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(54) [Title of Invention] NON-AQUEOUS ELECTROLYTE RECHARGEABLE BATTERY

(57) [Abstract] (Revised)

[Problem] To provide means by which excellent output properties can be achieved in a non-aqueous electrolyte rechargeable battery having a layered configuration.

[Resolution Means] A non-aqueous electrolyte rechargeable battery, having a positive electrode, wherein a positive electrode active material layer is formed on a surface of a positive electrode current collector, a negative electrode, wherein a negative electrode active material layer including is formed on a surface of a negative electrode current collector, and an electrolyte layer, and having a power generating element formed by layering three or more single battery layers having the positive electrode and the negative electrode facing each other, sandwiching the electrolyte layer, wherein the negative electrode active material includes at least one of a Si material selected from SiO_x (x represents an oxygen number satisfying the Si valence), which is a mixture of amorphous SiO_2 particles and Si particles, and a Si-containing alloy, and a carbon material selected from graphite, non-graphitizing carbon, and amorphous carbon, a capacity per unit area of the negative electrode active material layer of the layered single battery layer is substantially constant from outside to inside in the layering direction, and a thickness of the negative electrode active material layer decreases monotonically from inside to outside in the layering direction.

[Selected Drawing] None

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[Scope of Patent Claims]

[Claim 1]

A non-aqueous electrolyte rechargeable battery, comprising:

a positive electrode, wherein a positive electrode active material layer including a positive electrode active material is formed on a surface of a positive electrode current collector,

a negative electrode, wherein a negative electrode active material layer including a negative electrode active material is formed on a surface of a negative electrode current collector,

an electrolyte layer; and

a power generating element formed by layering three or more single battery layers having the positive electrode and the negative electrode facing each other, sandwiching the electrolyte layer, wherein:

the negative electrode active material includes at least one of a Si material selected from the group consisting of SiO_x (x represents an oxygen number satisfying the Si valence), which is a mixture of amorphous SiO_2 particles and Si particles, and a Si-containing alloy, and a carbon material selected from the group consisting of graphite, non-graphitizing carbon, and amorphous carbon;

a capacity per unit area of the negative electrode active material layer of the layered single battery layer is substantially constant from outside to inside in the layering direction; and

a thickness of the negative electrode active material layer decreases monotonically from inside to outside in the layering direction.

[Claim 2]

The non-aqueous electrolyte rechargeable battery according to claim 1, wherein a mixing ratio of the Si material in the negative electrode active material layer of the layered single battery layer is greater outside than inside in the layering direction.

[Claim 3]

The non-aqueous electrolyte rechargeable battery according to claim 1 or 2, wherein a capacity per unit mass of the Si material in the negative electrode active material layer of the layered single battery layer is greater outside than inside in the layering direction.

[Detailed Description of Invention]

[Technical Field]

[0001]

The present invention relates to a non-aqueous electrolyte rechargeable battery. The non-aqueous electrolyte rechargeable battery according to the present invention is used, for example, as a driving power source or an auxiliary power source for motors of vehicles such as electric vehicles, fuel cell vehicles, and hybrid electric vehicles.

[Background Art]

[0002]

In recent years, there has been demand to reduce the amount of carbon dioxide in order to combat global warming. Therefore, non-aqueous electrolyte rechargeable batteries, which have a low environmental impact, are increasingly being used not only in portable devices, but also in power supply devices for electrically powered vehicles such as hybrid electric vehicles (HEVs), electric vehicles (EVs), and fuel cell vehicles. Lithium-ion rechargeable batteries intended for use in electric vehicles must have a large capacity and a large area.

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[0003]

Conventionally, graphite and other carbon materials have been used for the negative electrode of lithium-ion rechargeable batteries due to their advantages in terms of charge-discharge cycle life and cost. However, carbon materials such as graphite are used for negative electrode active materials, which are charged and discharged by absorbing and releasing lithium ions into graphite crystals, and thus do not have a theoretical capacity of 372 mAh/g or higher, which is obtained from LiC_6 , a compound having the maximum amount of lithium incorporate therein. For this reason, obtaining capacities and energy densities that satisfy the practical usage level for vehicle use is difficult with only negative electrode active materials made of graphite and other carbon materials.

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[0004]

In contrast, a battery using a material that alloys with Li as the negative electrode active material has higher energy density than a battery using conventional carbon materials such as graphite, and is therefore expected to be used as a negative electrode active material for vehicle applications. For example, a Si material absorbs and releases 3.75 mol of lithium ions per 1 mol during charging and discharging, and $\text{Li}_{15}\text{Si}_4 (= \text{Li}_{3.75}\text{Si})$ has a theoretical capacity of 3600 mAh/g.

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[0005]

However, a rechargeable lithium-ion battery with a material that alloys with Li in the negative electrode, particularly Si material, has a large expansion and contraction at the negative electrode during charging and discharging. For example, in the case of graphite, the volume expansion when Li ions are absorbed is about 1.2 times that of graphite, whereas in the case of Si material, when Si and Li alloy, the volume changed from an amorphous state to a crystalline state, resulting in a large volume change of about 4 times, thereby reducing the cycle life of the electrode. Furthermore, in the case of a Si negative electrode active material, there is a trade-off between capacity and cycle durability, which makes it difficult to improve high cycle durability while demonstrating high capacity.

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[0006]

In order to solve these problems, an negative electrode active material for a lithium-ion

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rechargeable battery containing, as an example, an amorphous alloy having the formula: $\text{Si}_x\text{M}_y\text{Al}_z$ has been proposed (see, for example, patent document 1). In the formula, x, y, and z represent atomic percent values, where $x+y+z=100$, $x \geq 55$, $y < 22$, $z > 0$, and M is at least one metal selected from the group consisting of Mn, Mo, Nb, W, Ta, Fe, Cu, Ti, V, Cr, Ni, Co, Zr, and Y. According to the invention described in patent document 1, paragraph 0008 teaches that minimizing the content of metal M exhibits a favorable cycle life as well as high capacity by . Such also teaches that a mixture of graphite materials with low expansion exhibits a favorable cycle life.

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[Prior Art Documents]

[Patent Documents]

[0007]

[Patent Document 1] JP 2009-517850 A (Translation of PCT Application)

[Summary of Invention]

[Problem to Be Solved by Invention]

[0008]

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However, according to the examinations of the present inventors, the technology described in the above patent document 1 does not achieve sufficient output properties when used as a battery with a large multilayered configuration.

[0009]

The charge and discharge reactions of a lithium-ion rechargeable battery are accompanied by heat generation. In particular, large batteries, such as automotive batteries, use a multilayer structure battery consisting of multiple single battery layers, in which the positive and negative electrodes face each other via an electrolyte layer. However, with large multilayer batteries such as automotive batteries, there is concern that large temperature differences may occur between the inside of the layer (inner side in the layered direction) and the edge of the layer (outer side in the layered direction). That is, the inner side tends to be hotter than the outer side in the layering direction. This is believed to be due to the fact that heat generated by the charge-discharge reaction is dissipated into the battery packaging material as it approaches from the inside to the outside in the layering direction, and then from the battery packaging material to outside the system.

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[0010]

The present inventors discovered that the addition of Si material to carbon material as the negative electrode active material increases the electrode resistance, resulting in a particularly large temperature difference between the inside (inside of the layering direction) and the edge (outside of the layering direction) of the layer, which is accompanied by a large non-uniformity in battery properties. In multilayered batteries, in particularly, automotive batteries with a large number of layers, the temperature inside the layering direction (inner

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side) tends to rise even more. Therefore, single-cell layers on the inside of the layering direction activate the reaction more than the outer single-cell layers, resulting in variation in the rate properties of the single-cell layers. As a result, it becomes difficult to obtain stable high output properties.

[0011]

Therefore, the purpose of the present invention is to provide a means by which excellent output properties can be achieved in a non-aqueous electrolyte rechargeable battery with a layered structure, in which Si material and carbon material are used in mixture as the negative electrode active material.

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[Means for Solving Problem]

[0012]

The present inventors have conducted extensive research in order to solve the above problems. As a result, in a non-aqueous electrolyte rechargeable battery with a layered structure using a Si material and a carbon material as the negative electrode active material, the above problem can be solved by designing the thickness of the negative electrode active material layer of the outer single battery layer in the layering direction to be thinner than that of the negative electrode active material layer of the inner single battery layer, while keeping the capacity of the single battery layer constant, thereby completing the present invention.

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[0013]

That is, the present invention provides a non-aqueous electrolyte rechargeable battery with a layered structure, containing Si material and carbon material as the negative electrode active material, wherein the capacity per unit area of the negative electrode active material layer of a single battery layer is approximately constant and the thickness of the negative electrode active material layer decreases monotonically from the inside to the outside in the layering direction.

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[Effect of Invention]

[0014]

According to the present invention, it is possible to obtain uniform output properties for each multi-layered single battery layer by designing the outer single battery layer of a layered structure battery so that the negative electrode active material layer is thinner than the inner single battery layer, while maintaining the capacity. As a result, the output properties of the battery can be improved.

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[Brief Description of Drawings]

[0015]

[FIG. 1] FIG. 1 (A) illustrates a partial cross-sectional view of a lithium ion rechargeable battery with a layered structure consisting of multiple single-cell layers, while FIG. 1 (B) illustrates the change in rate properties of each single-cell layer relative to the layering

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direction of a lithium-ion rechargeable battery of the present embodiment and a conventional lithium-ion rechargeable battery of the same cell properties with a multiple single-cell layered structure.

[FIG. 2] is a cross-sectional schematic diagram illustrating the basic configuration of a flat (layered), non-bipolar lithium-ion rechargeable battery, as an embodiment of the non-aqueous electrolyte rechargeable battery of the present invention.

[FIG. 3] is a perspective view illustrating the appearance of a flat lithium ion rechargeable battery, which is a representative embodiment of a non-aqueous electrolyte rechargeable battery according to the present invention.

[FIG. 4] is a graph illustrating the relationship between the thickness of the negative electrode active material layer and the discharge rate properties (1C/0.1C) of a battery in which a mixture of Si and carbon materials is used as the negative electrode active material, when the capacity per unit area of the negative electrode active material layer is kept at an approximate constant.

