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NEGATIVE ELECTRODE MATERIAL FOR LITHIUM ION SECONDARY BATTERY, NEGATIVE ELECTRODE FOR LITHIUM ION SECONDARY BATTERY, AND LITHIUM ION SECONDARY BATTERY

Abstract

This negative electrode material for a lithium ion secondary battery may include composite particles. The composite particle may include a plurality of carbonaceous particles and a plurality of silicon particles. Each of the plurality of carbonaceous particles and the plurality of silicon particles may be amorphous. An average primary particle size of the plurality of silicon particles may be 1 nm or more and 50 nm or less. In the composite particle, a molar ratio of the silicon particles in the composite particle may be 15 mol % or more and 40 mol % or less, and a molar ratio of the carbonaceous particles may be 50 mol % or more and 80 mol % or less. The plurality of silicon particles may be bonded to one another.

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Background/Summary

CROSS-REFERENCE TO RELATED APPLICATIONS [0001] This application is a continuation of International Application No. PCT/JP2024/006053, filed Feb. 20, 2024, the entire content of which is incorporated herein by reference.

TECHNICAL FIELD

[0002] The present disclosure relates to a negative electrode material for a lithium ion secondary battery, a negative electrode for a lithium ion secondary battery, and a lithium ion secondary battery.

BACKGROUND ART

[0003] Lithium ion secondary batteries are widely used as power sources for mobile devices such as mobile phones and notebook computers and for hybrid cars.

[0004] The capacity of a lithium ion secondary battery depends mainly on an active material of an electrode. Graphite is generally used as a negative electrode active material, but there is a demand for a negative electrode active material with a higher capacity. For this reason, silicon (Si), which has a theoretical capacity far higher than that of graphite (372 mAh/g), has attracted attention.

[0005] A negative electrode active material including silicon undergoes significant volume expansion during charging. The volume expansion of the negative electrode active material causes a decrease in the cycle characteristics of the battery. When the negative electrode active material expands in volume, for example, the negative electrode active material is damaged, a conductive path between the negative electrode active materials is cut, peeling occurs at an interface between a negative electrode active material layer and a current collector, or cracks occur in a solid electrolyte interphase (SEI) coating film; and thereby, decomposition of an electrolytic solution is caused. This decreases the cycle characteristics of the battery.

[0006] For example, Patent Document 1 describes that the cycle characteristics are improved by defining the aspect ratio of a silicon particle and the inclination angle of the silicon particle with respect to the current collector.

CITATION LIST

Patent Document

[0007] Patent Document 1: Japanese Unexamined Patent Application, First Publication No. 2019-149333

SUMMARY OF DISCLOSURE

Technical Problems

[0008] The cycle characteristics are an important parameter, and it is desirable to be able to improve the cycle characteristics by a method other than the method described in Patent Document 1.

[0009] The present disclosure has been made in view of the above and other problems, and an object of the present disclosure is to provide a lithium ion secondary battery having excellent cycle characteristics.

Solution to Problem

[0010] The following solutions according to some embodiments of the present disclosure are provided to solve the above and other problems.

[0011] A negative electrode material for a lithium ion secondary battery according to a first aspect includes composite particles. The composite particle includes a plurality of carbonaceous particles and a plurality of silicon particles. Each of the plurality of carbonaceous particles and the plurality of silicon particles is amorphous. An average primary particle size of the plurality of silicon particles is 1 nm or more and 50 nm or less. In the composite particle, a molar ratio of the silicon particles is 15 mol % or more and 40 mol % or less, and a molar ratio of the carbonaceous particles is 50 mol % or more and 80 mol % or less. The plurality of silicon particles are bonded to each other.

Advantageous Effects of Disclosure

[0012] A lithium ion secondary battery using the negative electrode material for a lithium ion secondary battery according to some embodiments of the present disclosure has excellent cycle characteristics.

Description

BRIEF DESCRIPTION OF DRAWINGS

[0013] FIG. 1 a TEM image of a cross-section of a negative electrode material for a lithium ion secondary battery according to a first embodiment.

[0014] FIG. 2 a schematic diagram of a lithium ion secondary battery according to the first embodiment.

DESCRIPTION OF EMBODIMENTS

[0015] Hereinafter, embodiments will be described in detail with reference to the drawings as appropriate. In the drawings which will be used in the following description, featured portions may be enlarged for convenience in order to make the features easy to understand, and the dimensional ratios of constituent elements may be different from the actual ones. The materials, dimensions, and the like which will be exemplified in the following description are examples, and the present disclosure is not limited thereto and can be appropriately modified and carried out without changing the features of the present disclosure.

“Negative Electrode Material”

[0016] A negative electrode material according to a first embodiment is used in a lithium ion secondary battery and includes silicon particles. The negative electrode material according to the first embodiment functions as, for example, a negative electrode active material.

[0017] FIG. 1 is a cross-sectional view of the negative electrode material according to the first embodiment. The negative electrode material includes composite particles **1**.

[0018] The composite particle **1** is a secondary particle formed by aggregation of a plurality of particles. The average secondary particle size of the composite particles **1** is 1 μm or more and 10 μm or less, preferably 2 μm or more and 8 μm or less, and more preferably 3 μm or more and 7 μm or less.

[0019] When the average secondary particle size of the composite particles **1** is within the above-described range, the cycle characteristics are improved. If the composite particle **1** is too small, it becomes difficult to ensure sufficient strength and conductivity when a negative electrode active material layer is formed, and thus the used amounts of a binder and a conductive assistant increase. Since the binder and the conductive assistant are not active materials that perform charging and discharging, if the abundance ratio of these in the negative electrode active material layer increases, the capacity of the lithium ion secondary battery decreases. In addition, if the composite particle **1** is too large, the composite particle **1** is damaged due to expansion and contraction and thus a risk of a side reaction such as decomposition of the electrolytic solution occurring on a new surface

generated by the damage increases.

[0020] In a case in which the composite particles **1** are available in a particle state, a median size (D50) can be obtained as the average secondary particle size using a particle size distribution measuring device (for example, manufactured by Malvern Panalytical Ltd.). In a case in which the particle size distribution measuring device is used, for example, the average of the particle sizes of 50000 particles is obtained.

