DESCRIPTION KR20210128516A

{Two - Dimensional Silicon Nanostructures for storage of sodium ion and electrode comprising the same}

[0001]

The present invention relates to a two - dimensional silicon nanostructure for sodium ion storage and an electrode comprising the same, and more particularly, to a two - dimensional silicon nanostructure for sodium ion storage having high storage efficiency and electrochemical stability by intercalating sodium in the form of ions between sheet - shaped nanostructures and an electrode comprising the same.

[0002]

As demand for secondary batteries for energy storage devices, electric vehicles, mobile phones, etc. increases day by day, research is actively being conducted to replace lithium - ion - based secondary batteries, which are expensive and have unstable supply and demand of raw materials.

[0003]

Sodium accounts for 2.64 wt% of the earth's crust, making it about 1000 times more abundant than lithium, and thus has the advantage of being relatively inexpensive. In addition, sodium is a group 1 alkali metal like lithium, and has similar physical and chemical properties, so not only can a secondary battery be constructed by simply replacing lithium with sodium, but most of the electrode technology, cell assembly technology, and equipment infrastructure used in existing lithium secondary batteries can be utilized.

[0004]

However, the atomic radius of the sodium ion is about 130% larger than that of the lithium ion, it is 330% heavier, and has a potential 0.33 V higher than that of lithium, which makes it disadvantageous in terms of energy characteristics compared to using lithium ions.

For example, graphite, a representative negative electrode material for lithium - ion batteries, is almost inactive in sodium - ion batteries due to a mismatch between the internal lattice distance and sodium ions, which have a larger ionic radius than lithium ions, and shows low capacity.

[0005]

Silicon (Si), a representative alloy material used in lithium - ion secondary batteries, can store a large amount of lithium by reacting with lithium to form a Li₁₅Si₄ phase when used as an anode material for lithium - ion storage, thereby exhibiting a high theoretical capacity of approximately 4,212 mAh/g.

Similarly, it is theoretically possible to form a NaSi phase with sodium, but it has not been demonstrated whether an electrochemical reaction is possible. Therefore, the silicon has not received much attention as a cathode material for sodium ion storage, and research on it is insufficient.

[0006]

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[0007]

Accordingly, the problem to be solved by the present invention is to provide a sodium storage material and an electrode including the same.

[0008]

To solve the above problems, the present invention provides a two - dimensional silicon nanostructure for sodium ion storage comprising a siloxene compound including one or more siloxenes.

[0009]

In one embodiment of the present invention, the siloxane is in the form of nanosheets.

[0010]

In one embodiment of the present invention, the siloxane compound has a structure in which one or more siloxanes are laminated.

[0011]

In one embodiment of the present invention, the stacking spacing between the siloxanes is greater than the atomic size of a sodium ion.

[0012]

In one embodiment of the present invention, the lateral size of the particle of the siloxene compound is 500 to 10,000 nanometers.

[0013]

In one embodiment of the present invention, the two-dimensional silicon nanostructure for sodium ion storage has no pores of 2 to 50 nm, and the siloxane compound includes a functional group containing oxygen.

[0014]

In one embodiment of the present invention, the functional group including oxygen is included in an amount of 20 wt% to 50 wt% based on the total weight of the siloxene compound, and the functional group including oxygen is present outside the planar structure of the siloxene compound.

[0015]

The present invention also provides an electrode comprising the material described above, wherein the electrode is a sodium ion battery negative electrode.

[0016]

The present invention also provides a method for manufacturing a two-dimensional silicon nanostructure for storing sodium ions, comprising the steps of: mixing CaSi₂ with an acid solution and reacting it; and obtaining a siloxane compound synthesized in the reacting step, wherein the calcium ion of the CaSi2 is de-intercalated from the siloxane compound in the reacting step.

[0017]

In one embodiment of the present invention, the acid solution in the reacting step is hydrochloric acid (HCl), and the reaction formula of the reaction is as follows (1):

[0018]

3CaSi₂+ 6HCl + 3H₂O → Si₆H₃(OH)₃ + 3CaCl₂ + 3H₂↑ (1)

[0019]

The above reaction step is carried out at room temperature, and the hydrochloric acid (HCl) is used in excess of the equivalent ratio of the above reaction formula.

[0020]

The electrode material for sodium ion storage of the present invention comprises a siloxane compound having a structure in which nanosheet-shaped siloxanes are laminated, and intercalation/de-intercalation of sodium ions is easy in the siloxane compound, and has an excellent sodium ion storage capacity.

A sodium ion battery and a sodium ion capacitor including the above-mentioned sodium ion storage electrode material have the advantage of securing high capacity expression and stability compared to a sodium ion battery and a sodium ion capacitor including other silicon-based electrode materials.

