, 신성빌딩)
IV-1-2en	Address:	**(ShinSung Building, Yeoksam-dong)** **5th Floor, 233, Yeoksam-ro,** **Gangnam-gu, Seoul 06225** **Republic of Korea**
IV-1-3	전화번호	**+82-2-3453-0635**
IV-1-4	팩스번호	**+82-2-3453-0645**
IV-1-5	이메일 주소	**info@cheonmoon.com**
IV-1-5(a)	이메일 사용동의 수리관청, 국제조사기관, 국제사무국, 국제예비심사기관이 필요 시 이 이메일 주소를 사용하여 이 국제 출원과 관련하여 발행된 통지서를 송부할 것에 동의한다.	서면 통지서에 앞서 선람용 사본 송부
IV-1-6	대리인 코드	**9-2009-100001-0**
V	**지정국**	
V-1	**본 출원서의 제출로, 규칙 4.9(a)에 따라, 부여될 수 있는 모든 종류의 권리 보호를 위하여, 그리고 해당하는 경우 지역특허 및 국내특허 모두를 위하여 당해 국제출원일에 PCT에 기속되는 모든 체약국이 지정된다.**	
V-2	**V-2란은 출원서 제출시 또는 규칙 26의2.1에 의해 그 이후 출원서 제6기재란에 위 특정 관련 체약국의 국내 선출원에 대한 우선권주장이 포함되어 있을 경우 당해 체약국의 국내법에 의해 해당 국내 선출원의 효력이 상실되는 것을 방지하기 위한 목적으로 당해 체약국의 지정을 제외하는 데에만 사용될 수 있다 (지정 제외시 이의 취소 불가능).**	**KR**
VI-1	**선국내출원에 대한 우선권 주장**	
VI-1-1	출원일	**2015년 06월 24일 (24.06.2015)**
VI-1-2	출원번호	**10-2015-0090000**
VI-1-3	파리협약 당사국명 또는 WTO 회원국명	**KR**
VI-2	**우선권서류 신청** 수리관청에 대하여 위에 명시된 선출원의 인증등본을 준비하여 국제사무국에 송부하여 줄 것을 신청한다.	**VI-1**
VI-3	**인용에 의한 보완** 조약 제11조(1)(iii)(d) 또는 (e)에서 규정하는 국제출원의 요소, 또는 규칙 20.5(a)에서 규정하는 명세서, 청구 범위 또는 도면의 일부가 본 국제출원에는 포함되어 있지 않지만 조약 제11조(1)(iii) 규정의 요소 중 하나 이상이 수리관청에 최초로 접수된 날에 우선권주장의 기초가 된 선출원에 완전히 포함되어 있는 경우, 그 요소 또는 부분은 규칙 20.6 규정에 의한 확인을 조건으로, 규칙 20.6의 규정과 관련하여 본 국제출원에 있어서 인용에 의해 보완된다.	

PCT 출원서

출력(전자적 형태가 원본)

VII-1	**국제조사기관(ISA) 선택**	**대한민국 특허청 (ISA/KR)**	
VIII	**선언서**	선언서 개수	
VIII-1	발명자의 신원에 관한 선언	-	
VIII-2	국제출원일에 특허출원 및 특허를 받을 수 있는 출원인의 자격에 관한 선언	-	
VIII-3	국제출원일에 선출원의 우선권을 주장할 수 있는 출원인의 자격에 관한 선언	-	
VIII-4	발명자 선언(미국에 대한 지정의 경우에 한함)	-	
VIII-5	신규성을 해치지 아니하는 개시 또는 신규성 상실의 예외에 관한 선언	-	
IX	**체크 리스트**	용지 수	전자적 파일 첨부
IX-1	출원서(선언서 포함)	**5**	✓
IX-2	명세서	**10**	✓
IX-3	청구범위	**3**	✓
IX-4	요약서	**1**	✓
IX-5	도면	**1**	✓
IX-7	용지매수 소계	**20**	
	첨부 항목	서면 첨부	전자적 파일 첨부
IX-8	수수료 계산 용지	-	✓
IX-9	개별위임장 원본	-	✓
IX-20	**요약서에 수반되어야 할 도면 번호**	**1**	
IX-21	**국제출원의 출원 언어**	한국어	
X-1	**출원인, 대리인 또는 대표자의 서명 또는 날인**		
X-1-1	성명	특허법인 천문	
X-1-2	서명인의 성명	특허법인 천문	
X-1-3	권한 (출원서를 통해 서명자의 자격이 명백하지 않은 경우에는 그 자격도 표시)		

PCT 출원서

출력(전자적 형태가 원본)

수리관청 전용

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(71) 출원인: **엘에스엠트론 주식회사 (LS MTRON LTD.)** [KR/KR]; 14119 경기도 안양시 동안구 엘에스로 127, Gyeonggi-do (KR).

(72) 발명자: **김대영 (KIM, Dae Young)**; 16826 경기도 용인시 수지구 신수로 783 번길 22 (동천동, 영풍아파트) 101 동 1205 호, Gyeonggi-do (KR). **김승민 (KIM, Seung Min)**; 18105 경기도 오산시 양산로 460 (양산동, 세마이편한세상아파트) 105 동 1902 호, Gyeonggi-do (KR).

(74) 대리인: **특허법인 천문 (ASTRAN INT'L IP GROUP)**; 06225 서울시 강남구 역삼로 233, 5 층 (역삼동, 신성빌딩), Seoul (KR).

