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Manganese sulfate for battery materials

电池用硫酸锰

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Manganese sulfate for battery materials

1 Scope

This standard specifies the requirements, test methods, inspection rules, marking, labeling, packaging, transportation and storage of manganese sulfate for battery materials.

This standard applies to manganese sulfate for battery materials. This product is mainly used to prepare the positive electrode materials for secondary lithium battery (nickel-cobalt lithium manganate, lithium manganate, lithium-rich manganese-based cathode materials, etc.), which can also be used to make other manganese salts.

2 Normative references

The following documents are essential to the application of this document. For the dated documents, only the versions with the dates indicated are applicable to this document; for the undated documents, only the latest version (including all the amendments) are applicable to this standard.

GB/T 191-2008 Packaging - Pictorial marking for handling of goods

GB/T 6003.1-2012 Test sieves - Technical requirements and testing - Part 1: Test sieves of metal wire cloth

GB/T 6678 General principles for sampling chemical products

GB/T 6682-2008 Water for analytical laboratory use - Specification and test methods

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

GB/T 8946 General technical requirements of plastic woven sack

HG/T 2962-2010 Manganous sulphate for industrial use

HG/T 3696.1 Inorganic chemicals for industrial use - Preparations of standard and reagent solutions for chemical analysis - Part 1: Preparations of standard volumetric solutions

HG/T 3696.2 Inorganic chemicals for industrial use - Preparations of

5 Test methods

Warning: Some of the reagents used in this test method are corrosive and should be handled with care! If it is splashed on the skin or eyes, rinse immediately with water. In severe cases, seek medical attention immediately. The high-pressure hydrogen cylinder used in this test method shall be operated in accordance with the safe operation of high-pressure steel cylinders. After igniting the plasma, the screen door shall be opened as little as possible, to prevent high-frequency radiation from harming the body.

5.1 General provisions

The reagents and water used in this standard, unless otherwise specified, refer to analytical pure reagents and grade-3 water as specified in GB/T 6682-2008. The standard titration solution, preparations and products used in the tests are prepared in accordance with HG/T 3696.1, HG/T 3696.2, HG/T 3696.3, unless otherwise specified.

5.2 Appearance inspection

In natural light, use the visual observation method to judge the appearance on a white-backgrounded watch glass or white porcelain.

5.3 Determination of manganese sulfate content

5.3.1 Summary of method

In an ammonia-ammonium chloride buffer solution which has a pH of about 10, use the chrome black T as an indicator. Use the ethylenediaminetetraacetic acid disodium (EDTA) standard titration solution to titrate the solution until it changes from purple-red into pure blue, which is the end point. Based on the consumption of the titration solution, calculate the manganese sulfate content.

5.3.2 Reagents

5.3.2.1 Ascorbic acid.

5.3.2.2 Ammonia-ammonium chloride buffer solution A: pH ≈ 10.

5.3.2.3 Ethylenediaminetetraacetic acid disodium standard titration solution: c (EDTA) ≈ 0.05 mol/L.

5.3.2.4 Chrome black T indicator solution: 5 g/L.

5.3.3 Analytical procedures

determination result. When calculated by manganese sulfate ($MnSO_4 \cdot H_2O$), the absolute difference of the results of the two parallel determinations is not more than 0.5%. When calculated by manganese (Mn), the absolute difference of the results of the two parallel determinations is not more than 0.2%.

5.4 Determination of iron, zinc, copper, cadmium, potassium, sodium, calcium, magnesium, nickel, cobalt content

5.4.1 Summary of method

The specimen is dissolved by nitric acid. The inductively coupled plasma optical emission spectrometry is used to determine the tested elements (iron, zinc, copper, cadmium, potassium, sodium, calcium, magnesium, nickel, cobalt). The working curve method is used for quantification.

5.4.2 Reagents

5.4.2.1 Nitric acid solution: 1 + 1.

5.4.2.2 Nitric acid solution: 2 + 98.

5.4.2.3 Mixed standard solution I: 1 mL of solution contains 0.010 mg of cation (iron, zinc, copper, cadmium, nickel, cobalt).