[0021]

Figure 1 shows a reaction schematic diagram (a) of an electrode material for sodium ion storage manufactured according to one embodiment of the present invention, SEM (b and c), TEM (d) photographs, nitrogen adsorption/desorption (e and f), and XRD experiment (g) results.

Figure 2 shows the results of FT-IR (a), Raman spectrum (b), and XPS experiments (c, d, and e) of a sodium ion storage electrode material manufactured according to one embodiment of the present invention.

Figure 3 shows a CV graph (a) and a life characteristic graph (b) of a cathode system of one embodiment of the present invention.

Figure 4 shows the results of measuring the sodium ion storage capacity of graphite, which is widely used as an anode material in lithium ion secondary batteries.

[0022]

Hereinafter, the present invention will be described with reference to the attached drawings.

However, the present invention can be implemented in various different forms and is therefore not limited to the embodiments described herein.

And in order to clearly explain the present invention in the drawings, parts unrelated to the explanation are omitted, and similar parts are given similar drawing reference numerals throughout the specification.

[0023]

Throughout the specification, when a part is said to be "connected (connected, contacted, coupled)" to another part, this includes not only cases where it is "directly connected" but also cases where it is "indirectly connected" with another part in between.

Additionally, when a part is said to "include" a component, this does not mean that it excludes other components, unless otherwise specifically stated, but rather that it may include other components.

[0024]

The terminology used herein is for the purpose of describing particular embodiments only and is not intended to limit the invention.

Singular expressions include plural expressions unless the context clearly indicates otherwise.

In this specification, it should be understood that terms such as “include” or “have” are intended to specify the presence of a feature, number, step, operation, component, part or combination thereof described in the specification, but do not exclude in advance the possibility of the presence or addition of one or more other features, numbers, steps, operations, components, parts or combinations thereof.

[0025]

The present invention provides a nanostructure comprising siloxane as a material for storing sodium ions.

In the present invention, “siloxene” means a material having a basic skeleton in which a plurality of hexagonal rings composed of silicon (Si) elements are bonded and existing in a planar form, for example, in the form of a nanosheet.

[0026]

In the present invention, the “siloxene compound” is a compound in which one or more siloxenes are randomly distributed.

[0027]

It may be in the form of a tangle, a wide plate, or a shape aligned in one direction.

[0028]

It can be, for example, laminated in one direction.

[0029]

It is preferable that the spacing between the stacked one or more siloxane nanosheets is at a level where sodium can be intercalated or deintercalated in ionic form.

In particular, considering the size of the sodium ion, the spacing between the siloxane nanosheets is preferably 0.37 nm or more.

In the present invention, “ intercalation/de - intercalation ” means a phenomenon in which molecules, atoms and/or ions are inserted/released into the interlayer gap in a material having a layered structure, and the product of intercalation is called an interlayer compound.

[0030]

The siloxene compound of the sodium ion storage material according to one embodiment of the present invention may include a functional group containing oxygen, and through this functional group containing oxygen, the sheet - shaped siloxene compound can prevent aggregation between sheets by a steric effect and electrostatic repulsion, thereby maintaining a constant gap between the sheets.

[0031]

The functional group containing the oxygen is, for example, a group consisting of a hydroxyl group, a carbonyl group, an aldehyde group, a carboxylic acid ester group, a hydroperoxy group, and combinations thereof.

[0032]

One or more selected, for example, may be a hydroxyl group.

[0033]

In one embodiment of the present invention, the siloxane compound can be synthesized by a method using the reaction described in the following reaction scheme 1, for example, a method of de-intercalating calcium (Ca) ions present in CaSi₂ using hydrochloric acid (HCl):

[0034]

[Reaction Formula 1]

[0035]

3CaSi₂+ 6HCl + 3H₂O → Si₆H₃(OH)₃ + 3CaCl₂ + 3H₂↑

[0036]

Depending on the temperature at which the process of synthesizing a siloxene compound using the above method is performed, the inclusion of a functional group containing oxygen in the siloxene can be controlled, and the process of synthesizing the siloxene compound can be performed at 0 ° C. or higher, for example, 20 ° C. to 30 ° C., for example, 25 ° C.

[0037]

For example, if the temperature of the process for synthesizing the above siloxane compound is below 0 ° C, polysilane, which is a structure in which only hydrogen exists in a vertical direction in the hexagonal multiple structure of silicon, is formed, so a functional group containing oxygen may not exist.

In another example, when the temperature of the process for synthesizing the siloxene compound is room temperature (25 ° C), the synthesized siloxene compound may have an oxygen-containing functional group suitably substituted, and the oxygen-containing functional group may be included in a range of 20 to 50 wt% (for example, 33 wt%) based on the total weight of the synthesized siloxene compound. Additionally, the lateral size of the particles of the siloxene compound may be 500 to 10,000 nanometers.