[Embodiments of Invention]

[0016]

One embodiment of the present invention provides a non-aqueous electrolyte rechargeable battery, having a positive electrode, wherein a positive electrode active material layer including a positive electrode active material is formed on a surface of a positive electrode current collector, a negative electrode, wherein a negative electrode active material layer including a negative electrode active material is formed on a surface of a negative electrode current collector, and an electrolyte layer, and having a power generating element formed by layering three or more single battery layers having the positive electrode and the negative electrode facing each other, sandwiching the electrolyte layer, wherein the negative electrode active material includes at least one of a Si material selected from the group consisting of SiO_x (x represents an oxygen number satisfying the Si valence), which is a mixture of amorphous SiO_2 particles and Si particles, and a Si-containing alloy, and a carbon material selected from the group consisting of graphite, non-graphitizing carbon, and amorphous carbon, a capacity per unit area of the negative electrode active material layer of the layered single battery layer is substantially constant from outside to inside in the layering direction, and a thickness of the negative electrode active material layer decreases monotonically from inside to outside in the layering direction.

[0017]

Electric vehicles have been attracting attention in recent years as being environmentally friendly, but they have a shorter driving range than gasoline-powered vehicles, and this shorter driving range is particularly noticeable when air conditioning (cooling, heating) is in use. For this reason, non-aqueous electrolyte rechargeable batteries, particularly non-

aqueous electrolyte rechargeable batteries for electric vehicles, must have high output and high capacity in order to extend the driving distance on a single charge. In addition, improving durability (cycle characteristics) so that high output and high capacity are not degraded by repeated charging and discharging at high currents short periods of time is an important issue for batteries to be used in electric vehicles.

[0018]

In non-aqueous electrolyte rechargeable batteries having a multi-layered structure consisting of three or more single battery layers, the present inventors have found that the output properties of the batter are improved by using a mixture of Si material and carbon material as the negative electrode active material, by making the capacity per unit area of the negative electrode active material layer of the layered single battery layers constant between the outer and inner sides in the layering direction, and by configuring the thickness of the negative electrode active material layer to decrease monotonically from the inner side in the layering direction to the outer side.

[0019]

FIG. 1(A) illustrates a partial cross-sectional view of a non-aqueous electrolyte rechargeable battery with a multilayered structure, and FIG. 1 (B) illustrates how the rate properties of each single battery layer change with respect to the layering direction for a battery with a conventional layered structure consisting of multiple single battery layers with the same cell properties and fro the battery of the present embodiment. In automotive batteries with a large number of layers, the inner single-cell layer is more susceptible to temperature rise than the outer layer in the layering direction because it is not easy for heat to escape from the inner single-cell layer. Therefore, in conventional batteries with a multilayered structure, the inner single-cell layer has faster reaction rate and a relatively higher rate characteristic, while the outer single-cell layer has a slower reaction rate and a relatively lower rate characteristic. This causes variation in the output properties of the single cell layers, making it impossible to obtain sufficient output characteristics for the entire battery. In contrast to this, in the battery having a layered structure of the present embodiment, the thickness of the negative electrode active material layer is made relatively thin in the outer unit cell layers in the layering direction where the temperature is relatively low. As illustrated in FIG. 1 (B), due to the shorter diffusion distance of Li ions, the rate properties of the outer single-cell layer are improved, and the difference in rate properties with the inner single-cell layer in the layering direction can be reduced. In this case, it is possible to obtain a non-aqueous electrolyte rechargeable battery with stable output properties and little variation in output for each single battery layer by maintaining the capacity per unit area of the negative electrode active material layer of each single battery layer at an abbreviated constant level.

[0020]

In the present Specification, the capacity per unit area of the negative electrode active material layer is the charge capacity per unit area, and the capacity per unit area of the negative electrode active material layer of each single cell layer is approximately constant, meaning that the difference between the maximum or minimum value and the average value of the capacity per unit area of the negative electrode active material layer in the single battery layers constituting a battery is within $\pm 10\%$ of the average value.

[0021]

Preferably, the non-aqueous electrolyte rechargeable battery of the present embodiment has the mixing ratio of Si material in the negative electrode active material layer of the multi-layered single battery layer is outside > inside in the layering direction. It is preferable that the outer cell layers contain a larger amount of the Si material, which has a higher capacity than the carbon material, since this makes it easier to balance the output properties of each cell layer.

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[0022]

Additionally, the capacity per unit weight of the Si material in the negative electrode active material layer of the multi-layered single battery layers is preferable outside > inside in the layering direction. It is preferable to use a Si material having a high capacity per unit weight for the outer cell layers, since this makes it easier to balance the output properties of each cell layer.

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[0023]

The following is a description of the embodiment of the present invention with reference to the attached drawings. Note, in the description of the drawings, the same elements are given the same reference numerals and duplicated descriptions are omitted. Furthermore, the dimensional ratios in the drawings have been exaggerated for the convenience of explanation and may differ from the actual ratios.

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[0024]

[Non-aqueous electrolyte rechargeable battery]

FIG. 2 is a schematic cross-sectional diagram illustrating an overview of a flat multilayer battery, which is one embodiment of the battery of the present invention. By using a layered type, the battery can be made compact and high capacity. In the present Specification, an example of a flat layered, non-bipolar lithium-ion rechargeable battery as illustrated in FIG. 2 will be used to explain the details of the battery.

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[0025]

The above electrical connection configuration (electrode structure) in a lithium-ion rechargeable battery can be applied to both non-bipolar (internal parallel connection type) batteries and bipolar (internal series connection type) batteries.

[0026]

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When distinguishing between the types of electrolyte layers in a lithium-ion rechargeable battery, any of the conventionally known electrolyte layer types can be applied, including solution electrolyte batteries that use solution electrolytes such as non-aqueous electrolyte solutions in the electrolyte layer, and polymer batteries that use polymer electrolytes in the electrolyte layer. Such polymer batteries can be further divided into gel electrolyte batteries using polymer gel electrolytes (also simply referred to as gel electrolytes) and solid polymer (all solid state) batteries using polymer solid electrolytes (also simply referred to as polymer electrolytes).

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[0027]

Therefore, in the following description, a non-bipolar (internal parallel connection type) lithium ion rechargeable battery will be very simply described with reference to the drawings as an example of the lithium ion rechargeable battery of the present embodiment. However, the technical scope of the electric device according to the present invention and the lithium ion rechargeable battery according to the present embodiment should not be limited to these.

[0028]

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FIG. 2 is a schematic cross-sectional view showing the basic configuration of a flat, layered, non-bipolar non-aqueous electrolyte lithium ion rechargeable battery (hereinafter, simply referred to as a "layered battery"). As illustrated in FIG. 2, the layered battery 10 of the present embodiment has a structure in which the flat, rectangular power generating element 21, on which the charging and discharging reactions actually proceed, is sealed inside the battery exterior material 29, which is the outer body of the battery. Here, the power generating element 21 has a configuration in which a positive electrode, a separator 17, and a negative electrode are layered. The separator 17 contains a non-aqueous electrolyte (for example, a liquid electrolyte). The positive electrode has a structure in which positive electrode active material layers 15 are disposed on both sides of a positive electrode current collector 12. The negative electrode has a structure in which the negative electrode active material layer 13 is arranged on both sides of the negative electrode current collector 11. Specifically, the negative electrode, the electrolyte layer, and the positive electrode are layered in this order so that one positive electrode active material layer 15 and the adjacent negative electrode active material layer 13 face each other through the separator 17. As a result, the adjacent positive electrode, electrolyte layer and negative electrode constitute one single cell layer 19. Therefore, the layered battery 10 illustrated in FIG. 2 can be said to have a configuration in which a plurality of single battery layers 19 are layered and electrically connected in parallel.

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[0029]

Both outermost layer negative electrode current collectors located at the outermost layers of both power generating elements 21 have the negative electrode active material layer 13 on one side only, but the active material layer may be provided on both sides. In other words,

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rather than using a current collector dedicated to the outermost layer with an active material layer on only one side, a current collector with active material layers on both sides may be used as it is as a current collector for the outermost layer. In addition, by reversing the arrangement of the positive and negative electrodes from FIG. 2, the outermost positive electrode current collector may be positioned on both outermost layers of the power generating element 21, and the positive electrode active material layer may be disposed on one or both sides of the outermost positive electrode current collector.

[0030]

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The positive electrode current collector 12 and the negative electrode current collector 11 have a structure in which the positive electrode current collector plate (tab) 27 and the negative electrode collector plate (tab) 25, which are conductive to the respective electrodes (positive and negative electrodes), are attached to each other and conducted outside the battery outer packaging material 29, such that they are sandwiched between the ends of the battery outer packaging material 29. The positive electrode current collector 27 and the negative electrode collector 25 may be attached to the positive electrode current collector 12 and the negative electrode collector 11 of each electrode by ultrasonic welding, resistance welding, or the like, respectively, via positive electrode leads and negative electrode leads (not illustrated) as necessary.

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[0031]

Furthermore, the layered battery 10 of the present embodiment is composed of a monotonically decreasing thickness of the negative electrode active material layer from the inside to the outside in the layering direction, while keeping the capacity per unit area in the negative electrode active material layer of the single battery layer constant. That is, by controlling the thickness of the negative electrode active material layer in the unit cell layer formed by stacking multiple cells so as to monotonically decrease from the inside (also referred to as the interior, center, or central side) to the outside (also referred to as the exterior, end, or end side) in the layering direction, the output properties of the outer unit cell layer are improved and the variation in output properties within the battery are suppressed.

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[0032]

In a conventional non-aqueous electrolyte rechargeable battery having a layered structure in which a plurality of unit cell layers of the same configuration are layered, heat generation due to charging and discharging of the battery causes a distribution of in-plane temperature in the layering direction, i.e., a temperature difference occurs between the outside and inside of the layered structure. As a result, in the inner single-cell layer in the layering direction, the reaction is activated and the rate characteristic is high and the output characteristic is high, but in the outer single-cell layer, the rate characteristic is relatively low and the output characteristic is low.

