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Electrolyte for vanadium flow battery - test method

全钒液流电池用电解液 测试方法

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Electrolyte for vanadium flow battery - test method

1 Scope

This Standard specifies the terms and definitions, general requirements, sampling requirements and test methods for electrolytes for vanadium flow battery, including the determination methods of vanadium content, sulfate content, silicon content, iron content, nitrogen content, other elements (K, Na, Al) content, conductivity, density and viscosity.

This Standard applies to electrolytes for vanadium flow battery using sulfuric acid as a solvent.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the dated version applies to this document. For undated references, the latest edition (including all amendments) applies to this document.

GB/T 601-2002, Chemical reagent - Preparations of standard volumetric solutions

GB/T 602-2002, Chemical reagent - Preparations of standard solutions for impurity

GB/T 603-2002, Chemical reagent - Preparations of reagent solution for use in test methods

GB/T 622-2006, Chemical reagent - Hydrochloric acid

GB/T 625-2007, Chemical reagent - Sulfuric acid

GB/T 626-2006, Chemical reagent - Nitric acid

GB/T 629-1997, Chemical reagent - Sodium hydroxide

GB/T 633-1994, Chemical reagent - Sodium nitrite

GB/T 639-2008, Chemical reagent - Sodium carbonate anhydrous

GB/T 643-2008, Chemical reagent - Potassium permanganate

GB/T 652-2003, Chemical reagent - Barium chloride dihydrate

GB/T 657-2011, Chemical reagent - Hexammonium heptamolybdate tetrahydrate

3 Terms and definitions

The following terms and definitions are applicable to this Standard.

3.1

vanadium flow battery, VFB

Also known as vanadium flow battery system, which is an energy storage device that realizes the mutual conversion of electrical energy and chemical energy through the electrochemical reaction of vanadium ions with different valence states in the positive and negative electrolytes.

Note: A vanadium flow battery is mainly composed of power units (battery stacks or battery modules), energy storage units (electrolyte and storage tanks), electrolyte transport units (pipelines, valves, pumps, heat exchangers, etc.) and battery management systems.

3.2

electrolyte

Solution – containing vanadium ions of different valence states – with ionic conductivity.

3.3

electrolyte (3.5 valence)

When the molar concentration ratio of trivalent vanadium ions to tetravalent vanadium ions in the electrolyte is 1:1, its valence state is defined as 3.5, and the electrolyte is called electrolyte (3.5 valence).

3.4

positive electrolyte

The electrolyte when the battery is working has a different composition from the electrolyte (3.5 valence) due to the change in the valence state of vanadium ions. The positive electrolyte is the solution in the positive electrode storage tank of the battery, which contains only tetravalent and pentavalent vanadium ions.

3.5

negative electrolyte

The electrolyte when the battery is working has a different composition from the electrolyte (3.5 valence) due to the change in the valence state of vanadium ions. The negative electrolyte is the solution in the negative electrode storage tank of the battery, which contains only divalent and trivalent vanadium ions.

3.6

precipitation

The phenomenon that the active materials in the electrolyte accumulate or precipitate and separate from the solution.

3.7

active material

The material that accepts and releases electrical energy during redox reactions during the battery's bi-directional charging process.

Note: The active materials in the electrolyte for vanadium flow battery are vanadium ions of different valence states.

4 General requirements

When performing electrolyte testing, the following general requirements shall be followed:

a) Unless otherwise specified, the purity of reagents used in this Standard shall be analytical reagents or above; the preparations and products used shall be prepared in accordance with the provisions of GB/T 603-2002; the water for laboratory use shall comply with the specifications of Grade 3 water in GB/T 6682-2008.

b) The concentrations of standard volumetric solutions prepared in this Standard refer to the concentrations at room temperature. The analytical balance, weights, burettes, volumetric flasks, pipettes, etc. used in the calibration, direct preparation and use of standard volumetric solutions must be calibrated regularly.

c) When calibrating and using standard volumetric solutions, the titration speed shall generally be maintained at 1 mL/min ~ 3 mL/min.

d) Unless otherwise specified, standard volumetric solutions shall be stored at room temperature (15 °C ~ 25 °C) for no more than two months. If the solution becomes turbid, precipitates, changes in color, etc., it shall be re-prepared.

e) All solutions expressed in percentage (%) in this Standard are mass fractions, except for ethanol (95%) where the percentage (%) is volume fraction.

f) When testing with a cuvette in this Standard, ensure that the liquid to be tested is between 1/3 and 2/3 of the cuvette.

