DESCRIPTION KR102326642B1

Cathode for lithium - sulfur secondary battery comprising siloxene compound

[0001]

The present invention relates to a cathode for a lithium - sulfur secondary battery comprising a siloxane compound including one or more siloxanes and a cathode active material. Specifically, the present invention relates to a cathode for a lithium - sulfur secondary battery, to which a siloxane compound and a cathode active material are added, which are effective in fixing polysulfide, an intermediate product of a lithium - sulfur secondary battery.

[0002]

Recently, as the demand for portable electronic devices, electric vehicles, and energy storage systems has increased explosively, research on secondary batteries is actively underway. Since Sony launched the lithium - ion secondary battery (LIB) using graphite - based anode materials in 1991, lithium - ion secondary batteries have been known as the best secondary batteries to this day. However, recently, the battery capacity required for smartphones and electric vehicles has far exceeded the performance of lithium - ion secondary batteries, so the development of lithium - sulfur secondary batteries with higher energy density is deemed urgent.

[0003]

Lithium - sulfur secondary batteries are currently being actively researched as one of the most promising next - generation batteries because they are inexpensive, use sulfur, which is abundant on Earth, as a cathode active material, and have a high theoretical capacity (1,672 mAh/g).

41 The biggest obstacle to commercialization of lithium-sulfur secondary batteries is the elution of polysulfides, which are intermediate products, into the electrolyte, which causes performance degradation such as a decrease in the active material in the cathode and a decrease in the overall discharge capacity. Accordingly, the development of technology to suppress the dissolution of polysulfides while simultaneously maximizing sulfur utilization is urgently needed. In addition, most recent studies on lithium-sulfur secondary batteries use cathodes with low sulfur content (<2 mg sulfur/cm²), in which case the theoretical capacity is only about 3.2 mAh/cm², which is less than the capacity of commercial lithium-ion secondary batteries (4 mAh/cm²). Since the dissolution of the polysulfide mentioned above becomes more severe when the loading value is high, it is very important to test under high loading conditions (>6 mg sulfur/cm²) when developing a cathode capable of dissolution suppression.

[0004]

59 One object of the present invention is to provide a positive electrode for a lithium-sulfur secondary battery comprising a siloxane compound.

[0005]

64 Another object of the present invention is to provide a method for producing a positive electrode for a lithium-sulfur secondary battery comprising a siloxane compound.

[0006]

70 In order to solve the problems of polysulfide dissolution and low sulfur loading of the lithium-sulfur secondary battery mentioned above, the present invention was completed by discovering that a siloxane compound added to the positive electrode is effective in fixing polysulfide.

[0007]

77 One aspect of the present invention provides a cathode for a lithium-sulfur secondary battery comprising a siloxane compound including at least one siloxane and a cathode active material.

[0008]

In one embodiment of the present invention, the siloxane may be in the form of a nanosheet.

[0009]

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

[0010]

In one embodiment of the present invention, the stacking interval between the one or more siloxanes may be 0.2 nm or more.

[0011]

In one embodiment of the present invention, the siloxene compound may include a functional group containing oxygen.

[0012]

In one embodiment of the present invention, the oxygen - containing functional group of the siloxene compound can bind to polysulfide.

[0013]

In one embodiment of the present invention, the siloxane compound may be included in an amount of 0.1 wt% to 25 wt% based on the total weight of the positive electrode for a lithium - sulfur secondary battery.

[0014]

In one embodiment of the present invention, the positive electrode active material may include any one selected from the group consisting of inorganic sulfur (S₈, elemental sulfur), sulfur series compounds, and combinations thereof.

[0015]

In one embodiment of the present invention, the positive electrode for the lithium - sulfur secondary battery may include a current collector.

[0016]

In one embodiment of the present invention, the positive electrode for the lithium - sulfur secondary battery may additionally include a binder and/or a conductive material.

[0017]

One aspect of the present invention provides a lithium - sulfur secondary battery including the positive electrode for the lithium - sulfur secondary battery.

