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Electrolyte for vanadium flow battery

全钒液流电池用电解液

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Table of Contents

Electrolyte for vanadium flow battery

1 Scope

This Standard specifies the requirements for electrolyte for vanadium flow battery, test methods, inspection rules and marks, packaging, transportation, storage and the contents of quality certificates and order sheets (or contracts).

This Standard applies to electrolyte for vanadium flow battery in sulfuric acid system.

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 190-2009, *Packing symbol of dangerous goods*

GB/T 6678, *General principles for sampling chemical products*

GB/T 6680, *General rules for sampling liquid chemical products*

GB/T 6908-2008, *Analysis of water used in boiler and cooling system -- Determination of electrical conductivity*

GB/T 10247-2008, *Methods of viscosity measurement*

GB/T 11901-1989, *Water quality. Determination of suspended substance. Gravimetric method*

GB/T 19161-2016, *Packaging containers -- Composite intermediate bulk container*

GB/T 23942, *Chemical reagent -- General rules for inductively coupled plasma atomic emission spectrometry*

GB/T 30903, *Inorganic chemicals for industrial use -- Determination of impurity element -- Inductively coupled plasma mass spectrometry (ICP-MS)*

3 Requirements

3.1 Product classification

The products are divided into three varieties according to the different valence states of

11901-1989. It shall be resolved through negotiation between the supplier and the purchaser.

4.5 Physical properties

4.5.1 The conductivity testing is carried out in accordance with the provisions of 7.3 and 7.5 in GB/T 6908-2008.

4.5.2 The viscosity is tested in accordance with the provisions of Chapter 2 of GB/T 10247-2008. Use the Ubbelohde viscometer specified in A.3 of Annex A of GB/T 10247-2008. Depending on the actual viscosity, select a viscometer with size 0C, 0B or 1 specified in Table A.3 in Annex A of GB/T 10247-2008 for measurement.

5 Inspection rules

5.1 Inspection and acceptance

5.1.1 The product shall be inspected by the supplier to ensure that the product quality complies with the provisions of this Standard and the order sheet (or contract). A quality certificate shall be filled out.

5.1.2 The purchaser shall inspect the received products in accordance with the provisions of this Standard. If the inspection results are inconsistent with the provisions of this Standard and the order sheet (or contract), a written notification shall be submitted to the supplier within 30 days from the date of receipt of the product. The matter shall be resolved through negotiation between the supplier and the purchaser. If arbitration is needed, it can be entrusted to a unit recognized by both the supplier and the purchaser. Joint sampling at the purchaser's.

5.2 Batching

Products shall be submitted for acceptance in batches. Each batch shall consist of products of the same production batch, variety and grade. Each batch shall not exceed 30 m^3.

5.3 Inspection item

Before each batch of products leaves the factory, the main component content, impurity element content, additive content, insoluble impurities, and physical properties shall be inspected.

5.4 Sampling

5.4.1 To collect the samples for testing the main component content, impurity element content, additive content and physical properties, determine the number of sampling units in accordance with the provisions of GB/T 6678. From the selected packaging,

use a suitable sampler that complies with the provisions of GB/T 6680 to take equal amounts of samples from the upper, middle and lower parts of the packaging. Mix the removed sample evenly. Divide into 3 clean, dry polyethylene bottles. 1 is for supplier testing. 1 is for purchaser testing. Keep 1 sealed copy for future reference. Each sample volume is approximately 500 mL. The sample bottle shall be labeled with the specified content (according to GB/T 6678).

5.4.2 To collect samples for insoluble impurity testing, randomly select one package from each batch of products. From the selected packaging, use a suitable sampler that complies with the provisions of GB/T 6680 to take equal amounts of samples from the upper, middle and lower parts of the packaging. Mix the taken sample evenly. The sample volume is approximately 1100 mL.

5.5 Judgment of inspection results

5.5.1 If the content of the main ingredients fails to pass the inspection, the batch of products will be deemed to be unqualified.

