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[54] Title of the Invention:NANO ELECTROLYTIC COPPER FOIL SUITABLE
FOR LITHIUM-ION BATTERIES AND
PREPARATION METHOD THEREFOR**[57] Abstract**

Disclosed in the present invention are a nano electrolytic copper foil suitable for lithium-ion batteries and a preparation method therefor, wherein the electrolytic copper foil is composed of fine nano equiaxial crystals with an average grain size of ≤ 150 nm and no preferred orientation in an X-ray diffraction peak. A direct current electrodeposition process is adopted, and a nano electrolytic copper foil with a fine nano equiaxial crystal structure is prepared by rationally matching the composition of an electrolyte with electrodeposition process parameters, with the addition of a mixed organic additive. The electrolyte has a copper ion concentration of 30-120 g/l, and a sulfuric acid concentration of 50-350 g/l, the electrolytic deposition is carried out at 25°C to 65°C with the addition of the mixed organic additive, and the electrolyte has a flow rate of 0.5-5.0 m/s, and a current density of 0.5-5.0 A/cm². The mixed organic additive is composed of 1-15 mg/l thiourea, 1-15 mg/l bone glue, 0.1-5.0 mg/l chloride ions, and 0.005-0.05 mg/l Congo red. The prepared electrolytic copper foil has a thickness of ≤ 18 μ m, a tensile strength of ≥ 450 MPa, an elongation of $\geq 5\%$, and a rough surface roughness Rz of ≤ 0.40 μ m.

NANO ELECTROLYTIC COPPER FOIL SUITABLE FOR LITHIUM-ION BATTERIES AND PREPARATION METHOD THEREFOR

TECHNICAL FIELD

The present invention relates to a process for preparing an electrolytic copper foil, and relates more particularly to a method for preparing a nano electrolytic copper foil with a thickness of $\leq 18 \mu\text{m}$ for a high-performance lithium battery.

BACKGROUND ART

Human society in the 21st century is a society that attaches equal importance to energy, information, and the environment. High-energy batteries are closely related to the three major fields and will penetrate into all areas of human life. Lithium batteries are considered to be one of the high-energy batteries that can best meet the requirements of sustainable development of future society. At present, in addition to being widely used in traditional fields such as various electronic products, high-energy batteries have also been rapidly developed in emerging civilian fields such as portable electronic devices, built-in artificial organs, and robots. A preparation method for a negative electrode of a lithium-ion secondary battery is generally as follows: a negative electrode active material such as carbon powder processed into a paste is coated on the surface of a copper foil, and after drying, it is flattened. Then, it is wound together with a separator material and an aluminum foil coated with a positive electrode active material to obtain a lithium-ion secondary battery.

At present, there are two types of copper foils used as negative electrode current collectors for lithium-ion batteries: rolled copper foil and electrolytic copper foil. The cost of rolled copper foil is high, and the tensile strength of copper foil decreases due to recrystallization of rolled copper foil. After coating the negative electrode active material and drying, the operability is poor during rolling and other processes, and it is easy to break. Therefore, people have gradually shifted their focus to the electrolytic copper foil. The production process of electrolytic copper foil is divided into a roller method and a crawler method according to the form of devices. The roller method refers to a cathode device that is a cylindrical roller with its lower part immersed in an electrolyte and rotating continuously. Generally, the copper foil is formed by electrodeposition on a rotating cylindrical cathode in a $\text{CuSO}_4/\text{H}_2\text{SO}_4$ system. In an electrolytic cell, a fixed bow-shaped anode

is installed coaxially with the cathode roller, and a certain distance is maintained between the anode and the cathode. At present, this method is mostly used in the production of electrolytic copper foil.

In the existing production of a traditional electrolytic copper foil product, a certain amount of additive is generally added to an acidic copper sulfate electrolyte, and the additive is bone glue or cellulose. The process conditions are: 50-90 g/l copper, 100-250 g/l sulfuric acid, 3-12 mg/l bone glue, 1-5 g/l cellulose, an electrolysis temperature of 35°C to 55°C, an electrolyte flow rate of 0.5-3 m/s, and a current density of 0.4-0.8 A/cm². The tensile strength (350 MPa) and elongation (4%) of the electrolytic copper foil prepared under these conditions are relatively low, which cannot meet the requirements of lithium-ion battery special current collector materials for copper foil with high strength, high toughness, and low thickness. Therefore, it is necessary to develop a special electrolytic copper foil material suitable for lithium-ion batteries production, which develops toward low thickness ($\leq 18 \mu\text{m}$), and has higher tensile strength and elongation.