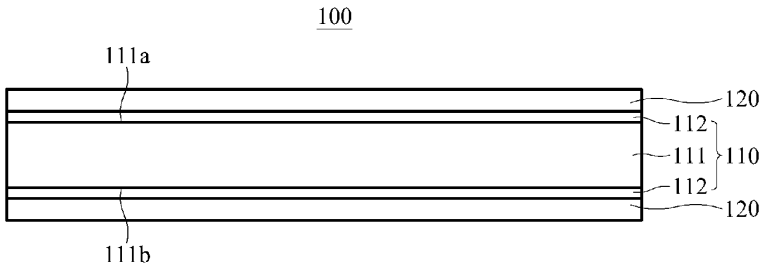
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공개:
— 국제조사보고서와 함께 (조약 제 21 조(3))

(54) **Title**: ELECTROLYTIC COPPER FOIL, CURRENT COLLECTOR INCLUDING SAME ELECTROLYTIC COPPER FOIL, ELECTRODE INCLUDING SAME CURRENT COLLECTOR, SECONDARY BATTERY INCLUDING SAME ELECTRODE, AND METHOD FOR MANUFACTURING SAME

(54) **발명의 명칭** : 전해 동박, 그 전해 동박을 포함하는 집전체, 그 집전체를 포함하는 전극, 그 전극을 포함하는 이차전지 및 이의 제조방법



(57) **Abstract**: Disclosed are an electrolytic copper foil which can guarantee a secondary battery having a high capacity maintaining rate, a current collector including the electrolytic copper foil, an electrode including the current collector, a secondary battery including the electrode, and a method for manufacturing the same. The electrolytic copper foil of the present invention comprises: a first surface; and a second surface opposite to the first surface, wherein each of the first surface and the second surface has 10 to 100 peak count roughnesses (Rpcs).

(57) **요약서**: 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전해 동박, 그 전해 동박을 포함하는 집전체, 그 집전체를 포함하는 전극, 그 전극을 포함하는 이차전지 및 이의 제조방법이 개시된다. 본 발명의 전해 동박은 제 1 면; 및 상기 제 1 면의 반대편의 제 2 면을 포함하되,상기 제 1 및 제 2 면들 각각은 10 내지 100 개의 피크 수 조도(peak count roughness: Rpc)를 갖는다.

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명세서

발명의 명칭: 전해 동박, 그것을 포함하는 집전체, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법

기술분야

[1] 본 발명은 전해 동박, 그것을 포함하는 집전체, 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 분야의 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] 한편, 이차전지가 충분히 높은 충전/방전 용량을 갖고 있다고 하더라도 충전/방전 사이클이 반복됨에 따라 이차전지의 충전/방전 용량이 급격히 감소한다면(즉, 용량 유지율이 낮다면 또는 수명이 짧다면), 소비자는 이차전지를 빈번하게 교체할 필요가 있을 것이고, 그로 인해 소비자 불편 및 자원 낭비가 초래될 것이다.

발명의 상세한 설명

기술적 과제

[7] 따라서, 본 발명은 위와 같은 관련 기술의 제한 및 단점들에 기인한 문제점들을 방지할 수 있는 전해 동박, 그것을 포함하는 집전체, 그것을 포함하는 전극, 그것을 포함하는 이차전지, 및 그것의 제조방법에 관한 것이다.

[8] 본 발명의 일 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전해 동박을 제공하는 것이다.

[9] 본 발명의 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는

집전체를 제공하는 것이다.

[10] 본 발명의 또 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전극을 제공하는 것이다.

[11] 본 발명의 또 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 제공하는 것이다.

[12] 본 발명의 또 다른 관점은, 높은 용량 유지율을 갖는 이차전지를 담보할 수 있는 전해 동박을 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.

과제 해결 수단

[14] 위와 같은 본 발명의 일 관점에 따라, 제1 면; 및 상기 제1 면의 반대 편의 제2 면을 포함하되, 상기 제1 및 제2 면들 각각은 10 내지 100 개의 피크 수 조도(peak count roughness: R_{pc})를 갖는 - 상기 제1 및 제2 면들 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값이고, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스틸-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 4mm의 단위 샘플링 길이당 0.5㎛의 상위 기준선(upper criteria line: C1) 위로 솟아 있는 유효 피크들의 개수이고, 상기 유효 피크들 중 이웃하는 유효 피크들 사이에는 -0.5㎛의 하위 기준선(lower criteria line: C2)보다 깊은 적어도 하나의 골(valley)이 존재함 -, 이차전지용 전해동박이 제공된다.

[15] 본 발명의 다른 관점에 따라, 10 내지 100 개의 피크 수 조도(R_{pc})를 각각 갖는 제1 및 제2 면들을 포함하는 전해동박; 및 상기 전해동박 상의 보호층을 포함하되, 상기 보호층은 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는, 이차전지용 집전체가 제공된다.

[16] 본 발명의 또 다른 관점에 따라, 10 내지 100 개의 피크 수 조도(R_{pc})를 각각 갖는 제1 및 제2 면들을 포함하는 전해동박을 포함하는 집전체; 및 상기 집전체 상의 활물질층을 포함하되, 상기 활물질층은, 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 선택되는 하나 이상의 활물질을 포함하는, 이차전지용 전극이 제공된다.

[17] 본 발명의 또 다른 관점에 따라, 양극(cathode); 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 포함하되, 상기 음극은, 10 내지 100 개의 피크 수 조도(R_{pc})를 각각 갖는 제1 및 제2 면들을 포함하는 전해동박을 포함하는 집전체; 및 상기 집전체 상의 활물질층을 포함하는, 이차전지가 제공된다.

[18] 본 발명의 또 다른 관점에 따라, 전해액 내에 서로 이격되게 배치된 양극판 및

회전 음극드럼을 통전시킴으로써 상기 회전 음극드럼 상에 구리를 석출시키는 전해동박 제조방법으로서, 구리 와이어를 열처리하는 단계; 상기 열처리된 구리 와이어를 산세하는 단계; 상기 산세된 구리 와이어를 상기 전해액에 투입하는 단계; 상기 구리 와이어가 상기 전해액에 투입된 상태에서 상기 양극판 및 회전 음극드럼을 통전시킴으로써 전기 도금을 수행하는 단계; 및 상기 전기 도금 중에 상기 전해액으로부터 고형 불순물을 제거하기 위한 연속 여과를 수행하는 단계를 포함하는, 전해동박 제조방법이 제공된다.

