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(71) Applicant (for all designated States except US): **DOW CORNING TORAY CO., LTD.** [JP/JP]; 5-1, Ohtemachi 1-chome, Chiyoda-ku, Tokyo, 1000004 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HARIMOTO, Yukinari** [JP/JP]; c/o Dow Corning Toray Co., Ltd., 507-1, Kishi, Yamakitamachi, Ashigarakamigun, Kanagawa, 2580112 (JP). **AKASAKA, Masayasu** [JP/JP]; c/o Dow Corning Toray Co., Ltd., 507-1, Kishi, Yamakitamachi, Ashigarakamigun, Kanagawa, 2580112 (JP). **FUKUI, Hiroshi** [JP/JP]; c/o Dow Corning Toray Co., Ltd., 507-1, Kishi, Yamakitamachi, Ashigarakamigun, Kanagawa,

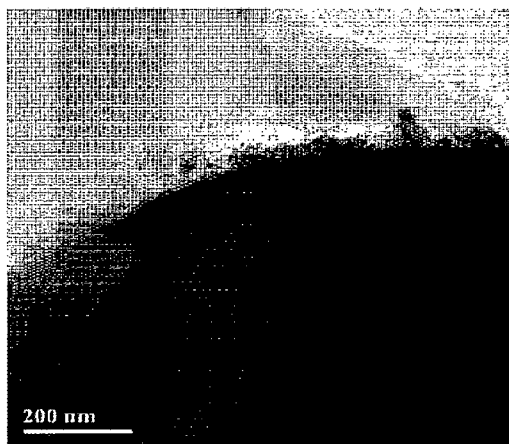
2580112 (JP). **EGUCHI, Katsuya** [JP/JP]; c/o Dow Corning Toray Co., Ltd., 507-1, Kishi, Yamakitamachi, Ashigarakamigun, Kanagawa, 2580112 (JP). **USHIO, Yoshito** [JP/JP]; c/o Dow Corning Toray Co., Ltd., 507-1, Kishi, Yamakitamachi, Ashigarakamigun, Kanagawa, 2580112 (JP). **PHAN, Son Thanh** [VN/JP]; c/o Dow Corning Toray Co., Ltd., 507-1, Kishi, Yamakitamachi, Ashigarakamigun, Kanagawa, 2580112 (JP).

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[Continued on next page]

(54) **Title:** METHOD FOR MANUFACTURING A CARBON SURFACE-COATED SILICON-CONTAINING CARBON-BASED COMPOSITE MATERIAL

**FIG. 5**

(57) **Abstract:** To provide a composite material suitable for use as an electrode of an electricity storage device, particularly for a lithium or lithium-ion secondary battery, an electrode active material constituted by the composite material, an electrode containing the active material, and an electricity storage device including the electrode. Using a carbon surface-coated silicon-containing carbon-based composite material as an electrode active material, the composite material obtained by: forming a cured product by crosslinking (A) a crosslinkable group-containing organic compound, and (B) a silicon-containing compound capable of crosslinking the crosslinkable group-containing organic compound; and baking a mixture of the cured product and (C) a carbonaceous matter.



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DESCRIPTION

METHOD FOR MANUFACTURING A CARBON SURFACE-COATED
SILICON-CONTAINING CARBON-BASED COMPOSITE MATERIAL

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FIELD OF THE INVENTION

[0001] The present invention relates to a carbon surface-coated silicon-containing carbon-based composite material and a method for manufacturing the same, an electrode active material constituted by the composite material, an electrode comprising the active material, and an electricity storage device comprising the electrode.

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DESCRIPTION OF THE PRIOR ART

[0002] Electricity storage devices and particularly lithium or lithium-ion secondary batteries are being investigated as a type of high energy density secondary battery. In many cases, a silicon-containing carbon material obtained by pyrolyzing a silicon polymer is used as a negative electrode material of such lithium-ion secondary batteries. For example, Japanese Unexamined Patent Application Publication No. H10-97853 and Solid State Ionics, 122, 71 (1999) describe fabricating an electrode usable in the manufacturing of a battery having a large capacity, low irreversible capacity, high density, and excellent safety behavior by using a polysilane and a coal tar pitch as precursors. Additionally, Japanese Unexamined Patent Application Publication No. H10-74506, Japanese Unexamined Patent Application Publication No. H10-275617, Japanese Unexamined Patent Application Publication No. 2004-273377, and J. Electrochem. Soc., 144, 2410 (1997) describe obtaining a battery having a large capacity, low irreversible capacity, high density, and excellent safety behavior by pyrolyzing a siloxane polymer and, thereafter, introducing lithium in order to form an electrode for a lithium or lithium-ion secondary battery.

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[0003] However, such lithium or lithium-ion secondary batteries that comprise an electrode including a silicon-containing carbon material have a problem in that practical performance is insufficient with regards to charge and discharge cycle characteristics and the like.

5 Prior Art Documents

Patent Documents

[0004] Patent Document 1: Japanese Unexamined Patent Application Publication No. H10-97853

Patent Document 2: Japanese Unexamined Patent Application Publication No. H10-74506

Patent Document 3: Japanese Unexamined Patent Application Publication No. H10-275617

10 Patent Document 4: Japanese Unexamined Patent Application Publication No. 2004-273377

Non-Patent Documents

[0005] Non-Patent Document 1: Solid State Ionics, 122, 71 (1999)

Non-Patent Document 2: J. Electrochem. Soc., 144, 2410 (1997)

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SUMMARY OF THE INVENTION

[0006] An object of the present invention is to provide a composite material suitable for use as an electrode of an electricity storage device, particularly for a lithium or lithium-ion secondary battery, an electrode active material constituted by the composite material, an electrode containing the active
20 material, and an electricity storage device including the electrode.

Solution to Problems

[0007] The object of the present invention is achieved by a method for manufacturing a carbon surface-coated silicon-containing carbon-based composite material characterized by obtaining a cured product by crosslinking (A) a crosslinkable group-containing organic compound (hereinafter referred to as "component (A)"), and (B) a silicon-containing compound (hereinafter referred to as
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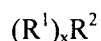
"component (B)") capable of crosslinking the crosslinkable group-containing organic compound; and baking a mixture of the cured product and (C) a carbonaceous matter (hereinafter referred to as "component (C)").

[0008] The baking is preferably performed at a temperature of from 300°C to 1,500°C in an inert gas or in a vacuum.

[0009] The crosslinkable group can be selected from the group consisting of aliphatic unsaturated groups, epoxy groups, acryl groups, methacryl groups, amino groups, hydroxyl groups, mercapto groups, and halogenated alkyl groups.

[0010] The component (A) may have an aromatic group.

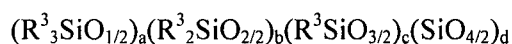
[0011] The component (A) is preferably an organic compound expressed by the following general formula.



In this formula, R^1 is a crosslinkable group; "x" is an integer greater than or equal to 1; and R^2 is an aromatic group with "x" valency.

[0012] The component (B) can be a siloxane, a silane, a silazane, a carbosilane, or a mixture thereof.

[0013] The component (B) is preferably a siloxane expressed by the following average unit formula.



In this formula, R^3 each independently represent a monovalent hydrocarbon group, a hydrogen atom, a halogen atom, an epoxy group-containing organic group, an acryl group- or methacryl

group-containing organic group, an amino group-containing organic group, a mercapto group-containing organic group, an alkoxy group, or a hydroxy group. "a", "b", "c", and "d" are numbers that are greater than or equal to 0 and less than or equal to 1, and that satisfy

"a"+"b"+"c"+"d"=1. However, "a", "b", and "c" cannot be 0 at the same time.

[0014] The component (C) can be a carbon black, a carbon fiber, a carbon nanofiber, a carbon nanotube, or a mixture thereof.

[0015] The crosslinking may be carried out via an addition reaction, a condensation reaction, a ring-opening reaction, or a radical reaction.

[0016] The cured product is preferably obtained by a hydrosilylation reaction of the component (A) having aliphatic unsaturated groups and the component (B) having silicon-bonded hydrogen atoms.

5 [0017] The cured product is preferably obtained by a radical reaction of the component (A) having aliphatic unsaturated groups and the component (B) having aliphatic unsaturated groups, acryl groups, methacryl groups, or silicon-bonded hydrogen atoms.

[0018] A surface of the cured product is preferably covered by the component (C).

[0019] The present invention relates to a carbon surface-coated silicon-containing carbon-based
10 composite material obtained via the manufacturing method described above.

[0020] The composite material is preferably constituted by particles having an average diameter from 5 nm to 50 μm .

[0021] An amount of carbon in the composite material can be set to from 1 to 50 mass (weight)%.

[0022] The composite material preferably has a carbon coating layer having a thickness from 5 nm to
15 2 μm .

[0023] The electrode active material of the present invention is constituted by the composite material described above. The electrode active material is preferably constituted by particles having an average diameter from 1 to 50 μm .

[0024] The electrode of the present invention includes the electrode active material described above,
20 and can be suitably used for electricity storage devices, especially for lithium or lithium-ion secondary batteries.

Effects of Invention

[0025] The composite material of the present invention can be used as a raw material for an electrode active material having high reversible capacity, stable charge and discharge cycle characteristics,
25 high initial charge and discharge efficiency, and little electrical potential loss when lithium is

discharged. Additionally, the composite material of the present invention uses inexpensive raw materials and can be manufactured via a simple manufacturing process.

[0026] The electrode active material of the present invention is suitable for use in an electricity storage device, particularly as an electrode of a lithium or lithium-ion secondary battery. Moreover, the electrode of the present invention can impart high reversible capacity, stable charge and discharge cycle characteristics, and high initial charge and discharge efficiency to a battery. As a result, the electricity storage device of the present invention can have high reversible capacity, stable charge and discharge cycle characteristics, and high initial charge and discharge efficiency.

Brief Description of the Drawings

[0027] FIG. 1 illustrates a lithium-ion secondary battery that is an example of the electricity storage device of the present invention.

FIG. 2 illustrates a lithium secondary battery that is an example of the electricity storage device of the present invention.

FIG. 3 is an electron photomicrograph of spherical silicon-containing crosslinked particles prepared in Practical Example 1.

FIG. 4 is an electron photomicrograph of the carbon-coated silicon-containing carbon-based composite material prepared in Practical Example 1.

FIG. 5 is a transmission electron photomicrograph of a cross-section of the carbon-coated silicon-containing carbon-based composite material prepared in Practical Example 1.

DETAILED DESCRIPTION OF THE INVENTION

[0028]

Composite Material

The composite material of the present invention can be obtained by a manufacturing method characterized by obtaining a cured product by crosslinking (A) a crosslinkable group-containing

organic compound, and (B) a silicon-containing compound capable of crosslinking the crosslinkable group-containing organic compound; and baking a mixture of the cured product and (C) a carbonaceous matter.

[0029] The crosslinkable group in the component (A) is not particularly limited provide that it is a

5 crosslinkable group. Examples thereof include aliphatic unsaturated groups, epoxy groups, acryl groups, methacryl groups, amino groups, hydroxyl groups, mercapto groups, and halogenated alkyl groups. Specific examples of the aliphatic unsaturated groups include vinyl groups, propenyl groups, butenyl groups, pentenyl groups, hexenyl groups, and similar alkenyl groups; acetyl groups, propynyl groups, pentynyl groups, and similar alkynyl groups. Specific examples of the epoxy
10 groups include glycidyl groups, glycidoxy groups, epoxycyclohexyl groups, 3-glycidoxypropyl groups, and 2-(3,4-epoxycyclohexyl) ethyl groups. Specific examples of the acryl groups include 3-acryloxypropyl groups. Specific examples of the methacryl groups include 3-methacryloxypropyl groups. Specific examples of the amino groups include 3-aminopropyl groups, and N-(2-aminoethyl)-3-aminopropyl groups. Specific examples of the hydroxyl groups include
15 hydroxyethyl groups, hydroxypropyl groups, and similar hydroxyalkyl groups; and hydroxyphenyl groups and similar hydroxyaryl groups. Specific examples of the mercapto groups include 3-mercaptopropyl groups. Specific examples of the halogenated alkyl groups include 3-chloropropyl groups.

[0030] Note that the component (A) may be mixture of an organic compound having one

20 crosslinkable group in a molecule and an organic compound having at least two crosslinkable groups in a molecule. In this case, a proportion of the latter compound in the mixture is not particularly limited, but, from the perspective of obtaining excellent crosslinkage, the content is preferably at least 15 mass (weight)% and more preferably at least 30 mass (weight)%.

[0031] The component (A) may be silicon-free or may include silicon.

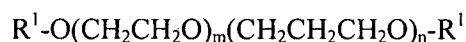
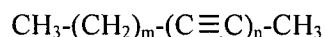
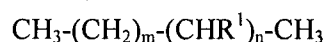
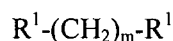
25 [0032] When the component (A) is silicon-free, the component (A) is preferably an organic

compound having at least one aromatic ring in a molecule because forming a graphene structure is facilitated due to excellent efficiency when carbonizing by heating.

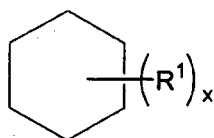
[0033] Examples of the component (A) described above include silicon-free aliphatic hydrocarbon compounds having a crosslinkable group at a molecular terminal and/or in the side molecular chains;

- 5 silicon-free aliphatic hydrocarbon compounds having a crosslinkable group at a molecular terminal and/or in the side molecular chains and hetero-atoms other than carbon atoms, such as, for example, nitrogen, oxygen, or boron atoms, in the molecular chain; silicon-free aromatic hydrocarbon compounds having a crosslinkable group in the molecule; and silicon-free cyclic fatty compounds having a crosslinkable group in the molecule and also hetero-atoms other than carbon atoms, such as,
- 10 for example, nitrogen, oxygen, or boron atoms.

