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Recycled black mass for lithium ion battery

锂离子电池用再生黑粉

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Recycled black mass for lithium ion battery

1 Scope

This document specifies the classification and grading, technical requirements, test methods, inspection rules, marking, packaging, transportation, storage and accompanying documents of recycled black mass for lithium-ion batteries.

This document applies to battery black mass obtained from the recycling of lithium-ion battery waste and used for subsequent recycling.

2 Normative references

The contents of the following documents constitute the essential terms of this document through normative references in the text. Among them, for dated references, only the version corresponding to that date applies to this document; for undated references, the latest version (including all amendments) applies to this document.

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

GB/T 8170 Rules of rounding off for numerical values and expression and judgement of limiting values

YS/T 1342 (all parts) Methods for chemical analysis of waste secondary battery

3 Terms and definitions

The following terms and definitions apply to this document.

3.1

Lithium ion battery scraps

Waste lithium ion batteries and their waste raw materials.

Note: Including scrapped lithium ion batteries, scrapped semi-finished products, waste raw materials generated in industrial production processes, as well as the lithium ion batteries that have lost their use value in daily life or circulation.

3.2

Black mass

out in accordance with the provisions of Appendix D.

6.1.3 The determination method of water-extractable total organic carbon (TOC) content in the product is shown in Appendix E.

6.1.4 The determination method of acid-insoluble matter content in the product is shown in Appendix F.

6.2 Loss on drying

The determination method of drying loss in the product is shown in Appendix G.

6.3 Mixtures or inclusions

6.3.1 The calculation method of the molar ratio of the main elements of the product is shown in Appendix H. The determination method of zinc, lead, chromium, cadmium, arsenic content in the product is shown in Appendix A.

6.3.2 Inclusions are detected by visual method; the determination method of product particle size is shown in Appendix I.

7 Inspection rules

7.1 Inspection and acceptance

7.1.1 Products are inspected by the supplier or a third-party inspection department. The supplier shall ensure that the product quality complies with the provisions of this document.

7.1.2 The buyer may inspect the received products in accordance with the provisions of this document. If the inspection results do not comply with the provisions of this document, the buyer shall submit the matter to the supplier within 30 days from the date of receipt of the product; the supplier and buyer shall negotiate to resolve the issue. If arbitration is required, the supplier and buyer shall jointly sample or negotiate at the buyer's place.

7.2 Group-batching

Each batch of products shall consist of products of the same class and grade; each batch of products shall not exceed 32 t. The group-batching method shall be carried out according to the supplier's incoming batch or determined by the supplier and buyer on-site.

7.3 Inspection items

Each batch of products shall be inspected for chemical composition, drying loss, mixed materials or inclusions.

Appendix A

(Informative)

Determination of nickel, cobalt, manganese, lithium, phosphorus, iron, zinc, lead, cadmium, chromium, arsenic content in recycled black mass for lithium-ion batteries - Inductively coupled plasma atomic emission spectrometry

A.1 Principle

The sample is dissolved in a hydrochloric acid-nitric acid mixture. In a nitric acid medium, the emission intensity of nickel, cobalt, manganese, lithium, phosphorus, iron, zinc, lead, cadmium, chromium, arsenic is measured on an inductively coupled plasma atomic emission spectrometer. The concentration of each element is found on the working curve and the mass fraction is calculated.

A.2 Reagents

Unless otherwise specified, the reagents used in this Appendix are reagents of analytical grade or above and distilled water or deionized water or water of equivalent purity.

A.2.1 Nitric acid (1 + 1).

A.2.2 Hydrochloric acid-nitric acid mixture: 3 volumes of hydrochloric acid ($\rho \approx 1.19$ g/mL) + 1 volume of nitric acid ($\rho \approx 1.42$ g/mL); mix well.

A.2.3 Nickel standard stock solution: National certified standard solution, wherein 1 mL of this solution contains 1 mg of nickel.

A.2.4 Cobalt standard stock solution: National certified standard solution, wherein 1 mL of this solution contains 1 mg of cobalt.

A.2.5 Manganese standard stock solution: National certified standard solution, wherein 1 mL of this solution contains 1 mg of manganese.

A.2.6 Lithium standard stock solution: National certified standard solution, wherein 1 mL of this solution contains 1 mg of lithium.

