

PREPARATION METHOD FOR SOLID ELECTROLYTE CONTAINING ANDERSON-TYPE POLYOXOMETALATE AND USE OF SOLID ELECTROLYTE

FIELD OF TECHNOLOGY

[0001] The present invention belongs to the field of solid-state electrolytes, and specifically, to a preparation method and use of a solid-state electrolyte containing Anderson-type polyoxometalate.

BACKGROUND

[0002] In recent years, lithium-ion batteries have been widely used in consumer electronics and electric (automobile) vehicles due to their high energy density. However, multiple safety incidents have occurred because their liquid electrolytes are flammable. Therefore, it is imperative to develop all-solid-state lithium batteries with enhanced safety. As the core component of solid-state batteries, electrolytes have advanced rapidly. Among all solid electrolytes, sulfide solid electrolytes have attracted widespread attention due to their superior mechanical properties, electrode interface compatibility, and highest room-temperature lithium-ion conductivity. However, sulfide electrolytes still face problems such as instability with lithium metal cathodes, poor compatibility with oxide anode materials, and insufficient conductivity, which limit their further application.

[0003] Polyoxometalates (POMs) are composed of structurally diverse cations and polyanionic clusters, with polyoxometal polyhedra of MO_x as basic structural units. According to the unique structure of the polyoxometalates, the polyanions in the polyoxometalates are characterized by large volume and a high number of negative charges. Moreover, surfaces of the polyanions contain abundant oxygen atoms that can donate electrons to electron acceptors; thus, the polyanions can be regarded as a soft base. Furthermore, metal ions on a polyanion framework possess unoccupied orbitals that can accept electrons; therefore, the polyanions can also be regarded as Lewis acids. Thus, under different conditions, the polyanions can function as Lewis acids and Lewis bases. Additionally, due to the strong electron-carrying and electron-releasing abilities of the polyanions, they are often regarded as electron reservoirs, indicating excellent redox properties.

[0004] Currently, the polyoxometalates are still preliminarily used in the battery field, mainly focusing on modification of anode materials and cathode materials (CN104051734A, CN107946592A, CN110752344A; the polyoxometalates involved are not Anderson-type polyoxometalates). There have been a few reports on the use of polyoxometalates as fillers for the modification of solid-state electrolytes. In 2018, Xiamen University reported a patent on the use of polyoxometalates to modify polymer solid-state electrolytes (CN108306046A). However, due to the low ionic conductivity and high ductility of polymer solid-state electrolytes, their application in all-solid-state batteries is limited. Nevertheless, this work provides a theoretical basis for using the polyoxometalates as the filler to modify sulfide solid-state electrolytes.

SUMMARY

[0005] To address the problems in the prior art, the present invention provides a preparation method and use of a solid-state electrolyte containing Anderson-type polyoxometalate, where the polyoxometalate is added as an additive to the solid-state electrolyte.

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

[0007] In a first aspect, the present invention provides a preparation method of a solid-state electrolyte containing Anderson-type polyoxometalate, and the method includes the following steps:

[0008] S1: mixing the polyoxometalate with a solid-state electrolyte, and performing ball milling on the resulting mixture to obtain a mixed electrolyte; and

[0009] S2: calcining the mixed electrolyte to obtain a polyoxometalate-modified solid-state electrolyte.

[0010] In Step S1, the polyoxometalate is the Anderson-type polyoxometalate, and a preparation method of the Anderson-type polyoxometalate includes:

[0011] dissolving a metal salt into deionized water under stirring, to obtain a metal salt solution;

[0012] dissolving ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$) or ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) in water, heating the resulting solution to boiling and

maintaining the solution in a boiling state, and dropwise adding the metal salt solution; and after dropwise addition, performing constant-temperature reaction, filtering the resulting reactant while hot, and performing constant-temperature standing and recrystallization, to obtain pure Anderson-type polyoxometalate.

[0013] The metal salt in the metal salt solution includes one or more of nitrates and sulfates of a metal, where the metal includes one or more of iron, nickel, copper, chromium, and cobalt. The metal salt is specifically one of $\text{Fe}_2(\text{SO}_4)_3$, $\text{Ni}(\text{NO}_3)_2$, CuSO_4 , $\text{Cr}(\text{NO}_3)_3$, and CoSO_4 . A mass ratio of the metal salt to ammonium molybdate or ammonium molybdate tetrahydrate is (2-4):(4-8). The metal salt solution is obtained by dissolving the metal salt in deionized water under stirring.

