

# **MXENE-COATED HARD CARBON-SOFT CARBON ANODE MATERIAL, PREPARATION METHOD AND USE THEREOF**

## **TECHNICAL FIELD**

5   **[0001]**   The present application relates to the technical field of anode materials for sodium-ion batteries, particularly to an MXene-coated hard carbon-soft carbon anode material, a preparation method and use thereof.

## **BACKGROUND ART**

10   **[0002]**   In recent years, the new energy industry has developed rapidly, and the cost of mainstream lithium batteries has increased due to the shortage of lithium resources. Sodium resources are much more abundant and evenly distributed than lithium resources. The cost of sodium carbonate is much lower than that of potassium carbonate. Developing sodium-ion batteries can solve the problem of lithium resource shortage. Although sodium-ion batteries  
15   have lower energy density than lithium-ion batteries, sodium-ion batteries have broad development prospects in energy storage fields with lower energy density requirements and cost sensitivity, such as energy storage power stations, data centers, 5G base stations, low-speed electric vehicles, and electric bicycles.

20   **[0003]**   Hard carbon materials are widely used in HEV/48V and some EV models due to advantages of large interlayer spacing, excellent low-temperature performance, and good fast-charging performance. Hard carbon materials are expected to become the preferred material for sodium-ion batteries in the future. However, due to the low specific capacity (300 mAh/g), low initial efficiency (80%), and low compaction density (1.0 g/cm<sup>3</sup>), the application of the hard carbon materials in sodium-ion batteries is limited. Although soft carbon materials show  
25   improvements in specific capacity (330 mAh/g), initial efficiency (85%), and compaction

density ( $1.3 \text{ g/cm}^3$ ), the soft carbon materials have a high voltage platform and the power performance is not as good as that of hard carbon materials, so the advantages over hard carbon materials are not obvious. Therefore, it is necessary to prepare a novel material with better power performance and higher efficiency by means of coating, doping, and the like to improve the defects of hard carbon or soft carbon materials and exert the synergistic effect between hard carbon materials and soft carbon materials.

## SUMMARY

**[0004]** To address the inherent defects of hard carbon and soft carbon materials, the present application provides an MXene-coated hard carbon-soft carbon anode material, a preparation method and use thereof. The MXene-coated hard carbon-soft carbon anode material prepared in the present application features a 3D interconnected network structure, exhibiting advantages of high specific capacity, high first-cycle Coulombic efficiency, excellent rate performance, and long cycle life, and can be used in sodium-ion batteries.

**[0005]** In a first aspect, the present application provides a method for preparing an MXene-coated hard carbon-soft carbon anode material, which adopts the following technical solution.

**[0006]** A method for preparing an MXene-coated hard carbon-soft carbon anode material, including the following steps:

**[0007]** S1, adding a phenolic resin, potassium permanganate, and oxalic acid into an ammonium persulfate aqueous solution with a mass concentration of 3% for oxidation to obtain an oxidized hard carbon precursor;

**[0008]** S2, uniformly dispersing the oxidized hard carbon precursor, an aminated asphalt, an amino acid, and a silane coupling agent in water, then reacting at  $150^\circ\text{C}$  for 3-4 hours to obtain a reaction mixture, filtering the reaction mixture to obtain a precipitate, and freeze-drying the precipitate at  $-38^\circ\text{C}$  for 24-28 hours to obtain a hard carbon-soft carbon precursor material;

**[0009]** S3, adding 6-8 mass parts of a surface-hydroxylated MXene to 20 mass parts of an aqueous solution of dodecyltrimethylammonium chloride with a mass concentration of 8 g/L, and stirring at room temperature to obtain a uniformly mixed solution;

**[0010]** S4, mixing 100 mass parts of the hard carbon-soft carbon precursor material with 10-20 mass parts of the mixed solution, stirring for 10-24 hours, then placing in an oven at 80-120°C, and curing for 12-24 hours to obtain a material A;

**[0011]** S5, heating the material A to 250-300°C at a rate of 4°C/min in an oxygen-containing atmosphere, holding for oxidation for 3-5 hours, then crushing and sieving to obtain a material B with an average particle size of 5-8 μm; and

**[0012]** S6, transferring the material B to a tube furnace, heating to 750°C-900°C at a rate of 5°C/min and holding for 2-5 hours, then heating to 1300°C-1500°C at a rate of 3°C/min for high-temperature carbonization for 1-5 hours, and cooling to room temperature to obtain the MXene-coated hard carbon-soft carbon anode material.

**[0013]** In the present application, the step S1 mainly converts the phenolic resin into the oxidized hard carbon precursor with a specific structure through a chemical reaction. This precursor has good electrochemical performance and structural stability, serving as the basis for the subsequent preparation of hard carbon-soft carbon anode material. The step S2 mainly performs a cross-linking reaction between the oxidized hard carbon precursor and aminated asphalt through a chemical reaction to form the hard carbon-soft carbon precursor material.

This precursor material has a high charge/discharge specific capacity and good cycling performance. The step S3 mainly improves the dispersibility of MXene in water by adding a surfactant for better coating on the hard carbon-soft carbon precursor material. The step S4 mainly forms the composite material with a 3D interconnected network structure by coating the MXene on the hard carbon-soft carbon precursor material through heating and curing. This composite material has the advantages of high charge/discharge specific capacity, high first-

cycle Coulombic efficiency, good rate performance, and long cycle life. The step S5 is mainly to further improve the performance of the composite material through high-temperature oxidation treatment. After this treatment, the charge/discharge specific capacity, first-cycle Coulombic efficiency, rate performance, and cycle life of the composite material are further improved. The step S6 mainly further enhances the performance of the composite material through high-temperature carbonization. After this treatment, the charge/discharge specific capacity, first-cycle Coulombic efficiency, rate performance, and cycle life of the composite material are further improved.