5 Sampling requirements

When sampling and testing the electrolyte, the following requirements shall be followed:

a) Before the products leave the factory, materials produced in one batch are sampled as a batch.

b) The number of samples to be taken for each batch of products shall be determined based on the uniformity of product mass.

c) Sampling shall be carried out in accordance with the requirements of 7.1.1.2 and 7.1.1.3 of GB/T 6680-2003.

6 Test methods

6.1 Appearance inspection

Visually inspect the color of the sample in a brightly lit room, where the color shall be dark green with no precipitation inside.

Note: This Clause is specifically for electrolyte (3.5 valence).

6.2 Determination of vanadium content

6.2.1 Principle

Use sulfuric-phosphoric acid buffer solution as the medium; titrate with potassium permanganate standard solution until a potential jump occurs; obtain the corresponding electrolyte volume based on the potential jump; calculate the corresponding vanadium ion concentration.

6.2.2 Reagents and solutions

The reagents used in the test shall meet the following requirements:

a) Potassium permanganate shall meet the requirements of GB/T 643-2008.

b) Sulfuric acid shall meet the requirements of GB/T 625-2007.

c) Phosphoric acid shall meet the requirements of GB/T 1282-1996.

d) Sodium oxalate shall meet the requirements of GB/T 1289-1994.

6.2.2.1 Preparation of solutions

The solutions used in the test shall be prepared as follows:

a) Sulfuric-phosphoric acid buffer solution. The volume fraction ratio is sulfuric acid (50%): phosphoric acid (50%): water = 1:1:1.

b) Sulfuric acid solution (10%). Measure 57 mL of 98% concentrated sulfuric acid into a beaker filled with water and dilute to 1 L.

c) Potassium permanganate. Standard solution of c_{KMnO_4} = 0.015 mol/L: Weigh 2.370 0 g of potassium permanganate; dissolve it in 1 L of water; boil slowly for 10 min ~ 15 min; place it in a dark place for one week; filter with a No. 4 glass filter pan; store in a brown bottle.

6.2.2.2 Calibration of potassium permanganate solution concentration

The calibration steps for potassium permanganate solution concentration are as follows:

a) Accurately weigh 1.000 0 g of standard sodium oxalate which has been dried at 105°C ~ 110°C for 2 h and cooled to room temperature in a desiccator.

b) Dissolve the weighed standard sodium oxalate in 100 mL of sulfuric acid solution (10%) and mix well.

c) Use the standard potassium permanganate solution prepared in 6.2.2.1 at 65 °C ~ 70 °C for titration, until the solution turns pink and remains unchanged for 30 seconds; record the volume V_1 of potassium permanganate solution consumed at this time.

d) For a blank test, use the standard potassium permanganate solution prepared in 6.2.2.1 at 65 °C ~ 70 °C to titrate 100 mL of sulfuric acid solution (10%), until the solution turns pink and remains unchanged for 30 seconds; record the volume V_2 of potassium permanganate solution consumed at this time.

6.2.2.3 Result calculation

Calculate the concentration of the calibrated potassium permanganate solution according to Formula (1):

$$c_{\mathrm{KMnO_4}} = 1000 \times \frac{m}{M(V_1 - V_2)} \qquad (1)$$

Where:

c_{KMnO_4} – concentration of the calibrated potassium permanganate standard solution, mol/L;

m – mass of sodium oxalate (accurate to 0.000 1 g), g;

M – molar mass of sodium oxalate, g/mol;

V_1 – volume of potassium permanganate consumed by the calibration solution, mL;

V_2 – volume of potassium permanganate consumed in the blank test, mL.

6.2.3 Test equipment

The instruments and accuracy used in the test shall meet the following requirements:

a) Potentiometric titrator: The potential accuracy is 0.1 mV.

b) Analytical balance: The accuracy is 0.000 1 g.

c) Other commonly used laboratory instruments.