SUMMARY OF THE INVENTION

An objective of the present invention is to propose a nano electrolytic copper foil suitable for lithium-ion batteries and a preparation method therefor. A mixed organic additive is added during the preparation of the electrolytic copper foil, so that the rough surface roughness of the electrolytic copper foil is reduced, the grains are refined to a nanometer level, the tensile strength and elongation of the copper foil are improved, there is no preferential orientation on the surface of the copper foil, and the mechanical properties in all directions are uniform and stable.

A nano electrolytic copper foil suitable for lithium-ion batteries of the present invention is composed of fine nano equiaxial crystals with an average grain size of $\leq 150 \text{ nm}$ and no preferred orientation in an X-ray diffraction peak.

A preparation method for a nano electrolytic copper foil of the present invention adopts a direct current electrodeposition process, wherein a nano electrolytic copper foil with a fine nano equiaxial crystal structure is prepared by rationally matching the composition of an electrolyte with electrodeposition process parameters, with the addition of a mixed organic additive; the electrolyte has a copper ion concentration of 30-120 g/l, and a sulfuric acid concentration of 50-350 g/l, the electrolytic deposition is carried out at 25°C to 65°C with the addition of the mixed organic additive, and the electrolyte has a flow rate of 0.5-5.0 m/s, and a current density of 0.5-5.0

A/cm²; and the mixed organic additive is composed of 1-15 mg/l thiourea, 1-15 mg/l bone glue, 0.1-5.0 mg/l chloride ions and 0.005-0.05 mg/l Congo red.

The prepared electrolytic copper foil has a thickness of $\leq 18 \mu\text{m}$, a tensile strength of ≥ 450 MPa, an elongation of $\geq 5\%$, and a rough surface roughness R_z of $\leq 0.40 \mu\text{m}$.

The nano electrolytic copper foil is used as a negative electrode current collector copper foil material of a lithium ion secondary battery.

The present invention has the following advantages: (1) it has high tensile strength, and the tensile strength is ≥ 450 MPa, which is 28% or more higher than the tensile strength of copper foil under traditional processes and is 150% or more higher than that of the national standard; (2) it has high elongation, and the elongation is $\geq 5\%$, which is 150% or more higher than that of the national standard; (3) the rough surface roughness of the copper foil is low, and the roughness R_z is $\leq 0.40 \mu\text{m}$, the grains are refined to the nanometer level, and the average grain size is ≤ 150 nm; and (4) there is no preferential orientation on the surface of the copper foil, and the mechanical properties in all directions are uniform and stable.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a scanning electron microscope photograph of a copper foil in Example 1.

FIG. 2 is a scanning electron microscope photograph of a copper foil in Example 2.

FIG. 3 is a scanning electron microscope photograph of a copper foil in Example 3.

FIG. 4 is a scanning electron microscope photograph of a cross section of an electrolytic copper foil.

FIG. 5 is a typical X-ray diffraction spectrum of a surface of an electrolytic copper foil.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be further described in detail below with reference to the accompanying drawings and examples.

The present invention relates to a nano-electrolytic copper foil suitable for lithium-ion batteries, wherein the electrolytic copper foil is composed of fine nano equiaxial crystals with an average grain size of ≤ 150 nm and no preferred orientation in an X-ray diffraction peak. Please refer to a scanning electron microscope image of a cross-section of an electrolytic copper foil

shown in FIG. 4, from which it can be seen that the copper foil is composed of fine equiaxial crystals. Please refer to a typical X-ray diffraction spectrum of a surface of an electrolytic copper foil shown in FIG. 5, which shows that there is no preferential orientation on the surface of the copper foil.

A preparation method for a nano electrolytic copper foil of the present invention adopts a direct current electrodeposition process, wherein: a nano electrolytic copper foil with a fine nano equiaxial crystal structure is prepared by rationally matching the composition of an electrolyte with electrodeposition process parameters, with the addition of a mixed organic additive; the electrolyte has a copper ion concentration of 30-120 g/l, and a sulfuric acid concentration is 50-350 g/l, the electrolytic deposition is carried out at 25°C to 65°C with the addition of the mixed organic additive, and the electrolyte has a flow rate of 0.5-5.0 m/s, and a current density of 0.5-5.0 A/cm²; and the mixed organic additive is composed of 1-15 mg/l thiourea, 1-15 mg/l bone glue, 0.1-5.0 mg/l chloride ions and 0.005-0.05 mg/l Congo red.