**[0014]** Preferably, in the step S1, a mass part ratio of the phenolic resin, potassium permanganate, oxalic acid, and ammonium persulfate aqueous solution with the mass concentration of 3% is 100: 20: 3: (90-100).

**[0015]** Preferably, in the step S2, a mass part ratio of the oxidized hard carbon precursor, aminated asphalt, amino acid, and silane coupling agent is 100: (10-15): (4-6): (2-3).

**[0016]** Preferably, in the step S2, the silane coupling agent is prepared by mixing  $\gamma$ -aminopropyl triethoxysilane and N-aminoethyl- $\gamma$ -aminopropyl triethoxysilane in a mass part ratio of 3: 2.

**[0017]** By adopting the above technical solution, the silane coupling agent can cross-link and carbonize the hard carbon precursor and a soft carbon precursor through coupling effect, thereby enhancing the structural stability of the composite material. This is crucial for improving the performance and cycle life of the battery. Improvement of specific capacity and energy density: a silicon-based material obtained after carbonization can increase the specific capacity of the composite material, thereby improving the energy density of the battery. This is of great significance for enhancing the endurance of the battery. The silane coupling agent prepared by mixing  $\gamma$ -aminopropyl triethoxysilane and N-aminoethyl- $\gamma$ -aminopropyl triethoxysilane in the mass part ratio of 3: 2 has a synergistic effect, which can better achieve

the above effects, thereby further improving the performance of the battery.

**[0018]** Preferably, in the step S2, a method for preparing the aminated asphalt includes: adding 30 g of N-(2-aminoethyl)-3-aminopropyl methyldimethoxysilane to 800 g of N-methylpyrrolidone and dispersing uniformly, then adding 120 g of an oxidized asphalt and mixing uniformly, reacting at 85°C for 4 hours, filtering and vacuum-drying a resulting precipitate at 85°C for 24 hours to obtain the aminated asphalt.

**[0019]** By adopting the above technical solution, the reaction between the N-(2-aminoethyl)-3-aminopropylmethyl dimethoxy silane and oxidized asphalt introduces amino functional groups, which can chemically react with hydroxyl/carboxyl groups on the surface of the oxidized hard carbon precursor to form amide groups connected by chemical bonds. The formation of these chemical bonds enhances the structural stability between hard carbon and soft carbon precursors, thereby improving the structural integrity and mechanical stability of a final composite material. The introduction of aminated asphalt not only improves the structural properties of the material but also enhances the conductivity and electrochemical activity of the electrode material. As an electron donor, the amino group can improve the electron transport capability of the material, thereby enhancing the charge-discharge efficiency and cycle stability of the battery. N-methylpyrrolidone as a solvent can effectively disperse the N-(2-aminoethyl)-3-aminopropylmethyl dimethoxy silane and oxidized asphalt, ensuring reaction uniformity. Additionally, conducting the reaction at a higher temperature (85°C) promotes a sufficient reaction between amino groups and oxidized asphalt, ensuring the homogeneity of the aminated asphalt. In summary, the preparation and use of aminated asphalt play an important role in improving the structural stability and electrochemical performance of the MXene-coated hard carbon-soft carbon anode material, and final battery performance. Through specific chemical reactions and process condition control, the material properties are optimized and enhanced, enabling this anode material to exhibit advantages such as high charge-discharge specific

capacity, high first-cycle Coulombic efficiency, excellent rate performance, and long cycle life in sodium-ion batteries.

**[0020]** Preferably, in the step S3, a method for preparing the surface-hydroxylated MXene includes the following steps:

5 **[0021]** S61, blending  $\text{Ti}_3\text{AlC}_2$ , LiF, and 8 mol/L of a HCl solution in a polypropylene reactor, and reacting at  $38^\circ\text{C}$  for 24 hours at a stirring rate of 300 rpm to obtain a multilayer MXene;

**[0022]** S62, centrifuging the multilayer MXene at a speed of 5000 rpm and washing with deionized water 5 times, then adding a lower-layer product to a gas-washing bottle, adding deionized water, introducing argon for 20 minutes and sonicating for 2-3 hours to obtain a  
10 mixture, centrifuging the mixture at a speed of 7000 rpm for 1 hour, collecting an upper black liquid as an MXene dispersion, and freeze-drying the MXene dispersion at  $-40^\circ\text{C}$  for 24 hours to obtain a MXene powder; and

**[0023]** S63, placing the MXene powder in a sodium hydroxide solution with a mass concentration of 20%, sonicating in an ice-water bath for 30-40 min under an air-free condition  
15 to obtain a mixed solution; then stirring the mixed solution at 600 rpm at room temperature for 10 hours, and finally freeze-drying at  $-40^\circ\text{C}$  for 24 hours to obtain the surface-hydroxylated MXene.