[0021] In a case in which the composite particles **1** are present in an electrode and it is difficult to separate the composite particles **1** from each other, the average secondary particle size can be obtained using at least 100 composite particles **1** observed in a cross-sectional image. The average secondary particle size measured using the particle size distribution measuring device and the average secondary particle size obtained from the cross-sectional image do not deviate significantly from each other, and they generally match each other.

[0022] First, a contrast threshold is set and the composite particles **1** are extracted from the image. Then, the sizes of at least 100 extracted composite particles **1** are obtained. The frequencies of the obtained sizes of the composite particles **1** are plotted graphically, and the most frequent value is taken as the average secondary particle size. In a case in which the shape of the composite particle **1** is irregular, the size of the major axis is used to calculate the average secondary particle size.

[0023] The composite particle **1** includes a plurality of carbonaceous particles and a plurality of silicon particles. The composite particle includes, for example, hydrogen, oxygen, nitrogen, and the like in addition to the carbonaceous particles and the silicon particles.

[0024] In a transmission electron microscope (TEM) image shown in FIG. **1**, the white portions are the silicon particles and the black portions are the carbonaceous particles. As shown in FIG. **1**, each of the plurality of silicon particles is bonded to an adjacent silicon particle. The silicon particles are bonded to adjacent silicon particles and connected in a network shape.

[0025] The molar ratio of the silicon particles in the composite particle **1** is, for example, 15 mol % or more and 40 mol % or less, and preferably 20 mol % or more and 30 mol % or less. The weight of silicon in the composite particle **1** can be measured by an inductively coupled plasma (ICP) emission spectrometry method or the like. In addition, as for the weight of the silicon in the composite particle **1**, proportions of elements other than the silicon (for example, oxygen, nitrogen, hydrogen, and carbon) are obtained using oxygen-nitrogen-hydrogen analysis (ONH analysis) and carbon-sulfur analysis (C—S analysis), and the weight of the silicon may be calculated on the basis of the proportions. The molar ratio of the silicon particles can be obtained from the weight of the silicon.

[0026] The molar ratio of the carbonaceous particle in the composite particle **1** is, for example, 50 mol % or more and 80 mol % or less, and preferably 60 mol % or more and 70 mol % or less. The weight of the carbonaceous particles can be measured by a high-frequency induction heating combustion-infrared absorption method or the like. The molar ratio of the carbonaceous particles can be obtained from the weight of the carbonaceous particles.

[0027] By controlling the molar ratio of the silicon particles and the carbonaceous particles in the composite particle **1**, it is possible to improve the cycle characteristics while ensuring the capacity of the lithium ion secondary battery. The silicon particles are a portion that contributes most to charging and discharging, and the molar ratio of the silicon particles affects the capacity of the lithium ion secondary battery. The carbonaceous particles function as a buffer when the silicon particles change in volume.

[0028] The presence of a predetermined amount of the carbonaceous particles in the composite particle **1** prevents damage to the composite particle **1** and improves the cycle characteristics of the lithium ion secondary battery.

[0029] The molar ratio of components other than the silicon particles and the carbonaceous particles (for example, hydrogen, oxygen, and nitrogen) in the composite particle **1** is preferably, for example, 15% or less.

[0030] The carbonaceous particles and the silicon particles are each amorphous. Lithium ions enter in an orientation direction of crystals. For this reason, in the crystals, a path through which the lithium ions can enter is limited. In contrast, in the amorphous carbonaceous particles and silicon particles, the crystal direction is not fixed to a predetermined direction, and thus the direction in which the lithium ions enter is not limited. When the carbonaceous particles and the silicon particles constituting the composite particle **1** are amorphous, the diffusion of the lithium ions in the composite particle **1** becomes uniform, and a local volume change in the composite particle **1** can be suppressed.

[0031] The silicon particles may be silicon in the form of a simple substance, may be silicon oxide (SiO_x : x satisfies, for example, $0.8 \leq x \leq 2$), or may be a silicon alloy represented by X_nSi . X is a cation. Examples of X include Ba, Mg, Al, Zn, Sn, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, W, Au, Ti, Na, K, and the like. n satisfies $0 \leq n \leq 0.5$.

[0032] The average primary particle size of the silicon particles is, for example, 1 nm or more and 50 nm or less, and preferably 3 nm or more and 30 nm or less. The average primary particle size of the silicon particles is obtained from the cross-sectional image of the composite particle **1**. The cross-sectional image can be obtained using a scanning electron microscope (SEM) or a transmission electron microscope (TEM). For example, the composite particle **1** is observed at a magnification of 100000 times using a scanning electron microscope JSM-7600 (manufactured by JEOL Ltd.), and the average primary particle size can be measured by subjecting the captured image to image processing. The average primary particle size of the silicon particles obtained by the image processing is approximately equal to the particle size of the silicon particle prepared before production.

[0033] The average primary particle size is obtained using image processing software HALCON (registered trademark, manufactured by MVTec Software GmbH). The software recognizes particles in the captured images and removes particles that are not captured in their entirety at the end portion of the observation field of view. When measuring the average primary particle size, a connecting portion that connects the particles is considered to be excluded. Specifically, as shown in FIG. 1, a portion connecting the particles also appears white, and thus this portion is excluded and only the particles are extracted. For example, among the white portions that can be observed in the image, a portion with a width of 1 nm or less is removed. Then, the shortest width (the shortest diameter of the circumscribing circle of the particle) is measured for each of the extracted particles, and the particle size is calculated from the shortest width. Such measurements are carried out for 200 particles to obtain a number-based cumulative particle size distribution, from which the average primary particle size can be calculated.

[0034] When the average primary particle size of the silicon particles is within the above-described range, an increase in the coating resistance of the electrolytic solution due to a side reaction caused by contact between the silicon particle and the electrolytic solution can be suppressed. In addition, when the average primary particle size of the silicon particles is within the above-described range, damage to the silicon particle due to expansion and contraction during charging and discharging can be suppressed.

