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(54) Title: POLYACID-BASED ELECTROLYTE CONDUCTOR MATERIAL AND PREPARATION METHOD AND APPLICATION THEREOF

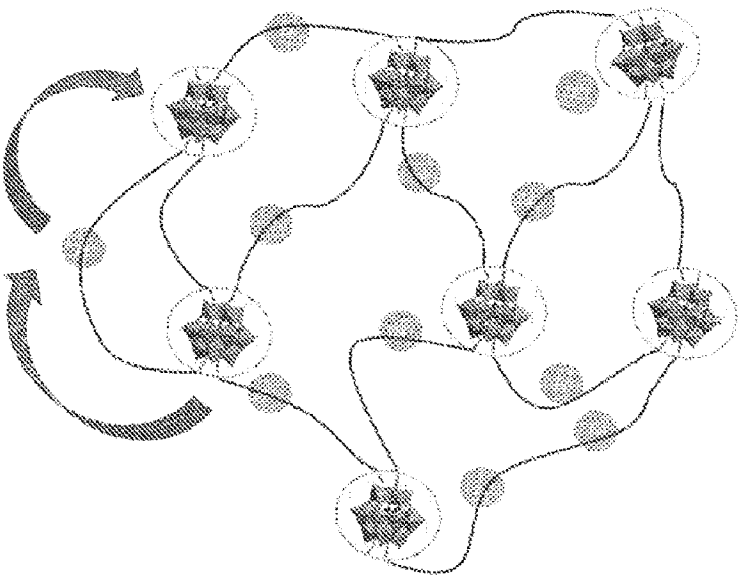

图 2

(57) Abrégé/Abstract:
A polyacid-based electrolyte conductor material and a preparation method and application thereof, specifically including two preparation methods: a solid-state melting method and a solvent method. The prepared polyacid-based electrolyte conductor material forms a three-dimensional network by means of hydrogen-bond interaction between the polyacid and the polymer, thereby realizing effective proton transfer. When the mass ratio of the polyacid is 70%, the conductivity of the conductor material may reach 1.01×10^{-2} S cm $^{-1}$ (- 80°C). In terms of mechanical properties, the viscosity of a sample is 273 Pa. s, guaranteeing the safety thereof as an electrolyte. The shear thinning behavior enables the polyacid-based electrolyte conductor material to have good processability.

Abstract

A POM-based electrolyte conductor material and a preparation method and application thereof, specifically including two preparation methods: a solid-state melting method and a solvent method. The prepared POM-based electrolyte conductor material forms a three-dimensional network by means of hydrogen-bond interaction between the POM and the polymer, thereby realizing effective proton transfer. When the mass ratio of the POM is 70%, the conductivity of the conductor material can reach 1.01×10^{-2} S cm^{-1} (at 80 °C). In terms of mechanical properties, the viscosity of a sample is 273 Pa•s, guaranteeing the safety thereof as an electrolyte. The shear thinning behavior enables the POM-based electrolyte conductor material good processability.

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POLYOXOMETALATE-BASED ELECTROLYTE CONDUCTOR MATERIAL AND PREPARATION METHOD AND APPLICATION THEREOF

Field of the Invention

The present invention belongs to the field of battery materials, and particularly relates to a polyoxometalate-based electrolyte conductor material and a preparation method and application thereof.

Background of the Invention

Improving the proton conductivity of electrolytes is the key to improving the efficiency of fuel cells and secondary batteries. At present, the proton conductor material that has been commercialized in proton exchange membrane fuel cells is perfluorosulfonic acid (Nafions), which has extremely high proton conductivity (> 10^{-2} S cm^{-1}) at a condition of high humidity (RH 100%) and low/medium temperature (< 373 K). However, Nafions are expensive and have poor stability and mechanical property. Therefore, it is an urgent problem to be solved to research and prepare conductor materials that can replace Nafions. The development of electrolyte conductor materials with good conductivity, mechanical property, and processability has a profound significance for the development of fuel cells, batteries, and capacitors.

Polyoxometalates (POMs) are nanoscale early transition metal-oxygen molecule clusters with a lower effective surface charge density, which endow them with very strong proton transmitting capability. In fact, Keggin-type POMs (e.g., $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) exhibit high proton conductivities comparable to Nafions at high humidity. Protons are transferred between POMs through the hydrogen-bond network formed by their crystal water. Therefore, the conductivity is greatly affected by humidity which limits the application of POMs as conductors.

POMs can form organic-inorganic hybrid materials with new functional performance in combination with different organic components. Therefore, researchers blend POMs with polymers to prepare a series of conductor materials with

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somewhat improved stability, but there is a very great gap between them and the commercial conductor materials in conductivity. How to prepare electrolyte conductor materials with ultra-high conductivity is still a big challenge for researchers.

Summary of the Invention

Aiming at the defects and deficiencies in the prior art, a primary objective of the present invention is to provide a POM-based electrolyte conductor material. In the prepared POM-based electrolyte conductor material, a three-dimensional network for transferring protons is formed by means of hydrogen-bond interaction between the POM and the polymer, thereby realizing effective transfer of protons by means of the movement of the polymer chains. This electrolyte conductor material has good proton conduction efficiency in low and medium temperature environments, and meanwhile, has superior processability, safety, and chemical stability.

Another objective of the present invention is to provide a preparation method of the above-described POM-based electrolyte conductor material.

Still another objective of the present invention is to provide an application of the above-described POM-based electrolyte conductor material.

The objectives of the present invention are achieved by the following technical solutions.

A preparation method of a POM-based electrolyte conductor material includes the following steps: mixing a POM with a polymer melt to obtain a blend, subjecting the blend to reacting under heating and stirring, then cooling to room temperature after the end of the reaction to prepare the POM-based electrolyte conductor material.

Preferably, a mass ratio of the POM to the polymer melt is 1 : 9 to 7 : 3.

Preferably, the heating and stirring is performed for a time of 5 to 48 hours, more preferably 12 hours, at a temperature of 60 to 80 °C and a stirring rate of 100 to 700 rpm.

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Preferably, the room temperature is 25 to 35 °C.

Preferably, the type of the POM is one of Keggin type POMs, Dawson type POMs, and Preyssler type POMs.

Preferably, a general chemical formula of the Keggin type POMs is $H_nXM_{12}O_{40}$ (M=Mo, W, or V; and X=P or As, and n=3; X=Si or Ge, and n=4; X=B or Al, and n=5; or X=Cu or Co, and n=6), and more preferably $H_3PW_{12}O_{40}$.