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[0033]

The present inventors discovered that, when a carbon material and a Si material are used as negative electrode active materials and the capacity per unit area of the negative electrode active material layer is designed to be approximately constant, the rate characteristics depend mainly on the thickness of the negative electrode active material layer rather than on the mixing ratio of the Si materials or the type of Si material. The smaller the thickness of the negative electrode active material layer, the higher the rate characteristic. By increasing the thickness of the negative electrode active material layer of the outer single-cell layer of the layered structure to be thinner than the negative electrode active material layer of the inner single-cell layer, the rate characteristics of the outer single-cell layer can be improved. As a result, the difference in rate characteristics between the inner single-cell layer and the rate characteristics of the inner single-cell layer can be reduced, and battery performance can be improved due to the suppression of variations in the rate characteristics of each single-cell layer.

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[0034]

Here, the ratio of (thickness of the negative electrode active material layer of the outermost single-cell layer)/(thickness of the negative electrode active material layer of the central single-cell layer) should be between 0.60 and 0.95, and between 0.70 and 0.90, although there is no particular restriction on the thickness variation between the inner and outer negative electrode active material layers in the single-cell layer in the layering direction. When the value of the above ratio is 0.95 or less, the effect of the present invention can be obtained remarkably. On the other hand, when the value is 0.60 or higher, it is easier to secure the battery capacity of the outer single-cell layer and a high-capacity battery can be obtained. Here, the thickness of the negative electrode active material layer of the outermost cell layer is the thickness of the negative electrode active material layer in the cell layer with the thinnest negative electrode active material layer, and the thickness of the negative electrode active material layer of the central cell layer is the thickness of the negative electrode active material layer in the cell layer with the thickest negative electrode active material layer.

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[0035]

Specifically, the thickness of the negative electrode active material layer of the outermost single battery layer is not limited as long as the thickness of the negative electrode active material layer decreases monotonically from outside to inside in the layering direction, for example, from 1 to 100 μm , with 45 to 70 μm being preferred, and 50 to 65 μm being more preferred. The thickness of the negative electrode active material layer of the central cell layer is, for example, 2 to 120 μm , preferably 50 to 90 μm , and more preferably 60 to 80 μm .

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[0036]

Here, as long as the number of single battery layers of the present embodiment of the non-

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aqueous electrolyte rechargeable battery is three or more layers, no particular limitation is set. Preferably, the number of single cell layers is from 3 to 10, more preferably from 3 to 7. Within the above range, the effects of the present invention can be obtained remarkably, and batteries with high output and high capacity can be obtained.

[0037]

In this form of non-aqueous electrolyte rechargeable battery of the present embodiment, it is sufficient that the thickness of the negative electrode active material layer for each unit cell layer is gradually changed from the inner side (center side) to the outer side (end side) in the layering direction. The thickness of the negative electrode active material layer may be graded in a staircase-like manner such that the thickness of the negative electrode active material layer changes for each number of single cell layers. For example, when there are 5 single battery layers (single cells) stacked, and the thickness of the negative electrode active material layer is in the order $A < B < C$, the thickness of the negative electrode active material layer includes a form in which the thickness of the negative electrode active material layer changes in the following order: outer-inner-outer: for each single battery layer, the thickness of the negative electrode active material layer may be graded as A-B-C-B-A so that the thickness of the layer varies. The thickness of the negative electrode active material layer may be graded in a staircase manner, such as A-A-B-A-A and A-B-B-B-A so that the thickness of the negative electrode active material layer changes for each of the several more single-cell layers. Also, the unit cell layer having the negative electrode active material layer with the greatest thickness may not be the innermost one, for example, A-B-B-C-B or A-B-B-C-A. However, it is not limited to these as long as the thickness of the negative electrode active material layer of the single battery layer decreases monotonically from the inside to the outside in the layering direction of the battery.

[0038]

It is preferred that in a battery in which the thickness of the negative electrode active material layer for each single battery layer is graded to monotonically decrease from the inside to the outside in the layering direction of the battery, the mixing ratio of Si material in the negative electrode active material layer of the layered single battery layers is outside > inside in the layering direction. By including more Si material, which has higher capacity compared to carbon material, in the outer single cell layer, the thickness of the negative electrode active material layer can be reduced without decreasing capacity. Conventionally, when Si material, which has a large volume change with charging/discharging, is mixed with carbon material as a negative electrode active material, it has been thought that the ratio of Si material in the mixture increases and the rate characteristic decreases. However, as indicated in the examples described later, the present inventors found that when the capacity per unit area of the negative electrode active material layer is fairly constant, the rate

characteristic depends mainly on the thickness of the negative electrode active material layer and is not significantly affected by the mixing ratio of the Si material. The migration rate of Li ions in the negative electrode active material layer depends on the thickness of the negative electrode active material layer, and the thinner the negative electrode active material layer, the higher the rate characteristic. Therefore, by making the mixing ratio of Si materials in the negative electrode active material layer of the single battery layer outer > inner in the stacking direction, it is easy to attain batteries with excellent output characteristics with little variation in rate characteristics for each single battery layer.

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[0039]

Here, in the negative electrode active material layer in the single cell battery layer, the change in the mixing ratio of the Si material between the inside and outside in the layering direction (the ratio of the mass of the Si material to the total mass of the negative electrode active material) is not particularly limited, but when the negative electrode active material layers of all the single cell battery layers contain a Si material and a carbon material, the ratio of (the mixing ratio of the Si material in the outermost cell layer)/(the mixing ratio of the Si material in the central cell layer) is, for example, not particularly limited, and is 1.1 to 30, more preferably 1.3 to 30, and further preferably 4 to 20. When the value of the above ratio is 1.1 or higher, the effect of the present invention can be obtained remarkably. On the other hand, when the value is less than 30, batteries with less variation in rate characteristics per single battery layer can be obtained. Here, the mixing ratio of the Si material in the negative electrode active material layer of the outermost cell layer is the mixing ratio of the Si material in the negative electrode active material layer of the single cell layer with the thinnest negative electrode active material layer, whereas the mixing ratio of the Si material in the central cell layer is the mixing ratio of the Si material in the negative electrode active material layer in the cell layer with the thickest negative electrode active material layer.

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[0040]

Specifically, the mixing ratio of Si material (the ratio of the mass of Si material to the total mass of the negative electrode active material) in the negative electrode active material layer of the outermost single battery layer should be less than 60 mass%, and 5 to 20 mass% is more preferred. The mixture ratio of the Si material in the central cell layer is preferably 0 to 20 mass%, and more preferably 1 to 10 mass%.

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[0041]

Here, it is preferred that the mixing ratio of the Si material in the negative electrode active material layer has at least one set of single cell layers in which the mixing ratio of the Si material is outside > inside in the layering direction in the adjacent single cell layers. In particular, it is preferable that the unit cell layers be provided with a step-like gradation from the inner side (center side) to the outer side (edge side) in the layering direction.

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[0042]

Similarly, when the capacity per unit area of the negative electrode active material layer in a battery using a mixture of carbon and Si materials as the negative electrode active material is fairly constant, the rate characteristic is independent of the type of Si material, and the thinner the negative electrode active material layer is, the higher the rate characteristic becomes. Therefore, it is preferable that the capacity per unit weight of the Si material in the negative electrode active material layer of the layered single battery layers in a battery graded to monotonically decrease from the inside to the outside in the layering direction of the battery, is outside > inside the layering direction.

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[0043]

For example, in the negative active material layer in a single battery layer, there is no restriction as to the change in capacity per unit weight of Si material between the inside and outside in the layering direction.

[0044]

Furthermore, it is possible to make the capacity per unit weight of Si material in the negative electrode active material layer in a battery in which the thickness of the negative electrode active material layer for each single battery layer is graded to monotonically decrease from the inside to the outside in the layering direction of the battery, so that the capacity per unit weight of Si material in the negative electrode active material layer is outside > inside the layering direction. Specifically, the capacity per unit weight of the Si material in the negative active material layer of each single battery layer should be 200-3700 mAh/g, and more preferably 600-1400 mAh/g. Within this range, it is possible to select the capacity per unit weight of the Si material in the negative electrode active material layer of each single battery layer to be outside > inside the layering direction.

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[0045]

Here, it is preferable to have at least one set of single battery layers where the capacity per unit weight of Si material in the negative electrode active material layer is outside > inside the layering direction in adjacent single battery layers. In particular, it is preferable that the unit cell layers be provided with a step-like gradation from the inner side (center side) to the outer side (edge side) in the layering direction.

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[0046]

The following is a description of the main components of the battery.

[0047]

<Active material layer>

The active material layer (13, 15) contains active material and further contains other additives as needed.

[0048]

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(Positive Electrode Active Material Layer)

The positive electrode active material layer 15 contains a positive electrode active material, and when necessary, further contains other additives such as a binder, a conductive agent, an electrolyte (a polymer matrix, an ion-conductive polymer, an electrolyte solution, and the like), and a lithium salt for enhancing ion conductivity.

[0049]

(Positive Electrode Active Material)

Examples of the positive electrode active material include lithium-transition metal composite oxides such as LiMn_2O_4 , LiCoO_2 , LiNiO_2 , $\text{Li}(\text{Ni-Mn-Co})\text{O}_2$, and those in which part of the transition metals in these oxides is replaced with other elements, lithium-transition metal phosphate compounds, and lithium-transition metal sulfate compounds. Preferably, lithium-transition metal composite oxide is used as the positive active material in terms of capacity and output characteristics. In some cases, two or more kinds of positive electrode active materials may be used in combination.

[0050]

More preferably, $\text{Li}(\text{Ni-Mn-Co})\text{O}_2$ and those in which some of these transition metals are replaced by other elements (hereinafter also referred to simply as "NMC composite oxides"). NMC composite oxides have a layered crystal structure in which lithium atomic layers and transition metal (Mn, Ni and Co in an ordered arrangement) atomic layers are layered alternately via oxygen atomic layers. Moreover, each transition metal contains one Li atom, and the amount of Li that can be extracted is twice that of spinel lithium manganese oxide, i.e., the supply capacity is twice that of spinel lithium manganese oxide, resulting in high capacity.