[0034] Specific examples of the aliphatic hydrocarbon compounds include compounds expressed by the following formulae:

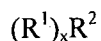


Formula 1



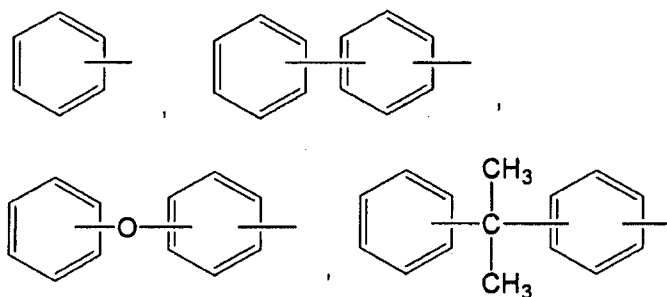
- 20 In the formulae, R^1 represents a crosslinkable group, and examples thereof include aliphatic unsaturated groups, epoxy groups, acryl groups, methacryl groups, amino groups, hydroxyl groups, mercapto groups, and halogenated alkyl groups. Specific examples are the same as the groups described above. Additionally, "m" and "n" are integers greater than or equal to 1; and "x" is an integer greater than or equal to 1.

[0035] Specific examples of the aromatic hydrocarbon compound include compounds expressed by the following general formula:



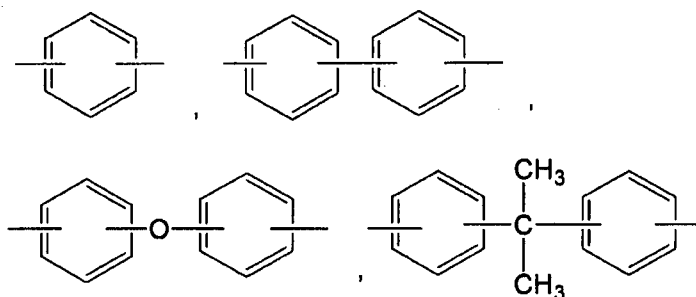
In this formula, R^1 is a crosslinkable group, and examples thereof are the same as the groups described above. Additionally, "x" is an integer greater than or equal to 1. R^2 represents an aromatic group with "x"-valency. Specifically, in this formula, when "x" is 1, R^2 represents a monovalent aromatic group, and specific examples thereof include the groups described below.

Formula 2



- 10 [0036] Specific examples of the aromatic hydrocarbon compound described above include α - or β -methylstyrene, α - or β -ethylstyrene, methoxystyrene, phenylstyrene, chlorostyrene, o-, m-, or p-methylstyrene, ethylstyrene, methylsilylstyrene, hydroxystyrene, cyanostyrene, nitrostyrene, aminostyrene, carboxystyrene, sulfoxystyrene, sodium styrenesulfonate, vinylpyridine, vinylthiophene, vinylpyrrolidone, vinylnaphthalene, vinylanthracene, and vinylbiphenyl.
- 15 [0037] Additionally, in the formula, when "x" is 2, R^2 represents a bivalent aromatic group, and specific examples thereof include the groups described below.

Formula 3



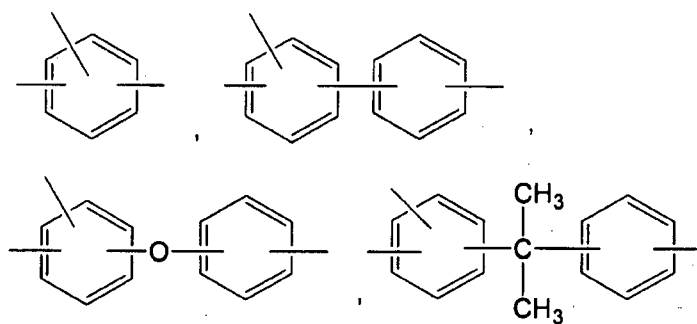
[0038] Specific examples of the aromatic hydrocarbon compound described above include divinylbenzene, divinylbiphenyl, vinylbenzylchloride, divinylpyrindine, divinylthiophene,

5 divinylpyrrolidone, divinylanthracene, divinylxylene, divinylethylbenzene, and divinylanthracene.

The aromatic hydrocarbon compound is preferably divinylbenzene because the pyrolyzing characteristics of the obtained cured product will be superior.

[0039] Additionally, in the formula, when "x" is 3, R² represents a trivalent aromatic group, and specific examples thereof include the groups described below.

10 Formula 4

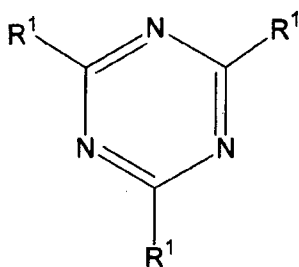


[0040] Specific examples of the aromatic hydrocarbon compound described above include trivinylbenzene and trivinylanthracene.

[0041] Additionally, specific examples of the aromatic compound comprising hetero-atoms include

15 aromatic compounds expressed by the following formula:

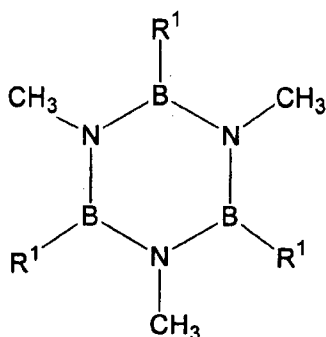
Formula 5



In this formula, R¹ is a crosslinkable group, and examples thereof are the same as the groups described above.

- 5 [0042] Additionally, specific examples of the cyclic compound having hetero-atoms include cyclic compounds expressed by the following formula:

Formula 6



In this formula, R¹ is a crosslinkable group, and examples thereof are the same as the groups described above.

10

[0043] The component (A) including silicon is not particularly limited provided that it has a crosslinkable group, and examples thereof include silicon-containing monomers, oligomers, and polymers. Examples thereof include silanes constituted by structural units having silicon-silicon bonds, silazanes constituted by structural units having silicon-nitrogen-silicon bonds, siloxanes constituted by structural units having silicon-oxygen-silicon bonds, carbosilanes constituted by structural units having silicon-carbon-silicon bonds, and mixtures thereof.

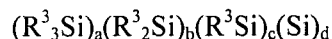
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[0044] Examples of silanes as the component (A) include those expressed by the following average

unit formula:



or the following average unit formula:



5 In these formulae,

R^3 each independently represent the crosslinkable group described above, a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic hydrocarbon group having from 1 to 20 carbons, an alkoxy group, a hydrogen atom, or a halogen atom.

"a", "b", "c", and "d" are each 0 or a positive number. However, "a"+"b"+"c"+"d"=1, and at least

10 one and preferably at least two

R^3 in the molecule are the crosslinkable group described above.

[0045] The saturated aliphatic hydrocarbon group is preferably an alkyl group, and the aromatic hydrocarbon group is preferably an aryl group and an aralkyl group.

[0046] The alkyl groups are preferably alkyl groups having from 1 to 12 carbons and more preferably

15 alkyl groups having from 1 to 6 carbon atoms. The alkyl groups are preferably any of the following: straight or branched chain alkyl groups, cycloalkyl groups, or cycloalkylene groups (alkyl groups that combine straight or branched chain alkylene groups (preferably methylene groups, ethylene groups, or similar alkylene groups having from 1 to 6 carbon atoms) with carbon rings (preferably rings having from 3 to 8 carbon atoms)).

20 [0047] The straight or branched chain alkyl groups preferably have from 1 to 6 carbon atoms and examples thereof include methyl groups, ethyl groups, n-propyl groups, isopropyl groups, butyl groups, t-butyl groups, pentyl groups, hexyl groups, and the like. Methyl groups are particularly preferable.

[0048] The cycloalkyl groups preferably have from 4 to 6 carbon atoms and examples thereof include
25 cyclobutyl groups, cyclopentyl groups, cyclohexyl groups, and the like. Cyclopentyl groups and

cyclohexyl groups are particularly preferable.

[0049] The aryl groups preferably have from 6 to 12 carbon atoms and examples thereof include phenyl groups, naphthyl groups, and tolyl groups.

[0050] The aralkyl groups preferably have from 7 to 12 carbon atoms. Examples of aralkyl groups with from 7 to 12 carbon atoms include benzyl groups, phenethyl groups, and phenylpropyl groups.

[0051] The hydrocarbon group may have a substituent and examples of said substituent include fluorine atoms, chlorine atoms, bromine atoms, iodine atoms, and similar halogen atoms; hydroxyl groups; methoxy groups, ethoxy groups, n-propoxy groups, isopropoxy groups, and similar alkoxy groups having from 1 to 6 carbons; amino groups; amide groups; nitro groups; epoxy groups; and the like. The substituent can be bonded at the hydrocarbon chain position, the saturated ring position, or the aromatic ring position.

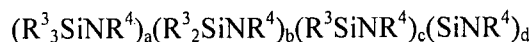
[0052] Examples of the alkoxy groups include methoxy groups, ethoxy groups, n-propoxy groups, and isopropoxy groups.

[0053] Examples of the halogen atoms include fluorine atoms, chlorine atoms, bromine atoms, and iodine atoms.

[0054] The silane described above can be manufactured by methods known in the art. Examples of methods thereof include the method comprising dehalogenation of halosilanes in the presence of an alkali metal described in *Macromolecules*, 23, 3423 (1990), etc.; the method comprising anionic polymerization of disilenes described in *Macromolecules*, 23, 4494 (1990), etc.; the method comprising dehalogenation of halosilanes via electrode reduction described in *J. Chem. Soc., Chem. Commun.*, 1161 (1990); *J. Chem. Soc., Chem. Commun.*, 897 (1992), etc; the method comprising dehalogenation of halosilanes in the presence of magnesium (see WO98/29476, etc.); the method comprising dehydration of hydrosilanes in the presence of metal catalysts (see Kokai H04-334551, etc.), and other methods.

[0055] Examples of silazane as the component (A) include those expressed by the following average

unit formula:



In this formula, R^3 each independently represent the crosslinkable group described above, a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic hydrocarbon group having from 1 to 20 carbons, an alkoxy group, a hydrogen atom, or a halogen atom.

R^4 represents a hydrogen atom or a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic hydrocarbon group having from 1 to 20 carbons.

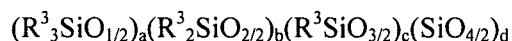
"a", "b", "c", and "d" are each 0 or a positive number, however, "a"+"b"+"c"+"d"=1.

At least one and preferably at least two R^3 in the molecule are the crosslinkable group described above.

Here, the saturated aliphatic hydrocarbon group, the aromatic hydrocarbon group, the alkoxy group, and the halogen atoms are the same as those defined above for the silane.

[0056] The silazane described above can be prepared by methods known in the art. Examples of methods for preparing the silazane include those methods described in U.S. Patent Nos. 4312970, 4340619, 4395460, 4404153, 4482689, 4397828, 4540803, 4543344, 4835238, 4774312, 4929742, and 4916200. An alternate method is also described in J. Mater. Sci., 22, 2609 (1987).

[0057] Examples of siloxanes as the component (A) include those expressed by the following average unit formula:



In this formula, R^3 each independently represent the crosslinkable group described above, a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic hydrocarbon group having from 1 to 20 carbons, an alkoxy group, a hydrogen atom, or a halogen atom. "a", "b", "c", and "d" are numbers that are greater than or equal to 0 and less than or equal to 1, and that satisfy "a"+"b"+"c"+"d"=1, however, "a", "b", and "c" cannot be 0 at the same time.

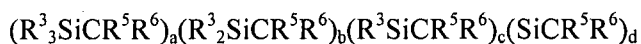
At least one and preferably at least two R^3 in the molecule are the crosslinkable group described above.

Here, the saturated aliphatic hydrocarbon group, the aromatic hydrocarbon group, the alkoxy group, and the halogen atoms are the same as those defined above for the silane.

5 [0058] The siloxane described above can be prepared by methods known in the art. The method for preparing the siloxane is not particularly limited, but the most general methods of preparation include hydrolysis of organochlorosilanes. These and other methods are disclosed by Noll in, Chemistry and Technology of Silicones, Chapter 5 (Translated 2nd German Issue, Academic Press, 1968).

[0059] Examples of carbosilane as the component (A) include those expressed by the following

10 average unit formula:



In this formula, R^3 each independently represent the crosslinkable group described above, a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic hydrocarbon group having from 1 to 20 carbons, an alkoxy group, a hydrogen atom, or a halogen atom.

R^5 and R^6 each independently represent a hydrogen atom or a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic hydrocarbon group having from 1 to 20 carbons.

"a", "b", "c", and "d" are each 0 or a positive number, however, "a"+"b"+"c"+"d"=1.

20 At least one and preferably at least two R^3 in the molecule are the crosslinkable group described above.

Here, the saturated aliphatic hydrocarbon group, the aromatic hydrocarbon group, the alkoxy group, and the halogen atoms are the same as those defined above for the silane.

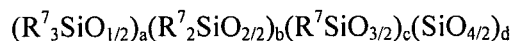
[0060] The carbosilane described above can be prepared by methods known in the art. Examples of methods for preparing the carbosilanes are described in Macromolecules, 21, 30 (1988) and U.S.

Patent 3293194.

[0061] The forms of the silane, silazane, siloxane, and carbosilane are not particularly limited, and may be solids, liquids, or paste-like forms, but, from the perspectives of handle-ability and the like, are preferably solids.