Preferably, a general chemical formula of the Dawson type POMs is $H_nX_2M_{18}O_{62}$ (M=Mo or W; X=P, As, S or V; and n=6).

Preferably, a general chemical formula of the Preyssler type POMs is $H_nYX_5M_{30}O_{110}$ (X=P; Y=Bi, Na, Ca, Eu or U; M=W; and n=12).

Preferably, the polymer is a polymer with one or more of hydroxyl, carboxylic acid group, and amino.

Preferably, the polymer with one or more of hydroxyl, carboxylic acid group, and amino is one of polyethylene glycol, polyacrylic acid, polyvinyl alcohol, and chitosan, and more preferably polyethylene glycol (PEG).

Preferably, the molecular weight of the polyethylene glycol is an average molecular weight of 400 to 300,000, and more preferably the polyethylene glycol is one or more of polyethylene glycol having an average molecular weight of 400 or 4,000 and six-arm star-shaped polyethylene glycol having an average molecular weight of 2,400.

A preparation method of a POM-based electrolyte conductor material includes the following steps: adding a polymer into a solvent to obtain a polymer solution; adding a POM into the solvent to obtain a POM solution; mixing the POM solution with the polymer solution to obtain a blend, subjecting the blend to reacting under heating and stirring, and after the end of the reaction, completely volatilizing the

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solvent to prepare the POM-based electrolyte conductor material.

Preferably, the polymer is added into the solvent to obtain the polymer solution, and a concentration range of the polymer solution is 0.1 g/mL to 1 g/mL.

Preferably, the POM is added into the solvent to obtain the POM solution, and a concentration range of the POM solution is 0.1 g/mL to 1 g/mL.

Preferably, a volume ratio of the POM solution to the polymer solution is 1 : 9 to 7 : 3.

Preferably, the heating and stirring is performed for a time of 5 to 48 hours, more preferably 12 hours, at a temperature of 40 to 60 °C and a stirring rate of 100 to 700 rpm.

Preferably, the solvent is water or tetrahydrofuran, and more preferably tetrahydrofuran.

Preferably, the type of the POM is one or more of Keggin type POMs, Dawson type POMs, and Preyssler type POMs.

Preferably, a general chemical formula of the Keggin type POMs is $H_nXM_{12}O_{40}$ (M=Mo, W or V; and X=P or As, and n=3; X=Si or Ge, and n=4; X=B or Al, and n=5; or X=Cu or Co, and n=6), and more preferably $H_3PW_{12}O_{40}$.

Preferably, a general chemical formula of the Dawson type POMs is $H_nX_2M_{18}O_{62}$ (M=Mo or W; X=P, As, S or V; and n=6).

Preferably, a general chemical formula of the Preyssler type POMs is $H_nYX_5M_{30}O_{110}$ (X=P; Y=Bi, Na, Ca, Eu or U; M=W; and n=12).

Preferably, the polymer is a polymer with one or more of hydroxyl, a carboxylic acid group, and amino.

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Preferably, the polymer with one or more of hydroxyl, a carboxylic acid group, and amino is one of polyethylene glycol, polyacrylic acid, polyvinyl alcohol, and chitosan, and more preferably polyethylene glycol.

Preferably, the molecular weight of the polyethylene glycol is an average molecular weight in a range of 400 to 300,000, and more preferably the polyethylene glycol is one or more of polyethylene glycol having an average molecular weight of 400 and 4,000 and six-arm star-shaped polyethylene glycol having an average molecular weight of 2,400.

A POM-based electrolyte conductor material is prepared by the preparation method of the POM-based electrolyte conductor material described above.

The POM-based electrolyte conductor material is applied in the fields of fuel cells, batteries, and super capacitors.

Compared with the prior art, the present invention has the following advantages and beneficial effects:

(1) the POM-based electrolyte conductor material of the present invention has very high proton conduction efficiency (to 1.01×10^{-2} S cm^{-1}) in low/medium temperature environments (80 °C).

(2) the preparation methods of the present invention are simple, have mild reaction conditions, are suitable for mass production, and have low cost.

(3) in the systems of the preparation methods of the present invention, the polyethylene glycol can combine with the POM through the hydrogen bond, thereby greatly increasing the proton conduction efficiency, and meanwhile, the viscosity of the sample is as high as 273 Pa•s, which guarantees the safety of the sample while used as an electrolyte.

(4) the POM-based electrolyte conductor material of the present invention has an obvious shear thinning behavior which ensures the good processability of the sample.

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Brief Description of the Drawings

Fig. 1 is small angle X-ray scattering curves of electrolyte conductor materials prepared by Examples 1 to 7.

Fig. 2 is a schematic diagram of the structure and proton conduction of an electrolyte conductor material prepared by an example of the present invention.

Fig. 3 is a Nyquist diagram of a PEG400 electrolyte conductor material prepared by Comparative example 1 at conditions of 25 °C, 50 °C, and 80 °C.

Fig. 4 is a Nyquist diagram of a PEG400-10%PW_{12} electrolyte conductor material prepared by Example 1 at conditions of 25 °C, 50 °C, and 80 °C.

Fig. 5 is a Nyquist diagram of a PEG400-20%PW_{12} electrolyte conductor material prepared by Example 2 at conditions of 25 °C, 50 °C, and 80 °C.

Fig. 6 is a Nyquist diagram of a PEG400-50%PW_{12} electrolyte conductor material prepared by Example 5 at conditions of 25 °C, 50 °C, and 80 °C.

Fig. 7 is a Nyquist diagram of a PEG400-70%PW_{12} electrolyte conductor material prepared by Example 7 at conditions of 25 °C, 50 °C, and 80 °C.

Fig. 8 is a Nyquist diagram of a PEG4000-60%PW_{12} electrolyte conductor material prepared by Example 8 at conditions of 25 °C, 50 °C, and 80 °C.

Fig. 9 is a Nyquist diagram of a PEG4000-70%PW_{12} electrolyte conductor material prepared by Example 9 at conditions of 25 °C, 50 °C, and 80 °C.

Fig. 10 is a Nyquist diagram of a SPEG2400-70%PW_{12} electrolyte conductor material prepared by Example 10 at conditions of 25 °C, 50 °C, and 80 °C.

Fig. 11 is a flowing graph of the electrolyte conductor materials prepared by

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Examples 1 to 7 and the electrolyte conductor material prepared by Comparative example 1.

Detailed Description of the Embodiments

Specific embodiments of the present invention will be further described in detail below with reference to the figures and examples. It should be pointed out that for an ordinary person skilled in the present field, several modifications and improvements can be made on the premise of without departing from the concept of the present invention. All these modifications and improvements shall fall within the scope of protection of the present invention.

