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DESCRIPTION CN106058232A

A kind of siloxane material, preparation method of silicon-based oxide and negative electrode material

[0001]

Technical Field

[0002]

The present invention belongs to the technical field of lithium-ion batteries, and in particular relates to a siloxane material, a preparation method of a silicon-based oxide, and a negative electrode material.

[0003]

Background Art

[0004]

Lithium-ion batteries are an ideal energy source for portable electronic devices, electric vehicles and energy storage systems. The development of new electrode materials with high specific energy, high power, good safety and low cost is a core issue in the field of lithium-ion battery research. The research on new negative electrode materials is of great significance to the development of a new generation of lithium-ion batteries.

[0005]

Currently, mature negative electrode materials for lithium-ion batteries are mainly graphite materials, with a specific capacity of only 372mAh/g, which cannot meet the future demand for high energy density of lithium-ion batteries.

As an emerging negative electrode material for lithium-ion batteries, silicon has a theoretical lithium insertion capacity of 4200mAh/g and is considered to be a very promising lithium-ion negative electrode material.

However, the huge lithium storage capacity leads to a huge volume change (>300%) of silicon during the process of lithium insertion and extraction. After multiple cycles, the internal stress of silicon accumulates, the silicon particles are pulverized, and the contact between the active ingredient and the conductive agent and binder deteriorates. At the same time, the huge volume expansion and contraction of the active ingredient silicon will lead to the instability of the SEI film on the electrode surface, the rupture and regeneration of the SEI film, and the continuous consumption of electrolyte, which affects the cycle stability of the silicon negative electrode material.

[0006]

Partial oxygen is introduced into pure silicon material to form silicon oxide. Silicon oxide material has a relatively high theoretical capacity (>2000mAh/g), a low lithium storage voltage platform, and a relatively small volume change rate during lithium insertion and extraction (<200%), and is considered to be a more practical negative electrode material. Suh et al. used Si and SiO_2 to evaporate and condense under high temperature conditions (T>5000°C), and prepared silicon oxide with different oxygen contents by controlling the ratio of O_2, H_2O and Ar.

The particle size of silicon oxide is micron-sized, and the capacity retention rate after 100 cycles at 0.1C is only 78% [Electrochemical behavior of SiOx anodes with variation of oxygen ratio for Li-ion batteries, Electrochemica Acta, 2014, 148, 111.]. However, this method has high energy consumption, high equipment requirements, is difficult to mass produce, and the prepared silicon oxide has low initial efficiency and poor cycle performance.

[0007]

Therefore, it is necessary to develop a new, low-cost silicon oxide preparation process so that the silicon oxide negative electrode material can effectively suppress the volume expansion problem of silicon and have a higher first coulombic efficiency, better cycle stability and good rate performance.

[0008]

Summary of the invention

[0009]

The purpose of the present invention is to provide a siloxane material, a method for preparing a silicon-based oxide and a negative electrode material. The negative electrode material prepared using the silicon-based oxide in the present invention as a raw material has good cycle stability.

[0010]

The present invention provides a siloxane material having a chemical formula shown in Formula 1:

[0011]

Si₆O_xH_y(OH)_{6-y}Formula 1;

[0012]

$1 \le x \le 6$, $1 \le y \le 6$;

[0013]

The siloxene material has Si-O-Si bonds, Si-H bonds, and Si-OH bonds.

[0014]

Preferably, the siloxene material has a structure shown in Formula 1-1 to Formula 1-4,

[0016]

The present invention provides a method for preparing a silicon-based oxide, comprising the following steps:

[0017]

Reacting calcium silicide in an acid solution to obtain siloxene;

[0018]

Heat treating siloxene at 300-1100 ° C. for 0.5-6 hours to obtain silicon-based oxide;

[0019]

The siloxene is the siloxene material mentioned above.

[0020]

Preferably, the acid solution comprises an acid and a solvent, and the acid comprises one or more of hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, boric acid, oxalic acid and an organic carboxylic acid;

[0021]

The solvent includes water and/or alcohol;

[0022]

The molar concentration of the acid solution is 0.1-10 mol/L.

[0023]

Preferably, the organic carboxylic acid is a C1-8 carboxylic acid.