[0051]

As described above, the NMC composite oxide also include composite oxides in which a part of the transition metal elements is substituted with other metal element. In such cases, other elements include Ti, Zr, Nb, W, P, Al, Mg, V, Ca, Sr, Cr, Fe, B, Ga, In, Si, Mo, Y, Sn, V, Cu, Ag, Zn, and the like. Preferably Ti, Zr, Nb, W, P, Al, Mg, V, Ca, Sr, and Cr. More preferably Ti, Zr, P, Al, Mg, and Cr. From the perspective of improving cycle characteristics, Ti, Zr, Al, Mg, and Cr are more preferable.

[0052]

NMC composite oxide has a high theoretical discharge capacity, and therefore preferably has a composition of the general formula (1): $\text{Li}_a\text{Ni}_b\text{Mn}_c\text{Co}_d\text{M}_x\text{O}_2$ (wherein a, b, c, d, and x in the formula satisfy $0.9 \leq a \leq 1.2$, $0 < b < 1$, $0 < c \leq 0.5$, $0 < d \leq 0.5$, $0 \leq x \leq 0.3$; M is at least one selected from Ti, Zr, Nb, W, P, Al, Mg, V, Ca, Sr, and Cr). Here, a represents the atomic ratio of Li, b represents the atomic ratio of Ni, c represents the atomic ratio of Mn, d represents the atomic ratio of Co, and x represents the atomic ratio of M. In the above general formula (1), the

relationship between b, c and d is not particularly limited and differs depending on the valence of M, and the like, but it is preferable that $b+c+d=1$ is satisfied. The composition of each element can be measured, for example, by inductively coupled plasma (ICP) emission spectrometry.

[0053]

In general, nickel (Ni), cobalt (Co), and manganese (Mn) are known to contribute to capacity and output properties in terms of improved material purity and electronic conductivity. Ti and others partially substitute transition metals in the crystal lattice. From the viewpoint of cycle properties, some of the transition elements may be substituted by other metal elements. In this case, $0 < x \leq 0.3$ in the general formula (1) is preferred. It is believed that the solid solution of at least one element selected from the group consisting of Ti, Zr, Nb, W, P, Al, Mg, V, Ca, Sr, and Cr stabilizes the crystal structure, and as a result, the capacity decrease of the battery can be prevented even after repeated charge/discharge cycles, and excellent and as a result, a decrease in the battery capacity can be prevented even when the battery is repeatedly charged and discharged, and excellent cycle properties can be attained.

[0054]

The above NMC composite oxides can be prepared by selecting various known methods, such as coprecipitation and spray-drying methods. It is preferable to use the coprecipitation method due to the ease of preparation of the composite oxide. Specifically, for example, a nickel-cobalt-manganese composite hydroxide is produced by a coprecipitation method as described in Special Publication JP 2011-105588 A. Thereafter, the NMC composite oxide can be obtained by mixing the nickel-cobalt-manganese composite hydroxide with a lithium compound and calcining the mixture.

[0055]

Of course, positive electrode active materials other than those mentioned above may be used.

[0056]

Although the average particle size of the positive electrode active material in the positive electrode active material layer is not particularly limited, from the viewpoint of high output, it is preferably from 1 to 100 μm , and more preferably from 1 to 25 μm . In the present Specification, the average particle size is measured using a particle size distribution measuring device and a laser diffraction/scattering method.

[0057]

In the positive electrode active material layer, it is preferable that the content of the positive electrode active material (in terms of solid content) is 80 to 99.5 mass%, and it is more preferable that the content is 85 to 99.5 mass%.

[0058]

From the viewpoint of high density, it is preferable that the density of the positive electrode active material layer be 2.5 to 3.8 g/cm^3 , and more preferable that it be 2.6 to 3.7 g/cm^3 .

[0059]

Moreover, from the viewpoint of high capacity, it is preferable that the coating amount (thickness) of one side of the positive electrode active material layer is 12 to 30 mg/cm^2 , and 15 to 28 mg/cm^2 is more preferable.

[0060]

(Binder)

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There is no particular limitation on the binder used for the positive electrode active material layer, but examples include the following materials. Examples include thermoplastic polymers such as polyethylene, polypropylene, polyethylene terephthalate (PET), polyether nitrile, polyacrylonitrile, polyimide, polyamide, cellulose, carboxymethyl cellulose (CMC) and its salts, ethylene-vinyl acetate copolymer, polyvinyl chloride, styrene-butadiene rubber (SBR), isoprene rubber, butadiene rubber, ethylene-propylene rubber, ethylene-propylene-diene copolymer, styrene-butadiene-styrene block copolymers and hydrogenated products thereof, and styrene-isoprene-styrene block copolymers and hydrogenated products thereof; fluororesins such as polyvinylidene fluoride (PVdF), polytetrafluoroethylene (PTFE), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), ethylene-tetrafluoroethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), ethylene-chlorotrifluoroethylene copolymer (ECTFE), and polyvinyl fluoride (PVF); fluororubbers such as vinylidene fluoride-hexafluoropropylene fluororubber (VDF-HFP fluororubber), vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene fluororubber (VDF-HFP-TFE fluororubber), vinylidene fluoride-pentafluoropropylene fluororubber (VDF-PFP fluororubber), vinylidene fluoride-pentafluoropropylene-tetrafluoroethylene fluororubber (VDF-PFP-TFE fluororubber), vinylidene fluoride-perfluoromethylvinyl ether-tetrafluoroethylene fluororubber (VDF-PFMVE-TFE fluororubber), and vinylidene fluoride-chlorotrifluoroethylene fluororubber (VDF-CTFE fluororubber); and epoxy resins and the like. These binders may be used alone or in combination of two or more.

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[0061]

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The content of the binder in the positive electrode active material layer is preferably 1 to $10 \text{ mass\%}$, and more preferably 1 to $8 \text{ mass\%}$.

[0062]

(Conductive Agent)

A conductive agent refers to an additive that is blended to improve the conductivity of the positive electrode active material layer or the negative electrode active material layer. Examples of conductive agents include carbon black such as acetylene black, ketjen black,

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and furnace black and the like. When the active material layer contains a conductive agent, an electronic network is effectively formed inside the active material layer, which can contribute to improving the output characteristics of the battery.

[0063]

The conductive agent the positive electrode active material layer is preferably 1 to 10 mass%, more preferably 1 to 8 mass%. The following effects are achieved by specifying the ratio (content) of conductive agent within the above range. In other words, the electronic conductivity can be sufficiently ensured without interfering with the electrode reaction, and the decrease in energy density due to the decrease in electrode density can be suppressed, and in turn, the energy density can be increased due to the increase in electrode density.

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[0064]

(Other Ingredients)

Examples of lithium salts include $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$, LiPF_6 , LiBF_4 , LiClO_4 , LiAsF_6 , LiCF_3SO_3 , and the like.

[0065]

Examples of ion-conducting polymers include polyethylene oxide (PEO) and polypropylene oxide (PPO) polymers.

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[0066]

The compounding ratio of the components contained in the positive electrode active material layer are not particularly limited. The composition ratio can be adjusted by appropriately referring to the known knowledge regarding lithium ion secondary batteries.

[0067]

The positive electrode (positive electrode active material layer) can be formed using any of the following methods: kneading sputtering, vapor deposition, CVD, PVD, ion plating, and thermal spraying, in addition to the usual method of applying (coating) a slurry.

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[0068]

The porosity of the positive electrode active material layer ranges from 10 to 45% by volume, preferably from 15 to 40% by volume, more preferably from 20 to 35% by volume, relative to the total volume of the positive electrode active material layer. If the porosity is within the above range, the pores in the active material layer can effectively function as a path for supplying the electrolyte (Li^+ ions) so as to impregnate the electrolyte into the active material layer and promote the electrode reaction without impairing the characteristics such as battery capacity or strength.

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[0069]

The thickness of the positive electrode active material layer (active material layer on one side of the current collector) is also not limited, and conventional known findings about batteries may be referenced as appropriate. To take one example, the thickness of the

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positive electrode active material layer is usually about 1 to 500 μm , preferably 50 to 100 μm , taking into consideration the intended use of the battery (emphasis on output, emphasis on energy, and the like) and ion conductivity.

[0070]

[Negative electrode active material layer]

In the non-aqueous electrolyte rechargeable battery of the present embodiment, the negative electrode active material layer 13 is provided with, as a negative electrode active material, at least one of a Si material which is one or more kinds selected from the group consisting of SiO_x (x represents the number of oxygen atoms satisfying the valence of Si) which is a mixture of amorphous SiO_2 particles and Si particles, and a Si-containing alloy, and a carbon material which is one or more kinds selected from the group consisting of graphite, non-graphitizing carbon, and amorphous carbon.

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[0071]

That is, the negative electrode active material layer 13 essentially contains, a material selected from the group consisting of SiO_x and Si-containing alloys (these are also collectively referred to as "Si materials") and/or a carbon material as the negative electrode active material. Preferably, the negative electrode active material layer 13 in each single cell battery layer contains both a Si material and a carbon material.

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[0072]

In the present specification, the Si material means SiO_x (where x represents the number of oxygen atoms satisfying the valence of Si), which is a mixture of amorphous SiO_2 particles and Si particles, and Si-containing alloys. Only one of these may be used as the Si material, or two or more may be used together. These Si materials are described in detail below.

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[0073]

(SiO_x)

SiO_x is a mixture of amorphous SiO_2 particles and Si particles, where x is the number of oxygen satisfying the valence of Si. There is no particular limitation on the specific value of x , which may be set as appropriate.

[0074]

Additionally, the above SiO_x may be conductive SiO_x particles wherein the surface of the SiO_x particle is coated with a conductive material by a mechanical surface fusion treatment. Such a configuration makes it easier for the Si in the SiO_x particles to desorb and insert lithium ions, allowing reactions in the active material to proceed more smoothly. In this case, the content of the conductive substance in the conductive SiO_x particles is preferably 1 to 30 mass%, and more preferably 2 to 20 mass%.