6.2.4 Determination steps

6.2.4.1 Determination of electrolyte (3.5 valence)

The concentration of electrolyte (3.5 valence) is tested as follows:

a) Accurately pipette 0.2 mL of the test solution into a beaker containing 40 mL of sulfuric-phosphoric acid buffer solution.

b) In a constant temperature water bath at 70 °C, titrate potentiometrically until two jump end points appear successively. According to the order of the time when the jumps occur, the corresponding volumes of potassium permanganate consumed are V_3 and V_4.

c) Calculate the corresponding vanadium concentration based on the volume of potassium permanganate consumed at the end point of the jump.

6.2.4.2 Determination of negative electrolyte

The concentration of negative electrolyte is determined as follows:

a) Accurately pipette 0.2 mL of the test solution into a beaker containing 40 mL of sulfuric-phosphoric acid buffer solution.

b) In a 70 °C constant temperature water bath, under the protection of argon, perform potentiometric titration until three jump end points appear successively. In the order of the time when the jumps occur, the corresponding volumes of potassium permanganate consumed are V_5, V_6 and V_7.

c) Calculate the corresponding vanadium concentration based on the volume of potassium permanganate consumed at the end point of the jump.

6.4.2 Reagents and solutions

The reagents and solutions used in the test and their requirements are as follows:

a) Silicon dioxide.

b) Sodium carbonate. Shall comply with the requirements of GB/T 639-2008.

c) Oxalic acid. Shall comply with the requirements of GB/T 9854-2008.

d) Ascorbic acid. Shall comply with the requirements of GB/T 15347-1994.

e) Ammonium molybdate. Shall comply with the requirements of GB/T 657-2011: 5% solution, used after filtration.

f) Sulfuric acid-oxalic acid mixture. Weigh 50 g of oxalic acid; place it in a 2 000 mL beaker; add 500 mL of water; slowly add 200 mL of sulfuric acid; after it dissolves, add 1 300 mL of water; mix well; cool to room temperature.

g) Ammonium ferrous sulfate. Shall comply with the requirements of GB/T 661-2011: 6% solution, 5 mL of sulfuric acid in 100 mL, used after filtration.

h) Ascorbic acid reducing agent (prepare before use). Weigh 4 g of ascorbic acid and 0.2 g of ammonium ferrous sulfate; dissolve them in water and dilute to 100 mL; add a few drops of sulfuric acid (98%).

i) Silicon standard solution.

   1) Silicone standard solution A. Weigh 1.070 0 g of pure silicon dioxide that has been dried at 105 °C ~ 110 °C for 1 h and cooled to room temperature in a desiccator; place it in a platinum crucible pre-filled with 6.000 0 g of sodium carbonate (not containing silicon dioxide); stir well and cover with a small amount of sodium carbonate; melt in a 900 °C high-temperature furnace for 30 min; take out and cool; place in a 500 mL plastic beaker; use boiling water to leach the molten block and dissolve it; take out the crucible; use water to rinse the solute on it; use water to dilute the solution in the beaker to the scale; shake well; store in a plastic bottle for later use. 1 mL of this solution contains 1 mg of silicon.

   2) Silicon standard solution B (prepare before use). Pipette 10 mL of silicon standard solution A into a 500 mL volumetric flask; use water to dilute to the mark; shake well. Store in a dry plastic bottle. 1 mL of this solution contains 0.02 mg of silicon.

6.4.3 Test equipment

The instruments and requirements used in the test are as follows:

a) Spectrophotometer. Its performance and operation shall conform to the relevant provisions of GB/T 7729-1987.

b) Other commonly used laboratory instruments.

6.4.4 Determination steps

6.4.4.1 Drawing of standard curve

Follow the steps below to draw the standard curve:

a) Accurately pipette 0.00, 1.00, 2.00, 3.00, and 5.00 mL of silicon standard solution B into 50 mL volumetric flasks, respectively.

b) Add 5 mL of ammonium molybdate solution respectively; use a small amount of water to rinse the bottle mouth; shake well.

c) After standing for 15 ~ 20 minutes, add 10 mL of sulfuric acid-oxalic acid mixture and quickly add 2 mL of ascorbic acid (4%).

d) Add water to dilute; fix the volume; shake well.

e) After 15 minutes, measure the absorbance at a wavelength of 660 nm using a 1 cm cuvette with the blank reagent as reference.

f) Draw a standard curve with the silicon content (in mg) as the abscissa and the corresponding absorbance as the ordinate.