- 5 [0062] Of these silicon-based polymer compounds, siloxanes constituted by units having silicon-oxygen-silicon bonds are preferable and polysiloxanes are more preferable in light of the following industrial benefits: the amount of silicon is not excessively low, such compounds have sufficient chemical stability, handling at room temperature in air is easy, raw material costs and fabrication process costs are low, and sufficient cost performance can be obtained.
- 10 [0063] The component (A) may be one type of the organic compound described above or may be a mixture of two or more types; and furthermore, may comprise a nitrogen-containing monomer such as acrylonitrile or the like as another component. In this case, a content of the nitrogen-containing monomer is preferably not more than 50 mass (weight)%, and more preferably is in a range from 10 to 50 mass (weight)%.
- 15 [0064] The component (B) is a silicon-containing compound capable of crosslinking the component (A). Examples of the component (B) described above include siloxanes, silanes, silazanes, carbosilanes, and mixtures thereof. Specific examples include monomers, oligomers, or polymers having Si-O-Si bonds and similar siloxanes; monomers, oligomers, or polymers having silane and Si-Si bonds and similar silanes; monomers, oligomers, or polymers having Si-(CH₂)_n-Si bonds and
- 20 similar silalkylenes; monomers, oligomers, or polymers having Si-(C₆H₄)_n-Si or Si-(CH₂CH₂C₆H₄CH₂CH₂)_n-Si bonds and similar silarylenes; monomers, oligomers, or polymers having Si-N-Si bonds and similar silazanes; silicon-containing copolymer compounds having at least two types of bonds selected from Si-O-Si bonds, Si-Si bonds, Si-(CH₂)_n-Si bonds, Si-(C₆H₄)_n-Si bonds, and Si-N-Si bonds; and mixtures thereof. Note that in the formula, "n" is an integer greater
- 25 than or equal to 1. The component (B) preferably has silicon-bonded hydrogen atoms.

[0065] Examples of siloxanes as the component (B) include those expressed by the following average unit formula:



In this formula, R^7 each independently represent a monovalent hydrocarbon group, a

5 hydrogen atom, a halogen atom, an epoxy group-containing organic group, an acryl group- or methacryl group-containing organic group, an amino group-containing organic group, a mercapto group-containing organic group, an alkoxy group, or a hydroxy group. "a", "b", "c", and "d" are numbers that are greater than or equal to 0 and less than or equal to 1, and that satisfy "a"+"b"+"c"+"d"=1. However, "a", "b", and "c" cannot be 0 at the same time.

10 [0066] Specific examples of the monovalent hydrocarbon groups represented by R^7 include alkyl groups, alkenyl groups, aralkyl groups, and aryl groups. The alkyl groups are preferably alkyl groups having from 1 to 12 carbon atoms and more preferably alkyl groups having from 1 to 6 carbon atoms. The alkyl groups may be any of the following: straight or branched chain alkyl groups, cycloalkyl groups, or cycloalkylene groups (alkyl groups that combine straight or branched

15 chain alkylene groups (preferably methylene groups, ethylene groups, or similar alkylene groups having from 1 to 6 carbon atoms) with carbon rings (preferably rings having from 3 to 8 carbon atoms)). The straight or branched chain alkyl groups preferably have from 1 to 6 carbon atoms and specific examples thereof include methyl groups, ethyl groups, n-propyl groups, isopropyl groups, butyl groups, t-butyl groups, pentyl groups, and hexyl groups. The cycloalkyl groups preferably

20 have from 4 to 6 carbon atoms and specific examples thereof include cyclobutyl groups, cyclopentyl groups, and cyclohexyl groups. The alkenyl groups preferably have from 2 to 12 carbon atoms, and more preferably from 2 to 6 carbon atoms. Specific examples of the alkenyl groups having from 2 to 6 carbons include vinyl groups, propenyl groups, butenyl groups, pentenyl groups, and hexenyl groups, of which vinyl groups are preferable. The aralkyl groups preferably have from 7 to 12

25 carbon atoms. Specific examples of the aralkyl groups with from 7 to 12 carbon atoms include

benzyl groups, phenethyl groups, and phenylpropyl groups. The aryl groups preferably have from 6 to 12 carbon atoms and specific examples thereof include phenyl groups, naphthyl groups, and tolyl groups. The monovalent hydrocarbon groups may have substituents. Specific examples of such substituents include fluorine atoms, chlorine atoms, bromine atoms, iodine atoms, or other halogens; hydroxyl groups; methoxy groups, ethoxy groups, n-propoxy groups, isopropoxy groups, or similar alkoxy groups. Specific examples of such substituted monovalent hydrocarbon groups include 3-chloropropyl groups, 3,3,3-trifluoropropyl groups, perfluorobutylethyl groups, and perfluorooctylethyl groups.

[0067] Specific examples of the halogen atoms represented by R^7 include fluorine atoms, chlorine atoms, bromine atoms, and iodine atoms, of which chlorine atoms are preferable.

[0068] Specific examples of the epoxy group-containing organic groups represented by R^7 include 3-glycidoxypropyl groups, 4-glycidoxybutyl groups, or similar glycidoxyalkyl groups; 2-(3,4-epoxycyclohexyl)-ethyl groups, 3-(3,4-epoxycyclohexyl)-propyl groups, or similar epoxycyclohexylalkyl groups; and 4-oxiranylbutyl groups, 8-oxiranyloctyl groups, or similar oxiranylalkyl groups. Glycidoxyalkyl groups are preferable and 3-glycidoxypropyl groups are particularly preferable.

[0069] Specific examples of the acryl group- or methacryl group-containing organic groups represented by R^7 include 3-acryloxypropyl groups, 3-methacryloxypropyl groups, 4-acryloxybutyl groups, and 4-methacryloxybutyl groups, of which 3-methacryloxypropyl groups are preferable.

[0070] Specific examples of the amino group-containing organic groups represented by R^7 include 3-aminopropyl groups, 4-aminobutyl groups, and N-(2-aminoethyl)-3-aminopropyl groups, of which 3-aminopropyl groups and N-(2-aminoethyl)-3-aminopropyl groups are preferable.

[0071] Specific examples of the mercapto group-containing organic groups represented by R^7 include 3-mercaptopropyl groups and 4-mercaptobutyl groups.

[0072] Specific examples of the alkoxy groups represented by R^7 include methoxy groups, ethoxy

groups, n-propoxy groups, and isopropoxy groups, of which methoxy groups and ethoxy groups are preferable.

[0073] In one molecule, at least one group and preferably at least two groups represented by R^7 are alkenyl groups, hydrogen atoms, halogen atoms, epoxy-containing organic groups, acryl-containing organic groups, methacryl-containing organic groups, amino-containing organic groups, mercapto-containing organic groups, alkoxy groups, or hydroxy groups.

[0074] "a", "b", "c", and "d" are numbers that are greater than or equal to 0 and less than or equal to 1, and that satisfy "a"+"b"+"c"+"d"=1. However, "a", "b", and "c" cannot be equal to 0 at the same time.

[0075] The aforementioned siloxanes may be structured at least from one of the structural units selected from $(R^7_3SiO_{1/2})$, $(R^7_2SiO_{2/2})$, $(R^7SiO_{3/2})$, and $(SiO_{4/2})$. Specific examples are the following: a straight chain polysiloxane composed of $(R^7_3SiO_{1/2})$ and $(R^7_2SiO_{2/2})$ units; a cyclic polysiloxane composed of $(R^7_2SiO_{2/2})$ units; a branched chain polysiloxane composed of $(R^7SiO_{3/2})$ and $(SiO_{4/2})$ units; a polysiloxane composed of $(R^7_3SiO_{1/2})$ and $(R^7SiO_{3/2})$ units; a polysiloxane composed of $(R^7_3SiO_{1/2})$ and $(SiO_{4/2})$ units; a polysiloxane composed of $(R^7SiO_{3/2})$ and $(SiO_{4/2})$ units; a polysiloxane composed of $(R^7_2SiO_{2/2})$ and $(R^7SiO_{3/2})$ units; a polysiloxane composed of $(R^7_2SiO_{2/2})$ and $(SiO_{4/2})$ units; a polysiloxane composed of $(R^7_3SiO_{1/2})$, $(R^7_2SiO_{2/2})$, and $(R^7SiO_{3/2})$ units; a polysiloxane composed of $(R^7_3SiO_{1/2})$, $(R^7_2SiO_{2/2})$, and $(SiO_{4/2})$ units; a polysiloxane composed of $(R^7_3SiO_{1/2})$, $(R^7SiO_{3/2})$, and $(SiO_{4/2})$ units; a polysiloxane composed of $(R^7_2SiO_{2/2})$, $(R^7SiO_{3/2})$, and $(SiO_{4/2})$ units; and a polysiloxane composed of $(R^7_3SiO_{1/2})$, $(R^7_2SiO_{2/2})$, $(R^7SiO_{3/2})$, and $(SiO_{4/2})$ units. The number of repetitions of the structural units expressed by each of $(R^7_3SiO_{1/2})$, $(R^7_2SiO_{2/2})$, $(R^7SiO_{3/2})$, and $(SiO_{4/2})$ is preferably within a range from 1 to 10,000, more preferably within a range from 1 to 1,000, and even more preferably within a range from 3 to 500.

[0076] The siloxanes described above can be prepared by methods known in the art. The method for preparing these siloxanes is not particularly limited, but the most general methods include

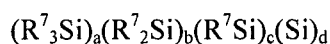
hydrolysis of organochlorosilanes. These and other methods are disclosed by Noll in, Chemistry and Technology of Silicones, Chapter 5 (Translated 2nd German Issue, Academic Press, 1968).

[0077] The siloxanes described above may be silicon-containing copolymer compounds with polymers. Examples of silicon-containing copolymer compounds that can be used as the siloxanes include silicon-containing copolymer compounds having Si-O-Si bonds and Si-Si bonds; silicon-containing copolymer compounds having Si-O-Si bonds and Si-N-Si bonds; silicon-containing copolymer compounds having Si-O-Si bonds and Si-(CH₂)_n-Si bonds; silicon-containing copolymer compounds having Si-O-Si bonds and Si-(C₆H₄)_n-Si bonds or Si-(CH₂CH₂C₆H₄CH₂CH₂)_n-Si bonds; and the like. In the formulae, "n" has the same meaning as defined above.

[0078] Furthermore, the silanes can be expressed by the following general formula:



or the following average unit formula:



In the formulae, R⁷ each independently represent a monovalent hydrocarbon group, a hydrogen atom, a halogen atom, an epoxy group-containing organic group, an acryl group- or methacryl group-containing organic group, an amino group-containing organic group, a mercapto group-containing organic group, an alkoxy group, or a hydroxy group. In one molecule, at least one group and preferably at least two groups represented by R⁷ are alkenyl groups, hydrogen atoms, halogen atoms, epoxy-containing organic groups, acryl-containing organic groups, methacryl-containing organic groups, amino-containing organic groups, mercapto-containing organic groups, alkoxy groups, or hydroxy groups. "a", "b", "c", and "d" are numbers that are greater than or equal to 0 and less than or equal to 1, and that satisfy "a"+"b"+"c"+"d"=1. However, "a", "b", and "c" cannot be equal to 0 at the same time.

[0079] The silanes are expressed by the general formula: R₄Si, or structured from at least one of the

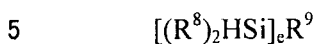
structural units selected from (R^7_3Si), (R^7_2Si), (R^7Si), and (Si). Specific examples are the following: a straight chain polysilane composed of (R^7_3Si) and (R^7_2Si) units; a cyclic polysilane composed of (R^7_2Si) units; a branched chain polysilane (polysilane) composed of (R^7Si) and (Si) units; a polysilane composed of (R^7_3Si) and (R^7Si) units; a polysilane composed of (R^7_3Si) and (Si) units; a polysilane composed of (R^7Si) and (Si) units; a polysilane composed of (R^7_2Si) and (R^7Si) units; a polysilane composed of (R^7_2Si) and (Si) units; a polysilane composed of (R^7_3Si), (R^7_2Si), and (R^7Si) units; a polysilane composed of (R^7_3Si), (R^7_2Si), and (Si) units; a polysilane composed of (R^7_3Si), (R^7Si), and (Si) units; a polysilane composed of (R^7_2Si), (R^7Si), and (Si) units; or a polysilane composed of (R^7_3Si), (R^7_2Si), (R^7Si), and (Si) units. The number of repetitions of the structural units expressed by each of (R^7_3Si), (R^7_2Si), (R^7Si), and (Si) is preferably within a range from 2 to 10,000, more preferably within a range from 3 to 1,000, and even more preferably within a range from 3 to 500.

[0080] The silanes described above can be manufactured by methods known in the art. Examples of methods thereof include the method comprising dehalogenation of halosilanes in the presence of an alkali metal described in *Macromolecules*, 23, 3423 (1990), etc.; the method comprising anionic polymerization of disilenes described in *Macromolecules*, 23, 4494 (1990), etc.; the method comprising dehalogenation of halosilanes via electrode reduction described in *J. Chem. Soc., Chem. Commun.*, 1161 (1990); *J. Chem. Soc., Chem. Commun.*, 897 (1992), etc; the method comprising dehalogenation of halosilanes in the presence of magnesium (see WO98/29476, etc.); the method comprising dehydration of hydrosilanes in the presence of metal catalysts (see Kokai H04-334551, etc.), and other methods.

[0081] The silanes described above may be silicon-containing copolymer compounds with other polymers. Examples of silicon-containing copolymer compounds that can be used as the silanes include silicon-containing copolymer compounds having Si-Si bonds and Si-O-Si bonds; silicon-containing copolymer compounds having Si-Si bonds and Si-N-Si bonds; silicon-containing copolymer compounds having Si-Si bonds and Si-(CH₂)_n-Si bonds; silicon-containing copolymer

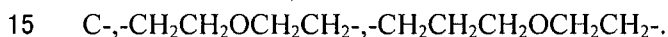
compounds having Si-Si bonds and Si-(C₆H₄)_n-Si bonds or Si-(CH₂CH₂C₆H₄CH₂CH₂)_n-Si bonds; and the like.

