

PREPARATION METHOD FOR SOLID-STATE ELECTROLYTE MEMBRANE AND USE THEREOF

FIELD OF TECHNOLOGY

[0001] The present invention relates to the technical field of energy storage, and particularly to a preparation method and use of a solid-state electrolyte membrane, which is specifically a preparation method of a solid-state electrolyte membrane prepared by an optimized binder.

BACKGROUND

[0002] With the continuous development of technology, people have increasingly stringent requirements for energy storage components. However, organic liquid electrolyte of conventional lithium batteries is flammable and explosive at high temperatures, leading to thermal runaway and posing significant safety hazards. Solid-state electrolytes are considered an effective solution to overcome the disadvantages of liquid batteries. Most solid-state electrolytes, especially ceramic electrolytes, are non-flammable, inherently non-volatile, and exhibit excellent thermal stability. The use of the solid-state electrolytes will fundamentally solve thermal runaway caused by flammable organic liquid electrolytes in conventional batteries. However, the current solid-state electrolyte sheets used in all-solid-state lithium batteries have high interfacial resistance, interfacial instability, and poor cycling stability caused by high thickness (0.5 mm-1.0 mm) and low ionic conductivity thereof. During the manufacturing process of the all-solid-state batteries, powder active materials need to be bonded by the binder. As an important inactive component in lithium batteries, the performance of the binder directly affects the electrochemical performance of the batteries. The binder should have sufficient elasticity to prevent active material particles from loosening, swelling and detachment due to their swelling and shrinkage during battery charge and discharge, and should facilitate conduction of electrons and ions during the battery charge and discharge.

[0003] For a long time, in the study of the all-solid-state lithium batteries, polyvinylidene fluoride (PVDF) as the binder and organic solvents such as N-methylpyrrolidone (NMP) as dispersants are mainly used. However, PVDF has inherent

shortcomings, such as poor electronic and ionic conductivity, and poor compatibility with lithium metal, which poses significant safety hazards. In addition, PVDF has a relatively high Young's modulus, resulting in insufficient flexibility of electrode sheets, degraded adhesion during battery charge and discharge, and high production cost. Therefore, it is of profound significance to develop new green binders (with favorable dispersibility, sufficient binding strength, and favorable electron/ion conduction) that can replace PVDF.

[0004] Patent Application No. CN201611112927.X discloses a "composite solid-state electrolyte membrane, preparation method thereof, and lithium-ion battery with the same." The composite solid-state electrolyte membrane includes a porous support material, a first composite binder layer coated on two side surfaces of the porous support material, and a second composite binder layer coated on the first composite binder layer; and the inorganic content of the second composite binder layer is lower than the inorganic content of the first composite binder layer. In this patent, the porous support material is added into the electrolyte membrane, thereby ensuring the flexibility of the membrane and enhancing the mechanical strength of the membrane. Moreover, the sandwich-structured electrolyte membrane can improve interfacial compatibility and enhance the cycling performance of the batteries. However, in the solution, the preparation process of the composite solid-state electrolyte membrane is relatively complicated, and the porous support material increases the thickness and weight of the electrolyte layer. Therefore, the existing technology still needs to be improved and developed.

SUMMARY

[0005] Aiming at the shortcomings of the prior art, the present invention provides a preparation method and use of a solid-state electrolyte membrane, which is specifically a solid-state electrolyte membrane prepared by an optimized binder and a preparation method thereof.

[0006] An objective of the present invention can be achieved by the following solution:

[0007] The present invention provides a preparation method of a solid-state electrolyte membrane, and the method includes the following steps:

[0008] Step 1: dispersing a polymer uniformly in an organic solvent to obtain solution A;

[0009] Step 2: adding a thiol-containing micromolecule to the solution A to obtain

solution B;

[0010] Step 3: adding a solid-state electrolyte to the solution B, followed by dispersing uniformly, to obtain solution C; and

[0011] Step 4: subjecting the solution C to electrolyte membrane preparation, followed by heat treatment and pressing, to prepare the solid-state electrolyte membrane.

[0012] Preferably, in Step 1, the polymer includes one or more of chitosan, chitin, a chitosan-poly(lactic acid) copolymer, and chitosan-poly(ethylene glycol)-dopamine.

[0013] Preferably, in Step 1, a mass percentage of the polymer in the solid-state electrolyte membrane is 1%-5%. A dosage ratio of the polymer to the organic solvent is 10-30 mg:10 mL. The solid-state electrolyte membrane consists of the polymer, the thiol-containing micromolecule, and the solid-state electrolyte.