The nano electrolytic copper foil obtained by the above preparation method has a thickness of $\leq 18\text{ }\mu\text{m}$, a tensile strength of $\geq 450\text{ MPa}$, an elongation of $\geq 5\%$, and a rough surface roughness Rz of $\leq 0.40\text{ }\mu\text{m}$.

In the present invention, a nano electrolytic copper foil with a fine nano equiaxial crystal structure is prepared by rationally matching the composition of the electrolyte with the electrodeposition process parameters while adding the mixed organic additive to improve the mechanical properties of the electrolytic copper foil. The prepared electrolytic copper foil has a small surface roughness, a high tensile strength, and a large elongation. The mixed organic additive is added in the preparation process of the electrolytic copper foil, and the composition of the electrolyte is rationally matched with the electrodeposition process parameters, so that the rough surface roughness of the electrolytic copper foil is reduced, the grains are refined to a nanometer level, the tensile strength and elongation of the copper foil are improved, there is no preferential orientation on the surface of the copper foil, and the mechanical properties in all directions are uniform and stable.

Example 1

A copper foil was prepared by adopting a direct current electrodeposition process. An electrolyte has a copper ion concentration of 50 g/l and a sulfuric acid concentration of 100 g/l.

Electrolysis is carried out at 35°C, the electrolyte has a flow rate of 1.0 m/s, and a current density of 0.6A/cm², and the unit composition of a mixed organic additive added to the electrolyte is as follows:

Thiourea	3 mg/l
Bone glue	3 mg/l
Chloride ion	0.1 mg/l
Congo red	0.005 mg/l

The prepared copper foil was tested by a material mechanical properties tester. It has a tensile strength of 500 MPa, an elongation of 5.0%, and a rough surface roughness of 0.40 μm. The average grain size is 146 nm, and its scanning electron microscope image is shown in FIG. 1. There is no preferential orientation on the surface of the copper foil.

Example 2

An preparation method includes an electrolyte having a copper concentration of 90 g/l and a sulfuric acid concentration of 250 g/l. Electrolysis is carried out at 55°C, the electrolyte has a flow rate of 1.0 m/s, and a current density of 1.0 A/cm², and the unit composition of an organic additive added to the electrolyte is as follows:

Thiourea	12 mg/l
Bone glue	12 mg/l
Chloride ion	5.0 mg/l
Congo red	0.02 mg/l

The prepared copper foil was tested by a material mechanical properties tester. It has a tensile strength of 645 MPa, an elongation of 6.2%, and a rough surface roughness of 0.38 μm. The average grain size is 120 nm, and its scanning electron microscope image is shown in FIG. 2. There is no preferential orientation on the surface of the copper foil.

Example 3

An preparation method includes an electrolyte having a copper concentration of 80 g/l and a sulfuric acid concentration of 200 g/l. Electrolysis is carried out at 50°C, the electrolyte has a

flow rate of 1.0 m/s, and a current density of 1.0 A/cm², and the unit composition of an organic additive added to the electrolyte is as follows:

Thiourea	9 mg/l
Bone glue	3 mg/l
Chloride ion	1.0 mg/l
Congo red	0.01 mg/l

The prepared copper foil was tested by a material mechanical properties tester. It has a tensile strength of 695 MPa and an elongation of 7.9%, and the rough surface roughness of the rough surface thereof is 0.38 μm . The average grain size is 100 nm, and its scanning electron microscope image is shown in FIG. 3. There is no preferential orientation on the surface of the copper foil.

According to the present invention, a nano electrolytic copper foil having a thickness of $\leq 18 \mu\text{m}$ for high-performance lithium batteries is prepared. The copper foil has high tensile strength and elongation. The tensile strength is $\geq 450 \text{ MPa}$, which is 28% or more higher than the tensile strength of copper foil under the traditional process, and is 150% or more higher than that of the national standard, and the elongation is $\geq 5\%$, which is 150% higher than that of the national standard. The rough surface roughness of the electrolytic copper foil is reduced, the grains are refined to the nanometer level, the average grain size is $\leq 150 \text{ nm}$, and there is no preferential orientation on the surface of the copper foil, and the mechanical properties in all directions are uniform and stable.