[0038]

In particular, in the present invention, CaSi2 is reacted with an acid solution (hydrochloric acid) in excess of the equivalent ratio at room temperature to suppress excessive oxidation reaction, thereby maintaining the two-dimensional siloxane planar structure and introducing a large amount of oxygen functional groups outside the planar structure.

[0039]

The electrode material for sodium ion storage of the present invention can be used as an electrode material for a sodium ion secondary battery described below.

[0040]

The present invention is described in more detail through the following examples and experimental examples.

[0042]

Example 1

[0043]

Manufacturing of materials for sodium ion storage

[0044]

A method for producing a sodium ion storage material according to one embodiment of the present invention comprises the steps of mixing CaSi₂ with an acid solution and reacting it; and obtaining a siloxane compound synthesized in the reacting step, wherein in the reacting step, calcium ions of the CaSi2 are de-intercalated from the siloxane compound produced.

[0045]

A method for manufacturing a sodium ion storage material according to one embodiment of the present invention is described in more detail as follows.

[0046]

20 g of CaSi₂ was slowly mixed with 80 g of concentrated hydrochloric acid (HCl, 37%) at 25 ℃, stirred for 12 hours under a nitrogen atmosphere, and then washed with acetone.
Afterwards, the siloxane compound was obtained by drying in a vacuum at 110 ° C for one day, thereby manufacturing an electrode material for sodium ion storage (Fig. 1 (a)).

[0047]

Example 2

[0048]

The siloxane compound recovered in Example 1 was mixed with a carboxymethyl cellulose sodium salt binder and a super P conductive agent in a mass ratio of 7:1:2, and then applied onto a carbon cloth (1.54 cm²) current collector to have an area loading of 4 mg/cm² to manufacture an electrode.
This electrode was tested as a working electrode in a CR2032 coin cell, with sodium metal as a counter electrode, glass fiber membrane (GFC) as a separator, and 1 M sodium perchlorate dissolved in ethylene carbonate:propylene carbonate (50:50, v/v) solution (200 mL) as an electrolyte.
To analyze the electrochemical properties, cyclic voltammetry (CV) was used in the range of 0.01 – 2.5 V vs.
The scan was performed at a rate of 0.1 mV/s in the Na/Na⁺ range, and the galvanostatic cycling with potential limitation (GCPL) method was used, also in the range of 0.01 – 2.5 V vs.
Charge and discharge were repeated at a current density of 200 mA/g in the Na/Na⁺ range.

[0050]

Experimental Example 1

[0051]

Morphological analysis of electrode materials for sodium ion storage

[0052]

1.1 Analysis of SEM and TEM results

[0053]

In order to observe the surface and morphology of the sodium ion storage electrode material obtained in Example 1 above, a scanning electron microscope (SEM) and a transmission electron microscope (TEM) were used.

[0054]

As a result of the observation, it was found that the siloxane compound was in the form of two-dimensional sheets laminated (Fig. 1 (b) and (c)), and the size of the sheets from the peeled and observed sample was found to be approximately 500 to 10,000 nm (Fig. 1 (d)).

[0056]

1.2 Analysis of nitrogen adsorption/desorption experiment results

[0057]

In order to observe the surface area and pore inclusion of the siloxene compound, a sodium ion storage material obtained in Example 1, a nitrogen adsorption/desorption experiment was performed.

[0058]

As a result of the experiment, it was confirmed that the surface area calculated from the results of the nitrogen adsorption/desorption experiment was very small, approximately 7 m²/g (Fig. 1 (e)), and it was confirmed that no pores existed in the range of approximately 2 to 50 nm (Fig. 1 (f)).

Therefore, it was confirmed that a sodium ion secondary battery with excellent reversible stability can be implemented because there are no pores contributing to the generation of sodium metal and SEI (solid-electrolyte-interphase) during discharge.

[0060]

1.3 XRD Results Analysis

[0061]

In order to confirm whether de-intercalation of Ca²⁺ was properly achieved in the sodium ion storage electrode material obtained in Example 1, the XRD pattern was analyzed.

[0062]

As a result of the experiment, it was confirmed that the peak corresponding to the existing CaSi₂ did not exist after HCl treatment, and it was confirmed that de-intercalation of Ca²⁺ was well achieved (Fig. 1 (g)).

[0063]

From the XRD results of Fig. 1 (h), it can be seen that the peak at 17.3° of the siloxene compound, which is a sodium ion storage material according to the present invention, is due to the graphitic stacking (001) of two-dimensional siloxene, and that the spacing between siloxene layers is approximately 0.52 nm, which is greater than the size of the solvated sodium ion of 0.37 nm. Also, the peak at 28° is due to the in-plane ordering (100) of the two-dimensional siloxane, which is composed of a hexagonal structure of Si (Si₆ ring structure) that is regularly arranged with a spacing of 0.32 nm. The remaining peaks are caused by small amounts of Si impurities present in CaSi₂.