[0014] Preferably, in Step 1, the organic solvent includes one or more of benzene, toluene, ethylbenzene, xylene, acetonitrile, N,N-dimethylformamide, N-methylpyrrolidone, isopropanol, and acetone.

[0015] Preferably, in Step 2, a mass percentage of the thiol-containing micromolecule in the solid-state electrolyte membrane is 0.1%-1%. The thiol-containing micromolecule has a molecular formula of HS-R-SH, and specifically includes one or more of 1,6-hexanedithiol, 1,2-ethanedithiol, 1,4-butanedithiol, 1,5-pentanedithiol, and 1,3-propanedithiol. In the present invention, the thiol-containing micromolecule is introduced into the preparation system of the solid-state electrolyte membrane, and the dosage of the polymer can be reduced, so that a sulfide electrolyte membrane with sufficient area, flexibility and high conductivity can be prepared. If the polymer contains thiol groups at two ends thereof, it is not easily soluble and thus cannot be used in the present invention. A thiol-excluding micromolecule cannot react with chitosan or electrolyte. The excessive dosage of the thiol-containing micromolecule will also lead to decreased conductivity.

[0016] Preferably, in Step 3, the solid-state electrolyte includes any one or more of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, $\text{Li}_7\text{P}_3\text{S}_{11}$, $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$, $\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_6\text{PS}_5\text{I}$, and $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$.

[0017] Preferably, in Step 4, a membrane preparation method for the electrolyte membrane preparation includes one of tape casting, vacuum filtration, and wet coating. In the vacuum filtration method, the vacuum filtration device used is a glass filter with a diameter of

45 mm, and a commercial separator (Celgard2400) is selected as the filter paper.

[0018] Preferably, in Step 4, a temperature for the heat treatment is 100°C-200°C and a duration for the heat treatment is 5 h-12 h. The heat treatment is performed in a glove box where water content and oxygen content are both less than 1 ppm, and the heat treatment is used to remove the solvent.

[0019] Preferably, in Step 4, a pressure for the pressing is 5 MPa-600 MPa.

[0020] In a second aspect, the present invention provides a solid-state electrolyte membrane prepared by the preparation method.

[0021] In a third aspect, the present invention provides use of the solid-state electrolyte membrane in a lithium battery.

[0022] Compared with the prior art, the present invention has the following beneficial effects:

[0023] In the present invention, chitosan and derivatives thereof are used as the binder to prepare the electrolyte membrane, and a trace amount of the thiol-containing micromolecule is added and can react with chitosan and sulfur in a sulfide electrolyte, improving bonding performance of chitosan. Meanwhile, the added micromolecules can act as a plasticizer, making the electrolyte membrane more flexible.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] Other features, objectives, and advantages of the present invention will become more apparent from the following detailed descriptions of non-restrictive examples with reference to the accompanying drawings:

[0025] FIG. 1 is a photograph of an electrolyte membrane prepared in Example 1;

[0026] FIG. 2 is a flow chart of reaction in Example 1;

[0027] FIG. 3 is an impedance diagram of an electrolyte in Example 1 and a comparative example;

[0028] FIG. 4 shows first-cycle charge-discharge data of a battery in Example 1 and a comparative example; and

[0029] FIG. 5 shows cycling data of the battery in Example 1 and a comparative example.

DESCRIPTION OF THE EXAMPLES

[0030] The present invention will be described in detail below with reference to the accompanying drawings and specific examples. The following examples are implemented based on the technical solution of the present invention, providing detailed examples and specific operating processes, which will help those skilled in the art to further understand the present invention. It should be noted that the protection scope of the present invention is not limited to the following examples. Various modifications and improvements made within the concept of the present invention fall within the protection scope of the present invention.

[0031] Example 1

[0032] The example provides a preparation method of a solid-state electrolyte membrane, and the method includes the following steps:

[0033] 1. Dissolve 20 mg of chitosan in 10 mL of toluene and stir for 2 h at a stirring speed of 500 rpm.

[0034] 2. Add 5 mg of 1,6-hexanedithiol to the above solution and stir for 2 h at the stirring speed of 500 rpm.

[0035] 3. Add 980 mg of finely ground $\text{Li}_6\text{PS}_5\text{Cl}$ powder to the chitosan solution and continue stirring for 5 h at a stirring speed of 800 rpm.

[0036] 4. Pour a dispersion into a vacuum filtration system (a glass filter with a diameter of 45 mm), followed by peeling off the membrane formed on a filter paper (Celgard2400), to obtain an independent membrane.

[0037] 5. Clamp the membrane between two glass slides and heat on a hot plate for 12 hours at 150°C to completely remove toluene.