In examples, the room temperature is 27 °C, the POM is a Keggin type POM $H_3PW_{12}O_{40}$, and a stirring rate is 300 rpm.

Example 1

1.0 g of POM was dissolved in 9.0 g of polyethylene glycol (PEG) melt having a relative molecular weight of 400 at 67 °C to obtain a blend A; the blend A was subjected to reacting for 12 hours under heating and stirring at 67 °C, and after the reaction ended, the temperature was cooled to room temperature to prepare a transparent POM-based electrolyte conductor material, which was denoted as PEG400-10%PW_{12}.

Example 2

2.0 g of POM was dissolved in 8.0 g of polyethylene glycol (PEG) melt having a relative molecular weight of 400 at 67 °C to obtain a blend A; the blend A was subjected to reacting for 12 hours under heating and stirring at 67 °C, and after the reaction ended, the temperature was cooled to room temperature to prepare a transparent POM-based electrolyte conductor material, which was denoted as PEG400-20%PW_{12}.

Example 3

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3.0 g of POM was dissolved in 7.0 g of polyethylene glycol (PEG) melt having a relative molecular weight of 400 at 67 °C to obtain a blend A; the blend A was subjected to reacting for 12 hours under heating and stirring at 67 °C, and after the reaction ended, the temperature was cooled to room temperature to prepare a transparent POM-based electrolyte conductor material, which was denoted as PEG400-30%PW_{12}.

Example 4

4.0 g of POM was dissolved in 6.0 g of polyethylene glycol (PEG) melt having a relative molecular weight of 400 at 67 °C to obtain a blend A; the blend A was subjected to reacting for 12 hours under heating and stirring at 67 °C, and after the reaction ended, the temperature was cooled to room temperature to prepare a transparent POM-based electrolyte conductor material, which was denoted as PEG400-40%PW_{12}.

Example 5

5.0 g of POM was dissolved in 5.0 g of polyethylene glycol (PEG) melt having a relative molecular weight of 400 at 67 °C to obtain a blend A; the blend A was subjected to reacting for 12 hours under heating and stirring at 67 °C, and after the reaction ended, the temperature was cooled to room temperature to prepare a transparent POM-based electrolyte conductor material, which was denoted as PEG400-50%PW_{12}.

Example 6

6.0 g of POM was dissolved in 4.0 g of polyethylene glycol (PEG) melt having a relative molecular weight of 400 at 67 °C to obtain a blend A; the blend A was subjected to reacting for 12 hours under heating and stirring at 67 °C, and after the reaction ended, the temperature was cooled to room temperature to prepare a transparent POM-based electrolyte conductor material, which was denoted as PEG400-60%PW_{12}.

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Example 7

7.0 g of POM was dissolved in 3.0 g of polyethylene glycol (PEG) melt having a relative molecular weight of 400 at 67 °C to obtain a blend A; the blend A was subjected to reacting for 12 hours under heating and stirring at 67 °C, and after the reaction ended, the temperature was cooled to room temperature to prepare a transparent POM-based electrolyte conductor material, which was denoted as PEG400-70%PW_{12}.

Example 8

6.0 g of POM was dissolved in 4.0 g of polyethylene glycol (PEG) melt having a relative molecular weight of 4,000 at 80 °C to obtain a blend A; the blend A was subjected to reacting for 12 hours under heating and stirring at 80 °C, and after the reaction ended, the temperature was cooled to room temperature to prepare a transparent POM-based electrolyte conductor material, which was denoted as PEG4000-60%PW_{12}.

Example 9

7.0 g of POM was dissolved in 3.0 g of polyethylene glycol (PEG) melt having a relative molecular weight of 4,000 at 80 °C to obtain a blend A; the blend A was subjected to reacting for 12 hours under heating and stirring at 80 °C, and after the reaction ended, the temperature was cooled to room temperature to prepare a transparent POM-based electrolyte conductor material, which was denoted as PEG4000-70%PW_{12}.

Example 10

7.0 g of POM was dissolved in 7 mL of tetrahydrofuran to obtain a solution A; 3.0 g of six-arm star-shaped polyethylene glycol having an average molecular weight of 2,400 was dissolved in 3 mL of tetrahydrofuran to obtain a solution B; the solution A was mixed with the solution B, and the mixture was subjected to reacting for 12

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hours under heating and stirring at 50 °C; and after the reaction ended, the solvent was volatilized to obtain a POM-based electrolyte conductor material, which was denoted as SPEG2400-70%PW_{12}.

Comparative example 1

10 g of polyethylene glycol having a relative molecular weight of 400 was subjected to reacting for 12 hours under heating and stirring at 67 °C, and after the reaction ended, the temperature was cooled to room temperature to obtain a transparent PEG400 electrolyte conductor material, which was denoted as PEG400.

Table 1 is test results for conductivity of the electrolyte conductor materials of Example 1, Example 2, Example 5, Example 7, Example 8, Example 9, Example 10, and Comparative example 1 at conditions of 25 °C, 50 °C, and 80 °C (at a relative humidity of 45%). A CHI660E electrochemical workstation purchased from CH Instruments, Inc. was used as a test instrument. During the tests, two platinum sheets were used as electrodes, a test frequency range was from 0.01 Hz to 100,000 Hz, EIS was used for test, and the proton conductivity was calculated by a formula $\sigma = L/(AR_b)$. R_b represented a resistance value, L represented a distance between the two platinum sheet electrodes, and A represented an area of the two electrodes.

Table 1 General chart of test results for conductivity

Sample	25 °C _ conductivity / S cm^{-1}	50 °C _ conductivity / S cm^{-1}	80 °C _ conductivity / S cm^{-1}
PEG400	7.4×10^{-6}	1.3×10^{-5}	2.9×10^{-5}
PEG400-10%PW_{12}	6.5×10^{-5}	1.8×10^{-4}	4.2×10^{-4}
PEG400-20%PW_{12}	1.4×10^{-4}	4.2×10^{-4}	1.0×10^{-3}
PEG400-50%PW_{12}	4.0×10^{-4}	1.2×10^{-3}	3.5×10^{-3}
PEG400-70%PW_{12}	1.4×10^{-3}	3.6×10^{-3}	1.0×10^{-2}
PEG4000-60%PW_{12}	1.8×10^{-3}	5.3×10^{-3}	1.2×10^{-2}
PEG4000-70%PW_{12}	1.6×10^{-3}	6.5×10^{-3}	1.6×10^{-2}

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SPEG2400-70%PW_{12}	6.1×10^{-4}	2.4×10^{-3}	8.8×10^{-3}

Conductivity values of the electrolyte conductor materials prepared by various examples are listed in Table 1, and it can be seen that: the conductivities of various samples increase as the temperature is increased; with the increase of the content of the POM, the conductivity of the prepared electrolyte conductor material is increased by three orders of magnitude, wherein the conductivity of the PEG400-70%PW_{12} sample can reach 1.01×10^{-2} S cm^{-1} at 80 °C; an electrolyte conductor material with very high proton conduction efficiency can also be obtained by blending a higher molecular weight polyethylene glycol with a POM; and the SPEG2400-70%PW_{12} sample prepared by the solvent method also has higher conductivity.