[0082] Examples of other silanes include silicon-containing compounds expressed by the general formula:

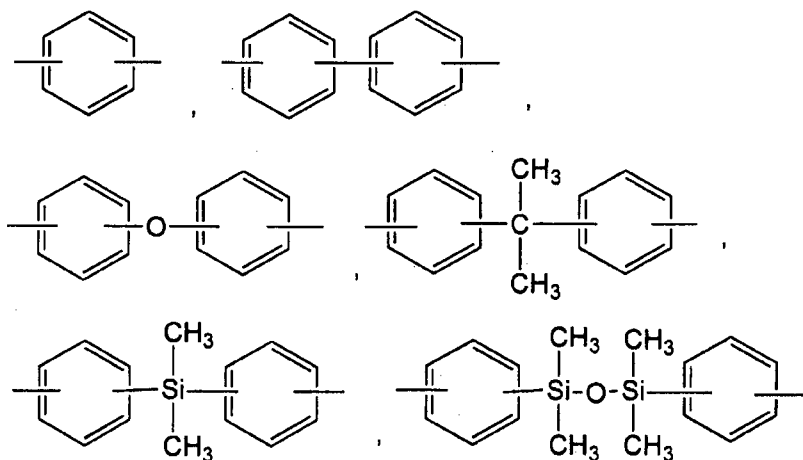


In this formula, R⁸ each represent substituted or unsubstituted monovalent hydrocarbon groups. "e" is an integer greater than or equal to 2, and R⁹ is an "e"-valent organic group. In this formula, examples of the monovalent hydrocarbon groups represented by R⁸ are the same as the monovalent hydrocarbon groups described as examples for R⁷. "e" is an integer greater than or

10 equal to 2, preferably an integer in a range from 2 to 6. When R⁹ is an "e"-valent organic group and "e" is equal to 2, R⁹ is a bivalent organic group. Specific examples thereof include alkylene groups, alkenylene groups, alkyleneoxyalkylene groups, arylene groups, aryleneoxyarylene groups, and arylene-alkylene-arylene groups. Even more specific examples include the groups expressed by the following formulae: -CH₂CH₂-, -CH₂CH₂CH₂-, -CH₂CH(CH₃)-, -CH=CH-, -C≡

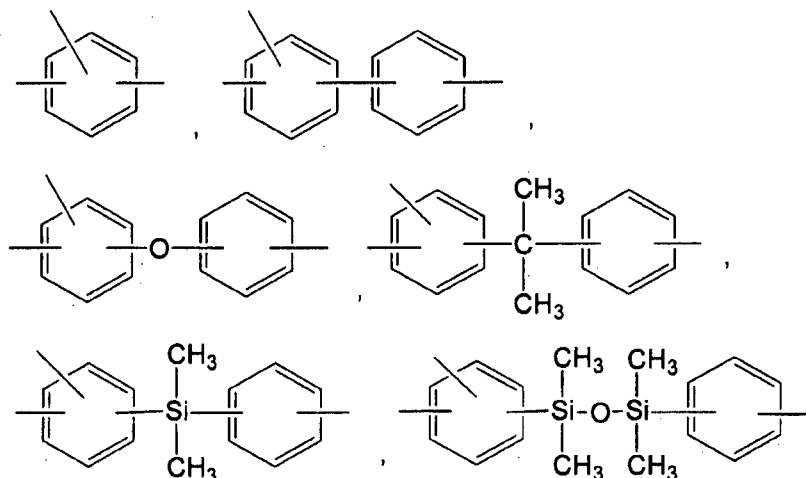


Formula 7



[0083] When "e" is equal to 3, R⁹ is a trivalent organic group. Specific examples thereof include the groups expressed by the following formulae:

Formula 8



[0084] Examples of the silazanes are those expressed, for example, by the following average unit formula:

$$(R^7_3SiNR^{10})_a(R^7_2SiNR^{10})_b(R^7SiNR^{10})_c(SiNR^{10})_d$$

In this formula, R^7 each independently represent a monovalent hydrocarbon group, a hydrogen atom, a halogen atom, an epoxy group-containing organic group, an acryl group- or methacryl group-containing organic group, an amino group-containing organic group, a mercapto group-containing organic group, an alkoxy group, or a hydroxy group. In one molecule, at least one group and preferably at least two groups represented by R^7 are alkenyl groups, hydrogen atoms, halogen atoms, epoxy-containing organic groups, acryl-containing organic groups, methacryl-containing organic groups, amino-containing organic groups, mercapto-containing organic groups, alkoxy groups, or hydroxy groups. R^{10} is a hydrogen atom or a substituted or unsubstituted monovalent hydrocarbon group. "a", "b", "c", and "d" are numbers that are greater than or equal to 0 and less than or equal to 1, and that satisfy "a"+"b"+"c"+"d"=1. However, "a", "b", and "c" cannot be equal to 0 at the same time. Examples of the monovalent hydrocarbon groups represented by R^{10} are the same as the examples of the monovalent hydrocarbon groups represented by R^7 . The moieties represented by R^{10} are preferably hydrogen atoms or alkyl groups, and particularly are preferably hydrogen atoms or methyl groups.

[0085] The silazanes contain units selected from at least one of the following structural units:

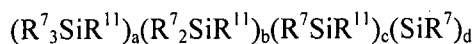
($R^7_3SiNR^{10}$), ($R^7_2SiNR^{10}$), (R^7SiNR^{10}), and ($SiNR^{10}$). Specific examples are the following: a straight chain polysilazane composed of ($R^7_3SiNR^{10}$) and ($R^7_2SiNR^{10}$) units; a cyclic polysilazane composed of ($R^7_2SiNR^{10}$) units; a branched chain polysilazane composed of (R^7SiNR^{10}) and ($SiNR^{10}$) units; a polysilazane composed of ($R^7_3SiNR^{10}$) and (R^7SiNR^{10}) units; a polysilazane composed of ($R^7_3SiNR^{10}$) and ($SiNR^{10}$) units; a polysilazane composed of (R^7SiNR^{10}) and ($SiNR^{10}$) units; a polysilazane composed of ($R^7_2SiNR^{10}$) and (R^7SiNR^{10}) units; a polysilazane composed of ($R^7_2SiNR^{10}$) and ($SiNR^{10}$) units; a polysilazane composed of ($R^7_3SiNR^{10}$), ($R^7_2SiNR^{10}$), and (R^7SiNR^{10}) units; a polysilazane composed of ($R^7_3SiNR^{10}$), ($R^7_2SiNR^{10}$), and ($SiNR^{10}$) units; a polysilazane composed of ($R^7_3SiNR^{10}$), (R^7SiNR^{10}), and ($SiNR^{10}$) units; a polysilazane composed of ($R^7_2SiNR^{10}$), (R^7SiNR^{10}), and ($SiNR^{10}$) units; and a polysilazane composed of ($R^7_3SiNR^{10}$), ($R^7_2SiNR^{10}$), (R^7SiNR^{10}), and ($SiNR^{10}$) units. The number of repetitions of the structural units expressed by each of ($R^7_3SiNR^{10}$), ($R^7_2SiNR^{10}$), (R^7SiNR^{10}), and ($SiNR^{10}$) is preferably within a range from 2 to 10,000, more preferably within a range from 3 to 1,000, and even more preferably within a range from 3 to 500.

[0086] The silazanes described above can be prepared by methods known in the art. Examples of methods for preparing the silazanes include those methods described in U.S. Patent Nos. 4312970, 4340619, 4395460, 4404153, 4482689, 4397828, 4540803, 4543344, 4835238, 4774312, 4929742, and 4916200. An alternate method is also described in J. Mater. Sci., 22, 2609 (1987).

[0087] The silazanes described above may be silicon-containing copolymer compounds with other polymers. Examples of silicon-containing copolymer compounds that can be used as the polysilazanes include silicon-containing copolymer compounds having Si-N-Si bonds and Si-O-Si bonds; silicon-containing copolymer compounds having Si-N-Si bonds and Si-Si bonds; silicon-containing copolymer compounds having Si-N-Si bonds and Si-(CH₂)_n-Si bonds; silicon-containing copolymer compounds having Si-N-Si bonds and Si-(C₆H₄)_n-Si bonds or

Si-(CH₂CH₂C₆H₄CH₂CH₂)_n-Si bonds; and the like. In the formulae, "n" has the same meaning as defined above.

[0088] The carbosilanes are expressed, for example, by the following average unit formula:



- 5 In this formula, R⁷ each independently represent a monovalent hydrocarbon group, a hydrogen atom, a halogen atom, an epoxy group-containing organic group, an acryl group- or methacryl group-containing organic group, an amino group-containing organic group, a mercapto group-containing organic group, an alkoxy group, or a hydroxy group. In one molecule, at least one group and preferably at least two groups represented by R⁷ are alkenyl groups, hydrogen atoms,
- 10 halogen atoms, epoxy-containing organic groups, acryl-containing organic groups, methacryl-containing organic groups, amino-containing organic groups, mercapto-containing organic groups, alkoxy groups, or hydroxy groups. R¹¹ is an alkylene group or an arylene group. "a", "b", "c", and "d" are numbers that are greater than or equal to 0 and less than or equal to 1, and that satisfy "a"+"b"+"c"+"d"=1. However, "a", "b", and "c" cannot be equal to 0 at the same time.
- 15 The alkylene group represented by R¹¹ may be expressed, for example, by the formula: -(CH₂)_n-, and the arylene group represented by R¹¹ can be expressed, for example, by the formula: -(C₆H₄)_n-. In the formulae, "n" has the same meaning as defined above.

- [0089] The carbosilanes are structured from at least one of the structural units expressed by the following: (R⁷₃SiR¹¹), (R⁷₂SiR¹¹), (R⁷SiR¹¹), and (SiR¹¹). Specific examples include a straight chain
- 20 polycarbosilane consisting of (R⁷₃SiR¹¹) and (R⁷₂SiR¹¹) units; a cyclic polycarbosilane consisting of (R⁷₂SiR¹¹) units; a branched chain polycarbosilane consisting of (R⁷SiR¹¹) and (SiR¹¹) units; a polycarbosilane consisting of (R⁷₃SiR¹¹) and (R⁷SiR¹¹) units; a polycarbosilane consisting of (R⁷₃SiR¹¹) and (SiR¹¹) units; a polycarbosilane consisting of (R⁷SiR¹¹) and (SiR¹¹) units; a polycarbosilane consisting of (R⁷₂SiR¹¹) and (R⁷SiR¹¹) units; a polycarbosilane consisting of
- 25 (R⁷₂SiR¹¹) and (SiR¹¹) units; a polycarbosilane consisting of (R⁷₃SiR¹¹), (R⁷₂SiR¹¹), and (R⁷SiR¹¹)

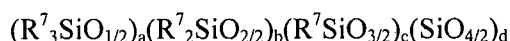
units; a polycarbosilane consisting of ($R^7_3SiR^{11}$), ($R^7_2SiR^{11}$), and (SiR^{11}) units; a polycarbosilane consisting of ($R^7_3SiR^{11}$), (R^7SiR^{11}), and (SiR^{11}) units; a polycarbosilane consisting of ($R^7_2SiR^{11}$), (R^7SiR^{11}), and (SiR^{11}) units; a polycarbosilane consisting of ($R^7_3SiR^{11}$), ($R^7_2SiR^{11}$), (R^7SiR^{11}), and (SiR^{11}) units; and similar structural units. The number of repetitions of the structural units

5 expressed by each of ($R^7_3SiR^{11}$), ($R^7_2SiR^{11}$), (R^7SiR^{11}), and (SiR^{11}) is preferably within a range from 2 to 10,000, more preferably within a range from 3 to 1,000, and even more preferably within a range from 3 to 500.

[0090] The carbosilanes described above can be prepared by methods known in the art. Examples of methods for preparing the carbosilanes are described in J. Dunogues, et al., *Macromolecules*, 21, 3
10 (1988) and U.S. Patent 3293194.

[0091] The carbosilanes described above may be silicon-containing copolymer compounds with other polymers. Examples of silicon-containing copolymer compounds that can be used as the carbosilanes include silicon-containing copolymer compounds having $Si-(CH_2)_n-Si$ bonds and $Si-O-Si$ bonds; silicon-containing copolymer compounds having $Si-(CH_2)_n-Si$ bonds and $Si-Si$ bonds;
15 silicon-containing copolymer compounds having $Si-(CH_2)_n-Si$ bonds and $Si-N-Si$ bonds; silicon-containing copolymer compounds having $Si-(CH_2)_n-Si$ bonds and $Si-(C_6H_4)_n-Si$ bonds; silicon-containing copolymer compounds having $Si-(C_6H_4)_n-Si$ bonds and $Si-O-Si$ bonds; silicon-containing copolymer compounds having $Si-(C_6H_4)_n-Si$ bonds and $Si-Si$ bonds; silicon-containing copolymer compounds having $Si-(C_6H_4)_n-Si$ bonds or
20 $Si-(CH_2CH_2C_6H_4CH_2CH_2)_n-Si$ bonds and $Si-N-Si$ bonds; and the like. In the formulae, "n" has the same meaning as defined above.

[0092] The component (b) is preferably a siloxane and more preferably a polysiloxane expressed by the following average unit formula:



25 In this formula, R^7 each independently represent a monovalent hydrocarbon group, a

hydrogen atom, a halogen atom, an epoxy group-containing organic group, an acryl group- or methacryl group-containing organic group, an amino group-containing organic group, a mercapto group-containing organic group, an alkoxy group, or a hydroxy group. "a", "b", "c", and "d" are numbers that are greater than or equal to 0 and less than or equal to 1, and that satisfy

5 "a"+"b"+"c"+"d"=1. However, "a", "b", and "c" cannot be 0 at the same time.

[0093] Specific examples of the crosslinking reaction include addition reactions such as a hydrosilylation reaction, a Michael addition reaction, a Diels-Alder reaction, and the like; condensation reactions such as dealcoholization, dehydrogenation, dewatering, deamination, and the like; ring-opening reactions such as epoxy ring-opening, ester ring-opening, and the like; and radical
10 reactions initiated by a peroxide, UV, or the like. Particularly, when the component (A) has aliphatic unsaturated groups and the component (B) has silicon-bonded hydrogen atoms, a mixture thereof can be hydrosilylation reacted in the presence of a hydrosilylation-reaction catalyst.

