

(19) Japan Patent Office (JP) (12) Japanese Unexamined Patent Application Publication (A) (11) Patent Application Publication No.
Japanese Patent Publication No. 2014-89855 (P2014-89855A)
 (43) Publication Date **May 15, 2014 (Heisei 26)**

(51) Int. Cl.	F I	Theme Code (Reference)
HO 1 M 4/48 (2010.01)	HO 1 M 4/48	4 G O 7 2
HO 1 M 4/36 (2006.01)	HO 1 M 4/36	A 4 G 1 4 6
CO 1 B 33/02 (2006.01)	HO 1 M 4/36	E 5 H O 5 O
CO 1 B 33/18 (2006.01)	CO 1 B 33/02	Z
CO 1 B 31/02 (2006.01)	CO 1 B 33/18	Z

Examination Request: Not Yet Total No. of Claims: 7 OL (Total 28 pages) Continued on last page

(21) Application No. Patent application 2012-238477 (P2012-238477)	(71) Applicant 000005810
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	F-term (reference): 4G072 AA01 AA38 BB05 BB20 DD04 GG02 TT30 UU30
	Continued on last page

(54) [Title of Invention] NEGATIVE ELECTRODE ACTIVE MATERIAL FOR NON-AQUEOUS RECHARGEABLE BATTERY AND NON-AQUEOUS RECHARGEABLE BATTERY

(57) [Abstract]

[Problem] To provide a non-aqueous rechargeable battery having high capacity and favorable storage characteristics, and a negative electrode active material used in the non-aqueous rechargeable battery.
 [Resolution Means] The above problem is solved by: a negative electrode active material for a non-aqueous rechargeable battery that includes a material containing Si and O as constituent elements, wherein a median particle diameter $D_{50\%}$ is 6 to 10 μm as determined by a laser diffraction/scattering method, and a full width at half maximum of an Si (220) diffraction peak is 0.6 to 1.0° as determined by an X-ray diffraction method using Cu K α radiation; and a non-aqueous rechargeable battery which uses the negative electrode active material for a non-aqueous rechargeable battery and a graphitic carbon material as negative electrode active materials.

[Selected Drawing] None

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[Scope of Patent Claims]

[Claim 1]

A negative electrode active material for a non-aqueous rechargeable battery comprising a material containing Si and O as constituent elements, wherein: median particle diameter D_{50} is 6 to 10 μm as determined by a laser diffraction/scattering method, and a full width at half maximum of an Si (220) diffraction peak is 0.6 to 1.0° as determined by an X-ray diffraction method using Cu K α radiation.

[Claim 2]

The negative electrode active material for a non-aqueous secondary battery according to claim 1, wherein the $D_{10\%}$ and $D_{90\%}$ determined by laser diffraction scattering are $D_{10\%}$: 4 μm or less and $D_{90\%}$: 14 μm or less.

[Claim 3]

The negative electrode active material for a non-aqueous rechargeable battery according to claim 1 or 2, wherein: the material containing Si and O as constituent elements is expressed by a general composition formula SiO_x (where $0.5 \leq x \leq 1.5$).

[Claim 4]

The negative electrode active material for a non-aqueous rechargeable battery according to claim 3, wherein: when measurement is carried out by an X-ray diffraction method using Cu K α radiation, the ratio I_a/I_b is 2.7 to 3.9, where I_a is an intensity of a diffraction peak derived from Si observed at a position of $2\theta=28.4^\circ$, and I_b is an intensity of a diffraction peak derived from SiO_2 observed at a position near $2\theta=21.2^\circ$.

[Claim 5]

The negative electrode active material for a non-aqueous rechargeable battery according to any of claims 1 to 4, wherein a composite thereof is formed using a carbon material.

[Claim 6]

The negative electrode active material for a non-aqueous rechargeable battery according to claim 5, wherein: in the Raman spectrum obtained by Raman spectroscopy analysis using a measurement laser having a wavelength of 532 nm, the ratio I_{510}/I_{1343} is 0.25 or less, where I_{510} is an intensity of a peak derived from Si at 510 cm^{-1} and I_{1343} is an intensity of a peak derived from carbon at 1343 cm^{-1} .

[Claim 7]

A non-aqueous rechargeable battery comprising: a positive electrode containing a positive electrode active material, a negative electrode containing a negative electrode active material, a non-aqueous electrolyte, and a separator, wherein:

the negative electrode active material for a non-aqueous rechargeable battery according to any of claims 1 to 6 and a graphite carbon material is used for the negative electrode active material.

[Detailed Description of Invention]

[Technical Field]

[0001]

The present invention relates to a non-aqueous rechargeable battery having high capacity and favorable storage characteristics, and to a negative electrode active material for forming the non-aqueous rechargeable battery.

[Background Art]

[0002]

Non-aqueous rechargeable batteries, including lithium-ion rechargeable batteries, are widely adopted as power sources for various portable devices due to their high voltage and high capacity. Furthermore, in recent years, applications thereof have expanded to include power tools such as electric tools, as well as medium- and large-scale applications such as electric vehicles and electric bicycles.

[0003]

In particular, batteries used in mobile phones and game consoles and the like, which are becoming increasingly miniaturized and multi-functional, require a further increased capacity, and as means to achieve this, research and development of electrode active materials which exhibit a high charge-discharge capacity are progressing. In particular, as an active material for a negative electrode, materials which may absorb and release more lithium (ions), such as silicon (Si) and tin (Sn), are attracting attention as alternatives to carbon materials such as graphite, which are adopted in conventional lithium-ion rechargeable batteries. In particular, SiO_x , which has a structure in which ultrafine silicon particles are dispersed in SiO_2 , has been reported to also possess excellent loading characteristics (see Patent Documents 1 and 2).

[0004]

However, it is known that because the SiO_x exhibits significant volume expansion and shrinkage during charge-discharge reactions, thus particles are pulverized during each charge-discharge cycle of a battery, which leads to problems such as the Si deposited on the surface reacting with the non-aqueous electrolyte solvent, causing irreversible capacity increase, and this reaction generating gas within the battery, causing swelling of the battery casing.

[0005]

In light of these circumstances, art has been proposed to improve the charge-discharge cycle characteristics of batteries and suppress swelling of the battery casing due to gas generation, by limiting the utilization rate of SiO_x to suppress volume expansion and shrinkage associated with charge-discharge reactions, or by using a non-aqueous electrolyte to which halogen-substituted cyclic carbonates (for example, 4-fluoro-1,3-dioxolan-2-one or the like) have been added (see Patent Document 3).

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[0006]

Furthermore, in non-aqueous rechargeable battery which uses SiO_x as a negative electrode, improvement of storage characteristics is also one problem thereof. Patent Document 4 discloses art that achieves this improvement by using a composite in which SiO_x used as a core thereof and a surface thereof is covered using carbon, and by defining a degree of carbon cover in the composite and a crystalline state of Si in SiO_x .

[Prior Art Documents]

[Patent Documents]

[0007]

[Patent Document 1] JP 2004-047404 A

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[Patent Document 2] JP 2005-259697 A

[Patent Document 3] JP 2008-210618 A

[Patent Document 4] International Publication No. 2012/036127

[Summary of Invention]

[Problem to Be Solved by Invention]

[0008]

The inventors of the present invention have conducted further studies on the art taught in Patent Document 4 in order to further improve storage characteristics of a non-aqueous rechargeable battery. In other words, an object of the present invention is to provide a non-aqueous rechargeable battery having high capacity and favorable storage characteristics, and a negative electrode active material for forming the non-aqueous rechargeable battery.

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[Means for Solving Problem]

[0009]

The negative electrode active material for a non-aqueous rechargeable battery of the present invention contains a material containing Si and O as constituent elements, a median particle diameter $D_{50\%}$ of 6 to 10 μm as determined by a laser diffraction/scattering method, and a full width at half maximum of an Si (220) diffraction peak of 0.6 to 1.0° as determined by an X-ray diffraction method using Cu $K\alpha$ radiation.

[0010]

Furthermore, the non-aqueous rechargeable battery of the present invention is a non-aqueous rechargeable battery having a positive electrode containing a positive electrode active material, a negative electrode containing a negative electrode active material, a non-aqueous electrolyte, and a separator, wherein: the negative electrode active material for a non-aqueous rechargeable battery of the present invention and a graphitic carbon material is used for the negative electrode active material.

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[Effect of Invention]

[0011]

According to the present invention, it is possible to provide a non-aqueous rechargeable battery having high capacity and favorable storage characteristics, and a negative electrode active material for forming the non-aqueous rechargeable battery.

[Brief Description of Drawings]

[0012]

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[FIG. 1] A schematic diagram illustrating an example of the non-aqueous rechargeable battery of the present invention, where (a) is a plan view thereof and (b) is a partial longitudinal cross-sectional view thereof.

[FIG. 2] A perspective view of the non-aqueous rechargeable battery illustrated in FIG. 1.

[Embodiments of Invention]

[0013]

As described above, the present inventors have conducted further studies of on the art taught in Patent Document 4 in order to further improve the storage characteristics of a non-aqueous rechargeable battery. As a result, the authors discovered that when a material containing Si and O as constituent elements is used as a negative electrode active material for a non-aqueous rechargeable battery, when a full width at half maximum of an Si (220) diffraction peak as determined by an X-ray diffraction method is within a defined range, and when a median particle diameter of the material takes a defined value, the storage characteristics of the non-aqueous rechargeable battery may be greatly improved, thus completing the present invention. The present invention will be described in detail below.

[0014]

<Negative electrode active material for non-aqueous secondary batteries>

The negative electrode active material for a non-aqueous rechargeable battery of the present invention contains a material that contains Si and O as constituent elements. When the negative electrode active material contains such a material, it is possible to provide a high capacity non-aqueous rechargeable battery.

[0015]

Furthermore, the negative electrode active material for a non-aqueous rechargeable battery of the present invention has a median particle diameter $D_{50\%}$ of 6 to 10 μm as determined by a laser diffraction/scattering method, and a full width at half maximum of an Si (220) diffraction peak of 0.6 to 1.0° as determined by an X-ray diffraction method using Cu K α radiation. In the negative electrode active material for a non-aqueous rechargeable battery containing Si and O as constituent elements, by setting the median particle diameter to $D_{50\%}$ to the above value and the full width at half maximum of an Si (220) diffraction peak to the above value, it becomes possible to maintain high capacity, suppress capacity degradation when stored in a charged state, and ensure high storage characteristics in a non-aqueous rechargeable battery using this material.

[0016]

In other words, if the median particle diameter $D_{50\%}$ of the negative electrode active material for non-aqueous rechargeable battery is too small, capacity degradation is likely to occur when the non-aqueous rechargeable battery using this material is stored in a charged state. Furthermore, if the median particle diameter $D_{50\%}$ of the negative electrode active material for a non-aqueous rechargeable battery is too large, a vicinity of a center of negative electrode active material particles becomes less likely to participate in a charge-discharge reaction, thus the capacity of the non-aqueous rechargeable battery using this material is reduced.

[0017]

Furthermore, if the full width at half maximum of the Si (220) diffraction peak in the negative electrode active material for a non-aqueous rechargeable battery is too small, the capacity of the non-aqueous rechargeable battery using this material is reduced. Furthermore, if the full width at half maximum of the Si (220) diffraction peak in the negative electrode active material for a non-aqueous rechargeable battery is too large, capacity degradation is likely to occur when the non-aqueous rechargeable battery using this material is stored in a charged state.