Fig. 1 shows small angle X-ray scattering curves of the electrolyte conductor materials prepared by Examples 1 to 7. It can be seen from Fig. 1 that: the prepared PEG400-PW_{12} nanocomposite material has no obvious crystal diffraction peak in the small angle X-ray scattering spectrum. It indicates that in the electrolyte conductor materials of the present invention, the POM clusters are uniformly dispersed in the polymer substrate, which achieves the nanoscale dispersion of the POM, and guarantees the structural stability of the sample.

Fig. 2 is schematic diagram for the structure and proton conduction of the electrolyte conductor material prepared by the example of the present invention. Wherein, islet shaped structures represent phosphotungstic acids and hydrogen-bond interaction between the phosphotungstic acids and the polymer components, solid lines connecting different islet structures represent the polymer chains of polyethylene glycol, and H^+ represents protons. It can be seen from Fig. 2 that: the polyethylene glycol and the POM form a three-dimensional network through hydrogen bonds, and the protons are effectively transferred in virtue of the movement of the polymer chain.

Fig. 3 is a Nyquist diagram of the PEG400 electrolyte conductor material prepared by Comparative example 1 at conditions of 25 °C, 50 °C, and 80 °C. Wherein, the conductivity of the electrolyte conductor material can be obtained from the intercept of the Nyquist plot with the real axis.

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Fig. 4 is a Nyquist diagram of the PEG400-10%PW_{12} electrolyte conductor material prepared by Example 1 at conditions of 25 °C, 50 °C, and 80 °C. Wherein, the conductivity of the electrolyte conductor material can be obtained from the intercept of the Nyquist plot with the real axis.

Fig. 5 is a Nyquist diagram of the PEG400-20%PW_{12} electrolyte conductor material prepared by Example 2 at conditions of 25 °C, 50 °C, and 80 °C. Wherein, the conductivity of the electrolyte conductor material can be obtained from the intercept of the Nyquist plot with the real axis.

Fig. 6 is a Nyquist diagram of the PEG400-50%PW_{12} electrolyte conductor material prepared by Example 5 at conditions of 25 °C, 50 °C, and 80 °C. Wherein, the conductivity of the electrolyte conductor material can be obtained from the intercept of the Nyquist plot with the real axis.

Fig. 7 is a Nyquist diagram of the PEG400-70%PW_{12} electrolyte conductor material prepared by Example 7 at conditions of 25 °C, 50 °C, and 80 °C. Wherein, the conductivity of the electrolyte conductor material can be obtained from the intercept of the Nyquist plot with the real axis.

It can be seen from Fig. 4 to Fig. 7 that the conductivity of the conductor is greatly increased with the addition of the POM. Meanwhile, it indicates that as the temperature is increased to 80 °C, the conductivity of the sample has an obvious rising tendency.

Fig. 8 is a Nyquist diagram of the PEG4000-60%PW_{12} electrolyte conductor material prepared by Example 8 at conditions of 25 °C, 50 °C, and 80 °C. Wherein, the conductivity of the electrolyte conductor material can be obtained from the intercept of the Nyquist plot with the real axis.

Fig. 9 is a Nyquist diagram of the PEG4000-70%PW_{12} electrolyte conductor material prepared by Example 9 at conditions of 25 °C, 50 °C, and 80 °C. Wherein, the conductivity of the electrolyte conductor material can be obtained from the

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intercept of the Nyquist plot with the real axis.

It can be seen from Fig. 8 and Fig. 9 that as the temperature is increased to 80 °C, the conductivity of the sample has an obvious rising tendency.

Fig. 10 is a Nyquist diagram of the SPEG2400-70%PW_{12} electrolyte conductor material prepared by Example 10 at conditions of 25 °C, 50 °C, and 80 °C. Wherein, the conductivity of the electrolyte conductor material can be obtained from the intercept of the Nyquist plot with the real axis. It can be seen from Fig. 10 that the POM-based electrolyte conductor material prepared by the solvent method also exhibits relatively high conductivity.

Fig. 11 is a flow graph of the electrolyte conductor materials prepared by Examples 1 to 7 and the electrolyte conductor material of Comparative example 1. It can be seen from Fig. 11 that the viscosity of the PEG400-70%PW_{12} sample is as high as 273 Pa•s at room temperature, which guarantees the safety of the sample used as an electrolyte. In addition, the obvious shear thinning behavior of the sample enables the sample to have good processability.

From the detailed description of the examples of the present invention with the above-described content, it can be understood that the conductivity of the POM-based electrolyte conductor material of the present invention is greatly increased as the temperature rises, under conditions of the temperature range of 25 °C to 80 °C and a relative humidity of 45%. During the preparation of the materials, the samples with the POM in a mass ratio of 70% can all have very high conductivity (at a temperature of 80 °C, the conductivity of PEG400-70%PW_{12} is 1.01×10^{-2} S cm^{-1}, the conductivity of PEG4000-70%PW_{12} is 1.64×10^{-2} S cm^{-1}, and the conductivity of SPEG2400-70%PW_{12} is 8.8×10^{-3} S cm^{-1}).

What is described above are preferred embodiments of the present invention and not intended to limit the present invention. It should be pointed out that an ordinary person skilled in the present technical field can make several improvements and modifications on the premise of without departing from the technical principle of the present inventions, and these improvements and modifications shall also be deemed as

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falling within the scope of protection of the present invention. Therefore, the content of without departing from the patented solution of the present invention, any simple amendment, equivalent change, and modification made to the above examples according to the essence of the patented technology of the present invention shall fall within the scope of protection of the patent of the present invention.

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Claims

1. A preparation method of a POM-based electrolyte conductor material, characterized in that, it comprises the following steps: mixing a POM with a polymer melt in a mass ratio of 1 : 9 to 7 : 3 to obtain a blend, subjecting the blend to reacting under heating and stirring, then cooling to room temperature after the end of the reaction to prepare the POM-based electrolyte conductor material.