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[0075]

SiO_x production method

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The method for producing SiO_x according to the present embodiment is not particularly limited, and such may be produced by utilizing various conventionally known methods. In other words, there is minimal difference in the amorphous state and properties depending on the production method, and therefore, all possible production methods can be applied.

[0076]

The following methods can be used to prepare SiO_x . First, Si powder and SiO_2 powder are combined as raw materials in predetermined proportions, mixed, granulated and dried, and then heated in an inert gas atmosphere (830°C or higher) or in a vacuum (1,100°C or higher and 1,600°C or lower) to form SiO (sublimation). The gaseous SiO generated by sublimation is vapor-deposited on a deposition substrate (substrate temperature is 450° C.or higher and 800° C.or lower) to deposit an SiO precipitate. Thereafter, the SiO precipitates are removed from the deposition substrate and pulverized using a ball mill or the like to obtain SiO_x powder.

[0077]

The value of x can be determined by fluorescent X-ray analysis. For example, this can be obtained by using the fundamental parameter method in X-ray fluorescent analysis using O-K α radiation. An example of an X-ray fluorescence analysis is the RIX3000 manufactured by Rigaku Electric Industry (Co., Ltd.). As for the conditions for X-ray fluorescence analysis, for example, rhodium (Rh) should be used as the target, the tube voltage should be 50 kV, and the tube current 50 mA. The x value obtained here is calculated from the intensity of the O-K α radiation detected in the measurement area on the substrate, and is therefore the average value for the measurement area.

[0078]

(Si-containing alloys)

The Si-containing alloy is not particularly limited as long as it is an alloy with another metal containing Si, and conventionally known findings may be referred to as appropriate. Here, as preferred embodiments of Si-containing alloys, $\text{Si}_x\text{Ti}_y\text{Ge}_z\text{A}_a$, $\text{Si}_x\text{Ti}_y\text{Zn}_z\text{A}_a$, $\text{Si}_x\text{Ti}_y\text{Sn}_z\text{A}_a$, $\text{Si}_x\text{Sn}_y\text{Al}_z\text{A}_a$, $\text{Si}_x\text{Sn}_y\text{V}_z\text{A}_a$, $\text{Si}_x\text{Sn}_y\text{C}_z\text{A}_a$, $\text{Si}_x\text{Zn}_y\text{V}_z\text{A}_a$, $\text{Si}_x\text{Zn}_y\text{Sn}_z\text{A}_a$, $\text{Si}_x\text{Zn}_y\text{Al}_z\text{A}_a$, $\text{Si}_x\text{Zn}_y\text{C}_z\text{A}_a$, $\text{Si}_x\text{Al}_y\text{C}_z\text{A}_a$, and $\text{Si}_x\text{Al}_y\text{Nb}_z\text{A}_a$ (wherein A is an unavoidable impurity in the formula; furthermore, x, y, z, and a represent values in mass%, where $0 < x < 100$, $0 < y < 100$, $0 \leq z < 100$, and $0 \leq a < 0.5$, and $x + y + z + a = 100$). More preferably, the alloy contains Si which further satisfies $0 < z < 100$ in the above formula. By using these Si-containing alloys as negative electrode active materials, the amorphous-crystalline phase transition can be suppressed and cycle life can be improved during Li alloying by appropriately selecting the prescribed first and second additive elements. This also results in a higher capacity than conventional negative electrode active materials, such as carbon-based negative electrode active materials.

[0079]

The average particle size of the SiO_x or Si-containing alloy, which is the Si material, is not

particularly limited as long as it is approximately the same as the average particle size of the negative electrode active material contained in the existing negative electrode active material layer 13. From the viewpoint of high output, the D50 of the secondary particle size is preferably in the range of 1 to 20 μm . The D90 of the secondary particle size is preferably in the range of 5 to 100 μm . Here, the secondary particle size of the Si material is the value obtained by the laser diffraction method. However, it goes without saying that there is no limitation to the above range, and it is possible to be out of the above range as long as the effect of the present embodiment can be effectively expressed. In addition, the shape of the Si material is not particularly limited, and may be spherical, elliptical, cylindrical, polygonal columnar, flaky, amorphous, or irregularly shaped.

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[0080]

Method for producing Si-containing alloy

The method of manufacturing the Si-containing alloys in this form is not particularly limited, and various conventionally known manufacturing methods can be used to produce the alloys. The following production methods are examples but not limited in any way to the production of Si-containing alloys.

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[0081]

First, a process is performed to mix raw materials of Si-containing alloys to obtain a mixed powder. In this process, the raw materials for the alloy are mixed with consideration to the composition of the Si-containing alloy to be obtained. The raw material for the alloy is not limited to any particular form, as long as the required ratio of the elements can be achieved as a Si-containing alloy. For example, it is possible to use a mixture of individual elements constituting a Si-containing alloy in the desired ratio, or an alloy, solid solution, or intermetallic compound with the desired elemental ratio. In addition, the raw materials are usually mixed in powder form. This produces a mixed powder consisting of raw materials.

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[0082]

Next, the mixed powder obtained above is subjected to an alloying treatment. In this way, Si-containing alloys can be obtained for use as negative electrode active materials for non-aqueous electrolyte rechargeable batteries.

[0083]

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The alloying treatment methods include solid, liquid, and vapor phase methods, such as mechanical alloying, arc plasma melting, casting, gas atomization, liquid quenching, ion beam sputtering, vacuum deposition, plating, and vapor phase chemical reaction methods. Among them, the mechanical alloying method is the preferred for alloying process. Alloying treatment via the mechanical alloying method is preferred because the phase state can be easily controlled. Furthermore, prior to the alloying process, a process for melting the raw material and a process for quenching and solidifying the molten material may be included.

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[0084]

By performing the alloying process described above, the structure can be made to consist of a matrix/silicide phase. In particular, when the alloying treatment time is 12 hours or longer, Si-containing alloys that are capable of exhibiting the desired cycle durability can be obtained. Note, that the duration of the alloying process is preferably 24 hours or more, more preferably 30 hours or more, even more preferably 36 hours or more, even more preferably 42 hours or more, and most preferably 48 hours or more. While there is no particular set upper limit for the time required for the alloying process, it normally should be no longer than 72 hours.

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[0085]

The above mentioned alloying process is usually performed in a dry atmosphere, however, the grain size distribution after the alloying process may have a very large range of sizes. For this reason, it is preferable to perform a milling and/or classification process to adjust the particle size.

[0086]

It is possible to control the particle size by classifying, pulverizing, or otherwise processing the particles obtained by the alloying process as appropriate. Examples of classification methods include air classification, mesh filtration, and sedimentation. In addition, the pulverization conditions are not limited, and the milling time, rotation speed, and the like using a suitable milling machine (for example, a device that can also be used in the mechanical alloying method, such as a planetary ball mill) should be set as appropriate. An example of pulverization conditions is the use of a planetary ball mill or other milling machine with a rotational speed of 200-400 rpm for 30 minutes to 4 hours.

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[0087]

In addition, the negative electrode active material layer can be formed by coating a negative electrode active material slurry containing the negative electrode active material, binder, conductivity aid, and solvent on the current collector, but further pulverization may be performed when preparing the negative electrode active material slurry. The pulverizing means is not particularly limited, and any known means can be appropriately adopted. The pulverization conditions are not particularly limited, and the grinding time, rotation speed, and the like may be appropriately set. An example of pulverization conditions is pulverize at a rotational speed of 200-400 rpm for 30 minutes to 4 hours. The pulverization process may be carried out in several parts with cooling time in between to prevent the solvent from being heated and denatured by the pulverization process.

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[0088]

(Carbon materials)

Carbon materials that may be used in the present invention are one or more selected from the group consisting of graphite, non-graphitizing carbon, and amorphous carbon. In detail,

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this is one or more selected from: graphite (graphite), which is a highly crystalline carbon such as natural graphite, artificial graphite, and the like; hard non-graphitizing carbon such as hard carbon; and amorphous carbon like carbon black, such as Ketjen black, acetylene black, channel black, lamp black, oil furnace black, thermal black, and the like. Of these, it is preferable to use graphite such as natural graphite or artificial graphite.

[0089]

In the present embodiment, the carbon material is used together with the above-mentioned Si material as the negative electrode active material to maintain higher cycle and rate characteristics, and also to exhibit well-balanced properties with high initial capacity.

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[0090]

As a result of the mixing of carbon materials, the initial capacity can be reduced due to the lower content of Si material in the negative electrode active material layer. However, since the carbon material itself is reactive with lithium ions, the degree of initial capacity reduction is relatively small. In other words, the negative electrode active material in this form has a greater effect of improving cycle characteristics compared to the effect of lowering initial capacity.

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[0091]

Furthermore, carbon materials are less likely to undergo volume changes when reacting with lithium ions, compared to Si materials such as SiO_x and Si-containing alloys. Therefore, even when the volume change of SiO_x or the Si-containing alloy is large, the effect of volume change of the negative electrode active material due to lithium reaction can be made relatively minor when the negative electrode active material as a whole is considered.

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[0092]

In addition, the inclusion of carbon materials can improve the electricity consumption (Wh). More specifically, the carbon material has a relatively low potential compared to the Si material. As a result, the relatively high potential of the Si material can be reduced. In this way, the potential of the entire negative electrode is reduced, which improves the power consumption (Wh). Such action is particularly advantageous when used, for example, in vehicle applications.

[0093]

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As for the shape of the carbon material, there are no limitations, and it can be spherical, elliptical, cylindrical, polygonal, scaly, or irregularly shaped.

[0094]

In some cases, a combination of negative electrode active material other than the two types of negative electrode active materials mentioned above may be used. Examples of the negative electrode active material that can be used in combination include lithium-transition metal composite oxides (for example, $\text{Li}_4\text{Ti}_5\text{O}_{12}$), metal materials, and lithium alloy-based

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negative electrode materials. Of course, other negative electrode active materials may be used.

[0095]

The negative electrode active material layer preferably contains a negative electrode active material represented by the following formula (1).