**[0024]** In the present application,  $\text{Ti}_3\text{AlC}_2$ , LiF, and 8 mol/L of the HCl solution are blended in the polypropylene reactor and reacted at  $38^\circ\text{C}$  for 24 hours at the stirring rate of 300 rpm to  
20 obtain the multilayer MXene. This step prepares the multilayer MXene from precursor  $\text{Ti}_3\text{AlC}_2$  through selective etching. The multilayer MXene is centrifuged at the speed of 5000 rpm and washed with deionized water 5 times. The lower-layer product was added to the gas-washing bottle, and then deionized water was added. Argon was introduced for 20 minutes, after which a resulting mixture was sonicated for 2-3 hours. The resulting mixture was centrifuged at the  
25 speed of 7000 rpm for 1 hour. The upper black liquid was collected as the MXene dispersion.

This step effectively separates and disperses MXene nanosheets through centrifugation and ultrasonic treatment. The MXene dispersion is freeze-dried at  $-40^{\circ}\text{C}$  for 24 hours to obtain the MXene powder. Then, the MXene powder is placed in the sodium hydroxide solution with the mass concentration of 20%, and subjected to ultrasonic treatment in the ice-water bath under the air-free condition for 30-40 minutes to obtain the mixed solution. The mixed solution is stirred at the speed of 600 rpm at room temperature for 10 hours, and freeze-dried at  $-40^{\circ}\text{C}$  for 24 hours to obtain the surface-hydroxylated MXene. This step successfully introduces hydroxyl groups onto the surface of MXene through ultrasonic treatment under an alkaline condition. The surface-hydroxylated MXene can form stronger interactions with the hard carbon-soft carbon precursor material, thereby enhancing the structural stability of the electrode material. This stable structure can effectively suppress the volume expansion during the charge-discharge processes, thereby improving the cycling stability of the battery. The introduction of surface hydroxyl groups increases the hydrophilicity of MXene, enabling MXene to coat the surface of the hard carbon-soft carbon material more uniformly and form a more complete conductive network. This helps to improve the conductivity of the electrode material, thereby enhancing the charge-discharge efficiency and rate performance of the battery. The introduction of hydroxyl groups may further increase active sites on the electrode surface, providing more positions for ion adsorption and intercalation, thereby increasing the specific capacity of the electrode material. In summary, through specific chemical reactions and process condition control, the surface hydroxylation of MXene is achieved, which not only improves the interaction between MXene and the hard carbon-soft carbon material but also optimizes the electrochemical performance of the electrode material, enabling this anode material to exhibit superior performance in sodium-ion batteries.

**[0025]** Preferably, in the step S61, a mass part ratio of the  $\text{Ti}_3\text{AlC}_2$ , LiF, and 8 mol/L of the HCl solution is 3: 4: (90-100).

**[0026]** Preferably, in the step S63, a mass part ratio of the MXene powder to the sodium hydroxide solution with the mass concentration of 20% is 3: 20.

**[0027]** In a second aspect, the present application provides an MXene-coated hard carbon-soft carbon anode material, which adopts the following technical solution.

5 **[0028]** As a general technical concept, the present application further provides the above MXene-coated hard carbon-soft carbon anode material, prepared by the above method for preparing the MXene-coated hard carbon-soft carbon anode material.

**[0029]** In a third aspect, the present application provides a use of the MXene-coated hard carbon-soft carbon anode material, which adopts the following technical solution.

10 **[0030]** As a general technical concept, the present application further provides a use of the MXene-coated hard carbon-soft carbon anode material in a preparation of an anode material for a sodium-ion battery.

**[0031]** In summary, the beneficial technical effects of the present application are:

**[0032]** 1. Enhancement of electrode structural stability: through the coating of the surface-  
15 hydroxylated MXene, an efficient and stable electrode structure is effectively constructed. This structure can suppress the volume expansion of a hard carbon-soft carbon electrode during the charge-discharge process, significantly improving the cycling stability and service life of the electrode in sodium-ion batteries.

**[0033]** 2. Improvement of electrochemical performance: the chemical reaction between  
20 hydroxyl/carboxyl groups on the surface of the oxidized hard carbon precursor and amino groups on the surface of the aminated asphalt forms amide groups connected by chemical bonds, enhancing the structural stability between materials. Meanwhile, the coupling effect of the silane coupling agent and the silicon-based material obtained after carbonization help to improve the specific capacity and energy density of the composite material, thereby enhancing  
25 the charge-discharge specific capacity and first-cycle Coulombic efficiency of the battery.

**[0034]** 3. Optimization of electrode surface performance: cross-linking and carbonization of the hard carbon precursor and soft carbon precursor using amphoteric compounds (amino acids) and coupling agents, followed by the coating of the surface-hydroxylated MXene, results in the MXene-coated hard carbon-soft carbon anode material with higher specific surface area and more active sites, facilitating potassium ion adsorption and intercalation, further improving the charge-discharge performance of the battery.

**[0035]** 4. Excellent rate performance and long cycle life: due to the unique two-dimensional structure and excellent conductivity of MXene, combined with the characteristics of hard carbon and soft carbon, this composite material maintains good electrochemical performance under high current density, exhibiting excellent rate performance. Moreover, the 3D interconnected network structure of the material helps to alleviate the volume change during cycling, ensuring a long cycle life.

#### **DETAILED DESCRIPTION**

**[0036]** The embodiments of the present application will be described in detail below with reference to examples. However, those skilled in the art will understand that the following examples are only used to illustrate the present application and should not be construed as limiting the scope of the present application. For examples where specific conditions are not specified, they shall be performed under conventional conditions or manufacturer-recommended conditions. Reagents or instruments without specified manufacturers are conventional products available commercially.

