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(54) Title: SILICON-CONTAINING CARBON-BASED COMPOSITE MATERIAL

(57) Abstract: The present invention relates to a silicon-containing carbon-based composite material obtained by heat-treating a cured product containing (A) a crosslinkable organic compound having at least one n aromatic group, and (B) a silicon-containing compound that can crosslink component (A). The composite material according to the present invention can be used for an electrode of an electricity storage device, particularly for a sodium or sodium-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.

DESCRIPTION

SILICON-CONTAINING CARBON-BASED COMPOSITE MATERIAL

TECHNICAL FIELD

[0001] The present invention relates to a silicon-containing carbon-based composite material, an electrode-active material constituted by the composite material, an electrode comprising the electrode-active material, and an electricity storage device comprising the electrode, and particularly relates to a sodium or sodium-ion secondary battery.

[0002] Priority is claimed on Japanese Patent Application No. 2012-017368 filed on January 30, 2012, the content of which is incorporated herein by reference.

BACKGROUND ART

[0003] Lithium ion batteries are used as secondary batteries with high energy density in various everyday applications. Furthermore, automotive applications have gained popularity recently, and the lithium ion battery market is expected to continue to expand in the future.

[0004] Lithium ion batteries normally use a carbon material such as graphite for the negative electrode, and a transition metal oxide containing lithium for the positive electrode. During charging and discharging, lithium ions migrate between the positive and negative electrodes through an electrolyte solution where an electrolyte salt containing lithium has been dissolved.

[0005] On the other hand, research focusing on sodium as the alkali metal has also been performed. The theoretical capacity is less than half that of lithium, and the voltage of the cell is reduced by a potential difference of 0.33 V. However, from the perspective of natural resources, sodium has richer reserves than lithium, and is attractive as a substitute metal. In this case, materials that can store and discharge sodium ions instead of lithium ions can be used.

[0006] In particular, Japanese Unexamined Patent Application Publication No. 2007-35588 discloses that graphite and silicon that can store and discharge lithium ions have little or no capability of storing and discharging sodium ions. Therefore, the application publication discloses that carbon materials that have a specific crystalline structure can be used as negative electrode materials that can store and discharge sodium ions.

[0007] Furthermore, WO2010/109889 discloses that sufficient sodium ion storage and discharge is possible when using hard carbon, and that a sodium ion secondary battery can be provided that suppresses a drop in battery performance due to the negative electrode-active material.

[0008] Similarly, the storage and discharge of sodium ions by hard carbon has also been disclosed in the Journal of the Electrochemical Society, 148 (8) A803 (2001), and in Electrochimica Acta, 47 (2002) 3303-3307.

[0009] However, when these carbon materials are used as the negative electrode in a sodium-ion battery, battery performance such as long-term cycle properties and the like

cannot be sufficiently demonstrated.

DISCLOSURE OF INVENTION

Technical Problems

[0010] An object of the present invention is to provide a composite material suitable for use as an electrode of a sodium or sodium-ion secondary battery, an electrode-active material constituted by the composite material, an electrode containing the electrode-active material, and an electricity storage device, particularly a sodium or sodium-ion secondary battery, including the electrode.

Solution to Problems

[0011] The object of the present invention can be achieved by a silicon-containing carbon-based composite material obtained by heat-treating a cured product from a crosslinking reaction between a crosslinkable organic compound having at least one aromatic group (A) and a silicon-containing compound (B) that can crosslink with component (A).

[0012] The heat-treating is preferably performed at a temperature from 300°C to 1,500°C in an inert gas or in a vacuum.

[0013] The component (A) can have at least one crosslinkable group 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.

[0014] The component (A) is preferably an organic compound expressed by the following general formula:
$(R^1)_xR^2$
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.

[0015] The component (A) may include silicon. The component (A) is preferably a siloxane, a silane, a silazane, a carbosilane, or a mixture thereof.

[0016] The siloxane is preferably expressed by the average unit formula:
$(R^3{}_3SiO_{1/2})_a(R^3{}_2SiO_{2/2})_b(R^3SiO_{3/2})_c(SiO_{4/2})_d$
wherein
R^3 each independently represents a crosslinkable group, a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic 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 R^3 in the molecule is an aromatic group; and
at least one R^3 in the molecule is a crosslinkable group.

[0017] The component (B) is preferably a siloxane, a silane, a silazane, a carbosilane, or a mixture thereof.

[0018] The siloxane is preferably expressed by the average unit formula:
$(R^7{}_3SiO_{1/2})_a(R^7{}_2SiO_{2/2})_b(R^7SiO_{3/2})_c(SiO_{4/2})_d$
wherein
R^7 each independently represents 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. In the above formula, "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.

[0019] The crosslinking may be carried out via an addition reaction, a condensation reaction, a ring-opening reaction, or a radical reaction.

[0020] The cured product may be obtained via a hydrosilylation reaction of the component (A) having aliphatic unsaturated groups and the component (B) having silicon-bonded hydrogen atoms.

[0021] The cured product may be obtained via a hydrosilylation reaction of the component (A) having silicon-bonded hydrogen atoms and the component (B) having aliphatic unsaturated groups.

[0022] The cured product may be 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.

[0023] The cured product may be obtained by a radical reaction of the component (A) having aliphatic unsaturated groups, acryl groups, methacryl groups, or silicon-bonded hydrogen atoms and the component (B) having aliphatic unsaturated groups.

[0024] The silicon-containing carbon-based composite material of the present invention is preferably amorphous. The silicon-containing carbon-based composite material of the present invention is preferably constituted by particles having an average diameter from 5 nm to 50 μm.

[0025] 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.

[0026] The electrode of the present invention includes the electrode-active material described above, and can be suitably used for sodium or sodium-ion secondary batteries.

Advantageous Effects of Invention

[0027] The silicon-containing carbon-based composite material of the present invention has high reversible capacity and stable charge and discharge cycle characteristics. Furthermore, the silicon-containing carbon-based composite material of the present invention is suitable for an electricity storage device, and particularly as an electrode for a sodium or sodium-ion secondary battery. Additionally, the silicon-containing carbon-based composite material of the present invention uses inexpensive raw materials and can be manufactured via a simple manufacturing process.

[0028] The electrode-active material of the present invention is suitable for use in an electricity storage device, particularly as an electrode of a sodium or sodium-ion secondary battery. Moreover, the electrode of the present invention can impart high reversible capacity, and stable charge and discharge cycle characteristics to a battery. As a result, the sodium or sodium-ion secondary battery of the present invention can have high reversible capacity, and stable charge and discharge cycle characteristics.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] FIG. 1 illustrates an example of the sodium-ion secondary battery of the present invention.

[0030] FIG. 2 illustrates an example of the sodium secondary battery of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[0031] Composite Material

The silicon-containing carbon-based composite material of the present invention can be obtained by a manufacturing method comprising the steps of: crosslinking (A) a crosslinkable organic compound having at least one aromatic group, and (B) a silicon-containing compound capable of crosslinking the component (A); and heat-treating the obtained closslikned or cured product. The silicon-containing carbon-based composite material of the present invention can electrochemically store sodium ions.

[0032] Component (A) is an organic compound that can crosslink, and generally contains a crosslinkable group. The crosslinkable group of the component (A) is not particularly limited provided that it is a 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 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 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.

[0033] Note that the component (A) may be a mixture of an organic compound having one 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)%.

[0034] The component (A) has at least one aromatic group in a molecule. The aromatic group is not particularly limited, but monovalent aromatic groups and divalent aromatic groups are preferable, and monovalent aromatic groups are more preferable. The monovalent aromatic group can be an aryl group having from 6 to 20 carbon atoms such as a phenyl group, tolyl group, xylyl group and the like; an aralkyl group having from 7 to 20 carbon atoms such as a benzyl group, phenethyl group and the like; other monovalent aromatic groups such as a styryl group, biphenyl group and the like; and groups wherein the hydrogen atoms bonded to the carbon atoms of these groups are substituted at least partially by fluorine or a similar halogen atom, or an organic group having carbinol groups, epoxy groups, glycidyl groups, acyl groups, carboxyl groups, amino groups, methacryl groups, mercapto groups, amide groups, oxyalkylene groups, and the like. The aryl or aralkyl groups are preferably unsubstituted aryl groups or aralkyl groups having from 6 to 20 carbon atoms, more preferably unsubstituted aryl groups or aralkyl groups having from 6 to 10 carbon atoms, and even more preferably a phenyl group. Examples of divalent aromatic groups include arylene groups such as phenylene groups and biphenylene groups.

