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Bipolar Membrane

双极膜

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Bipolar Membrane

1 Scope

This Document specifies the requirements, test methods, inspection rules, marking, packaging, transportation and storage of bipolar membranes.

This Document applies to the research and development, production, inspection and use of bipolar membrane products.

2 Normative References

The provisions in following documents become the essential provisions of this Document through reference in 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) is applicable to this Document.

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

GB/T 601-2016 Chemical Reagent - Preparations of Standard Volumetric Solutions

GB/T 4456 Polyethylene blown film for packaging applications

GB/T 6543 Single and double corrugated boxes for transport packages

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

GB/T 9174 General specification for transport packages of general cargo

GB/T 9969 General Principles for Preparation of Instructions for Use of Industrial Products

GB/T 14436 General Principles of Industrial Product Guarantee Documents

GB/T 20103-2006 Technical terms for membrane separation

HG/T 5112-2016 Diffusion dialysis anion exchange membrane

HY/T 166.1-2013 Ion-exchange membrane - Part 1: Electro-driven membrane

3 Terms and Definitions

For the purposes of this Document, the terms and definitions given in GB/T 20103-2006 and

HY/T 166.1-2013 and the following apply.

3.1 Bipolar membrane

A membrane with a multi-layer functional structure composed of anion and cation exchange layers and a transition layer with water dissociation catalysis in the middle.

[Source: GB/T 20103-2006, 3.l.7, modified]

3.2 Ion exchange capacity

The amount of ions in an ion exchange membrane that are in charge balance with the fixed groups.

NOTE: The unit of ion exchange capacity is: mol/kg (dry membrane).

[Source: GB/T 20103-2006, 3.1.13]

3.3 Bursting strength

Apply fluid pressure perpendicular to the membrane surface on the membrane, the critical pressure at which the membrane begins to leak or rupture.

NOTE: The unit of bursting strength is MPa.

[SOURCE: GB/T 20103-2006, 3.1.21]

3.4 Dimensional changes

The extent to which the geometric dimensions of a membrane change when it is transferred from one solution to another.

NOTE: The dimensional change rate is expressed as the percentage change of length, width or thickness.

3.5 Area resistance

The resistance value of a film specimen of a certain area.

Note: The unit of area resistance is: $\Omega \cdot cm^2$.

[SOURCE: GB/T 20103-2006, 3.1.19]

3.6 Trans-membrane voltage

in a given solution, the trans-membrane flow of a certain amount of charged ions results in a potential difference on both sides of the membrane.

NOTE: The unit of trans-membrane voltage is: V.

The trans-membrane voltage of the bipolar membrane at a current density of 100 mA/cm^2 shall be no greater than 1.5V.

4.8 Tolerance of chemical reagent

If the bipolar membrane is soaked in 6 mol/L hydrochloric acid solution for 2000 h, the decrease rate of bursting strength shall be no greater than 10%. If the bipolar membrane is soaked in 6 mol/L sodium hydroxide solution for 2000 h, the decrease rate of bursting strength shall be no greater than 10%.

4.9 Generation rate of acid or base

At a current density of 40 mA/cm^2, the generation rate of acid or base of the bipolar membrane shall be no less than 0.15 mol/ (m^2 • min).

5 Test Methods

5.1 Appearance

The visual inspection and inspection results shall meet the requirements of 4.1.

5.2 Thickness deviation

The inspection of thickness deviation shall be carried out according to the test methods specified in 6.2 of HG/T 5112-2016.

5.3 Ion exchange capacity

5.3.1 Test conditions

The test shall be carried out in a constant temperature room at 25°C ± 1°C.

5.3.2 Test principle

The dissociable ions attracted to the fixed groups in the membrane can equivalently exchange with counter ions in the solution. The exchange capacity of the membrane is determined by titrating the dissociable ions exchanged with the counter ions in the solution.

5.3.3 Apparatus

The apparatus for the test is as follows:

a) Base burette: 25.0 mL:

b) Brown acid burette; 25.0 mL;

c) Volumetric flask: 100 mL;

d) Triangular flask with stopper: 250 mL;

e) Analytical balance: 100 g, accuracy of 0.001 g:

f) Dryer;

g) Oven: 300°C. Temperature control accuracy 1°C.