**[0037]** Preparation Example 1: Preparation of aminated asphalt

**[0038]** The method for preparing the aminated asphalt was as follows: 30 g of N-(2-aminoethyl)-3-aminopropyl methyldimethoxysilane was added to 800 g of N-methylpyrrolidone and dispersed uniformly. A resulting mixture was then mixed with 120 g of

an oxidized asphalt and reacted at 85°C for 4 hours. After the reaction, a resulting product was filtered to obtain a precipitate and the precipitate was vacuum-dried at 85°C for 24 hours to obtain the aminated asphalt.

**[0039]** Preparation Example 2: Preparation of surface-hydroxylated MXene

5 **[0040]** The method for preparing the surface-hydroxylated MXene included the following steps.

**[0041]** S61, 3 g of  $\text{Ti}_3\text{AlC}_2$ , 4 g of LiF, and 90 g of 8 mol/L of a HCl solution were blended in a polypropylene reactor and reacted at 38°C for 24 hours at a stirring rate of 300 rpm to obtain a multilayer MXene.

10 **[0042]** S62, the multilayer MXene was centrifuged at a speed of 5000 rpm and washed with deionized water 5 times. A lower-layer product was added to a gas-washing bottle, then deionized water was added. Argon was introduced for 20 minutes, after which a resulting mixture was sonicated for 2 hours. The resulting mixture was centrifuged at a speed of 7000 rpm for 1 hour. An upper black liquid was collected as an MXene dispersion. Finally, the  
15 MXene dispersion was freeze-dried at -40°C for 24 hours to obtain a MXene powder.

**[0043]** S63, 3 g of the MXene powder was placed in 20 g of a sodium hydroxide solution with a mass concentration of 20% to obtain a mixture. The mixture was sonicated in an ice-water bath for 30 minutes under an oxygen-free condition to obtain a mixed solution. Subsequently, the mixed solution was stirred at a speed of 600 rpm at room temperature for 10  
20 hours to obtain a product. Finally, the product was freeze-dried at -40°C for 24 hours to obtain the surface-hydroxylated MXene.

**[0044]** Preparation Example 3: Preparation of surface-hydroxylated MXene

**[0045]** The method for preparing the surface-hydroxylated MXene included the following steps.

25 **[0046]** S61, 3 g of  $\text{Ti}_3\text{AlC}_2$ , 4 g of LiF, and 100 g of 8 mol/L of a HCl solution were blended

in a polypropylene reactor and reacted at 38°C for 24 hours at a stirring rate of 300 rpm to obtain a multilayer MXene.

**[0047]** S62, the multilayer MXene was centrifuged at a speed of 5000 rpm and washed with deionized water 5 times. A lower-layer product was added to a gas-washing bottle, then deionized water was added. Argon was introduced for 20 minutes, after which a resulting mixture was sonicated for 3 hours. The resulting mixture was centrifuged at a speed of 7000 rpm for 1 hour. An upper black liquid was collected as an MXene dispersion. Finally, the MXene dispersion was freeze-dried at -40°C for 24 hours to obtain a MXene powder.

**[0048]** S63, 3 g of the MXene powder was placed in 20 g of a sodium hydroxide solution with a mass concentration of 20% to obtain a mixture. The mixture was sonicated in an ice-water bath for 40 minutes under an oxygen-free condition to obtain a mixed solution. Subsequently, the mixed solution was stirred at a speed of 600 rpm at room temperature for 10 hours to obtain a product. Finally, the product was freeze-dried at -40°C for 24 hours to obtain the surface-hydroxylated MXene.

**[0049]** Preparation Example 4: Preparation of surface-hydroxylated MXene

**[0050]** The method for preparing the surface-hydroxylated MXene included the following steps.

**[0051]** S61, 3 g of  $\text{Ti}_3\text{AlC}_2$ , 4 g of LiF, and 95 g of 8 mol/L of a HCl solution were blended in a polypropylene reactor and reacted at 38°C for 24 hours at a stirring rate of 300 rpm to obtain a multilayer MXene.

**[0052]** S62, the multilayer MXene was centrifuged at a speed of 5000 rpm and washed with deionized water 5 times. A lower-layer product was added to a gas-washing bottle, then deionized water was added. Argon was introduced for 20 minutes, after which a resulting mixture was sonicated for 2.5 hours. The resulting mixture was centrifuged at 7000 rpm for 1 hour. An upper black liquid was collected as an MXene dispersion. Finally, the MXene

dispersion was freeze-dried at -40°C for 24 hours to obtain a MXene powder.

**[0053]** S63, 3 g of the MXene powder was placed in 20 g of a sodium hydroxide solution with a mass concentration of 20% to obtain a mixture. The mixture was sonicated in an ice-water bath for 35 minutes under an oxygen-free condition to obtain a mixed solution.

5 Subsequently, the mixed solution was stirred at a speed of 600 rpm at room temperature for 10 hours to obtain a product. Finally, the product was freeze-dried at -40°C for 24 hours to obtain the surface-hydroxylated MXene.