[0014] A ratio of the metal salt to the deionized water used for dissolution is 1 g-5 g:20-100 mL. A ratio of ammonium molybdate or ammonium molybdate tetrahydrate to the deionized water used for dissolution is 3 g-10 g:50 mL-160 mL.

[0015] During the dropwise addition of the metal salt solution, HCl is added in real time to adjust the pH within the range of 2-5.

[0016] A temperature for the constant-temperature reaction is 90°C-110°C, and a duration for the constant-temperature reaction is 20 min-60 min.

[0017] A duration for the constant-temperature standing is 10 h-12 h, and the number of recrystallization is 2-4 times.

[0018] A structural formula of the Anderson-type polyoxometalate is: $(\text{MH}_4)[\text{MMo}_6\text{O}_{18}(\text{OH})_6]^{(6-X)-}$ ($X=1,2,3,4,5$), where M is selected from one of Fe, Ni, Cu, Cr, and Co.

[0019] In Step S1, a stoichiometric ratio of the polyoxometalate to the solid-state electrolyte is (1-5):(70-95). The solid-state electrolyte is a sulfide electrolyte, including $\text{Li}_6\text{PS}_5\text{Cl}$.

[0020] In Step S1, a ball milling speed is 300 r/min-600 r/min, and a ball milling duration is 2 h-8 h. Ball milling is performed using a high-energy planetary ball mill under sealing conditions and with a ball-to-material mass ratio of (30-50):1, and a zirconia ball milling bead has a diameter of 2 mm-5 mm. A preferred material weight for ball milling is 1 g-10 g. A ball milling method is a solid-phase method, while solvent mixing is a liquid-phase

method. In the liquid-phase method, a solvent is introduced; even after drying, residual solvent molecules are inevitably left in an electrolyte system, thereby affecting the ionic conductivity of the electrolyte. The solid-phase method of the present invention, in which binders or other polymeric macromolecules are not required, can completely address this problem.

[0021] In Step S2, a calcination temperature is 400°C-700°C, a calcination duration is 6 h-9 h, and a heating rate during calcination is 0.1°C/min-1°C/min. The purpose of calcination is to remove impurity phases generated during the preparation of polyoxometalate and form a dense solid-state electrolyte. If the temperature is too low, impurities cannot be completely removed. After calcination, a sulfide solid-state electrolyte modified by filling voids with polyoxometalate is obtained. Due to the solid-solid contact between solid-state electrolyte particles, voids are inevitably formed, leading to an interface problem. The nanoscale polyoxometalate of the present invention just fills these voids during ball milling, thereby solving the interface problem to a certain extent and enhancing the electrochemical performance of the all-solid-state battery. The heating rate is controlled based on two main considerations: on one hand, for safety, if the heating rate is too fast, a quartz tube is prone to burst; on the other hand, the heating rate directly affects the purity of the product.

[0022] In a second aspect, the present invention further provides use of the solid-state electrolyte containing Anderson-type polyoxometalate in preparation of a composite anode material, where the use specifically includes: mixing an anode material, the solid-state electrolyte containing Anderson-type polyoxometalate, and a vapor-grown carbon fiber (VGCF) and performing ball milling on the resulting mixture to prepare the composite anode material. The anode material includes NCM811.

[0023] In a third aspect, the present invention further provides use of the solid-state electrolyte containing Anderson-type polyoxometalate in an all-solid-state battery.

[0024] Compared with the prior art, the present invention has the following beneficial effects:

[0025] (1) Compared with conventional solid-state electrolytes, the modified solid-state electrolyte has increased density, thereby achieving better interface contact with electrodes during the assembly of the all-solid-state battery.

[0026] (2) The ionic conductivity of the modified solid-state electrolyte is improved.

[0027] (3) Due to the increased density of the modified solid-state electrolyte and the formation of a relatively good interface, the cycling stability in the all-solid-state battery is also enhanced.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028] 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:

[0029] FIG. 1 is an infrared spectrum of FePOM prepared in Example 1;

[0030] FIG. 2 is an impedance spectrum of a modified solid-state electrolyte in Example 1; and

[0031] FIG. 3 is a 300-cycle curve graph of an all-solid-state battery prepared from a material at a rate of 0.1C in Example 1.