[0038] 6. Further press the obtained electrolyte membrane at a pressure of 300 MPa, so that the electrolyte membrane is denser, with a thickness of about 100 μm . The prepared electrolyte membrane is shown in FIG. 1. In the electrolyte membrane, the thiol-containing micromolecule can react with sulfur in chitosan and a sulfide electrolyte, as shown in FIG. 2.

[0039] 7. Subject the electrolyte membrane to AC impedance test to analyze the conductivity of the electrolyte membrane. As shown in FIG. 3, the conductivity is 2.2 mS/cm, and higher than the conductivity of 0.5 mS/cm in Comparative Example 1.

[0040] 8. Preparation of all-solid-state battery: press an In-Li foil onto a stainless steel plug with a diameter of 12 mm at the pressure of 300 MPa. Then, press a circular solid-state electrolyte membrane with a diameter of 12 mm onto the In-Li foil in a mold at the pressure of 300 MPa. Next, uniformly press 25 mg of anode material (which is a composite anode of 70% wt NCM811:30% wt $\text{Li}_6\text{PS}_5\text{Cl}$) onto the other side thereof at 100 MPa, and perform charge-discharge testing at room temperature. First-cycle charge-discharge data of the battery at a rate of 0.1C is shown in FIG. 4, and a first-cycle discharge capacity thereof is 144.9 mAh/g; and the cycling data of the battery is shown in FIG. 5.

[0041] **Example 2**

[0042] The example provides a preparation method of a solid-state electrolyte membrane, and the method includes the following steps:

[0043] 1. Dissolve 20 mg of a chitosan-polylactic acid copolymer in 10 mL of toluene and stir for 2 h at a stirring speed of 500 rpm.

[0044] 2. Add 5 mg of 1,6-hexanedithiol to the above solution and stir for 2 h at the stirring speed of 500 rpm.

[0045] 3. Add 980 mg of finely ground $\text{Li}_6\text{PS}_5\text{Cl}$ powder to the chitosan-polylactic acid copolymer solution obtained in Step 2 and continue stirring for 5 h at a stirring speed of 800 rpm.

[0046] 4. Pour a dispersion into a vacuum filtration system (a glass filter with a diameter of 45 mm), followed by peeling off the membrane formed on a filter paper (Celgard2400), to obtain an independent membrane.

[0047] 5. Clamp the membrane between two glass slides and heat on a hot plate for 12 hours at 150°C to completely remove toluene.

[0048] 6. Further press the obtained electrolyte membrane at a pressure of 300 MPa, so that the electrolyte membrane is denser, with a thickness of about 100 μm .

[0049] 7. Subject the electrolyte membrane to AC impedance test to analyze the conductivity of the electrolyte membrane.

[0050] 8. Preparation of all-solid-state battery: press an In-Li foil onto a stainless steel plug with a diameter of 12 mm at the pressure of 300 MPa. Then, press a circular solid-state electrolyte membrane with a diameter of 12 mm onto the In-Li foil in a mold at the pressure of

300 MPa. Next, uniformly press 25 mg of anode material (which is a composite anode of 70% wt NCM811:30% wt $\text{Li}_6\text{PS}_5\text{Cl}$) onto the other side thereof at a pressure of 100 MPa. Perform battery charge-discharge testing.

[0051] Example 3

[0052] The example provides a preparation method of a solid-state electrolyte membrane, and the method includes the following steps:

[0053] 1. Dissolve 20 mg of chitosan-polyethylene glycol-dopamine in 10 mL of toluene and stir for 2 h at a stirring speed of 500 rpm.

[0054] 2. Add 5 mg of 1,6-hexanedithiol to the above solution and stir for 2 h at the stirring speed of 500 rpm.

[0055] 3. Add 980 mg of finely ground $\text{Li}_6\text{PS}_5\text{Cl}$ powder to the chitosan-polyethylene glycol-dopamine solution obtained in Step 2 and continue stirring for 5 h at a stirring speed of 800 rpm.

[0056] 4. Pour a dispersion into a vacuum filtration system (a glass filter with a diameter of 45 mm), followed by peeling off the membrane formed on a filter paper (Celgard2400), to obtain an independent membrane.

[0057] 5. Clamp the membrane between two glass slides and heat on a hot plate for 12 hours at 150°C to completely remove toluene.

[0058] 6. Further press the obtained electrolyte membrane at a pressure of 300 MPa, so that the electrolyte membrane is denser, with a thickness of about 100 μm .

[0059] 7. Subject the electrolyte membrane to AC impedance test to analyze the conductivity of the electrolyte membrane.