CLAIMS

1. A nano electrolytic copper foil suitable for lithium-ion batteries, characterized in that the electrolytic copper foil is composed of fine nano equiaxial crystals with an average grain size of ≤ 150 nm and no preferred orientation in an X-ray diffraction peak.
2. A preparation method for the nano electrolytic copper foil according to claim 1, adopting a direct current electrodeposition process, characterized in that: a nano electrolytic copper foil with a fine nano equiaxial crystal structure is prepared by rationally matching the composition of an electrolyte with electrodeposition process parameters, with the addition of a mixed organic additive; the electrolyte has a copper ion concentration of 30-120 g/l, and a sulfuric acid concentration is 50-350 g/l, the electrolytic deposition is carried out at 25°C to 65°C with the addition of the mixed organic additive, and the electrolyte has a flow rate of 0.5-5.0 m/s, and a current density of 0.5-5.0 A/cm²; and the mixed organic additive is composed of 1-15 mg/l thiourea, 1-15 mg/l bone glue, 0.1-5.0 mg/l chloride ions and 0.005-0.05 mg/l Congo red.
3. The preparation method for the nano electrolytic copper foil according to claim 2, wherein: the electrolyte has a copper ion concentration of 50 g/l, and a sulfuric acid concentration of 100 g/l, the mixed organic additive includes 3 mg/l thiourea, 3 mg/l bone glue, 0.1 mg/l chloride ions and 0.005 mg/l Congo red, the electrolysis is carried out at 35°C, and the electrolyte has a flow rate of 1.0 m/s, and a current density of 0.6 A/cm².
4. The preparation method for the nano electrolytic copper foil according to claim 2, wherein: the copper ion concentration in the electrolyte is 90 g/l, the sulfuric acid concentration is 250 g/l, the mixed organic additive includes 12 mg/l thiourea, 12 mg/l bone glue, 5.0 mg/l chloride ions and 0.02 mg/l Congo red, and the electrolysis is carried out at 55°C, and the flow rate of the electrolyte is 1.0 m/s, and the current density is 1.0 A/cm².
5. The preparation method for the nano electrolytic copper foil according to claim 2, wherein: the copper ion concentration in the electrolyte is 80 g/l, the sulfuric acid concentration is 200 g/l, the mixed organic additive includes 9 mg/l thiourea, 3 mg/l bone glue, 1.0 mg/l chloride ions and

0.01 mg/l Congo red, the electrolysis is carried out at 50°C, and the flow rate of the electrolyte is 1.0 m/s, and the current density is 1.0 A/cm².

6. The preparation method for the nano electrolytic copper foil according to claim 2 or 3 or 4 or 5, wherein: the prepared electrolytic copper foil has a thickness of $\leq 18\text{ }\mu\text{m}$, a tensile strength of $\geq 450\text{ MPa}$, an elongation of $\geq 5\%$, and a rough surface roughness Rz of $\leq 0.40\text{ }\mu\text{m}$.

7. The preparation method for the nano electrolytic copper foil according to claim 2 or 3 or 4 or 5, wherein: the prepared electrolytic copper foil is used as a negative electrode current collector copper foil material of a lithium ion secondary battery.