[0035] Note that the component (A) may be a mixture of an organic compound having one aromatic group in a molecule and an organic compound having at least two aromatic groups in a molecule. In this case, a proportion of the latter compound in the mixture is not particularly limited, but the content is preferably at least 25 mass (weight)% and more preferably at least 50 mass (weight)%.

[0036] The component (A) may be silicon-free or may include silicon.

[0037] 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 of a graphene structure is facilitated due to excellent efficiency when carbonizing by heating.

[0038] Specific examples of the component (A) described above include aromatic hydrocarbon compounds that contain a crosslinkable group in the molecule, but do not contain a silicon atom, and aromatic compounds that have a crosslinkable group in the molecule, that have a hetero atom other than a carbon atom such as a nitrogen atom, oxygen atom, boron atom, and the like, and that do not contain silicon atoms.

[0039] Specific examples of the aromatic compound include those expressed by the following general formula:

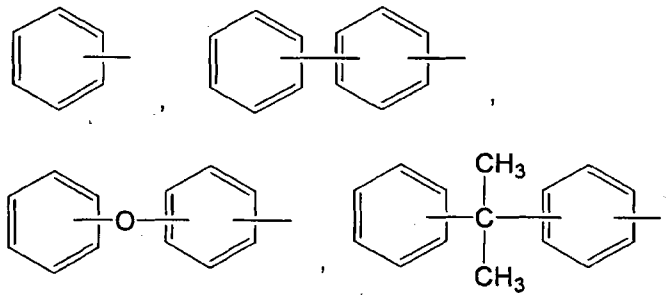
$(R^1)_xR^2$

wherein

R^1 is a crosslinkable group;

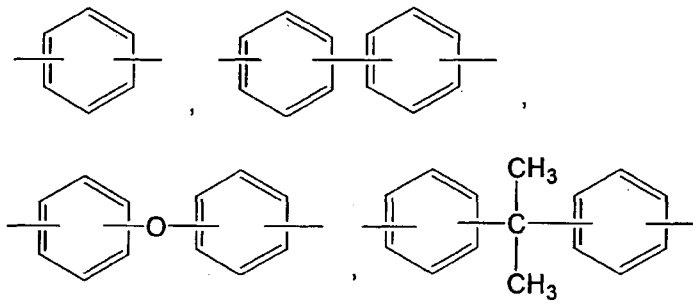
"x" is an integer greater than or equal to 1, preferably 1 or 2, and more preferably 1; and R^2 is an aromatic group with "x" valency.

[0040] Specifically, in this formula, when "x" is 1, R^2 represents a monovalent aromatic group, and specific examples thereof include the groups described below.



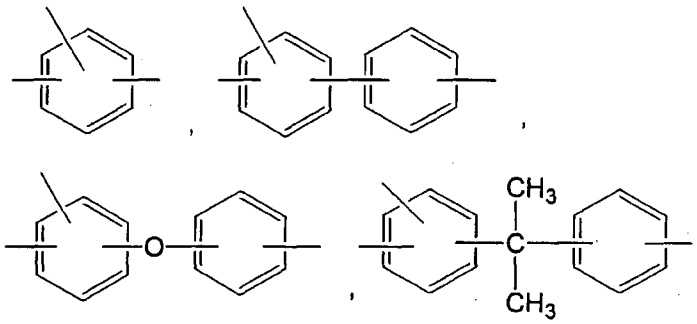
[0041] Specific examples of the aromatic hydrocarbon compound described above include α- or β-methylstyrene, α- or β-ethylstyrene, methoxystyrene, phenylstyrene, chlorostyrene, o-, m-, or p-methylstyrene, ethylstyrene, methylsilylstyrene, hydroxystyrene, cyanostyrene, nitrostyrene, aminostyrene, carboxystyrene, sulfoxystyrene, sodium styrenesulfonate, vinylpyridine, vinylthiophene, vinylpyrrolidone, vinylnaphthalene, vinylanthracene, and vinylbiphenyl.

[0042] Additionally, in the formula, when "x" is 2, R^2 represents a bivalent aromatic group, and specific examples thereof include the groups described below.



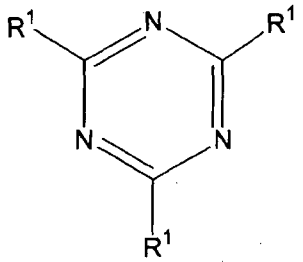
[0043] Specific examples of the aromatic hydrocarbon compound described above include divinylbenzene, divinylbiphenyl, vinylbenzylchloride, divinylpyrindine, divinylthiophene, divinylpyrrolidone, divinylnaphthalene, divinylxylene, divinylethylbenzene, and divinylanthracene. The aromatic hydrocarbon compound is preferably divinylbenzene because the pyrolyzing characteristics of the obtained cured product will be superior.

[0044] Additionally, in the formula, when "x" is 3, R^2 represents a trivalent aromatic group, and specific examples thereof include the groups described below.



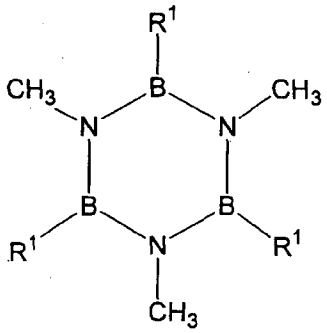
[0045] Specific examples of the aromatic hydrocarbon compound described above include trivinylbenzene and trivinylnaphthalene.

[0046] Additionally, specific examples of the aromatic compound comprising hetero-atoms include aromatic compounds expressed by the following formula:



In this formula, R^1 is a crosslinkable group, and examples thereof are the same as the groups described above.

[0047] Additionally, specific examples of the cyclic compound having hetero-atoms include cyclic compounds expressed by the following formula:



in this formula, R^1 is a crosslinkable group, and examples thereof are the same as the groups described above.

[0048] 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.

[0049] Examples of silanes as the component (A) include those expressed by the following average unit formula:

$R^3{}_4Si$
or the following average unit formula:
$(R^3{}_3Si)_a(R^3{}_2Si)_b(R^3Si)_c(SiO)_d$
wherein, R^3 each independently represents the crosslinkable group described above, a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic 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;
at least one R^3 in the molecule is an aromatic group; and
at least one R^3 in the molecule and preferably at least two are the crosslinkable groups.
Here, the aromatic group is the same as those defined above.

[0050] The saturated aliphatic hydrocarbon group is preferably an alkyl group, and the aromatic hydrocarbon group is preferably an aryl group and an aralkyl group.

[0051] The alkyl groups are preferably alkyl groups having from 1 to 12 carbons and more preferably 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)).

[0052] 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.

[0053] The cycloalkyl groups preferably have from 4 to 6 carbon atoms and examples thereof include cyclobutyl groups, cyclopentyl groups, cyclohexyl groups, and the like. Cyclopentyl groups and cyclohexyl groups are particularly preferable.

[0054] The aryl groups preferably have from 6 to 12 carbon atoms and examples thereof include phenyl groups, naphthyl groups, and tolyl groups.

[0055] 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.

[0056] 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.

[0057] Examples of the alkoxy groups include methoxy groups, ethoxy groups, n-propoxy groups, and isopropoxy groups.

[0058] Examples of the halogen atoms include fluorine atoms, chlorine atoms, bromine

atoms, and iodine atoms.

[0059] 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 Japanese Unexamined Patent Application Publication No. H04-334551, etc.), and other methods.

[0060] Examples of silazane as the component (A) include those expressed by the following average unit formula:
$(R^3{}_3SiNR^4)_a(R^3{}_2SiNR^4)_b(R^3SiNR^4)_c(SiNR^4)_d$
wherein
R^3 each independently represents the crosslinkable group described above, a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic 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 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 R^3 in the molecule is an aromatic group; and
at least one R^3 in the molecule and preferably at least two are the crosslinkable groups.
Here, the aromatic group is the same as those defined above. The saturated aliphatic hydrocarbon group, the alkoxy group, and the halogen atoms are the same as those defined above for the silane.