[0024]

Preferably, the organic carboxylic acid comprises one or more of formic acid, glacial acetic acid, propionic acid, 2-propionic acid, valeric acid, n-hexanoic acid, butyric acid, trichloroacetic acid, trifluoroacetic acid and 2-methylpropionic acid.

[0025]

Preferably, the alcohol comprises a C1-6 aliphatic alcohol;

[0026]

The volume ratio of the alcohol to water is (0.1-1):1.

[0027]

Preferably, the alcohol includes one or more of methanol, ethanol, isopropanol, glycerol, butanol, pentanol, n-hexanol, 2-methoxyethanol and 2-ethoxyethanol.

[0028]

The present invention provides a negative electrode material, which is made of materials including silicon-based materials and carbon materials;

[0029]

The silicon-based material includes a siloxane material and/or a silicon-based oxide;

[0030]

The siloxane material is the siloxane material described above; the silicon-based oxide is the silicon-based oxide prepared by the preparation method described above.

[0031]

Preferably, the negative electrode material contains carbon, and the mass fraction of the carbon is 5 to 60%.

[0032]

The present invention provides a siloxene material having a chemical formula shown in Formula 1: Si₆O_xH_y(OH)_{6-y}; 1≤x≤6, 1≤y≤6; the siloxene material has a Si-O-Si bond, a Si-H bond and a Si-OH bond.

The siloxene material in the present invention has Si-O-Si bonds, Si-H bonds and Si-OH bonds at the same time, and the preparation process is simple and easy to prepare on a large scale. The negative electrode material prepared by using the siloxene material in the present invention can effectively suppress the volume expansion problem of silicon, so that the negative electrode material has higher cycle stability, higher first coulomb efficiency and good rate performance.

Experimental results show that the negative electrode material made of silicon-based oxide in the present invention has a first lithium desorption capacity of 845 to 1329 mAh/g at 150 mA/g, a first coulombic efficiency of 65.2 to 84.1%, a capacity retention rate of 75.0 to 85.3% after 200 cycles, and a capacity retention rate of 71.1 to 86.0% at 1.5 A/g.

[0033]

BRIEF DESCRIPTION OF THE DRAWINGS

[0034]

In order to more clearly illustrate the embodiments of the present invention or the technical solutions in the prior art, the drawings required for use in the embodiments or the description of the prior art will be briefly introduced below. Obviously, the drawings described below are only embodiments of the present invention. For ordinary technicians in this field, other drawings can be obtained based on the provided drawings without paying creative work.

[0035]

FIG1 is an infrared image of siloxene in Example 1 of the present invention;

[0036]

FIG2 is an XRD diagram of the siloxane material and the silicon-based oxide and carbon composite negative electrode material obtained in Example 1 of the present invention;

[0037]

FIG3 is a TEM image of the negative electrode material obtained in Example 1 of the present invention;

[0038]
FIG4 is a SAD diagram of the negative electrode material obtained in Example 1 of the present invention;

[0039]
FIG5 is a high rate charge and discharge curve of the negative electrode material in Example 1 of the present invention at the 100th cycle;

[0040]
FIG. 6 is a graph showing the high-cycle performance of the negative electrode material in Example 1 of the present invention.

[0041]
DETAILED DESCRIPTION

[0042]
The present invention provides a siloxane material having a chemical formula shown in Formula 1:

[0043]
Si₆O_xH_y(OH)_{6-y}Formula 1;

[0044]
$1\leq x\leq 6, 1\leq y\leq 6$;

[0045]
The siloxene material has Si-O-Si bonds, Si-H bonds, and Si-OH bonds.

[0046]
In the present invention, x is preferably 1, 2, 3 or 4; y is preferably 3, 4 or 5; specifically, the siloxene material has the structure shown in Formula 1-1 to Formula 1-4:

[0048]

The present invention preferably prepares the above-mentioned siloxene material according to the following steps, including the following steps:

[0049]

Calcium silicide is reacted in an acid solution to obtain siloxane.

[0050]

In the present invention, the calcium silicide (CaSi₂) is preferably layered calcium silicide, and the layered calcium silicide undergoes a chemical reaction in an acid solution, and is separated after the calcium element is stripped off to obtain a siloxane material.