A.2.7 Phosphorus standard stock solution: National certified standard solution, wherein 1 mL of this solution contains 1 mg of phosphorus.

A.2.8 Iron standard stock solution: National certified standard solution, wherein 1 mL of this solution contains 1 mg of iron.

A.2.9 Zinc standard stock solution: National certified standard solution, wherein 1 mL of this solution contains 1 mg of zinc.

A.2.10 Lead standard stock solution: National certified standard solution, wherein 1 mL

of this solution contains 1 mg of lead.

A.2.11 Cadmium standard stock solution: National certified standard solution, wherein 1 mL of this solution contains 1 mg of cadmium.

A.2.12 Chromium standard stock solution: National certified standard solution, wherein 1 mL of this solution contains 1 mg of chromium.

A.2.13 Arsenic standard stock solution: National certified standard solution, wherein 1 mL of this solution contains 1 mg of arsenic.

A.2.14 Nickel, cobalt, manganese mixed standard solution: Pipette 10.00 mL of nickel standard stock solution (A.2.3), cobalt standard stock solution (A.2.4), manganese standard stock solution (A.2.5) to a 100 mL volumetric flask; dilute to the mark with water; mix well. 1 mL of this solution contains 100 μg of nickel, cobalt, manganese, respectively.

A.2.15 Iron and lithium mixed standard solution: Take 10.00 mL of iron standard stock solution (A.2.8) and lithium standard stock solution (A.2.6); place them in a 100 mL volumetric flask; dilute to the mark with water and mix well. 1 mL of this solution contains 100 μg of iron and lithium each.

A.2.16 Phosphorus, zinc, lead, cadmium, chromium, arsenic mixed standard solution: Take 10.00 mL of phosphorus standard stock solution (A.2.7), zinc standard stock solution (A.2.9), lead standard stock solution (A.2.10), cadmium standard stock solution (A.2.11), chromium standard stock solution (A.2.12), arsenic standard stock solution (A.2.13); place them in a 100 mL volumetric flask; dilute to the mark with water; mix well. 1 mL of this solution contains 100 μg of phosphorus, zinc, lead, cadmium, chromium, arsenic each.

A.2.17 Lithium standard solution: Pipette 10.00 mL of lithium standard stock solution (A.2.6) into a 100 mL volumetric flask; dilute to scale with water; mix well. 1 mL of this solution contains 100 μg of lithium.

A.2.18 Phosphorus and iron mixed standard solution: Pipette 10.00 mL of phosphorus standard stock solution (A.2.7) and iron standard stock solution (A.2.8) into a 100 mL volumetric flask; dilute to scale with water; mix well. 1 mL of this solution contains 100 μg of phosphorus and iron, respectively.

A.2.19 Mixed standard solution of zinc, lead, cadmium, chromium, arsenic, nickel, cobalt, manganese: Take 10.00 mL of zinc standard stock solution (A.2.9), lead standard stock solution (A.2.10), cadmium standard stock solution (A.2.11), chromium standard stock solution (A.2.12), arsenic standard stock solution (A.2.13), nickel standard stock solution (A.2.3), cobalt standard stock solution (A.2.4), manganese standard stock solution (A.2.5); place them in a 100 mL volumetric flask; dilute to the mark with water; mix well. 1 mL of this solution contains 100 μg of each element of zinc, lead, cadmium,

Perform two tests in parallel and take the average value.

A.5.3 Blank test

Perform a blank test with the test material.

A.5.4 Determination

A.5.4.1 Conventional digestion

A.5.4.1.1 Place the sample (A.5.1.1) in a 1000 mL beaker; moisten with a small amount of water; add 60 mL of hydrochloric acid-nitric acid mixture (A.2.2); cover with a watch glass; heat until completely dissolved; cool to room temperature; transfer to a 500 mL volumetric flask; dilute to scale with water; mix well, to obtain the test solution 1.

A.5.4.1.2 Filter test solution 1 (A.5.4.1.1) with filter paper to obtain a filtrate. Take 2.00 mL of the filtrate of test solution 1 (A.5.4.1.1); place it in a 200 mL volumetric flask; add 8 mL of nitric acid (A.2.1); dilute to scale with water; mix well, to obtain test solution 2 (the dilution factor is 100 times).