[0018]

Note that for a main Si-derived peak detected during measurement by X-ray diffraction, in addition to the (220) diffraction peak, a (111) diffraction peak is also known; however, the (220) diffraction peak does not receive an effect from, for example, a broad peak derived from SiO₂ when compared to the (111) diffraction peak, and therefore the full width at half maximum of the (220) diffraction peak may be determined more easily. Therefore, in the present invention, the negative electrode active material for a non-aqueous rechargeable battery is set to have a full width at half maximum of the Si (220) diffraction peak at a defined value.

[0019]

In the present specification, the median particle diameter $D_{50\%}$ of the negative electrode active material for a non-aqueous rechargeable battery is a value determined by laser diffraction/scattering as described above, but more specifically, it is a particle size at 50% of a cumulative volume-based fraction measured by dispersing the negative electrode active material in a non-dissolving medium using a laser diffraction particle size analyzer (for example, "LA-920" manufactured by Horiba).

[0020]

Furthermore, from the viewpoint of more favorable storage characteristics of the non-aqueous rechargeable battery using the negative electrode active material for a non-aqueous rechargeable battery of the present invention, it is preferable that $D_{10\%}$ (particle size at 10% of the cumulative volume-based fraction) of the negative electrode active material for a non-aqueous rechargeable battery, which is determined by the same method as the median particle diameter $D_{50\%}$, is 4 μm or more.

[0021]

Moreover, from the viewpoint of suppressing damage to a separator by the negative electrode active

material and more favorable reliability of the non-aqueous rechargeable battery using the negative electrode active material for a non-aqueous rechargeable battery of the present invention, it is preferable that $D_{90\%}$ (particle size at 90% of the cumulative volume-based fraction) of the negative electrode active material for a non-aqueous rechargeable battery, which is determined by the same method as the median particle diameter $D_{50\%}$, is 14 μm or less.

[0022]

A material containing Si and O as constituent elements may be not only an Si oxide, but also a composite oxide of Si and another metal, and may also contain microcrystalline or amorphous phases of Si or another metal.

[0023]

Among materials containing Si and O as constituent elements, a material having a structure in which a fine Si phase is dispersed in an amorphous SiO_2 matrix is particularly preferable. This material is represented by the general composition formula SiO_x (where $0.5 \leq x \leq 1.5$). For example, in a structure where Si is dispersed in an amorphous SiO_2 matrix, if the molar ratio of SiO_2 to Si is 1:1, the empirical formula is represented as SiO .

[0024]

SiO_x is preferably a composite material formed by combining with a carbon material; for example, it is desirable that the surface of SiO_x is coated with a carbon material. Because SiO_x has poor conductivity, when using it as a negative electrode active material, a conductive additive such as a carbon material is necessary to ensure good battery characteristics. When a composite material is formed by compositing SiO_x and carbon material, a conductive network in the negative electrode can be favorably formed, thereby improving load characteristics of the battery, compared to using, for example, a material obtained by simply mixing SiO_x and a conductive additive such as carbon material.

[0025]

Examples of composites of SiO_x and carbon materials include, as mentioned above, those in which the surface of SiO_x is coated with a carbon material, as well as granulated bodies of SiO_x and carbon materials.

[0026]

Furthermore, by further compositing the above composite material, of which the surface of the SiO_x is covered using carbon material, with a conductive material (such as carbon material), it becomes possible to form an even more favorable conductive network in the negative electrode, thus making it possible to realize a non-aqueous rechargeable battery having higher capacity and excellent battery characteristics (for example, charge-discharge cycle characteristics). Examples of composites of SiO_x covered using carbon material include granules in which further granulating a mixture of carbon material and SiO_x covered with carbon material, and the like.

[0027]

Furthermore, as the SiO_x whose surface is covered using carbon material, in which a surface of a composite of SiO_x and carbon material having a lower specific resistance value than the SiO_x (for example, granules) is further covered with carbon material, may also be preferably used. When SiO_x and carbon material are dispersed within the granules, a more favorable conductive network can be formed, thus battery characteristics such as heavy load discharge characteristics can be further improved in a non-aqueous rechargeable battery having a negative electrode containing SiO_x as the negative electrode active material.

[0028]

Carbon materials that may be used to form an SiO_x composite preferably include, for example, low-crystallinity carbon, carbon nanotubes, vapor-phase growth carbon fibers, and the like.

[0029]

The carbon material is preferably at least one type of material selected from the group consisting of fibrous or coiled carbon material, carbon black (including acetylene black and Ketjen black), artificial graphite, graphitizable carbon, and non-graphitizable carbon. Fibrous or coiled carbon materials are preferable because they easily form a conductive network and have a large surface area. Carbon black (including acetylene black and Ketjen black), graphitizable carbon, and non-graphitizable carbon are preferable because they have high electrical conductivity and high liquid retention, and furthermore, they have a property of easily maintaining contact to SiO_x particles even when these particles expand and shrink.

[0030]

When the non-aqueous rechargeable battery is formed using the negative electrode active material for a non-aqueous rechargeable battery of the present invention, a graphitic carbon material is also used as the negative electrode active material, however this graphitic carbon material may also be used as carbon

material for a composite of SiO_x and a carbon material. Graphitic carbon material also has high electrical conductivity and high liquid retention similar to carbon black and the like, and furthermore, this material has a property of easily maintaining contact to SiO_x particles even when these particles expand and shrink, making this material preferable for use in SiO_x composite formation.

[0031]

Among the carbon materials exemplified above, a fibrous carbon material is particularly preferable for one used when the SiO_x composite is composed of granules. Fibrous carbon material is suitable because of the thin, thread shape and high flexibility thereof, allowing this material to follow the expansion and shrinkage of SiO_x during battery charge-discharge; additionally, the high bulk density of this material allows formation of many contact points to the SiO_x particles. Examples of fibrous carbon include polyacrylonitrile (PAN) carbon fibers, pitch carbon fibers, vapor-phase growth carbon fibers, carbon nanotubes and the like, and any of these may be used.

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[0032]

Note that the fibrous carbon material may also be formed, for example, on the surface of SiO_x particles by a vapor-phase method.

[0033]

Whereas the specific resistance value of SiO_x is typically 10^3 to 10^7 $\text{k}\Omega\text{cm}$, the specific resistance value of the carbon material exemplified above is usually 10^{-5} to 10 $\text{k}\Omega\text{cm}$.

[0034]

Furthermore, the composite of SiO_x and carbon material may further include a material layer (a material layer including non-graphitizable carbon) that covers the carbon material covering layer on the particle surface.

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[0035]

In the composite of SiO_x and carbon material, from the viewpoint of favorably exhibiting the effect of compositing with the carbon material, the ratio between SiO_x and carbon material is preferably such that the carbon material is 5 parts by mass or more, and more preferably 10 parts by mass or more, relative to 100 parts by mass of SiO_x . Furthermore, in the composite, when the proportion of the carbon material composited with SiO_x is too large, this leads to a decrease in the amount of SiO_x in the negative electrode mixture layer, and there is a risk that the effect of increasing capacity becomes small. Therefore, the carbon material is preferably 50 parts by mass or less, and more preferably 40 parts by mass or less, relative to 100 parts by mass of SiO_x .

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[0036]

SiO_x can be obtained, for example, by the following method.

[0037]

SiO_x may be obtained by a method such as heating a mixture of Si and SiO_2 and cooling and precipitating the generated silicon oxide gas. Furthermore, by pulverizing and classifying the obtained SiO_x , the $D_{50\%}$, $D_{10\%}$, and $D_{90\%}$ can be set to the above values. Note that classification may be performed after the CVD treatment described below.

[0038]

By adjusting the temperature and time during heat treatment of SiO_x in an inert gas atmosphere, the full width at half maximum of the Si (220) diffraction peak can be controlled to the above value. The heat treatment temperature is preferably 900 to 1400°C , and the heat treatment time is preferably 0.1 to 10 hours.

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[0039]

With respect to the SiO_x after the heat treatment, when measurement is performed by an X-ray diffraction method using Cu $K\alpha$ radiation, it is preferable that the ratio I_a/I_b between the intensity I_a of the diffraction peak derived from Si observed at a position of $2\theta = 28.4^\circ$ and the intensity I_b of the diffraction peak derived from SiO_2 observed at a position near $2\theta = 21.2^\circ$ be 2.7 to 3.9. If SiO_x satisfies the above value for I_a/I_b , it can be understood that, along with particle growth of Si, SiO_2 molecules become more favorably arranged. That is, if SiO_x satisfies the above value for I_a/I_b , it has been favorably heat-treated, and the effect of improving storage characteristics of a non-aqueous rechargeable battery using the same becomes more favorable.

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[0040]

Note that, in the present specification, the intensity I_a of the diffraction peak derived from Si observed at a position of $2\theta = 28.4^\circ$ means the peak height at the position where the peak top of the same diffraction peak is present, and the intensity I_b of the diffraction peak derived from SiO_2 observed at a position near $2\theta = 21.2^\circ$ means the peak height at the position where the peak top of the same diffraction peak is present.

[0041]

Furthermore, the composite of the above SiO_x and carbon material can be obtained, for example, by the following method.

[0042]

First, a method for production in which SiO_x is composited will be described. A dispersion in which SiO_x is dispersed in a dispersion medium is prepared, and the dispersion is sprayed and dried to produce composite particles including a plurality of particles. Ethanol or the like, for example, may be used as the dispersion medium. Usually, it is suitable for the spraying of the dispersion to be carried out in an atmosphere of 50 to 300°C . In addition to the above method, similar composite particles can also be produced by a granulation method via a mechanical method such as one using a vibration-type or planetary-type ball mill or a rod mill.

[0043]

Note that, in a case of producing granules of SiO_x and a carbon material having a smaller specific resistance value than SiO_x , the carbon material is added into a dispersion in which SiO_x is dispersed in a dispersion medium, and composite particles (granules) may be formed using this dispersion, by a method similar to that used in the case of compositing SiO_x . Furthermore, granules of SiO_x and carbon material can also be produced by a granulation method via a mechanical method similar to that described above.

[0044]

Next, in a case where a composite is formed by covering the surface of SiO_x particles (SiO_x composite particles, or granules of SiO_x and carbon material) with carbon material, for example, the SiO_x particles and a hydrocarbon-based gas are heated in a gas phase, and carbon generated by thermal decomposition of the hydrocarbon-based gas is deposited on the surface of the particles. In this manner, according to a vapor-phase growth (CVD) method, the hydrocarbon-based gas is diffused throughout the composite particles, and since a thin and uniform film (carbon material covering layer) including a carbon material having conductivity can be formed on the surface of the particles and in pores on the surface, conductivity can be imparted to the SiO_x particles with good uniformity by a small amount of carbon material.

[0045]

In the production of SiO_x covered with carbon material, the treatment temperature (ambient temperature) of the vapor-phase growth (CVD) method varies depending on the type of hydrocarbon-based gas, but is usually suitably 600 to 1200°C , within which is preferably 700°C or higher, and more preferably 800°C or higher. This is because a higher treatment temperature results in less residual impurities and enables formation of a covering layer that includes carbon having high conductivity.

[0046]

Furthermore, in controlling the full width at half maximum of the Si (220) diffraction peak in SiO_x to the above value, instead of the above heat treatment, heat treatment in this CVD method may also be used, and in this case, the number of process steps can be reduced, which is more preferable. When controlling the full width at half maximum of the Si (220) diffraction peak to the above value by heat treatment in the CVD method, the treatment temperature in the CVD method is preferably 900°C or higher.