[0018]

One aspect of the present invention provides a method for producing a positive electrode for a lithium - sulfur secondary battery, comprising: a step of producing a siloxene compound; a step of mixing and processing the siloxene compound and a positive electrode active material to produce a positive electrode for a lithium - sulfur secondary battery;

[0019]

In one embodiment of the present invention, the step of preparing the siloxene compound can be performed at a temperature of 0 ° C. or higher.

[0020]

The present invention provides a positive electrode for a lithium - sulfur secondary battery containing a siloxene compound, thereby fixing polysulfide, which is an intermediate product during charging and discharging of a lithium - sulfur secondary battery, to the positive electrode to suppress its dissolution, and increasing the sulfur content, which is a positive electrode active material, thereby enabling the provision of a lithium - sulfur secondary battery having high capacity and high energy density.

[0021]

The effects of the present invention are not limited to the effects described above, and should be understood to include all effects that can be inferred from the detailed description of the present invention or the composition of the invention described in the claims.

[0022]

Figure 1 shows a reaction schematic diagram (a) of a siloxane compound 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 siloxane compound manufactured according to one embodiment of the present invention.

Figure 3 shows the results of an experiment on the sulfur active material adsorption capacity of a siloxane compound manufactured according to one embodiment of the present invention.

Figure 4 shows the results of a cycling test of a lithium - sulfur secondary battery manufactured according to one embodiment of the present invention and a comparative example.

Figure 5 shows a separator and a lithium metal portion of a lithium - sulfur secondary battery manufactured according to one embodiment of the present invention and a comparative example.

Figure 6 shows the CV (a to d) and GCPL (e) experimental results of lithium - sulfur secondary batteries manufactured according to one embodiment and a comparative example of the present invention.

Figure 7 shows the XPS experimental results of lithium - sulfur secondary batteries manufactured according to one embodiment and a comparative example of the present invention.

[0023]

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 that are not related to the explanation are omitted.

[0024]

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.

[0025]

212 When it is said in this specification that a part such as a layer, film, region, or plate is “ over ” another part, this includes not only the case where it is “ directly over ” the other part, but also the case where there is another part in between.

[0026]

218 The terminology used herein is for the purpose of describing particular embodiments only and is not intended to limit the invention.
220 Singular expressions include plural expressions unless the context clearly indicates otherwise.

[0028]

225 One aspect of the present invention provides a cathode for a lithium - sulfur secondary battery comprising a siloxane compound including one or more siloxanes and a cathode active material.

[0029]

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

[0030]

237 In the present invention, the “ siloxene compound ” may be in the form of one or more siloxenes randomly distributed, aligned in a wide plate, or aligned in one direction, for example, in the form of being laminated in one direction.

[0031]

243 The stacking gap between the one or more stacked siloxanes provides a space capable of adsorbing and/or fixing polysulfide, an intermediate product generated during charging and discharging of a lithium - sulfur secondary battery.

[0032]

249 The spacing between the one or more laminated siloxanes may be 0.2 nm or more, for example, 0.4 nm or more.

[0033]

The above siloxene compound may contain a functional group containing oxygen.

[0034]

The functional group containing oxygen of the above siloxene compound can bind to the polysulfide.

[0035]

The functional group containing the oxygen may be, for example, one or more selected from the group consisting of a hydroxyl group, a carbonyl group, an aldehyde group, a carboxylic acid ester group, a hydroperoxy group, and combinations thereof, for example, a hydroxyl group.

[0036]

The functional group including the oxygen may be included in an amount of 20 wt% to 50 wt%, for example, 33 wt%, based on the total weight of the siloxene compound.

[0037]

As used herein, “polysulfide” includes both polysulfide ions (S_x^{2-,}, where x is 8, 6, 4 or 2) and lithium polysulfide (Li₂S_x or LiS_x⁻, where x is 8, 6, 4 or 2).

[0038]

Most of the lithium-sulfur secondary battery research conducted to date has utilized low sulfur contents (≤2 mg/cm²), so even if 100% efficiency is assumed, the areal capacity is approximately 3.35 mAh/cm², which is lower than the maximum areal capacity of existing lithium-ion secondary batteries (approximately 4 mAh/cm²).