[0096]

$$\alpha \text{ (Si material)} + \beta \text{ (carbon material)} \quad (1)$$

In formula (1), the Si material is one or more selected from the group consisting of SiO_x (x is the number of oxygen atoms satisfying the valence of Si), which is a mixtures of amorphous SiO_2 particles and Si particles, and Si-containing alloys, as described above. As described above, carbon materials are one or more selected from the group consisting of graphite, non-graphitizing carbon, and amorphous carbon. Further, α and β represent the mass% of each component in the negative electrode active material layer, and are within the ranges of $80 \leq \alpha + \beta \leq 98$, $0.1 \leq \alpha \leq 40$, and $58 \leq \beta \leq 97.9$.

[0097]

As is clear from formula (1), the content of the Si material (α) in the negative electrode active material layer is preferably 0.1 to 40 mass%. The content of carbon material (β) is 58 to 97.9 mass%. Furthermore, their total content ($\alpha + \beta$) is 80 to 98 mass%.

[0098]

The mixing ratio of the Si material and the carbon material in the negative electrode active material is not particularly limited and can be appropriately selected depending on the desired application, and the like. In the present embodiment, it is preferable to use a relatively low content of Si material and a relatively high content of carbon material as the mixing ratio of Si material and carbon material. In particular, it is preferred that the Si material content (α) in the negative electrode active material is 0.5 to 40 mass%, 1 to 30 mass% is more preferred, and 1 to 20 mass% is even more preferred. When the content of Si material in the negative electrode active material layer is 0.1 mass% or more, a high initial capacity can be obtained. On the other hand, when the Si material content is 40 mass% or less, high cycle properties can be obtained. The content (β) of the carbon material in the negative electrode active material is preferably in the range of 58 to 97.5 mass%, more preferably 68 to 97 by mass%, and even more preferably 78 to 97 by mass%. When the content of carbon material in the negative electrode active material layer is 58 mass% or more, high cycle properties can be obtained. On the other hand, when the content of the carbon material is 97.9 mass% or less, a high initial capacity can be obtained.

[0099]

The total content of Si material and carbon material ($\alpha + \beta$) in the negative electrode active material layer is not particularly limited and can be selected according to the desired

application, and the like. The total content ($\alpha+\beta$) of the Si material and the carbon material in the negative electrode active material layer is, for example, 80 to 98 mass%, preferably 85 to 97 mass%, and more preferably 90 to 97 mass%. When the total content of Si material and carbon material in the negative electrode active material layer is 80 mass% or more, it is preferred because the weight energy density is higher. On the other hand, when the total content of the Si material and the carbon material is 98 mass% or less, the contents of the binder and the conductive agent can be sufficiently ensured, and thus favorable battery performance can be obtained.

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[0100]

(Binder)

In the present embodiment, the negative electrode active material layer preferably contains a binder. The binder contained in the negative electrode active material layer preferably contains a water-based binder. In addition to the ease of procuring water as a raw material, water based binders have the advantage that capital investment in the production line can be significantly reduced and environmental impact can be reduced because it is only water vapor that is generated during drying.

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[0101]

The aqueous binder refers to a binder that uses water as a solvent or dispersion medium, and specific examples of the aqueous binder include thermoplastic resins, polymers having rubber elasticity, water-soluble polymers, and mixtures of these. Here, the binder using water as a dispersion medium includes all those expressed as latex or emulsion, and refers to a polymer emulsified with water or suspended in water, such as polymer latexes emulsion-polymerized in a self-emulsifying system.

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[0102]

Specific examples of the aqueous binder include styrene-based polymers (styrene-butadiene rubber (SBR), styrene-vinyl acetate copolymer, styrene-acrylic copolymer, and the like), acrylonitrile-butadiene rubber, methyl methacrylate-butadiene rubber, (meth)acrylic polymers (polyethyl acrylate, polyethyl methacrylate, polypropyl acrylate, polymethyl methacrylate (methyl methacrylate rubber), polypropyl methacrylate, polyisopropyl acrylate, polyisopropyl methacrylate, polybutyl acrylate, polybutyl methacrylate, polyhexyl acrylate, , polyhexyl methacrylate, polyethylhexyl acrylate, polyethylhexyl methacrylate, polylauryl acrylate, polylauryl methacrylate, and the like), polytetrafluoroethylene, polyethylene, polypropylene, ethylene-propylene copolymer, polybutadiene, butyl rubber, fluororubber, polyethylene oxide, polyepichlorohydrin, polyphosphazene, polyacrylonitrile, polystyrene, ethylene-propylene-diene copolymer, polyvinylpyridine, chlorosulfonated polyethylene, polyester resin, phenol resin, epoxy resin, and the like. These aqueous binders may be used alone or in a combination of two or more types.

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[0103]

From the viewpoint of binding properties, the aqueous binder preferably contains at least one rubber-based binder selected from the group consisting of styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber, methyl methacrylate-butadiene rubber, and methyl methacrylate rubber. Furthermore, the aqueous binder preferably contains styrene-butadiene rubber (SBR) because of its good binding properties.

[0104]

When a aqueous binder is used, it is preferable to use a thickener in combination. This is because although the aqueous binder has a strong binding property (binding effect), it does not have a sufficient thickening property. Therefore, merely adding a aqueous binder to the aqueous slurry during electrode production does not provide a sufficient thickening effect. Therefore, a thickening agent having excellent viscosity-increasing properties is used to impart viscosity to the aqueous binder. The thickener is not particularly limited, and examples thereof include polyvinyl alcohol (average polymerization degree is preferably 200 to 4000, more preferably 1000 to 3000, and saponification degree is preferably 80 mol% or more, more preferably 90 mol% or more) and modified products thereof (1 to 80 mol% saponification product of vinyl acetate units of copolymers having a molar ratio of ethylene/vinyl acetate = (2/98) to (30/70), 1 to 50 mol% partial acetalization product of polyvinyl alcohol, and the like), starch and modified products thereof (oxidized starch, phosphated starch, cationic starch, and the like), cellulose derivatives (carboxymethylcellulose (CMC), methylcellulose, hydroxypropylcellulose, hydroxyethylcellulose, and salts thereof, and the like), polyvinylpyrrolidone, polyacrylic acid (salt), polyethylene glycol, copolymers of (meth)acrylamide and/or (meth)acrylate salts [(meth)acrylamide polymers, (meth)acrylamide-(meth)acrylate salt copolymers, (meth)acrylate alkyl (carbon number 1 to 4) ester-(meth)acrylate salt copolymers, and the like], styrene-maleate copolymers, Mannich-modified polyacrylamide, formalin condensation resins (urea-formalin resin, melamine-formalin resin, and the like), polyamidopolyamine or dialkylamine-epichlorohydrin copolymers, polyethyleneimine, casein, soybean protein, synthetic protein, and galactomannan derivatives. These thickeners may be used alone or in a combination of two or more types.

[0105]

When styrene-butadiene rubber (SBR), which is suitable as the aqueous binder, is used, it is preferable to use the following thickeners in combination from the viewpoint of improving the coatability. Suitable thickening agents for use in combination with styrene-butadiene rubber (SBR) include polyvinyl alcohol and its modifications, starch and its modifications, cellulose derivatives (such as carboxymethyl cellulose (CMC), methyl cellulose, hydroxyethyl cellulose, and salts thereof), polyvinylpyrrolidone, polyacrylic acid (salts), or polyethylene glycol. Among these, it is preferable to combine styrene-butadiene rubber (SBR) with

carboxymethyl cellulose (CMC) or a salt thereof (CMC (salt)). The mass ratio of the SBR (aqueous binder) to the thickener is not particularly limited, but it is preferable that the SBR (aqueous binder):thickener content ratio is 1:(0.3 to 0.7).

[0106]

When the negative electrode active material layer contains a binder, the content of the aqueous binder in the binder used in the negative electrode active material layer is preferably 80 to 100 mass%, more preferably 90 to 100 mass%, and still more preferably 100 mass%. Examples of binders other than the aqueous binder include binders used in the positive electrode active material layer.

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[0107]

The amount of the binder contained in the negative electrode active material layer is not particularly limited as long as it is an amount capable of binding the active material, but is preferably 0.5 to 15 mass%, more preferably 1 to 10 mass%, even more preferably 1 to 8 mass%, particularly preferably 1 to 4 mass%, and most preferably 1.5 to 3.5 mass%, relative to 100 mass% of the total amount of the negative electrode active material layer. Since the aqueous binder has a high binding strength, an active material layer can be formed by adding a smaller amount of the aqueous binder than with an organic solvent binder. The amount of the thickener contained in the negative electrode active material layer is determined from the content mass ratio of the aqueous binder (SBR) to the thickener, the amount of the binder contained in the negative electrode active material layer, and the content of the aqueous binder in the binder contained in the negative electrode active material layer.

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[0108]

In addition to active materials and binders, the negative electrode active material layer further contains other additives such as conductivity aids, electrolytes (polymer matrix, ion-conductive polymers, electrolyte, and the like), and lithium salts to enhance ion conductivity, in addition to the thickening agents described above, as needed.

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[0109]

(Conductive agent)

A conductive agent refers to an additive that is blended to improve the conductivity of the positive electrode active material layer or the negative electrode active material layer. Examples of the carbon material include, but are not limited to, carbon black such as acetylene black, carbon black, furnace black, and other carbon powders, such as channel black and thermal black, and various carbon fibers such as vapor grown carbon fiber (VGCF; registered trademark). When the active material layer contains a conductive agent, an electronic network is effectively formed inside the active material layer, which can contribute to improving the output characteristics of the battery.

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[0110]

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The conductivity aid in the negative electrode active material layer is preferably 0.1 to 10 mass%, more preferably 0.5 to 8 mass%. The following effects are achieved by specifying the ratio (content) of conductive agent within the above range. In other words, the electronic conductivity can be sufficiently ensured without interfering with the electrode reaction, and the decrease in energy density due to the decrease in electrode density can be suppressed, and in turn, the energy density can be increased due to the increase in electrode density.