[0047]

As a liquid source of the hydrocarbon-based gas, toluene, benzene, xylene, mesitylene, and the like may be used, but toluene, which is easy to handle, is particularly preferable. The hydrocarbon-based gas may be obtained by vaporizing these (for example, by bubbling with nitrogen gas). Additionally, methane gas, acetylene gas, and the like may also be used.

[0048]

Furthermore, after the surface of the SiO_x particles (SiO_x composite particles, or granules of SiO_x and carbon material) is covered with carbon material by the vapor-phase growth (CVD) method, at least one type of organic compound selected from the group consisting of petroleum-based pitch, coal-based pitch,

thermosetting resins, and condensates of naphthalenesulfonate and aldehydes is attached to a covering layer containing carbon material, after which the particles to which the organic compound is attached may be fired. [0049]

Specifically, a dispersion is prepared in which SiO_x particles covered with carbon material (SiO_x composite particles, or granules of SiO_x and carbon material) and the organic compound are dispersed in a dispersion medium, and this dispersion is sprayed and dried to form particles covered with the organic compound, and the particles covered with the organic compound are fired. [0050]

As the pitch, isotropic pitch may be used, and as the thermosetting resin, phenol resin, furan resin, furfural resin, and the like may be used. As the condensate of naphthalenesulfonate and aldehydes, a naphthalenesulfonate-formaldehyde condensate may be used. [0051]

As the dispersion medium for dispersing the SiO_x particles covered with carbon material and the organic compound, for example, water, alcohols (such as ethanol), and the like may be used. Usually, it is suitable for the spraying of the dispersion to be carried out in an atmosphere of 50 to 300°C. The firing temperature is usually suitably 600 to 1200°C, within which 700°C or higher is preferable, and 800°C or higher is more preferable. This is because a higher treatment temperature results in less residual impurities and enables formation of a covering layer that includes a high-quality carbon material having high conductivity. However, the treatment temperature needs to be equal to or lower than the melting point of SiO_x . [0052]

In a Raman spectrum obtained when Raman spectroscopy analysis is performed using a measurement laser having a wavelength of 532 nm for a composite of SiO_x and carbon material (particularly SiO_x covered with carbon material), it is preferable that the ratio I_{510}/I_{1343} between the intensity I_{510} of the peak at 510 cm^{-1} derived from Si and the intensity I_{1343} of the peak at 1343 cm^{-1} derived from carbon be 0.25 or less. [0053]

More specifically, I_{510}/I_{1343} is obtained by performing mapping measurement of the composite by micro-Raman spectroscopy (range: $80 \times 80 \mu\text{m}$, step: $2 \mu\text{m}$), averaging all spectra within the measurement range, measuring each intensity of the Si peak (near 510 cm^{-1}) and the carbon (C) peak (near 1343 cm^{-1}), and calculating the ratio thereof. [0054]

In the case of a composite of SiO_x and carbon material in which I_{510}/I_{1343} satisfies the above value, since the proportion of portions of the SiO_x particle surface that are not covered with the carbon material (portions where the SiO_x particle surface is exposed) is small, the effect of improving conductivity due to compositing SiO_x with carbon material is more remarkably exhibited. Therefore, during the production of the composite of SiO_x and carbon material, it is desirable to adjust conditions (for example, in the case of the above CVD method, the treatment temperature, treatment time, concentration of the liquid source of the carbon material in the treatment environment, and the like) such that I_{510}/I_{1343} satisfies the above value. [0055]

<Non-aqueous rechargeable battery>

The non-aqueous rechargeable battery of the present invention has a positive electrode containing a positive electrode active material, a negative electrode containing a negative electrode active material, a separator, and a non-aqueous electrolyte. The negative electrode active material may use the negative electrode active material for a non-aqueous rechargeable battery of the present invention and a graphitic carbon material. There are no particular restrictions on other configurations and structures, and various configurations and structures used in conventionally known non-aqueous rechargeable batteries may be applied. [0056]

(Negative electrode)

A negative electrode having a structure in which a negative electrode mixture layer containing a negative electrode active material and a binder or the like is provided on one surface or both surfaces of a current collector, for example, is used as the negative electrode according to the non-aqueous rechargeable battery

of the present invention.

[0057]

As described above, the negative electrode active material is used in combination with the negative electrode active material for a non-aqueous rechargeable battery of the present invention and the graphitic carbon material.

[0058]

The negative electrode active material for a non-aqueous rechargeable battery of the present invention has a higher capacity than carbon materials that are conventionally used as negative electrode active materials for non-aqueous rechargeable batteries. However, since the amount of volume change associated with charge and discharge of the battery is large, in a non-aqueous rechargeable battery using a negative electrode having a negative electrode mixture layer with a high content of the negative electrode active material for a non-aqueous rechargeable battery of the present invention, the negative electrode (negative electrode mixture layer) may undergo significant volume change and deteriorate due to repeated charge and discharge, resulting in a decrease in capacity (that is, a decrease in charge-discharge cycle characteristics). Graphitic carbon materials are widely used as negative electrode active materials for non-aqueous rechargeable batteries, and while they have relatively large capacity, the amount of volume change associated with charge-discharge of the battery is smaller in comparison to that of the negative electrode active material for a non-aqueous rechargeable battery of the present invention. Therefore, by using the negative electrode active material for a non-aqueous rechargeable battery of the present invention in combination with the graphitic carbon material as the negative electrode active material, it is possible to suppress, to the extent possible, a decrease in the effect of improving battery capacity due to a reduction in the amount of use of the negative electrode active material for a non-aqueous rechargeable battery of the present invention, while effectively suppressing deterioration in charge-discharge cycle characteristics of the battery. As a result, it is possible to obtain a non-aqueous rechargeable battery having higher capacity and excellent charge-discharge cycle characteristics.

[0059]

Graphitic carbon materials conventionally used as negative electrode active materials for non-aqueous rechargeable batteries are suitably used as the graphitic carbon material. Specifically, examples include natural graphite such as flake graphite; pyrolytic carbons; and artificial graphite obtained by graphitizing graphitizable carbon such as mesophase carbon microbeads (MCMB) and carbon fibers at 2800°C or higher.

[0060]

In the negative electrode according to the non-aqueous rechargeable battery of the present invention, from the viewpoint of favorably ensuring the effect of increasing capacity by using the negative electrode active material for a non-aqueous rechargeable battery of the present invention, the content of the negative electrode active materials is preferably 1% by mass or more, and more preferably 3% by mass or more. Furthermore, from the viewpoint of more effectively avoiding problems due to volume change of the negative electrode active material for a non-aqueous rechargeable battery of the present invention, the content of the negative electrode active material for a non-aqueous rechargeable battery of the present invention in the total negative electrode active materials is preferably 20% by mass or less, and more preferably 15% by mass or less.

[0061]

Specific examples of the binder used in the negative electrode mixture layer include, for example, polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), styrene-butadiene rubber (SBR), and carboxymethyl cellulose (CMC), and the like.

[0062]

Furthermore, a conductive material may be further added to the negative electrode mixture layer as a conductive additive. Such a conductive material is not particularly limited as long as it does not undergo a chemical change within the non-aqueous rechargeable battery. Examples include carbon black (thermal black, furnace black, channel black, Ketjen black, acetylene black, and the like), carbon fibers, metal powders (copper, nickel, aluminum, silver, and the like), metal fibers, and polyphenylene derivatives (those described in JP S59-20971 A), and the like, and one kind or two or more kinds thereof may be used. Among these, carbon black is preferred, and Ketjen black or acetylene black are more preferred.

[0063]

The particle size of the carbon material used as the conductive additive is, for example, a median particle diameter ($D_{50\%}$) measured by the same method as that for the negative electrode active material for a non-aqueous rechargeable battery of the present invention, and is preferably 0.01 μm or more, more preferably 0.02 μm or more, and preferably 10 μm or less, more preferably 5 μm or less.

[0064]

The negative electrode is produced, for example, through a step of preparing a paste-like or slurry-like negative electrode mixture-containing composition in which a negative electrode active material and a

binder, and further a conductive additive as needed, are dispersed in a solvent such as N-methyl-2-pyrrolidone (NMP) or water (the binder may be dissolved in the solvent), coating the composition onto one surface or both surfaces of a current collector, drying, and then performing a pressing treatment as needed. However, the negative electrode is not limited to one produced by the above production method, and may be one produced by another production method.

[0065]

The thickness of the negative electrode mixture layer is preferably 10 to 100 μm per one surface of the current collector. The density of the negative electrode mixture layer is calculated from the mass and thickness of the negative electrode mixture layer per unit area laminated on the current collector, and is preferably 1.0 to 1.9 g/cm^3 . Furthermore, for the composition of the negative electrode mixture layer, for example, the total amount of the negative electrode active material is preferably 80% to 99% by mass, the amount of the binder is preferably 1% to 20% by mass, and when a conductive additive is used, the amount thereof is preferably 1% to 10% by mass.

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[0066]

A copper foil, a nickel foil, a punching metal, a mesh, an expanded metal, or the like may be used as the current collector for the negative electrode, but a copper foil is usually used. In order to obtain a battery with high energy density, when reducing the overall thickness of the negative electrode, the upper limit of the thickness of the negative electrode current collector is preferably 30 μm , and the lower limit is preferably 5 μm in order to ensure mechanical strength.

[0067]

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(Positive electrode)

A positive electrode with a structure having, on one or both surfaces of the current collector, a positive electrode mixture layer including a positive electrode active material, a binder, a conductive additive, or the like, for example, may be used for the positive electrode of the non-aqueous rechargeable battery of the present invention.

[0068]

The positive electrode mixture layer uses a lithium-containing transition metal oxide or the like capable of occluding and releasing lithium (Li) ions. As Li-containing transition metal oxides, those conventionally known and used in non-aqueous rechargeable batteries specifically include Li_yCoO_2 (where $0 \leq y \leq 1.1$), Li_zNiO_2 (where $0 \leq z \leq 1.1$), Li_eMnO_2 (where $0 \leq e \leq 1.1$), $\text{Li}_a\text{Co}_b\text{M}^{1-b}\text{O}_2$ (where M^1 is at least one type of metal element selected from the group consisting of Mg, Mn, Fe, Ni, Cu, Zn, Al, Ti, Ge, and Cr, where $0 \leq a \leq 1.1$ and $0 < b < 1.0$), and $\text{Li}_c\text{Ni}_{1-d}\text{M}^{2-d}\text{O}_2$ (where M^2 is at least one metallic element selected from the group consisting of Mg, Mn, Fe, Co, Cu, Zn, Al, Ti, Ge, and Cr, where $0 \leq c \leq 1.1$ and $0 < d < 1.0$), Li-containing transition metal oxides having a layered structure such as $\text{Li}_f\text{Mn}_g\text{Ni}_h\text{Co}_{1-g-h}\text{O}_2$ (where $0 \leq f \leq 1.1$, $0 < g < 1.0$, and $0 < h < 1.0$), and only one of these may be used, or two or more may be used in combination.

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[0069]

The same binders as those exemplified above for the negative electrode mixture layer may be used as the binder for the positive electrode mixture layer. The same binders as those exemplified above for the negative electrode mixture layer may be used as the binder for the positive electrode mixture layer.

[0070]

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The positive electrode is produced, for example, through a step of preparing a paste-like or slurry-like positive electrode mixture-containing composition in which a positive electrode active material, a binder, and a conductive additive are dispersed in a solvent such as NMP (the binder may be dissolved in the solvent), coating the composition onto one surface or both surfaces of the current collector, drying, and then performing pressing treatment as needed. However, the positive electrode is not limited to one produced by the above production method, and may be one produced by another production method.