[0039]

Therefore, in order to develop a lithium-sulfur secondary battery with high energy density, the sulfur content must be 6 mg/cm² or higher, the mass ratio of the sulfur active material in the cathode and the sulfur utilization rate must be maximized, and the mass of the electrolyte in the battery must be minimized.

[0040]

302 In lithium - sulfur secondary batteries, when discharged, the cyclic S₈ is converted into linear lithium polysulfide (Li₂S_x, where x is 3 to 8), and a stepwise reduction behavior is exhibited at a specific voltage.
306 Therefore, there is a problem that when an intermediate of lithium polysulfide is formed during charge/discharge and the intermediate is dissolved in the organic electrolyte and eluted or an insoluble final product (Li₂S) is deposited inside and on the surface of the positive electrode pores, it leads to a decrease in positive electrode active material and a decrease in capacity.

[0041]

314 The functional group containing the oxygen is present in a direction perpendicular to the basic skeleton of the siloxene compound, and helps in the adsorption of lithium polysulfide, which is an intermediate product of a lithium - sulfur secondary battery, thereby controlling the elution of lithium polysulfide into the organic electrolyte.

[0042]

321 The degree of substitution of the functional group containing the oxygen can be controlled by controlling the synthesis temperature of the siloxene compound.
323 For example, a siloxane compound synthesized at room temperature can be used as a cathode for a lithium - sulfur secondary battery to effectively control the elution of polysulfide into the organic electrolyte.

[0043]

329 The siloxane compound of the present invention can easily induce penetration of linear lithium polysulfide, and the functional groups containing oxygen facilitate trapping of polysulfide through adsorption, thereby preventing loss of sulfur active material in the positive electrode and maximizing utilization efficiency.

[0044]

336 In one embodiment of the present invention, the width of the siloxene compound may be 0.02 μm² to 100 μm²_,, for example, 0.04 μm² to 60 μm², and the thickness of the siloxene compound may be 0.2 μm to 12 μm, for example, 0.5 μm to 8 μm.

[0045]

In one embodiment of the present invention, the siloxane compound may be included in an amount of 0.1 wt% to 25 wt%, for example, 0.2 wt% to 21 wt%, for example, 0.6 wt% to 14.6 wt%, based on the total weight of the positive electrode for a lithium-sulfur secondary battery.

[0046]

If the above siloxane compound is included in an amount of less than 0.1 wt%, the adsorption capacity of polysulfide may be insufficient, and if it is included in an amount of more than 25 wt%, the performance may be further reduced due to low electrical conductivity of the anode.

[0047]

In one embodiment of the present invention, the cathode active material may be any one selected from the group consisting of inorganic sulfur (S₈, elemental sulfur), sulfur compounds, for example, cyclic-S₈, Li₂S₆ dissolved in catholyte, organosulfur compounds, and carbon-sulfur polymers ((C₂S_x)_n, x is 2.5 to 50, n≥2), and combinations thereof, for example, Li₂S₆.

[0048]

The above lithium-sulfur secondary battery stores and generates electrical energy by utilizing an oxidation-reduction reaction in which the oxidation number of S decreases as the S-S bond is broken during a reduction reaction (during discharge) and the oxidation number of sulfur (S) increases during an oxidation reaction (during charge) and the S-S bond is formed again.

[0049]

In one embodiment of the present invention, the sulfur may be included in an amount of 4 mg/cm² or more, for example, 6 mg/cm² to 10 mg/cm².

If the above sulfur is included at less than 4 mg/cm², it may exhibit a low energy density that makes commercialization difficult.

[0050]

382 In one embodiment of the present invention, the positive electrode for the lithium - sulfur secondary battery may include a current collector.

[0051]

388 The above current collector acts as a passage to transfer electrons from the outside to cause an electrochemical reaction in the active material or to receive electrons from the active material and allow them to flow to the outside, and is not particularly limited as long as it is conductive and does not cause a chemical change in the battery.
393 For example, it may include any one selected from the group consisting of carbon (C), nickel (Ni), stainless steel (SUS), aluminum (Al), molybdenum (Mo), chromium (Cr), titanium (Ti), and combinations thereof, for example, carbon (C).