[0035] The carbonaceous particles are composited with the silicon particles. Examples of the carbonaceous particles include graphite, graphene, carbides formed after sintering pitches, carbides formed after sintering resins, and the like. The carbonaceous particles may be of two or more types.

[0036] The pitches may be coal-based pitches, petroleum-based pitches, or synthetic pitches, and examples of the pitches include coal tar, light tar oil, medium tar oil, heavy tar oil, naphthalene oil, anthracene oil, coal tar pitch, pitch oil, mesophase pitch, oxygen-crosslinked petroleum pitch, heavy oil, coke, low molecular weight heavy oil, derivatives of these, and the like.

[0037] Examples of the resins include a thermoplastic resin such as polyvinyl alcohol, a phenol resin, an epoxy resin, a melamine resin, a urea resin, an aniline resin, a cyanate resin, a furan resin, a ketone resin, an unsaturated polyester resin, a urethane resin, modified products of these, and the

like. Examples of the phenol resin include a novolac type phenol resin, a resol type phenol resin, and the like. Examples of the epoxy resin include a bisphenol type epoxy resin, a novolac type epoxy resin, and the like. Examples of the resins include polyethylene, polystyrene, an acrylonitrile-styrene (AS) resin, an acrylonitrile-butadiene-styrene (ABS) resin, polypropylene, polyethylene terephthalate, polycarbonate, polyacetal, polyphenylene ether, polybutylene terephthalate, polyphenylene sulfide, polysulfone, polyether sulfone, polyether ether ketone, polyvinyl chloride, and the like.

[0038] The carbonaceous particles preferably include graphite or graphene. The sp² bonds in the graphite or graphene have high electronic conductivity and allow the lithium ions to be supplied uniformly to the silicon particles.

[0039] The surface of the composite particle **1** may be further coated with carbon or carbon nanotubes. The carbon or carbon nanotubes support the conductivity between the composite particles **1**. When the surface of the composite particle **1** is coated with carbon or carbon nanotubes, the conductive network between the composite particles **1** can be easily maintained even in a case in which the volume of the composite particle **1** is changed.

[0040] The negative electrode material according to the first embodiment can be produced by carrying out a core producing step and a coating layer producing step.

[0041] In the core producing step, the composite particles **1** are produced. The composite particles **1** can be produced by mixing the silicon particles and the carbon source in an organic solvent. The molar ratio of the silicon particles to the carbonaceous particles in the composite particle **2** can be adjusted by the mixing ratio of the silicon particles and the carbon source.

[0042] Examples of the carbon source include graphite, graphene, pitches, resins, and the like. As the pitches and resins, those described above can be used. The carbon source is preferably at least one selected from the group consisting of graphite, graphene, a novolac-type phenolic resin, a resol-type phenolic resin, a coal-based pitch, and a petroleum-based pitch. Two or more carbon sources may be used. The carbon source affects the powder resistivity of the negative electrode active material.

[0043] The organic solvent is, for example, methanol, ethanol, tetrahydrofuran, or the like. A dispersant may be added to the organic solvent. By adding a dispersant, the carbonaceous particles uniformly cover the silicon particles during compositing. Such a composite particle **1** has excellent electronic conductivity and is less likely to cause a side reaction with the electrolytic solution during charging and discharging.

[0044] Next, a mixture obtained after the mixing is dried. Through the drying, the organic solvent is removed from the mixture and powder is obtained. A drying method is not particularly limited, but may be, for example, a spray drying method.

[0045] Next, the powder obtained after the drying is subjected to a heat treatment. Through the heat treatment step, the resin or resin composition serving as the carbon source burns incompletely and carbonizes to become the carbonaceous particles. In this way, the silicon particles and the carbonaceous particles are composited with each other.

[0046] The heat treatment of the mixture is preferably carried out at a heat treatment temperature of 350 to 1200° C. If the heat treatment temperature is low, the carbon source is not sufficiently carbonized, and this may cause lithium to be trapped during charging and discharging. When the lithium is trapped, the initial efficiency of the lithium ion secondary battery is decreased. If the heat treatment temperature is high, the silicon particles react with the carbonaceous particles, and an excess amount of silicon carbide is produced. Among silicon compounds, the silicon carbide has a small contribution to charging and discharging, and reduces the conductivity of the lithium ions, and this causes a decrease in the discharge capacity of the lithium ion secondary battery.

[0047] In addition, the heat treatment time is preferably 1 hour or more and 72 hours or less. The heat treatment atmosphere is preferably a reducing atmosphere such as a nitrogen atmosphere or an argon atmosphere.

[0048] Next, the particles after the compositing are irradiated with a laser or an electron beam to perform a thermal welding treatment for the silicon particles and the carbonaceous particles. By carrying out the thermal welding treatment, a network structure in which the silicon particles are connected to each other is formed.

[0049] In the coating layer producing step, carbon or carbon nanotubes are attached to the surface of the composite particle **1**. The coating layer producing step may not be carried out. The carbon or carbon nanotubes coat the surface of the composite particle **1** by a chemical vapor deposition (CVD) or electrostatic adsorption method.

[0050] The negative electrode material according to the first embodiment has excellent cycle characteristics for the lithium ion secondary battery. This is because the negative electrode material includes predetermined composite particles **1**. The composite particle **1** includes a predetermined molar ratio of the silicon particles and the carbonaceous particles, and thus it is possible to improve the cycle characteristics while ensuring the capacity of the lithium ion secondary battery.

[0051] In addition, in the composite particle **1**, the silicon particles constituting the composite particle **1** are connected to each other, and thus the strength of the particle is high and the particle is not easily damaged. When the composite particle **1** is damaged, a new surface is exposed, and this causes an irreversible reaction of the electrolytic solution. The lithium ions are used in the irreversible reaction of the electrolytic solution, and this causes a decrease in the cycle characteristics of the lithium ion secondary battery.

[0052] In addition, as the silicon particles spread in a network-like pattern, the reaction area with the lithium ions increases, and thus the charge and discharge reactions of the lithium ion secondary battery become smooth.