[0094] Specific examples of the hydrosilylation-reaction catalyst include fine platinum powder, platinum black, fine platinum-carrying silica powder, fine platinum-carrying activated carbon,
15 chloroplatinic acid, platinum tetrachloride, an alcoholic solution of chloroplatinic acid, an olefin complex of platinum, and an alkenylsiloxane complex of platinum. The amount in which the hydrosilylation-reaction catalyst can be used is not particularly limited. However, the catalyst is preferably used in such an amount that, in terms of mass (weight), the content of metal atoms in the catalyst is in a range from 0.1 to 1,000 ppm, and more preferably in a range from 1 to 500 ppm, with
20 respect to a total weight of the component (A) and the component (B).

[0095] When the component (A) has aliphatic unsaturated groups and the component (B) has silicon-bonded hydrogen atoms, the respective amounts thereof are not particularly limited.

However, the contents are such that the silicon-bonded hydrogen atoms in the component (B) are in a range from 0.1 to 50 moles, preferably in a range from 0.1 to 30 moles, and more preferably in a
25 range from 0.1 to 10 moles, per one mole of the aliphatic unsaturated groups in the component (A).

A reason for this is because when the amount of the component (B) is less than the lower limit of the range described above, the carbonization yield when baking the obtained cured product will tend to decline. On the other hand, when the amount exceeds the range described above, the characteristics as an electrode active material of the silicon-containing carbon-based composite material obtained by baking the obtained cured product will tend to decline.

[0096] When the component (A) comprises aliphatic unsaturated groups and the component (B) comprises aliphatic unsaturated groups, acryl groups, methacryl groups, or silicon-bonded hydrogen atoms, a mixture thereof can be radical reacted by a radical initiator using heat and/or light.

[0097] Specific examples of the radical initiator include dialkyl peroxides, diacyl peroxides, peroxy

esters, peroxy dicarbonates, and similar organic peroxides; and organic azo compounds. Specific examples of the organic peroxides include dibenzoyl peroxide, bis-p-chlorobenzoyl peroxide, bis-2,4-dichlorobenzoyl peroxide, di-t-butyl peroxide, dicumyl peroxide, t-butyl perbenzoate, 2,5-bis(t-butyl peroxy)-2,3-dimethylhexane, t-butyl peracetate, bis(o-methylbenzoyl peroxide), bis(m-methylbenzoyl peroxide), bis(p-methylbenzoyl peroxide), 2,3-dimethylbenzoyl peroxide, 2,4-dimethylbenzoyl peroxide, 2,6-dimethylbenzoyl peroxide, 2,3,4-trimethylbenzoyl peroxide, 2,4,6-trimethylbenzoyl peroxide, and similar methyl group-substituted benzoyl peroxides; t-butyl perbenzoate, dicumyl peroxide, 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane, t-butylperoxy isopropyl monocarbonate, and t-butyl peroxyacetate; and mixtures thereof. Additionally, specific examples of the organic azo compounds include 2,2'-azobisisobutyronitrile, 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis-isobutylvaleronitrile, and 1,1'-azobis(1-cyclohexanecarbonitrile).

[0098] The amount in which the radical initiator can be used is not particularly limited, but is preferably in a range from 0.1 to 10 mass (weight)%, and more preferably in a range from 0.5 to 5 mass (weight)%, with respect to the total weight of the component (A) and the component (B).

[0099] When the component (A) comprises aliphatic unsaturated groups and the component (B)

comprises aliphatic unsaturated groups, acryl groups, methacryl groups, or silicon-bonded hydrogen atoms, the amounts thereof are not particularly limited. However, the contents are such that the aliphatic unsaturated groups, acryl groups, methacryl groups, or silicon-bonded hydrogen atoms in the component (B) are in a range from 0.1 to 50 moles, preferably in a range from 0.1 to 30 moles, and more preferably in a range from 0.1 to 10 moles, per one mole of the aliphatic unsaturated groups in the component (A). A reason for this is because when the amount of the component (B) is less than the lower limit of the range described above, the carbonization yield when baking the obtained cured product will tend to decline. On the other hand, when the amount exceeds the range described above, the characteristics as an electrode active material of the silicon-containing carbon-based composite material obtained by baking the obtained cured product will tend to decline.

[0100] When forming the cured product obtained by crosslinking the component (A) and the component (B), the cured product is formed, for example, by manufacturing according to methods I or II described below, and then subjecting the product to a step of baking. I: After mixing the component (A) and the component (B), the mixture is precured at a temperature not greater than 300°C, and preferably at a temperature between 60°C and 300°C. The subsequent baking step is preferably carried out after pulverizing the obtained precured mixture so that an average diameter of particles thereof is from 0.1 to 30 μm and preferably from 1 to 20 μm . II: Particularly, the cured product preferably used in the present invention is constituted by spherical particles. In order to form these spherical particles, for example, a crosslinkable composition comprising the component (A) and the component (B) is preferably crosslinked by spraying said crosslinkable composition into hot air or crosslinked after emulsifying or dispersing said crosslinkable composition in a non-compatible medium.

[0101] When one of the component (A) and the component (B) has aliphatic unsaturated groups and the other has silicon-bonded hydrogen atoms, fine particles of the cured product can be obtained by spraying a crosslinkable composition comprising the component (A), the component (B), and the

hydrosilylation-reaction catalyst in particulate form into hot-air, and crosslinking by hydrosilylation reaction.

[0102] On the other hand, fine particles of the cured product can be formed by adding a crosslinkable composition comprising the component (A), the component (B), and the hydrosilylation-reaction catalyst to an aqueous solution of an emulsifier, emulsifying by agitation to form fine particles of the crosslinkable composition, and, thereafter, crosslinking by hydrosilylation reaction.

[0103] The emulsifier is not particularly limited, and specific examples thereof include ionic surfactants, nonionic surfactants, and mixtures of ionic surfactants and nonionic surfactants.

Particularly, from the perspective of obtaining excellent uniform dispersion and stability of the

oil-in-water emulsion produced by mixing the crosslinkable composition and water, the emulsifier is preferably a mixture of one or more types of ionic surfactant and one or more types of nonionic surfactant.

[0104] Moreover, by using silica (colloidal silica) or a metallic oxide such as titanium oxide in combination with the emulsifier and carbonizing while the silica is retained on the surface of the

cured product particles, a stable layer can be formed on the carbon surface, carbonization yield can be increased, and surface oxidation occurring when allowing the carbon material to sit can be suppressed.

[0105] The diameter of the cured product particles is not particularly limited, but in order to form a silicon-containing carbon-based composite material, through baking, with an average diameter from

1 to 20 μm , which is suitable for an electrode active material, the average diameter is preferably in a range from 5 to 30 μm , and more preferably is in a range from 5 to 20 μm .

[0106] Because the crosslinking of the cured product particles obtained as described above can be further promoted and the carbonization yield via baking can be increased, the cured product particles are preferably further subjected to heat treating in air at a temperature from 150°C to 300°C.

[0107] The silicon-containing carbon-based composite material of the present invention can be

obtained via a process of heat treating (baking) the cured product of the component (A) and the component (B) along with a carbonaceous matter (C).

[0108] Prior to the baking process, the carbonaceous matter (C) is preferably coated on a surface of the cured product obtained by crosslinking the component (A) and the component (B) to form

5 composite particles. An amount of the component (C) coated on the surface of the cured product of the component (A) and the component (B) is preferably from 0.5 to 20 mass (weight)%, more preferably from 1 to 10 mass (weight)%, and even more preferably from 1 to 5 mass (weight)% in the composite particles.

[0109] The method of preparing the composite particles is not particularly limited, and examples

10 thereof include (i) a method of mixing/agitating the cured product obtained by crosslinking the component (A) and the component (B), and the carbonaceous matter (C) while supplying mechanical energy; and, when preparing the cured particles by crosslinking the component (A) and the component (B) in an emulsified state in an aqueous dispersing medium, (ii) a method of adsorbing the carbonaceous matter (C) on the surface of the cured product by dispersing the carbonaceous
15 matter (C) in the aqueous dispersing medium.

[0110] The pulverizing apparatus, mixing device, and surface treating device used when (i)

mixing/agitating the cured product obtained by crosslinking the component (A) and the component (B), and the carbonaceous matter (C) while supplying mechanical energy are not particularly limited.

The pulverizing, mixing, and surface treating may be performed using a dry method or a wet method.

20 [0111] Examples of the pulverizing apparatus include apparatuses that pulverize by pressure or

striking, such as jaw crushers, gyratory crushers, roll crushers, roll mills, automatic mortars, and the like; apparatuses where a strike plate is fixed around a high-speed rotating rotor, that pulverize products using shearing forces and the like caused by the rotor and the strike plate such as hammer
mills, impact crushers, pin mills, atomizers, pulverizers, and the like; apparatuses where a roll or ball

25 is pressed against the top of a ring and rotated, the product being pulverized by being placed between

the ring and the roll or ball and crushed such as ring roller mills, ring ball mills, centrifugal roller mills, ball bearing mills, angmills, and the like; pulverizing apparatus provided with a cylindrical pulverizing chamber, that pulverize by a ball or rod being inserted into the pulverizing chamber as a crusher and rotated or oscillated such as pot mills, ball mills, oscillating mills, planetary ball mills, and the like; pulverizing apparatuses provided with a cylindrical pulverizing chamber, where a ball or beads are inserted into the pulverizing chamber as a crusher and pulverizing is performed via shearing forces and frictional action caused by a disk-like or annular agitating mechanism inserted into the crushing medium such as tower mills, attritors, sand mills, and the like; and pulverizing apparatuses where a medium such as high-pressure air or the like is blasted from a nozzle and caused to impact particles as an ultra high speed jet, and the product is pulverized by the impact of the particles such as jet mills and the like.

[0112] Examples of the mixing device include mixers that have a mixing shaft in a mixing vessel, where a mixing blade is attached to the shaft and particles are mixed such as super mixers, high-speed mixers, Henschel mixers, and the like; continuous mixers comprising a main shaft provided with a vertical cylinder having a particle insertion opening and a mixing blade, where the main shaft is supported by an upper bearing and the discharge side is free such as Flexomix mixers and the like; and continuous mixers where mixing is performed by loading raw material into an upper portion of a disk having an agitation pin, and rotating the disk at a high speed to produce shearing forces such as flow jet mixers, spiral pin mixers, and the like.

[0113] Examples of the surface treating device include Hybridizer®, manufactured by Nara Machinery Co., Ltd., Mechanofusion® and Nobilta™, manufactured by Hosokawa Micron Ltd., and the like.

[0114] When preparing the cured product particles by crosslinking the component (A) and the component (B) in an emulsified state in an aqueous dispersing medium (ii), the composite particles can be obtained by removing the water after adsorbing the carbonaceous matter (C) on the surface of

the cured product by dispersing the carbonaceous matter (C) in the aqueous dispersing medium. In this case, preferably the component (A) and the component (B) are emulsified in the aqueous dispersing medium and, thereafter, the carbonaceous matter (C) is dispersed in the emulsion.

[0115] The baking conditions are not particularly limited, but baking is preferably carried out in an inert gas or in vacuum at a temperature of from 300°C to 1,500°C. Examples of the inert gas include nitrogen, helium, and argon. Note that the inert gas may comprise hydrogen gas or similar reducing gases. Thus, the composite material of the present invention may contain trace amounts of hydrogen. The baking temperature is more preferably in a range from 500°C to 1,000°C. Baking time is not particularly limited, but can be set to a range from 10 minutes to 10 hours, and preferably is set to a range from 30 minutes to 3 hours.

[0116] The heating method and type of the carbonization furnace is not particularly limited, and carbonization can be carried out in a fixed-bed type or a fluidized-bed type carbonization furnace, provided that the furnace is capable of heating the product to an appropriate temperature. Specific examples of the carbonization furnace include Reidhammer furnace, tunnel furnace, single type furnace, Oxynon furnace, roller hearth kiln, pusher kiln, batch type rotary kiln, and continuous type rotary kiln.

[0117] The carbonaceous matter (C) is not particularly limited provided that it is constituted mainly by carbon, and examples thereof include activated carbon, natural graphite, artificial graphite, various coke powders, and mesophase carbon; vapor-grown carbon fibers, pitch-based carbon fibers, PAN (Polyacrylonitrile) -based carbon fibers, and similar carbon fibers; acetylene black, furnace black, ketjen black, gas black, and similar carbon blacks; carbon nanofiber; carbon nanotube; and the like.

[0118] The silicon-containing carbon-based composite material of the present invention can be constituted by particles having an average diameter from 5 nm to 50 μm . The average diameter is preferably from 10 nm to 40 μm , more preferably from 100 nm to 30 μm , and even more preferably from 1 μm to 20 μm .

[0119] An amount of the carbon included in the silicon-containing carbon-based composite material of the present invention is preferably from 1 to 50 mass (weight)%, more preferably from 5 to 30 mass (weight)%, and even more preferably from 5 to 20 mass (weight)%. When the amount is within this range, even when using the silicon-containing carbon-based composite material of the present invention alone as the electrode active material, the silicon-containing carbon-based composite material will have suitable conductivity, and declines in the charge and discharge capacity of the electrode can be suppressed.

[0120] The surface of the silicon-containing carbon-based composite material of the present invention has a coating layer constituted from carbon. A thickness of the carbon coating layer is not particularly limited, but is preferably from 5 nm to 2 μ m, more preferably from 10 nm to 1 μ m, and even more preferably from 20 nm to 100 nm. The core portion covered by the carbon coating layer is the baked product of the cured product of the component (A) and the component (B).

[0121] The silicon-containing carbon-based composite material obtained by the process described above has silicon, carbon, and oxygen as main components and can be expressed by the following average composition formula: $\text{Si}_{1.00}\text{C}_f\text{O}_g\text{H}_h$. In this formula, "f", "g", and "h" are numbers that satisfy $0.5 < f < 100$, $0 \leq g < 5$, and $0 \leq h < 10$, respectively. Preferably, $1.5 < f < 70$, and more preferably, $2.0 < f < 50$.

[0122] The obtained carbon surface-coated silicon-containing carbon-based composite material can be used as the electrode active material. The electrode active material of the present invention can be in a particulate form and, in this case, the average diameter thereof is preferably from 1 to 50 μ m, more preferably from 1 to 40 μ m, and even more preferably from 1 to 30 μ m.