[0052]

399 In one embodiment of the present invention, the positive electrode for the lithium - sulfur secondary battery may additionally include a binder and/or a conductive material.

[0053]

405 The above binder is added to bind the active material and the conductive material, and the active material and the current collector, and may be a thermoplastic resin or a thermosetting resin.
408 The above binder is, for example, polyethylene, polypropylene, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), styrene - butadiene rubber (SBR), tetrafluoroethylene - perfluoro alkyl vinyl ether copolymer, vinylidene fluoride - hexafluoropropylene copolymer, vinylidene fluoride - chlorotrifluoroethylene copolymer, ethylene - tetrafluoroethylene copolymer, polychlorotrifluoroethylene, vinylidene fluoride - pentafluoro propylene copolymer, propylene - tetrafluoroethylene copolymer, ethylene - chlorotrifluoroethylene copolymer, vinylidene fluoride - hexafluoropropylene - tetrafluoroethylene copolymer, vinylidene fluoride - perfluoromethyl vinyl ether - tetrafluoro ethylene copolymer, ethylene - acrylic acid copolymer, polyvinyl alcohol (PVA), polyacrylic acid (PAA), polymethacrylic acid (PMA), Any one selected from the group consisting of polymethyl methacrylate (PMMA), polyacrylamide (PAM), polymethacrylamide, polyacrylonitrile (PAN), polymethacrylonitrile, polyimide (PI), alginic acid, alginate, chitosan, carboxymethyl cellulose (CMC), starch, hydroxypropyl cellulose, regenerated cellulose, polyvinyl pyrrolidone, and combinations thereof, for example, polyvinylidene fluoride (PVDF), but is not limited

thereto, and any one that can be used as a binder in the art is possible.

[0054]

The conductive material is not particularly limited as long as it is conductive and does not cause a chemical change in the battery, and examples thereof include any one selected from the group consisting of graphite such as natural graphite or artificial graphite; carbon black such as carbon black, acetylene black, Ketjen black, Denka black, channel black, furnace black, lamp black, summer black, and the like; graphene; conductive fibers such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), carbon fibers, or metal fibers; metal powders such as carbon fluoride, aluminum, and nickel powder; conductive whiskers such as zinc oxide and potassium titanate; conductive metal oxides such as titanium oxide; polyphenylene derivatives, and combinations thereof. For example, Super P may be used.

[0056]

One aspect of the present invention provides a lithium - sulfur secondary battery including a positive electrode for a lithium - sulfur secondary battery.

[0057]

The above lithium - sulfur secondary battery includes a cathode, an anode, and an electrolyte and a separator present between them.

[0058]

The above positive electrode may be a positive electrode for a lithium - sulfur secondary battery according to one embodiment of the present invention.

[0059]

The composition of the negative electrode, separator, and electrolyte of the above lithium - sulfur secondary battery is not particularly limited in the present invention, and follows what is known in the field.

[0060]

The above negative electrode includes a negative active material formed on a negative electrode current collector.

[0061]

The above negative electrode current collector may include any one selected from the group consisting of carbon (C), nickel (Ni), stainless steel (SUS), aluminum (Al), molybdenum (Mo), chromium (Cr), titanium (Ti), and combinations thereof, and may include, for example, carbon (C).

[0062]

As the negative electrode active material, a lithium metal or lithium alloy that can reversibly intercalate or de-intercalate lithium ions (Li⁺) and can reversibly form a lithium-containing compound by reacting with lithium ions can be used.

[0063]

The above lithium alloy may be an alloy of a metal selected from the group consisting of, for example, lithium (Li) and sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), francium (Fr), beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), radium (Ra), aluminum (Al), and tin (Sn).