“Lithium Ion Secondary Battery”

[0053] FIG. **2** is a schematic diagram of a lithium ion secondary battery according to the first embodiment. A lithium ion secondary battery **100** shown in FIG. **2** includes a power generating element **40**, an exterior body **50**, and an electrolyte (for example, a non-aqueous electrolytic solution). The exterior body **50** covers the periphery of the power generating element **40**. The power generating element **40** is connected to the outside via a pair of terminals **60** and **62** connected to the power generating element **40**. The non-aqueous electrolytic solution is accommodated in the exterior body **50**. Although FIG. **2** illustrates an example in which one power generating element **40** is provided inside the exterior body **50**, a plurality of power generating elements **40** may be stacked.

(Power Generating Element)

[0054] The power generating element **40** includes a separator **10**, a positive electrode **20**, and a negative electrode **30**. The power generating element **40** may be a laminated body in which these are laminated, or a wound body obtained by winding a structure in which these are laminated.

<Positive Electrode>

[0055] The positive electrode **20** includes, for example, a positive electrode current collector **22** and a positive electrode active material layer **24**. The positive electrode active material layer **24** is in contact with at least one surface of the positive electrode current collector **22**.

[Positive Electrode Current Collector]

[0056] The positive electrode current collector **22** is, for example, a conductive sheet material. The positive electrode current collector **22** is a thin metal sheet made of, for example, aluminum, copper, nickel, titanium, stainless steel, or the like. Aluminum, which is light in weight, is suitably used for the positive electrode current collector **22**. The average thickness of the positive electrode current collector **22** is, for example, 10 μm or more and 30 μm or less.

[Positive Electrode Active Material Layer]

[0057] The positive electrode active material layer **24** includes, for example, a positive electrode active material. The positive electrode active material layer **24** may include a conductive assistant and a binder as necessary.

[0058] The positive electrode active material includes an electrode active material capable of reversibly progressing the absorption and release of the lithium ions, the deintercalation and intercalation of the lithium ions, or the doping and dedoping of the lithium ions and counter anions.

[0059] The positive electrode active material is, for example, a composite metal oxide. Examples of the composite metal oxide include lithium cobalt oxide ($\text{LiCoO}_{0.5}\text{O}_{1.5}$), lithium nickel oxide ($\text{LiNiO}_{0.5}\text{O}_{1.5}$), lithium manganese oxide ($\text{LiMnO}_{0.5}\text{O}_{1.5}$), spinel lithium manganese oxide ($\text{LiMn}_{0.5}\text{O}_{2}\text{O}_{0.4}$), a compound of a general formula:

$\text{LiNi}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{M}_{0.5}\text{O}_{2}$ (in the general formula, $x+y+z+a=1$, $0 \leq x < 1$, $0 \leq y < 1$, $0 \leq z < 1$, $0 \leq a < 1$, and M is one or more elements selected from Al, Mg, Nb, Ti, Cu, Zn, and Cr), a lithium vanadium compound ($\text{LiVO}_{0.5}\text{O}_{1.5}$), olivine type $\text{LiMPO}_{0.5}\text{O}_{1.5}$ (wherein M represents one or more elements selected from Co, Ni, Mn, Fe, Mg, Nb, Ti, Al, and Zr, or VO), lithium titanate ($\text{Li}_{0.5}\text{Ti}_{1.5}\text{O}_{12}$), $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{Al}_{0.5}\text{O}_{2}$ ($0.9 < x+y+z < 1.1$), and the like. The positive electrode active material may be an organic material. For example, the positive electrode active material may be polyacetylene, polyaniline, polypyrrole, polythiophene, or polyacene.

[0060] The positive electrode active material may be a lithium-free material. Examples of the lithium-free material include $\text{FeF}_{0.3}$, a conjugated polymer including an organic conductive material, a Chevrel phase compound, a transition metal chalcogenide, a vanadium oxide, a niobium oxide, and the like. As the lithium-free material, only one material may be used, or a plurality of materials may be used in combination with each other. In a case in which the positive electrode active material is the lithium-free material, for example, discharging is first performed. Lithium is intercalated into the positive electrode active material by discharging. In addition, lithium may be chemically or electrochemically pre-doped to the positive electrode active material that is the lithium-free material.

[0061] The conductive assistant enhances electronic conductivity between the positive electrode active materials. Examples of the conductive assistant include carbon powder, carbon nanotubes, a carbon material, metal fine powder, a mixture of a carbon material and metal fine powder, a conductive oxide, and the like. Examples of the carbon powder include carbon black, acetylene black, ketjen black, and the like. Examples of the fine metal powder include copper powder, nickel powder, stainless steel powder, iron powder, and the like.

[0062] The amount of the conductive assistant in the positive electrode active material layer **24** is not particularly limited. For example, the amount of the conductive assistant relative to the total mass of the positive electrode active material, the conductive assistant, and the binder is 0.5 mass % or more and 20 mass % or less, and preferably 1 mass % or more and 5 mass % or less.

[0063] The binder in the positive electrode active material layer **24** binds the positive electrode active materials together. As the binder, a known binder can be used. The binder is preferably one that is insoluble in the electrolytic solution, has oxidation resistance, and has adhesive properties. The binder is, for example, a fluororesin. Examples of the binder include polyvinylidene fluoride (PVDF), polyvinyl alcohol (PVA), polytetrafluoroethylene (PTFE), polyamide (PA), polyimide (PI), polyamideimide (PAI), polybenzimidazole (PBI), polyethersulfone (PES), polyacrylic acid and its copolymers, metal ion crosslinked products of polyacrylic acid and its copolymers, maleic anhydride grafted polypropylene (PP) or polyethylene (PE), and mixtures thereof. The binder used in the positive electrode active material layer is particularly preferably PVDF.

[0064] The amount of the binder in the positive electrode active material layer **24** is not particularly limited. For example, the amount of the binder relative to the total mass of the positive electrode active material, the conductive assistant, and the binder is 1 mass % or more and 15 mass % or less, and preferably 1.5 mass % or more and 5 mass % or less. If the amount of the binder is low, the adhesive strength of the positive electrode **20** is weakened. If the amount of the binder is high, the binder is electrochemically inactive and does not contribute to the discharge capacity, and thus the energy density of the lithium ion secondary battery **100** becomes low.

