GB

NATIONAL STANDARD OF THE

PEOPLE'S REPUBLIC OF CHINA

ICS 29.050

Q 53

GB/T 30836-2014

Lithium titanium oxide and its carbon composite anode materials for lithium ion battery

锂离子电池用钛酸锂及其炭符合负极材料

Issued on: June 24, 2014 **Implemented on: April 01, 2015**

Issued by: General Administration of Quality Supervision, Inspection and Quarantine;
Standardization Administration of the People's Republic of China.

Table of Contents

Lithium titanium oxide and its carbon composite anode materials for lithium ion battery

1 Scope

This Standard specifies the terms and definitions, classification and code, technical requirements, test methods, inspection rules, as well as packaging, marking, storage and transportation of lithium titanium oxide and its carbon composite anode materials for lithium ion battery.

This Standard applies to lithium titanium oxide and its carbon composite anode materials for lithium ion battery (hereinafter referred to as lithium titanate oxide anode materials). Lithium titanate oxide for electrochemical capacitors can also be used with reference to this Standard.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

GB/T 191, Packaging - Pictorial marking for handling of goods

GB/T 5162, Metallic powders - Determination of tap density

GB/T 6283, Chemical products - Determination of water - Karl Fischer method (general method)

GB/T 6388, Transport package shipping mark

GB/T 6682, Water for analytical laboratory use - Specification and test methods

GB/T 9724, Chemical reagent - General rule for the determination of pH

GB/T 13732, General rules for sampling inspection of bulk materials with uniform size

GB/T 19077.1, Particle size analysis - Laser diffraction methods - Part 1: General principles

GB/T 19587, Determination of the specific surface area of solids by gas adsorption using the BET method

GB/T 20123, Steel and iron - Determination of total carbon and sulfur content Infrared absorption method after combustion in an induction furnace (routine method)

GB/T 24533-2009, Graphite negative electrode materials for lithium ion battery

DZ/T 0064.49, Methods for analysis of groundwater quality - Part 49: Determination of carbonate, bicarbonate ions, hydroxy - Titrimetric method

JCPDS (00-049-0207), Lithium titanate X-ray powder diffraction standard pattern

IEC 62321, Electrotechnical products - Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

lithium titanium oxide and its carbon composite anode materials

Lithium titanate oxide, or carbon composite lithium titanate oxide materials which realize the charging and discharging of lithium ion batteries when working together with the cathode material in a certain system. During the charging process, the lithium titanate oxide anode material accepts the insertion of lithium ions, and during the discharging process, the lithium ions are released.

4 Classification and code

4.1 Product classification

The carbon-free lithium titanate oxide anode material is represented by LTO, and the carbon composite lithium titanate oxide anode material is represented by LTO@C, where LTO represents lithium titanate oxide, @ represents the composite of the two materials, and C represents carbon:

-- Carbon-free lithium titanate oxide anode materials (LTO) are divided into three categories, respectively represented as LTO-I, LTO-II, and LTO-III. Their specific performance requirements are detailed in Table 2;

-- Carbon composite lithium titanate oxide anode materials (LTO@C) are divided into three categories, respectively represented as LTO@C-I, LTO@C-II, and LTO@C-III. Their specific performance requirements are detailed in Table 2.

Perform visual observation under natural light conditions.

6.2 Particle size D_{50}

Carry out the measurement in accordance with the measurement method specified in GB/T 19077.1.

6.3 Moisture content

Determine the moisture content according to the direct potentiometric titration method specified in GB/T 6283.

6.4 pH

Successively weigh 1.000 g ± 0.001 g (accurate to 0.000 1 g) of sample and 50.00 g ± 0.01 g (accurate to 0.000 1 g) of water into a 100 mL beaker. After stirring, sonicate for 10 minutes and let stand to obtain the solution to be tested. Measure the solution to be tested with reference to the measurement method specified in GB/T 9724, and the measurement result is the pH value of the sample.

6.5 Tap density

Carry out the measurement in accordance with the measurement method specified in GB/T 5162.

6.6 Powder compaction density

Carry out the measurement according to the measurement method specified in Appendix L of GB/T 24533-2009.

6.7 True density

Carry out the measurement according to the measurement method specified in Appendix E of GB/T 24533-2009.

6.8 BET specific surface area

Carry out the determination according to the volumetric method for measuring powder BET specific surface area specified in GB/T 19587.

6.9 Carbon content

Carry out the measurement in accordance with the measurement method specified in GB/T 20123.

6.10 Lithium content

Carry out the measurement according to the measurement method specified in Appendix A.

6.11 Iron content

Carry out the measurement according to the measurement method specified in Appendix H of GB/T 24533-2009.

6.12 Crystal structure

Carry out the measurement according to the measurement method specified in Appendix B.

6.13 Anatase TiO_2 peak intensity ratio I_{101}/I_{111}

Carry out the measurement according to the measurement method specified in Appendix B.