[19] 위와 같은 본 발명에 대한 일반적 서술은 본 발명을 예시하거나 설명하기 위한 것일 뿐으로서, 본 발명의 권리범위를 제한하지 않는다.

발명의 효과

[20] 본 발명에 의하면, 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

[21] 첨부된 도면은 본 발명의 이해를 돕고 본 명세서의 일부를 구성하기 위한 것으로서, 본 발명의 실시예들을 예시하며, 발명의 상세한 설명과 함께 본 발명의 원리들을 설명한다.

[22] 도 1은 본 발명의 일 실시예에 따른 이차전지용 전극의 단면도이고,

[23] 도 2는 스틸-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일을 예시한다.

발명의 실시를 위한 형태

[24] 이하에서는 첨부된 도면을 참조하여 본 발명의 실시예들을 상세하게 설명한다.

[25] 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.

[26] 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 절연시켜 주는 분리막(separator)을 포함한다.

[27] 도 1은 본 발명의 일 실시예에 따른 이차전지용 전극의 단면도이다.

[28] 도 1에 예시된 바와 같이, 본 발명의 일 실시예에 따른 이차전지용 전극(100)은 집전체(110) 및 활물질층(120)을 포함한다. 도 1은 상기 집전체(110)의 상하면 모두 위에 형성된 활물질층(120)을 예시하고 있으나, 본 발명이 이에 국한되는 것은 아니며, 상기 활물질층(120)은 상기 집전체(110)의 일 면 상에만 형성될

수도 있다.

[29] 리튬 이차전지에 있어서, 양극 활물질과 결합되는 양극 집전체로서는 알루미늄 호일(foil)이 사용되고 음극 활물질과 결합되는 음극 집전체로서는 동박이 사용되는 것이 일반적이다.

[30] 본 발명의 일 실시예에 의하면, 상기 이차전지용 전극(100)은 음극이고, 상기 집전체(110)는 음극 집전체이며, 상기 활물질층(120)은 음극 활물질을 포함한다.

[31] 음극 집전체인 본 발명의 집전체(110)는 3 내지 20 ㎛의 두께 및 30 내지 60 kgf/mm^{2}의 인장강도를 갖는 전해 동박(111)을 포함한다. 또한, 도 1에 예시된 바와 같이, 상기 집전체(110)는 상기 전해 동박(111) 상의 보호층(112)을 더 포함할 수 있다. 도 1은 상기 전해 동박(111)의 상하면 모두 위에 형성된 보호층(112)을 예시하고 있으나, 본 발명이 이에 국한되는 것은 아니며, 상기 보호층(112)은 상기 전해 동박(111)의 일 면 상에만 형성될 수도 있다.

[32] 본 발명의 전해 동박(111)은 전기도금을 통해 회전 음극드럼 상에 형성될 수 있으며, 전기도금 과정에서 상기 회전 음극드럼과 접촉하였던 제1 면[일명 "샤이니 면(Shiny surface)"](111a) 및 상기 제1 면의 반대 편의 제2 면[일명 "매트 면(Matte surface)"](111b)을 갖는다.

[33] 샤이니 면(111a)이 매트 면(111b)에 비해 더 낮은 조도를 갖는 것이 일반적이기는 하지만 본 발명이 이에 국한되는 것은 아니며 샤이니 면(111a)의 조도가 매트 면(111b)의 조도와 동일하거나 더 높을 수도 있다. 여기서, 샤이니 면(111a)과 매트 면(111b)의 조도는 10점 평균조도(ten-point mean roughness: R_{zJIS})를 의미한다.

[34] 상기 활물질층(120)은, 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 선택되는 하나 이상의 활물질을 음극 활물질로서 포함한다.

[35] 이차전지의 충방전 용량을 증가시키기 위하여, Si를 소정량 포함한 음극 활물질들의 혼합물로 상기 활물질층(120)이 형성될 수 있다.

[36] 한편, 이차전지의 충방전이 반복됨에 따라 활물질층(120)의 수축 및 팽창이 번갈아 발생하고, 이것은 상기 활물질층(120)과 상기 집전체(110)의 분리를 유발하여 이차전지의 충방전 효율을 저하시킨다. 따라서, 이차전극이 일정 수준 이상의 용량 유지율 및 수명을 확보하기 위해서는(즉, 이차전지의 충방전 효율 저하를 억제하기 위해서는), 상기 집전체(110)가 상기 활물질에 대하여 우수한 코팅성을 가짐으로써 상기 집전체(110)와 활물질층(120)의 접착 강도가 높아야 한다.

[37] 거시적 관점에서 볼 때, 상기 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)의 10점 평균조도(R_{zJIS})가 작을수록, 상기 집전체(110)를 포함하는 이차전지의 충방전 효율이 대체로 덜 저하되는 경향이 있다.

[38] 따라서, 본 발명의 일 실시예에 따른 전해 동박(111)의 샤이니 면(111a)과 매트

면(111b) 각각은 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖는다. 상기 샤이니 면(111a) 또는 매트 면(111b)이 2㎛를 초과하는 10점 평균조도(R_{zJIS})를 갖는다면 상기 집전체(110)와 활물질층(120) 사이의 접촉 균일성이 일정 수준에 미치지 못할 것이고, 따라서 이차전지가 업계에서 요구되는 90% 이상의 용량 유지율을 만족하지 못할 것이다.

[39] 그러나, 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)이 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖는다고 하더라도, 그러한 전해 동박(111)이 반드시 90% 이상의 이차전지 용량 유지율을 담보할 수 있는 것이 아님이 본 출원인에 의해 밝혀졌다. 즉, 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)의 낮은 10점 평균조도(R_{zJIS})(예를 들어, 2㎛ 이하)가 90% 이상의 이차전지 용량 유지율에 대한 충분 조건이 될 수 없다.