2. The preparation method of a POM-based electrolyte conductor material according to claim 1, characterized in that, the heating and stirring is performed for a time of 5 to 48 hours at a temperature of 60 to 80 °C and a stirring rate of 100 to 700 rpm.

3. A preparation method of a POM-based electrolyte conductor material, characterized in that, it comprises the following steps: adding a polymer into a solvent to obtain a polymer solution at a concentration of 0.1 g/mL to 1 g/mL; adding a POM into the solvent to obtain a POM solution at a concentration of 0.1 g/mL to 1 g/mL; mixing the POM solution with the polymer solution in a volume ratio of 1 : 9 to 7 : 3 to obtain a blend, subjecting the blend to reacting under heating and stirring, and after the end of the reaction, completely volatilizing the solvent to prepare the POM-based electrolyte conductor material.

4. The preparation method of a POM-based electrolyte conductor material according to claim 3, characterized in that, the heating and stirring is performed for a time of 5 to 48 hours at a temperature of 40 to 60 °C and a stirring rate of 100 to 700 rpm; and the solvent of the polymer solution and the POM solution is water or tetrahydrofuran.

5. The preparation method of the POM-based electrolyte conductor material according to claims 1 or 3, characterized in that, the POM is one or more of Keggin type POMs, Dawson type POMs, and Preyssler type POMs; and

the polymer is a polymer with one or more of hydroxyl, carboxylic acid group, and amino.

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6. The preparation method of the POM-based electrolyte conductor material according to claim 5, characterized in that,

a general chemical formula of the Keggin type POMs is $H_nXM_{12}O_{40}$, where M=Mo, W or V; and X=P or As, and n=3; X=Si or Ge, and n=4; X=B or Al, and n=5; or X=Cu or Co, and n=6;

a general chemical formula of the Dawson type POMs is $H_nX_2M_{18}O_{62}$, where M=Mo or W; X=P, As, S or V; and n=6; and

a general chemical formula of the Preyssler type POMs is $H_nYX_5M_{30}O_{110}$, where X=P; Y=Bi, Na, Ca, Eu or U; M=W; and n=12.

7. The preparation method of the POM-based electrolyte conductor material according to claim 5, characterized in that, the polymer with one or more of hydroxyl, carboxylic acid group, and amino is one of polyethylene glycol, polyacrylic acid, polyvinyl alcohol, and chitosan; and the Keggin type POM is $H_3PW_{12}O_{40}$.

8. The preparation method of the POM-based electrolyte conductor material according to claim 7, characterized in that, the polyethylene glycol has an average molecular weight of 400 to 300,000.

9. A POM-based electrolyte conductor material prepared by the preparation method of the POM-based electrolyte conductor material according to any one of claims 1 to 8.

10. An application of the POM-based electrolyte conductor material according to claim 9 in the fields of fuel cells, lithium ion batteries, and supercapacitors.

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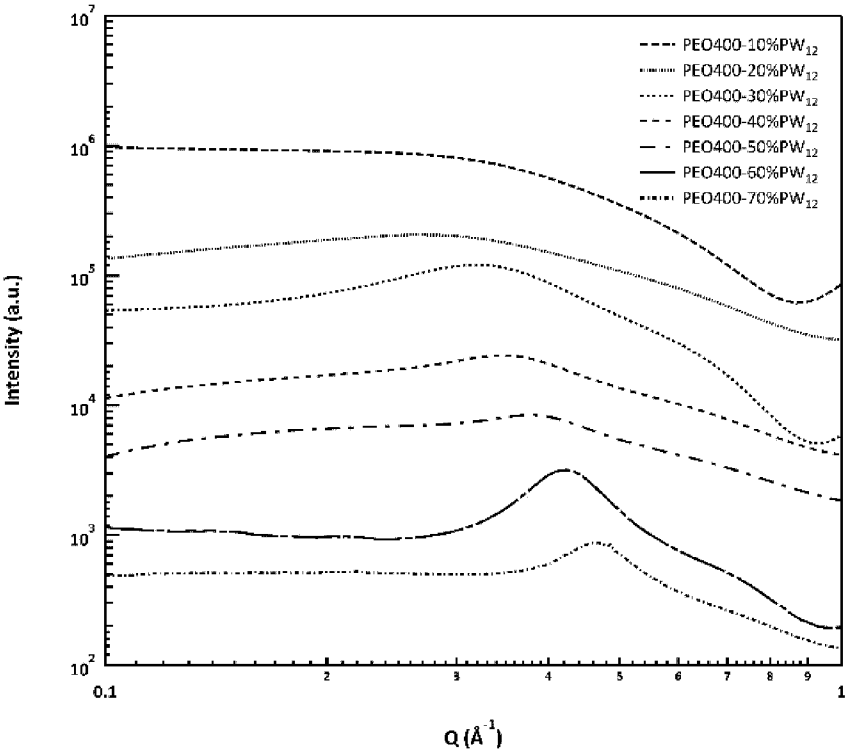