A.5.4.1.3 On the inductively coupled plasma atomic emission spectrometer (A.3.1), measure the emission intensity of nickel, cobalt, manganese, lithium, phosphorus, iron, zinc, lead, cadmium, chromium, arsenic in the blank test solution (A.5.3), the filtrate of test solution 1 (A.5.4.1.1), test solution 2 (A.5.4.1.2). Calculate the mass concentration (ρ) of each element to be measured after blank correction from the working curve.

A.5.4.2 Microwave digestion

A.5.4.2.1 Place the sample (A.5.1.2) in a digestion tank; add 10 mL of hydrochloric acid-nitric acid mixture (A.2.2); seal it and place it in a microwave digester for digestion. After digestion, transfer it to a 200 mL volumetric flask; dilute it to the scale with water; mix it well, to obtain test solution 3.

A.5.4.2.2 Filter test solution 3 (A.5.4.2.1) with filter paper to obtain a filtrate. Take 5.00 mL of the filtrate of test solution 3 (A.5.4.2.1); place it in a 200 mL volumetric flask; add 8 mL of nitric acid (A.2.1); dilute to the mark with water; mix well, to obtain test solution 4 (its dilution factor is 40 times).

A.5.4.2.3 Determine the emission intensity of nickel, cobalt, manganese, lithium, phosphorus, iron, zinc, lead, cadmium, chromium, arsenic in the blank test solution (A.5.2), the filtrate of test solution 3 (A.5.4.2.1), the test solution 4 (A.5.4.2.2), on an inductively coupled plasma atomic emission spectrometer (A.3.1). Calculate the mass concentration (ρ) of each element to be measured after blank correction from the working curve.

A.6 Drawing of working curve

A.6.1 Class I black mass

A.6.1.1 Pipette 0 mL, 2.00 mL, 4.00 mL, 6.00 mL, 8.00 mL of iron and lithium mixed standard solution (A.2.15) to a group of 100 mL volumetric flasks; pipette 0 mL, 4.00 mL, 8.00 mL, 12.00 mL, 16.00 mL of nickel, cobalt, manganese mixed standard solution (A.2.14) to the above group of 100 mL volumetric flasks; pipette 0 mL, 0.10 mL, 0.20 mL, 0.30 mL, 0.40 mL of phosphorus, zinc, lead, cadmium, chromium, arsenic mixed standard solution (A.2.16) to the above group of 100 mL volumetric flasks; add 4 mL of nitric acid (A.2.1) to each; dilute to the mark with water; mix well; transfer into a dry polyethylene bottle.

A.6.1.2 Measure the emission intensity of nickel, cobalt, manganese, lithium, phosphorus, iron, zinc, lead, cadmium, chromium, arsenic in a series of standard solutions on an inductively coupled plasma atomic emission spectrometer; draw a working curve with the mass concentration of the element to be measured as the abscissa and the corresponding emission intensity (minus the excitation intensity of the "zero" solution) as the ordinate.

A.6.2 Class II black mass

A.6.2.1 Pipette 0 mL, 2.00 mL, 4.00 mL, 6.00 mL, 8.00 mL of lithium standard solution (A.2.17) to a set of 100 mL volumetric flasks; pipette 0 mL, 4.00 mL, 8.00 mL, 12.00 mL, 16.00 mL of phosphorus and iron mixed standard solution (A.2.18) to the above set of 100 mL volumetric flasks; pipette 0 mL, 0.10 mL, 0.20 mL, 0.30 mL, 0.40 mL of zinc, lead, cadmium, chromium, arsenic, nickel, cobalt, manganese mixed standard solution (A.2.19) to the above set of 100 mL volumetric flasks; add 4 mL of nitric acid (A.2.1) to each; dilute to the mark with water; mix well; transfer into a dry polyethylene bottle.

A.6.2.2 Determine the emission intensity of nickel, cobalt, manganese, lithium, phosphorus, iron, zinc, lead, cadmium, chromium, arsenic in a series of standard solutions, on an inductively coupled plasma atomic emission spectrometer. Draw a working curve with the mass concentration of the element to be measured as the horizontal axis and the corresponding emission intensity (minus the excitation intensity of the "zero" solution) as the vertical axis.