[0111]

(Lithium salt)

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The lithium salt is contained in the negative electrode active material layer as a result of the above electrolyte permeating into the negative electrode active material layer. Therefore, the specific form of the lithium salt that can be contained in the negative electrode active material layer is the same as that of the lithium salt that constitutes the electrolyte. Examples of lithium salts include $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$, LiPF_6 , LiBF_4 , LiClO_4 , LiAsF_6 , LiCF_3SO_3 , and the like.

[0112]

(Ion Conductive Polymer)

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Examples of ion-conducting polymers include polyethylene oxide (PEO) and polypropylene oxide (PPO) polymers.

[0113]

The compounding ratio of the components contained in the negative electrode active material layer are not particularly limited. The composition ratio can be adjusted by appropriately referring to the known knowledge regarding lithium ion secondary batteries.

[0114]

The average particle size of the carbon material is not particularly limited, but the secondary particle size D50 is preferably 1 to 50 μm , and more preferably 2 to 25 μm . Here, the secondary particle size of the carbon material is the value obtained by the laser diffraction method. In this case, in comparison with the average particle size of the above Si material, the average particle size of the carbon material may be the same as or different from the average particle size of the Si material, but is preferably different. It is more preferable that the average particle size of the Si material is smaller than the average particle size of the carbon material.

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[0115]

The porosity of the negative electrode active material layer ranges from 10 to 45% by volume, preferably from 15 to 40% by volume, more preferably from 20 to 35% by volume, relative to the total volume of the negative electrode active material layer. If the porosity is within the above range, the pores in the active material layer can effectively function as a path for supplying the electrolyte (Li^+ ions) so as to impregnate the electrolyte into the active material layer and promote the electrode reaction without impairing the characteristics such

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as battery capacity or strength.

[0116]

In this embodiment, the density of the negative electrode active material layer is not particularly limited, but from the viewpoint of high density, it is preferably 1.5 to 1.8 g/cm³, and more preferably 1.5 to 1.7 g/cm³.

[0117]

The coating amount (area weight) of the negative electrode active material layer on one side is not particularly limited, but is preferably 5 to 20 mg/cm², and more preferably 8 to 15 mg/cm². When the coating amount on one side of the negative electrode active material layer is 20 mg/cm² less, the rate characteristics of the battery can be improved. On the other hand, if the coating amount on one side of the negative electrode active material layer is 5 mg/cm² or more, a sufficient capacity can be ensured.

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[0118]

The thickness of the negative electrode active material layer (active material layer on one side of the current collector) is also not limited, and conventional known findings about batteries may be referenced as appropriate. To take one example, the thickness of the negative electrode active material layer is usually about 1 to 500 μm, preferably 50 to 150 μm, taking into consideration the intended use of the battery (emphasis on output, emphasis on energy, and the like) and ion conductivity.

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[0119]

<Current collector>

Current collectors (11, 12) are made of a conductive material. The size of the current collector is determined according to the intended use of the battery. For example, if the battery is to be used in a large battery that requires high energy density, a current collector with a large area is used.

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[0120]

There is no particular limitation on the thickness of the current collector. The thickness of the current collector is usually about 1 to 100 μm.

[0121]

There is no particular limitation on the shape of the current collector. In the stacked battery 10 illustrated in FIG. 2, in addition to the current collecting foil, a mesh shape (such as an expanded grid) or the like may be used.

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[0122]

There are no restrictions on the materials that make up the current collector. For example, a metal, a conductive polymer material, or a resin in which a conductive filler is added to a non-conductive polymer material may be used.

[0123]

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Specific examples of metals include aluminum, nickel, iron, stainless steel, titanium, and copper. In addition to these, a clad material of nickel and aluminum, a clad material of copper and aluminum, or a plated material of a combination of these metals can be preferably used. Alternatively, the foil may be a metal foil having a surface coated with aluminum. Among these, aluminum, stainless steel, copper and nickel are preferred from the viewpoints of electronic conductivity, battery operating potential, adhesion of the negative electrode active material to the current collector by sputtering, and the like.

[0124]

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Examples of the conductive polymer material include polyaniline, polypyrrole, polythiophene, polyacetylene, polyparaphenylene, polyphenylenevinylene, polyacrylonitrile, and polyoxadiazole. Such conductive polymer materials have sufficient conductivity without the addition of a conductive filler, and are therefore advantageous in terms of facilitating the production process and reducing the weight of the current collector.

[0125]

Examples of non-conductive polymeric materials include polyethylene (PE; high density polyethylene (HDPE), low density polyethylene (LDPE), and the like), polypropylene (PP), polyethylene terephthalate (PET), polyethernitrile (PEN), polyimide (PI), polyamideimide (PAI), polyamide (PA), polytetrafluoroethylene (PTFE), styrene-butadiene rubber (SBR), polyacrylonitrile (PAN), polymethyl acrylate (PMA), polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), polyvinylidene fluoride (PVdF), and polystyrene (PS). Such non-conductive polymeric materials may have excellent electric potential resistance or solvent resistance.

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[0126]

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A conductive filler may be added to the above conductive polymer material or non-conductive polymer material, if necessary. In particular, when the resin serving as the base material of the current collector is made of only a non-conductive polymer, a conductive filler is inevitably required to impart conductivity to the resin.

[0127]

The conductive filler can be any material having electrical conductivity without any particular limitation. For example, materials having excellent electrical conductivity, potential resistance, or lithium ion blocking properties include metals and conductive carbon. The metal is not particularly limited, but preferably includes at least one metal selected from the group consisting of Ni, Ti, Al, Cu, Pt, Fe, Cr, Sn, Zn, In, Sb, and K, or an alloy or metal oxide containing such a metal. The conductive carbon is not particularly limited. Preferably, the filler contains at least one selected from the group consisting of acetylene black, Vulcan, black pearl, carbon nanofiber, Ketjen black, carbon nanotube, carbon nanohorn, carbon nanoballoon, and fullerene.

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[0128]

The amount of the conductive filler added is not particularly limited as long as it is an amount that can impart sufficient conductivity to the current collector, and is generally about 5 to 35 mass%.

[0129]

<Separator (electrolyte layer)>

The separator has a function of retaining the electrolyte to ensure lithium ion conductivity between the positive electrode and the negative electrode, and a function of acting as a partition between the positive electrode and the negative electrode.

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[0130]

Examples of the form of the separator include a porous sheet separator made of a polymer or fiber that absorbs and retains the electrolyte, and a nonwoven fabric separator.

[0131]

As the separator made of a porous sheet of polymer or fiber, for example, a microporous sheet (microporous membrane) may be used. Specific examples of the porous sheet made of the polymer or fiber include polyolefins such as polyethylene (PE) and polypropylene (PP); laminates of a plurality of these laminates (for example, a laminate having a three-layer structure of PP/PE/PP), polyimide, aramid, hydrocarbon resins such as polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP), and microporous (microporous membrane) separators made of glass fibers.

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[0132]

The thickness of the microporous (microporous membrane) separator cannot be unequivocally defined because it varies depending on the application. As an example, in applications such as secondary batteries for driving motors in electric vehicles (EVs), hybrid electric vehicles (HEVs), fuel cell vehicles (FCVs), and the like, a single layer or multiple layers having a thickness of 4 to 60 μm is desirable. The microporous (microporous membrane) separator desirably has a maximum pore size of 1 μm or less (usually a pore size of about several tens of nm).

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[0133]

As the nonwoven fabric separator, conventionally known materials such as cotton, rayon, acetate, nylon, polyester; polyolefins such as PP and PE; polyimide, aramid, and the like may be used alone or in combination. The bulk density of the nonwoven fabric is not particularly limited as long as sufficient battery characteristics can be obtained with the impregnated electrolyte. Furthermore, the thickness of the nonwoven fabric separator may be the same as that of the electrolyte layer, and is preferably 5 to 200 μm , and particularly preferably 10 to 100 μm .

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[0134]

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As described above, the separator also includes an electrolyte. The electrolyte is not particularly limited as long as it can exhibit such functions, and a liquid electrolyte or a gel polymer electrolyte is used. By using a gel polymer electrolyte, the distance between the electrodes is stabilized, the occurrence of polarization is suppressed, and durability (cycle characteristics) is improved.

[0135]

The liquid electrolyte functions as a carrier for lithium ions. The liquid electrolyte constituting the electrolyte layer has a form in which a lithium salt is dissolved in an organic solvent that serves as a plasticizer. Examples of organic solvents used include ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate and other carbonates. In addition, as the lithium salt, compounds that can be added to the active material layer of an electrode, such as $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$, LiPF_6 , LiBF_4 , LiClO_4 , LiAsF_6 , LiTaF_6 , and LiCF_3SO_3 , can be similarly used. The liquid electrolyte may further contain additives other than the above components. Specific examples of such additives include vinylene carbonate, methylvinylene carbonate, dimethylvinylene carbonate, phenylvinylene carbonate, diphenylvinylene carbonate, ethylvinylene carbonate, diethylvinylene carbonate, vinyl ethylene carbonate, 1,2-divinylethylene carbonate, 1-methyl-1-vinyl ethylene carbonate, 1-methyl-2-vinyl ethylene carbonate, 1-ethyl-1-vinyl ethylene carbonate, 1-ethyl-2-vinyl ethylene carbonate, vinyl vinylene carbonate, allyl ethylene carbonate, vinyloxymethyl ethylene carbonate, allyloxymethyl ethylene carbonate, acryloxymethyl ethylene carbonate, methacryloxymethyl ethylene carbonate, ethynyl ethylene carbonate, propargyl ethylene carbonate, ethynyloxymethyl ethylene carbonate, propargyloxyethylene carbonate, methylene ethylene carbonate, and 1,1-dimethyl-2-methylene ethylene carbonate. Vinylene carbonate, methyl vinylene carbonate, and vinyl ethylene carbonate are particularly preferred, with vinylene carbonate and vinyl ethylene carbonate being more preferred. Only one type of these additives may be used, or two or more may be used in combination.