[0123] The electrode active material comprising the carbon surface-coated silicon-containing carbon-based composite material of the present invention has high reversible capacity and stable charge and discharge cycle characteristics, and can be used in the manufacturing of an electrode that has little electrical potential loss when lithium is discharged, via a simple manufacturing process.

Thus, the electrode active material can be suitably used as an electrode active material for nonaqueous electrolyte secondary batteries. The electrode active material is particularly suitable as the active material of electrodes of lithium or lithium-ion secondary batteries.

[0124]

5 Electrode

The electrode of the present invention is characterized by comprising the electrode active material described above. The form and method for fabricating the electrode are not particularly limited. Examples of the method for fabricating the electrode of the present invention include methods in which the electrode is fabricated by mixing the silicon-containing carbon-based composite material with a binder, and methods in which the electrode is fabricated by mixing the silicon-containing carbon-based composite material with a binder and a solvent, contact binding or coating the obtained paste on a current collector and, thereafter, drying the electrode. Moreover, a thickness of the paste coated on the current collector is, for example, about from 30 to 500 μm and preferably about from 50 to 300 μm . Means for drying after coating are not particularly limited, but heating under vacuum drying is preferable. A thickness of the electrode material on the current collector after drying is about from 10 to 300 μm and preferably about from 20 to 200 μm . When the silicon-containing carbon-based composite material is fibrous, the electrode can be fabricated by orienting the material in a single axial direction and forming the material into a fabric or similar structure, or bundling or weaving metal, conducting polymer, or similar conductive fibers.

Terminals may be incorporated as necessary when forming the electrode.

[0125] The current collector is not particularly limited, and specific examples thereof include metal meshes and foils made from copper, nickel, alloys thereof, and the like.

[0126] Specific examples of the binder include fluorine-based (e.g. polyvinylidene fluoride and polytetrafluoroethylene) resins and styrene-butadiene resins. An amount in which the binder is used

is not particularly limited, but a lower limit thereof is in a range from 5 to 30 parts by mass (weight)

and preferably in a range from 5 to 20 parts by mass (weight), per 100 parts by mass (weight) of the silicon-containing carbon-based composite material. When the amount of the binder used is outside these ranges, for example, bonding strength of the silicon-containing carbon-based composite material on the surface of the current collector will be insufficient; and an insulating layer, which is a cause of increased internal resistance of the electrode, may form. A method for preparing the paste is not particularly limited, and examples thereof include methods in which a mixed liquid (or dispersion) comprising the binder and an organic solvent is mixed with the silicon-containing carbon-based composite material.

[0127] A solvent that can dissolve or disperse the binder is generally used as the solvent, and specific examples thereof include N-methylpyrrolidone, N,N-dimethylformamide, and similar organic solvents. An amount in which the solvent is used is not particularly limited provided that when mixed with the binder, the mixture thereof has a paste-like form, but generally the amount is in a range from 0.01 to 500 parts by mass (weight), preferably in a range from 0.01 to 400 parts by mass (weight), and more preferably in a range from 0.01 to 300 parts by mass (weight), per 100 parts by mass (weight) of the silicon-containing carbon-based composite material.

[0128] Additives may be compounded in the electrode of the present invention as desired. For example, a conductivity promoter may be added to the electrode during manufacturing. An amount in which the conductivity promoter is used is not particularly limited, but is in a range from 2 to 60 parts by mass (weight), preferably in a range from 5 to 40 parts by mass (weight), and more preferably in a range from 5 to 20 parts by mass (weight) per 100 parts by mass (weight) of the silicon-containing carbon-based composite material. When the amount is within this range, conductivity will be excellent and declines in the charge and discharge capacity of the electrode can be suppressed.

[0129] Examples of the conductivity promoter include carbon blacks (e.g. ketjen black, acetylene black), carbon fibers, carbon nanotubes, and the like. A single conductivity promoter may be used

or a combination of two or more types of conductivity promoters can be used. The conductivity promoter can, for example, be mixed with the paste comprising the silicon-containing carbon-based composite material, the binder, and the solvent.

[0130] Graphite or a similar electrode active material may be compounded in the electrode of the present invention as another optional additive.

[0131] Electricity storage device

The electricity storage device of the present invention is characterized by comprising the electrode described above. Examples of the electricity storage device include lithium primary batteries, lithium secondary batteries, lithium-ion secondary batteries, capacitors, hybrid capacitors (redox capacitors), organic radical batteries, and dual carbon batteries, of which lithium or lithium-ion secondary batteries are preferable. The lithium-ion secondary battery may be manufactured according to a generally known method using battery components including a negative electrode comprising the electrode described above, a positive electrode capable of storing and discharging lithium, an electrolyte solution, a separator, a current collector, a gasket, a sealing plate, a case, and the like. The lithium secondary battery may be manufactured according to a generally known method using battery components including a positive electrode constituted by the electrode described above, a negative electrode constituted by metallic lithium, an electrolyte solution, a separator, a current collector, a gasket, a sealing plate, a case, and the like.

[0132] Preferable forms (lithium or lithium-ion secondary batteries) of the battery of the present invention are illustrated in detail in FIGS. 1 and 2.

[0133] FIG. 1 is a schematic breakdown cross sectional view of a lithium-ion secondary battery (button battery) that is an example of the battery of the present invention.

[0134] The lithium-ion secondary battery illustrated in FIG. 1 comprises a cylindrical case 1 having a bottom and an open top, a cylindrical gasket 2 that is open on both ends and has an inner circumference that is substantially the same as the outer circumference of the case 1, a washer 3, a

SUS plate 4, a current collector 5, a negative electrode 6 having the silicon-containing carbon-based composite material of the present invention as an electrode active material thereof, a separator 7, a positive electrode 8, a current collector 9, and a sealing plate 10.

[0135] The washer 3, having a substantially ring-like shape and a size that is slightly smaller than the inner circumference of the case 1 is housed in the case 1 of the lithium-ion secondary battery illustrated in FIG. 1. The SUS plate 4, having a substantially disc-like shape and a size that is slightly smaller than the inner circumference of the case 1, is stacked on the washer 3. The current collector 5 and the negative electrode 6, both having substantially disc-like shapes and sizes that are slightly smaller than the inner circumference of the case 1, are provided on the SUS plate 4. The separator 7, which is a single-layer disc-like member and has a size substantially the same as the inner circumference of the case 1, is stacked on the negative electrode 6. The separator 7 is impregnated with an electrolyte solution. Note that the separator 7 may be constituted by two or more disc-like members. The positive electrode 8, having a size that is substantially the same as that of the negative electrode 6, and the current collector 9 having a size that is substantially the same as that of the current collector 5 are provided on the separator 7. The current collector 5 is constituted by a mesh, foil, or the like made from copper, nickel, or similar metal, and the current collector 9 is constituted by a mesh, foil, or the like made from aluminum or a similar metal. The current collector 5 and the current collector 9 are bonded and integrated with the negative electrode 6 and the positive electrode 8, respectively.

[0136] With the lithium-ion secondary battery illustrated in FIG. 1, the gasket 2 is fitted on a wall face of the case 1 and; furthermore, an inner circumferential face of the cylindrical sealing plate 10, having a bottom and an open lower face and a size that is slightly larger than that of the gasket 2, is fitted on an outer circumferential face of the gasket 2. Thereby, the case 1 is insulated from the sealing plate 10 by the gasket 2, and a button battery having the case 1, the gasket 2, the washer 3, the SUS plate 4, the current collector 5, the negative electrode 6, the separator 7, the positive

electrode 8, the current collector 9, and the sealing plate 10, with a common axis, is formed.

[0137] The positive electrode 8 in the lithium-ion secondary battery illustrated in FIG. 1 is not particularly limited and, for example, can be constituted by positive electrode active materials, conductivity promoters, binders, and the like. Examples of the positive electrode active materials include LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and similar metallic oxides; LiFePO_4 , $\text{Li}_2\text{FeSiO}_4$, and similar polyanion oxides; spinel LiMn_2O_4 ; and the like. A single positive electrode active material may be used or a combination of two or more types of positive electrode active materials can be used.

Examples of the conductivity promoters and the binders include those described above.

[0138] FIG. 2 is a breakdown cross sectional view of a lithium secondary battery (button battery) that is an example of the battery of the present invention, fabricated according to the Practical Examples.

[0139] The lithium secondary battery illustrated in FIG. 2 comprises a cylindrical case 1 having a bottom and an open top, a cylindrical gasket 2 that is open on both ends and has an inner circumference that is substantially the same as the outer circumference of the case 1, a washer 3, a SUS plate 4, a negative electrode 6 constituted by metallic lithium, a separator 7, a positive electrode 8 having the silicon-containing carbon-based composite material of the present invention as an electrode active material thereof, a current collector 9', and a sealing plate 10.

[0140] The washer 3, having a substantially ring-like shape and a size that is slightly smaller than the inner circumference of the case 1 is housed in the case 1 of the lithium secondary battery illustrated in FIG. 2. The SUS plate 4, having a substantially disc-like shape and a size that is slightly smaller than the inner circumference of the case 1, is stacked on the washer 3. The negative electrode 6, having a substantially disc-like shape and a size that is slightly smaller than the inner circumference of the case 1, is provided on the SUS plate 4. The separator 7, which is a single-layer disc-like member and has a size substantially the same as the inner circumference of the case 1, is stacked on the negative electrode 6. The separator 7 is impregnated with an electrolyte solution. Note that the separator 7 may be constituted by two or more disc-like members. The positive electrode 8 and

the current collector 9', having sizes that are substantially the same as that of the negative electrode 6, are provided on the separator 7. The current collector 9' is constituted by a mesh, foil, or the like made from copper, nickel, or similar metal, and is bonded and integrated with the positive electrode 8.

5 [0141] With the lithium secondary battery illustrated in FIG. 2, the gasket 2 is fitted on a wall face of the case 1 and; furthermore, an inner circumferential face of the cylindrical sealing plate 10, having a bottom and an open lower face and a size that is slightly larger than that of the gasket 2, is fitted on an outer circumferential face of the gasket 2. Thereby, the case 1 is insulated from the sealing plate 10 by the gasket 2, and a button battery having the case 1, the gasket 2, the washer 3, the SUS plate 4, 10 the negative electrode 6, the separator 7, the positive electrode 8, the current collector 9', and the sealing plate 10, with a common axis, is formed.

[0142] The electrolyte solutions included in the lithium or lithium-ion secondary batteries illustrated in FIGS. 1 and 2 are not particularly limited, and commonly known electrolyte solutions can be used. For example, a non-aqueous lithium or lithium-ion secondary battery can be manufactured by using a 15 solution in which an electrolyte is dissolved in an organic solvent as the electrolyte solution.

Examples of the electrolyte include LiPF_6 , LiClO_4 , LiBF_4 , LiClF_4 , LiAsF_6 , LiSbF_6 , LiAlO_4 , LiAlCl_4 , LiCl , LiI , and similar lithium salts. Examples of the organic solvent include carbonates (e.g. propylene carbonate, ethylene carbonate, diethyl carbonate), lactones (e.g. γ -butyrolactone), chained ethers (e.g. 1,2-dimethoxyethane, dimethylether, diethylether), cyclic ethers (e.g. tetrahydrofuran, 20 2-methyltetrahydrofuran, dioxolane, 4-methyldioxolane), sulfolanes (e.g. sulfolane), sulfoxides (e.g. dimethyl sulfoxide), nitriles (e.g. acetonitrile, propionitrile, benzonitrile), amides (e.g. N,N-dimethylformamide, N,N-dimethylacetamide), polyoxyalkylene glycols (e.g. diethyleneglycol), and similar aprotic solvents. A single organic solvent may be used or a mixed solvent comprising two or more types of organic solvents can be used. A concentration of the electrolyte per one liter 25 of the electrolyte solution is, for example, about from 0.3 to 5 moles, preferably about from 0.5 to 3

moles, and more preferably about from 0.8 to 1.5 moles.

[0143] The separators 4 in the lithium or lithium-ion secondary batteries illustrated in FIGS. 1 and 2 are not particularly limited, and a commonly known separator can be used. Examples thereof include porous polypropylene nonwovens, porous polyethylene nonwovens, and other polyolefin-based porous films.

[0144] The electricity storage device of the present invention is not limited to the examples illustrated in FIGS. 1 and 2 and, for example, can be applied to various forms such as stacked, packed, button, gum, battery pack, and rectangular batteries. Utilizing the characteristics of light-weight, high capacity, and high energy density, the electricity storage device of the present invention, particularly the lithium or lithium-ion secondary battery, is suitable for use as a power supply for video cameras, computers, word processors, portable stereos, cellular phones, and other mobile, small electronic devices; a power supply for hybrid vehicles and electric vehicles; and a power supply for electricity storage.

15 INDUSTRIAL APPLICABILITY

[0145] The electrode active material of the present invention has high reversible capacity and stable charge and discharge cycle characteristics, and has high initial charge and discharge efficiency.

Therefore, the electrode active material of the present invention is suitable for an electrode of an electricity storage device, particularly of a lithium or lithium-ion secondary battery. Additionally,

the electrode active material of the present invention uses inexpensive raw materials, and can be manufactured via a simple manufacturing process. Moreover, the electrode of the present invention can impart high reversible capacity, stable charge and discharge cycle characteristics, and high initial charge and discharge efficiency to a battery. As a result, the electricity storage device of the present invention can have high reversible capacity, stable charge and discharge cycle characteristics, and high initial charge and discharge efficiency.

Examples

[0146] Hereinafter, examples will be used to describe the composite material, electrode active material, electrode, and electricity storage device of the present invention in more detail, but the present invention is not limited to these examples. In these examples, observations via X-ray diffraction, scanning electron microscope, transmission electron microscope, and energy dispersive x-ray analysis; and evaluations of the battery characteristics were carried out as described below.