Respectively, pipette 1.00 mL of iron (Fe), Zinc (Zn), Copper (Cu), Cadmium (Cd), Nickel (Ni), Cobalt (Co) standard stock solution which are prepared according to HG/T 3696.2. Place them in 100 mL volumetric flasks. Use the nitric acid solution (see 5.4.2.2) to dilute it to the mark. Shake it uniformly. It may also use the solution of the national standard substance with certificate for accurate dilution. This solution is prepared before use.

5.4.2.4 Mixed standard solution II: 1 mL of solution contains 0.050 mg of cations (potassium, sodium, calcium, magnesium).

Respectively, pipette 5.00 mL of Potassium (K), Sodium (Na), calcium (Ca), Magnesium (Mg) standard stock solution which are prepared according to HG/T 3696.2. Place them in 100 mL volumetric flasks. Use the nitric acid solution (see 5.4.2.2) to dilute it to the mark. Shake it uniformly. It may also use the solution of the national standard substance with certificate for accurate dilution. This solution is prepared before use.

5.4.2.5 Water: It complies with the specifications of grade-2 water of GB/T 6682-2008.

5.4.3 Instruments and equipment

Inductively coupled plasma optical emission spectrometer.

5.4.4 Analytical procedures

5.4.4.1 Preparation of test solution

Weigh about 1.0 g of the specimen, accurate to 0.0002 g. Place it into a 100 mL beaker. Use a small amount of water to wet it. Add 2 mL of nitric acid solution (see 5.4.2.1). Cover the watch glass. On a pressure-regulated electric furnace, use low-temperature to heat to evaporate it almost dry. After cooling it down, add a small amount of water to dissolve it. Rinse the solution into a 100 mL volumetric flask. Use water to dilute it to the mark. Shake it uniformly. According to the conditions of samples and instruments, dilute it if necessary.

5.4.4.2 Drawing of working curve

Take four 100 mL volumetric flasks. Respectively, add 0.00 mL, 1.00 mL, 2.00 mL, 6.00 mL of mixed standard solution I. Use the nitric acid solution (see 5.4.2.2) to the dilute it to the mark. Shake it uniformly. This solution is used to determine the content of iron, zinc, copper, cadmium, nickel, cobalt.

Take four 100 mL volumetric flasks. Respectively, add 0.00 mL, 0.50 mL, 2.00 mL, 3.00 mL of mixed standard solution II. Use the nitric acid solution (see 5.4.2.2) to the dilute it to the mark. Shake it uniformly. This solution is used to determine the content of potassium, sodium, calcium, magnesium.

Under the optimal determination conditions of the inductively coupled plasma optical emission spectrometry, lead the above series of standard solution into the inductively coupled plasma optical emission spectrometry. The wavelength of the analytical spectrum is as shown in Appendix A (or otherwise selected according to the instrument’s instruction manual). Determine the spectral intensity of each tested element. Use the mass concentration of the standard solution (μg/mL) as the abscissa and the corresponding emission intensity as the ordinate, to draw the working curve.

5.4.4.3 Determination

Under the same conditions as in 5.4.4.2, determine the spectral intensity of each element to be tested in the test solution. Use the working curve to obtain the mass concentration of the element to be tested.