DESCRIPTION OF THE EXAMPLES

[0032] The present invention will be described in detail below with reference to the accompanying drawings and specific examples. The following examples are implemented under the technical solutions of the present invention, providing detailed examples and specific operating procedures, 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.

[0033] In the examples and comparative examples of the present invention, the charge and discharge performance is tested by the following steps:

[0034] Preparation of NCM811 composite anode material: NCM811, the prepared modified solid-state electrolyte, and vapor-grown carbon fiber (VGCF) are weighed at a mass ratio of 16:3:1 and placed into a 25 mL zirconia ball milling jar, with a total material mass of 1 g and a ball-to-material mass ratio of 20:1. The diameter of the zirconia ball milling bead used is 3 mm. Then, the sealed ball milling jar is fixed onto a high-energy planetary ball mill and subjected to ball milling for 4 h at 400 r/min. Finally, the NCM811 composite anode material

is obtained. Then, Li/In serves as a cathode and the modified solid-state electrolyte serves as the electrolyte, the all-solid-state battery is assembled and the charge-discharge performance thereof is tested.

[0035] Example 1

[0036] The example provides a preparation method of a solid-state electrolyte containing Anderson-type polyoxometalate, and the method includes the following steps:

[0037] (1) Preparation of Fe-based polyoxometalate (FePOM):

[0038] 1.2 g of $\text{Fe}_2(\text{SO}_4)_3$ is weighed into 20 mL of deionized water, stirred until dissolved, to obtain $\text{Fe}_2(\text{SO}_4)_3$ solution. 5.3 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ is dissolved in 80 mL water, and heated to boiling; and the $\text{Fe}_2(\text{SO}_4)_3$ solution is added dropwise into the boiled dissolving solution under stirring. As the $\text{Fe}_2(\text{SO}_4)_3$ solution is continuously added, the dissolving solution gradually changes from colorless to deep red. pH is monitored in real time, and the pH of the solution is adjusted with a hydrochloric acid and kept at 2.8; the solution is subjected to constant-temperature reaction for 1 h, and filtered while hot; and after 12 h, brownish-red flaky crystals are precipitated. The crystals are recrystallized once in an 80°C water bath to obtain pure Fe-based polyoxometalate (4.9 g). The infrared spectrum of the prepared FePOM is shown in FIG. 1.

[0039] (2) Preparation of modified $\text{Li}_6\text{PS}_5\text{Cl}$ solid-state electrolyte ($\text{Li}_6\text{PS}_5\text{Cl}$ -FePOM):

[0040] The sample and $\text{Li}_6\text{PS}_5\text{Cl}$ from Example 1 are weighed at a stoichiometric ratio of 5:95, well mixed in a zirconia ball milling jar, with a total material mass of 1 g and a ball-to-material mass ratio of 30:1. The diameter of the zirconia ball milling bead used is 5 mm.

[0041] Then, the sealed ball milling jar is fixed onto a high-energy planetary ball mill and subjected to ball milling for 7 h at 550 r/min. Next, the material is scraped from the wall of the ball milling jar, the obtained powder is tableted, vacuum-sealed in a quartz tube, and calcined in a muffle furnace for 7 h at 550°C with a heating rate of 0.5°C/min. After cooled to room temperature, the modified flake-like sulfide solid-state electrolyte material is taken out of a glove box, ground, and bottled for later use.

[0042] (3) Preparation of NCM811 composite anode material:

[0043] NCM811, $\text{Li}_6\text{PS}_5\text{Cl}$ -FePOM prepared in Step 2, and vapor-grown carbon fiber (VGCF) are weighed at a mass ratio of 16:3:1 and placed into a 25 mL zirconia ball milling jar,

with a total material mass of 1 g and a ball-to-material mass ratio of 20:1. The diameter of the zirconia ball milling bead used is 3 mm. Then, the sealed ball milling jar is fixed onto a high-energy planetary ball mill and subjected to ball milling for 4 h at 400 r/min. Finally, the NCM811 composite anode material is obtained.