[0061] The silazane described above can be prepared by methods known in the art. Examples of methods for preparing the polysilazane 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).

[0062] Examples of siloxanes as the component (A) include those expressed by the following average unit formula:
$(R^3{}_3SiO_{1/2})_a(R^3{}_2SiO_{2/2})_b(R^3SiO_{3/2})_c(SiO_{4/2})_d$
wherein
R^3 each independently represents the crosslinkable group described above, a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic 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 R^3 in the molecule is an aromatic group; and
at least one R^3 in the molecule and preferably at least two are the crosslinkable groups.

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

[0063] 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).

[0064] Examples of carbosilane as the component (A) include those expressed by the following average unit formula:
$(R^3{}_3SiCR^5R^6)_a(R^3{}_2SiCR^5R^6)_b(R^3SiCR^5R^6)_c(SiCR^5R^6)_d$
wherein
R^3 each independently represents the crosslinkable group described above, a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic group having from 1 to 20 carbons, an alkoxy group, a hydrogen atom, or a halogen atom;
R^5 and R^6 each independently represents a hydrogen atom or a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic 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 R^3 in the molecule is an aromatic group; and
at least one R^3 in the molecule and preferably at least two are the crosslinkable groups.
Here, the aromatic group is the same as those defined above. The saturated aliphatic hydrocarbon group, the alkoxy group, and the halogen atoms are the same as those defined above for the silane.

[0065] The carbosilane described above can be prepared by methods known in the art. Examples of methods for preparing the carbosilane are described in Macromolecules, 21, 30 (1988) and U.S. Patent 3293194.

[0066] 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 handleability and the like, are preferably solids.

[0067] 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.

[0068] 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)%.

[0069] The component (B) is a silicon-containing compound capable of crosslinking the

component (A). Examples of the component (B) described above include silanes, silazanes, siloxanes, carbosilanes, and mixtures thereof. Specifically, the silane, silazane, siloxane, and carbosilane can be selected from silanes of monomers, oligomers, and polymers and the like having a Si-Si bond, silazanes of monomers, oligomers, and polymers and the like having a Si-N-Si bond, siloxanes of monomers, oligomers, and polymers and the like having a Si-O-Si bond, and carbosilanes of monomers, oligomers, and polymers and the like having a Si-C-Si bond.

[0070] Furthermore, examples of component (B) include silalkylenes of monomers, oligomers, and polymers and the like having a Si-$(CH_2)_n$-Si bond, silarylenes of monomers, oligomers, and polymers and the like having a Si-$(C_6H_4)_n$-Si or Si-$(CH_2CH_2C_6H_4CH_2CH_2)_n$-Si bond, silicon-containing copolymer compounds having at least two types of bonds selected from Si-O-Si bonds, Si-Si bonds, Si-$(CH_2)_n$-Si bonds, Si-$(C_6H_4)_n$-Si bonds, and Si-N-Si bonds. Note that in the formulae, n is an integer greater than or equal to 1.

[0071] The component (B) preferably has silicon-bonded hydrogen atoms.

[0072] A silane as the component (B) can be expressed for example by the general formula:
$R^7{}_4Si$
or the following average unit formula:
$(R^7{}_3Si)_a(R^7{}_2Si)_b(R^7Si)_c(Si)_d$
wherein
R^7 each independently represents 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. In the above formula, “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.

[0073] 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 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 have 4 to 6 carbon atoms and specific examples thereof include cyclobutyl groups, cyclopentyl groups, and cyclohexyl groups. The alkenyl groups preferably have 2 to 12 carbon atoms, and more preferably 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 7 to 12 carbon atoms. Specific examples of the aralkyl groups with 7 to 12 carbon atoms include benzyl groups, phenethyl groups, and phenylpropyl groups. The aryl groups preferably have 6 to 12 carbon atoms and specific examples thereof include phenyl groups, naphthyl groups, and tolyl groups. The aforementioned 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.

[0074] 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.

[0075] 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.

[0076] 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.

[0077] 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.

[0078] Specific examples of the mercapto group-containing organic groups represented by R^7 include 3-mercaptopropyl groups and 4-mercaptobutyl groups.

[0079] 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.

[0080] 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.

[0081] “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.

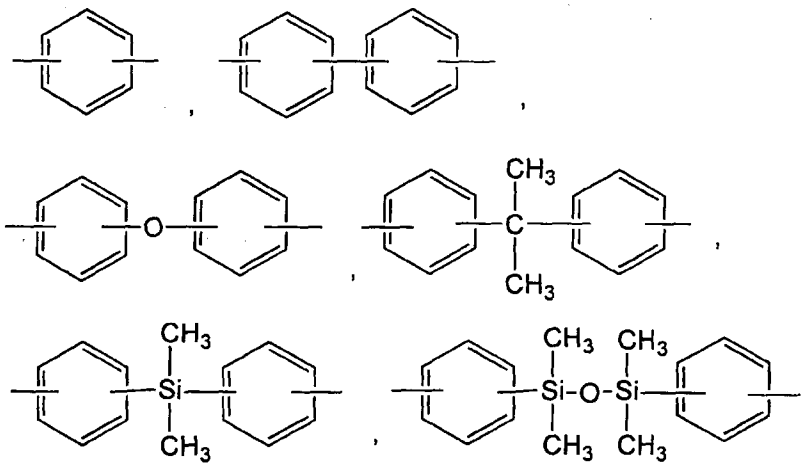
[0082] The silanes are expressed by the general formula: R^7_4Si, or structured from at least one of the structural units selected from (R^7_3Si), (R^7_2Si), (R^7Si), and (Si). Specific examples are the following: a straight chain polysilane composed of (R^7_3Si) and (R^7_2Si) units; a cyclic polysilane composed of (R^7_2Si) units; a branched chain polysilane (polysiline) 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 repeated 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.

[0083] The aforementioned silanes 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 Japanese Unexamined Patent Application Publication No. H04-334551, etc.), and other methods.

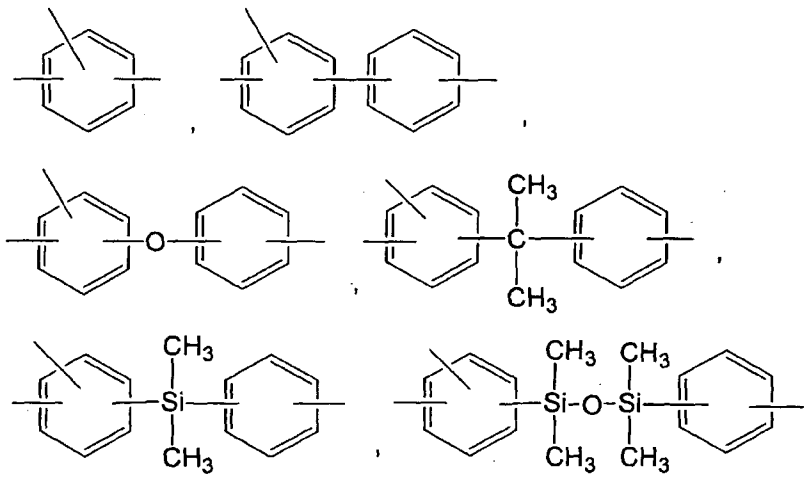
[0084] The silanes described above may be silicon-containing copolymer compounds with other polymers. Examples of silicon-containing copolymer compounds that can be used as the silanes include silicon-containing copolymer compounds having Si-Si bonds and Si-O-Si bonds; silicon-containing copolymer compounds having Si-Si bonds and Si-N-Si bonds; silicon-containing copolymer compounds having Si-Si bonds and Si-$(CH_2)_n$-Si bonds; silicon-containing copolymer compounds having Si-Si bonds and Si-$(C_6H_4)_n$-Si bonds or Si-$(CH_2CH_2C_6H_4CH_2CH_2)_n$-Si bonds; and the like.