[0071]

The thickness of the positive electrode mixture layer is, for example, preferably 10 to 100 μm per one surface of the current collector, and the density of the positive electrode mixture layer is calculated from the mass and thickness of the positive electrode mixture layer per unit area laminated on the current collector, and is preferably 3.0 to 4.5 g/cm^3 . In addition, for the composition of the positive electrode mixture layer,

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for example, the amount of the positive electrode active material is preferably 60% to 95% by mass, the amount of the binder is preferably 1% to 15% by mass, and the amount of the conductive additive is preferably 3% to 20% by mass.

[0072]

For the current collector for the positive electrode, one similar to those conventionally used for positive electrodes of non-aqueous rechargeable batteries may be used, and for example, an aluminum foil having a thickness of 10 to 30 μm is preferable.

[0073]

(Separator)

A separator having sufficient strength and capability of retaining a large amount of non-aqueous electrolyte is preferable as the separator according to the non-aqueous rechargeable battery of the present invention. A microporous membrane made of a polyolefin such as polyethylene (PE) or polypropylene (PP), having a thickness of 5 to 50 μm and a porosity of 30 to 70%, may be used. The microporous membrane constituting the separator may be, for example, one using only PE or only PP, may contain an ethylene-propylene copolymer, or may be a laminate of a PE microporous membrane and a PP microporous membrane.

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[0074]

Furthermore, a laminated separator composed of a porous layer (A) mainly containing a resin having a melting point of 140°C or lower, and a porous layer (B) mainly containing a resin having a melting point of 150°C or higher or an inorganic filler having a heat resistance temperature of 150°C or higher may be used as the separator for the non-aqueous rechargeable battery. Here, “melting point” means a melting temperature measured using a differential scanning calorimeter (DSC) in accordance with the JIS K 7121 standard, and “heat resistance temperature of 150°C or higher” means that, at the least, no deformation such as softening is observed at 150°C.

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[0075]

The porous layer (A) of the laminated separator is mainly for ensuring a shutdown function, and when the non-aqueous rechargeable battery reaches a temperature equal to or higher than the melting point of the resin that is the main component of the porous layer (A), the resin in the porous layer (A) melts and blocks the pores of the separator, thereby causing the shutdown that suppresses the progress of the electrochemical reaction.

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[0076]

PE, for example, may be used as the resin having a melting point of 140°C or lower, which is the main component of the porous layer (A), and examples of the form thereof include a substrate such as a microporous membrane used in non-aqueous rechargeable batteries or a nonwoven fabric, coated with PE particles. Here, the volume of the resin having a melting point of 140°C or lower, which is the main component in all constituent components of the porous layer (A) is 50% by volume or more, and more preferably 70% by volume or more. When the porous layer (A) is formed of the PE microporous membrane, it is 100% by volume.

[0077]

The porous layer (B) of the laminated separator is one provided with a function of preventing a short circuit due to direct contact between the positive electrode and the negative electrode even when the internal temperature of the non-aqueous rechargeable battery rises, and this function is ensured by a resin having a melting point of 150°C or higher or an inorganic filler having a heat resistance temperature of 150°C or higher. That is, when the battery reaches high temperatures, even if the porous layer (A) shrinks, the porous layer (B), which is less likely to shrink, can prevent a short circuit due to direct contact between the positive and negative electrodes that may occur when the separator undergoes thermal shrinkage. Furthermore, since this heat-resistant porous layer (B) acts as a skeleton of the separator, thermal shrinkage of the porous layer (A), that is, thermal shrinkage of the separator as a whole, can also be suppressed.

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[0078]

When the porous layer (B) is formed mainly of a resin having a melting point of 150°C or higher, examples of the form thereof include a form in which a microporous membrane formed of a resin having a melting point of 150°C or higher (for example, the above-mentioned PP battery microporous membrane) is laminated on the porous layer (A), and a coated and laminated form in which a composition (coating liquid) for forming the porous layer (B) containing fine particles of a resin having a melting point of 150°C or higher is coated onto the porous layer (A) to laminate the porous layer (B) containing fine particles of a resin having a melting point of 150°C or higher.

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[0079]

Examples of the resin constituting the fine particles of the resin having a melting point of 150°C or higher include various crosslinked polymers such as crosslinked polymethyl methacrylate, crosslinked polystyrene, crosslinked polydivinylbenzene, crosslinked styrene-divinylbenzene copolymers, polyimide, melamine resin, phenol resin, and benzoguanamine-formaldehyde condensates; and heat-resistant polymers such as PP, polysulfone, polyethersulfone, polyphenylene sulfide, PTFE, polyacrylonitrile, aramid, and polyacetal.

[0080]

The particle size of the fine particles of the resin having a melting point of 150°C or higher is the average particle diameter ($D_{50\%}$) measured by the same method as that for the negative electrode active material for a non-aqueous rechargeable battery of the present invention, and is, for example, preferably 0.01 μm or more, more preferably 0.1 μm or more, and preferably 10 μm or less, more preferably 2 μm or less.

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[0081]

Since the amount of the fine particles of the resin having a melting point of 150°C or higher is the main component contained in the porous layer (B), the amount thereof is 50% by volume or more, preferably 70% by volume or more, more preferably 80% by volume or more, and even more preferably 90% by volume or more, in the total volume of the constituent components of the porous layer (B) (total volume excluding pores).

[0082]

When the porous layer (B) is formed mainly of an inorganic filler having a heat resistance temperature of 150°C or higher, examples thereof include a coated and laminated form in which a composition (coating liquid) for forming the porous layer (B) containing an inorganic filler having a heat resistance temperature of 150°C or higher is coated onto the porous layer (A) to laminate the porous layer (B) containing the inorganic filler having a heat resistance temperature of 150°C or higher.

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[0083]

The inorganic filler for the porous layer (B) is not particularly limited as long as it has a heat resistance temperature of 150°C or higher, is stable with respect to the non-aqueous electrolyte of the non-aqueous rechargeable battery, and is electrochemically stable such that it is not easily oxidized or reduced within the operating voltage range of the non-aqueous rechargeable battery. However, from the viewpoint of dispersion and the like, fine particles are preferable, and alumina, silica, and boehmite are preferable. Alumina, silica, and boehmite have high oxidation resistance and allow the particle size and shape to be adjusted to desired values and the like, making it easy to precisely control the porosity of the porous layer (B). Note that the inorganic filler having a heat resistance temperature of 150°C or higher may be used alone as one exemplified above or in a combination of two or more kinds. Furthermore, the inorganic filler having a heat resistance temperature of 150°C or higher and the fine particles of a resin having a melting point of 150°C or higher may be used in combination.

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[0084]

The shape of the inorganic filler having a heat resistance temperature of 150°C or higher for the porous layer (B) is not particularly limited, and various shapes such as substantially spherical (including perfectly spherical), substantially ellipsoidal (including ellipsoidal), and plate-like shapes may be used.

[0085]

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Furthermore, the average particle diameter of the inorganic filler having a heat resistance temperature of 150°C or higher for the porous layer (B) (the average particle diameter of plate-like fillers and other shaped fillers; the same applies hereinafter) is preferably 0.3 μm or more, more preferably 0.5 μm or more, because if it is too small, ion permeability decreases. Moreover, if the inorganic filler having a heat resistance temperature of 150°C or higher is too large, electrical characteristics tend to deteriorate, and therefore the average particle diameter thereof is preferably 5 μm or less, more preferably 2 μm or less. The average particle diameter of the inorganic filler having a heat resistance temperature of 150°C or higher in the present specification is an average particle diameter ($D_{50\%}$) obtained by the same method as that for the negative electrode active material.

[0086]

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Since the inorganic filler having a heat resistance temperature of 150°C or higher in the porous layer (B) is the main component contained in the porous layer (B), the amount thereof in the porous layer (B) is 50% by volume or more, preferably 70% by volume or more, more preferably 80% by volume or more, and even

more preferably 90% by volume or more, in the total volume of the constituent components of the porous layer (B) (total volume excluding pores). By setting the content of the inorganic filler in the porous layer (B) to a high level as described above, even when the non-aqueous rechargeable battery reaches high temperatures, thermal shrinkage of the separator as a whole can be effectively suppressed, and the occurrence of short circuits due to direct contact between the positive electrode and the negative electrode can be more effectively suppressed.

[0087]

Note that, when using, in combination, inorganic fillers having a heat resistance temperature of 150°C or higher and fine particles of resin having a melting point of 150°C or higher, it is sufficient that these two materials together constitute the main body of the porous layer (B). Specifically, the total amount of these should be 50% or more by volume of the total volume of the constituent components of the porous layer (B) (total volume excluding the void portion), preferably 70% or more by volume, more preferably 80% or more by volume, and even more preferably 90% or more by volume. This makes it possible to ensure the same effect as when the inorganic filler in the porous layer (B) is given a high content as described above.

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[0088]

It is preferable to include an organic binder in the porous layer (B) for purposes such as binding together fine particles of resin having a melting point of 150°C or higher, or inorganic fillers having a heat resistance temperature of 150°C or higher, integrating the porous layer (B) with the porous layer (A), or the like. Examples of organic binders include ethylene-vinyl acetate copolymers (EVA, those containing 20 to 35 mol% of structural units derived from vinyl acetate), ethylene-acrylic acid copolymers such as ethylene-ethyl acrylate copolymer, fluororubber, SBR, CMC, hydroxyethylcellulose (HEC), polyvinyl alcohol (PVA), polyvinyl butyral (PVB), polyvinylpyrrolidone (PVP), crosslinked acrylic resins, polyurethanes, epoxy resins, and the like. In particular, heat-resistant binders having a heat resistance temperature of 150°C or higher are preferably used. One type of the organic binders exemplified above may be used alone, or two or more may be used in combination.

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[0089]

Among the organic binders exemplified above, highly flexible binders such as EVA, ethylene-acrylic acid copolymer, fluororubber, SBR, and the like are preferred. Specific examples of such highly flexible organic binders include Mitsui DuPont Polychemical's "Evaflex series (EVA)", Nippon Unicar's EVA, Mitsui DuPont Polychemical's "Evaflex-E EA series (ethylene-acrylic acid copolymer)", Nippon Unicar's EEA, Daikin Industries' "Dai-Latex series (fluororubber)", JSR's "TRD-200 1 (SBR)", Nippon Zeon's "BM-400B (SBR)", and the like.

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[0090]

When the organic binder is used in the porous layer (B), it may be used in the form of an emulsion dissolved in the solvent of a composition used for formation of the porous layer (B) described later.

[0091]

The coated and laminated separator may be manufactured by, for example, coated the composition used for formation of the porous layer (B) (a liquid composition such as a slurry or the like), containing fine particles of resin having a melting point of 150°C or higher or an inorganic filler having a heat resistance temperature of 150°C or higher, onto the surface of a microporous membrane for forming the porous layer (A), and drying it to a predetermined temperature to manufacture the porous layer (B).

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[0092]

The composition used for formation of the porous layer (B) contains fine particles of resin having a melting point of 150°C or higher, or an inorganic filler having a heat resistance temperature of 150°C or higher, as well as an organic binder and the like as needed, and is a composition in which these are dispersed in a solvent (including a dispersion medium; the same applies below). Note that the organic binder may also be dissolved in a solvent. The solvent used in the composition used for formation of the porous layer (B) may be any solvent that can uniformly disperse inorganic fillers and the like, or that can uniformly dissolve or disperse organic binders. For example, common organic solvents such as aromatic hydrocarbons such as toluene, furans such as tetrahydrofuran, and ketones such as methyl ethyl ketone and methyl isobutyl ketone,

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are preferably used. Note that alcohols (such as ethylene glycol and propylene glycol), various propylene oxide-based glycol ethers such as monomethyl acetate, or the like may be added to these solvents as appropriate with the aim of controlling interfacial tension. In addition, when the organic binder is water-soluble, water may be used as a solvent, such as when using it as an emulsion, or the like. The interfacial tension can also be controlled by adding alcohols (methyl alcohol, ethyl alcohol, isopropyl alcohol, ethylene glycol, and the like) in this case as well, as appropriate.