[0064]

The above negative electrode may additionally include a binder for bonding the negative electrode active material and the conductive material and for bonding to the current collector.
The above binder is added to bind the active material and the conductive material, and the active material and the current collector, and may be a thermoplastic resin or a thermosetting resin.
The above binder is, for example, polyethylene, polypropylene, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), styrene-butadiene rubber (SBR), tetrafluoroethylene-perfluoro alkyl vinyl ether copolymer, vinylidene fluoride-hexafluoropropylene copolymer, vinylidene fluoride-chlorotrifluoroethylene copolymer, ethylene-tetrafluoroethylene copolymer, polychlorotrifluoroethylene, vinylidene fluoride-pentafluoro propylene copolymer, propylene-tetrafluoroethylene copolymer, ethylene-chlorotrifluoroethylene copolymer, vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene copolymer, vinylidene fluoride-perfluoromethyl vinyl ether-tetrafluoro ethylene copolymer, ethylene-acrylic acid copolymer, polyvinyl alcohol (PVA), polyacrylic acid (PAA), polymethacrylic acid (PMA), Any one selected from the group consisting of polymethyl methacrylate (PMMA), polyacrylamide (PAM), polymethacrylamide, polyacrylonitrile (PAN), polymethacrylonitrile, polyimide (PI), alginic acid, alginate, chitosan, carboxymethyl cellulose (CMC), starch,

hydroxypropyl cellulose, regenerated cellulose, polyvinyl pyrrolidone, and combinations thereof may be used, but is not necessarily limited thereto, and any one that can be used as a binder in the relevant technical field may be used.

[0065]

544 The above separator is a physical separator that has the function of physically separating electrodes, and can be used without special restrictions if it is used as a normal separator.

547 Additionally, the separator separates or insulates the positive and negative electrodes from each other while enabling the transport of lithium ions between the positive and negative electrodes.

550 These membranes may be made of porous, non - conductive or insulating materials.

551 The above separator may be an independent member such as a film, or a coating layer added to the anode and/or cathode.

553 For example, a porous polymer film, for example, a porous polymer film made of a polyolefin polymer such as an ethylene homopolymer, a propylene homopolymer, an ethylene/butene copolymer, an ethylene/hexene copolymer, and an ethylene/methacrylate copolymer, may be used alone or in a laminated manner, but is not limited thereto.

[0066]

561 The positive electrode, negative electrode, and separator included in the lithium - sulfur secondary battery can be prepared according to conventional components and manufacturing methods, respectively, and the external shape of the lithium - sulfur secondary battery is not particularly limited, but may be cylindrical, box - shaped, pouch - shaped, or coin - shaped, for example, coin - shaped.

[0068]

569 One aspect of the present invention provides a method for producing a positive electrode for a lithium - sulfur secondary battery, comprising: a step of producing a siloxene compound; a step of mixing and processing the siloxene compound and a positive electrode active material to produce a positive electrode for a lithium - sulfur secondary battery;

[0069]

577 First, the present invention includes a step of preparing a siloxane compound.

[0070]

The step of preparing the above siloxene compound can be performed, for example, by a method of de-intercalating Ca ions present in CaSi₂ using hydrochloric acid (HCl), and the related reaction formula is described in the following equation 1:

[0071]

[Formula 1]

[0072]

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

[0073]

In this specification, “intercalation/de-intercalation” refers to a phenomenon in which molecules, atoms, and/or ions are inserted/released into the interlayer gap in a material having a layered structure.

The products of intercalation are called intercalation compounds.

[0074]

Depending on the temperature at which the step of producing the above siloxene compound is performed, the inclusion of a functional group containing oxygen in the siloxene can be controlled.

[0075]

In one embodiment of the present invention, the process of synthesizing the siloxene compound can be performed at a temperature of 0 ° C. or higher, for example, 20 ° C. to 30 ° C., for example, 25 ° C.

[0076]

If the temperature of the process for synthesizing the above siloxane compound is less than 0 ° C, polysilane, which is a structure in which no functional group containing oxygen exists and only hydrogen exists in a vertical direction in the hexagonal multiple structure of silicon, can be formed.

[0077]

For example, when synthesized at room temperature (25 ° C.), the synthesized siloxene compound has an appropriately substituted functional group containing oxygen, so that in this case, the elution of polysulfide from the positive electrode for a lithium - sulfur secondary battery into the organic electrolyte can be effectively controlled.

[0078]

For example, when synthesized at room temperature, oxygen may be included at 33 wt% based on the total weight of the synthesized siloxene compound.

[0079]

Next, the present invention includes a step of manufacturing a cathode for a lithium - sulfur secondary battery by mixing and processing the siloxane compound manufactured in the above step and the cathode active material.