[40] 특히, 이차전지의 고용량화를 위하여 상기 활물질층(120)이 Si를 포함할 경우 전해 동박(111)의 10점 평균조도(R_{zJIS})와 이차전지의 용량 유지율 사이의 연관성이 더욱 낮은 것으로 드러났다.

[41] 본 출원인은, 연구를 거듭한 결과, 90% 이상의 용량 유지율을 안정적으로 확보함에 있어서 전해 동박(111)의 피크 수 조도(peak count roughness: R_{pc})가 중요한 인자임을 밝혀내었다.

[42] 이하에서는, 도 2를 참조하여 전해 동박(111)의 피크 수 조도(R_{pc})를 설명한다.

[43] 본 명세서에서 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b) 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값을 지칭하며, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스틸-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 4mm의 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 피크 수 조도(R_{pc})의 측정에 이용되는 "유효 피크"가 될 수는 없으며, "유효 피크" 개수를 구함에 있어서 상기 피크들 중 상대적으로 더 낮은 피크는 무시된다.

[44] 본 발명에 의하면, 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)은 10 내지 100 개(count)의 피크 수 조도(R_{pc})를 각각 갖는다.

[45] 상기 피크 수 조도(R_{pc})가 10개 미만인 경우 이차전지의 용량 유지율의 열화가 발생하는데, 이것은 이차전지의 충방전시 국부적으로 돌출된 산(mountain)에 응력이 집중되기 때문인 것으로 파악된다.

[46] 반면, 피크 수 조도(R_{pc})가 100개를 초과하는 경우에도 이차전지의 용량 유지율의 열화가 마찬가지로 발생하는데, 이것은 너무 많은 산들로 인해 상기 전해 동박(111) 상에 활물질이 균일하게 코팅되지 못하기 때문인 것으로

판단된다.

[47] 본 발명의 일 실시예에 의하면 상기 집전체(110)의 양 면들 모두에 활물질이 코팅되기 때문에, 상기 전해 동박(111)의 샤이니 면(111a)과 매트 면(111b)의 피크 수 조도(R_{pc}) 차이는 60개 이하인 것이 바람직하다. 상기 피크 수 조도(R_{pc}) 차이가 60개를 초과하면 양 면들(111a, 111b)의 표면 형상의 차이로 인해 이차전지의 용량 유지율 열화가 발생한다.

[48] 전술한 바와 같이, 본 발명의 이차전지용 집전체(110)는 상기 전해 동박(111) 상의 보호층(112)을 더 포함할 수 있다. 상기 보호층(112)은 상기 전해 동박(111)의 방청 처리를 통해 형성될 수 있다. 즉, 본 발명의 전해 동박(111)은 그대로 집전체로서 사용될 수도 있지만, 크롬산염, 벤조트리아졸, 및/또는 실란계 화합물로 방청 처리(anticorrosion treatment)되는 것이 바람직하다. 이와 같은 방청 처리는 전해 동박(111)의 부식을 방지하고, 내열성을 향상시키며, 활물질층(120)과의 접착 강도를 높여 이차 전지의 충방전 효율 저하를 억제시킬 수 있다.

[49] 이하에서는, 본 발명의 일 실시예에 따른 전해 동박의 제조방법을 구체적으로 설명한다.

[50] 상기 전해 동박(111)의 제조에 이용되는 제박기는 전해액이 담겨진 전해조, 상기 전해액 내에서 서로 이격되어 있는 회전 음극드럼 및 양극판을 포함한다.

[51] 50 내지 100 g/L의 구리 이온, 50 내지 150 g/L의 황산 및 50 ppm 이하의 염소 이온을 포함하는 전해액에 하이드록시에틸 셀룰로오스(HEC), 유기 황화물, 유기 질화물, 및/또는 티오요소(thiourea)계 화합물과 같은 유기 첨가제를 소량 첨가한 후, 10 내지 80 A/dm^{2}의 전류밀도로 40 내지 60 ℃에서 상기 회전 음극드럼 표면에 구리를 전착함으로써 전해 동박(111)을 제조한다.

[52] 상기 전해 동박(111)의 샤이니 면(111a)의 10점 평균조도(R_{zJIS}) 및 피크 수 조도(R_{pc})는 회전 음극드럼 표면(전기도금에 의해 구리가 석출되는 면)의 연마 정도에 의존한다.

[53] 본 발명에 의하면, 상기 샤이니 면(111a)이 10 내지 100 개의 피크 수 조도(R_{pc}) 및 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖도록 하기 위하여, #800 내지 #1500의 입도(Grit)를 갖는 연마 브러시로 상기 회전 음극드럼의 표면이 연마된다.

[54] 상기 전해 동박(111)의 매트 면(111b)의 10점 평균조도(R_{zJIS}) 및 피크 수 조도(R_{pc})는 전기도금에 이용되는 전해액의 조성(특히, 유기 불순물 및 금속 불순물의 농도), 전기도금의 전류 밀도 등에 의존한다.

[55] 본 발명에 의하면, 상기 매트 면(111b)이 10 내지 100 개의 피크 수 조도(R_{pc}) 및 2㎛ 이하의 10점 평균조도(R_{zJIS})를 갖도록 하기 위하여, 상기 전해액 내 유기 불순물 및 금속 불순물의 농도가 각각 1g/L 이하 및 10g/L 이하로 제어되며, 10 내지 80 A/dm^{2}의 전류밀도로 상기 전기도금이 수행된다.