5.3.4 Chemical reagents

Sodium hydroxide, hydrochloric acid, silver nitrate, sodium sulfate, potassium hydrogen phthalate, sodium chloride, phenol hydroxide, potassium chromate, pure water.

Among them, sodium chloride and potassium hydrogen phthalate are the primary reagents, and the rest are of analytically pure. The used standard solution is prepared in accordance with the provisions of GB/T 601-2016; and the pure water shall comply with the secondary water standard specified in GB/T 6682-2008.

5.3.5 Test procedures

5.3.5.1 Preparation of membrane sample

Randomly select a membrane from the membranes to be tested; and randomly select a square membrane with a side length of 10 cm from the upper, middle, and lower parts of the membrane as a membrane sample.

5.3.5.2 Pretreatment of membrane sample

The pretreatment procedures for membrane samples are as follows:

a) Take the membrane sample prepared in 5.3.5.1, soak it in pure water for no less than 24 h, and take it out;

b) Soak the membrane sample in 1 L of sodium hydroxide solution [c (NaOH) = 1.0 mol/L] for 2.5 h ± 0.5 h. Take it out; wash it with pure water until neutral; and then transfer it to 1 L hydrochloric acid solution [c(HCI) = 1.0 mol/L]; soak for 2.5 h±0.5 h. Take it out; and wash with pure water until neutral;

c) Repeat the Procedure b) for twice;

d) Transfer to hydrochloric acid solution [c(HCl) = 1.0 mol/L], the soaking time shall be no less than 24 h;

e) Take out the membrane sample. Wash with pure water until neutral; use silver nitrate solution to detect no chloride ions; place in pure water; and set aside.

5.3.5.3 Determination of moisture content

The determination of moisture content shall be carried out according to the test method specified in 6.3 of HY/T 166.1-2013.

5.3.5.4 Determination of ion exchange capacity of cation exchange layer

The procedures for measuring the ion exchange capacity of the cation exchange layer are as follows:

a) Take a membrane sample after pretreatment in 5.3.5.2; and use filter paper to absorb the surface moisture. Quickly cut into square pieces with a side length of no more than 1 cm. Weigh in a weighing bottle of known weight. Weigh the wet membrane of the membrane sample (recorded as W) and put it into a triangular flask with a stopper;

b) Add 50 mL of sodium sulfate solution [$c(Na_2SO_4)$ = 1.0mol/L] to the triangular flask with a stopper; shake it every 0.5h; and the soaking time shall be no less than 2 h:

c) Use phenolphthalein as the indicator and titrate with sodium hydroxide standard solution [c(NaOH) = 0.1 mol/L] until pink appears and does not fade for 15 s as the end point. Record the consumed volume of the sodium hydroxide standard solution (recorded as V_{NaOH});

d) Repeat Procedures a), b), and c) for 3 times; and use the average value of the ion exchange capacity calculated from the test values measured on three parallel samples as the ion exchange capacity of the cation exchange layer.

5.3.5.5 Determination of ion exchange capacity of anion exchange layer

The procedures for measuring the ion exchange capacity of the anion exchange layer are as follows:

a) Follow procedures a), b), c) in 5.3.5.4;

b) Add 5 mL of potassium chromate solution as an indicator to the triangular flask in a); and titrate with the silver nitrate standard solution [$c(AgNO_3$=0.1 mol/L) until a brick-red precipitate just appears in the solution and does not disappear as the end point. Record the consumed volume of the silver nitrate standard solution (recorded as V_{AgNO_3});

c) Repeat procedures a) and b) for 3 times. Use the average value of the exchange capacity calculated from the test values measured on 3 parallel samples as the ion exchange capacity of the anion exchange layer.

5.3.6 Data processing

The ion exchange capacity of the cation exchange layer of the bipolar membrane is calculated according to Formula (1); while the ion exchange capacity of the anion exchange layer is calculated according to Formula (2).

characterize the degree of change in the geometric dimensions of the membrane.

5.5.3 Instruments

The instruments required for the test are as follows·

a) Spiral micrometer: graduation value of 0.01 mm;

b) Vernier caliper: graduation value of 0.1 mm.