[0085] Examples of other silanes include silicon-containing compounds expressed by the general formula:
$[(R^8)_2HSi]_eR^9$
wherein
R^8 are each independently substituted or unsubstituted monovalent hydrocarbon groups;
"e" is an integer greater than or equal to 2; and
R^9 is an "e"-valent organic group. In this formula, examples of the monovalent hydrocarbon groups represented by R^8 are the same as the monovalent hydrocarbon groups described as examples for R^7. "e" is an integer greater than or equal to 2, preferably an integer in a range from 2 to 6. When R^9 is an "e"-valent organic group and "e" is equal to 2, R^9 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:-CH_2CH_2-, -$CH_2CH_2CH_2$-, -$CH_2CH(CH_3)$-, -CH=CH-, -C≡C-, -$CH_2CH_2OCH_2CH_2$-, -$CH_2CH_2CH_2OCH_2CH_2$-,



[0086] When "e" is equal to 3, R^9 is a trivalent organic group. Specific examples thereof include the groups expressed by the following formulae:



[0087] Examples of silazane as the component (B) include those expressed by the following average unit formula:
$(R^7{}_3SiNR^{10})_a(R^7{}_2SiNR^{10})_b(R^7SiNR^{10})_c(SiNR^{10})_d$
wherein
R^7 each independently represents 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. In the above formula, "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. 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.

[0088] 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 ($R^7_3SiNR^{10}$), (R^7SiNR^{10}), and ($SiNR^{10}$) units; a polysilazane composed ($R^7_2SiNR^{10}$), (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 repeated 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.

[0089] The silazanes 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).

[0090] 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-$(CH_2)_n$-Si bonds; silicon-containing copolymer compounds having Si-N-Si bonds and Si-$(C_6H_4)_n$-Si bonds or Si-$(CH_2CH_2C_6H_4CH_2CH_2)_n$-Si bonds; and the like. In the formulae, "n" has the same meaning as defined above.

[0091] Examples of siloxane as the component (B) include those expressed by the following average unit formula:
$(R^7_3SiO_{1/2})_a(R^7_2SiO_{2/2})_b(R^7SiO_{3/2})_c(SiO_{4/2})_d$
wherein
R^7 each independently represents 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. In the above formula, "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.

[0092] 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 repeated 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.

[0093] The aforementioned siloxanes can be prepared by methods known in the art. There are no special restrictions with regard to the method for the siloxane preparation, but the most common method consists of 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).

[0094] 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-(CH_2)$_n$-Si bonds; silicon-containing copolymer compounds having Si-O-Si bonds and Si-(C_6H_4)$_n$-Si bonds or Si-($CH_2CH_2C_6H_4CH_2CH_2$)$_n$-Si bonds; and the like. In the formulae, "n" has the same meaning as defined above.

[0095] Examples of carbosilane as the component (B) include those expressed by the following average unit formula:
$(R^7_3SiR^{11})_a(R^7_2SiR^{11})_b(R^7SiR^{11})_c(SiR^7)_d$
wherein
R^7 each independently represents 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^{11} is an alkylene group or an arylene group. In the above formula, "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. The alkylene group represented by R^{11} may be expressed, for example, by the formula: -(CH_2)$_n$-, and the arylene group represented by R^{11} can be expressed, for

example, by the formula: $-(C_6H_4)_n-$. In the formulae, "n" has the same meaning as defined above.

[0096] The carbosilanes are structured from at least one of the structural units expressed by the following: $(R^7{}_3SiR^{11})$, $(R^7{}_2SiR^{11})$, (R^7SiR^{11}), and (SiR^{11}). Specific examples include a straight chain polycarbosilane consisting of $(R^7{}_3SiR^{11})$ and $(R^7{}_2SiR^{11})$ units; a cyclic polycarbosilane consisting of $(R^7{}_2SiR^{11})$ units; a branched chain polycarbosilane consisting of (R^7SiR^{11}) and (SiR^{11}) units; a polycarbosilane consisting of $(R^7{}_3SiR^{11})$ and (R^7SiR^{11}) units; a polycarbosilane consisting of $(R^7{}_3SiR^{11})$ and (SiR^{11}) units; a polycarbosilane consisting of (R^7SiR^{11}) and (SiR^{11}) units; a polycarbosilane consisting of $(R^7{}_2SiR^{11})$ and (R^7SiR^{11}) units; a polycarbosilane consisting of $(R^7{}_2SiR^{11})$ and (SiR^{11}) units; a polycarbosilane consisting of $(R^7{}_3SiR^{11})$, $(R^7{}_2SiR^{11})$, and (R^7SiR^{11}) 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 repeated structural units 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.

[0097] The aforementioned carbosilanes 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.

[0098] 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; 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 $Si-(CH_2CH_2C_6H_4CH_2CH_2)_n-Si$ bonds and Si-N-Si bonds; and the like. In the formulae, "n" has the same meaning as defined above.

[0099] The component (B) is preferably a siloxane and more preferably a polysiloxane expressed by the following average unit formula:
$(R^7{}_3SiO_{1/2})_a(R^7{}_2SiO_{2/2})_b(R^7SiO_{3/2})_c(SiO_{4/2})_d$
wherein
R^7 each independently represents 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. In the above formula, "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.

[0100] The crosslinking reaction is not particularly limited so long as component (A) and component (B) can be crosslinked, but specific examples include addition reactions such as hydrosilylation reactions, Michael addition reactions, Diels-Alder reactions, and the like; condensation reactions such as dealcoholization, dehydrogenation, dehydration, deamination, and the like; ring opening reactions such as epoxy ring-opening reactions and ester ring-opening reactions and the like; and radical reactions initiated by a peroxide or UV or the like. Particularly, when the component (A) has an aliphatic unsaturated group and the component (B) has a silicon-bonded hydrogen atom, or when the component (A) has a silicon-bonded hydrogen atom and the component (B) has an aliphatic unsaturated group, the reaction can be a hydrosilylation reaction in the presence of a hydrosilylation-reaction catalyst.

[0101] Specific examples of the hydrosilylation-reaction catalyst include fine platinum powder, platinum black, fine platinum-carrying silica powder, fine platinum-carrying activated carbon, 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 respect to a total weight of the component (A) and the component (B).

[0102] When the component (A) has aliphatic unsaturated groups and the component (B) has silicon-bonded hydrogen atoms or when the component (A) has silicon-bonded hydrogen atoms and the component (B) has aliphatic unsaturated groups, the respective amounts thereof are not particularly limited. However, the contents are such that the silicon-bonded hydrogen atoms in the component (B) or the component (A) 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) or the component (B). One reason for this is because when the amount of the silicon-bonded hydrogen atoms 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.

[0103] 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 and when component (A) comprises aliphatic unsaturated groups, acryl groups, methacryl groups, or silicon-bonded hydrogen atoms and the component (B) comprises aliphatic unsaturated groups, a mixture thereof can be radical-reacted by a radical initiator using heat and/or light.

[0104] 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).

[0105] 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).

[0106] 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 and when the component (A) comprises aliphatic unsaturated groups, acryl groups, methacryl groups, or silicon-bonded hydrogen atoms and the component (B) comprises aliphatic unsaturated groups, 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 one of the components 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 other of the components. One reason for this is because when the amount of the aliphatic unsaturated groups, the acryl groups, the methacryl groups, or the silicon-bonded hydrogen atoms 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.

[0107] 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 heat-treating (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 may be carried out at this point or may be 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: When forming the cured product into 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 by emulsifying or dispersing said crosslinkable composition in a non-compatible medium.

[0108] 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.

[0109] 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.

[0110] 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.

[0111] 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.

[0112] 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 5 nm to 50 μm, which is suitable for an electrode-active material, the average diameter is preferably in a range from 5 nm to 100 μm, more preferably is in a range from 0.1 to 80 μm, and even more preferably is in a range from 0.5 to 80 μm.

[0113] 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.

[0114] 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).

[0115] The baking conditions are not particularly limited, but baking is preferably carried out in an inert gas or in a vacuum at a temperature 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. 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 a Reidhammer furnace, tunnel-type furnace, single-type furnace, oxynon furnace, a roller hearth kiln, a pusher kiln, batch type rotary kiln, and continuous rotary kiln and the like.

[0117] If a continuous furnace such as a roller hearth kiln, pusher kiln, and continuous rotary kiln is used, the step of forming a cured product by a crosslinking reaction between the component (A) and component (B) and the step of baking the cured product can be continuously performed. Furthermore, the step of forming the cured product by a crosslinking reaction of the component (A) and component (B), the baking step, and the surface coating treatment step such as sputtering and thermal chemical vapor deposition can also be continuously performed in a continuous furnace. If a continuous furnace such as a roller hearth kiln, pusher kiln, or continuous rotary kiln is used, the concentration of oxygen in each process environment can be strictly controlled, so there is an advantage that the amount of oxygen atoms and hydrogen atoms in the silicon-containing carbon-based composite material that is obtained can be easily controlled and adjusted.