<Negative Electrode>

[0065] The negative electrode **30** includes, for example, a negative electrode current collector **32** and a negative electrode active material layer **34**. The negative electrode active material layer **34** is formed on at least one surface of the negative electrode current collector **32**.

[Negative Electrode Current Collector]

[0066] The negative electrode current collector **32** is, for example, a conductive sheet material. As the negative electrode current collector **32**, a material that is the same as the positive electrode current collector **22** can be used.

[Negative Electrode Active Material Layer]

[0067] The negative electrode active material layer **34** includes a negative electrode active material and a binder. The negative electrode active material layer may include a conductive assistant, a dispersion stabilizer, and the like, as necessary. As the negative electrode active material, the above-mentioned negative electrode material is used. By using the above-mentioned negative electrode material as the negative electrode active material, the cycle characteristics of the lithium ion secondary battery **100** are improved.

[0068] As the conductive assistant and the binder, materials that are the same as those of the positive electrode **20** can be used. Examples of the binder in the negative electrode **30** may include cellulose, styrene-butadiene rubber, ethylene-propylene rubber, polyimide resin, polyamide-imide resin, acrylic resin, or the like, in addition to those exemplified for the positive electrode **20**. The cellulose may be, for example, carboxymethyl cellulose (CMC).

<Separator>

[0069] The separator **10** is sandwiched between the positive electrode **20** and the negative electrode **30**. The separator **10** separates the positive electrode **20** and the negative electrode **30** from each other and prevents a short circuit between the positive electrode **20** and the negative electrode **30**. The separator **10** extends in-plane along the positive electrode **20** and the negative electrode **30**. The lithium ions can pass through the separator **10**.

[0070] The separator **10** has, for example, an electrically insulating porous structure. The separator **10** is, for example, a monolayer or laminated body of a polyolefin film. The separator **10** may be a stretched film of a mixture of polyethylene, polypropylene, and the like. The separator **10** may be a nonwoven fabric of a fiber made of at least one constituent material selected from the group consisting of cellulose, polyester, polyacrylonitrile, polyamide, polyethylene, and polypropylene. The separator **10** may be, for example, a solid electrolyte. The solid electrolyte is, for example, a polymer solid electrolyte, an oxide-based solid electrolyte, or a sulfide-based solid electrolyte. The separator **10** may be an inorganic coated separator. The inorganic coated separator is formed by applying a mixture of a resin such as PVDF or CMC and an inorganic substance such as alumina or silica on the surface of the above-mentioned film. The inorganic coated separator has excellent heat resistance and suppresses the deposition (precipitation) of a transition metal eluted from the positive electrode onto the surface of the negative electrode.

<Electrolytic Solution>

[0071] The electrolytic solution is enclosed in the exterior body **50** and is impregnated in the power generating element **40**. The electrolytic solution is not limited to a liquid electrolyte, but may be a solid electrolyte. The non-aqueous electrolytic solution includes, for example, a non-aqueous solvent and an electrolytic salt. The electrolytic salt is dissolved in the non-aqueous solvent.

[0072] The solvent is not particularly limited as long as it is a solvent generally used in the lithium ion secondary battery. The solvent includes, for example, any one of a cyclic carbonate compound, a chain carbonate compound, a cyclic ester compound, and a chain ester compound. The solvent may include these compounds in any mixture ratio. Examples of the cyclic carbonate compound include ethylene carbonate (EC), propylene carbonate (PC), fluoroethylene carbonate, vinylene carbonate, and the like. Examples of the chain carbonate compound include diethyl carbonate (DEC), ethyl methyl carbonate (EMC), and the like. Examples of the cyclic ester compound

include γ -butyrolactone, and the like. Examples of the chain ester compound include propyl propionate, ethyl propionate, ethyl acetate, and the like.

[0073] The electrolytic salt is, for example, a lithium salt. Examples of the electrolyte include LiPF_6 , LiClO_4 , LiBF_4 , LiCF_3SO_3 , $\text{LiCF}_3\text{CF}_2\text{SO}_3$, $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$, $\text{LiN}(\text{CF}_3\text{CF}_2\text{CO})_2$, LiBOB , $\text{LiN}(\text{FSO}_2)_2$, and the like. As the lithium salt, one of these compounds or a mixture of two or more thereof may be used. From the viewpoint of the degree of electrolytic dissociation, the electrolyte preferably includes LiPF_6 . The dissociation rate of the electrolytic salt in the carbonate solvent at room temperature is preferably 10% or more.

[0074] The electrolytic solution is preferably one in which LiPF_6 is dissolved in the carbonate solvent, for example. The concentration of LiPF_6 is, for example, 1 mol/L. In a case in which the polyimide resin includes a large amount of aromatic, the polyimide resin may exhibit charging behavior similar to that of soft carbon. In a case in which the electrolytic solution is a carbonate electrolytic solution solvent including a cyclic carbonate, lithium can be reacted uniformly with the polyimide. In this case, the cyclic carbonate is preferably ethylene carbonate, fluoroethylene carbonate, or vinylene carbonate.

<Exterior Body>

[0075] The exterior body **50** seals the power generating element **40** and the non-aqueous electrolytic solution therein. The exterior body **50** prevents leakage of the non-aqueous electrolytic solution to the outside and prevents moisture and the like from entering the inside of the lithium ion secondary battery **100** from the outside.

[0076] As shown in FIG. 1, the exterior body **50** has a metal foil **52** and a resin layer **54** laminated on each side of the metal foil **52**. The exterior body **50** is a metal laminate film in which both sides of the metal foil **52** are coated with a polymer film (the resin layer **54**).

[0077] The metal foil **52** may be, for example, an aluminum foil. As the resin layer **54**, a polymer film such as polypropylene can be used. The material constituting the resin layer **54** may be different between the inner side and the outer side. For example, as the material on the outer side, a polymer with a high melting point, for example, polyethylene terephthalate (PET), polyamide (PA), or the like can be used, and as the material of the polymer film on the inner side, polyethylene (PE), polypropylene (PP), or the like can be used.