A.7 Test data processing

The content of each element to be measured is calculated as the mass fraction w_x of the element, according to formula (A.1):

$$w_x = \frac{(\rho_1 - \rho_2) \cdot V_1 \cdot n \times 10^{-6}}{m_1} \times 100\% \quad \cdots\cdots (A.1)$$

Where:

x - Nickel, cobalt, manganese, lithium, phosphorus, iron, zinc, lead, chromium,

Appendix B

(Normative)

Determination of phosphorus content in recycled black mass for lithium-ion batteries - Quinoline phosphomolybdic acid weight method

B.1 Principle

In an acidic medium, orthophosphate reacts with quinoline molybdic acid precipitant to form a yellow quinoline phosphomolybdic acid precipitate, which is filtered, washed, dried, weighed to determine the phosphorus content.

B.2 Reagents and materials

Unless otherwise specified, the reagents used in this Appendix are reagents of analytical purity or above and distilled water or deionized water or water of equivalent purity.

B.2.1 Hydrochloric acid ($\rho \approx 1.19$ g/mL).

B.2.2 Quinoline molybdate reagent is prepared as follows:

a) Solution A - Weigh 70 g of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) in a 400 mL beaker; dissolve it with 100 mL water;

b) Solution B - Weigh 60 g of citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) in a 1000 mL beaker; dissolve it with 150 mL water; add 85 mL of nitric acid ($\rho \approx 1.42$ g/mL);

c) Solution C - Add solution A to solution B; mix well;

d) Solution D - Mix 35 mL of nitric acid ($\rho \approx 1.42$ g/mL) and 100 mL water in a 400 mL beaker; add 5 mL of quinoline;

e) Solution E - Add solution D to solution C; mix well. Let stand overnight; filter with a glass crucible or filter paper; add 280 mL of acetone to the filtrate; dilute with water to 1000 mL; store in a polyethylene bottle or barrel.

Note: The reagent shall be stored in a dark place, away from light and heat.

B.3 Instruments and equipment

B.3.1 Oven: with automatic temperature controller, which can control the temperature at 180 °C ± 5 °C.

B.3.2 Glass sand core crucible: G4, 30 mL.

B.4 Sample

Appendix C

(Normative)

Determination of iron content in recycled black mass for lithium-ion batteries - Titanium trichloride reduction-potassium dichromate titration method

C.1 Principle

After the sample is dissolved in hydrochloric acid, a small amount of trivalent iron is reduced to divalent iron with titanium trichloride, using sodium tungstate as an indicator, to generate "tungsten blue"; the excess trivalent titanium is oxidized with potassium dichromate standard solution. In sulfuric acid-phosphoric acid medium, sodium diphenylamine sulfonate is used as an indicator; divalent iron is titrated with potassium dichromate standard solution.

C.2 Reagents and materials

Unless otherwise specified, all reagents used in this appendix are analytical grade or higher and distilled water or deionized water or water of equivalent purity.

C.2.1 Hydrochloric acid ($\rho \approx 1.19$ g/mL).

C.2.2 Sulfuric acid-phosphoric acid mixed acid: Slowly add 15 mL of sulfuric acid ($\rho \approx 1.84$ g/mL) to 70 mL water; add 15 mL of phosphoric acid ($\rho \approx 1.69$ g/mL) after cooling; mix well.

C.2.3 Titanium trichloride solution (1 + 9): take 10 mL of titanium trichloride solution (mass fraction of about 15%); add 30 mL of hydrochloric acid (1 + 1); dilute to 100 mL with water; mix well.

C.2.4 Potassium dichromate standard titration solution [$c_{1/6K_2Cr_2O_7} \approx 0.0500$ mol/L]: Weigh 2.4516 g of standard potassium dichromate (pre-dried at 140 °C ~150 °C for 2 h; placed in a desiccator; cooled to room temperature); dissolve it in water; transfer it into a 1000 mL volumetric flask; dilute to the scale with water; mix well.

C.2.5 Sodium tungstate solution (10%): Weigh 10 g of sodium tungstate and dissolve it in appropriate amount of water; add 5.00 mL of phosphoric acid ($\rho \approx 1.69$ g/mL); dilute to 100 mL with water; mix well.

C.2.6 Sodium diphenylamine sulfonate indicator solution (5 g/L): Weigh 0.50 g of sodium diphenylamine sulfonate; dissolve it in water; dilute to 100 mL with water; mix well; store in a brown bottle.

C.3 Instruments

Digital display bottle-top burette or acid burette, 25 mL.