[0093]

The composition used for formation of the porous layer (B) preferably has a solid content of, for example, 10 to 80% by mass, which includes fine particles of resin having a melting point of 150°C or higher or an inorganic filler having a heat resistance temperature of 150°C or higher, an organic binder, and the like.

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[0094]

In the laminated separator, the porous layer (A) and the porous layer (B) do not necessarily have to be just one layer each, and there may be a plurality of layers thereof in the separator. For example, the configuration may be porous layers (A) disposed on both sides of the porous layer (B), or porous layers (B) disposed on both sides of the porous layer (A). However, increasing the number of layers may increase the thickness of the separator, potentially leading to an increase in the internal resistance of the battery and a decrease in energy density. Therefore, it is not preferable to have too many layers, and it is preferable that the total number of porous layers (A) and porous layers (B) within the laminated separator be five or less.

[0095]

The thickness of the separator for the non-aqueous rechargeable battery (a separator composed of a microporous membrane made of polyolefin, or the laminated separator) is more preferably 10 to 30 μm.

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[0096]

In addition, in the laminated separator, the thickness of the porous layer (B) [or the total thickness thereof if the separator has a plurality of porous layers (B)] is preferably 3 μm or more, from the viewpoint of more effectively exerting the aforementioned effects of the porous layer (B). However, if the porous layer (B) is too thick, it may cause a decrease in the energy density of the battery, or the like, so it is preferable that the thickness of the porous layer (B) be 8 μm or less.

[0097]

Furthermore, in the laminated separator, the thickness of the porous layer (A) [or the total thickness thereof if the separator has a plurality of porous layers (A); the same applies below.] is preferably 6 μm or more, and more preferably 10 μm or more, from the viewpoint of more effectively exhibiting the effects (particularly the shutdown effect) due to the use of the porous layer (A). However, if the porous layer (A) is too thick, it may cause a decrease in the energy density of the battery, and moreover, the force that causes the porous layer (A) to shrink due to heat may increase, reducing its effect in suppressing the thermal shrinkage of the separator as a whole. Because of this, the thickness of the porous layer (A) is preferably 25 μm or less, more preferably 20 μm or less, and even more preferably 14 μm or less.

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[0098]

The porosity of the separator as a whole is preferably 30% or more in a dried state, in order to ensure electrolyte retention and have favorable ion permeability. On the other hand, from the viewpoint of ensuring separator intensity and preventing internal short circuits, it is preferable that the porosity of the separator be 70% or less in a dried state. The porosity P (%) of the separator can be calculated by determining the sum for each component i using the following formula (1), from the thickness of the separator, the mass per unit area, and the density of the constituent components.

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$$P = \{1 - (m/t) / (\sum a_i \cdot \rho_i)\} \times 100 \quad (1)$$

Here, in the above formula, a_i is the ratio of component i when the total mass is 1, ρ_i is the density of component i (g/cm³), m is the mass per unit area of the separator (g/cm²), and t is the thickness of the separator (cm).

[0099]

In addition, in the case of the laminated separator, in formula (1), the porosity P (%) of the porous layer (A) can also be determined using formula (1) by setting m as the mass per unit area of the porous layer (A)

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(g/cm²) and t as the thickness of the porous layer (A) (cm). The porosity of the porous layer (A) obtained by this method is preferably 30 to 70%.

[0100]

Furthermore, in the case of the laminated separator, in formula (1), the porosity P (%) of the porous layer (B) can also be determined using formula (1) by setting m as the mass per unit area of the porous layer (B) (g/cm²) and t as the thickness of the porous layer (B) (cm). The porosity of the porous layer (B) obtained by this method is preferably 20 to 60%.

[0101]

The separator is preferably one having high mechanical intensity, for example, it is preferable that the puncture intensity thereof is 3 N or more. As mentioned above, the negative electrode active material for a non-aqueous rechargeable battery of the present invention undergoes significant volume expansion and shrinkage during charging and discharging. As the charge-discharge cycle is repeated, the expansion and shrinkage of the negative electrode as a whole will also cause mechanical damage to the separator it faces. If the puncture intensity of the separator is 3 N or higher, favorable mechanical intensity is ensured, and the mechanical damage to the separator may be mitigated.

[0102]

The aforementioned laminated separators may be cited as separators having a puncture intensity of 3 N or higher, and in particular, a separator is preferred in which a porous layer (A) mainly composed of a resin having a melting point of 140°C or lower is laminated with a porous layer (B) mainly containing an inorganic filler having a heat resistance temperature of 150°C or higher. This is thought to be because the inorganic filler has high mechanical intensity, which may compensate for the mechanical intensity of the porous layer (A) and increase the overall mechanical intensity of the separator.

[0103]

The puncture intensity may be measured by the following method. A separator is fixed onto a plate having a 2-inch diameter hole, such that there are no wrinkles or bends. A hemispherical metal pin having a tip diameter of 1.0 mm is then lowered onto the measurement sample at a speed of 120 mm/min, and the force at the time of a hole being opened in the separator is measured five times. Then, the average value is determined for the three measurements excluding the maximum and minimum values from the five measurements mentioned above, and this is taken as the puncture intensity of the separator.

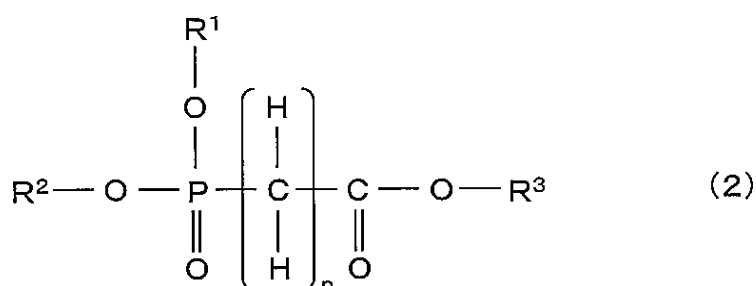
[0104]

(Nonaqueous electrolyte)

In the non-aqueous rechargeable battery of the present invention, it is preferable to use a non-aqueous electrolyte solution that is a solution in which lithium salt is dissolved in an organic solvent and contains a phosphonoacetate compound that satisfies general formula (2).

[0105]

[Chem. 1]



[0106]

In the above general formula (2), R¹, R², and R³ each independently represent an alkyl group, alkenyl group, or alkynyl group having 1 to 12 carbon atoms, which may be substituted with a halogen atom; and n is an integer from 0 to 6.

[0107]

Examples of the phosphonoacetate compound include, for example, the following compounds.

[0108]

<Compounds for which n=0 in the general formula (2)>

Trimethyl phosphonoformate, methyl diethyl phosphonoformate, methyl dipropyl phosphonoformate, methyl dibutyl phosphonoformate, triethyl phosphonoformate, ethyl dimethyl phosphonoformate, ethyl dipropyl phosphonoformate, ethyl dibutyl phosphonoformate, tripropyl phosphonoformate, propyl dimethyl phosphonoformate, propyl diethyl phosphonoformate, propyl dibutyl phosphonoformate, tributyl phosphonoformate, butyl dimethyl phosphonoformate, butyl diethyl phosphonoformate, butyl dipropyl phosphonoformate, methyl bis(2,2,2-trifluoroethyl) phosphonoformate, ethyl bis(2,2,2-trifluoroethyl) phosphonoformate, propyl bis(2,2,2-trifluoroethyl) phosphonoformate, butyl bis(2,2,2-trifluoroethyl) phosphonoformate, and the like. 10

[0109]

<Compounds for which n=1 in the general formula (2)>

Trimethylphosphonoacetate, methyldiethylphosphonoacetate, methyldipropylphosphonoacetate, methyldibutylphosphonoacetate, triethylphosphonoacetate, ethyldimethylphosphonoacetate, ethyldipropylphosphonoacetate, ethyldibutylphosphonoacetate, tripropylphosphonoacetate, propyldimethylphosphonoacetate, propyldiethylphosphonoacetate, propyldibutylphosphonoacetate, tributylphosphonoacetate, butyldimethylphosphonoacetate, butyldiethylphosphonoacetate, butyldipropylphosphonoacetate, methylbis(2,2,2-trifluoroethyl)phosphonoacetate, ethylbis(2,2,2-trifluoroethyl)phosphonoacetate, propylbis(2,2,2-trifluoroethyl)phosphonoacetate, butylbis(2,2,2-trifluoroethyl)phosphonoacetate, allyldimethylphosphonoacetate, allyldiethylphosphonoacetate, 2-propynyldimethylphosphonoacetate, 2-propynyl(diethylphosphono)acetate, and the like. 20

[0110]

<Compounds for which n=2 in the general formula (1)>

Trimethyl 3-phosphonopropionate, methyl 3-(diethylphosphono)propionate, methyl 3-(dipropylphosphono)propionate, methyl 3-(dibutylphosphono)propionate, triethyl 3-phosphonopropionate, ethyl 3-(dimethylphosphono)propionate, ethyl 3-(dipropylphosphono)propionate, ethyl 3-(dibutylphosphono)propionate, tripropyl 3-phosphonopropionate, propyl 3-(dimethylphosphono)propionate, propyl 3-(diethylphosphono)propionate, propyl 3-(dibutylphosphono)propionate, tributyl 3-phosphonopropionate, butyl 3-(dimethylphosphono)propionate, butyl 3-(diethylphosphono)propionate, butyl 3-(dipropylphosphono)propionate, methyl 3-(bis(2,2,2-trifluoroethyl)phosphono)propionate, ethyl 3-(bis(2,2,2-trifluoroethyl)phosphono)propionate, propyl 3-(bis(2,2,2-trifluoroethyl)phosphono)propionate, butyl 3-(bis(2,2,2-trifluoroethyl)phosphono)propionate, and the like. 30

[0111]

<Compounds for which n=3 in the general formula (2)>

Trimethyl 4-phosphonobutyrate, methyl 4-(diethylphosphono)butyrate, methyl 4-(dipropylphosphono)butyrate, methyl 4-(dibutylphosphono)butyrate, triethyl 4-phosphonobutyrate, ethyl 4-(dimethylphosphono)butyrate, ethyl 4-(dipropylphosphono)butyrate, ethyl 4-(dibutylphosphono)butyrate, tripropyl 4-phosphonobutyrate, propyl 4-(dimethylphosphono)butyrate, propyl 4-(diethylphosphono)butyrate, propyldibutylphosphono)butyrate, tributyl 4-phosphonobutyrate, butyl 4- 40

(dimethylphosphono)butyrate, butyl 4-(diethylphosphono)butyrate, butyl 4-(dipropylphosphono)butyrate, and the like.

[0112]

The content of the phosphonoacetate compound represented by the general formula (2) in the non-aqueous electrolyte solution used in the non-aqueous rechargeable battery is preferably 0.1% by mass or more, and more preferably 0.5% by mass or more, from the viewpoint of ensuring a good effect in favorably suppressing battery swelling under high-voltage charging conditions and especially when stored at high temperatures. On the other hand, if the amount of the phosphonoacetate compound in the non-aqueous electrolyte solution is too high, it may degrade the battery's load characteristics, charge-discharge cycle characteristics, and storage characteristics. Therefore, the content of the phosphonoacetate compound represented by the general formula (2) in the non-aqueous electrolyte solution used in the non-aqueous rechargeable battery is preferably 5% by mass or less, and more preferably 2.5% by mass or less.