5.5.2 If the impurity element content test fails, the batch of products will be deemed unqualified.

5.5.3 If the test of insoluble impurities fails, the batch of products will be deemed unqualified.

6 Marks, packaging, transportation, storage and quality certificate

6.1 Marks

The following marks (or labels) shall be printed on the outer packaging of the electrolyte:

a) Name of supplier;

b) Product name;

c) Product batch number;

d) Reference to this Standard;

e) The product packaging shall be marked with the "Corrosive substances" that complies with the provisions of GB 190-2009.

6.2 Packaging, transportation and storage

6.2.1 Products shall be stored in plastic containers that are resistant to sulfuric acid

Annex A

(Informative)

Determination of vanadium ion content in vanadium electrolyte

A.1 Scope

This appendix specifies the method for determination of vanadium ion content in vanadium electrolyte. The measurement range of positive trivalent vanadium ion content is 0.00 mol/L~2.50 mol/L. The measurement range of positive tetravalent vanadium ion content is 0.00 mol/L~2.50 mol/L.

A.2 Principle

There are two adjacent valence states of vanadium ions in the electrolyte solution. Based on the redox reaction between potassium permanganate and low-valent vanadium, in a phosphate buffer solution, the electrolyte sample is titrated with a standard titration solution of potassium permanganate, and the low-valent vanadium ions are gradually oxidized until they are pentavalent. Each sudden jump in potential corresponds to a change in the valence state of vanadium. According to the consumed volume of potassium permanganate standard solution corresponding to the potential jump point, calculate the content of vanadium ions in each valence state and total vanadium.

A.3 Reagents and materials

The reagents and water used in this appendix, unless otherwise specified, shall be reagents confirmed to be analytically pure and water that meets the requirements for grade three water in GB/T 6682.

The standard titration solutions, preparations and products required in the test shall be prepared in accordance with the provisions of GB/T 601 and GB/T 603, unless other requirements are specified.

A.3.1 Sodium oxalate: benchmark working reagent.

A.3.2 Sulfuric acid: 8+92.

A.3.3 Potassium permanganate standard titration solution: c (1/5 $KMnO_4$) is approximately 0.15 mol/L.

A.3.3.1 Preparation

Weigh 4.0 g of potassium permanganate (excellent grade pure) and dissolve it in 1 L of water. Heat to boiling. Keep at a slight boil for 1 h. Cool down. Replenish water to 1 L.

Place in a dark place for two weeks and filter with a treated 3# sand core funnel. Rinse the brown reagent bottle with a small amount of filtrate. Discard the lotion. Transfer the potassium permanganate filtrate to the reagent bottle. Store it in a dark place at room temperature for calibration.

The treatment of the sand core funnel means that the sand core funnel is slowly boiled in potassium permanganate solution of the same concentration for 5 min.

A.3.3.2 Calibration

Accurately weigh 0.08 g of the sodium oxalate reference reagent (A.3.1) that have been dried to constant weight in an electric oven at 105℃~110℃ into a 250 mL beaker. Add 60 mL of sulfuric acid (A.3.2). Add a small amount of water to dissolve. Add water to about 150 mL. Heat to 65°C in a water bath. Use potentiometric titration equipment (A.4.1). Titrate to the end point with potassium permanganate standard titration solution (A.3.3.1) while it is hot. Do a blank test at the same time. The titration end point is determined in accordance with the relevant regulations of GB/T 9725.

The concentration of potassium permanganate standard titration solution [c(1/5 $KMnO_4$)], expressed in moles per liter (mol/L), is calculated according to formula (A.1):

$$c\left(\frac{1}{5}KMnO_4\right)=\frac{m\times 1\ 000}{(V_1-V_2)M} \qquad \cdots\cdots(A.1)$$

Where,

m - The accurate value of the mass of sodium oxalate, in grams (g);

V_1 - The value of the volume of potassium permanganate standard titration solution (A.3) consumed by the titration, in milliliters (mL);

V_2 - The value of the volume of potassium permanganate standard titration solution (A.3) consumed by the blank test, in milliliters (mL);

M - The value of the molar mass of sodium oxalate, in grams per mole (g/mol) [M (1/2 $Na_2C_2O_4$) =66.999].

A.3.4 Phosphoric acid: ρ =1.70 g/mL, guaranteed reagent.