5.5.4 Test procedures

5.5.4.1 Determination of base dimensional changes

The procedures for measuring the base dimensional changes are as follows:

a) Randomly cut a membrane sample with a length of 10cm and a width of 5cm on the bipolar membrane. Carry out pretreatment of membrane samples according to the provisions of 5.3.5.2;

b) Choose any 3 corners and make 3 marks about 1cm away from the sides.

c) Place it in pure water and soak it for no less than 24 h. Take it out in the wet state; use a spiral micrometer to measure the thickness of 5 points at the 4 corners and in the middle of the sample membrane; and take the average value as L_{OZ}. Use a vernier caliper to measure the lengthwise spacing L_{OX} between the marks; and the widthwise spacing L_{OY} between the marks.

d) Take it out from pure water. Soak in 1L of sodium hydroxide solution [c(NaOH) = 2.0 mol/L]; soak for no less than 24 h. Take it out in a wet state; and use a spiral micrometer to measure the thickness of 5 pints at the 4 corners and in the middle of the sample membrane; take the average value as L_{BZ}. Use a vernier caliper to measure the lengthwise spacing L_{BX} and the widthwise spacing L_{BY} between the marks.

5.5.4.2 Determination of acidic dimensional changes

The procedures for determining the acidic dimensional changes are as follows:

a) Follow procedures a), b), c) in 5.5.4.1;

b) Take it out from the pure water; soak it in 1 L of hydrochloric acid solution [c(HCl) = 2.0 mol/L] for no less than 24 h. Take it out and use a spiral micrometer to measure the thickness of 5 points at the 4 corners and in the middle of the sample membrane.; take the average thickness as L_{AZ}. Use a vernier caliper to measure the lengthwise spacing L_{AX} and the widthwise spacing L_{AY} between the marks.

5.5.5 Data processing

The test shall be carried out in a constant temperature room at 25°C±1°C.

5.7.2 Test principle

Place the bipolar membrane in an electrodialysis membrane stack containing electrode plates; introduce the sodium chloride solution with a certain concentration. A DC electric field is applied on both sides of the bipolar membrane; and the voltage of the electrodialysis membrane stack under different current densities is measured. Calculate the average value of the single trans-membrane voltage. Plot current density – voltage curve to determine the trans-membrane voltage at 100 mA/cm^2.

5.7.3 Apparatus

The apparatus required for the test is as follows:

a) Trans-membrane voltage testing equipment: See Appendix A.1 for the schematic diagram of the device.

b) Electrodialysis membrane stack: The electrodialysis membrane stack is mainly composed of 2 water distribution plates with electrode plates, 6 non-reflux separators and 5 bipolar membranes. The electrode plate material should be titanium coated with ruthenium and iridium. The separator should be a general separator for electrodialysis. See Appendix A.2 for the schematic diagram of the device;

c) Platinum sheet or copper sheet: Specification width is 10 mm, length is 50 mm, thickness is 0.1mm; 2 pieces;

d) Multimeter: Accuracy 0.01 V.

5.7.4 Chemical reagents

Sodium chloride solution [c(NaCl)] = 0.5 mol/L].

5.7.5 Test procedures

The test procedures for trans-membrane voltage of bipolar membrane are as follows:

a) Take 5 membrane samples with a length of 300 mm and a width of 100 mm, pretreat them according to the provisions of 5.3.5.2. Use filter paper to absorb the surface solution; and assemble them and the separator in the middle of the electrode plate according to Appendix A.2.

b) During the assembly process, place two platinum sheets attached to the electrode plate and close to the membrane, so that one end of the platinum sheet is completely submerged in the effective area of the membrane stack for water flow, and the other end extends to the outer end of the membrane stack;

5.7.6.2 Draw the current density-voltage curve based on the calculation results of 5.7.6.1.

5.7.6.3 Determine the trans-membrane voltage $U_{m.100}$ at a current density of 100 mA/cm^2 on the current density-voltage curve drawn in 5.7.6 2.

5.8 Tolerance of chemical reagent

5.8.1 Test conditions

The test is carried out in a constant temperature room at 25°C ± 1°C.

5.8.2 Test principle

Soak the bipolar membrane in chemical reagents with a certain concentration. The interaction between the bipolar membrane and chemical reagents can cause damage to the membrane such as embrittlement and reduced bursting strength.