[0080]

The step of manufacturing the positive electrode for the above lithium - sulfur secondary battery can be performed, for example, through a process of casting onto a current collector.

[0081]

The above current collector acts as a passage to transfer electrons from the outside to cause an electrochemical reaction in the active material or to receive electrons from the active material and allow them to flow to the outside, and is not particularly limited as long as it is conductive and does not cause a chemical change in the battery.

For example, it may include any one selected from the group consisting of carbon (C), nickel (Ni), stainless steel (SUS), aluminum (Al), molybdenum (Mo), chromium (Cr), titanium (Ti), and combinations thereof, for example, carbon (C).

[0082]

The above casting process can be performed by applying a liquid and/or semi - liquid material, such as the positive electrode slurry, by radiation onto a solid and/or semi - solid material, such as the current collector.

The above casting process is performed using a method common in the relevant technical field, and the method of performing the process is not limited.

[0084]

670 Hereinafter, preferred examples are presented to help understand the present invention.
672 However, it is obvious that the following examples are only intended to illustrate the present invention and the scope of the present invention is not limited to the following examples.

[0086]

678 Example

[0087]

682 Manufacturing example 1.
683 Preparation of siloxane compounds

[0088]

687 CaSi₂5 g was added to a mixed solution of 3.79 g of hydrochloric acid (HCl, 35%) and 0.94 g of water, stirred at 30 ° C for 6 hours under a nitrogen atmosphere, and then washed with acetone.
690 Afterwards, the siloxane compound was obtained by drying at 110 ° C for one day (Fig. 1 (a)).

[0090]

695 Example 1.
696 Manufacturing of lithium - sulfur secondary batteries

[0091]

700 1.1. Manufacturing of lithium - sulfur secondary battery cathode

[0092]

704 70 mg of the siloxane compound obtained in the above Manufacturing Example 1, 20 mg of Super P as a conductive agent, and 10 mg of polyvinylidene fluoride (PVDF) as a binder were added to 1 ml of N - methylpyrrolidone as a solvent, and the contents were dispersed through ultrasonic treatment for 3 hours, and then stirred

on a stirring plate overnight to prepare a siloxane compound slurry.

[0093]

1 M Li₂S₆ was prepared by adding 50 mg of Li₂S (99.9% Alfa - Aesar, Haverhill, Miami, USA) and 48 mg of sulfur to 20 ml of 1,3 - dioxolane (DOL) and 1,2 - dimethoxyethane (DME) (1:1 by volume) containing 1 M LiTFSI.

[0094]

After casting 6 mg of the above siloxane compound on a carbon collector with a diameter of 14 mm, it was dried in a vacuum oven at 120 ° C for 24 hours.

[0096]

1.2. Manufacturing of lithium - sulfur secondary batteries

[0097]

A carbon collector cast with the above - mentioned siloxane compound was added to the coin cell, and 83 μl of Li₂S₆ (1 M) was injected, followed by sequentially stacking a separator, 117 μl of an electrolyte containing 1,3 - dioxolane (DOL) and 1,2 - dimethoxyethane (DME) (1:1 volume ratio) containing 1 M LiTFSI dissolved therein and 1 wt% LiNO₃, lithium foil, a spacer, and a spring, to manufacture a lithium - sulfur secondary battery.

[0099]

Examples 2 to 3.
Manufacturing of lithium - sulfur secondary batteries

[0100]

A lithium - sulfur secondary battery was obtained by performing the same method as in Example 1, except that 17 μl and 50 μl of Li₂S₆(1 M) were injected instead of 83 μl in Example 1.

[0102]

Comparative examples 1 to 3.
Manufacturing of lithium - sulfur secondary batteries

[0103]

A lithium - sulfur secondary battery was obtained by performing the same method as in Example 1, except that the siloxane compound was not added and Li₂S₆(1 M) was injected at 83 μl, 17 μl, and 50 μl, respectively, in Example 1.1.

[0105]

Experimental example 1.