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[0113]

In addition, it is preferable that the non-aqueous electrolyte solution used in the non-aqueous rechargeable battery contains 1,3-dioxane. When a non-aqueous electrolyte solution containing 1,3-dioxane is used, its effect may improve the load characteristics and high-temperature storage characteristics of the non-aqueous rechargeable battery, especially when charged at high voltage. In addition, 1,3-dioxane is more preferably used in combination with a phosphonoacetate compound represented by the general formula (2), in which case the charge-discharge cycle characteristics of the non-aqueous rechargeable battery may be further improved.

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[0114]

The 1,3-dioxane content in the non-aqueous electrolyte solution used in the non-aqueous rechargeable battery is preferably 0.1% by mass or more, and more preferably 0.5% by mass or more, from the viewpoint of improving the battery's load characteristics when charged at high voltage and its capacity recovery after high-temperature storage, as well as ensuring the effect of improving the battery's charge-discharge cycle characteristics when combined with the phosphonoacetate compound represented by the general formula (2). On the other hand, when the amount of 1,3-dioxane in the non-aqueous electrolyte solution is too high, the load characteristics, charge/discharge cycle characteristics, and storage characteristics of the battery may be reduced. Therefore, the content of 1,3-dioxane in the non-aqueous electrolyte solution used in the non-aqueous rechargeable battery is preferably 5% by mass or less, and more preferably 2.5% by mass or less.

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[0115]

In addition, it is preferable to use a non-aqueous electrolyte solution that also contains halogen-substituted cyclic carbonates. Halogen-substituted cyclic carbonates act on the negative electrode to suppress the reaction between the negative electrode and the non-aqueous electrolyte solution components. Therefore, by using a non-aqueous electrolyte solution that also contains halogen-substituted cyclic carbonates, a non-aqueous rechargeable battery having favorable charge-discharge cycle characteristics can be obtained.

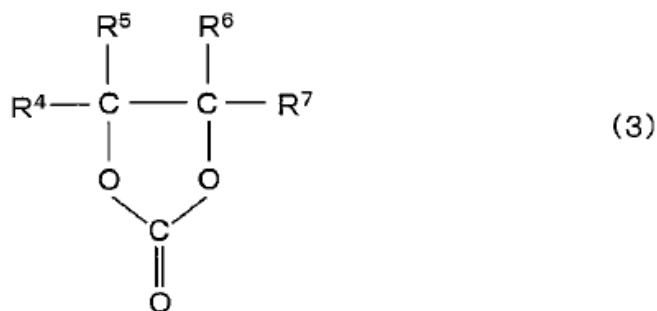
[0116]

Compounds represented by the following general formula (3) may be used as halogen-substituted cyclic carbonates.

[0117]

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[Chem. 2]



[0118]

In the general formula (3) above, R^4 , R^5 , R^6 , and R^7 represent hydrogen, a halogen, or an alkyl group having 1 to 10 carbon atoms, and some or all of the hydrogen atoms in the alkyl group may be substituted with a halogen, and at least one of R^4 , R^5 , R^6 , and R^7 is a halogen, and R^4 , R^5 , R^6 , and R^7 may be different from each other, or two or more may be the same. When R^4 , R^5 , R^6 , and R^7 are alkyl groups, the fewer the carbon atoms therein, the more preferable. Fluorine is particularly preferred as the halogen.

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[0119]

Among such halogen-substituted cyclic carbonates, 4-fluoro-1,3-dioxolan-2-one (FEC) is particularly preferred.

[0120]

For the non-aqueous electrolyte solution used in the non-aqueous rechargeable battery, the content of halogen-substituted cyclic carbonate is preferably 0.1% by mass or more, and more preferably 0.5% by mass or more, from the viewpoint of more favorably ensuring an effect from the use thereof. However, when the content of halogen-substituted cyclic carbonate in the non-aqueous electrolyte solution is too high, the effect of improving storage characteristics may be reduced. Therefore, the content of the halogen-substituted cyclic carbonate in the non-aqueous electrolyte solution used in the non-aqueous rechargeable battery is preferably 10% by mass or less, and more preferably 5% by mass or less.

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[0121]

Further, it is preferable for the non-aqueous electrolyte solution to be an electrolyte containing vinylene carbonate (VC). VC acts on the negative electrode (especially negative electrodes using carbon materials as the negative electrode active material) and has the effect of suppressing the reaction between the negative electrode and the non-aqueous electrolyte solution components. Therefore, by using a non-aqueous electrolyte solution that also contains VC, a non-aqueous rechargeable battery having more favorable charge/discharge cycle characteristics may be obtained.

[0122]

The content of VC in the non-aqueous electrolyte solution used in the non-aqueous rechargeable battery is preferably 0.1% by mass or more, and more preferably 1.0% by mass or more, from the viewpoint of more favorably ensuring an effect from the use thereof. However, if the content of VC in the non-aqueous electrolyte solution is too high, the effect of improving storage characteristics may be reduced. Therefore, the content of VC in the non-aqueous electrolyte solution used in the non-aqueous rechargeable battery is preferably 10% by mass or less, and more preferably 4.0% by mass or less.

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[0123]

The lithium salt used in the non-aqueous electrolyte solution is not particularly limited, as long as it dissociates in the solvent to form Li^+ ions and does not easily undergo side reactions such as decomposition within the voltage range used for the battery. For example, inorganic lithium salts such as LiClO_4 , LiPF_6 , LiBF_4 , LiAsF_6 , LiSbF_6 , and the like, and organic lithium salts such as LiCF_3SO_3 , LiCF_3CO_2 , $\text{Li}_2\text{C}_2\text{F}_4(\text{SO}_3)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, $\text{LiC}_n\text{F}_{2n+1}\text{SO}_3$ ($n \geq 2$), $\text{LiN}(\text{RfOSO}_2)_2$ [where Rf is a fluoroalkyl group], and

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the like may be used.

[0124]

The concentration of this lithium salt in the non-aqueous electrolyte solution is preferably 0.5 to 1.5 mol/L, and more preferably 0.9 to 1.25 mol/L.

[0125]

The organic solvent used in the non-aqueous electrolyte solution is not particularly limited, as long as it dissolves the lithium salt and does not cause side reactions such as decomposition within the voltage range used for the battery. Examples include cyclic carbonates such as ethylene carbonate, propylene carbonate, butylene carbonate, and the like; acyclic carbonates such as dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, and the like; acyclic esters such as methyl propionate and the like; cyclic esters such as γ -butyrolactone; acyclic ethers such as dimethoxyethane, diethyl ether, 1,3-dioxolane, diglyme, triglyme, tetraglyme, and the like; cyclic ethers such as 1,4-dioxane, tetrahydrofuran, 2-methyltetrahydrofuran, and the like; nitriles such as acetonitrile, propionitrile, methoxypropionitrile, and the like; and sulfite esters such as ethylene glycol sulfite; and the like, and two or more of these may also be used in a mixture thereof. Note that, to achieve a battery having more favorable characteristics, it is desirable to use a combination of solvents that can obtain high conductivity, such as a mixed solvent of ethylene carbonate and an acyclic carbonate.

[0126]

In addition, additives such as anhydrides, sulfonic acid esters, dinitriles, 1,3-propanesalton, diphenyl disulfide, cyclohexylbenzene, biphenyl, fluorobenzene, t-butylbenzene, and the like (including their derivatives) may be added as appropriate to the non-aqueous electrolyte solution used in the non-aqueous rechargeable battery in order to further improve charge-discharge cycle characteristics and enhance safety such as high-temperature storability and overcharge prevention.

[0127]

Furthermore, an electrolyte which has been gelled by adding a known gelling agent such as a polymer to the aforementioned non-aqueous electrolyte solution (a gel electrolyte) may also be used for the non-aqueous electrolyte solution of the non-aqueous rechargeable battery.

[0128]

(Battery Form)

The form of the non-aqueous rechargeable battery of the present invention is not particularly limited. For example, such may be coin-shaped, button-shaped, sheet-shaped, laminated, cylindrical, flat, rectangular, large-scale such as those used in electric vehicles, or the like. Note that, when using the negative electrode active material for a non-aqueous rechargeable battery of the present invention, swelling problems tend to occur particularly in batteries constructed using rectangular (prismatic) or flat cans having a small thickness relative to their width, laminate film outer casings, or the like. However, the non-aqueous rechargeable battery of the present invention may effectively suppress the occurrence of such battery swelling, and this effect is particularly pronounced when using rectangular or flat batteries having the aforementioned outer casings (cans).

[0129]

When introducing the positive electrode, the negative electrode, and the separator into the non-aqueous rechargeable battery of the present invention, a laminated electrode assembly may be used in which the positive electrode and the negative electrode are laminated having a separator in between, or a wound electrode assembly may be used in which the positive electrode and the negative electrode are laminated having a separator therebetween and further wound in a spiral shape. In addition, depending on the form of the battery, a plurality of positive or negative electrodes may be used in these laminated electrode assemblies or wound electrode assemblies.

[0130]

In the laminated electrode assembly or wound electrode assembly used in the non-aqueous rechargeable battery, when using the laminated separator, it is preferable that the porous layer (B) be disposed such that it faces at least the positive electrode, especially when using a separator in which a porous layer (A) mainly composed of a resin having a melting point of 140°C or less is laminated with a porous layer (B) mainly composed of an inorganic filler having a heat resistance temperature of 150°C or more. In this case, a porous layer (B) mainly containing an inorganic filler having a heat resistance temperature of 150°C or higher, which has superior oxidation resistance, faces the positive electrode. This allows for better suppression of the oxidation of the separator by the positive electrode, thereby improving the battery's storage characteristics at

high temperatures and the charge-discharge cycle characteristics thereof. In addition, when additives such as vinylene carbonate, cyclohexylbenzene, or the like are added to the non-aqueous electrolyte, they may form a film on the positive electrode side, clogging the pores of the separator and significantly degrading the battery's performance. Therefore, by facing a relatively porous layer (B) toward the positive electrode, an effect of suppressing clogging of the pores can be anticipated.

[0131]

On the other hand, if one surface of the laminated separator is the porous layer (A), it is preferable that the porous layer (A) made to face the negative electrode. This suppresses, for example, the absorption of molten thermoplastic resin from the porous layer (A) into the electrode mixture layer during shutdown, allowing it to be utilized to close the pores of the separator with good efficiency.

[0132]

In addition, in the electrode body used in the non-aqueous rechargeable battery (the laminated electrode assembly or the wound electrode assembly), it is preferable that p/n is 1.0 to 3.6, where p is the mass of the positive electrode active material contained in the positive electrode and n is the mass of the negative electrode active material contained in the negative electrode. By setting the p/n ratio to 3.6 or less, the utilization rate of the negative electrode active material may be reduced, thereby limiting the charging capacity. This suppresses, during battery charging and discharging, the volume expansion and shrinkage of the material containing Si and O as constituent elements that is used as the negative electrode active material, and better suppresses the deterioration of the battery's charge-discharge cycle characteristics due to pulverization and the like of the material particles. In addition, by setting the p/n ratio to 1.0 or higher, a higher battery capacity may be ensured.

[0133]

Because the non-aqueous rechargeable battery of the present invention has various favorable battery characteristics, including storage characteristics, these characteristics may be leveraged for preferred use in various applications where conventionally known non-aqueous rechargeable batteries are adopted, including power supply applications for small-scale, multi-functional portable devices.