A.3.5 Ferrous ammonium sulfate solution: 40 g/L.

A.4 Instruments and equipment

A.4.1 The indicating electrode of the potentiometric titration measuring device uses a platinum electrode. A saturated calomel electrode is used as the reference electrode. The potentiometer measurement accuracy is ±0.1 mV.

Annex B

(Informative)

Determination of sulfate content in vanadium electrolyte

B.1 Scope

This appendix specifies the method for the determination of sulfate in vanadium energy storage medium. The measurement range is 2.00 mol/L~5.50 mol/L.

B.2 Principle

Add hydroxylamine hydrochloride to the sample to reduce the possible n-pentavalent vanadium to prevent the n-pentavalent vanadium from forming barium vanadate precipitation under weakly acidic conditions. Adjust the pH value to 3.1~4.4 to prevent trace dissolution of barium sulfate under strong acid. Add carbon dioxide-free barium chloride solution as a precipitant to cause sulfate radicals to form barium sulfate precipitate. Add a small amount of pulp and boil to expand the precipitated grains. After burning at 810℃ (when the temperature is higher than 850℃, barium sulfate is easily melted and decomposed) and then weighed to obtain the weight of barium sulfate. After calculation, the sulfate content is obtained.

B.3 Reagents and materials

The reagents and water used in this appendix, unless otherwise specified, shall be reagents confirmed to be analytically pure and water that meets the requirements for grade three water in GB/T 6682.

The standard titration solutions, preparations and products required in the test shall be prepared in accordance with the provisions of GB/T 601 and GB/T 603 unless other requirements are specified.

B.3.1 Hydroxylammonium hydrochloride.

B.3.2 Sodium hydroxide solution: 500 g/L.

B.3.3 Hydrochloric acid solution: 5 mol/L.

B.3.4 Barium chloride solution: 100 g/L.

B.3.5 Quantitative pulp.

B.3.6 Silver nitrate solution: 10 g/L. Dissolve 1.0 g of silver nitrate in a small amount of water. Dilute to 100 mL with water. Mix well. If there is precipitation, it needs to be filtered before use.

B.4 Instruments and equipment

B.4.1 Use an analytical balance to weigh. The accuracy is 0.0001 g.

B.4.2 Other instruments and equipment are general laboratory instruments and equipment

B.5 Analysis steps

B.5.1 Accurately pipette 1.00 mL of electrolyte into a 500 mL beaker pre-filled with 300 mL of hot water.

B.5.2 Add 0.5 g of hydroxylamine hydrochloride (B.3.1). Use pH test paper to measure the pH value (3.1~4.4). If it exceeds the range, use sodium hydroxide solution (B.3.2) or hydrochloric acid solution (B.3.3) to adjust the pH value to 3.1~4.4.

B.5.3 Heat to boil and remove.

B.5.4 Add 25 mL of barium chloride solution (B.3.4) quickly (within 1 s, continuously pour water) under constant and rapid stirring.

B.5.5 Add a small amount of quantitative pulp (B.3.5). Heat it to boil while stirring constantly. Remove and let stand for 20 min.

B.5.6 Filter with medium speed quantitative filter paper. Wash first with the pouring method. Then transfer the precipitate to filter paper. Wash the precipitate with hot water until the filtrate remains clear within 5 min after adding 10 mL of silver nitrate solution (B.3.6) to 10 mL of the filtrate.

B.5.7 Place the precipitate, pulp and filter paper obtained in step B.5.6 into a porcelain crucible that has been previously heated at 810°C, cooled in a desiccator and weighed. Burn in an electric furnace at 810°C for 30 min. Take it out. Place in a desiccator to cool to room temperature and then weigh.

B.6 Result calculation

Calculate the content of sulfate [c (SO_4^{2-})] according to formula (B.1), in moles per liter (mol/L):

$$c(SO_4^{2-}) = \frac{m_0}{V_0 \times 233.40} \times 1\,000 \qquad \cdots\cdots (B.1)$$

Where,

m_0 - The mass of barium sulfate, in grams (g);

V_0 - The sample volume, in milliliters (mL);

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