[0118] The silicon-containing carbon-based composite material of the present invention, obtained as described above, is characterized by having a chemical composition expressed by the formula: $SiO_xC_yH_z$. In this formula, "x" is from 0.8 to 1.7, preferably from 0.8 to 1.6, more preferably from 0.8 to 1.5, and even more preferably from 0.9 to 1.2. "y" is in a range from 1.4 to 8.0, preferably from 1.7 to 7.5, more preferably from 2.0 to 6.0, and even more preferably from 2.5 to 4.5. "z" is in a range from 0.1 to 1.5, preferably from 0.2 to 1.0, and more preferably from 0.3 to 0.9. When the moieties of the chemical composition are within the ranges described above, reversible capacity and charge and discharge cycle characteristics will be enhanced and, particularly, initial charge and discharge efficiency will be enhanced.

[0119] The chemical composition of the silicon-containing carbon-based composite material can be controlled by pre-adjusting the ratios of oxygen atoms, carbon atoms, and hydrogen atoms per one silicon atom in the cured product by changing the type of the component (A) and/or the component (B) used, and the volume ratio of the component (A) to the component (B) when curing. The component (A) preferably includes silicon atoms, the component (A) preferably contains a silicon-bonded aromatic group and/or the component (B) also has an aromatic group, and both component (A) and component (B) contain a silicon-bonded aromatic group, because control of the value of "y" after baking is facilitated when an aromatic group bonded to a silicon atom is present in particular. Additionally, the chemical composition of the silicon-containing carbon-based composite material can be controlled by adjusting the heat-treating atmosphere, flow rate of the inert gas, rate of temperature increase, and heat-treating time, when baking.

[0120] The silicon-containing carbon-based composite material preferably has oxygen atoms and carbon atoms bonded to the silicon atoms, and an amorphous structure. The structure described above can be confirmed by ^{29}Si MAS NMR or an X-ray diffraction analysis. If the silicon-containing carbon-based composite material is crystallized, the charge and discharge cycle characteristics and the initial charging and discharging efficiency may decline.

[0121] The surface of the silicon-containing carbon-based composite material of the present invention may be further subjected to a surface coating treatment by metal or carbon.

[0122] The method of coating the surface of the silicon-containing carbon-based composite material with carbon can be selected as desired. For example, a carbon layer derived from a vapor deposition carbon source (D1) may be thermal chemical vapor deposited on the surface of the silicon-containing carbon-based composite material in a non-oxidation atmosphere at a temperature of 800°C or higher. Additionally, a silicon-containing carbon-based composite material covered with a carbon phase derived from an organic material to be carbonized by heating can be obtained by mixing an organic material carbonized by heating (D2) and the silicon-containing carbon-based composite material, and then baking the obtained mixture.

[0123] The apparatus used for the thermal chemical vapor deposition is not particularly limited provided that it has means for heating to not less than 800°C in a non-oxidation atmosphere, and may be appropriately selected depending on the purpose thereof. Apparatuses using continuous methods and/or batch methods can be used, and specific examples thereof include fluidized bed-furnaces, revolving furnaces, vertical moving bed furnaces, tunnel furnaces, batch furnaces, batch-type rotary kilns, and continuous rotary kilns.

[0124] Specific examples of the vapor deposition carbon source (D1) used in the thermal chemical vapor deposition include methane, ethane, ethylene, acetylene, propane, butane, butene, pentane, isobutane, hexane, and similar aliphatic hydrocarbons or mixtures thereof; benzene, divinylbenzene, monovinylbenzene, ethylvinylbenzene, toluene, xylene, styrene, ethylbenzene, diphenylmethane, naphthalene, phenol, cresol, nitrobenzene, chlorobenzene, indene, coumarone, pyridine, anthracene, phenanthrene, and similar aromatic hydrocarbons; gas light oil, creosote oil, anthracene oil, or cracked naphtha tar oil obtained in a tar distillation process; exhaust gas produced in the baking process; and mixtures thereof. Generally, methane or acetylene is used.

[0125] The non-oxidation atmosphere can be formed by introducing the vapor deposition carbon source gas or flash gas thereof; argon gas, helium gas, hydrogen gas, nitrogen gas, or similar non-oxidizing gases; or a gas mixture thereof into the thermal chemical vapor deposition apparatus.

[0126] Baking may be carried out in the same way when mixing the organic material to be carbonized by heating (D2) and the silicon-containing carbon-based composite material and then baking to obtain a silicon-containing carbon-based composite material coated with a carbon phase derived from the organic material carbonized by heating. Specific examples of the organic material to be carbonized by heating (D2) include paraffin that is in a liquid or a wax-like state at room temperature; polyethylene, polypropylene, polystyrene, polymethyl methacrylate, urethane resins, AS resins, ABS resins, polyvinyl chloride, polyacetal, aromatic polycarbonate resins, aromatic polyester resins, coal tar, phenolic resins, epoxy resins, urea resins, melamine resins, fluoro resins, imide resins, furan resins, and mixtures thereof. Among these, aromatic polycarbonate resins, aromatic polyester resins, coal tar, phenolic resins, fluoro resins, imide resin, furan resins, and similar high molecular aromatic compounds and melamine resins are preferable. This is because forming of a graphene structure is facilitated due to the excellent

efficiency when carbonizing by heating.

[0127] When coating the surface of the silicon-containing carbon-based composite material with carbon, an amount of the carbon applied is preferably from 0.5 to 50 mass (weight)%, more preferably from 1 to 30 mass (weight)%, and even more preferably from 1 to 20 mass (weight)% of the mass (weight) of the silicon-containing carbon-based composite material. When the amount is within this range, even when using the silicon-containing carbon-based composite material alone as the electrode-active material, the silicon-containing carbon-based composite material will have suitable conductivity, and declines in the charging and discharging capacity of the electrode can be suppressed.

[0128] The method of coating the surface of the silicon-containing carbon-based composite material with metal can be selected as desired. For example, a metal coating of gold, silver, copper, iron, zinc, platinum, aluminum, cobalt, nickel, titanium, palladium, stainless steel, and the like can be formed on the surface of the silicon-containing carbon-based composite material by vacuum deposition, sputtering, electroplating, or electroless plating. Of these, nickel and copper are preferable as a surface coating metals.

[0129] 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.

[0130] The electrode-active material comprising the 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 sodium ion 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 sodium or sodium-ion secondary batteries.

[0131] 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 30 to 500 μm and preferably about 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 10 to 300 μm and preferably about 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.

[0132] 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.

[0133] 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.

[0134] 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.

[0135] 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.

[0136] 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.

[0137] Graphite or a similar electrode-active material may be compounded in the electrode of the present invention as another optional additive.

[0138] The sodium or sodium-ion secondary battery of the present invention is characterized by comprising the electrode described above. The sodium-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 sodium, an electrolyte solution, a separator, a current collector, a gasket, a sealing plate, a case, and the like. The sodium 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 sodium, an electrolyte solution, a separator, a current collector, a gasket, a sealing plate, a case, and the like.

[0139] Preferable forms (sodium or sodium-ion secondary batteries) of the battery of the present invention are illustrated in detail in FIGS. 1 and 2.

[0140] FIG. 1 is a schematic breakdown cross-sectional view of a sodium-ion secondary battery (button battery) that is an example of the battery of the present invention.

[0141] The sodium-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.

[0142] 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 sodium-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.

[0143] With the sodium-ion secondary battery illustrated in FIG. 1, the gasket 2 is fitted on a wall face of the case 1; and 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.

[0144] The positive electrode 8 in the sodium-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 positive electrode-active materials include $NaMn_2O_4$, $NaNiO_2$, $NaCoO_2$, $NaFeO_2$, $NaNi_{0.5}Mn_{0.5}O_2$, $NaCrO_2$ 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.

[0145] FIG. 2 is a breakdown cross-sectional view of a sodium secondary battery (button battery) that is an example of the battery of the present invention, fabricated according to the Practical Examples.

[0146] The sodium 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 sodium, 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.

[0147] 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 sodium-ion 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.

[0148] With the sodium secondary battery illustrated in FIG. 2, the gasket 2 is fitted on a wall face of the case 1; and 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 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.