[Examples]

[0134]

The present invention will be described in detail below based on examples. However, the present invention is not limited thereto.

[0135]

<Synthesis of lithium-containing composite oxide A containing Ni>

Ammonia water, whose pH was adjusted to approximately 12 by the addition of sodium hydroxide, was placed in a reaction vessel. A mixed aqueous solution containing nickel sulfate, cobalt sulfate, and manganese sulfate at concentrations of 2.4 mol/dm^3 , 0.8 mol/dm^3 , and 0.8 mol/dm^3 , respectively, and ammonia water at a concentration of 25% by mass were added dropwise thereto while vigorously stirring, using a metering pump at rates of $23 \text{ cm}^3/\text{min}$ and $6.6 \text{ cm}^3/\text{min}$, respectively, to synthesize a co-precipitated compound (spherical co-precipitated compound) of Ni, Co, and Mn. Note that, during this process, the temperature of the reaction solution was maintained at 50°C , and an aqueous sodium hydroxide solution having a concentration of 6.4 mol/dm^3 was simultaneously added dropwise so that the pH of the reaction solution was maintained near 12. Furthermore, nitrogen gas was bubbled in at a flow rate of $1 \text{ dm}^3/\text{min}$.

[0136]

The aforementioned co-precipitated compound was washed with water, filtered, and dried to obtain a hydroxide containing Ni, Co, and Mn in a molar ratio of 6:2:2. 0.196 mol of this hydroxide and 0.204 mol of $\text{LiOH} \cdot \text{H}_2\text{O}$ were dispersed in ethanol to form a slurry, which was then mixed in a planetary ball mill for 40 minutes and dried at room temperature to obtain a mixture. Next, the mixture was placed in an alumina crucible and heated to 600°C in a dry air flow of $2 \text{ dm}^3/\text{min}$. This was followed by holding the mixture at that temperature for 2 hours to preheat, and further raising the temperature to 900°C and firing for 12 hours to synthesize lithium-containing composite oxide A.

[0137]

The obtained lithium-containing composite oxide A was washed with water, then heat-treated at 850°C for 12 hours in air (oxygen concentration of approximately 20 vol%), and subsequently pulverized into a powder using a mortar and pestle. After pulverization, the lithium-containing composite oxide A was stored in a desiccator.

[0138]

The composition of the lithium-containing composite oxide A was analyzed using ICP as follows. First, 0.2 g of the lithium-containing composite oxide A was collected and placed in a 100 mL container. Subsequently, 5 mL of pure water, 2 mL of aqua regia, and 10 mL of pure water were added in sequence, the mixture was heated and dissolved, and after cooling, was further diluted 25 times and the composition thereof was analyzed using ICP (JARRELASH "ICP-757") (calibration curve method). From the obtained results, upon deriving the composition of the lithium-containing composite oxide A, the composition was found to be represented by $\text{Li}_{1.02}\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$.

[0139]

<Synthesis of lithium-containing composite oxide B containing Ni>

Ammonia water, whose pH was adjusted to approximately 12 by the addition of sodium hydroxide, was placed in a reaction vessel. A mixed aqueous solution containing nickel sulfate, manganese sulfate, and cobalt sulfate at concentrations of 3.76 mol/dm^3 , 0.21 mol/dm^3 , and 0.21 mol/dm^3 , respectively, and ammonia water at a concentration of 25% by mass were added dropwise thereto while vigorously stirring, using a metering pump at rates of $23 \text{ cm}^3/\text{min}$ and $6.6 \text{ cm}^3/\text{min}$, respectively, to synthesize a co-precipitated compound (spherical co-precipitated compound) of Ni, Mn, and Co. Note that, during this process, the temperature of the reaction solution was maintained at 50°C , and an aqueous sodium hydroxide solution having a concentration of 6.4 mol/dm^3 was simultaneously added dropwise so that the pH of the reaction solution was maintained near 12. Furthermore, nitrogen gas was further bubbling at a flow rate of $1 \text{ dm}^3/\text{min}$ in order to cause the reaction in an inert atmosphere.

[0140]

The aforementioned co-precipitated compound was washed with water, filtered, and dried to obtain a hydroxide containing Ni, Mn, and Co in a molar ratio of 90:5:5. 0.196 mol of this hydroxide, 0.204 mol of $\text{LiOH}\cdot\text{H}_2\text{O}$, and 0.001 mol of TiO_2 were dispersed in ethanol to form a slurry, which was then mixed in a planetary ball mill for 40 minutes and dried at room temperature to obtain a mixture. Next, the mixture was placed in an alumina crucible and heated to 600°C in a dry air flow of $2 \text{ dm}^3/\text{min}$. This was followed by holding the mixture at that temperature for 2 hours to preheat, and further raising the temperature to 800°C and firing for 12 hours to synthesize lithium-containing composite oxide B. The obtained lithium-containing composite oxide B was pulverized into a powder using a mortar and pestle, and then stored in a desiccator.

[0141]

The composition of this lithium-containing composite oxide B was analyzed using the calibration curve method employing ICP described above. From the obtained results, upon deriving the composition of the lithium-containing composite oxide B, the composition was found to be represented by $\text{Li}_{1.02}\text{Ni}_{0.895}\text{Co}_{0.05}\text{Mn}_{0.05}\text{Ti}_{0.005}\text{O}_2$.

[0142]

Example 1

<Production of positive electrode>

A positive electrode mixture-containing paste was prepared by uniformly mixing 70 parts by mass of LiCoO_2 , which is the positive electrode active material, 30 parts by mass of $\text{LiMn}_{0.2}\text{Ni}_{0.6}\text{Co}_{0.2}\text{O}_2$, which is the lithium-containing composite oxide A, 1 part by mass of artificial graphite and 1 part by mass of Ketjen black, which are conductive additives, and 10 parts by mass of PVDF, which is a binder, using NMP as a solvent. The positive electrode mixture-containing paste was intermittently coated onto both sides of a current collector made of aluminum foil having a thickness of $15 \mu\text{m}$, adjusting the thickness as needed. After drying, a calendaring treatment was performed to adjust the thickness of the positive electrode mixture layer so that the total thickness was $130 \mu\text{m}$. The positive electrode was then manufactured by cutting it to a width of 54.5 mm . Furthermore, tabs were welded to the exposed portion of the aluminum foil of the positive electrode to form a lead portion.

[0143]

<Production of negative electrode>

An aqueous negative electrode mixture-containing paste was prepared by mixing: 98% parts by mass of a mixture which has mixed together a material in which the SiO surface is covered with carbon (the amount of carbon in the composite is 20% by mass; hereinafter referred to as "SiO/carbon composite") and graphitic carbon having a median particle diameter D_{50} of $16 \mu\text{m}$, in a mass ratio of 5:95; 1.0 parts by mass of an aqueous CMC solution having a concentration of 1% by mass and having a viscosity adjusted to the range of 1500 to 5000 $\text{mPa}\cdot\text{s}$; and 1.0 parts by mass of SBR, using ion-exchanged water having a specific

conductivity of $2.0 \times 10^5 \Omega/\text{cm}$ or higher as the solvent.

[0144]

Note that the SiO/carbon composite was obtained by CVD treatment of SiO, whose particle size distribution had been adjusted by pulverization and classification, using toluene as the liquid source, at a processing temperature of 1100°C and a processing time of 4 hours. The SiO/carbon composite obtained after CVD treatment had $D_{10\%}$ at $5 \mu\text{m}$, $D_{50\%}$ at $9 \mu\text{m}$, and $D_{90\%}$ at $13 \mu\text{m}$, having a full width at half maximum of the Si (220) diffraction peak of 0.8° , I_a/I_b at 3.3, and I_{510}/I_{1343} at 0.10.

[0145]

The negative electrode mixture-containing paste was intermittently coated onto both sides of a current collector made of copper foil having a thickness of $8 \mu\text{m}$, adjusting the thickness as needed. After drying, a calendering treatment was performed to adjust the thickness of the negative electrode mixture layer so that the total thickness was $110 \mu\text{m}$. The negative electrode was then manufactured by cutting it to a width of 55.5 mm . Furthermore, tabs were welded to the exposed portion of the copper foil of this negative electrode to form a lead portion.

[0146]

<Production of separator>

A dispersion was prepared by adding 5 kg of ion-exchanged water and 0.5 kg of a dispersant (aqueous polycarboxylate ammonium salt, solid content concentration 40% by mass) to 5 kg of boehmite having a median particle diameter $D_{50\%}$ of $1 \mu\text{m}$, and pulverizing the mixture in a ball mill having an internal volume of 20 L and a rotation rate of 40 cycles/minute for 10 hours. The treated dispersion was vacuum-dried at 120°C and observed using a scanning electron microscope (SEM), revealing that the boehmite's form was substantially plate-shaped.

[0147]

0.5 g of xanthan gum was added as a thickening agent to 500 g of the dispersion, and 17 g of resin binder dispersion (modified polybutyl acrylate, solid content 45% by mass) was added as a binder. The mixture was stirred having a three-in-one motor for 3 hours to prepare a uniform slurry [slurry for forming porous layer (B), solid content ratio 50% by mass].

[0148]

A microporous separator made of PE for non-aqueous rechargeable batteries [porous layer (A): thickness $12 \mu\text{m}$, porosity 40%, average pore size $0.08 \mu\text{m}$, melting point of PE 135°C] was subjected to corona discharge treatment (discharge amount $40 \text{ W} \cdot \text{min}/\text{m}^2$), and a slurry for forming the porous layer (B) was coated onto this treated surface using a microgravure coater. By drying, a porous layer (B) having a thickness of $4 \mu\text{m}$ was formed to obtain a laminated separator. The porous layer (B) in this separator had a mass per unit area of $5.5 \text{ g}/\text{m}^2$, a volume content of 95% by volume of boehmite, and a porosity of 45%.

[0149]

<Preparation of non-aqueous electrolyte solution>

A solution was prepared by dissolving LiPF_6 as a lithium salt at a concentration of $1.1 \text{ mol}/\text{dm}^3$ in a mixed solvent in which EC, MEC, and DMC are mixed in a volume ratio of 1:1:1, and then further adding FEC in an amount equal to 2.0% by mass, VC in an amount equal to 2.0% by mass, 2-propynyl (diethylphosphono)acetate in an amount equal to 1.0% by mass, and 1,3-dioxane in an amount equal to 1.0% by mass.

[0150]

<Construction of battery>

The positive electrode and negative electrode obtained as described above were stacked while interposing the porous layer (B) of the separator therebetween so that the porous layer (B) faces the positive electrode, and the wound electrode assembly was produced by winding into a spiral shape. The obtained wound electrode assembly was made into a flat shape by flattening, placed in an aluminum alloy can measuring 5 mm thick, 42 mm wide, and 61 mm high, and the aforementioned non-aqueous electrolyte solution was injected into it.

[0151]

After injecting the non-aqueous electrolyte solution, the can was sealed to produce a non-aqueous rechargeable battery having the structure illustrated in FIG. 1 and the appearance illustrated in FIG. 2. This battery features a slit vent at the top of the can to release pressure if the internal pressure rises.

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[0152]

Here, the battery illustrated in FIG. 1 and FIG. 2 will be described. FIG. 1(a) is a plan view, and FIG. 1(b) is a partial cross-sectional view thereof. As illustrated in FIG. 1(b), a positive electrode 1 and a negative electrode 2 are wound into a spiral shape via a separator 3 as described above, and then pressurized to become flattened to form a flattened wound electrode assembly 6, which is housed together with the electrolyte in a prismatic can 4. However, in order to avoid complexity, FIG. 1 does not show metal foil, electrolytes, or the like used as current collectors in the production of the positive electrode 1 and the negative electrode 2. In addition, the individual layers of the separator are not illustrated separately.