[0051]

In the present invention, the acid solution comprises an acid and a solvent, the acid comprises an inorganic acid and/or an organic acid, the inorganic acid comprises one or more of hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, boric acid and oxalic acid, more preferably comprises hydrochloric acid and/or nitric acid; the organic acid is preferably an organic carboxylic acid, more preferably an organic carboxylic acid of C1 to 8, most preferably one or more of formic acid, glacial acetic acid, propionic acid, 2-propionic acid, valeric acid, n-hexanoic acid, butyric acid, trichloroacetic acid, trifluoroacetic acid and 2-methylpropionic acid; specifically, in an embodiment of the present invention, it can be formic acid and glacial acetic acid, formic acid and propionic acid, propionic acid and 2-propionic acid, valeric acid and n-hexanoic acid, n-hexanoic acid and butyric acid, butyric acid and trichloroacetic acid, trichloroacetic acid and trifluoroacetic acid, trifluoroacetic acid and 2-methylpropionic acid, formic acid, glacial acetic acid and propionic acid, propionic acid, 2-propionic acid, valeric acid or n-hexanoic acid.

[0052]

In the present invention, the solvent includes water and/or alcohol, and the alcohol preferably includes C1-6 alcohol, more preferably C1-C6 aliphatic alcohol, and most preferably one or more of methanol, ethanol, isopropanol, glycerol, butanol, pentanol, n-hexanol, 2-methoxyethanol and 2-ethoxyethanol; specifically, in an embodiment of the present invention, it can be methanol and ethanol, methanol and isopropanol, methanol and glycerol, ethanol and butanol, ethanol and glycerol, isopropanol and glycerol, glycerol and butanol, glycerol and pentanol, butanol and pentanol, n-hexanol and 2-methoxyethanol, 2-methoxyethanol and 2-ethoxyethanol, methanol, ethanol and isopropanol, ethanol, isopropanol, glycerol and butanol, pentanol, n-hexanol, 2-methoxyethanol or 2-ethoxyethanol.

In the present invention, the volume ratio of the alcohol to water is preferably (0.1-1):1, more preferably (0.2-0.8):1, and most preferably (0.4-0.6):1; when the alcohol is a mixture of multiple alcohols, the present invention has no special requirements on the amount of different alcohols used, the solvent is mainly water, and the addition of alcohol is only an auxiliary effect.

[0053]

In the present invention, the molar concentration of the acid in the acid solution is 0.1-10 mol/L, preferably 0.5-8 mol/L, most preferably 2-5 mol/L, specifically, in an embodiment of the present invention, it can be 2 mol/L, 5 mol/L or 10 mol/L.

[0054]

In the present invention, the reaction temperature is preferably 20 to 35 ° C., more preferably 25 to 30 ° C.; the reaction time is preferably 2 to 25 hours, more preferably 5 to 20 hours, and most preferably 10 to 15 hours.

The present invention preferably carries out the above reaction under oxygen atmosphere.

[0055]

After the calcium silicide completes the reaction in the acid solution, the present invention preferably performs solid-liquid separation on the mixed solution obtained by the reaction, removes the liquid, and obtains siloxene. In the present invention, the solid-liquid separation method is preferably stirring and/or ultrasonic treatment followed by centrifugation. The stirring time is preferably 2 to 20 hours, more preferably 5 to 15 hours. Specifically, in the embodiments of the present invention, it can be 2 hours, 5 hours or 20 hours; the stirring is preferably magnetic stirring or electric stirring; the ultrasonic treatment time is preferably 2 to 40 hours, more preferably 5 to 20 hours; the ultrasound frequency is preferably 20 to 50 kHz.

More preferably, it is 30 to 40 kHz.

[0056]

In the present invention, the solid product obtained after centrifugation is repeatedly washed with deionized water until it becomes neutral to obtain a siloxene aqueous solution, and then further freeze-dried or dried in an inert or vacuum atmosphere to obtain siloxene, which is in a powder state.

[0057]

The present invention also provides a method for preparing silicon-based oxide, comprising the following steps:

[0058]

Calcium silicide is reacted in an acid solution to obtain siloxane

[0059]

Heat treating siloxene at 300-1200 ° C. for 0.5-6 hours to obtain silicon-based oxide;

[0060]

The siloxene is the siloxene material mentioned above.