[0149] The electrolyte solutions included in the sodium or sodium-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 sodium or sodium-ion secondary battery can be manufactured by using a solution in which an electrolyte is dissolved in an organic solvent as the electrolyte solution. Examples of electrolyte include $NaClO_4$,

$NaPF_6$, $NaBF_4$, CF_3SO_3Na, $NaAsF_6$, $NaB(C_6H_5)_4$, CH_3SO_3Na, CF_3SO_3Na, $NaN(SO_2CF_3)_2$, $NaN(SO_2C_2F_5)_2$, $NaC(SO_2CF_3)_3$, $NaN(SO_3CF_3)_2$ and the like. 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, 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 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.

[0150] The separators 7 in the sodium or sodium-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.

[0151] The sodium and sodium-ion secondary battery 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.

Industrial Applicability

[0152] The silicon-containing carbon-based composite material of the present invention is suitable for an electrode-active material and electrodes for sodium or sodium-ion secondary batteries with stable charge and discharge properties that have high reversible capacity. Additionally, the silicon-containing carbon-based composite material of the present invention uses inexpensive raw materials and can be manufactured via a simple manufacturing process. Moreover, the electrode-active material and the electrode of the present invention can impart high reversible capacity, and stable charge and discharge cycle characteristics to a battery. As a result, the sodium or sodium-ion secondary battery of the present invention can have high reversible capacity, stable charge and discharge cycle characteristics, and high initial charge and discharge efficiency.

EXAMPLES

[0153] Hereinafter, the present invention will be described in detail based on Practical Examples and Comparative Examples. However, the present invention is not limited to these Practical Examples. In the Practical Examples and Comparative Examples, elemental analyses and evaluations of the battery characteristics were carried out as described below.

[0154] Elemental analyses

C, H, and N analyses: Calculated from the sum of amounts of each element detected via an oxygen transfer combustion method, a TCD detection method and a high frequency combustion method, and an infra-red absorption detection method.

Device: NCH-21 (manufactured by Sumika Chemical Analysis Service, Ltd.) and

CS-LS600 (manufactured by LECO Japan Corporation)
O analysis: High-temperature carbon reaction, NDIR detection method
Device: EMGA-2800 (manufactured by Horiba, Ltd.)
Si analysis: ICP detection was performed after breaking down the sample by carbonizing, alkali melting, and acidic dissolving.
Device: iCAP6500 DuoView (manufactured by Thermo Fisher Scientific K.K.)

[0155] Battery characteristics
Sodium insertion and extraction capacities of the silicon-containing carbon-based composite material of the present invention were measured as described below. The measuring of the sodium insertion and extraction capacities was performed using a constant current withan HJ1010m SM8A (manufactured by Hokuto Denko Corporation). At the first cycle, the theoretical capacity with respect to the weight of the silicon-containing carbon-based composite material was 700 mAh, and current value was adjusted to be 70 mA with respect to the weight of the silicon-containing carbon-based composite material. The capacity when the battery voltage reached 0.005 V, and the current value was 1/10 was considered to be the sodium insertion capacity. The capacity until battery voltage reached 1.5 V was considered to be the sodium extraction capacity. When switching between the sodium insertion and extraction, circuits were left in an open state for 30 minutes. Note, for cycle characteristics, the capacity obtained in the first cycle was considered to be the theoretical capacity. For the second and subsequent cycles, measurements using the same conditions as the first cycle were performed at a current value corresponding to 0.1 C. The sodium extraction capacity of the third cycle was considered to be the reversible capacity, and the capacity maintenance ratio after the cycle test was expressed as a ratio of the sodium extraction capacity after the cycle test to said sodium extraction capacity.

[0156] Practical Example 1
Preparation of the silicon-containing cured product
A crosslinkable composition was prepared by mixing 775 g of DVB570 (manufactured by Nippon Steel Chemical Co., Ltd.; Main components: divinylbenzene 57.0 mass (weight)% and vinyl ethylbenzene 38.9% mass (weight)%; proportion of divinylbenzene included in the main components: about 60 mass (weight)%); 531 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 about one mole of the silicon-bonded hydrogen atoms in the copolymer is included per one mole of vinyl groups in the DVB570); and a 1,3-divinyltetramethyl disiloxane platinum complex platinum catalyst (included in an amount so that 10 ppm of metallic platinum is included). Thereafter, a cured product was prepared by curing the obtained composition in nitrogen at a temperature of 120°C.

[0157] Preparation of the silicon-containing carbon-based composite material
1,200 g of the cured product were placed in an SSA-S grade alumina crucible and the crucible was set in a degreasing oven. Thereafter, a state of reduced pressure was maintained in the degreasing oven for 10 minutes, and then high purity nitrogen (99.99%) was used to return the oven to a normal pressure. This operation was repeated a total of one time. Thereafter, the temperature was raised at a rate of 2°C/minute while supplying high purity nitrogen at a flow rate of 2 L/minute, and the cured product was baked for two hours at a temperature of 600°C. The obtained baked product was pulverized using an air jet pulverizer, and then classified using a high precision air

classifier. 800 g of the baked product obtained after the pulverizing and classifying were placed in a carbon crucible, and the crucible was set in an Oxynon furnace. Thereafter, the baked product was baked for one hour at a temperature of 1,000°C while supplying 4 vol.% hydrogen-containing high purity nitrogen at a flow rate of 10 L/minute and, thereby, a silicon-containing carbon-based composite material was obtained. The chemical composition of the silicon-containing carbon-based composite material is shown in Table 1.

[0158] Fabrication of the electrode

85 mass (weight)% of the silicon-containing carbon-based composite material obtained above and 5 mass (weight)% of carbon black were mixed for 15 minutes. Thereafter, a 5 mass (weight)% polyvinylidene fluoride-containing N-methyl-2-pyrrolidone solution was added in an amount such that the polyvinylidene fluoride was 10 mass (weight)% of the solid content. Furthermore, an appropriate amount of N-methyl-2-pyrrolidone was added and the mixture was stirred. Thereby, a slurry-like mixture was obtained. Then, the slurry-like mixture was coated on a copper foil roll. The electrode obtained as a result was stored for 12 hours or longer in a vacuum at a temperature of 85°C and, thereby, an electrode having a thickness of about 60 μm was fabricated.

[0159] Fabrication and evaluation of the secondary battery

The above electrode was used for a coin-type sodium secondary battery. And, metallic sodium was used for and a counterelectrode; a mixed solvent comprising ethylene carbonate and diethyl carbonate at a volume ratio of 1:1, in which sodium hexafluorophosphate was dissolved at a ratio of 1 mol/L, was used as the electrolyte solution; and a polyethylene nonwoven was used as the separator to fabricate the coin-type sodium secondary battery. The characteristics of the battery of Practical Example 1 are shown in Table 2.

[0160] Practical Example 2

(Preparation of cured product containing silicon and silicon-containing carbon-based composite material)

A crosslinkable composition was prepared by mixing about 3000 g of a diphenyl bis(dimethylvinylsiloxy)silane (vinyl group content: 14.06 mass (weight)%); about 990 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 diphenyl bis(dimethylvinylsiloxy)silane); and a 1,3-divinyltetramethyl disiloxane platinum complex platinum catalyst (included in an amount so that 5 ppm of metallic platinum is included). Next, this composition was cured at 200°C in a nitrogen environment containing 1% hydrogen using a device (Rotary kiln) produced by Takasago Industry Co., Ltd., and then the temperature was increased to 1000°C, and heat-treating was performed for one hour to obtain approximately 2450 g of baked product. The baked product was pulverized using a device (laboratory jet mill) produced by Nippon Pneumatic Mfg. Co., Ltd. to obtain the silicon-containing carbon-based composite material.

[0161] Fabrication of the electrode

An electrode having a thickness of about 40 μm was fabricated in the same way as that of Practical Example 1.

[0162] Fabrication and evaluation of the secondary battery
Measurements were performed the same as in Practical Example 1. The characteristics of the battery of Practical Example 2 are shown in Table 2.