[0153]

The can 4 is made of aluminum alloy and constitutes the battery's outer casing; this can 4 also serves as the positive electrode terminal. An insulator 5 made of a PE sheet is disposed at the bottom of the can 4, and a positive electrode lead 7 and a negative electrode lead 8 are drawn out from a flat wound electrode assembly 6 consisting of the positive electrode 1, the negative electrode 2, and the separator 3, respectively, which are connected to one end of the positive electrode 1 and the negative electrode 2. In addition, a stainless steel terminal 11 is attached to an aluminum alloy sealing lid plate 9 that seals the opening of the can 4 via a PP insulating packing 10, and a stainless steel lead plate 13 is attached to this terminal 11 via an insulator 12.

[0154]

Moreover, this lid plate 9 is then inserted into the opening of the can 4, and the joint between the two is welded, thereby sealing the opening of the can 4 and creating a sealed environment inside the battery. In addition, in the battery illustrated in FIG. 1, a non-aqueous electrolyte solution inlet 14 is provided on the lid plate 9. A sealing member is welded to this non-aqueous electrolyte solution inlet 14 while being inserted therein, for example by laser welding or the like, to ensure the battery's airtightness (therefore, in the batteries illustrated in FIG. 1 and FIG. 2, the non-aqueous electrolyte solution inlet 14 is actually the non-aqueous electrolyte solution inlet and the sealing member, but it is illustrated as the non-aqueous electrolyte solution inlet 14 for the sake of clarity). Furthermore, the lid plate 9 is provided with a split vent 15 as a mechanism to expel internal gas to the outside when the battery temperature rises.

[0155]

In the battery of this Example 1, the positive electrode lead body 7 is directly welded to the lid plate 9 so that the can 4 and the lid plate 9 function as the positive electrode terminal, and the negative electrode lead body 8 is welded to the lead plate 13 so that the negative electrode lead body 8 and the terminal 11 are electrically connected via the lead plate 13 so that the terminal 11 functions as the negative electrode terminal. However, depending on the material and the like of the can 4, the positive and negative polarities thereof may be reversed.

[0156]

FIG. 2 is a schematic perspective view illustrating the external appearance of the battery illustrated in FIG. 1. FIG. 2 is intended to illustrate that the battery is a prismatic battery, whereas FIG. 1 illustrates the battery in a general manner and only illustrates certain components of the battery. In addition, in FIG. 1, the inner circumference portion of the electrode body is not illustrated in cross-section.

[0157]

Examples 2-5 and Comparative Examples 1-4

A negative electrode was produced in the same manner as in Example 1, with the exception that the SiO/carbon composite was changed to one having the configuration illustrated in Table 1. A non-aqueous rechargeable battery was then produced in the same manner as in Example 1, with the exception that these negative electrodes were used. Incidentally, the amount of carbon in the SiO/carbon composite was adjusted by the CVD treatment time. Specifically, the CVD treatment time for the SiO/carbon composite used in Example 3 was 2.4 hours, and the CVD treatment time for the SiO/carbon composite used in Comparative Example 1 was 3 hours.

[0158]

Example 6

A positive electrode was produced in the same manner as in Example 1, with the exception that the lithium-containing composite oxide B was used instead of the lithium-containing composite oxide A. A non-aqueous rechargeable battery was then produced in the same manner as in Example 1, with the exception that this positive electrode was used.

[0159]

The following storage tests (7-day storage test at 25°C, 7-day storage test at 45°C, and 30-day storage test at 45°C) were performed on each non-aqueous rechargeable battery in the Examples and Comparative Examples.

[0160]

<Storage test at 25°C for 7 days>

For each battery in the Examples and Comparative Examples, constant current-constant voltage charging was performed at 25°C using a constant current of 1 C and a constant voltage of 4.35 V (total charging time: 3 hours), followed by constant current discharge at 1 C (discharge termination voltage: 2.7 V), and the initial discharge capacity (mAh) was measured.

[0161]

For each of the batteries after measuring the initial discharge capacity, constant current-constant voltage charging was performed at 25°C using a constant current of 0.5 C and a constant voltage of 4.35 V (total charging time: 1 hour), and then they were stored in a constant temperature bath at 25°C for 7 days. Thereafter, each battery was removed from the constant temperature bath and discharged at a constant current of 1 C (discharge termination voltage: 2.7 V).

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[0162]

For each of the batteries after storage, constant current-constant voltage charging and constant current discharging were performed under the same conditions as when the initial discharge capacity was measured, and the discharge capacity after 7 days of storage at 25°C was determined. Then, the capacity retention rate was calculated by dividing the discharge capacity after 7 days of storage at 25°C by the initial discharge capacity and expressing the result as a percentage.

[0163]

<Storage test at 45°C for 7 days>

For each battery in the Examples and Comparative Examples (batteries subjected to a 7-day storage test at 25°C are differentiated), the initial discharge capacity and the discharge capacity after a 7-day storage at 45°C were measured in the same manner as for the 7-day storage test at 25°C, except that the storage temperature in the constant temperature bath was changed to 45°C, and the capacity retention rate was calculated.

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[0164]

<Storage test at 45°C for 30 days>

For each battery in the Examples and Comparative Examples (batteries subjected to a 7-day storage test at 25°C and those subjected to a 7-day storage test at 45°C are differentiated), the initial discharge capacity and the discharge capacity after storage for 30 days at 45°C were measured in the same manner as for the 45°C storage test for 7 days, with the exception that the storage time in the thermostatic bath was changed to 30 days, and the capacity retention rate was calculated.

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[0165]

Table 1 shows the composition of the SiO/carbon composite used in the negative electrode, and Table 2 shows the evaluation results thereof. Note that the initial discharge capacity in Table 2 is shown as a relative value in which the value for the non-aqueous rechargeable battery in Example 1 set to 100, based on the value measured during a 7-day storage test at 25°C.

[0166]

[0167]

	SiO/carbon composite						
	D _{10%} (μm)	D _{50%} (μm)	D _{90%} (μm)	Si(220) Diffraction peak width at half maximum (°)	I _a /I _b	Amount of carbon in the complex (mass%)	I ₅₁₀ /I ₁₃₄₃
Example 1	5	9	13	0.8	3.3	20	0.10
Example 2	4	7	12	0.8	3.3	20	0.10
Embodiment 3	5	9	13	0.8	3.3	12	0.20
Embodiment 4	5	9	13	0.6	3.6	20	0.10
Embodiment 5	5	9	13	1.0	2.9	20	0.10
Embodiment 6	5	9	13	0.8	3.3	20	0.10
Comparative Example 1	3	5	9	0.8	3.2	15	0.15
Comparative Example 2	5	9	13	0.4	4.1	20	0.10
Comparative Example 3	5	9	13	1.2	2.5	20	0.10
Comparative Example 4	6	11	16	0.8	3.4	20	0.10

[Table 1]

(25)

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[Table 2]

	Initial discharge capacity (%)	Storage characteristics: Capacity retention rate (%)		
		Storage test at 25°C for 7 days	Storage test at 45°C for 7 days	Storage test at 45°C for 30 days
Example 1	100	100	99	98
Example 2	100	100	98	97
Example 3	101	100	98	97
Example 4	99	100	99	98
Example 5	100	100	99	97
Example 6	106	100	99	98
Comparative Example 1	101	100	98	92
Comparative Example 2	92	100	99	98
Comparative Example 3	101	100	98	91
Comparative Example 4	92	100	99	98

[0168]

As is clear from Tables 1 and 2, the non-aqueous rechargeable batteries of Examples 1 to 6, in which the negative electrode active material was a combination of SiO having a median particle diameter $D_{50\%}$ and an appropriate full width at half maximum of the Si (220) diffraction peak, and graphitic carbon, demonstrated excellent storage characteristics of large initial discharge capacity and high capacity retention rates after 7 days of storage at 25°C, 7 days of storage at 45°C, and 30 days of storage at 45°C.

[0169]

In contrast, the battery in Comparative Example 1, which used SiO having a median particle diameter $D_{50\%}$ that was too small, and the battery in Comparative Example 3, which used SiO having a full width at half maximum of the Si (220) diffraction peak that was too large, exhibited inferior storage characteristics of poor capacity retention after 30 days of storage at 45°C. In addition, the battery in Comparative Example 2, which used SiO having a full width at half maximum of the Si (220) diffraction peak that was too small, and the battery in Comparative Example 4, which used SiO having a median particle diameter $D_{50\%}$ that was too large, had low initial discharge capacity.

[Description of Reference Numerals]

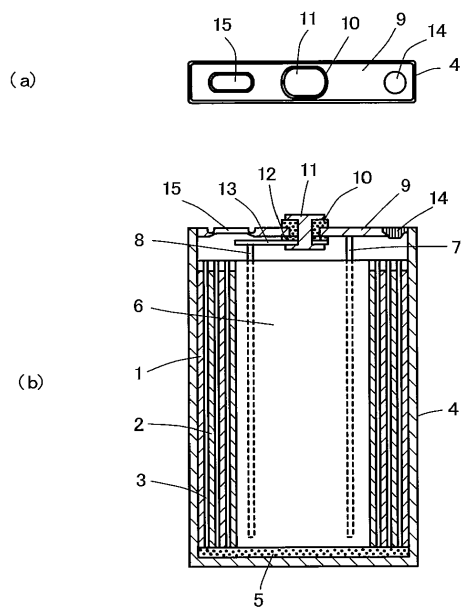
[0170]

- 1 Positive electrode
- 2 Negative electrode
- 3 Separator

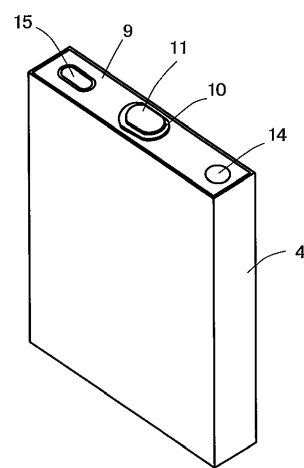
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[Figure 1]



[Figure 2]



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(51) Int.Cl.	FI	Theme Code (Reference)
	C01B 31/02	101Z
F-Term (Reference)	4G146 AA01 AD17 AD23 AD25 BA12 BB23 BC09 BC34B BC37B 5H050 AA08 AA09 BA15 CA07 CA08 CA09 CA29 CB02 CB08 CB29 DA03 HA02 HA05 HA13	

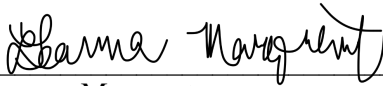


DECLARATION OF TRANSLATOR

I, Leanna Marquart, hereby declare as follows:

1. I personally performed the attached translation from Japanese into English of Foreign Patent Publication No. JP2014089855A, published/issued May 15, 2014, and entitled "非水二次電池用負極活物質および非水二次電池" ("NEGATIVE ELECTRODE ACTIVE MATERIAL FOR NON-AQUEOUS RECHARGEABLE BATTERY AND NON-AQUEOUS RECHARGEABLE BATTERY").
2. The attached translation is, to the best of my knowledge and belief, a true, full, and accurate English translation of the above-identified Japanese-language document.
3. I am competent to perform this translation because I have an M.S. in biochemistry and 8 years of translation experience..
4. I declare under penalty of perjury under the laws of the United States that the foregoing is true and correct, and I further declare that I am aware that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of any patent or proceeding resulting therefrom.

Dated: 6-11-26



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