Fig. 1

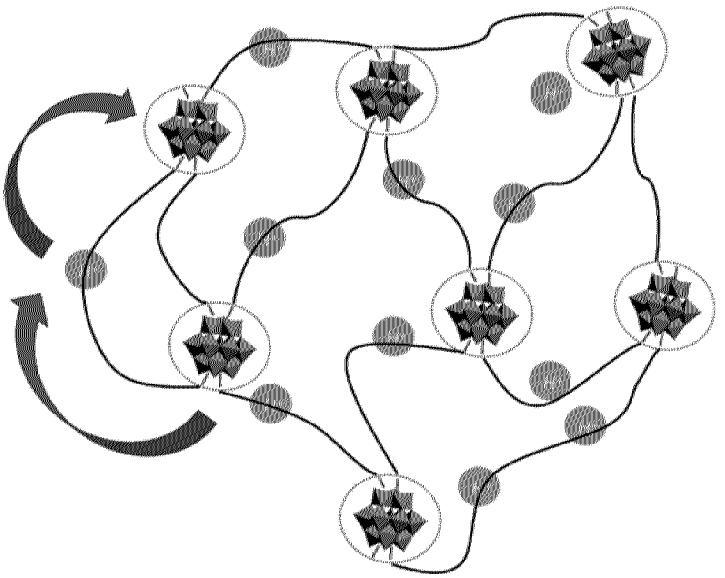

Fig. 2

Date Reçue/Date Received 2021-12-24

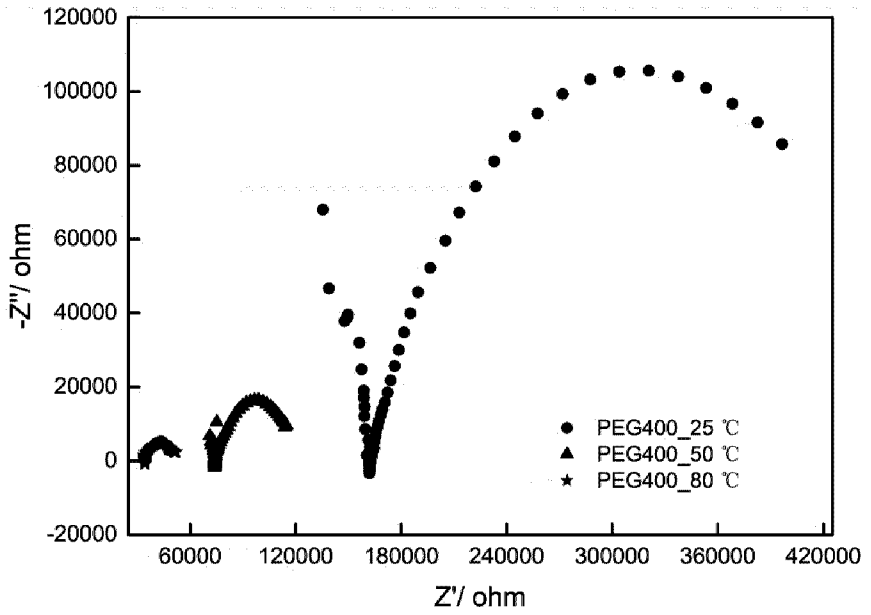

Fig. 3

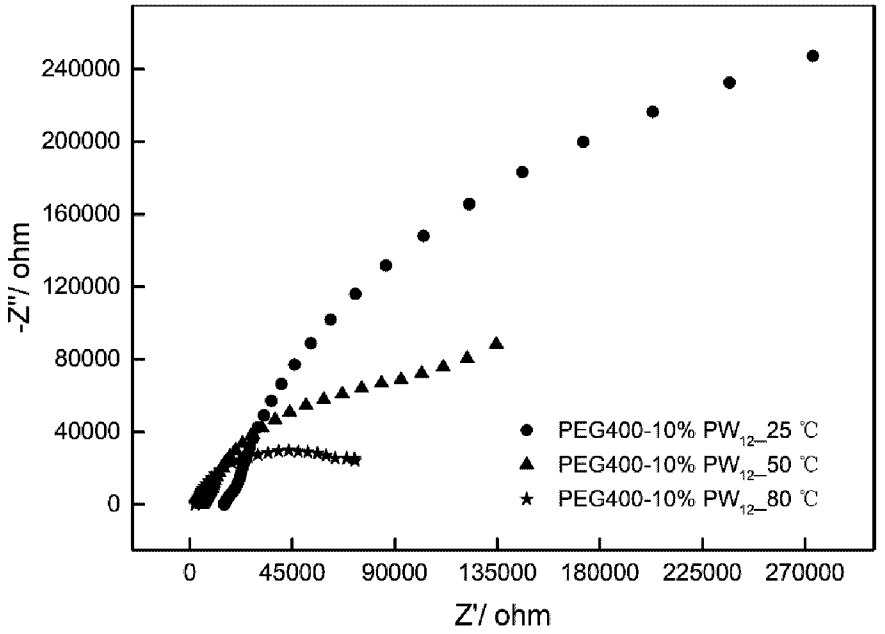

Fig. 4

Date Reçue/Date Received 2021-12-24

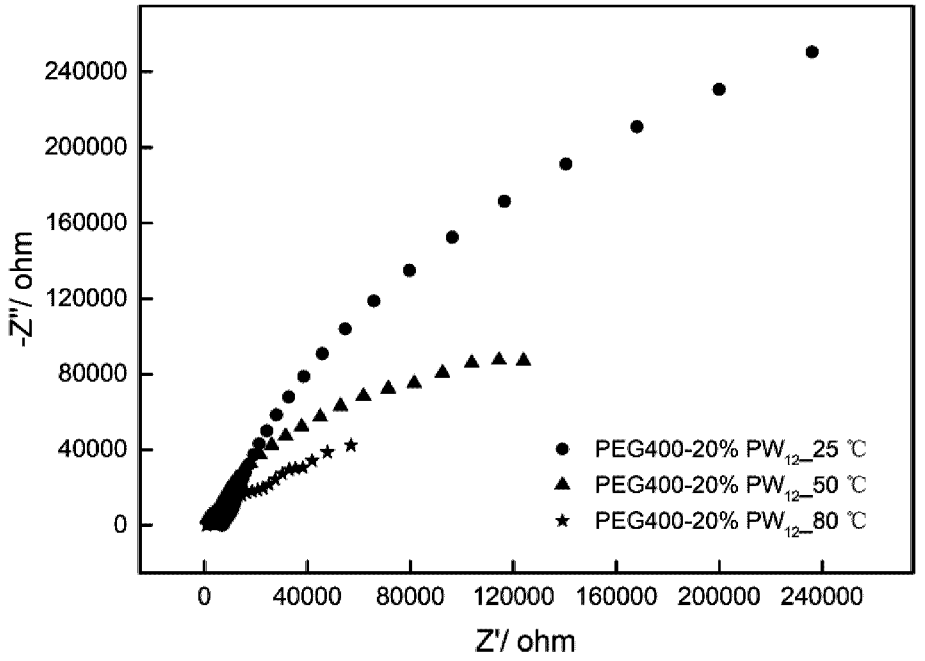