[0163] Practical Example 3
Preparation of the silicon-containing cured product
A crosslinkable composition was prepared by mixing 3.0 g of a diphenyl bis(dimethylvinylsiloxy)silane (vinyl group content: 14.06 mass (weight)%); 0.98 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 diphenyl bis(dimethylvinylsiloxy)silane); and a 1,3-divinyltetramethyl disiloxane platinum complex platinum catalyst (included in an amount so that 10 ppm of metallic platinum is included). Thereafter, a cured product was prepared by curing the obtained composition in nitrogen at a temperature of 150°C.

[0164] Preparation of the silicon-containing carbon-based composite material
3.7 g of the cured product were placed in an SSA-S grade alumina crucible and the crucible was set in a degreasing oven. Thereafter, a state of reduced pressure was maintained in the degreasing oven for 10 minutes, and then high purity nitrogen (99.99%) was used to return the oven to a normal pressure. This operation was repeated a total of one time. Thereafter, the temperature was raised at a rate of 2°C/minute while supplying high purity nitrogen at a flow rate of 2 L/minute, and the cured product was baked for two hours at a temperature of 600°C. The obtained baked product was pulverized using a ball mill and classified using a 300 mesh. 2.2 g of the baked product obtained after the pulverizing and classifying was placed in an SSA-S grade alumina crucible and the crucible was set in a muffle furnace. Thereafter, a state of reduced pressure was maintained in the muffle furnace for 60 minutes, and then high purity nitrogen (99.99%) was used to return the oven to a normal pressure. This operation was repeated a total of one time. Thereafter, the temperature was raised at a rate of 5°C/minute while supplying high purity argon at a flow rate of 100 mL/minute, and the cured product was baked for one hour at a temperature of 1,000°C. Thereby, a silicon-containing carbon-based composite material was obtained. The chemical composition of the silicon-containing carbon-based composite material is shown in Table 1.

[0165] Fabrication of the electrode
An electrode having a thickness of about 40 μm was fabricated in the same way as that of Practical Example 1.

[0166] Fabrication and evaluation of the secondary battery
Measurements were performed the same as in Practical Example 1. The characteristics of the battery of Practical Example 4 are shown in Table 2.

[0167] Practical Example 4
Preparation of the silicon-containing cured product
A crosslinkable composition was prepared by mixing 6.38 g of a diphenyl bis(dimethylhydrogensiloxy)silane (silicon-bonded hydrogen atom content: 0.66 mass (weight)%); 3.63 g of a cyclic methylvinylpolysiloxane (viscosity: 4 mPa·s; silicon-bonded

vinyl group content: 31.4 mass (weight)%; included in an amount such that about one mole of the silicon-bonded vinyl groups in the cyclic is included per one mole of silicon-bonded hydrogen atoms in the diphenyl bis(dimethylhydrogensiloxy)silane); and a 1,3-divinyltetramethyl disiloxane platinum complex platinum catalyst (included in an amount so that 10 ppm of metallic platinum is included). Thereafter, a cured product was prepared by curing the obtained composition in nitrogen at a temperature of 150°C.

[0168] Preparation of the silicon-containing carbon-based composite material
The same procedures as practical example 3 were performed, except that 9.04 g of the cured product was added, and 1.78 g of the baked product was added. The chemical composition of the obtained silicon-containing carbon-based composite material is shown in Table 1.

[0169] Fabrication of the electrode
An electrode having a thickness of about 50 μm was fabricated in the same way as that of Practical Example 1.

[0170] Fabrication and evaluation of the secondary battery
Measurements were performed the same as in Practical Example 1. The characteristics of the battery of Practical Example 5 are shown in Table 2.

[0171] Practical Example 5
Preparation of the silicon-containing cured product
A crosslinkable composition was prepared by mixing 7.83 g of a diphenylsiloxane capped at both molecular terminals with dimethylhydrogensiloxy groups (manufactured by Dow Corning Toray Co., Ltd.; viscosity: 118 mPa·s; silicon-bonded hydrogen atom content: 0.32 mass (weight)%); 2.18 g of a cyclic methylvinylpolysiloxane (viscosity: 4 mPa·s; silicon-bonded vinyl group content: 31.4 mass (weight)%; included in an amount such that about one mole of the silicon-bonded vinyl groups in the cyclic is included per one mole of silicon-bonded hydrogen atoms in the diphenylsiloxane capped at both molecular terminals with dimethylhydrogensiloxy groups); and a 1,3-divinyltetramethyl disiloxane platinum complex platinum catalyst (included in an amount so that 10 ppm of metallic platinum is included). Thereafter, a cured product was prepared by curing the obtained composition in nitrogen at a temperature of 150°C.

[0172] Preparation of the silicon-containing carbon-based composite material
The same procedures as practical example 3 were performed, except that 9.04 g of the cured product was added, and 2.12 g of the baked product was added. The chemical composition of the obtained silicon-containing carbon-based composite material is shown in Table 1.

[0173] Fabrication of the electrode
An electrode having a thickness of about 40 μm was fabricated in the same way as that of Practical Example 1.

[0174] Fabrication and evaluation of the secondary battery
Measurements were performed the same as in Practical Example 1. The characteristics of the battery of Practical Example 6 are shown in Table 2.

[0175] Practical Example 6

Preparation of the silicon-containing cured product
A crosslinkable composition was prepared by mixing 15.49 g of DVB570 (manufactured by Nippon Steel Chemical Co., Ltd.; Main components: divinylbenzene 57.0 mass (weight)% and vinyl ethylbenzene 38.9% mass (weight)%; proportion of divinylbenzene included in the main components: about 60 mass (weight)%); 2.65 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 about 0.25 moles of the silicon-bonded hydrogen atoms in the copolymer is included per one mole of vinyl groups in the DVB570); and a 1,3-divinyltetramethyl disiloxane platinum complex platinum catalyst (included in an amount so that 10 ppm of metallic platinum is included). Thereafter, a cured product was prepared by curing the obtained composition in nitrogen at a temperature of 120°C.

[0176] Preparation of the silicon-containing carbon-based composite material
4 g of the cured product described above was placed in a carbon crucible and said crucible was set in an Oxynon furnace. Thereafter, the cured product was baked for one hour at a temperature of 1,000°C while supplying 4 vol.% hydrogen-containing high purity nitrogen at a flow rate of 10 L/minute. The obtained baked product was pulverized using a ball mill and classified using a 300 mesh. Thereby, a silicon-containing carbon-based composite material was obtained. The chemical composition of the silicon-containing carbon-based composite material is shown in Table 1.

[0177] Fabrication of the electrode
An electrode having a thickness of about 40 μm was fabricated in the same way as that of Practical Example 1.

[0178] Fabrication and evaluation of the secondary battery
Measurements were performed the same as in Practical Example 1. The characteristics of the battery of Practical Example 6 are shown in Table 2.

[0179] Comparative Example 1
Fabrication of the electrode
70 mass (weight)% of crushed semiconductor grade silicon (d50 = 3 μm), 15 mass (weight)% of acetylene black were added, and then 7.5 mass (weight)% of carboxymethyl cellulose (degree of polymerization 500, manufactured by Tokyo Chemical Industry Co., Ltd.), and suitable quantities of polyacrylic acid (molecular weight 25,000, manufactured by Wako Pure Chemical Industries, Ltd.) and pure water were added and mixed for 15 minutes. Thereafter, pure water was added and the mixture was stirred for 15 minutes. Thereby, a slurry-like mixture was obtained. Then, the slurry-like mixture was coated on a copper foil roll. The electrode obtained as a result was stored for 12 hours or longer in a vacuum at a temperature of 85°C and, thereby, an electrode having a thickness of about 30 μm was fabricated.

[0180] Fabrication and evaluation of the secondary battery
Other than setting the constant current for the charging and discharging measurements to 0.1 mA, measurements were performed the same as in Practical Example 1. The characteristics of the battery of Comparative Example 1 are shown in Table 2.

[0181] Comparative Example 2

Preparation of the silicon-containing cured product
A crosslinkable composition was prepared by mixing 10 g of a tetramethyldivinyldisiloxane (manufactured by Dow Corning Toray Co., Ltd.); 6.7 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 about one mole of the silicon-bonded hydrogen atoms in the copolymer is included per one mole of vinyl groups in the tetramethyldivinyldisiloxane); and a 1,3-divinyltetramethyl disiloxane platinum complex platinum catalyst (included in an amount so that 10 ppm of metallic platinum is included). Thereafter, a cured product was prepared by curing the obtained composition in nitrogen at a temperature of 120°C.