6.14 Rutile TiO_2 peak intensity ratio I_{110}/I_{111}

Carry out the measurement according to the measurement method specified in Appendix B.

6.15 First reversible specific capacity

Carry out the measurement according to the measurement method specified in Appendix G of GB/T 24533-2009. Some of the measurement parameters are as follows: the mass fractions of the sample, conductive electrode, and binder are 80% ~ 90%, 2% ~ 10%, and 2% ~ 10% respectively; the experimental battery is measured at 20 °C ~ 25 °C; the limited charging voltage is 2.5 V; the end of discharge voltage is 1.0 V; the charge and discharge current rate is 1 C.

6.16 First coulombic efficiency

Measure according to the measurement method specified in Appendix G of GB/T 24533-2009, and the test parameters are the same as 6.15.

6.17 Magnetic substance content

Carry out the measurement according to the measurement method specified in Appendix K of GB/T 24533-2009.

6.18 Residual alkali content

Weigh 5.000 g ± 0.005 g (accurate to 0.000 1 g) of the sample into a 100 mL beaker; add 50 mL of water, sonicate for 5 minutes; filter and add water to fix the volume in a 100 mL volumetric flask; shake well; let stand until tested. Measure the solution to be tested according to the measurement method specified in DZ/T 0064.49, and the measurement result is the residual alkali content of the sample.

6.19 Anion content (Cl^-, SO_4^{2-})

7.1.3.2 The effective storage period of spare samples is 12 months.

7.2 Inspection

7.2.1 Ex-factory inspection

Inspect the physical and chemical properties, electrochemical properties, magnetic substance content, total sulfur content, restricted substance content, residual alkali content, etc. of each batch of samples, and deliver them only after the inspection is qualified.

7.2.2 Type inspection

Inspect all technical requirements specified in this Standard. Carry out the type inspection when one of the following situations occurs:

a) when there are changes in raw material models, suppliers, etc.;

b) when there are changes in the production process;

c) when the production equipment which has been stopped for more than half a year is put into production again for the first time;

d) when customers have special requirements.

7.3 Acceptance rules

7.3.1 A product that meets all the technical indicators required by a certain category in Table 2 is a qualified product. If an indicator fails to meet the requirements of this category, double samples shall be taken from the sampling bags of the same batch of products for re-inspection of the unqualified items, and the re-inspection results will be used as the final result. Products that do not fall into the product categories in Table 2 or have special requirements shall be determined through negotiation between the supply and demand parties.

7.3.2 The inspection department of the manufacturer shall ensure that the products delivered meet the requirements specified in this Standard, and send a product quality inspection report to the receiving party at the same time as each batch of products leaves the factory.

7.3.3 The receiving party has the right to accept products in accordance with this Standard and the right to reject products that do not meet the requirements of this Standard.

7.3.4 The receiving party shall conduct acceptance inspection of the product within one month after receiving the product. If there is any objection, a spare sample shall be used for re-inspection. If there is still a dispute, it shall be arbitrated by the superior quality supervision department.

8 Packaging, marking

8.1 Pack according to the net weight of 25 kg per package. Special packaging requirements shall be agreed upon by both parties.

8.2 Pack in a dry environment, and first put the product into waterproof packaging. Special packaging requirements shall be agreed upon by both parties.

8.3 The packaged products are then packaged in composite bags, plastic barrels, paper barrels, etc.

8.4 The marking of lithium titanate oxide anode material shall comply with the requirements in GB/T 191. There shall be an eye-catching marking on the front of each product packaging bag. The marking shall include the following:

a) product name;

b) model and specifications;

c) number of the standard implemented;

d) net weight;

e) manufacturer name;

f) manufacturing date, production batch number or production date and serial number;

g) warning instructions;

h) other identifications.

It can also be marked according to customer needs.

9 Storage and transportation

9.1 Product transportation markings shall comply with the regulations on transportation packaging receipt and delivery markings in GB/T 6388.

9.2 Products shall be stored in a ventilated and dry warehouse.

9.3 Products shall be stacked neatly and cleanly, and markings such as registered trademark, production batch number, and production date shall be clear and easy to identify.

9.4 Avoid mixing storage and transportation with items that may cause product deterioration or damage packaging bags.

Appendix A

(Normative)

Determination method of lithium content

A.1 Scope of application

This Appendix is applicable to the determination of lithium content in samples by inductively coupled plasma-atomic emission spectrometry.

A.2 Method summary

Dissolve the sample with a mixed acid of concentrated sulfuric acid and concentrated hydrochloric acid (volume ratio 1:3), and measure the lithium content using an inductively coupled plasma-atomic emission spectrometer under selected optimal conditions.

A.3 Reagents and materials

Unless otherwise specified, the water used in the tests in this Standard refers to grade-3 water meeting the requirements in GB/T 6682, and the reagents used in the tests are all analytical reagents.