**[0054]** Preparation Comparative Example 1: Preparation of MXene

**[0055]** It was basically the same as Preparation Example 4, except that the step S63 was  
10 omitted.

**[0056]** Example 1

**[0057]** A method for preparing an MXene-coated hard carbon-soft carbon anode material included the following steps.

**[0058]** S1, 100 g of a phenolic resin, 20 g of potassium permanganate, and 3 g of oxalic acid  
15 were added into 90 g of an ammonium persulfate aqueous solution with a mass concentration of 3% for oxidation to obtain an oxidized hard carbon precursor.

**[0059]** S2, 100 g of the oxidized hard carbon precursor, 10 g of the aminated asphalt prepared in Preparation Example 1, 4 g of an amino acid, and 2 g of a silane coupling agent were uniformly dispersed in water and reacted at 150°C for 3 hours. A reaction product was filtered  
20 to obtain a precipitate, and the precipitate was freeze-dried at 38°C for 24 hours to obtain a hard carbon-soft carbon precursor material. The silane coupling agent was prepared by mixing  $\gamma$ -aminopropyl triethoxysilane and N-aminoethyl- $\gamma$ -aminopropyl triethoxysilane in a mass part ratio of 3: 2.

**[0060]** S3, 6 g of a surface-hydroxylated MXene was added to 20 g of an aqueous solution  
25 of dodecyltrimethylammonium chloride with a mass concentration of 8 g/L, and stirred at room

temperature to obtain a uniformly mixed solution. The surface-hydroxylated MXene was prepared in Preparation Example 2.

**[0061]** S4, 100 g of the hard carbon-soft carbon precursor material was mixed with 10 g of the mixed solution and stirred for 10 hours to obtain a mixture. Then, the mixture was placed in an oven at 80°C and cured for 24 hours to obtain a material A.

**[0062]** S5, the material A was heated to 250°C at a rate of 4°C/min in an oxygen-containing atmosphere, and held for oxidation for 5 hours. Then, an oxidation product was crushed and sieved to obtain a material B with an average particle size of 5 μm.

**[0063]** S6, the material B was transferred to a tube furnace, heated to 750°C at a rate of 5°C/min, and held for 5 hours. Then, the material B was heated to 1300°C at a rate of 3°C/min for high-temperature carbonization for 5 hours and cooled to room temperature to obtain the MXene-coated hard carbon-soft carbon anode material.

**[0064]** Example 2

**[0065]** A method for preparing an MXene-coated hard carbon-soft carbon anode material included the following steps.

**[0066]** S1, 100 g of a phenolic resin, 20 g of potassium permanganate, and 3 g of oxalic acid were added into 100 g of an ammonium persulfate aqueous solution with a mass concentration of 3% for oxidation to obtain an oxidized hard carbon precursor.

**[0067]** S2, 100 g of the oxidized hard carbon precursor, 15 g of the aminated asphalt prepared in Preparation Example 1, 6 g of an amino acid, and 3 g of a silane coupling agent were uniformly dispersed in water and reacted at 150°C for 4 hours. A reaction product was filtered to obtain a precipitate, and the precipitate was freeze-dried at 38°C for 28 hours to obtain a hard carbon-soft carbon precursor material. The silane coupling agent was prepared by mixing γ-aminopropyl triethoxysilane and N-aminoethyl-γ-aminopropyl triethoxysilane in a mass part ratio of 3: 2.

**[0068]** S3, 8 g of a surface-hydroxylated MXene was added to 20 g of an aqueous solution of dodecyltrimethylammonium chloride with a mass concentration of 8 g/L, and stirred at room temperature to obtain a uniformly mixed solution. The surface-hydroxylated MXene was prepared in Preparation Example 3.

5 **[0069]** S4, 100 g of the hard carbon-soft carbon precursor material was mixed with 20 g of the mixed solution and stirred for 24 hours to obtain a mixture. Then, the mixture was placed in an oven at 120°C, and cured for 12 hours to obtain a material A.

**[0070]** S5, the material A was heated to 300°C at a rate of 4°C/min in an oxygen-containing atmosphere, and held for oxidation for 3 hours. Then, an oxidation product was crushed and  
10 sieved to obtain a material B with an average particle size of 8 μm.

**[0071]** S6, the material B was transferred to a tube furnace, heated to 900°C at a rate of 5°C/min, and held for 2 hours. Then, the material B was heated to 1500°C at a rate of 3°C/min for high-temperature carbonization for 1 hour, and cooled to room temperature to obtain the MXene-coated hard carbon-soft carbon anode material.

15 **[0072]** Example 3

**[0073]** A method for preparing an MXene-coated hard carbon-soft carbon anode material included the following steps.

**[0074]** S1, 100 g of a phenolic resin, 20 g of potassium permanganate, and 3 g of oxalic acid were added into 95 g of an ammonium persulfate aqueous solution with a mass concentration  
20 of 3% for oxidation to obtain an oxidized hard carbon precursor.

**[0075]** S2, 100 g of the oxidized hard carbon precursor, 13 g of the aminated asphalt prepared in Preparation Example 1, 5 g of an amino acid, and 2.5 g of a silane coupling agent were uniformly dispersed in water and reacted at 150°C for 3.5 hours. A reaction product was filtered to obtain a precipitate, and the precipitate was freeze-dried at 38°C for 26 hours to obtain a  
25 hard carbon-soft carbon precursor material. The silane coupling agent was prepared by mixing

$\gamma$ -aminopropyl triethoxysilane and N-aminoethyl- $\gamma$ -aminopropyl triethoxysilane in a mass part ratio of 3: 2.