Fig. 5

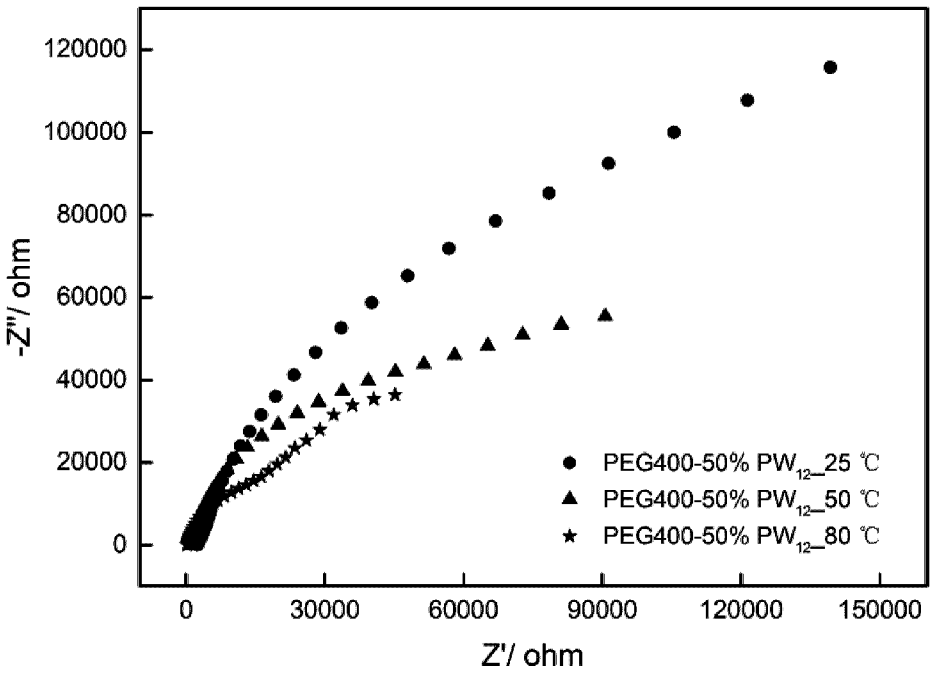

Fig. 6

Date Reçue/Date Received 2021-12-24

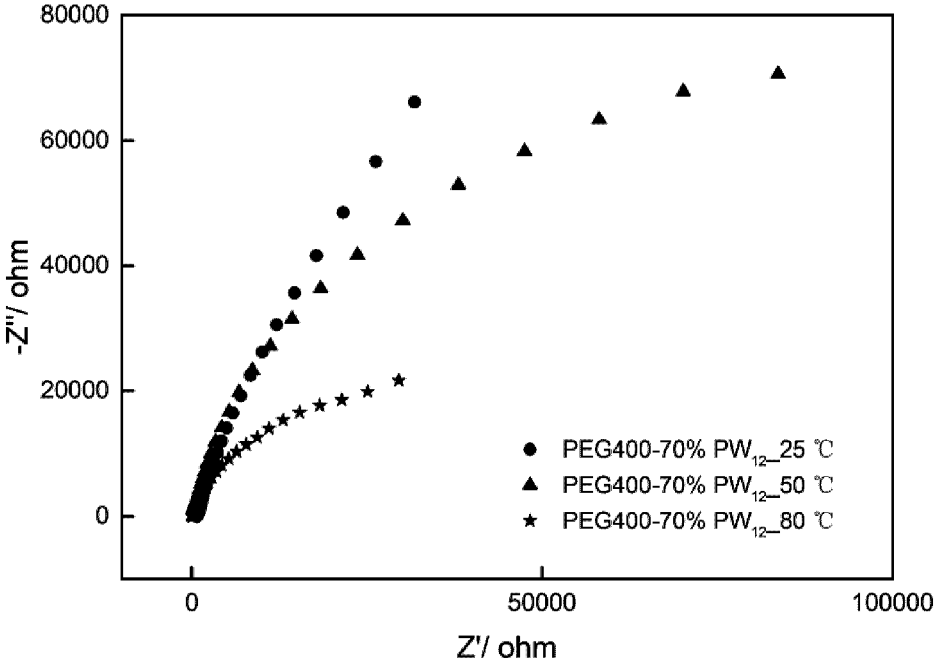

Fig. 7

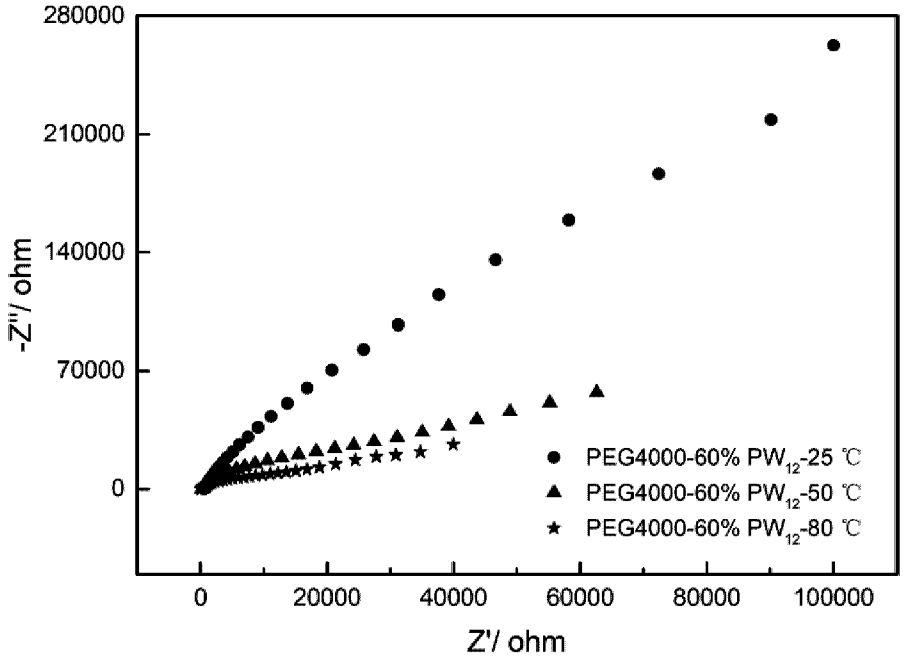

Fig. 8

Date Reçue/Date Received 2021-12-24