A.3.1 Concentrated sulfuric acid

ρ1.84 g/mL.

A.3.2 Concentrated hydrochloric acid

ρ1.19 g/mL.

A.3.3 Argon gas

Volume fraction not less than 99.999%.

A.3.4 Lithium standard solution

Concentration 1 000 μg/mL, national certified reference material which can be stored for 1 year.

A.3.5 Preparation of stock standard solution

Take 5.00 mL of lithium standard solution (see A.3.4) in a 100 mL volumetric flask; add 2 mL of concentrated hydrochloric acid (see A.3.2); adjust the volume to the mark; shake well; prepare it a stock standard solution with a lithium ion concentration of 50 μg/mL.

A.3.6 Preparation of series standard solutions

Accurately measure 0 mL, 1.00 mL, 2.00 mL, 5.00 mL, and 10.00 mL of lithium ion stock standard solutions (see A.3.5) into five 100 mL volumetric flasks; add 2 mL of concentrated hydrochloric acid (see A.3.2) to each; dilute to the mark; shake well; prepare it standard blank and series standard solutions with lithium ion concentrations of 0 μg/mL, 0.50 μg/mL, 1.00 μg/mL, 2.50 μg/mL, and 5.00 μg/mL. The ion content in the solution to be tested shall be within the range of the standard curve.

A.4 Instruments and apparatuses

A.4.1 Inductively coupled plasma-atomic emission spectrometer.

A.4.2 Heating plate or digestion device of equivalent performance (working temperature range: 50 °C ~ 400 °C).

A.4.3 Analytical balance (sensitivity: 0.000 1 g).

A.5 Analysis steps

A.5.1 Number of determinations

Take two samples for parallel sample testing and take their arithmetic average.

A.5.2 Blank test

Do a blank test with the sample.

A.5.3 Standard curve

Linear correlation coefficient ≥0.999 5.

A.5.4 Preparation of sample solution to be tested

Weigh 0.10 g ± 0.02 g (accurate to 0.000 1 g) of sample into a 50 mL beaker; add 9 mL of concentrated hydrochloric acid (see A.3.2) and 3 mL of concentrated sulfuric acid (see A.3.1); place it on the heating plate (see A.4.2); digest completely; cool to room temperature; filter and dilute to volume. Properly dilute the sample solution to a constant volume (referring to the preparation method of the stock standard solution for dilution) to ensure that the lithium ion concentration in the sample solution to be tested is within the standard curve.

A.5.5 Determination

After the instrument is running stably, according to the conditions in Table A.1, inject the blank and the series standard solutions (see A.3.6) of the standard sample sequentially for measurement; draw a standard curve; then measure the sample blank and the sample solution to be tested (see A.5.4) in the same method, and correct the results by subtracting the blank.

Appendix B

(Normative)

Determination method of material crystal structure and residual TiO_2

B.1 Scope of application

This Appendix is applicable to the crystal structure of the sample tested by the X-ray diffractometer, as well as the qualitative content of the anatase TiO_2 and rutile TiO_2 residues.

B.2 Method summary

Take the crystal as a stack of many parallel atomic planes. When X-rays are irradiated onto the atomic plane, the scattered waves of all atoms have the same phase in the reflection direction of the atomic plane, which is the direction of enhanced interference. Since X-rays can penetrate into the interior, to make the internal atoms become the source of scattering waves, the diffracted ray is regarded as the result of the superposition of the amplitudes of the reflected waves reflected by many parallel atomic planes. The condition for interference enhancement is that the phase difference of the scattered waves of atoms on any adjacent atomic plane in the crystal in the reflection direction of the atomic plane is an integer multiple of 2π, or the optical path difference is equal to an integer multiple of the wavelength. It can be seen from Figure B.1 that the conditions for interference enhancement are: $2d \sin\theta = n\lambda$, where n is an integer, which is called the reflection series, θ is the angle between the incident ray and the reflecting surface, which is called the grazing angle, 2θ is called the diffraction angle, and the above equation is called the Bragg equation. X-rays diffract on different atomic planes, and appear as diffraction lines at different diffraction angle positions in the diffraction pattern. The X-ray diffractometer automatically records the diffraction line pattern of the lithium titanate oxide anode material in the range of $10° \sim 90°$, and compares the obtained diffraction pattern with the standard X-ray powder diffraction patterns of lithium titanate oxide, anatase TiO_2 and rutile TiO_2, to analyze the crystal structure of the lithium titanate oxide material, and calculate the anatase TiO_2 and rutile TiO_2 residues, which are represented by the "peak intensity ratio" of the designated diffraction peaks of lithium titanate oxide and anatase TiO_2 and rutile TiO_2.

This is an excerpt of the PDF (Some pages are marked off intentionally)

------ The End ------