<Terminal>

[0078] The terminals **62** and **60** are connected to the positive electrode **20** and the negative electrode **30**, respectively. The terminal **62** connected to the positive electrode **20** is a positive terminal, and the terminal **60** connected to the negative electrode **30** is a negative terminal. The terminals **60** and **62** serve to electrically connect the power generating element to the outside. The terminals **60** and **62** are formed from a conductive material such as aluminum, nickel, or copper. A connection method may be welding or screwing. The terminals **60** and **62** are preferably protected with insulating tape to prevent a short circuit.

“Method of Manufacturing Lithium Ion Secondary Battery”

[0079] The lithium ion secondary battery **100** is produced by preparing the negative electrode **30**, the positive electrode **20**, the separator **10**, the electrolytic solution, and the exterior body **50**, and assembling them. An example of a method of manufacturing the lithium ion secondary battery **100** will be described below.

[0080] The negative electrode **30** is produced, for example, by sequentially carrying out a slurry producing step, an electrode application step, a drying step, and a rolling step.

[0081] The slurry producing step is a step of mixing a negative electrode active material, a binder, a conductive assistant, and a solvent to make a slurry. As the negative electrode active material, the above-mentioned negative electrode material is used. When a dispersion stabilizer is added to the

slurry, it is possible to suppress aggregation of the negative electrode active material.

[0082] The slurry producing step is a step of mixing a negative electrode active material, a binder, a conductive assistant, and a solvent to make a slurry. The solvent is, for example, water, N-methyl-2-pyrrolidone, or the like. The composition ratio, by mass, of the negative electrode active material, the conductive material, and the binder is preferably 70 wt % to 100 wt %: 0 wt % to 10 wt %: 0 wt % to 20 wt %. The mass ratio of these is adjusted such that the total is 100 wt %. A container used for producing the slurry is preferably made of a metal such as SUS.

[0083] The negative electrode active material may be a material composited by mixing active material particles and a conductive material while a shearing force is applied thereto. When the active material particles are mixed while the shear force is applied thereto to the extent that the active material particles are not altered, the surfaces of the active material particles are coated with the conductive material. In addition, the particle size of the negative electrode active material can be adjusted by the degree of mixing. In addition, the produced negative electrode active material may be sieved to make the particle size uniform.

[0084] The electrode application step is a step of applying the slurry to the surface of the negative electrode current collector **32**. A method of applying a slurry is not particularly limited. For example, a slit die coating method or a doctor blade method can be used as the method of applying a slurry. The slurry is applied, for example, at room temperature.

[0085] The drying step is a step of removing the solvent from the slurry. For example, the negative electrode current collector **32** on which the slurry is applied is dried in an atmosphere of 80° C. or higher and 350° C. or lower.

[0086] The rolling step is carried out as necessary. The rolling step is a step of applying a pressure to the negative electrode active material layer **34** to adjust the density of the negative electrode active material layer **34**. The rolling step is carried out, for example, using a roll press apparatus.

[0087] The positive electrode **20** can be produced in the same procedure as that for the negative electrode **30**. As the separator **10** and the exterior body **50**, commercially available products can be used.

[0088] Next, the produced positive electrode **20** and negative electrode **30** are laminated such that the separator **10** is located between them; and thereby, the power generating element **40** is produced. In a case in which the power generating element **40** is a wound body, the positive electrode **20**, the negative electrode **30**, and the separator **10** are wound with one end side thereof as an axis.

[0089] Finally, the power generating element **40** is enclosed in the exterior body **50**. The non-aqueous electrolytic solution is injected into the exterior body **50**. After the non-aqueous electrolytic solution is injected, the pressure is reduced, heating is performed, and the like, and thus the non-aqueous electrolytic solution is impregnated into the power generating element **40**. The exterior body **50** is sealed by applying heat or the like; and thereby, the lithium ion secondary battery **100** is obtained. Instead of injecting the electrolytic solution into the exterior body **50**, the power generating element **40** may be immersed in the electrolytic solution. After the liquid is injected into the power generating element, the power generating element is preferably left to stand for 24 hours.

[0090] The lithium ion secondary battery **100** according to the first embodiment has excellent cycle characteristics because the negative electrode active material includes a negative electrode material having a predetermined shape.

[0091] The embodiments of the present disclosure have been described in detail with reference to the drawings, but configuration, combinations thereof, and the like in the embodiments are merely examples, and additions, omissions, substitutions, and other modifications in the configurations are possible without departing from the features of the present disclosure.

EXAMPLES

Example 1

[0092] A positive electrode slurry was applied to one surface of an aluminum foil having a thickness of 15 μm . The positive electrode slurry was produced by mixing a positive electrode active material, a conductive assistant, a binder, and a solvent.

[0093] As the positive electrode active material, Li.sub.xCoO.sub.2 was used. As the conductive assistant, acetylene black was used. As the binder, polyvinylidene fluoride (PVDF) was used. As the solvent, N-methyl-2-pyrrolidone was used. The positive electrode slurry was produced by mixing 97 parts by mass of the positive electrode active material, 1 part by mass of the conductive assistant, 2 parts by mass of the binder, and 70 parts by mass of the solvent. The amount of the positive electrode active material carried in a positive electrode active material layer after drying was 25 mg/cm^2 . The solvent was removed from the positive electrode slurry in a drying furnace to make the positive electrode active material layer. The positive electrode active material layer was pressed using a roll press to produce a positive electrode.

[0094] Next, a negative electrode active material to be added to a negative electrode slurry was prepared. First, silicon particles having an average primary particle size of 5 nm and a carbon source were mixed and sintered to produce a composite particle. After the composite particle was produced, a thermal welding treatment was performed using a laser such that the silicon particles were connected to each other. The state in which the silicon particles were connected to each other in the composite particle was observed from an SEM image. The average secondary particle diameter of the composite particles was 8.6 μm .

[0095] Next, the negative electrode slurry was produced using this negative electrode active material. As the conductive assistant, carbon black was used. As the binder, a polyimide resin was used. As the solvent, N-methyl-2-pyrrolidone was used. The negative electrode slurry was produced by mixing 90 parts by mass of the negative electrode active material, 5 parts by mass of the conductive assistant, and 5 parts by mass of the binder in the N-methyl-2-pyrrolidone.