**[0076]** S3, 7 g of a surface-hydroxylated MXene was added to 20 g of an aqueous solution of dodecyltrimethylammonium chloride with a mass concentration of 8 g/L, and stirred at room temperature to obtain a uniformly mixed solution. The surface-hydroxylated MXene was prepared in Preparation Example 4.

**[0077]** S4, 100 g of the hard carbon-soft carbon precursor material was mixed with 15g of the mixed solution and stirred for 16 hours to obtain a mixture. Then, the mixture was placed in an oven at 100°C and cured for 18 hours to obtain a material A.

**[0078]** S5, the material A was heated to 280°C at a rate of 4°C/min in an oxygen-containing atmosphere, and held for oxidation for 4 hours. Then, an oxidation product was crushed and sieved to obtain a material B with an average particle size of 7  $\mu$ m.

**[0079]** S6, the material B was transferred to a tube furnace, heated to 820°C at a rate of 5°C/min, and held for 3.5 hours. Then, the material B was heated to 1400°C at a rate of 3°C/min for high-temperature carbonization for 3 hours and cooled to room temperature to obtain the MXene-coated hard carbon-soft carbon anode material.

**[0080]** Comparative Example 1

**[0081]** It was basically the same as Example 3, except that in the step S2, an equivalent amount of oxidized asphalt was used instead of the aminated asphalt.

**[0082]** Comparative Example 2

**[0083]** It was basically the same as Example 3, except that in the step S3, an equivalent amount of MXene prepared in Preparation Comparative Example 1 was used instead of the surface-hydroxylated MXene.

**[0084]** Comparative Example 3

**[0085]** It was basically the same as Example 3, except that in the step S2, the silane coupling

agent was  $\gamma$ -aminopropyl triethoxysilane.

**[0086]** Comparative Example 4

**[0087]** It was basically the same as Example 3, except that in the step S2, the silane coupling agent was N-aminoethyl- $\gamma$ -aminopropyl triethoxysilane.

5 **[0088]** Performance testing

**[0089]** 1. The MXene-coated hard carbon-soft carbon anode materials prepared in Examples 1-3 and Comparative Examples 1-4 were respectively made into button-type sodium-ion batteries for testing.

**[0090]** The MXene-coated hard carbon-soft carbon anode material, a conductive agent Super  
10 P, and carboxymethyl cellulose were mixed in a mass ratio of 8:1:1 with water to form a slurry. The slurry was stirred for 24 hours, and then coated on a carbon-coated (150  $\mu\text{m}$  thickness) copper foil, and dried in an oven at 80°C for 24 hours to obtain a dried electrode. The dried electrode was cut into 12 mm discs with a loading capacity of 1-1.4  $\text{mg}/\text{cm}^2$ . A sodium foil was used as a counter electrode, a lithium metal sheet was used as a counter electrode, a  
15 polyethylene propylene (PEP) composite film was used as a separator, and  $\text{LiPF}_6/\text{EC}+\text{DEC}$  (the concentration of  $\text{LiPF}_6$  was 1.3 mol/L, and the volume ratio of EC to DEC was 1:1) was used as an electrolyte. The battery was assembled in a glove box filled with argon.

**[0091]** The electrochemical performance testing was performed on a Wuhan LAND CT2001A battery tester with a charge-discharge voltage range of 0.005-2.0V and a charge-  
20 discharge rate of 0.1C. The specific capacity at the 2C rate of the material was also tested and the rate performance (2C/0.1C) was calculated. Test results are shown in Table 1.

**[0092]** Table 1 Electrochemical Performance Test Results

| Item      | Initial discharge capacity (mAh/g) | Initial discharge efficiency (%) | Rate (2C/0.1C)/% |
|-----------|------------------------------------|----------------------------------|------------------|
| Example 1 | 374.6                              | 96.9                             | 95.2             |
| Example 2 | 375.4                              | 97.3                             | 95.8             |
| Example 3 | 375.2                              | 97.1                             | 95.5             |

|                       |       |      |      |
|-----------------------|-------|------|------|
| Comparative Example 1 | 352.4 | 94.2 | 92.2 |
| Comparative Example 2 | 348.3 | 93.1 | 90.4 |
| Comparative Example 3 | 370.3 | 95.3 | 93.8 |
| Comparative Example 4 | 369.2 | 95.2 | 93.4 |

**[0093]** As shown in Table 1, the MXene-coated hard carbon-soft carbon anode material prepared in the present application exhibits high initial discharge capacity, high initial discharge efficiency, and high rate performance when made into sodium-ion batteries. The structural stability between materials is enhanced by chemical reactions between hydroxyl/carboxyl groups on the surface of the oxidized hard carbon precursor and amino groups on the surface of the aminated asphalt to form amide groups connected by chemical bonds. Simultaneously, the coupling effect of the silane coupling agent and silicon-based materials obtained after carbonization are used to increase the specific capacity and the energy density of the composite material. Through cross-linking and carbonization of the hard carbon precursor and the soft carbon precursor by an amphoteric compound (amino acid) and the coupling agent, and followed by coating with the surface-hydroxylated MXene, the MXene-coated hard carbon-soft carbon anode material is obtained, which significantly improves the high charge/discharge specific capacity, high first-cycle Coulombic efficiency, excellent rate performance, and long cycle life of the battery.