[0182] Preparation of the silicon-containing carbon-based composite material
4 g of the cured product described above was placed in a carbon crucible and said crucible was set in an Oxynon furnace. Thereafter, the cured product was baked for one hour at a temperature of 1,000°C while supplying 4 vol.% hydrogen-containing high purity nitrogen at a flow rate of 10 L/minute. The obtained baked product was pulverized using a ball mill and classified using a 300 mesh. Thereby, a silicon-containing carbon-based composite material was obtained. 4 g of the cured product was degreased, pulverized, and classified at 600°C similar to practical example 3, and then 2 g was placed in a carbon container during baking, and the container was placed in an Oxynon furnace. Thereafter, the baked product was baked for one hour at a temperature of 1,100°C while supplying 4 vol.% hydrogen-containing high purity nitrogen at a flow rate of 10 L/minute and, thereby, a silicon-containing carbon-based composite material was obtained. The chemical composition of the silicon-containing carbon-based composite material is shown in Table 1.

[0183] Fabrication of the electrode
An electrode having a thickness of about 30 μm was fabricated in the same way as that of Practical Example 1.

[0184] Fabrication and evaluation of the secondary battery
Measurements were performed the same as in Practical Example 1. The characteristics of the battery of Comparative Example 2 are shown in Table 2.

[0185]

Table 1

	Si	O	C	H
Practical Example 1	1.0	1.1	5.3	0.8
Practical Example 3	1.0	0.9	2.6	0.4
Practical Example 4	1.0	0.9	2.8	0.4
Practical Example 5	1.0	1.0	4.2	0.6
Practical Example 6	1.0	1.7	7.9	1.4
Comparative Example 2	1.0	0.8	1.3	0.3

[0186]

Table 2

	Sodium extraction capacity of 1st cycle (mAh/g)	Sodium extraction capacity of 3rd cycle (mAh/g)	Sodium extraction capacity retention rate after 50 cycles (%)
Practical Example 1	156	174	91
Practical Example 2	78	118	93
Practical Example 3	76	118	102
Practical Example 4	95	134	92
Practical Example 5	128	150	81
Practical Example 6	118	142	92
Comparative Example 1	28	-	-
Comparative Example 2	6.6	-	-

[0187] Reference Numerals

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

CLAIMS

1. A silicon-containing carbon-based composite material capable of electrochemically storing sodium ions, obtained by heat-treating a cured product from a crosslink reaction between (A) a crosslinkable organic compound having at least one aromatic group,
and (B) a silicon-containing compound capable of crosslinking the component (A).

2. The silicon-containing carbon-based composite material of Claim 1, wherein the heat-treating is carried out in an inert gas or in a vacuum at a temperature from 300 to 1,500°C.

3. The silicon-containing carbon-based composite material of Claim 1 or 2, wherein the component (A) comprises at least one crosslinkable group 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.

4. The silicon-containing carbon-based composite material of any of Claims 1 to 3, wherein the component (A) is an organic compound expressed by the general formula:
$(R^1)_xR^2$
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.

5. The silicon-containing carbon-based composite material of any of Claims 1 to 3, wherein the component (A) includes silicon atoms.

6. The silicon-containing carbon-based composite material of Claim 5, wherein the component (A) is a silane, a silazane, a siloxane, a carbosilane, or a mixture thereof.

7. The silicon-containing carbon-based composite material of Claim 6, wherein the siloxane is expressed by the average unit formula:
$(R^3{}_3SiO_{1/2})_a(R^3{}_2SiO_{2/2})_b(R^3SiO_{3/2})_c(SiO_{4/2})_d$
wherein
R^3 each independently represents a crosslinkable group, a monovalent substituted or unsubstituted saturated aliphatic hydrocarbon group or aromatic 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 R^3 in the molecule is an aromatic group; and
at least one R^3 in the molecule is a crosslinkable group.

8. The silicon-containing carbon-based composite material of any of Claims 1 to 7, wherein the component (B) is a silane, a silazane, a siloxane, a carbosilane, or a mixture thereof.

9. The silicon-containing carbon-based composite material of Claim 8, wherein the siloxane is expressed by the average unit formula:
$(R^7{}_3SiO_{1/2})_a(R^7{}_2SiO_{2/2})_b(R^7SiO_{3/2})_c(SiO_{4/2})_d$
wherein
R^7 each independently represents 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; however, 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; and
"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.

10. The silicon-containing carbon-based composite material of any of Claims 1 to 9, wherein the crosslinking is carried out via an addition reaction, a condensation reaction, a ring-opening reaction, or a radical reaction.

11. The silicon-containing carbon-based composite material of any of Claims 1 to 10, 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.

12. The silicon-containing carbon-based composite material of any of Claims 1 to 10, wherein the cured product is obtained by a hydrosilylation reaction of the component (A) having silicon-bonded hydrogen atoms and the component (B) having aliphatic unsaturated groups.

13. The silicon-containing carbon-based composite material of any of Claims 1 to 10, 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.

14. The silicon-containing carbon-based composite material of any of Claims 1 to 10, wherein the cured product is obtained by a radical reaction of the component (A) having aliphatic unsaturated groups, acryl groups, methacryl groups, or silicon-bonded hydrogen atoms and the component (B) having aliphatic unsaturated groups.

15. The silicon-containing carbon-based composite material of any of Claims 1 to 14 that is amorphous.

16. The silicon-containing carbon-based composite material of any of Claims 1 to 15, that is a particulate having an average diameter from 5 nm to 50 μm.

17. An electrode-active material constituted by the silicon-containing carbon-based

composite material described in any of Claims 1 to 16.

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

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 sodium or sodium-ion secondary battery.

FIG. 1

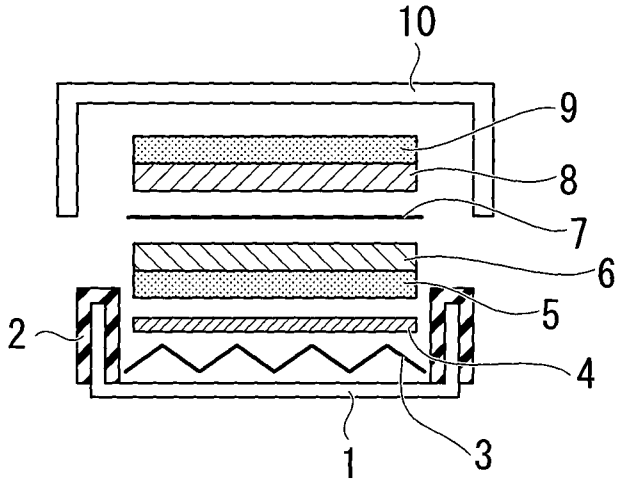
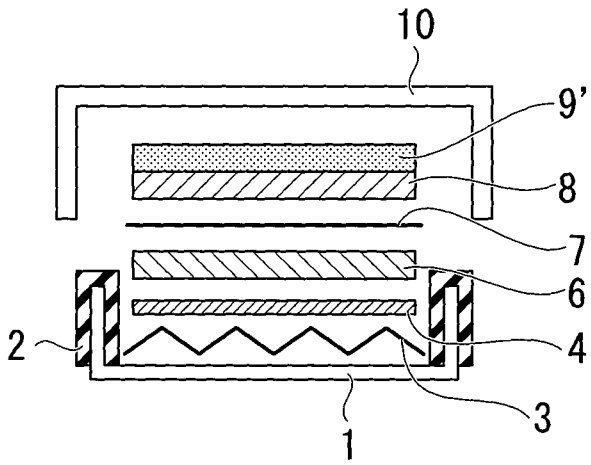


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2013/051686

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/38 H01M4/62 H01M10/054 H01M4/133 H01M4/587
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.
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L	examples 1-10 claims 1-21	1-20

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L	column 1, line 10 - line 16; claims 1-4	1-20

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L	column 1, line 6 - line 13; claims 1-89	1-20

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 May 2013	11/06/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Götz, Heide

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2013/051686

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	THOMAS P ET AL: "Electrochemical insertion of sodium into hard carbons", ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 47, no. 20, 5 August 2002 (2002-08-05), pages 3303-3307, XP004373165, ISSN: 0013-4686, DOI: 10.1016/S0013-4686(02)00250-5 the whole document -----	21

1

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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