[0096] Then, the negative electrode slurry was applied onto one surface of a copper foil having a thickness of 10 μm and dried. The amount of the negative electrode active material carried in a negative electrode active material layer after drying was 2.5 mg/cm^2 . The negative electrode active material layer was pressed using a roll press and then sintered in a nitrogen atmosphere at 300° C. or higher for 5 hours.

[0097] Next, an electrolytic solution was produced. In a solvent of the electrolytic solution, fluoroethylene carbonate (FEC): ethylene carbonate (EC): diethyl carbonate (DEC)=10% by volume: 20% by volume: 70% by volume. In addition, an additive for improving output, an additive for suppressing gas, an additive for improving cycle characteristics, and an additive for improving safety performance were added to the electrolytic solution. As an electrolytic salt, LiPF.sub.6 was used. The concentration of LiPF.sub.6 was 1 mol/L.

(Production of Lithium Ion Secondary Battery for Evaluation)

[0098] The produced negative electrode and positive electrode were laminated with a separator (porous polyethylene sheet) interposed between them such that the positive electrode active material layer and the negative electrode active material layer faced each other, to obtain a laminated body. This laminated body was inserted into an exterior body made of an aluminum laminate film and heat-sealed except for one portion on the periphery thereof to form a closed portion. Finally, after the electrolytic solution was injected into the exterior body, a remaining portion was heat-sealed while reducing the pressure using a vacuum sealer, to produce a lithium ion secondary battery. The produced lithium ion secondary battery was left to stand for 24 hours.

(Measurement of Capacity Retention Rate after 300 Cycles)

[0099] The cycle characteristics of the lithium ion secondary battery were measured. The cycle characteristics were measured using a secondary battery charging and discharging test device (manufactured by Hokuto Denko Corporation).

[0100] The battery was charged at a constant current charge rate of 1 C (a current value at which charging was completed in 1 hour when constant current charging was performed at 25° C.) until a

battery voltage reached 4.2 V, and then discharged at a constant current discharge rate of 1.0 C until the battery voltage reached 2.5 V. The discharge capacity after the completion of charging and discharging was detected to obtain a battery capacity $Q_{\text{sub.1}}$ before the cycle test. The battery capacity $Q_{\text{sub.1}}$ was 2099 mAh/g.

[0101] The battery whose battery capacity $Q_{\text{sub.1}}$ was obtained above was again charged using the secondary battery charging and discharging test device at a constant current charge rate of 1 C until a battery voltage reached 4.2 V, and then discharged at a constant current discharge rate of 1 C until the battery voltage reached 2.5 V. The above-described charging and discharging was counted as one cycle, and 300 cycles of charging and discharging were performed. Thereafter, the discharge capacity after 300 cycles of charging and discharging was detected to obtain a battery capacity $Q_{\text{sub.2}}$ after 300 cycles. From the battery capacities $Q_{\text{sub.1}}$ and $Q_{\text{sub.2}}$ obtained above, a capacity retention rate E after 300 cycles was obtained. The capacity retention rate E was obtained by $E = Q_{\text{sub.2}}/Q_{\text{sub.1}} \times 100$. The capacity retention rate of Example 1 was 93%.

Examples 2 and 3

[0102] Examples 2 and 3 differ from Example 1 in that the average primary particle size of the silicon particles constituting the composite particle was changed. Other conditions were the same as in Example 1, and the capacity retention rate after 300 cycles was obtained.

Examples 4 to 6

[0103] Examples 4 to 6 differ from Example 1 in that the molar ratio of the silicon particles and the carbonaceous particles constituting the composite particle was changed. The molar ratio of the silicon particles and the carbonaceous particles was changed by adjusting the amounts of the silicon particles and the carbon source when producing the composite particle. Other conditions were the same as in Example 1, and the capacity retention rate after 300 cycles was obtained.

Example 7

[0104] Example 7 differs from Example 1 in that carbon was attached to the surface of the composite particle. The attachment of the carbon was performed by a chemical vapor deposition (CVD) method using acetylene gas. Other conditions were the same as in Example 1, and the capacity retention rate after 300 cycles was obtained.

Comparative Example 1

[0105] Comparative Example 1 differs from Example 1 in that the thermal welding treatment by laser irradiation was not carried out after the compositing treatment. In the composite particle of Comparative Example 1, no connection between the silicon particles was observed. Other conditions were the same as in Example 1, and the capacity retention rate after 300 cycles was obtained.

Comparative Examples 2 and 3

[0106] Comparative Examples 2 and 3 differ from Example 1 in that the molar ratio of the silicon particles and the carbonaceous particles constituting the composite particle was changed. The molar ratio of the silicon particles and the carbonaceous particles was changed by adjusting the amounts of the silicon particles and the carbon source when producing the composite particle. Other conditions were the same as in Example 1, and the capacity retention rate after 300 cycles was obtained.

Comparative Examples 4 and 5

[0107] Comparative Examples 4 and 5 differ from Example 1 in that the average primary particle size of the silicon particles constituting the composite particle was changed. Other conditions were the same as in Example 1, and the capacity retention rate after 300 cycles was obtained.

[0108] The results of Examples 1 to 7 and Comparative Examples 1 to 5 were summarized in the following table. The negative electrode active materials of Examples 2 to 7 and Comparative Examples 1 to 5 were also affected by variations in manufacturing conditions in addition to the intentionally changed parameters, and some of them were deviated from the various parameters of the negative electrode active material of Example 1.