[56] 또한, 본 발명에 의하면, 상기 전해액 내 유기 불순물 및 금속 불순물의 농도를 각각 1g/L 이하 및 10g/L 이하로 제어하기 위하여, 고순도 구리 와이어를

전해액에 투입하기 전에 600 내지 800℃(예를 들어, 약 700℃)의 고온에서 열처리하여 유기물을 태운 후 황산 등의 산으로 산세(acid cleaning) 한다. 또한, 전기도금 중에 상기 전해액으로부터 유기 불순물 및 금속 불순물을 포함하는 고형 불순물을 제거하기 위한 연속 여과를 수행함으로써 상기 전해액 내의 유기 불순물 및 금속 불순물의 농도를 각각 1g/L 이하 및 10g/L 이하로 유지시킨다.

[57] 이어서, 크롬산염(chromate), 벤조트리아졸(benzotriazole: BTA), 및/또는 실란계 화합물(silane compound)을 이용한 방청 처리(anticorrosion treatment)를 통해 상기 전해 동박(111)의 샤이니 면(111a) 및/또는 매트 면(111b) 상에 보호층(112)을 형성함으로써 본 발명의 집전체(110)를 제조할 수 있다.

[58] 예를 들어, 1 내지 10 g/L의 중크롬산 칼륨 용액에 상기 전해 동박(111)을 상온에서 2 내지 20초 침지시킴으로써 상기 보호층(112)을 형성할 수 있다.

[59] 이어서, 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 선택되는 하나 이상의 음극 활물질을 상기 집전체(110) 상에 코팅함으로써 본 발명의 이차전지용 전극(즉, 음극)을 제조한다.

[60] 예를 들어, 탄소 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 집전체(110) 상에 20 내지 60㎛ 두께로 상기 슬러리를 도포하고, 110 내지 130℃에서 0.5 내지 1.5 ,ton/cm^2의 압력으로 프레스한다.

[61] 이상의 방법으로 제조된 본 발명의 이차전지용 전극(음극)과 함께 통상의 양극, 전해질, 및 분리막을 이용하여 리튬 이차전지를 제조할 수 있다.

[62]

[63] 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.

[64]

[65] *** 전해 동박의 제조**

[66] 실시예 1 내지 4 및 비교예 1 내지 4

[67] i) 구리 와이어 열처리 여부/온도, ii) 전기 도금 수행시 연속 여과 수행 여부, 및/또는 iii) 회전 음극 드럼의 표면 연마에 이용된 연마 브러시의 입도를 아래의 표 1과 같이 변경한 것을 제외하고는 동일한 조건 하에서 전해 동박들을 각각 제조하였다.

[68] 이어서, 상기 전해 동박들의 샤이니 면 및 매트 면의 피크 수 조도(R_{pc})를 Mahr社의 Mahrsurf M300 조도계를 이용하여 각각 측정하였고, 그 결과를 아래의 표 1에 나타내었다.

[69] 전술한 바와 같이, 샤이니 면과 매트 면 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값이며, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스틸-아이언 테스트 스케쥴(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 4mm의 단위 샘플링 길이당 0.5㎛의 상위 기준선(C1) 위로 솟아 있는 유효 피크들의 개수이다.

[70] 상위 기준선(C1) 위로 솟아 있는 이웃하는 피크들 사이에 -0.5㎛의 하위 기준선(C2)보다 깊은 골이 하나도 존재하지 않는 경우에는, "유효 피크" 개수를 구함에 있어서 상기 피크들 중 상대적으로 더 낮은 피크는 무시되었다.

[71] [표1]

	구리 와이어 열처리 온도(℃)	연속 여과 수행 여부	연마 브러시 입도(#)	매트 면의 R_{pc}(count)	샤이니 면의R_{pc}(count)	R_{pc} 차이 (count)
실시예1	720	○	1200	13	42	29
실시예2	700	○	1400	20	24	4
실시예3	680	○	800	39	98	59
실시예4	660	○	1000	98	89	9
비교예1	810	○	1600	8	9	1
비교예2	-	○	700	112	128	16
비교예3	-	×	1200	181	47	134
비교예4	670	○	600	47	139	92

[72]

[73] <u>* 이차전지의 제조</u>

[74] <u>실시예 5 내지 8 및 비교예 5 내지 8</u>

[75] 실시예 1 내지 4 및 비교예 1 내지 4의 전해 동박들을 10g/L의 중크롬산 칼륨 용액에 10초 동안 각각 침지시킴으로써 전해 동박 상에 보호층이 형성된 집전체들을 얻었다. 이어서, 음극 활물질용으로 시판되는 탄소 100 중량부에 SBR 2 중량부 및 CMC 2 중량부를 혼합한 후 증류수를 용제로 이용하여 슬러리를 제조하였다. 10cm의 폭을 갖는 상기 집전체들 상에 상기 슬러리를 닥터 블레이드를 이용하여 50㎛의 두께로 각각 도포하고 120℃에서 건조시킨 후 1 ton/cm^2의 압력으로 프레스함으로써 총8개의 이차전지용 음극들을 제조하였다.

[76] 이와 같이 제조된 이차전지용 음극들 각각과 함께 전해액 및 이차전지용 양극을 이용하여 총8개의 이차전지들을 제조하였다. 상기 전해액과 양극은 아래와 같이 준비되었다.

[77] 에틸렌카보네이트(EC) 및 에틸렌메틸카보네이트(EMC)를 1:2의 비율로 혼합한 비수성 유기용매에 용질로서 $LiPF_6$를 1M 용해시킨 것을 기본 전해액으로 하고, 이 기본 전해액 99.5 중량%와 숙신산 무수물(succinic anhydride) 0.5 중량%를 혼합하여 상기 전해액을 제조하였다.

[78] 또한, 리튬망간산화물($Li_{1.1}Mn_{1.85}Al_{0.05}O_4$)과 orthorhombic 결정구조의 리튬망간산화물(o-$LiMnO_2$)을 90:10(중량비)로 혼합하여 양극 활물질을 제조하였다. 상기 양극 활물질과 카본블랙을 결착제인 폴리비닐리덴플루오라이드(PVDF)와 85:10:5(중량비)로 유기용매인 NMP와 혼합하여 슬러리를 제조하였다. 상기 슬러리를 두께 20㎛의 알라미늄 호일의 양면에 도포한 후 건조시킴으로써 상기 양극을 제조하였다.