6.4.4.2 Sample determination

Follow the steps below to test the silicon content:

a) Use a pipette to transfer 2 mL of the sample to be tested into a 100 mL volumetric flask; fix the volume; shake well.

b) Transfer 10 mL of the solution prepared in step a) into a 50 mL volumetric flask.

c) Repeat steps b) ~ e) of 6.4.4.1.

d) Obtain the corresponding silicon content m on the standard curve according to the measured absorbance.

6.4.5 Result calculation

The silicon content is calculated according to Formula (9):

$$c_{\mathrm{Si}} = \frac{m}{V} \qquad (9)$$

Where:

c_{Si} – content of silicon in the sample, mg/L;

m – silicon content obtained from the standard curve according to the sample absorbance, mg;

V – sample volume, mL.

6.5 Determination of iron content

6.5.1 Principle

Directly absorb the sample to be tested and use sodium hydroxide to neutralize it; use hydroxylamine hydrochloride to reduce the high-valent iron and eliminate the interference of copper at the same time. In a solution with a pH value of 3 ~ 5, low-valent iron reacts with o-phenanthroline to form an orange-red complex, which is determined by spectrophotometry.

6.5.2 Reagents and solutions

The reagents and solutions used in the test and their requirements are as follows:

a) Hydroxylamine hydrochloride. Shall comply with the requirements of GB/T 6685-2007: 10% solution.

b) Sodium hydroxide. Shall comply with the requirements of GB/T 629-1997: 10% solution.

c) 1,10-phenanthroline (o-phenanthroline). Shall comply with the requirements of HG/T 4018-2008: 0.1% solution.

d) Iron wire. The iron content shall be above 99.99%.

e) Sodium acetate. Shall comply with the requirements of GB/T 694-1995.

f) Acetic acid. Shall comply with the requirements of GB/T 676-2007.

g) Nitric acid. Shall comply with the requirements of GB/T 626-2006.

6.5.3 Solution preparation

The solutions and preparation steps used in the test are as follows:

a) Sodium acetate-acetic acid buffer solution. Weigh 4.000 0 g of sodium acetate and dissolve it in an appropriate amount of water; add 27 mL of acetic acid (36%); use water to dilute to 100 mL; mix well.

b) 0.1% o-phenanthroline solution. Weigh 0.100 0 g of o-phenanthroline and place it in a small amount of water; add two drops of 1+1 hydrochloric acid; dissolve it; use water to dilute it to 100 mL; store it in a brown bottle.

c) Iron standard solution. Solution A, 1 mL contains 0.1 mg of iron; Solution B, 1 mL contains 0.01 mg of iron.

  1) Preparation method of solution A. Weigh 0.100 0 g of pure iron wire with an iron content of more than 99.99% and place it in a 100 mL beaker; add 10 mL of 1+1 nitric acid and dissolve it under slight heat; use a small amount of water to wash the wall of the beaker; heat to remove nitrogen oxides; after cooling, transfer it to a 1 000 mL volumetric flask; use water to dilute it; fix the volume; shake well.

  2) Preparation method of solution B. When using, accurately pipette 10 mL of Solution A; place it in a 100 mL volumetric flask; use water to dilute; fix the volume; shake well.

6.5.4 Test equipment

The instruments and requirements used in the test are as follows:

a) Spectrophotometer. The operation shall comply with the relevant provisions of GB/T 7729-1987.

b) Other commonly used laboratory instruments.

6.5.5 Determination steps

6.5.5.1 Drawing of standard curve

The standard curve is drawn according to the following steps:

a) Accurately pipette 0.00, 1.00, 2.00, 3.00, 5.00, and 6.00 mL of iron standard solution B into 50 mL volumetric flasks, respectively.

b) Use water to dilute to about 25 mL; use sodium hydroxide (10%) to adjust the pH to 3 ~ 5; shake well.

c) Add 5 mL of hydroxylamine hydrochloride (10%) solution, 5 mL of acetic acid-sodium acetate buffer solution, and 5 mL of o-phenanthroline solution (0.1%) in sequence.

d) Place at room temperature for 30 minutes; dilute to volume; shake well.

e) Measure the absorbance at a wavelength of 510 nm using the blank reagent as a reference.

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