Morphological analysis of siloxene compounds

[0106]

1.1 Analysis of SEM and TEM results

[0107]

In order to observe the surface and morphology of the siloxane compound obtained in the above Manufacturing Example 1, a scanning electron microscope (SEM) and a transmission electron microscope (TEM) were used.

[0108]

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 was found to be approximately 500 nm from the peeled and observed sample (Fig. 1 (d)).

[0110]

1.2 Analysis of nitrogen adsorption/desorption experiment results

[0111]

In order to observe the surface area and pore inclusion of the siloxane compound obtained in the above Manufacturing Example 1, a nitrogen adsorption/desorption experiment was performed.

[0112]

796 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 there were no micropores with a size of approximately 2 nm, mesopores with a size of 2 nm to 50 nm, or macropores with a size of 50 nm or more (Fig. 1 (f)).

796 Therefore, it was found that there was no physical adsorption of polysulfide by micropores.

[0114]

806 1.3 XRD Results Analysis

[0115]

810 To confirm whether de-intercalation of Ca²⁺ was successfully achieved in the siloxane compound obtained in the above Manufacturing Example 1, the XRD pattern was analyzed.

[0116]

816 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)).

[0118]

822 1.4 FT-IR Results Analysis

[0119]

826 In order to confirm the functional group present in the siloxane compound obtained in the above Manufacturing Example 1, the results of FT-IR were analyzed.

[0120]

831 As a result of the analysis, peaks corresponding to wavenumbers 2150 cm⁻¹, 1060 cm⁻¹, and 460 cm⁻¹ were identified, 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)).

[0122]

1.5 Analysis of Raman spectrum results

[0123]

In order to confirm whether multiple hexagonal structures (in-plane structures) exist in the siloxene compound obtained in the above Manufacturing Example 1, the Raman spectrum was analyzed.

[0124]

The analysis results showed a gentle peak due to the vibrational energy of the Si-Si bond 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 did not affect the in-plane structure as intended and the oxidation reaction proceeded only outside the in-plane structure.

[0126]

1.6. XPS Results Analysis

[0127]

To confirm the mass content of the surface of the siloxane compound obtained in the above Manufacturing Example 1, the XPS results were analyzed.

[0128]

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 de-intercalation of Ca was well achieved, and the mass of oxygen was 45.6 atom%, 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)).

[0129]

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

[0130]

883 element
884 Content (mass%)
885 Content (atom%)
886 carbon
887 3.45
888 6.28
889 oxygen
890 33.37
891 45.6
892 silicon
893 56.46
894 44.09
895 calcium

2

899 .21
900 1.21
901 chlorine

4

905 .51
906 2.82
907 Total
908 100
909 100

[0132]

913 Experimental example 2.
914 Sulfur - active substance adsorption capacity of siloxane compounds

[0133]

918 In order to confirm the sulfur active material adsorption capacity of the siloxene compound obtained in the above Manufacturing Example 1, 0 mg, 50 mg, 100 mg, and 300 mg of the siloxene compound were added to 20 ml of 1 M Li₂S₆, and left at room temperature for 4 hours.

[0134]

As a result of the experiment, it was found that the samples with added siloxane compounds became transparent, indicating that lithium polysulfide (Li₂S₆) was adsorbed. In addition, it was found that the higher the content of siloxene compound, the more transparent it became (Figure 3).

[0136]

Experimental example 3.
Charge and discharge experiments of lithium - sulfur secondary batteries

[0137]

3.1 Cycling test of lithium - sulfur secondary battery

[0138]

In order to confirm the capacity per unit area of the lithium - sulfur secondary batteries manufactured in Examples 1 to 3 and Comparative Examples 1 to 3, a charge/discharge cycle stability test was conducted.

[0139]

The experimental results confirmed that the performance of the siloxane compound became more prominent as the sulfur content increased. In addition, when looking at the utilization efficiency of sulfur, it increased by about 10% or more in Examples 1 to 3 compared to Comparative Examples 1 to 3. Specifically, it was confirmed that when the sulfur loading amount was 6 mg/cm² (Example 3 and Comparative Example 3), it increased from 41% to 52%, and when the sulfur loading amount was 10 mg/cm² (Example 1 and Comparative Example 1), it increased from 31% to 44% (Fig. 4), and through this, it was confirmed that the increase in utilization efficiency was greater as the sulfur loading amount increased.