[79]

[80] 위와 같이 제조된 실시예 5 내지 8 및 비교예 5 내지 8의 이차전지들의 용량 유지율을 아래의 방법으로 측정하였고, 그 결과를 표 2에 나타내었다.

[81] * 이차전지의 방전용량 유지율

[82] 4.3V의 충전작동전압 및 3.4V의 방전작동전압으로 양극의 g당 용량을 측정하였고, 고온 수명을 평가하기 위하여 50℃에서 0.2 C의 전류밀도로 50회으 충/방전 실험을 수행하였으며, 방전용량 유지율을 아래의 식 1에 따라 산출하였다.

[83] 식 1: 방전용량 유지율(%) = (50회차의 방전용량/1회차의 방전용량)×100

[84] 참고로, 업계에서 요구되는 이차전지의 방전용량 유지율은 90% 이상이다.

[85] [표2]

	전해 동박 매트 면의 R_{pc}(count)	전해 동박 샤이니 면의 R_{pc}(count)	전해 동박 양면들의 R_{pc} 차이 (count)	이차전지의 방전용량 유지율(%)
실시예5	13	42	29	95
실시예6	20	24	4	97
실시예7	39	98	59	93
실시예8	98	89	9	94
비교예5	8	9	1	84
비교예6	112	128	16	85
비교예7	181	47	134	85
비교예8	47	139	92	87

[86] 위 표 2로부터, 전해 동박의 샤이니 면과 매트 면 중 어느 하나라도 100개(count)를 초과하는 피크 수 조도(R_{pc})를 가질 경우 그러한 전해 동박을 이용하여 제조된 이차전지의 방전용량 유지율은 업계에서 요구되는 90% 이상을

만족시키지 못함을 알 수 있다(비교예 6-8). 너무 많은 산들로 인해 전해 동박 상에 활물질이 균일하게 코팅되지 못하였기 때문인 것으로 판단된다.

[87] 또한, 전해 동박의 샤이니 면과 매트 면이 10개 미만의 피크 수 조도(R_{pc})를 가질 경우 그러한 전해 동박을 이용하여 제조된 이차전지의 방전용량 유지율은 업계에서 요구되는 90% 이상을 만족시키지 못함을 알 수 있는데(비교예 5), 이것은 이차전지의 충방전시 국부적으로 돌출된 산에 응력이 집중되었기 때문인 것으로 파악된다.

청구범위

[청구항 1] 제1 면(111a); 및
상기 제1 면(111a)의 반대 편의 제2 면(111b)을 포함하되,
상기 제1 및 제2 면들(111a, 111b) 각각은 10 내지 100 개의 피크 수 조도(peak count roughness: R_{pc})를 갖는 - 상기 제1 및 제2 면들(111a, 111b) 각각의 피크 수 조도(R_{pc})는 임의의 3개 지점들의 피크 수 조도(R_{pc})의 평균값이고, 상기 지점들 각각의 피크 수 조도(R_{pc})는 스틸-아이언 테스트 스케줄(SEP 1940) 규격에 따라 얻어진 표면 조도 프로파일에서 4mm의 단위 샘플링 길이당 0.5㎛의 상위 기준선(upper criteria line: C1) 위로 솟아 있는 유효 피크들의 개수이고, 상기 유효 피크들 중 이웃하는 유효 피크들 사이에는 -0.5㎛의 하위 기준선(lower criteria line: C2)보다 깊은 적어도 하나의 골(valley)이 존재함 -,
이차전지용 전해동박.

[청구항 2] 제1항에 있어서,
상기 제1 및 제2 면들(111a, 111b)의 피크 수 조도(R_{pc}) 차이는 60개 이하인,
이차전지용 전해동박.

[청구항 3] 제1항에 있어서,
상기 제1 및 제2 면들(111a, 111b) 각각은 2㎛ 이하의 10점 평균조도(ten-point mean roughness: R_{zJIS})를 갖는,
이차전지용 전해동박.

[청구항 4] 제1항에 있어서,
3 내지 20 ㎛의 두께 및 30 내지 60 kgf/mm^{2}의 인장강도를 갖는,
이차전지용 전해동박.

[청구항 5] 제1항 내지 제4항 중 어느 한 항의 전해동박(111); 및
상기 전해동박 상의 보호층(112)을 포함하되,
상기 보호층(112)은 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는,
이차전지용 집전체.

[청구항 6] 제5항에 있어서,
상기 보호층(112)은 상기 전해동박(111)의 상기 제1 및 제2 면들(111a, 111b) 위에 형성된,
이차전지용 집전체.

[청구항 7] 제1항 내지 제4항 중 어느 한 항의 전해동박(111)을 포함하는 집전체(110); 및
상기 집전체 상의 활물질층(120)을 포함하되,
상기 활물질층(120)은, 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 선택되는 하나 이상의 활물질을 포함하는,
이차전지용 전극.

[청구항 8] 제7항에 있어서,
상기 활물질층(120)은 Si를 포함하는,
이차전지용 전극.

[청구항 9] 제7항에 있어서,
상기 집전체(110)는 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는 보호층(112)을 더 포함하고,
상기 보호층(112)은 상기 전해동박(111)과 상기 활물질층(120) 사이에 배치된,
이차전지용 전극.

[청구항 10] 양극(cathode);
음극(anode)(100);
상기 양극과 음극 사이에서 리튬 이온이 이동할 수 있는 환경을 제공하는 전해질(electrolyte); 및
상기 양극과 상기 음극(100)을 전기적으로 절연시켜 주는
분리막(separator)을 포함하되,
상기 음극(100)은,
제1항 내지 제4항 중 어느 한 항의 전해동박(111)을 포함하는 집전체(110); 및
상기 집전체(110) 상의 활물질층(120)을 포함하는,
이차전지.