[0061]

In the present invention, the preparation method of the siloxane material is the same as the preparation method described above, which will not be described in detail herein.

[0062]

Specifically, the silicon-based oxide in the present invention can be prepared by any one of the following two methods:

[0063]

1) heat treating the siloxene at 300-600 ° C. for 0.5-6 hours to obtain silicon-based oxide.

[0064]

In method 1), the temperature of the heat treatment is preferably 300-600 ° C, more preferably 350-550 ° C, and most preferably 400-500 ° C; the time of the heat treatment is preferably 0.5-6 hours, more preferably 1-5 hours, and most preferably 2-4 hours; the present invention achieves the above-mentioned heat treatment temperature by heating, and the heating rate is preferably 2-20 ° C/min, more preferably 3-15 ° C/min, and most preferably 5-10 ° C/min.

The present invention preferably performs the above heat treatment under a vacuum atmosphere, an inert atmosphere, and a reducing atmosphere, or a combination of these atmospheres. Specifically, it may be a vacuum atmosphere, an argon atmosphere, a mixed atmosphere of hydrogen and argon, a hydrogen atmosphere, or a mixed atmosphere of carbon monoxide and nitrogen.

In the present invention, the vacuum degree of the vacuum atmosphere is preferably ≤10-⁵Torr.

The silicon-based oxide obtained by the method is amorphous silicon-based oxide.

[0065]

2) The siloxene or the silicon-based oxide obtained by method 1) is heat-treated at 600-1100 ° C. for 0.5-4 hours to obtain silicon-based oxide.

[0066]

In method 2), the temperature of the heat treatment is preferably 600-1100 ° C, more preferably 850-1050 ° C, and most preferably 850-950 ° C; the time of the heat treatment is preferably 0.5-4 hours, more preferably 1-3.5 hours, and most preferably 2-3 hours; the present invention achieves the above-mentioned heat treatment temperature by heating, and the heating rate is preferably 2-20 ° C/min, more preferably 3-15 ° C/min, and most preferably 5-10 ° C/min.

The present invention preferably performs the above heat treatment under a vacuum atmosphere, an inert atmosphere, and a reducing atmosphere, or a combination of these atmospheres. Specifically, it may be a vacuum atmosphere, an argon atmosphere, a mixed atmosphere of hydrogen and argon, a hydrogen atmosphere, or a mixed atmosphere of carbon monoxide and nitrogen.

In the present invention, the vacuum degree of the vacuum atmosphere is preferably ≤10-⁵Torr.

At a high temperature of 800-1200 ° C., siloxane or the silicon-based oxide in method 1) undergoes a disproportionation reaction, and the obtained silicon-based oxide is a mixture in which silicon particles are uniformly dispersed among amorphous silicon oxides.

[0067]

The present invention also provides a negative electrode material, which is made of materials including silicon-based materials and carbon materials;

[0068]

The silicon-based material includes a siloxane material and/or a silicon-based oxide;

[0069]

The siloxene material is the siloxene material mentioned above, and the silicon-based oxide is the silicon-based oxide mentioned above.

[0070]

In the present invention, the negative electrode material contains carbon, and the mass fraction of carbon in the negative electrode material is preferably 5-60%, more preferably 5-50%, and most preferably 10-50%. Specifically, in an embodiment of the present invention, it can be 5%, 10%, 29%, 35% or 60%.

[0071]

The present invention preferably prepares the negative electrode material according to any one of the following three preparation methods.

[0072]

a) mixing the silicon-based material with the carbon material and performing heat treatment to obtain a negative electrode material.

[0073]

In the present method, the carbon material preferably includes an organic carbon source or graphene oxide, and the organic carbon source preferably includes one or more of sugars, organic acids, asphalt, polypyrrole or polyaniline, and more preferably includes one or more of sucrose, glucose, maltose, citric acid, asphalt, epoxy resin, phenolic resin, acrylic resin and furfural resin; specifically, in an embodiment of the present invention, it can be a mixture of sucrose and glucose, a mixture of maltose and citric acid, a mixture of asphalt and epoxy resin, a mixture of phenolic resin, acrylic acid and furfural resin, a mixture of sucrose, maltose, glucose and citric acid, or a mixture of asphalt, epoxy resin, phenolic resin and furfural resin.