5.4.5 Calculation of results

The content of the element to be tested is calculated by the mass fraction w_3 of the element to be tested, which is calculated according to formula (3):

$$w_3 = \frac{\rho_i \times 100 \times 10^{-6}}{m} \times 100\% \qquad \cdots\cdots\cdots\cdots\cdots (3)$$

Where:

Use water to dilute it to 100 mL. Use sodium hydroxide solution to adjust the pH of solution o 1.0 ~ 1.5 (use precision pH test paper to check it). Transfer this solution into a 250 mL separatory funnel. Use water to dilute it to about 200 mL. Add 2 mL of Pyrrolidine dithiocarbamate (APDC) solution. Mix it. Use trichloromethane to extract it for two times. Add 20 mL for each extraction. Collect the extract (that is, the organic phase) into a 50 mL beaker. Put it in steam bath to evaporate it dry (this operation must be carried out in a ventilation hood). Add 3 mL of nitric acid in the residue. Continue evaporation to almost dry. Add 0.5 mL of nitric acid and 10 mL of water. Heat it until the solution volume is about 3 mL ~ 5 mL. Transfer it into a 10 mL volumetric flask. Use water to dilute it to the mark. Shake it uniformly.

5.5.4 Preparation of test solution

Weigh appropriate amount of specimen (2 g for the first-grade product; 1 g for the qualified product), accurate to 0.01 g. Place it into a 150 mL beaker. Add 30 mL of water. Add 1 mL of hydrochloric acid. Cover the watch glass. Heat to boil it for 5 min. Cool it down. Use water to dilute it to 100 mL. Use sodium hydroxide solution to adjust the pH of solution to 1.0 ~ 1.5 (use precision test paper to check it). The rest operation is same as that in 5.5.3 “Transfer this solution into a 250 mL separatory funnel …… Transfer it into a 10 mL volumetric flask. Use water to dilute it to the mark. Shake it uniformly.”

5.5.5 Determination

Select the air-acetylene flame. At the wavelength of 283.3 nm, use water to zero it. Determine the absorbance of the standard solution and the test solution. The absorbance of the test solution shall be not more than that of the standard solution.

5.6 Determination of water insoluble content

Follow the requirements of clause 5.7 in HG/T 2962-2010 to make determination.

5.7 Determination of pH

Follow the requirements of clause 5.8 in HG/T 2962-2010 to make determination.

5.8 Determination of fineness

5.8.1 Instruments and equipment

Test sieve: The piece Φ200 x 50-0.4/0.25 GB/T 6003.1-2012. It is equipped with a sieve cover and a sieve bottom.

5.8.2 Analytical procedures

Weigh about 50 ± 0.1 g of specimen. Place it in a test sieve. Add the sieve cover and sieve bottom to perform sieving. When there is no sieving residue above the sieve, it indicates that they all pass.

5.9 Determination of silicon content

5.9.1 Reagents

5.9.1.1 Sulfuric acid solution: 6 + 94.

5.9.1.2 Hydrofluoric acid solution: 1 + 9.

5.9.1.3 Ammonium molybdate solution: 75 g/L.

Weigh 75 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$]. Dissolve it in warm water. After cooling it down, use water to dilute it to 1000 mL. Filter it before use.

5.9.1.4 Ammonium ferrous sulfate solution: 150 g/L.

Weigh 150 g of ammonium ferrous sulfate [$(NH_4)_6 Fe(SO_4)_2 \cdot 6H_2O$]. Dissolve it in 500 mL of water. Add 100 mL of sulfuric acid solution (1 + 9). Use water to dilute it to 1000 mL. Shake it uniformly.

5.9.1.5 Silicon standard solution: 1 mL of solution contains 0.010 mg of silicon (Si).

Pipette 1.00 mL of silicon (Si) standard stock solution which is prepared according to HG/T 3696.2. Place it in a 100 mL plastic volumetric flask. Use water to dilute it to the mark. Shake it uniformly. This solution is prepared before use.

5.9.2 Instruments and equipment

5.9.2.1 Spectrophotometer: A cuvette equipped with a path length of 1 cm.

5.9.2.2 Constant-temperature water bath: The temperature can be controlled at 50 °C ± 2 °C.

5.9.2.3 Beaker (polytetrafluoroethylene).

5.9.2.4 Volumetric flask (polytetrafluoroethylene).

5.9.3 Analytical procedures

5.9.3.1 Preparation of test solution

Weigh about 2.0 g of the specimen, accurate it to 0.0002 g. Place it in a 200 mL beaker. Use a small amount of water to wet it. Cover the watch glass. Slowly add sulfuric acid solution. In the water bath, use low temperature to heat to m - The value of the mass of the specimen, in grams (g).