[0044] Application Example 1

[0045] Assembly of all-solid-state battery: 100 mg of modified $\text{Li}_6\text{PS}_5\text{Cl}$ solid-state electrolyte ($\text{Li}_6\text{PS}_5\text{Cl}$ -FePOM) is weighed into a 10 mm stainless steel tableting mold, and an electrolyte sheet is pressed at a pressure of 360 MPa. Then, 10 mg of the composite anode material prepared by the above method is added to one side of the electrolyte sheet and pressed again at a pressure of 150 MPa. The product obtained by pressing is demolded and then loaded into a special battery testing mold. Next, a 9 mm lithium-indium sheet (with a thicknesses of 30 micrometers and 100 micrometers, respectively) is added to the other side of the electrolyte sheet. Finally, an Al sheet current collector is installed on an anode side, and a Cu current collector is installed on a cathode side to complete encapsulation. A battery mold is removed and placed into a battery fixture, and pressed by applying a pressure of 50 MPa to obtain a sandwich-structured all-solid-state battery. The assembled all-solid-state battery is subjected to capacitance discharge test. As shown in FIG. 2, at room temperature and at a rate of 0.1C, the first-cycle charge specific capacity may be up to 251 mAh/g. The 300-cycle curve graph of the all-solid-state battery is shown in FIG. 3 at the rate of 0.1C.

[0046] Example 2

[0047] The example provides a preparation method of a solid-state electrolyte containing Anderson-type polyoxometalate, and the method includes the following steps:

[0048] (1) Preparation of Cu-based polyoxometalate:

[0049] 0.48 g of $\text{Cu}_2(\text{SO}_4)_3$ is weighed into 20 mL of deionized water, and stirred until dissolved, to obtain Cu_2SO_4 solution. 5.3 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ is dissolved in 80 mL water, and heated to boiling, and the Cu_2SO_4 solution is added dropwise into the boiled dissolving solution under stirring. As the Cu_2SO_4 solution is continuously added, the dissolving solution gradually changes from colorless to light blue. pH is monitored in real time, and the pH of the solution is adjusted with a hydrochloric acid and kept at 2.8; the solution is subjected to constant-temperature reaction for 1 h, and filtered while hot; and after 12 h, blue flaky crystals

are precipitated. The crystals are recrystallized once in an 80°C water bath to obtain pure Cu-based polyoxometalate (2.8 g).

[0050] (2) Preparation of modified $\text{Li}_6\text{PS}_5\text{Cl}$ -CuPOM solid-state electrolyte ($\text{Li}_6\text{PS}_5\text{Cl}$ -CuPOM):

[0051] The sample and $\text{Li}_6\text{PS}_5\text{Cl}$ from Example 1 are weighed at a stoichiometric ratio of 5:95, well mixed in a zirconia ball milling jar, with a total material mass of 1 g and a ball-to-material mass ratio of 30:1. The diameter of the zirconia ball milling bead used is 5 mm. Then, the sealed ball milling jar is fixed onto a high-energy planetary ball mill and subjected to ball milling for 7 h at 550 r/min. Next, the material is scraped from the wall of the ball milling jar, the obtained powder is tableted, vacuum-sealed in a quartz tube, and calcined in a muffle furnace for 7 h at 550°C with a heating rate of 0.5°C/min. After cooled to room temperature, the modified flake-like sulfide solid-state electrolyte material is taken out of a glove box, ground, and bottled for later use.

[0052] (3) Preparation of NCM811 composite anode material:

[0053] NCM811, $\text{Li}_6\text{PS}_5\text{Cl}$ -CuPOM prepared in Step 2, and vapor-grown carbon fiber (VGCF) are weighed at a mass ratio of 16:3:1 and placed into a 25 mL zirconia ball milling jar, with a total material mass of 1 g and a ball-to-material mass ratio of 20:1. The diameter of the zirconia ball milling bead used is 3 mm. Then, the sealed ball milling jar is fixed onto a high-energy planetary ball mill and subjected to ball milling for 4 h at 400 r/min. Finally, the NCM811 composite anode material is obtained.

[0054] Application Example 2

[0055] Assembly of all-solid-state battery: 100 mg of modified $\text{Li}_6\text{PS}_5\text{Cl}$ solid-state electrolyte ($\text{Li}_6\text{PS}_5\text{Cl}$ -CuPOM) is weighed into a 10 mm stainless steel tableting mold, and an electrolyte sheet is pressed at a pressure of 360 MPa. Then, 10 mg of the composite anode material prepared by the above method is added to one side of the electrolyte sheet and pressed again at a pressure of 150 MPa. The product obtained by pressing is demolded and then loaded into a special battery testing mold. Next, a 9 mm lithium-indium sheet (with a thicknesses of 30 micrometers and 100 micrometers, respectively) is added to the other side of the electrolyte sheet. Finally, an Al sheet current collector is installed on an anode side, and a Cu current collector is installed on a cathode side to complete encapsulation. A battery mold is removed

and placed into a battery fixture, and pressed by applying a pressure of 50 MPa to obtain a sandwich-structured all-solid-state battery. The assembled all-solid-state battery is subjected to capacitance discharge test. At room temperature and at a rate of 0.1C, the first-cycle charge specific capacity may be up to 184 mAh/g.