[0140]

Additionally, after 100 cycles, the battery was opened and the separator and lithium metal parts were confirmed through photographic images.

[0141]

In the case of the lithium - sulfur secondary battery of Comparative Example 2, it was confirmed that the yellow color indicating the presence of polysulfide remained not only in the lithium metal but also in the separator after charging and discharging (Fig. 5 (a)). Under the same conditions, in the case of the lithium - sulfur secondary battery of Example 1, no yellow residue was observed in the lithium metal and separator (Fig. 5 (b)). These results demonstrate the adsorption capacity of siloxane compounds for polysulfides, indicating that they can effectively play a role in fixing active materials within the anode.

[0143]

3.2 Analysis of CV and GCPL results of lithium - sulfur secondary batteries

[0144]

In order to confirm the discharge capacity of the lithium - sulfur secondary battery manufactured in Example 1 and Comparative Example 1, cyclic voltammetry (CV) and charge/discharge curve (GCPL) experiments were performed.

[0145]

First, CV experiments were performed by varying the scan rate from 0.01 mV/s to 0.04 mV/s, and the kinetic mechanism was analyzed using the power - law relationship. The above analysis method derives a linear relationship (log - log) from the currents of peak 1 generated in the oxidation process, peak 2 generated in the reduction process, and peak 3, and analyzes the slopes of each. The closer the slope is to 0.5, the closer the process is to diffusion - controlled, and the closer it is to 1, the closer the process is to surface reaction.

[0146]

As a result of the experiment, the biggest difference between Example 1 and Comparative Example 1 was that the slope value was reversed at peak 2, and Example 1 induced a larger current at peak 2. The reduction step from Li₂S₄ to Li₂S is greatly restricted by space. In Comparative Example 1, the second reduction step was gradually pushed out due to insufficient space for the sulfur active material to react, whereas in Example 1, the electrode adsorbed more sulfur active material, helping the conversion from Li_2S_4 to Li_2S. It was found that the discharge capacity was generated by the space created when the siloxane compound was placed on the three - dimensional current collector while casting the additive onto the electrode (Fig. 6 (a), (b) and (c)).

[0147]

In the CV experiment with a scan rate of 0.01 mV/s, the open circuit voltage (OCV) was observed to be 2.1 V vs. Li/Li^+ and 2.3 V vs. It was found that the lithium - sulfur secondary battery of Example 1 had a higher voltage - to - current ratio (V/Li^+) than the lithium - sulfur secondary battery of Comparative Example 1, and thus self - discharge was found to occur relatively less, with a V/V ratio of about 2.1 V vs. When looking at the peak current density near Li/Li^+, it was found that it had a greater discharge capacity (Fig. 6 (d)).

[0148]

GCPL experimental results 2.1 V vs. It was confirmed that the expression of discharge capacity near Li/Li^+ was significantly different at about 7.0 mAh/cm^2 (Fig. 6 (e)).

[0149]

This is thought to be because the polysulfide (Li_2S_n, n is 4 to 8) is well fixed to the siloxane compound, which allows the reaction to occur better within the anode, thereby increasing the sulfur utilization rate.

[0151]

Experimental example 4.

XPS Results Analysis of Lithium - Sulfur Secondary Battery

[0152]

To determine the chemical structure of the sulfur active material in the cathode after charge and discharge, ex - situ XPS analysis was performed. Sulfur - containing materials undergo a stepwise oxidation/reduction reaction to form polysulfides, which are intermediate products between S₈ and Li₂S. Polysulfides have a binding energy between S₈ (164 eV) and Li₂S (160 eV).

In the case of Example 1, the formation of polysulfide could be confirmed from the presence of a peak having a binding energy of about 162 eV, but in the case of Comparative Example 1, the formation of polysulfide could not be confirmed because there was no peak around 164 eV to 160 eV (Fig. 7).

Therefore, it was found that a reduction reaction actually occurred during the discharge process when a siloxane compound was present, which means that the chemical adsorption ability for polysulfide actually exists.

[0154]

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.

[0155]

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.