5.8.3 Chemical reagents

Hydrochloric acid solution [c(HCl) =6 mol/L], sodium hydroxide solution [c(Na0H) = 6 mol/L].

5.8.4 Test procedures

5.8.4.1 Acid tolerance of chemical reagent

The test procedures for acid tolerance of chemical reagents are as follows:

a) Pretreat 6 square membrane samples with a side length of 5 cm in accordance with the provisions of 5.3.5.2;

b) Take 3 membrane samples, test the bursting strength of the membrane sample according to the test method in 5.4; and record the average bursting strength of the 3 membrane samples as P_{A0};

c) Put the remaining 3 membrane samples into the conical flask and add 150 mL of the prepared hydrochloric acid solution. The membrane samples shall be submerged below the liquid level. The effective concentration of the hydrochloric acid solution shall be ensured during the test;

d) Shake every 24 h for 2 min;

e) After the soaking time reaches 2000 h, take out the membrane sample and wash it with pure water until it is neutral. Test the bursting strength of the membrane sample according to the bursting strength test method; and record the average bursting strength of the 3 membrane samples as P_A.

5.8.4.2 Base tolerance of chemical reagent

P_{B0} – value of bursting strength of membrane sample before soaking in the sodium hydroxide solution, in MPa;

P_B – value of bursting strength of membrane sample after soaking in the sodium hydroxide solution, in MPa.

5.9 Generation rate of acid and base

5.9.1 Test conditions

The test shall be carried out in the constant temperature room at 25°C±1°C.

5.9.2 Test principle

Place the bipolar membrane in an electrodialysis membrane stack containing electrode plates; introduce the sodium sulfate solution. Apply a DC electric field on both sides of the bipolar membrane; measure the amount of acid and base produced in the acid-base chamber under fixed current density conditions, and calculate the generation rate of acid or base.

5.9.3 Apparatus

The apparatus required for the test is as follows:

a) Testing device for generation rate of acid or base: See Appendix A.3 for the schematic diagram of the device:

b) Test membrane stack: The effective area length of the membrane in the membrane stack is no less than 210 mm and the width is no less than 90 mm. The electrodialysis membrane stack mainly consists of 2 water distribution plates with electrode plates, 4 non-reflux separators, 1 bipolar member, as well as perfluorinated sulfonic acid anode membranes. The electrode plate material should be titanium coated with ruthenium and iridium. The separator should be a general separator for electrodialysis. The perfluorinated sulfonic acid anode membranes should use a membrane with stable market performance. Schematic diagram of the device can refer to Appendix A.4.

5.9.4 Chemical reagents

Sodium sulfate solution [$c(Na_2SO_4)$ = 0.5 mol/L].

5.9.5 Test procedures

The test procedures for the generation rate of acid or base of the bipolar membrane are as follows:

a) Follow the pretreatment procedures in 5.3.5.2 to process 1 membrane sample with a length of 300 mm and a width of 100 mm, and 2 perfluorinated sulfonic acid anode membranes with a length of 300 mm and a width of 100 mm; and assemble them with

a) Certificate of conformity;

b) Test report of membrane performance;

c) Trademark, product number;

d) Production date:

e) Name and address of the manufacturer;

f) Execution standard number of the product.

7.2 Packaging

7.2.1 Inner packaging

The inner packaging of the bipolar membrane uses high-density polyethylene blown membrane, which shall comply with the provisions of GB/T 4456.

7.2.2 Outer packaging

The outer packaging of bipolar membrane contains the following contents:

a) Use corrugated cartons, which shall comply with the provisions of GB/T 6543;

b) The provisions of GB/T 9174 shall be complied with during transportation,

c) Storage and transportation markings shall comply with the provisions of GB/T 191.

7.2.3 Packaging box

The packaging box of the bipolar membrane contains the following contents·

a) The packaging box shall be attached with a packing list, inspection certificate, instructions for use and other documents;

b) The inspection certificate shall be written in compliance with the provisions of GB/T 14436;

c) The instructions for use should be written in compliance with the provisions of GB/T 9969.

7.3 Transportation

During the transportation, loading and unloading process of bipolar membranes, they shall not be subject to severe impact, bumping, throwing, squeezing, rain and stains; and shall also avoid contact with corrosive chemical reagents.

7.4 Storage

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