[0056] Example 3

[0057] The example provides a preparation method of a solid-state electrolyte containing Anderson-type polyoxometalate, and the method includes the following steps:

[0058] (1) Preparation of Ni-based polyoxometalate:

[0059] 0.55g $\text{Ni}(\text{NO}_3)_2$ is weighed into 20 mL of deionized water, and stirred until dissolved, to obtain $\text{Ni}(\text{NO}_3)_2$ solution. 5.3 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ is dissolved in 80 mL water, and heated to boiling, and the $\text{Ni}(\text{NO}_3)_2$ solution is added dropwise into the boiled dissolving solution under stirring. As the $\text{Ni}(\text{NO}_3)_2$ solution is continuously added, the solution gradually changes from colorless to dark red. pH is monitored in real time, and the pH of the solution is adjusted with a hydrochloric acid and kept at 2.8; the solution is subjected to constant-temperature reaction for 1 h, and filtered while hot; and after 12 h, sky-blue flaky crystals are precipitated. The crystals are recrystallized once in an 80°C water bath to obtain pure Ni-based polyoxometalate (2.1 g).

[0060] (2) Preparation of modified $\text{Li}_6\text{PS}_5\text{Cl}$ solid-state electrolyte ($\text{Li}_6\text{PS}_5\text{Cl}$ -NiPOM):

[0061] The sample and $\text{Li}_6\text{PS}_5\text{Cl}$ from Example 1 are weighed at a stoichiometric ratio of 5:95, well mixed in a zirconia ball milling jar, with a total material mass of 1 g and a ball-to-material mass ratio of 30:1. The diameter of the zirconia ball milling bead used is 5 mm. Then, the sealed ball milling jar is fixed onto a high-energy planetary ball mill and subjected to ball milling for 7 h at 550 r/min. Next, the material is scraped from the wall of the ball milling jar, the obtained powder is tableted, vacuum-sealed in a quartz tube, and calcined in a muffle furnace for 7 h at 550°C with a heating rate of 0.5°C/min. After cooled to room temperature, the modified flake-like sulfide solid-state electrolyte material is taken out of a glove box, ground, and bottled for later use.

[0062] (3) Preparation of NCM811 composite anode material:

[0063] NCM811, $\text{Li}_6\text{PS}_5\text{Cl}$ -NiPOM prepared in Step 2, and vapor-grown carbon fiber (VGCF) are weighed at a mass ratio of 16:3:1 and placed into a 25 mL zirconia ball milling jar,

with a total material mass of 1 g and a ball-to-material mass ratio of 20:1. The diameter of the zirconia ball milling bead used is 3 mm. Then, the sealed ball milling jar is fixed onto a high-energy planetary ball mill and subjected to ball milling for 4 h at 400 r/min. Finally, the NCM811 composite anode material is obtained.

[0064] Application Example 3

[0065] Assembly of all-solid-state battery:

[0066] 100 mg of modified $\text{Li}_6\text{PS}_5\text{Cl}$ solid-state electrolyte ($\text{Li}_6\text{PS}_5\text{Cl}$ -NiPOM) is weighed into a 10 mm stainless steel tableting mold, and an electrolyte sheet is pressed at a pressure of 360 MPa. Then, 10 mg of the composite anode material prepared by the above method is added to one side of the electrolyte sheet and pressed again at a pressure of 150 MPa. The product obtained by pressing is demolded and then loaded into a special battery testing mold. Next, a 9 mm lithium-indium sheet (with a thicknesses of 30 micrometers and 100 micrometers, respectively) is added to the other side of the electrolyte sheet. Finally, an Al sheet current collector is installed on an anode side, and a Cu current collector is installed on a cathode side to complete encapsulation. A battery mold is removed and placed into a battery fixture, and pressed by applying a pressure of 50 MPa to obtain a sandwich-structured all-solid-state battery. The assembled all-solid-state battery is subjected to capacitance discharge test. At room temperature and at a rate of 0.1C, the first-cycle charge specific capacity may be up to 191 mAh/g.