## **[0094]** 2. Pouch Cell Testing

**[0095]** An anode was prepared using the MXene-coated hard carbon-soft carbon anode materials from each example and comparative example, a cathode was prepared using a ternary material ( $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ) as a cathode material,  $\text{LiPF}_6$  (the solvent was EC + DEC, the volume ratio was 1:1, and the concentration of the  $\text{LiPF}_6$  was 1.3 mol/L) was used as an electrolyte, and Celgard 2400 was used as a separator to prepare 2Ah pouch cells.

**[0096]** The preparation method of the anode was the same as that in the testing of button-

type sodium-ion battery.

**[0097]** For the preparation of the cathode, a PVDF binder, a SP conductive agent and a solvent (N-methylpyrrolidone) were added to the cathode material in a weight ratio of 93: 3: 4: 140 and stirred uniformly to prepare a cathode slurry. The cathode slurry was coated on an aluminum foil, dried, rolled, and cut to obtain cathode sheets.

## **[0098]** 2.1 Rate Performance Testing

**[0099]** Testing was performed at a charge-discharge voltage range of 2.8-4.2V, a test temperature of 25±3.0°C. The pouch cell was charged at 1.0C, 2.0C, 3.0C, 5.0C, and discharged at 1.0C. Constant current ratio and temperature of the pouch cell of the pouch cell were measured under different charging modes. Results are shown in Table 2.

**[00100]** Table 2 Rate Performance

| Item                  |                          | 1C    | 2C    | 3C    | 5C    |
|-----------------------|--------------------------|-------|-------|-------|-------|
| Example 1             | Constant current ratio/% | 97.88 | 93.78 | 87.56 | 79.26 |
|                       | Temperature/°C           | 26.2  | 27.2  | 30.8  | 33.7  |
| Example 2             | Constant current ratio/% | 98.1  | 94.12 | 87.95 | 79.53 |
|                       | Temperature/°C           | 26.4  | 27.6  | 30.9  | 33.9  |
| Example 3             | Constant current ratio/% | 97.96 | 93.94 | 87.82 | 79.82 |
|                       | Temperature/°C           | 26.3  | 27.5  | 30.8  | 33.6  |
| Comparative Example 1 | Constant current ratio/% | 95.23 | 88.57 | 84.21 | 73.42 |
|                       | Temperature/°C           | 28.3  | 30.7  | 36.4  | 38.6  |
| Comparative Example 2 | Constant current ratio/% | 94.56 | 87.61 | 83.68 | 72.56 |
|                       | Temperature/°C           | 28.7  | 31.3  | 37.6  | 39.8  |
| Comparative Example 3 | Constant current ratio/% | 96.11 | 91.26 | 84.97 | 75.36 |
|                       | Temperature/°C           | 27.2  | 29.8  | 33.6  | 35.5  |
| Comparative Example 4 | Constant current ratio/% | 96.34 | 91.45 | 85.24 | 74.62 |
|                       | Temperature/°C           | 27.1  | 29.6  | 33.4  | 35.2  |

**[00101]** As can be seen from Table 2, the rate charging performance of the pouch cell made of the MXene-coated hard carbon-soft carbon anode material obtained in the examples of the present application is significantly better than that of the comparative examples, and the

charging time is shorter, indicating that the MXene-coated hard carbon-soft carbon anode material of the present application exhibits excellent fast-charging performance. MXene can be coated onto the hard carbon-soft carbon precursor material through heat curing to form a composite material with a 3D interconnected network structure, which enhances the diffusion rate of lithium ions during the charge-discharge process and improves the rate performance.

## **[00102]** 2.2 Cycling Performance Testing

**[00103]** The pouch cells prepared by using MXene-coated hard carbon-soft carbon anode materials prepared in each example and comparative example as the anode materials were tested as follows: under a 2C/2C charge-discharge rate with a voltage range of 2.8-4.2 V, 100, 300 and 800 charge-discharge cycles were carried out in sequence, and the capacity retention rate of the cells was tested. The results are shown in Table 3.

**[00104]** Table 3 Cycling Performance

| Item                  | Capacity retention rate after 100 cycles/% | Capacity retention rate after 300 cycles/% | Capacity retention rate after 800 cycles/% |
|-----------------------|--------------------------------------------|--------------------------------------------|--------------------------------------------|
| Example 1             | 100                                        | 99.23                                      | 96.4                                       |
| Example 2             | 100                                        | 99.58                                      | 96.9                                       |
| Example 3             | 100                                        | 99.45                                      | 97.3                                       |
| Comparative Example 1 | 100                                        | 98.78                                      | 94.6                                       |
| Comparative Example 2 | 100                                        | 98.54                                      | 94.3                                       |
| Comparative Example 3 | 100                                        | 99.03                                      | 95.4                                       |
| Comparative Example 4 | 100                                        | 99.12                                      | 95.2                                       |

**[00105]** As can be seen from Table 3, the preparation method of the present application forms a composite material with a 3D interconnected network structure by coating MXene onto the hard carbon-soft carbon precursor material. The synergistic effect among these components can reduce the irreversible capacity, increase the number of lithium ions during the charge-discharge process, and improve the cycling performance.

**[00106]** The above-described examples are only used to explain and illustrate the technical solution of the present application, and not to limit it. Although the above-described examples

provide specific explanations of the present application, related technical personnel should understand that modifications or equivalent substitutions can still be made to the specific embodiments of the present application, and any modifications and equivalent substitutions that do not depart from the spirit and scope of the present application should be included in the scope of the present application.