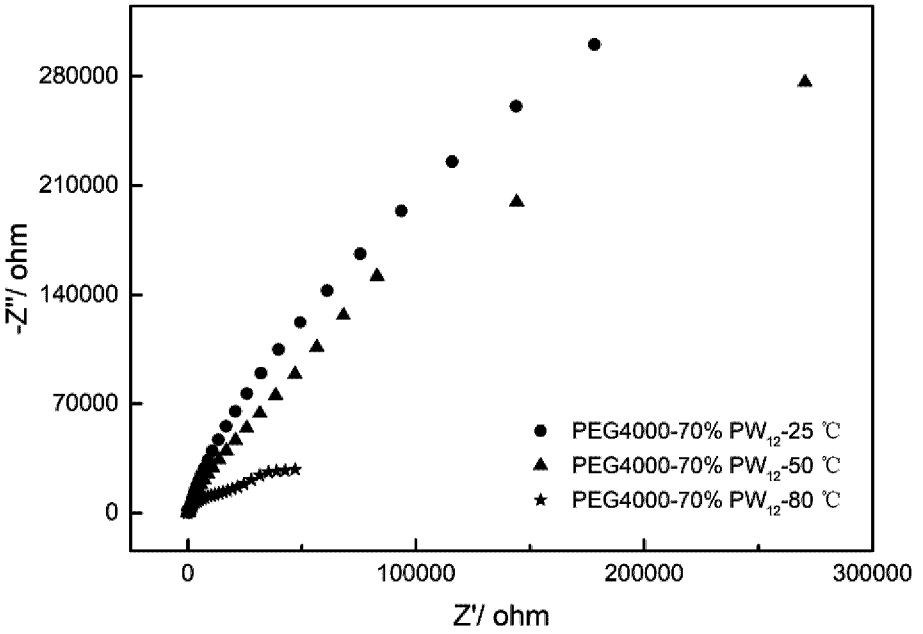

Fig. 9

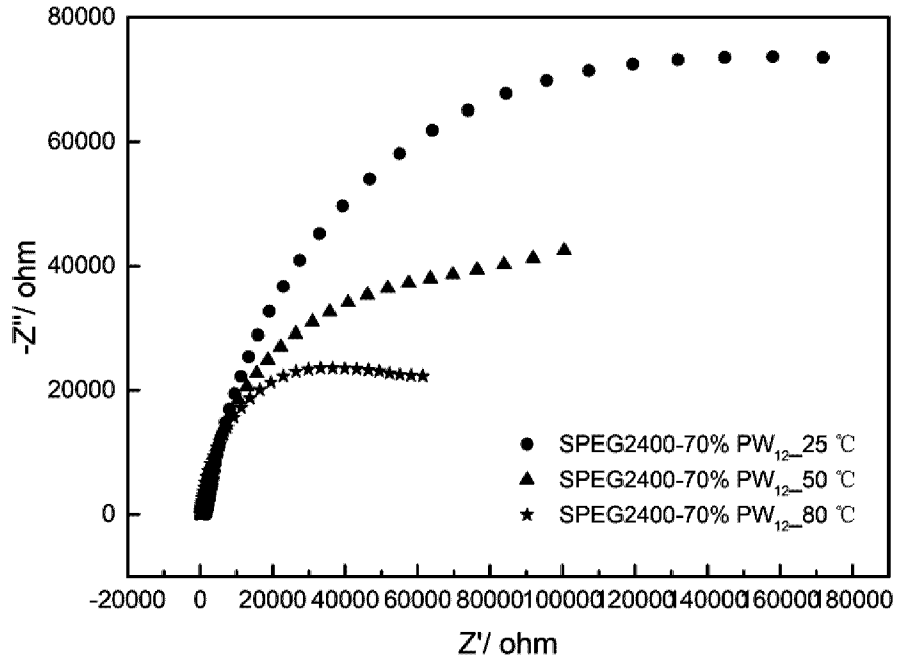

Fig. 10

Date Reçue/Date Received 2021-12-24

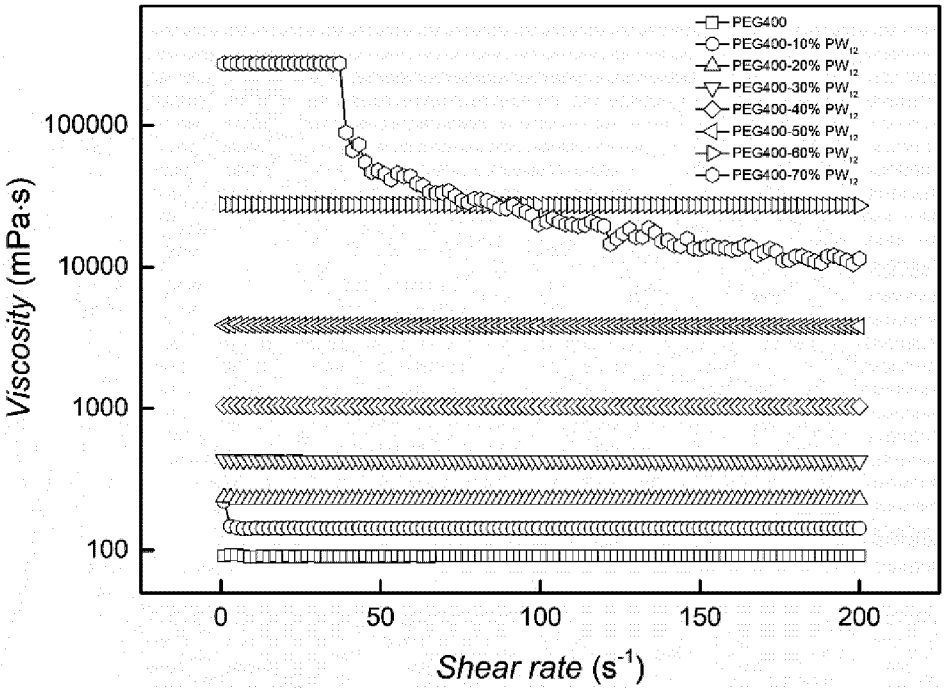

Fig. 11

Date Reçue/Date Received 2021-12-24

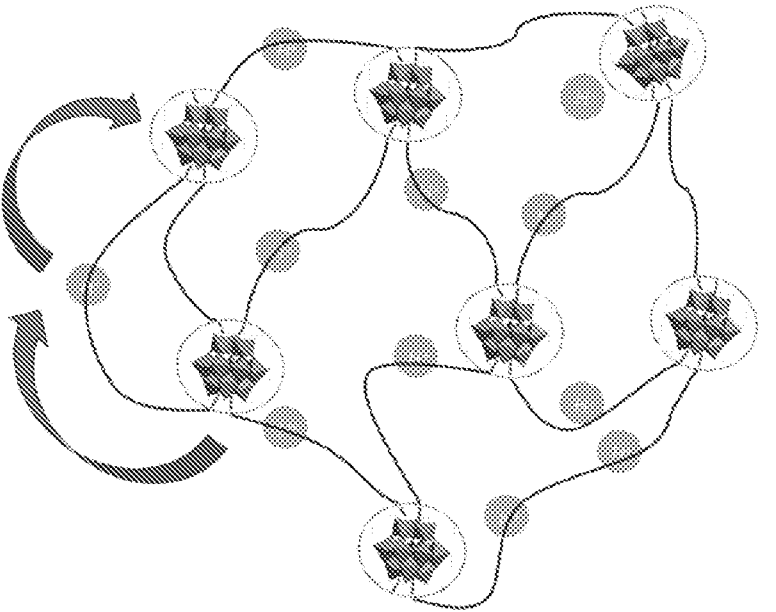

图 2