[청구항 11] 제10항에 있어서,
상기 집전체(110)는 크롬산염, 벤조트리아졸 및 실란 화합물 중 적어도 하나를 포함하는 보호층(112)을 더 포함하고,
상기 보호층(112)은 상기 전해동박(111)과 상기 활물질층(120) 사이에 배치된,
이차전지.

[청구항 12] 전해액 내에 서로 이격되게 배치된 양극판 및 회전 음극드럼을 통전시킴으로써 상기 회전 음극드럼 상에 구리를 석출시키는
전해동박(111) 제조방법에 있어서,
구리 와이어를 열처리하는 단계;
상기 열처리된 구리 와이어를 산세하는 단계;
상기 산세된 구리 와이어를 상기 전해액에 투입하는 단계;
상기 구리 와이어가 상기 전해액에 투입된 상태에서 상기 양극판 및 회전 음극드럼을 통전시킴으로써 전기 도금을 수행하는 단계; 및
상기 전기 도금 중에 상기 전해액으로부터 고형 불순물을 제거하기 위한

연속 여과를 수행하는 단계를 포함하는,
전해동박 제조방법.

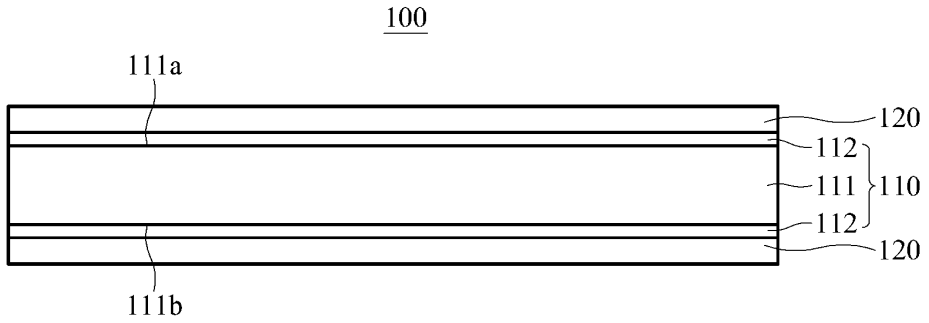
[청구항 13] 제12항에 있어서,
상기 전기 도금 중에 상기 전해액 내의 유기 불순물 및 금속 불순물의 농도가 1g/L 이하 및 10g/L 이하로 각각 유지되는,
전해동박 제조방법.

[청구항 14] 제12항에 있어서,
상기 구리 와이어의 열처리 단계는 600 내지 800℃에서 수행되는,
전해동박 제조방법.

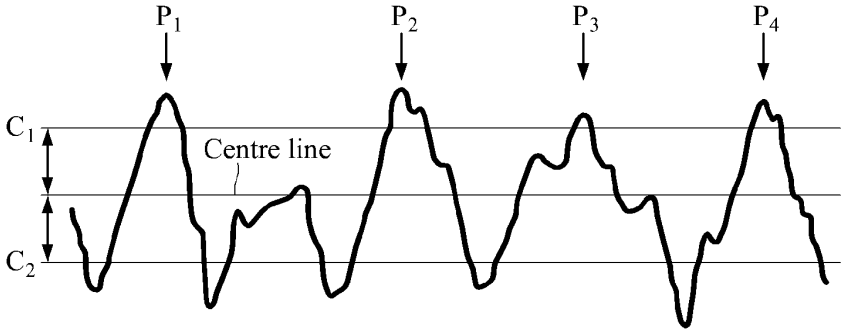
[청구항 15] 제12항에 있어서,
상기 전해액은 50 내지 100 g/L의 구리 이온, 50 내지 150 g/L의 황산, 50 ppm 이하의 염소 이온, 및 유기 첨가제를 포함하는,
전해동박 제조방법.

[청구항 16] 제15항에 있어서,
상기 유기 첨가제는 하이드록시에틸 셀룰로오스(HEC), 유기 황화물, 유기 질화물, 티오요소(thiourea)계 화합물, 또는 이들 중 2 이상의 혼합물인,
전해동박 제조방법.

[도1]


100
111a
120
112
111
110
112
120
111b

[도2]


P1
P2
P3
P4
C1
Centre line
C2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2016/004449

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/66(2006.01)i, H01M 10/052(2010.01)i, C25D 1/04(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)

H01M 4/66; H05K 1/05; B32B 15/20; C25D 7/06; H01M 4/64; H05B 33/26; H05B 33/02; C25D 1/04; B32B 15/08; H01M 2/02; H01M 10/052

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility models and applications for Utility models: IPC as above
Japanese Utility models and applications for Utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS (KIPO internal) & Keywords: rechargeable battery, electrolytic copper foil, peak number illuminance, tensile strength, average illumination, collector, electrode for secondary battery

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2000-182623 A (NIPPON DENKAI KK.) 30 June 2000 See paragraphs [0018]-[0044]; and claims 1-5.	12-16
A		1-11
A	JP 2014-135175 A (MITSUI MINING & SMELTING CO., LTD.) 24 July 2014 See paragraph [0021]; and claims 1-14.	1-16
A	KR 10-1449342 B1 (ILJIN MATERIALS CO., LTD.) 13 October 2014 See claims 1-3, 12 and 13.	1-16
A	KR 10-2014-0090069 A (CHANG CHUN PETROCHEMICAL CORPORATION) 16 July 2014 See claims 1-11.	1-16
A	US 2001-0051282 A1 (YATES, C. B. et al.) 13 December 2001 See claims 1-12.	1-16

☐ 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
29 JULY 2016 (29.07.2016)	**29 JULY 2016 (29.07.2016)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office Government Complex-Daejeon, 189 Seonsa-ro, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2016/004449