[0067] **Comparative Example 1**

[0068] The example provides a preparation method of a solid-state electrolyte containing Anderson-type polyoxometalate, and steps of the preparation method are basically the same as those in Example 1, except that a wet ball milling method is used. Following a same procedure, Fe-based polyoxometalate (FePOM) and $\text{Li}_6\text{PS}_5\text{Cl}$ are mixed; 10 mL of acetonitrile solvent is added to a ball milling jar and then vacuum dried for 12 h to remove the solvent, and subsequently the resulting mixture is calcined.

[0069] **Comparative Example 2**

[0070] The example provides a preparation method of a solid-state electrolyte containing Anderson-type polyoxometalate, and steps of the preparation method are basically the same as those in Example 1, except that no calcination is performed after ball milling.

[0071] Comparative Example 3

[0072] The example provides a preparation method of a solid-state electrolyte containing Anderson-type polyoxometalate, and steps of the preparation method are basically the same as those in Example 1, except that a calcination temperature is 200°C.

[0073] Electrolyte sheets prepared in various examples and comparative examples are tested using same methods as those in the application examples. The test results are as follows:

Table 1

	Test thickness (mm)	Impedance value (Ω)	Ionic conductivity (mS/cm)
Example 1	0.785	25	4
Comparative Example 1	0.701	75	1.5
Comparative Example 2	0.730	63	1.7
Comparative Example 3	0.751	90	1.1

[0074] The above describes the specific examples of the present invention. It should be understood that the present invention is not limited to the specific examples described above. Various modifications or changes may be made within the scope of the claims by those skilled in the art, which do not affect the substantive content of the present invention.

WHAT IS CLAIMED IS:

1. A preparation method of a solid-state electrolyte containing Anderson-type polyoxometalate, comprising the following steps:

S1: mixing the polyoxometalate with a solid-state electrolyte, and performing ball milling on the resulting mixture to obtain a mixed electrolyte; and

S2: calcining the mixed electrolyte to obtain a polyoxometalate-modified solid-state electrolyte.

2. The preparation method according to claim 1, wherein in Step S1, the polyoxometalate is the Anderson-type polyoxometalate, and a preparation method of the Anderson-type polyoxometalate is as follows:

dissolving ammonium molybdate or ammonium molybdate tetrahydrate in water, heating the resulting solution to boiling and maintaining the solution in a boiling state, and dropwise adding a metal salt solution; after dropwise addition, performing constant-temperature reaction, filtering the resulting reactant while hot, and performing constant-temperature standing and recrystallization, to obtain the Anderson-type polyoxometalate.

3. The preparation method according to claim 2, wherein a metal salt in the metal salt solution comprises one or more of nitrates and sulfates of a metal, wherein the metal comprises one or more of iron, nickel, copper, chromium, and cobalt; and a mass ratio of the metal salt to ammonium molybdate tetrahydrate is (2-4):(4-8).

4. The preparation method according to claim 2, wherein a temperature for the constant-temperature reaction is 90°C-110°C, and a duration for the constant-temperature reaction is 20 min-60 min.

5. The preparation method according to claim 2, wherein a structural formula of the Anderson-type polyoxometalate is: $(\text{MH}_4)_x[\text{MMo}_6\text{O}_{18}(\text{OH})_6]^{(6-x)-}$, wherein X is 1, 2, 3, 4, or 5, and M comprises one of Fe, Ni, Cu, Cr, or Co.

6. The preparation method according to claim 1, wherein in Step S1, a stoichiometric ratio of the polyoxometalate to the solid-state electrolyte is (1-5):(70-95).

7. The preparation method according to claim 1, wherein in Step S1, a ball milling speed is 300 r/min-600 r/min, and a ball milling duration is 2 h-8 h.

8. The preparation method according to claim 1, wherein in Step S2, a calcination

temperature is 400°C-700°C, a calcination duration is 6 h-9 h, and a heating rate during calcination is 0.1°C/min-1°C/min.

9. Use of the solid-state electrolyte containing Anderson-type polyoxometalate according to claim 1 in an all-solid-state battery.

10. Use of the solid-state electrolyte containing Anderson-type polyoxometalate according to claim 1 in preparation of a composite anode material, specifically comprising: mixing a anode material, the solid-state electrolyte containing Anderson-type polyoxometalate, and a vapor-grown carbon fiber and performing ball milling on the resulting mixture to prepare the composite anode material.