[0060] 8. Preparation of all-solid-state battery: press an In-Li foil onto a stainless steel plug with a diameter of 12 mm at the pressure of 300 MPa. Then, press a circular solid-state electrolyte membrane with a diameter of 12 mm onto the In-Li foil in a mold at the pressure of 300 MPa. Next, uniformly press 25 mg of anode material (which is a composite anode of 70% wt NCM811:30% wt $\text{Li}_6\text{PS}_5\text{Cl}$) onto the other side thereof at a pressure of 100 MPa. Perform charge-discharge testing.

[0061] Comparative Example

[0062] The comparative example provides a preparation method of a solid-state

electrolyte membrane, and the method includes the following steps:

[0063] 1. Dissolve 20 mg of chitosan in 10 mL of toluene and stir for 2 h at a stirring speed of 500 rpm.

[0064] 2. Add 980 mg of finely ground $\text{Li}_6\text{PS}_5\text{Cl}$ powder to the chitosan solution obtained in Step 1 and continue stirring for 5 h at a stirring speed of 800 rpm.

[0065] 3. Pour a dispersion into a vacuum filtration system (a glass filter with a diameter of 45 mm), followed by peeling off the membrane formed on a filter paper (Celgard2400). This offers poor membrane formation property.

[0066] 4. Clamp the membrane between two glass slides and heat on a hot plate for 12 hours at 150°C to completely remove toluene.

[0067] 5. Further press the obtained electrolyte membrane at a pressure of 300 MPa, so that the electrolyte membrane is denser.

[0068] 6. Subject the electrolyte membrane to AC impedance test to analyze the conductivity of the electrolyte membrane.

[0069] 7. Preparation of all-solid-state battery: press an In-Li foil onto a stainless steel plug with a diameter of 12 mm at the pressure of 300 MPa. Then, press a circular solid-state electrolyte membrane with a diameter of 12 mm onto the In-Li foil in a mold at the pressure of 300 MPa. Next, uniformly press 25 mg of anode material onto the other side thereof at a pressure of 100 MPa. Perform charge-discharge testing. A first-cycle discharge capacity thereof is 111.4 mAh/g.

[0070] It should be understood that the applications of the present invention are not limited to the above examples. For those skilled in the art, improvements or modifications can be made based on the above descriptions, and all such improvements and modifications should fall within the scope of protection of the appended claims of the present invention.

WHAT IS CLAIMED IS:

1. A preparation method of a solid-state electrolyte membrane, comprising the following steps:

Step 1: dispersing a polymer uniformly in an organic solvent to obtain solution A;

Step 2: adding a thiol-containing micromolecule to the solution A to obtain solution B;

Step 3: adding a solid-state electrolyte to the solution B, followed by dispersing uniformly, to obtain solution C; and

Step 4: subjecting the solution C to electrolyte membrane preparation, followed by heat treatment and pressing, to prepare the solid-state electrolyte membrane;

the polymer comprises one or more of chitosan, chitin, a chitosan-polylactic acid copolymer, and chitosan-polyethylene glycol-dopamine; and a mass percentage of the polymer in the solid-state electrolyte membrane is 1%-5%;

wherein in Step 2, a mass percentage of the thiol-containing micromolecule in the solid-state electrolyte membrane is 0.1%-1%; and the thiol-containing micromolecule comprises one or more of 1,6-hexanedithiol, 1,2-ethanedithiol, 1,4-butanedithiol, 1,5-pentanedithiol, and 1,3-propanedithiol;

wherein in Step 3, the solid-state electrolyte comprises one or more of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, $\text{Li}_7\text{P}_3\text{S}_{11}$, $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$, $\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_6\text{PS}_5\text{I}$, and $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$.

2. The preparation method according to claim 1, wherein in Step 1, the organic solvent comprises one or more of benzene, toluene, ethylbenzene, xylene, acetonitrile, N,N-dimethylformamide, N-methylpyrrolidone, isopropanol, and acetone.

3. The preparation method according to claim 1, wherein in Step 4, a membrane preparation method for the electrolyte membrane preparation comprises one of tape casting, vacuum filtration, and wet coating.

4. The preparation method according to claim 1, wherein in Step 4, a temperature for the heat treatment is 100°C-200°C and a duration for the heat treatment is 5 h-12 h.

5. The preparation method according to claim 1, wherein in Step 4, a pressure for the pressing is 5 MPa-600 MPa.

6. A solid-state electrolyte membrane prepared by the preparation method according to claim 1.

7. Use of the solid-state electrolyte membrane according to claim 6 in a lithium battery.