[0074]

In method a), the present invention has no special restriction on the amount of the carbon material used, as long as the carbon content in the prepared negative electrode material is ensured to be between 5% and 60%.

[0075]

In the present invention, the temperature of the heat treatment in the method a) is preferably 600-1100 ° C, more preferably 700-1000 ° C, and most preferably 800-1000 ° C; the time of the heat treatment in the method a) is preferably 1-8 hours, more preferably 3-6 hours, and most preferably 4-5 hours.

[0076]

b) mixing the silicon-based material with the carbon nanomaterial and performing heat treatment to obtain a negative electrode material.

[0077]

In the present invention, the carbon nanomaterial preferably includes one or more of carbon nanotubes, carbon nanofibers, nanographite, graphene, carbon black and nano-activated carbon, and more preferably includes a mixture of carbon nanotubes and carbon nanofibers, a mixture of nanographite and graphene, a mixture of carbon black, nanographite and carbon nanotubes, or a mixture of carbon nanofibers, nanographite, graphene, carbon black and nano-activated carbon; the carbon nanomaterial can be in a powder state or a carbon nanomaterial slurry dispersed in an aqueous solution or an organic solution system.

[0078]

In method b), the present invention has no special limitation on the amount of the carbon material used, as long as the carbon content in the prepared negative electrode material is ensured to be between 5% and 60%.

In the present invention, the mixing in method b) is mechanical mixing, and the mechanical mixing method is a mechanical mixing method commonly used by those skilled in the art.

[0079]

In the present invention, the temperature of the heat treatment in the method b) is preferably 80-1100 ° C, and there are two typical temperature ranges, 80-300 ° C or 600-1100 ° C, more preferably 80-200 ° C or 700-1000 ° C, and most preferably 80-150 ° C or 700-970 ° C; the time of the heat treatment in the method b) is preferably 0.5-12 hours, more preferably 1-6 hours, and most preferably 1-3 hours.

[0080]

c) mixing the silicon-based material with a carbon source and performing chemical vapor deposition to obtain a negative electrode material.

[0081]

In the present invention, the carbon source preferably includes one or more of C1-6 alkanes, C1-6 alkenes and C1-6 alkynes, and more preferably includes one or more of methane, ethylene and acetylene.

The present invention has no special restriction on the amount of the carbon source used in the chemical vapor deposition, as long as the carbon content in the prepared negative electrode material is ensured to be between 5% and 60%.

[0082]

In the present invention, the temperature of the chemical vapor deposition is preferably 600-1100 ° C, more preferably 700-1050 ° C, and most preferably 800-1000 ° C; the time of the chemical vapor deposition is preferably 30-240 min, more preferably 40-150 min, and most preferably 40-90 min.

[0083]

After the chemical vapor deposition process, the negative electrode material obtained is coated with a carbon layer.

[0084]

The present invention provides a siloxene material having a chemical formula shown in Formula 1: Si₆O_xH_y(OH)_{6-y}; $1 \leq x \leq 6$, $1 \leq y \leq 6$; the siloxene material has a Si-O-Si bond, a Si-H bond and a Si-OH bond.

The siloxene material in the present invention has Si-O-Si bonds, Si-H bonds and Si-OH bonds at the same time. The negative electrode material made of the siloxene material in the present invention can effectively suppress the volume expansion problem of silicon, so that the negative electrode material has higher cycle stability, higher first coulomb efficiency and good rate performance.

Experimental results show that the capacity retention rate of the negative electrode material made of silicon-based oxide in the present invention after 200 cycles is between 74% and 86%, the first coulombic efficiency is as high as 84.1%, and the capacity is 1329 mAh/g under 150 mA/g.

[0085]

In order to further illustrate the present invention, a siloxane material, a method for preparing a silicon-based oxide and a negative electrode material provided by the present invention are described in detail below in conjunction with embodiments, but they should not be construed as limiting the scope of protection of the present invention.