TABLE-US-00001 TABLE 1 Average Capacity Silicon Carbon secondary primary particle
Carbonaceous Network coating Capacity particle particle molar particle of presence Discharge
retention size size ratio molar ratio silicon or capacity rate (μm) (nm) (mol %) (mol %) particle
absence (mAh/g) (%) Example 1 8.6 5 21.8 64.1 Presence Absence 2099 93 Example 2 8.5 1 20.8
66.5 Presence Absence 2110 92 Example 3 7.8 50 24.0 64.9 Presence Absence 2198 89 Example 4
5.6 7 15.0 80.0 Presence Absence 2163 90 Example 5 6.5 4 25.1 68.3 Presence Absence 2307 91
Example 6 3.4 25 40.0 50.0 Presence Absence 2485 87 Example 7 4.3 43 31.2 5.0 Presence
Presence 2221 92 Comparative 5.4 3 21.2 65.1 Absence Absence 2097 54 Example 1 Comparative
4.7 15 15.0 85.0 Presence Absence 2263 45 Example 2 Comparative 3.5 32 50.0 37.0 Presence
Absence 2615 21 Example 3 Comparative 8.4 60 25.6 68.3 Presence Absence 2326 52 Example 4
Comparative 7.5 0.5 24.1 65.2 Presence Absence 2208 59 Example 5

[0109] Examples 1 to 7 had higher capacity retention rates and better cycle characteristics than Comparative Examples 1 to 5.

REFERENCE SIGNS LIST

[0110] **1** Composite particle [0111] **10** Separator [0112] **20** Positive electrode [0113] **22** Positive electrode current collector [0114] **24** Positive electrode active material layer [0115] **30** Negative electrode [0116] **32** Negative electrode current collector [0117] **34** Negative electrode active material layer [0118] **40** Power generating element [0119] **50** Exterior body [0120] **52** Metal foil [0121] **54** Resin layer [0122] **60, 62** Terminal [0123] **100** Lithium ion secondary battery

Claims

1. A negative electrode material for a lithium ion secondary battery, comprising composite particles, wherein each of the composite particles includes a plurality of carbonaceous particles and a plurality of silicon particles, wherein each of the plurality of carbonaceous particles and the plurality of silicon particles is amorphous, wherein an average primary particle size of the plurality of silicon particles is 1 nm or more and 50 nm or less, wherein in the composite particles, a molar ratio of the silicon particles is 15 mol % or more and 40 mol % or less, and a molar ratio of the carbonaceous particles is 50 mol % or more and 80 mol % or less, and wherein the plurality of silicon particles are bonded to one another.
2. The negative electrode material for a lithium ion secondary battery according to claim 1, wherein a surface of each of the composite particles is coated with carbon or carbon nanotubes.
3. The negative electrode material for a lithium ion secondary battery according to claim 1, wherein in the composite particles, a molar ratio of the silicon particles is 20 mol % or more and 30 mol % or less, and a molar ratio of the carbonaceous particles is 60 mol % or more and 70 mol % or less.
4. The negative electrode material for a lithium ion secondary battery according to claim 1, wherein an average secondary particle size of the composite particles is 1 μm or more and 10 μm or less.
5. The negative electrode material for a lithium ion secondary battery according to claim 4, wherein the average secondary particle size of the composite particles is 2 μm or more and 8 μm or less.
6. The negative electrode material for a lithium ion secondary battery according to claim 5, wherein the average secondary particle size of the composite particles is 3 μm or more and 7 μm or less.
7. The negative electrode material for a lithium ion secondary battery according to claim 1, wherein the silicon particles include silicon in a form of a simple substance; SiO_x , wherein x satisfies $0.8 \leq x \leq 2$; or a silicon alloy represented by X_nSi , wherein X is a cation, and n satisfies $0 \leq n \leq 0.5$.
8. The negative electrode material for a lithium ion secondary battery according to claim 7, wherein X includes at least one selected from the group consisting of Ba, Mg, Al, Zn, Sn, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, W, Au, Ti, Na, and K.
9. The negative electrode material for a lithium ion secondary battery according to claim 1, wherein the average primary particle size of the plurality of silicon particles is 3 nm or more and 30 nm or less.

- 10.** The negative electrode material for a lithium ion secondary battery according to claim 1, wherein the carbonaceous particles include at least one from the group consisting of graphite, graphene, carbides formed after sintering pitches, and carbides formed after sintering resins.
- 11.** The negative electrode material for a lithium ion secondary battery according to claim 10, wherein the pitches are coal-based pitches, petroleum-based pitches, or synthetic pitches.
- 12.** The negative electrode material for a lithium ion secondary battery according to claim 11, wherein the pitches include at least one of coal tar, light tar oil, medium tar oil, heavy tar oil, naphthalene oil, anthracene oil, coal tar pitch, pitch oil, mesophase pitch, oxygen-crosslinked petroleum pitch, heavy oil, coke, or low molecular weight heavy oil, or derivatives of thereof.
- 13.** The negative electrode material for a lithium ion secondary battery according to claim 10, the resins include a thermoplastic resin.
- 14.** The negative electrode material for a lithium ion secondary battery according to claim 13, wherein the thermoplastic resin includes a polyvinyl alcohol, a phenol resin, an epoxy resin, a melamine resin, a urea resin, an aniline resin, a cyanate resin, a furan resin, a ketone resin, an unsaturated polyester resin, or a urethane resin, or modified products thereof.
- 15.** The negative electrode material for a lithium ion secondary battery according to claim 14, wherein the resins include one of polyethylene, polystyrene, an acrylonitrile-styrene (AS) resin, an acrylonitrile-butadiene-styrene (ABS) resin, polypropylene, polyethylene terephthalate, polycarbonate, polyacetal, polyphenylene ether, polybutylene terephthalate, polyphenylene sulfide, polysulfone, polyether sulfone, polyether ether ketone, or polyvinyl chloride.
- 16.** The negative electrode material for a lithium ion secondary battery according to claim 10, wherein the carbonaceous particles include graphite or graphene.
- 17.** The negative electrode material for a lithium ion secondary battery according to claim 1, wherein the composite particles further includes hydrogen, oxygen, and/or nitrogen.
- 18.** The negative electrode material for a lithium ion secondary battery according to claim 17, wherein a molar ratio of the hydrogen, oxygen, and/or nitrogen in the composite particles is 15 mol % or less.
- 19.** A negative electrode for a lithium ion secondary battery, comprising the negative electrode material for a lithium ion secondary battery according to claim 1.
- 20.** A lithium ion secondary battery comprising the negative electrode for a lithium ion secondary battery according to claim 19, a positive electrode, and an electrolyte.
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