[0147]

X-ray diffraction

10 Device: RINT 2000 (manufactured by Rigaku Corporation)

X-ray generator: Target Cu

Tube voltage: 40 kV

Tube current: 40 mA

$2\theta=10-90$

15 Divergence slit: $2/3^\circ$

Divergence height: 10 mm

Scattering slit: $2/3^\circ$

Receiving slit: 0.3 mm

[0148]

20 Scanning electron microscope: SEM

Device: JSM-5800LV (manufactured by JEOL Ltd.)

[0149]

Transmission electron microscope: TEM

Device: JEOL 2100F TEM (manufactured by JEOL Ltd.)

25 [0150]

Energy dispersive x-ray analysis: EDX

Device: JED-2100 (manufactured by JEOL Ltd.)

[0151]

Evaluation of battery characteristics

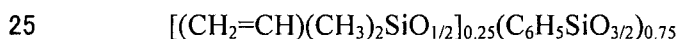
- 5 Charge and discharge characteristics of the lithium secondary battery using the composite material of the present invention were measured as described below using an HJR-110m SM6 (manufactured by Hokuto Denko Corporation). Charging was performed using a constant current of 0.1C (70.0 mAh/g), which is 1/10 of the theoretical capacity (700 mAh/g, expressed as 1.0C), per 1 g (mass) of the silicon-containing carbon-based composite material. The charging was considered
- 10 complete at the point when the current value became 1/10 after the battery voltage had reached 0.02 V and the voltage had been kept constant. The charging capacity was calculated at this point. Additionally, discharging was performed at a constant current of 0.1 C and was considered complete when the battery voltage reached 1.5 V. The discharging capacity was calculated at this point. The cycle characteristics were evaluated under the same conditions. Initial charging and
- 15 discharging efficiency (CE%) was expressed as a percentage (%) of the discharging capacity with respect to the charging capacity in the first cycle. A capacity maintenance ratio after the cycle test was expressed as a percentage (%) of the charging capacity after 10 cycles with respect to the initial charging capacity.

[0152]

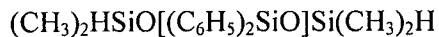
20 Practical Example 1

Preparation of the silicon-containing crosslinked particles

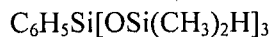
A solution comprising 2.4 g of polystyrene at a degree of polymerization of about 2,000 and 3.0 g of toluene; and a silicone composition comprising 24 g of an organopolysiloxane expressed by the formula:



2.4 g of an organopolysiloxane expressed by the formula:



and 2.4 g of an organopolysiloxane expressed by the formula:



5 were mixed to form a uniform solution. Next, the obtained solution was mixed with 0.01 g of a 1,3-divinyltetramethyl disiloxane platinum complex and 0.1 g of a methyl tris(1,1-dimethyl-2-propynoxy) silane, and the components were stirred evenly at room temperature. Thereafter, the silicone composition was crosslinked by being put in a 110°C oven for 30 minutes. As a result, a gel-like substance having white turbidity was obtained. This gel-like substance was
10 heated under reduced pressure in order to remove the toluene, and a white solid product was obtained. Observation of a cross-section of the obtained solid under a SEM showed that the silicon-containing crosslinked particles were uniformly dispersed in the polystyrene. The silicon-containing crosslinked particles were extracted with toluene, and were confirmed to have a regular spherical shape with an average diameter of 2.5 μm (FIG. 3).

15 [0153]

Preparation of the carbon-coated silicon-containing carbon-based composite material

Black particles were obtained by mixing 4.75 g of the silicon-containing crosslinked particles obtained above and 0.25 g of acetylene black for five minutes in a ball mill. The particles were placed into an SSA-S grade alumina crucible and baked in a muffle furnace for two hours at 600°C in
20 a nitrogen atmosphere, followed by one hour at 1,000°C. After cooling, black particles were obtained at a 75% yield. An amount of carbon coated on the surface of the obtained carbon surface-coated silicon-containing carbon-based composite material was 6.6 mass (weight)% of the silicon-containing carbon-based composite material. Subjecting the obtained black particles to SEM observation revealed that the black particles were spherical particles having an average
25 diameter of about 2.45 μm (FIG. 4). Additionally, observation of a cross section of the material

using a transmission electron microscope (hereinafter referred to as "TEM") and an energy dispersive x-ray analysis (hereinafter referred to as "EDX") thereof revealed that the black particles were composite particles in which the cores of the particles were constituted mainly of the SiOC component and the surfaces of the particles were coated with carbon particles having a diameter from 30 to 40 nm. (FIG. 5)

[0154]

Fabrication of the electrode

107.58 parts by mass (weight) of the silicon-containing carbon-based composite material obtained above and 6.94 parts by mass (weight) of acetylene black were mixed for 15 minutes in a mortar. Thereafter, 12.00 parts by mass (weight) of polyvinylidene fluoride was added and the components were further mixed for 15 minutes. Then, N-methyl-2-pyrrolidone was mixed in as a solvent in order to obtain a slurry-like mixture, which was then coated on a copper foil roll at a thickness of about 250 μm by means of a doctor blade method. Thereafter, the coated foil roll was dried under vacuum for not less than 12 hours at 85°C, and an electrode having a thickness of about 40 μm was obtained.

[0155]

Fabrication and evaluation of the secondary battery

Metallic lithium was used for the electrode as a counterelectrode; a mixed solvent comprising ethylene carbonate and diethyl carbonate at a volume ratio of 1:1, in which lithium hexafluorophosphate was dissolved at a ratio of 1 mol/L, was used as the electrolyte solution; and a polypropylene nonwoven was used as the separator to fabricate a coin-type lithium secondary battery. Then, the battery characteristics of the lithium secondary battery were evaluated according to the evaluation methods of battery characteristics described above. The battery characteristics are shown in Table 1.

[0156]

Practical Example 2

Preparation of the silicon-containing crosslinked particles

A crosslinkable composition was prepared by mixing 15.49 g of DVB570 (manufactured by Nippon Steel Chemical Co., Ltd.; Main components: divinylbenzene and vinyl ethylbenzene; proportion of divinylbenzene included in the main components: 60 mass (weight)%; and 9.51 g of a methyl hydrogen siloxane copolymer capped at both molecular terminals with trimethylsiloxy groups (viscosity: 20 mPa·s; silicon-bonded hydrogen atoms content: 1.58 mass (weight)%; included in an amount such that one mole of the silicon-bonded hydrogen atoms in the copolymer is included per one mole of vinyl groups in the DVB570). Thereafter, 25 g of an aqueous solution of 10 mass (weight)%-polyoxyethylene secondary alkyl ether (Sanonic SS120, manufactured by Sanyo Chemical Industries, Ltd.; HLB=14.5) was added. Then, a water-based emulsion of the crosslinkable composition was prepared by emulsifying the mixture using a homo-disper (rotation speed: 5000 rpm).

[0157] Next, a water-based emulsion of a platinum-based catalyst having a 1,3-divinyltetramethyl disiloxane platinum complex as a main component (average diameter of the emulsion = 0.05 μm ; platinum metal concentration = 0.05 mass (weight)%) that was prepared separately was uniformly mixed with the water-based emulsion of the crosslinkable composition at an amount, in terms of mass (weight), such that 20 ppm of platinum metal was included with respect to the crosslinkable composition, and mixed at 60°C for 60 minutes. Thereafter, cured product particles having an average diameter from 1 to 5 μm were prepared by removing the water.

[0158]

Preparation of the carbon-coated silicon-containing carbon-based composite material

Black particles were obtained by mixing 4.75 g of the silicon-containing crosslinked particles obtained above and 0.25 g of acetylene black for five minutes in a ball mill. As in Practical

Example 1, the cured product particles were placed into an SSA-S grade alumina crucible and baked. After cooling, black particles were obtained at a 62% yield. An amount of carbon coated on the surface of the obtained carbon surface-coated silicon-containing carbon-based composite material was 7.6 mass (weight)% of the silicon-containing carbon-based composite material. Subjecting the
5 obtained black particles to SEM, TEM, and EDX observation revealed that the black particles were spherical particles having an average diameter of about from 1.0 to 5.0 μm , constituted mainly of the SiOC component, and that the black particles were composite particles in which the surfaces of the particles were coated with carbon particles having a diameter from 30 to 40 nm.

[0159] Fabrication of the electrode and a secondary battery using the silicon-containing carbon-based
10 composite material described in this Practical Example and evaluation thereof was carried out the same as in Practical Example 1. The battery characteristics are shown in Table 1.

[0160]

Practical Example 3

Preparation of the silicon-containing crosslinked particles

15 A crosslinkable composition was prepared by mixing 100 g of DVB630 (manufactured by Nippon Steel Chemical Co., Ltd.; Main components: divinylbenzene and vinyl ethylbenzene; proportion of divinylbenzene included in the main components: 63.6 mass (weight)%); 153.4 g of a dimethylsiloxane-methyl hydrogen siloxane copolymer capped at both molecular terminals with trimethylsiloxy groups (viscosity: 45 mPa·s; silicon-bonded hydrogen atoms content: 0.76 mass
20 (weight)%; included in an amount such that one mole of the silicon-bonded hydrogen atoms in the copolymer is included per one mole of vinyl groups in the DVB630); an isopropyl alcohol solution of chloroplatinic acid (included in an amount such that 10 ppm of platinum metal was included with respect to the total weight of the DVB630 and the dimethylsiloxane-methyl hydrogen siloxane copolymer); and 0.1 g of 2-methyl-3-butyne-2-ol. This mixture was cured in nitrogen at a
25 temperature of 80°C for 30 minutes and then further cured for 60 minutes at 200°C. Thereafter, the

cured product was cooled and crushed using a pulverizer having a clearance set to 20 μm . Thereby, particles having an average diameter of about 15 μm were obtained.

[0161]

Preparation of the carbon-coated silicon-containing carbon-based composite material

5 Black particles were obtained by mixing 4.75 g of the silicon-containing crosslinked particles obtained above and 0.25 g of ketjen black for five minutes in a ball mill. As in Practical Example 1, the particles were placed into an SSA-S grade alumina crucible and baked. After cooling, black particles were obtained at a 62% yield. An amount of carbon coated on the surface of the obtained carbon surface-coated silicon-containing carbon-based composite material was 7.6 mass (weight)%
10 of the silicon-containing carbon-based composite material. Subjecting the obtained black particles to SEM, TEM, and EDX observation revealed that the black particles were particles having an average diameter of about from 10.0 to 15.0 μm , constituted mainly of the SiOC component, and that the black particles were composite particles in which the surfaces of the particles were coated with carbon particles having a diameter from 30 to 40 nm.

15 [0162] Fabrication of the electrode and a secondary battery using the silicon-containing carbon-based composite material described in this Practical Example and evaluation thereof was carried out the same as in Practical Example 1. The battery characteristics are shown in Table 1.

[0163]

Practical Example 4

20 Preparation of the silicon-containing crosslinked particles

A crosslinkable composition was prepared by mixing 500 g of an organopolysiloxane expressed by the formula: $[(\text{CH}_3)_2(\text{CH}_2=\text{CH})\text{SiO}]_2(\text{C}_6\text{H}_5)_2\text{Si}$
951 g of a methyl hydrogen siloxane copolymer capped at both molecular terminals with trimethylsiloxy groups (viscosity: 20 mPa·s; silicon-bonded hydrogen atoms content: 1.58 mass
25 (weight)%; included in an amount such that 1.2 moles of the silicon-bonded hydrogen atoms in the

copolymer is included per one mole of vinyl groups in the organopolysiloxane); an isopropyl alcohol solution of chloroplatinic acid (included in an amount such that, in terms of mass (weight), 10 ppm of platinum metal was included with respect to the total weight of the organopolysiloxane and the methyl hydrogen siloxane copolymer); and 2-methyl-3-butyne-2-ol (included in an amount such that, in terms of mass (weight), 200 ppm of 2-methyl-3-butyne-2-ol was included with respect to the total weight of the RMS organopolysiloxane and the methyl hydrogen siloxane copolymer). Then, this mixture was sprayed using a rotating nozzle into a spray drier (diameter = 2 meters, height = 4 meters) having a hot-air entrance temperature of 200°C. Thereafter, the product was collected from the spray drier using a cyclone. Thus, spherical cured product particles having a diameter from 2 to 50 µm were prepared.

[0164]

Preparation of the carbon-coated silicon-containing carbon-based composite material

Black particles were obtained by mixing 4.75 g of the silicon-containing crosslinked particles obtained above and 0.25 g of acetylene black for five minutes in a Hybridizer®, manufactured by Nara Machinery Co., Ltd. As in Practical Example 1, the particles were placed into an SSA-S grade alumina crucible and baked. After cooling, black particles were obtained at an 80% yield. An amount of carbon coated on the surface of the obtained carbon surface-coated silicon-containing carbon-based composite material was 6.1 mass (weight)% of the silicon-containing carbon-based composite material. Subjecting the obtained black particles to SEM, TEM, and EDX observation revealed that the black particles were composite particles having an average diameter of about from 2.0 to 50.0 µm in which the cores of the particles were constituted mainly of the SiOC component, and the surfaces of the particles were coated with carbon particles having a diameter from 30 to 40 nm.

[0165] Fabrication of the electrode and a secondary battery using the silicon-containing carbon-based composite material described in this Practical Example and evaluation thereof was carried out the

same as in Practical Example 1. The battery characteristics are shown in Table 1.

[0166]

Practical Example 5

Other than changing the compounded amount of the acetylene black to 0.05 g, the carbon
5 coated silicon-containing crosslinked particles of this Practical Example were prepared the same as
those in Practical Example 4. The battery characteristics are shown in Table 1.

[0167]

Practical Example 6

Other than changing the compounded amount of the acetylene black to 0.15 g, the carbon
10 coated silicon-containing crosslinked particles of this Practical Example were prepared the same as
those in Practical Example 4. The battery characteristics are shown in Table 1.

[0168]

Practical Example 7

Other than changing the compounded amount of the acetylene black to 0.50 g, the carbon
15 coated silicon-containing crosslinked particles of this Practical Example were prepared the same as
those in Practical Example 4. The battery characteristics are shown in Table 2.