[0086]

Example 1

[0087]

2.5 g of calcium silicide powder was weighed, mixed with 250 mL of a 5 mol/L hydrochloric acid aqueous solution under air atmosphere, subjected to 20 kHz ultrasonic reaction for 20 h, then centrifuged, repeatedly washed with deionized water until neutral, and freeze-dried to obtain siloxane powder.

[0088]

The siloxane powder was heated in an Ar atmosphere with a flow rate of 200 sccm, and the temperature was raised to 900 ° C at 5 ° C/min. Ethylene gas with a flow rate of 200 sccm was introduced. After keeping at 900 ° C for 45 minutes, the ethylene gas was turned off, and the sample was cooled to room temperature in a 200 sccm Ar atmosphere to obtain a negative electrode material.

[0089]

The present invention conducts an infrared test on the siloxene obtained in this embodiment, and the result is shown in FIG1 . FIG1 is an infrared image of the siloxene in Example 1 of the present invention. From the infrared spectrum of the siloxene in FIG1 , it can be seen that the siloxene has 465, 807, 1060, and 1180 cm-¹ vibration peaks corresponding to Si-O-Si vibrations, indicating that oxygen is embedded in the Si-Si bond, 643, 875, and 895 cm-¹ are Si-H vibration peaks, and 3200-3400 and 3615 cm-¹ are Si-OH vibration peaks. The infrared spectrum shows that the siloxene prepared in Example 1 of the present invention has Si-O-Si bonds, and Si-H and Si-OH are also present.

[0090]

The present invention performs XRD test on the siloxane and negative electrode material obtained in this embodiment, and the result is shown in FIG2 , which is an XRD graph of the siloxane and silicon-based oxide negative electrode material obtained in Example 1 of the present invention.

As shown in Figure 2, the diffraction peaks of silicon and graphite in the prepared siloxane and negative electrode materials are relatively broad, indicating that the size of the silicon particles is small, the crystallinity of the graphite is poor, and the amorphous SiO_x is not obvious due to the large amount of coated carbon.

[0091]

The present invention carried out transmission electron microscopy (TEM) testing and electron diffraction (SAD) testing on the negative electrode material obtained in this embodiment, and the results are shown in Figures 3 and 4. Figure 3 is a TEM image of the negative electrode material obtained in Example 1 of the present invention; Figure 4 is a SAD image of the negative electrode material obtained in Example 1 of the present invention.

The TEM image shows that nano-scale silicon particles are uniformly dispersed in the amorphous SiO_x, and the SAD image shows that the crystalline material is silicon nanoparticles.

[0092]

The present invention tests the cycle performance of the negative electrode material obtained in this embodiment, and the results are shown in Figures 5 and 6. Figure 5 is the 100th cycle high-rate charge and discharge curve of the negative electrode material in Example 1 of the present invention; Figure 6 is a high-rate cycle performance graph of the negative electrode material in Example 1 of the present invention.

FIG5 shows that the negative electrode material prepared by the present invention can realize fast charge and discharge of lithium-ion batteries. At a rate of 7.5 A/g, fast charge and discharge can be achieved in only about 3 minutes, and the discharge capacity is nearly 360 mAh/g. After 200 cycles, the capacity remains basically unchanged.

The results in Figure 6 show that the material prepared in Example 1 has a charging capacity of 749, 625 and 360 mAh/g at 1.5 A/g, 3.0 A/g and 7.5 A/g rates, respectively.

The results show that the negative electrode material prepared by the present invention has good rate performance and can achieve rapid charging and discharging of the material.

[0093]

Example 2

[0094]

2.5 g of calcium silicide powder was weighed, mixed with 250 mL of 10 mol/L hydrochloric acid aqueous solution under air atmosphere, reacted for 5 h, ultrasonically treated at 50 kHz for 10 h, then centrifuged, repeatedly washed with deionized water until neutral, and vacuum dried to obtain siloxane powder.

[0095]

593 The siloxane powder was heated in an Ar atmosphere with a flow rate of 200 sccm, and the temperature was raised to 850 ° C at a rate of 5 ° C/min. Ethylene gas with a flow rate of 100 sccm was introduced. After keeping at 850 ° C for 30 minutes, the ethylene gas was turned off, and the sample was cooled to room temperature in a 200 sccm Ar atmosphere to obtain a negative electrode material.