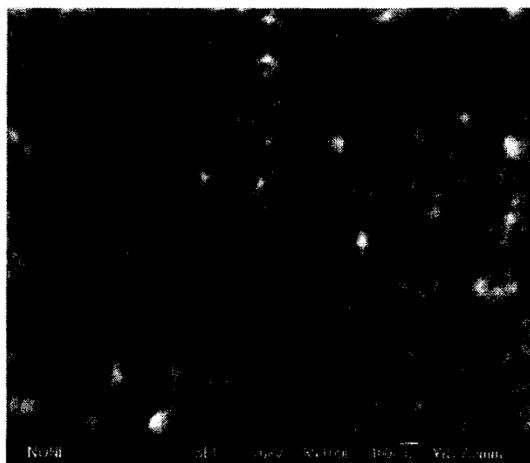


FIG. 1

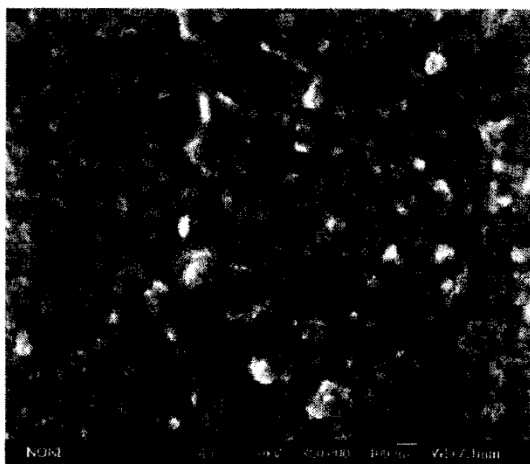


FIG. 2



FIG. 3

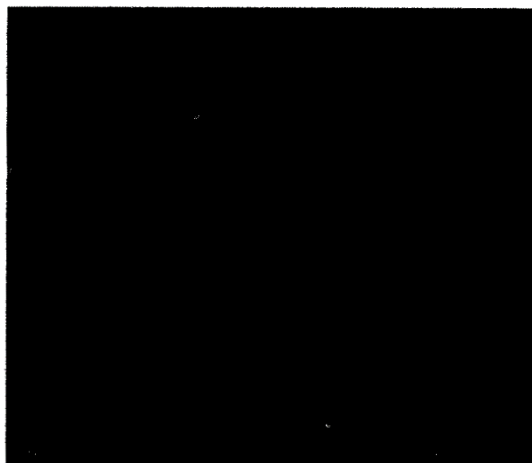


FIG. 4

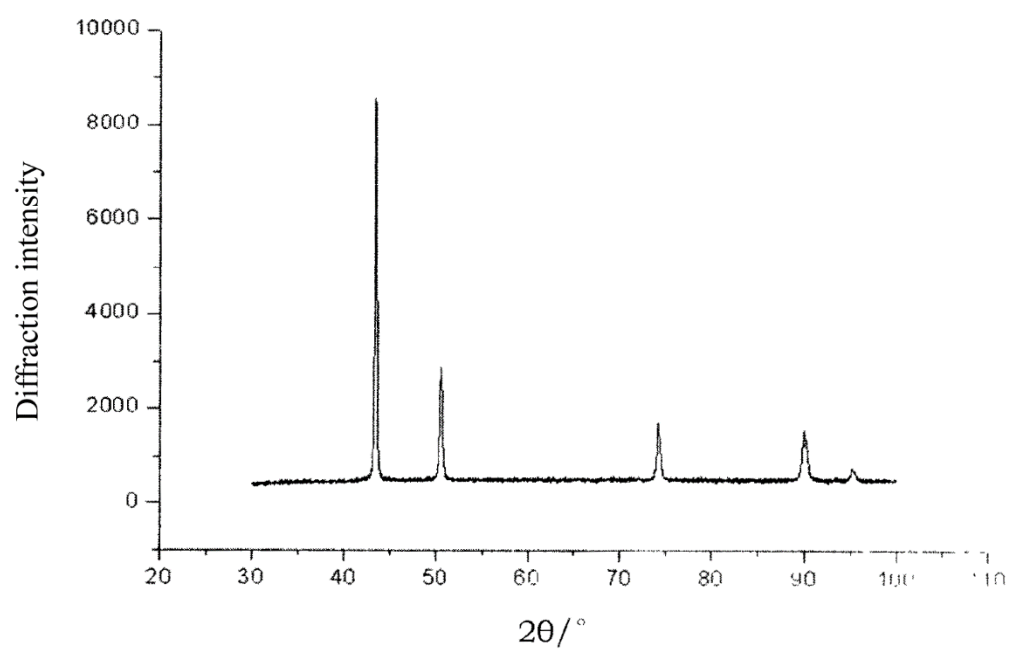


FIG. 5



TRANSLATOR'S CERTIFICATE OF TRANSLATION

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Questel Project Number: FRPC2420071UT-L_Q

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I, Chris Yien, a translator fluent in the Chinese and English languages, on behalf of Questel, do solemnly and sincerely declare that the following is, to the best of my knowledge and belief, a true and correct translation of the document(s) listed below in a form that best reflects the intention and meaning of the original text.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I further declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

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