[0169]

Practical Example 8

Other than changing the acetylene black to a vapor grown carbon fiber (hereinafter referred to
20 as "VGCF"; diameter= 125 nm; length= 10 μ m; BET surface area= 13 cm²/g), the carbon coated
silicon-containing crosslinked particles of this Practical Example were prepared the same as those in
Practical Example 4. The battery characteristics are shown in Table 2.

[0170]

Practical Example 9

25 Other than changing the compounded amount of the VGCF to 0.05 g, the carbon coated

silicon-containing crosslinked particles of this Practical Example were prepared the same as those in Practical Example 8. The battery characteristics are shown in Table 2.

[0171]

Practical Example 10

5 Other than changing the VGCF to a carbon nanotube (average diameter= 11 nm; maximum length= 10 μm ; BET surface area= 300 m^2/g), the carbon coated silicon-containing crosslinked particles of this Practical Example were prepared the same as those in Practical Example 8. The battery characteristics are shown in Table 2.

[0172]

10 Comparative Example 1

Preparation of the silicon-containing crosslinked particles

A crosslinkable composition was prepared by mixing 15.49 g of DVB570 (manufactured by Nippon Steel Chemical Co., Ltd.; Main components: divinylbenzene and vinyl ethylbenzene; proportion of divinylbenzene included in the main components: 60 mass (weight)%); and 9.51 g of a
15 methyl hydrogen siloxane copolymer capped at both molecular terminals with trimethylsiloxy groups (viscosity: 20 $\text{mPa}\cdot\text{s}$; silicon-bonded hydrogen atoms content: 1.58 mass (weight)%; included in an amount such that one mole of the silicon-bonded hydrogen atoms in the copolymer is included per one mole of vinyl groups in the DVB570). Thereafter, 25 g of an aqueous solution of 10 mass (weight)%-polyoxyethylene secondary alkyl ether (Sanonic SS120, manufactured by Sanyo
20 Chemical Industries, Ltd.; HLB=14.5) was added. Then, a water-based emulsion of the crosslinkable composition was prepared by emulsifying the mixture using a homo-disper (rotation speed: 5000 rpm). Next, a water-based emulsion of a platinum-based catalyst having a 1,3-divinyltetramethyl disiloxane platinum complex as a main component (average diameter of the emulsion = 0.05 μm ; platinum metal concentration = 0.05 mass (weight)%) that was prepared
25 separately was uniformly mixed with the water-based emulsion of the crosslinkable composition at

an amount, in terms of mass (weight), such that 20 ppm of platinum metal was included with respect to the crosslinkable composition, and mixed at 60°C for 60 minutes. Thereafter, cured product particles having an average diameter from 1 to 5 μm were prepared by removing the water.

[0173] Preparation of the silicon-containing carbon-based composite material

- 5 As in Practical Example 1, the cured product particles were placed into an SSA-S grade alumina crucible and baked. After cooling, black particles were obtained at a 62% yield. Subjecting the obtained black particles to SEM and EDX observation revealed that the black particles were spherical particles having an average diameter of about from 1.0 to 5.0 μm , constituted mainly of the SiOC component.

10 [0174]

Fabrication of the electrode

- 107.58 parts by mass (weight) of the obtained silicon-containing carbon-based composite material and 6.94 parts by mass (weight) of acetylene black were mixed for 15 minutes in a mortar. Thereafter, 12.00 parts by mass (weight) of polyvinylidene fluoride was added and the components
15 were further mixed for 15 minutes. Then, N-methyl-2-pyrrolidone was mixed in as a solvent in order to obtain a slurry-like mixture, which was then coated on a copper foil roll at a thickness of about 250 μm by means of a doctor blade method. Thereafter, the coated foil roll was dried under vacuum for not less than 12 hours at 85°C, and an electrode having a thickness of about 40 μm was obtained.

20 [0175]

Fabrication and evaluation of the secondary battery

Fabrication of a secondary battery and evaluation thereof was carried out the same as in Practical Example 1. The battery characteristics are shown in Table 2.

[0176]

Comparative Example 2

99.40 parts by mass (weight) of the silicon-containing carbon-based composite material obtained in Comparative Example 1 and 14.58 parts by mass (weight) of acetylene black were mixed for 15 minutes in a mortar. Thereafter, 12.00 parts by mass (weight) of polyvinylidene fluoride was added and the components were further mixed for 15 minutes. Then, N-methyl-2-pyrrolidone was mixed in as a solvent in order to obtain a slurry-like mixture, which was then coated on a copper foil roll at a thickness of about 250 μm by means of a doctor blade method. Thereafter, the coated foil roll was dried under vacuum for not less than 12 hours at 85°C, and an electrode having a thickness of about 40 μm was obtained. Fabrication of the electrode and a secondary battery and evaluation thereof was carried out the same as in Practical Example 1. The battery characteristics are shown in Table 2.

[0177]

Table 1

	Practical Example 1	Practical Example 2	Practical Example 3	Practical Example 4	Practical Example 5	Practical Example 6
Initial discharging capacity (mAh/g)	812	842	700	759	743	603
CE%	68	66	67	70	69	68
Capacity maintenance ratio (%) After 10 cycles	95	90	96	98	90	95

[0178]

Table 2

	Practical Example 7	Practical Example 8	Practical Example 9	Practical Example 10	Comparative Example 1	Comparative Example 2
Initial discharging capacity (mAh/g)	603	810	812	830	820	750
CE%	63	68	68	70	60	55
Capacity maintenance ratio (%) After 10 cycles	97	95	90	98	65	60

REFERENCE NUMERALS

- 5 [0179]
- 1: Case
- 2: Gasket
- 3: Washer
- 4: SUS plate
- 10 5: Current collector
- 6: Negative electrode
- 7: Separator
- 8: Positive electrode
- 9, 9': Current collector
- 15 10: Sealing plate

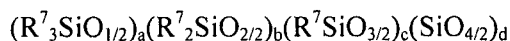
CLAIMS

1. A method for manufacturing a carbon surface-coated silicon-containing carbon-based composite material characterized by: obtaining a cured product by crosslinking (A) a crosslinkable
5 group-containing organic compound (hereinafter referred to as "component (A)"), and (B) a silicon-containing compound (hereinafter referred to as "component (B)") capable of crosslinking the crosslinkable group-containing organic compound; and baking a mixture of the cured product and (C) a carbonaceous matter (hereinafter referred to as "component (C)").
- 10 2. The manufacturing method of claim 1, wherein the baking is performed at a temperature from 300°C to 1,500°C in an inert gas or in a vacuum.
3. The manufacturing method of claim 1 or 2, wherein the crosslinkable group is selected from the group consisting of aliphatic unsaturated groups, epoxy groups, acryl groups, methacryl groups,
15 amino groups, hydroxyl groups, mercapto groups, and halogenated alkyl groups.
4. The manufacturing method of any of claims 1 to 3, wherein the component (A) has an aromatic group.
- 20 5. The manufacturing method of any of claims 1 to 4, wherein the component (A) is an organic compound expressed by the general formula:
$$(R^1)_x R^2$$

wherein R^1 is a crosslinkable group; "x" is an integer greater than or equal to 1; and R^2 is an aromatic group with "x" valency.

6. The manufacturing method of any of claims 1 to 5, wherein the component (B) is a siloxane, a silane, a silazane, a carbosilane, or a mixture thereof.

7. The manufacturing method of any of claims 1 to 6, wherein the component (B) is preferably a siloxane expressed by the average unit formula:



wherein, R^7 each independently represent a monovalent hydrocarbon group, a hydrogen atom, a halogen atom, an epoxy group-containing organic group, an acryl group- or methacryl group-containing organic group, an amino group-containing organic group, a mercapto group-containing organic group, an alkoxy group, or a hydroxy group; "a", "b", "c", and "d" are numbers that are greater than or equal to 0 and less than or equal to 1, and that satisfy "a"+"b"+"c"+"d"=1; however, "a", "b", and "c" cannot be 0 at the same time.

8. The manufacturing method of any of claims 1 to 7, wherein the component (C) is a carbon black, a carbon fiber, a carbon nanofiber, a carbon nanotube, or a mixture thereof.

9. The manufacturing method of any of claims 1 to 8, wherein the crosslinking is carried out via an addition reaction, a condensation reaction, a ring-opening reaction, or a radical reaction.

10. The manufacturing method of any of claims 1 to 9, wherein the cured product is obtained by a hydrosilylation reaction of the component (A) having aliphatic unsaturated groups and the component (B) having silicon-bonded hydrogen atoms.

11. The manufacturing method of any of claims 1 to 9, wherein the cured product is obtained by a radical reaction of the component (A) having aliphatic unsaturated groups and the component (B)

having aliphatic unsaturated groups, acryl groups, methacryl groups, or silicon-bonded hydrogen atoms.

12. The manufacturing method of any of claims 1 to 11, wherein a surface of the cured product is
5 covered by the component (C).

13. A carbon surface-coated silicon-containing carbon-based composite material obtained via the manufacturing method described in any of claims 1 to 12.

10 14. The composite material of claim 13, wherein the silicon-containing carbon-based composite material is constituted by particles having an average diameter from 5 nm to 50 μm .

15. The composite material of claim 13 or 14, wherein an amount of carbon included therein is from 1 to 50 mass (weight)%.

15

16. The composite material of any of claims 13 to 15, comprising a carbon coating layer having a thickness from 5 nm to 2 μm .

17. An electrode active material constituted by the composite material described in any of claims 13
20 to 16.

18. The electrode active material of claim 17, constituted by particles having an average diameter from 1 to 50 μm .

25 19. An electrode comprising the electrode active material described in claim 17 or 18.

20. An electricity storage device comprising the electrode of claim 19.

21. The electricity storage device of claim 20, which is a lithium or lithium-ion secondary battery.

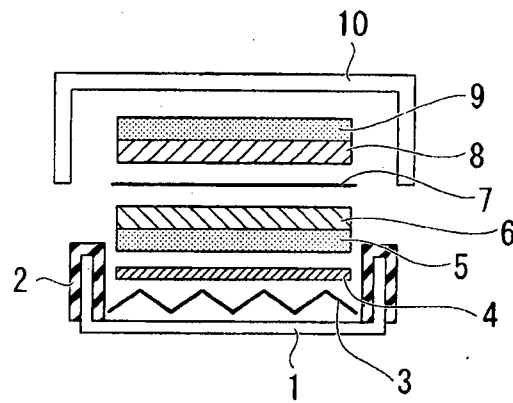


FIG. 1

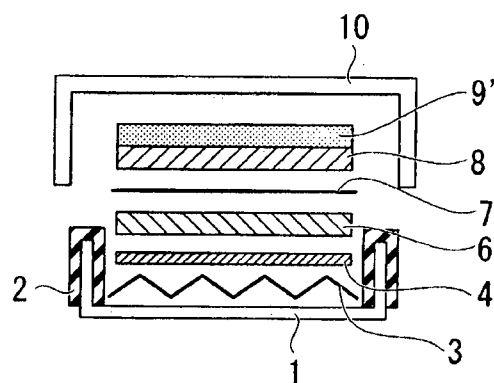


FIG. 2

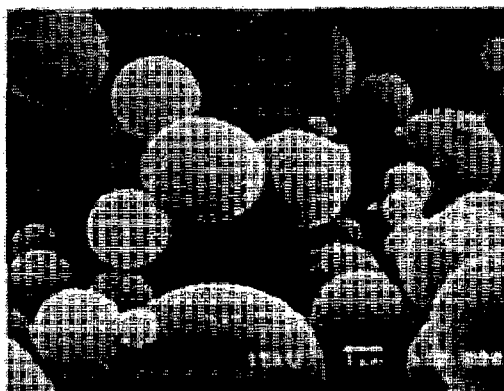


FIG. 3

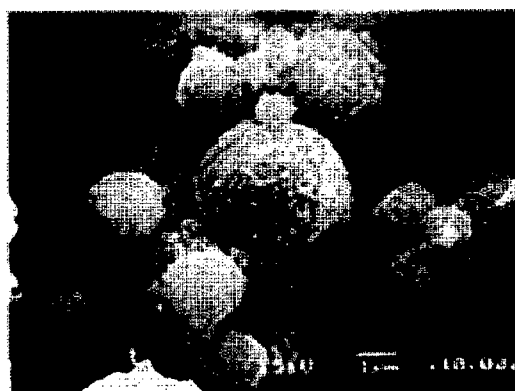


FIG. 4

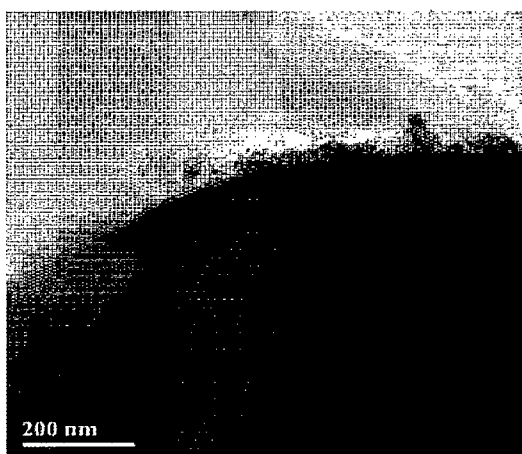


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2012/052440

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M4/133 H01M4/587 H01M4/38 H01M4/134
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, FSTA, INSPEC, PAJ, IBM-TDB, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/252864 A1 (CAREL MARK [US] ET AL) 8 October 2009 (2009-10-08)	13-21
A	paragraphs [0008], [0015], [0016], [0040] - [0044] claims 1,4,5 figure 1	1-12
X	US 2005/136330 A1 (MAO ZHENHUA [US] ET AL) 23 June 2005 (2005-06-23)	13-21
A	paragraphs [0018], [0026], [0030], [0031], [0043], [0046] - [0049], [0054] examples 1-3	1-12



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

16 May 2012

Date of mailing of the international search report

29/05/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Götz, Heide

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2012/052440

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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