C.4 Sample

The sample particle size shall not be greater than 0.25 mm.

C.5 Test steps

C.5.1 Test material

Weigh 3.00 g of sample (C.4), accurate to 0.0001 g.

C.5.2 Parallel test

Perform two tests in parallel; take the average value.

C.5.3 Blank test

Perform a blank test with the test material.

C.5.4 Determination

C.5.4.1 Place the sample (C.5.1) in a 250 mL beaker; moisten it with a small amount of water; add 25 mL of hydrochloric acid (C.2.1); immediately cover it with a watch glass; shake it gently to mix. If there is a violent reaction, open the watch glass after the violent reaction ends; add water to the 100 mL mark of the beaker; cover it with a watch glass again; heat it on a 200 °C ± 5 °C hot plate for 20 min; cool it to room temperature; rinse the watch glass with a small amount of water; filter it with a fast filter paper; wash the beaker and filter paper with water for 5 ~ 7 times. Collect the filtrate in a 250 mL volumetric flask; dilute it to the mark with water; mix it; set it aside. This is the test solution A, which is also used for the determination of phosphorus content.

C.5.4.2 According to Table C.1, transfer a certain volume of the test solution A (C.5.4.1) to a 250 mL beaker; rinse the inner wall of the conical flask with a small amount of water; add 5 mL of hydrochloric acid (C.2.1); heat to near boiling on an electric hot plate in a fume hood; add 4 drops of sodium tungstate solution (C.2.5) drop by drop while shaking the conical flask while it is hot; add titanium trichloride solution (C.2.3) drop by drop while shaking, until the solution turns light blue. Place it in a cold water tank to cool to room temperature; titrate with potassium dichromate standard titration solution (C.2.4), until the blue color just fades (when the copper concentration in the test solution is high, the blue color will fade quickly even if potassium dichromate is not added); do not count the consumed volume of potassium dichromate standard titration solution (C.2.4). Add 50 mL of water, 10 mL of sulfuric acid-phosphoric acid mixed acid (C.2.2), 4 drops of sodium diphenylamine sulfonate indicator solution (C.2.6); titrate with potassium dichromate standard titration solution (C.2.4) to stable purple color (does not disappear in 30 seconds), which is taken as the end point.

Appendix D

(Normative)

Determination of water-soluble fluoride content in recycled black mass for lithium-ion batteries - Fluoride ion selective electrode method

D.1 Principle

Mix the sample and water at a ratio of 1:10; shake on a fully automatic flip shaker; filter to obtain the filtrate; test the fluoride (in terms of fluoride ions) in the filtrate by the fluoride ion selective electrode method.

D.2 Reagents and materials

Unless otherwise specified, the reagents used in this appendix are reagents of analytical grade or above and distilled water or deionized water or water of equivalent purity.

D.2.1 Fluorine standard stock solution I: National certified standard solution, 1000 mg/L.

D.2.2 Fluorine standard stock solution II: Transfer 10 mL of fluorine standard stock solution I (D.2.1) to a 100 mL volumetric flask; dilute to the mark with water. The concentration of fluorine in this solution is 100 mg/L.

D.2.3 Fluorine standard stock solution III: Transfer 10 mL of fluorine standard stock solution II (D.2.2) to a 100 mL volumetric flask; dilute to the mark with water. The concentration of fluorine in this solution is 10 mg/L.

D.2.4 Total ionic strength regulator (TISAB): Weigh 58.8 g of trisodium citrate and 85 g of sodium nitrate; dissolve in 800 mL water; adjust pH to 5.0 ~ 6.0 with nitric acid ($\rho \approx 1.42$ g/mL); dilute to 1000 mL with water; mix well.

D.3 Instruments

D.3.1 Ion meter: Equipped with fluoride ion selective electrode, display accuracy 0.01 mV.

D.3.2 Fully automatic flip oscillator: Flip device with a rotation speed of 30 r/min ± 2 r/min.

D.3.3 Extraction bottle: Wide-mouth bottle with screw cap and inner cover, 2 L, made of inert material (glass or polyethylene, etc.) that cannot leach or adsorb the contained components.

D.3.4 Balance: Maximum range not less than 110 g, sensitivity not less than ±0.01 g.

D.3.5 Pipette: Adjustable. The maximum range is 10 mL; the accuracy is 0.01 mL.

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