## WHAT IS CLAIMED IS:

1. A method for preparing an MXene-coated hard carbon-soft carbon anode material, characterized by comprising the following steps:

S1, adding a phenolic resin, potassium permanganate, and oxalic acid into an ammonium persulfate aqueous solution with a mass concentration of 3% for oxidation to obtain an oxidized hard carbon precursor;

S2, uniformly dispersing the oxidized hard carbon precursor, an aminated asphalt, an amino acid, and a silane coupling agent in water, and then reacting at 150°C for 3-4 hours to obtain a reaction mixture, filtering the reaction mixture to obtain a precipitate, and freeze-drying the precipitate at -38°C for 24-28 hours to obtain a hard carbon-soft carbon precursor material;

S3, adding 6-8 mass parts of a surface-hydroxylated MXene to 20 mass parts of an aqueous solution of dodecyltrimethylammonium chloride with a mass concentration of 8 g/L, and stirring at room temperature to obtain a uniformly mixed solution;

S4, mixing 100 mass parts of the hard carbon-soft carbon precursor material with 10-20 mass parts of the mixed solution, stirring for 10-24 hours, then placing in an oven at 80-120°C, and curing for 12-24 hours to obtain a material A;

S5, heating the material A to 250-300°C at a rate of 4°C/min in an oxygen-containing atmosphere, holding for oxidation for 3-5 hours, then crushing and sieving to obtain a material B with an average particle size of 5-8 μm; and

S6, transferring the material B to a tube furnace, heating to 750°C-900°C at a rate of 5°C/min and holding for 2-5 hours, then heating to 1300°C-1500°C at a rate of 3°C/min for high-temperature carbonization for 1-5 hours, and cooling to room temperature to obtain the MXene-coated hard carbon-soft carbon anode material.

2. The method for preparing the MXene-coated hard carbon-soft carbon anode material

according to claim 1, characterized in that, in the step S1, a mass part ratio of the phenolic resin, potassium permanganate, oxalic acid, and ammonium persulfate aqueous solution with the mass concentration of 3% is 100: 20: 3: (90-100).

3. The method for preparing the MXene-coated hard carbon-soft carbon anode material according to claim 1, characterized in that, in the step S2, a mass part ratio of the oxidized hard carbon precursor, aminated asphalt, amino acid, and silane coupling agent is 100: (10-15): (4-6): (2-3).

4. The method for preparing the MXene-coated hard carbon-soft carbon anode material according to claim 1, characterized in that, in the step S2, the silane coupling agent is prepared by mixing  $\gamma$ -aminopropyl triethoxysilane and N-aminoethyl- $\gamma$ -aminopropyl triethoxysilane in a mass part ratio of 3:2.

5. The method for preparing the MXene-coated hard carbon-soft carbon anode material according to claim 1, characterized in that, in the step S2, a method for preparing the aminated asphalt comprises: adding 30 g of N-(2-aminoethyl)-3-aminopropyl methyldimethoxysilane to 800 g of N-methylpyrrolidone and dispersing uniformly, then adding 120 g of an oxidized asphalt and mixing uniformly, reacting at 85°C for 4 hours, filtering and vacuum-drying a resulting precipitate at 85°C for 24 hours to obtain the aminated asphalt.

6. The method for preparing the MXene-coated hard carbon-soft carbon anode material according to claim 1, characterized in that, in the step S3, a method for preparing the surface-hydroxylated MXene comprises the following steps:

S61, blending  $\text{Ti}_3\text{AlC}_2$ , LiF, and 8 mol/L of a HCl solution in a polypropylene reactor, and reacting at 38°C for 24 hours at a stirring rate of 300 rpm to obtain a multilayer MXene;

S62, centrifuging the multilayer MXene at a speed of 5000 rpm and washing with deionized water 5 times, then adding a lower-layer product to a gas-washing bottle, adding deionized water, introducing argon for 20 minutes and sonicating for 2-3 hours to obtain a

mixture, centrifuging the mixture at a speed of 7000 rpm for 1 hour, collecting an upper black liquid as an MXene dispersion, and freeze-drying the MXene dispersion at -40°C for 24 hours to obtain a MXene powder; and

S63, placing the MXene powder in a sodium hydroxide solution with a mass concentration of 20%, sonicating in an ice-water bath for 30-40 min under an air-free condition to obtain a mixed solution; then stirring the mixed solution at a speed of 600 rpm at room temperature for 10 hours, and finally freeze-drying at -40°C for 24 hours to obtain the surface-hydroxylated MXene.

7. The method for preparing the MXene-coated hard carbon-soft carbon anode material according to claim 6, characterized in that, in the step S61, a mass part ratio of the  $\text{Ti}_3\text{AlC}_2$ , LiF, and 8 mol/L of the HCl solution is 3: 4: (90-100).

8. The method for preparing the MXene-coated hard carbon-soft carbon anode material according to claim 1, characterized in that, in the step S63, a mass part ratio of the MXene powder to the sodium hydroxide solution with the mass concentration of 20% is 3:20.

9. An MXene-coated hard carbon-soft carbon anode material, prepared by the method for preparing the MXene-coated hard carbon-soft carbon anode material according to any one of claims 1-8.

10. Use of the MXene-coated hard carbon-soft carbon anode material according to claim 9 in a preparation of an anode material for a sodium-ion battery.