[0096]

600 Example 3

[0097]

604 Weigh 2.5 g of calcium silicide powder, mix it with 250 mL of a mixed solution of 0.1 mol/L hydrochloric acid water and ethanol in an air atmosphere, where the volume ratio of water to ethanol is 0.1, treat it with 10 Hz ultrasound for 15 h, then centrifuge it, wash it repeatedly with deionized water until it is neutral, and dry it in an Ar atmosphere to obtain siloxane powder.

[0098]

611 The siloxane powder was heated in an Ar atmosphere with a flow rate of 100 sccm, and the temperature was raised to 850 ° C at a rate of 10 ° C/min. Acetylene gas with a flow rate of 200 sccm was introduced. After being kept at 600 ° C for 30 minutes, the acetylene gas was turned off, and the sample was cooled to room temperature in an Ar atmosphere of 200 sccm to obtain a negative electrode material.

[0099]

618 Example 4

[0100]

622 2.5 g of calcium silicide powder was weighed, mixed with 250 mL of a 5 mol/L hydrochloric acid aqueous solution under air atmosphere, subjected to ultrasonic reaction at 40 kHz for 15 h, then centrifuged, repeatedly washed with deionized water until neutral, and freeze-dried to obtain siloxane powder.

[0101]

628 The siloxane powder was heated in an Ar atmosphere with a flow rate of 200 sccm, and the temperature was raised to 1000 ° C at 15 ° C/min. Methane gas with a flow rate of 150 sccm was introduced. After being kept at 1100 ° C for 40 minutes, the methane gas was turned off, and the sample was cooled to room temperature in a 200 sccm Ar atmosphere to obtain a negative electrode material.

[0102]

Example 5

[0103]

Weigh 2.5 g of calcium silicide powder, mix it with 250 mL of a mixed solution of 2 mol/L hydrochloric acid water and ethanol under air atmosphere, wherein the volume ratio of water to ethanol is 1, stir and react for 20 h, then centrifuge, repeatedly wash with deionized water until neutral, and obtain siloxane powder after vacuum drying.

[0104]

The siloxane powder was heated in a N₂ atmosphere with a flow rate of 200 sccm, and the temperature was raised to 900 ° C at 10 ° C/min. Ethylene gas with a flow rate of 20 sccm was introduced. After being kept at 900 ° C for 4 hours, the ethylene gas was turned off, and the sample was cooled to room temperature in a 200 sccm N₂ atmosphere to obtain the negative electrode material.

[0105]

Embodiments 6 to 10

[0106]

The siloxenes in Examples 1 to 5 were mixed with the carbon precursors in Table 1, respectively, and then heat-treated according to the heat treatment parameters in Table 1 to obtain negative electrode materials.

[0107]

Examples 11 to 15

[0108]

The siloxenes in Examples 1 to 5 were mixed with the carbon nanomaterials in Table 1 respectively, and then heat-treated according to the heat treatment parameters in Table 1 to obtain negative electrode materials.

[0109]

Table 1 Preparation parameters of negative electrode materials in Examples 6 to 15 of the present invention

[0111]

Embodiments 16 to 30

[0112]

The siloxene in Examples 1 to 15 is first heat-treated according to the heat treatment parameters in Table 2 to obtain heat-treated siloxene, i.e., silicon-based oxide;

[0113]

Then, the silicon-based oxides were respectively prepared according to the preparation methods of the negative electrode materials in Examples 1 to 15 to obtain negative electrode materials, except that the siloxanes in Examples 1 to 15 were replaced by the silicon-based oxides in Examples 16 to 30 in sequence.

[0114]

Table 2 Thermal treatment parameters of siloxane in Examples 16 to 30 of the present invention

[0117]

The present invention tests the electrochemical properties of the negative electrode materials obtained in Examples 1 to 30, and the results are shown in Table 3.

[0118]

Table 3 Electrochemical properties of negative electrode materials obtained in Examples 1 to 30 of the present invention

[0121]

The above is only a preferred embodiment of the present invention. It should be pointed out that for ordinary technicians in this technical field, several improvements and modifications can be made without departing from the principle of the present invention. These improvements and modifications should also be regarded as the scope of protection of the present invention.