Take the arithmetic mean of the results of parallel determination as the determination result. The absolute difference between the two parallel determination results is not more than 20% of the arithmetic mean.

5.10 Determination of fluorine content

5.10.1 Reagent

5.10.1.1 Hydrochloric acid solution: 1 + 4.

5.10.1.2 Nitric acid solution: 1 + 15.

5.10.1.3 Sodium hydroxide solution: 100 g/L.

5.10.1.4 Buffer solution.

Dissolve 270 g of sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) and 24 g of citric acid ($C_6H_8O_7 \cdot H_2O$) in 800 mL of water. Use water to dilute it to 1000 mL.

5.10.1.5 Fluoride standard solution: 1 mL of solution contains 0.01 mg of fluorine (F).

Pipette 1.00 mL of fluoride standard stock solution as prepared according to the requirements of HG/T 3696.2. Place it in a 100 mL volumetric flask. Use water to dilute it to the mark. Shake it uniformly. This solution shall be prepared before use.

5.10.1.6 Bromocresol green indicator solution: 1 g/L.

5.10.2 Instruments and equipment

5.10.2.1 Fluoride ion selective electrode.

5.10.2.2 Saturated calomel electrode.

5.10.2.3 Potentiometer.

5.10.2.4 Electromagnetic stirrer and stirring rod.

5.10.3 Analytical procedures

5.10.3.1 Drawing of the working curve

According to the fluorine content in the specimen, pipette the appropriate amount of fluoride standard solution into a set of 50 mL volumetric flask, respectively. Add 1 mL of hydrochloric acid solution, 5 drops of buffer solution, 2 drops of bromocresol green indicator solution. Use the sodium hydroxide continuously or by the same shift of the same enterprise using the same materials under the same production conditions. Each batch of products shall not exceed 5 t.

6.3 Follow the requirements of GB/T 6678 to determine the number of sampling units. When sampling, insert the sampler vertically from the top of the package to the 3/4 depth of the material layer. The specimen as taken for each package shall be not less than 50 g. Mix the sample taken uniformly. Use the quartering method to reduce it to about 500 g. Contain it into two dry and clean jars or plastic bags. Seal it. Attach the label. Indicate the manufacturer name, product name, grade, batch number, sampling date, name of sampling personnel. One jar (plastic bag) is used for inspection and the other is retained for reference.

6.4 If one indicator of the inspection results fails to meet the requirements of this standard, it shall take sample from double quantity of packages for re-inspection. Even there is only one indicator in the re-inspection results fails to meet the requirements of this standard, the entire batch of products is unqualified.

6.5 Use the comparison method of the rounding-off value according to GB/T 8170 to determine whether the inspection results comply with standard.

7 Markings, labels

7.1 The package of manganese sulfate for batteries shall be clearly marked with the following contents: the name of the manufacturer, the address of the factory, the name of the product, the grade, the net content, the batch number or the date of manufacture, the serial number of this standard, the sign of “Avoid rain” and “Avoid sun exposure” as specified in GB/T 191-2008.

7.2 Each batch of exit-battery manganese sulfate products for battery shall be attached with the quality certificate. Its content includes the name of the manufacturer, the address of the factory, the name of the product, the grade, the net content, the batch number or the date of manufacture, the certificate of the product quality in accordance with this standard, the serial number of this standard.

8 Packaging, transportation and storage

8.1 The manganese sulfate for battery sulfuric uses double-layer package. The inner package is made of polyethylene plastic film bag. The outer package is made of plastic woven bag. Its performance and inspection method shall comply with the requirements of GB/T 8964. The inner packaging bag is tied by the nylon rope or other similar quality rope, or otherwise sealed by other equivalent methods. The outer package is stitched by a sewing machine. The

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