[0065]

1.4 FT-IR Results Analysis

[0066]

In order to confirm the functional groups present in the sodium ion storage electrode material obtained in Example 1 above, the results of FT-IR were analyzed.

[0067]

As a result of the analysis, peaks corresponding to wavenumbers 2150 cm⁻¹ and 3000~3500 cm⁻¹ were confirmed, and through this, it was found that surface functional groups such as oxygen functional groups or hydroxyl groups existed in the siloxene compound (Fig. 2 (a)). In particular, the present invention can maintain a stable two-dimensional silicon structure while inducing oxygen functional groups on the surface. That is, it is known that high temperatures can cause excessive oxidation, which can cause oxidation and damage to two-dimensional structures, but the sodium ion storage material according to the present invention is synthesized at room temperature and has a wide two-dimensional structure, large gaps, a surface without micropores, and a highly stacked two-dimensional structure. As a result, the intercalation capacity of sodium ions can be increased.

[0069]

1.5 Analysis of Raman spectrum results

[0070]

In order to confirm whether multiple hexagonal structures (in - plane structures) exist in the sodium ion storage electrode material obtained in the above Example 1, the Raman spectrum was analyzed.

[0071]

The analysis results showed a gentle peak due to the vibrational energy of Si - Si bonds between 400 cm^{- 1} and 550 cm^{- 1} (Fig. 2 (b)). In particular, the peak at 470 cm^{- 1} indicates Si composed of a hexagonal structure (Si₆ ring structure). Therefore, it was confirmed that the synthesis at room temperature aimed at partial oxidation proceeded with the oxidation reaction only outside the hexagonal in - plane structure. Contrary to popular belief, de - intercalation of Ca at room temperature did not affect the in - plane structure of siloxane, which is thought to be because the oxidation reaction was inhibited by using an excess (2 - fold) of concentrated hydrochloric acid.

[0073]

1.6. XPS Results Analysis

[0074]

In order to confirm the mass content of the surface of the sodium ion storage electrode material obtained in Example 1 above, the XPS results were analyzed.

[0075]

As a result of the experiment, the mass of calcium was 1.21 atom%, the mass of chlorine was 2.82 atom%, which was almost non - existent, indicating that Ca de - intercalation was well achieved. Oxygen was 33.37 wt% (45.6 atom%), which was within the range of 20 to 50 wt%, indicating that a siloxane compound containing a large amount of oxygen functional groups and hydroxyl groups was well formed. The high - resolution spectra of Si 2p and O 1s confirmed the presence of bonds of Si - Si (99 eV), Si - O (102 eV), Si - OH (531 eV), and Si - O (533 eV) (Fig. 2 (c), (d), and (e)).

[0076]

The contents of the elements in the experimental results are shown in Table 1 below:

[0077]

element
Content (mass%)
Content (atom%)
carbon
3.45
6.28
oxygen
33.37
45.6
silicon
56.46
44.09
calcium

2
.21
1.21
chlorine

4
.51
2.82
Total
100
100

[0078]

Experimental example 2

[0079]

Sodium ion storage capacity experiment

[0080]

In order to evaluate the stability and storage characteristics of the cathode system of the present invention in the coin cell manufactured in Example 2 above, CV (cyclic voltammetry) and life characteristics were measured, and the results are shown in Fig. 3.

[0081]

As a result of the experiment, the cathode system of the present invention shows a gentle curve without a special redox peak (a in Fig. 3), which confirms that storage of sodium ions through intercalation is the main mechanism.

[0082]

The results of the charge - discharge test using GCPL showed that in the initial cycle, instability was observed due to some silica (SiO₂) impurities or side reactions of the electrolyte, but after a certain number of cycles, the discharge capacity was maintained very stably up to 500 cycles (Fig. 3b).

[0083]

Figure 4 shows the results of measuring the sodium ion storage capacity of graphite, which is widely used as an anode material in lithium ion secondary batteries.

[0084]

Referring to Figure 4, it can be confirmed that under the same GCPL conditions, graphite cannot store sodium ions at all. As mentioned above, the two - dimensional structure of graphite has an interlayer spacing of less than 0.37 nm, making intercalation of solvated sodium ions impossible.

[0085]

The above description of the present invention is for illustrative purposes only, and those skilled in the art will appreciate that the present invention can be easily modified into other specific forms without changing the technical idea or essential characteristics of the present invention.
Therefore, it should be understood that the embodiments described above are exemplary in all respects and not limiting.
For example, each component described as a single entity may be implemented in a distributed manner, and likewise, components described as distributed may be implemented in a combined manner.

[0086]

The scope of the present invention is indicated by the claims described below, and all changes or modifications derived from the meaning and scope of the claims and their equivalent concepts should be interpreted as being included in the scope of the present invention.