Patent document cited in search report	Publication date	Patent family member	Publication date
JP 2000-182623 A	30/06/2000	JP 3850155 B2	29/11/2006
JP 2014-135175 A	24/07/2014	EP 2945467 A1	18/11/2015
		US 2015-0340639 A1	26/11/2015
		WO 2014-109081 A1	17/07/2014
KR 10-1449342 B1	13/10/2014	TW 201523992 A	16/06/2015
		WO 2015-069075 A1	14/05/2015
KR 10-2014-0090069 A	16/07/2014	CN 103911633 A	09/07/2014
		JP 2014-132106 A	17/07/2014
		JP 5696179 B2	08/04/2015
		US 2014-0193660 A1	10/07/2014
		US 9365942 B2	14/06/2016
US 2001-0051282 A1	13/12/2001	US 6372113 B2	16/04/2002

Form PCT/ISA/210 (patent family annex) (January 2015)

국 제 조 사 보 고 서

국제출원번호
PCT/KR2016/004449

A. 발명이 속하는 기술분류(국제특허분류(IPC))

H01M 4/66(2006.01)i, H01M 10/052(2010.01)i, C25D 1/04(2006.01)i

B. 조사된 분야

조사된 최소문헌(국제특허분류를 기재)
H01M 4/66; H05K 1/05; B32B 15/20; C25D 7/06; H01M 4/64; H05B 33/26; H05B 33/02; C25D 1/04; B32B 15/08; H01M 2/02; H01M 10/052

조사된 기술분야에 속하는 최소문헌 이외의 문헌
한국등록실용신안공보 및 한국공개실용신안공보: 조사된 최소문헌란에 기재된 IPC
일본등록실용신안공보 및 일본공개실용신안공보: 조사된 최소문헌란에 기재된 IPC

국제조사에 이용된 전산 데이터베이스(데이터베이스의 명칭 및 검색어(해당하는 경우))
eKOMPASS(특허청 내부 검색시스템) & 키워드: 이차전지, 전해동박, 피크 수 조도, 인장강도, 평균조도, 집전체, 이차전지용 전극

C. 관련 문헌

카테고리*	인용문헌명 및 관련 구절(해당하는 경우)의 기재	관련 청구항
X	JP 2000-182623 A (NIPPON DENKAI KK) 2000.06.30 단락 [0018]-[0044]; 및 청구항 1-5 참조.	12-16
A		1-11
A	JP 2014-135175 A (MITSUI MINING & SMELTING CO., LTD.) 2014.07.24 단락 [0021]; 및 청구항 1-14 참조.	1-16
A	KR 10-1449342 B1 (일진머티리얼즈 주식회사) 2014.10.13 청구항 1-3, 12 및 13 참조.	1-16
A	KR 10-2014-0090069 A (창춘 페트로케미칼 컴퍼니 리미티드) 2014.07.16 청구항 1-11 참조.	1-16
A	US 2001-0051282 A1 (YATES, C. B. 등) 2001.12.13 청구항 1-12 참조.	1-16

☐ 추가 문헌이 C(계속)에 기재되어 있습니다.

☒ 대응특허에 관한 별지를 참조하십시오.

* 인용된 문헌의 특별 카테고리:

"A" 특별히 관련이 없는 것으로 보이는 일반적인 기술수준을 정의한 문헌

"E" 국제출원일보다 빠른 출원일 또는 우선일을 가지나 국제출원일 이후에 공개된 선출원 또는 특허 문헌

"L" 우선권 주장에 의문을 제기하는 문헌 또는 다른 인용문헌의 공개일 또는 다른 특별한 이유(이유를 명시)를 밝히기 위하여 인용된 문헌

"O" 구두 개시, 사용, 전시 또는 기타 수단을 언급하고 있는 문헌

"P" 우선일 이후에 공개되었으나 국제출원일 이전에 공개된 문헌

"T" 국제출원일 또는 우선일 후에 공개된 문헌으로, 출원과 상충하지 않으며 발명의 기초가 되는 원리나 이론을 이해하기 위해 인용된 문헌

"X" 특별한 관련이 있는 문헌. 해당 문헌 하나만으로 청구된 발명의 신규성 또는 진보성이 없는 것으로 본다.

"Y" 특별한 관련이 있는 문헌. 해당 문헌이 하나 이상의 다른 문헌과 조합하는 경우로 그 조합이 당업자에게 자명한 경우 청구된 발명은 진보성이 없는 것으로 본다.

"&" 동일한 대응특허문헌에 속하는 문헌

국제조사의 실제 완료일	국제조사보고서 발송일
2016년 07월 29일 (29.07.2016)	2016년 07월 29일 (29.07.2016)

ISA/KR의 명칭 및 우편주소
대한민국 특허청
(35208) 대전광역시 서구 청사로 189,
4동 (둔산동, 정부대전청사)
팩스 번호 +82-42-481-8578

심사관
김동석
전화번호 +82-42-481-5405

서식 PCT/ISA/210 (두 번째 용지) (2015년 1월)

국제조사보고서
대응특허에 관한 정보

국제출원번호
PCT/KR2016/004449

국제조사보고서에서 인용된 특허문헌	공개일	대응특허문헌	공개일
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JP 2014-135175 A	2014/07/24	EP 2945467 A1	2015/11/18
		US 2015-0340639 A1	2015/11/26
		WO 2014-109081 A1	2014/07/17
KR 10-1449342 B1	2014/10/13	TW 201523992 A	2015/06/16
		WO 2015-069075 A1	2015/05/14
KR 10-2014-0090069 A	2014/07/16	CN 103911633 A	2014/07/09
		JP 2014-132106 A	2014/07/17
		JP 5696179 B2	2015/04/08
		US 2014-0193660 A1	2014/07/10
		US 9365942 B2	2016/06/14
US 2001-0051282 A1	2001/12/13	US 6372113 B2	2002/04/16