[0136]

The gel polymer electrolyte has a configuration in which the above liquid electrolyte is injected into a matrix polymer (host polymer) made of an ion-conductive polymer. The use of a gel polymer electrolyte as the electrolyte is advantageous in that it eliminates the fluidity of the electrolyte and makes it easy to block ionic conductivity between the layers. Examples of the ion-conductive polymer used as the matrix polymer (host polymer) include polyethylene oxide (PEO), polypropylene oxide (PPO), polyethylene glycol (PEG), polyacrylonitrile (PAN), polyvinylidene fluoride-hexafluoropropylene (PVdF-HEP), poly(methyl methacrylate) (PMMA), and copolymers thereof.

[0137]

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The matrix polymer of the gel electrolyte can exhibit excellent mechanical strength by forming a crosslinked structure. To form a crosslinked structure, a polymerizable polymer for forming the polymer electrolyte (for example, PEO or PPO) may be subjected to a polymerization treatment such as thermal polymerization, ultraviolet polymerization, radiation polymerization, or electron beam polymerization using an appropriate polymerization initiator. [0138]

Furthermore, the separator is preferably a separator in which a heat-resistant insulating layer is laminated on a porous substrate such as a porous sheet separator or a nonwoven fabric separator (separator with a heat-resistant insulating layer). The heat-resistant insulating layer is a ceramic layer that includes inorganic particles and a binder. The heat-resistant insulating layer-attached separator has a high heat resistance, that is, a melting point or thermal softening point of 150 °C or higher, preferably 200 °C or higher. By providing the heat-resistant insulating layer, the internal stress of the separator that increases when the temperature rises is alleviated, and therefore the effect of suppressing thermal shrinkage can be obtained. As a result, it is possible to prevent the induction of short circuits between the battery electrodes, resulting in a battery configuration in which performance degradation due to temperature rise is less likely to occur. Furthermore, by providing the heat-resistant insulating layer, the mechanical strength of the separator with the heat-resistant insulating layer is improved, and the separator is less likely to break. Furthermore, due to the effect of suppressing thermal shrinkage and the high mechanical strength, the separator is less likely to curl during the battery manufacturing process. [0139]

The inorganic particles in the heat-resistant insulating layer contribute to the mechanical strength of the heat-resistant insulating layer and the effect of suppressing thermal shrinkage. The material used as the inorganic particles is not particularly limited. Examples include oxides (SiO_2 , Al_2O_3 , ZrO_2 , TiO_2), hydroxides, and nitrides of silicon, aluminum, zirconium, and titanium, as well as composites thereof. These inorganic particles may be derived from mineral resources such as boehmite, zeolite, apatite, kaolin, mullite, spinel, olivine, and mica, or may be artificially produced. Furthermore, only one type of these inorganic particles may be used, or two or more may be used in combination. Among these, from the viewpoint of cost, it is preferable to use silica (SiO_2) or alumina (Al_2O_3), and it is more preferable to use alumina (Al_2O_3). [0140]

The weight of the heat-resistant particles is not particularly limited, but is preferably 5 to 15 g/m². This range is preferable in that sufficient ion conductivity is obtained and heat resistance strength is maintained. [0141]

The binder in the heat-resistant insulating layer serves to bond the inorganic particles together and between the inorganic particles and the porous substrate. The binder allows the heat-resistant insulating layer to be formed stably and prevents peeling between the porous substrate and the heat-resistant insulating layer.

[0142]

The binder used in the heat-resistant insulating layer is not particularly limited, and examples of the binder that can be used include compounds such as carboxymethyl cellulose (CMC), polyacrylonitrile, cellulose, ethylene-vinyl acetate copolymer, polyvinyl chloride, styrene-butadiene rubber (SBR), isoprene rubber, butadiene rubber, polyvinylidene fluoride (PVdF), polytetrafluoroethylene (PTFE), polyvinyl fluoride (PVF), and methyl acrylate. Of these, it is preferable to use carboxymethyl cellulose (CMC), methyl acrylate, or polyvinylidene fluoride (PVdF). Only one type of these compounds may be used, or two or more may be used in combination.

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[0143]

The content of the binder in the heat resistant insulating layer is preferably 2 to 20 mass% relative to 100 mass% of the heat resistant insulating layer. When the binder content is 2 mass% or more, the peel strength between the heat resistant insulating layer and the porous substrate can be increased, and the vibration resistance of the separator can be improved. On the other hand, when the content of the binder is 20 mass% or less, the gaps between the inorganic particles are appropriately maintained, so that sufficient lithium ion conductivity can be ensured.

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[0144]

The heat shrinkage rate of the separator with a heat resistant insulation layer is preferably 10% or less in both MD and TD after being held for 1 hour under conditions of 150°C and 2 gf/cm². By using such a material with high heat resistance, it is possible to effectively prevent the separator from shrinking even if the amount of heat generated by the positive electrode increases and the temperature inside the battery reaches 150°C. As a result, it is possible to prevent the induction of short circuits between the battery electrodes, resulting in a battery configuration in which performance degradation due to temperature rise is less likely to occur.

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[0145]

<Current collector plate (tab)>

In a lithium ion rechargeable battery, a current collector (tab) electrically connected to a current collector is extended from the laminate film that is the casing of the battery in order to extract current outside the battery.

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[0146]

The material constituting the current collector plate is not particularly limited, and any known highly conductive material that has been conventionally used as a current collector

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plate for lithium ion secondary batteries may be used. The current collector plate is preferably made of a metal material such as aluminum, copper, titanium, nickel, stainless steel (SUS), or an alloy thereof. From the viewpoints of light weight, corrosion resistance, and high electrical conductivity, aluminum and copper are more preferable, and aluminum is particularly preferable. The positive electrode current collector plate (positive electrode tab) and the negative electrode current collector plate (negative electrode tab) may be made of the same material or different materials.

[0147]

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Furthermore, there is no particular limitation on the removal of tabs 58 and 59 illustrated in FIG. 3. The positive electrode tab 58 and the negative electrode tab 59 may be pulled out from the same side, or the positive electrode tab 58 and the negative electrode tab 59 may each be divided into multiple tabs and pulled out from each side; this is not limited to what is illustrated in FIG. 3.

[0148]

<Seal portion>

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The seal portion is a part specific to series-stacked batteries, and has the function of preventing leakage of the electrolyte layer. In addition, it is also possible to prevent contact between adjacent current collectors in the battery and short circuits caused by slight irregularities in the ends of the laminated electrodes.

[0149]

The constituent material of the seal portion is not particularly limited, but may be polyolefin resin such as polyethylene or polypropylene, epoxy resin, rubber, polyimide, or the like. Of these, it is preferable to use polyolefin resins from the viewpoints of corrosion resistance, chemical resistance, film-forming properties, and economic efficiency.

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[0150]

<Positive electrode terminal lead and negative electrode terminal lead>

The negative electrode and positive electrode terminal leads may be made of any material that is used in known stacked secondary batteries. Note that the portion removed from the battery casing is preferably covered with a heat-resistant insulating heat-shrinkable tube or the like to prevent it from coming into contact with peripheral devices or wiring, causing an electric leakage and affecting products (for example, automobile parts, particularly electronic devices, and the like).

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[0151]

<Battery casing>

As the battery casing, a conventionally known metal can case may be used. Alternatively, the power generating element 21 may be packaged in a laminate film 29 as illustrated in FIG. 2 as a casing. The laminate film may have a three-layer structure in which, for example,

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polypropylene, aluminum, and nylon are laminated in this order. By using such a laminate film, it is possible to easily open the exterior casing, add the capacity recovery material, and reseal the exterior casing. A laminate film is preferable because it has high output, excellent cooling performance, and can be suitably used for batteries for large devices such as EVs and HEVs. In addition, since the collective pressure applied from the outside to the power generation element can be easily adjusted and the thickness of the electrolyte layer can be easily adjusted to the desired thickness, it is more preferable that the casing be made of a laminate film containing aluminum (for example, a bag made of an aluminum laminate sheet). As the laminate film containing aluminum, the above aluminum laminate film in which polypropylene, aluminum, and nylon are laminated in this order may be used.

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[0152]

[Cell size]

FIG. 3 is a perspective view depicting the appearance of a flat lithium-ion rechargeable battery, a typical embodiment of a rechargeable battery. Like this lithium ion rechargeable battery, a preferred embodiment of the present invention provides a flat laminate battery having a configuration in which the power generating element is encapsulated in a battery casing made of a laminate film containing aluminum.

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[0153]

As illustrated in FIG. 3, the flat lithium ion rechargeable battery 50 has a flat rectangular shape, with a positive electrode tab 58 and a negative electrode tab 59 extending from both sides thereof for extracting electric power. The power generating element 57 is wrapped in the battery casing 52 of the lithium ion rechargeable battery 50 and its periphery is heat sealed, and the power generating element 57 is sealed with the positive electrode tab 58 and the negative electrode tab 59 extended to the outside. Here, the power generating element 57 corresponds to the power generating element 21 of the lithium ion rechargeable battery 10 illustrated in FIG. 2 described above. The power generating element 57 is formed by stacking a plurality of unit cell layers (single cells) 19, each of which is made up of a positive electrode (positive electrode active material layer) 15, an electrolyte layer 17, and a negative electrode (negative electrode active material layer) 13.

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[0154]

Furthermore, there is no particular limitation on the removal of tabs 58 and 59 illustrated in FIG. 3. The positive electrode tab 58 and negative electrode tab 59 may be pulled out from the same side, or the positive electrode tab 58 and negative electrode tab 59 may be divided into multiple tabs and taken out from each side, and the like, not limited to those illustrated in FIG. 3.

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[0155]

In a typical electric vehicle, the battery storage space is about 170 liters. Since the cells

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and auxiliary devices such as charge/discharge control devices are stored in this space, the efficiency of the storage space for the cells is usually around 50%. The efficiency with which cells can be loaded into this space is the factor that determines the driving range of an electric vehicle. If the size of the single cell becomes smaller, the loading efficiency is reduced, making it impossible to ensure a sufficient driving range.

[0156]

Therefore, in the present invention, it is preferable that the battery structure in which the power generating element is covered with a casing is large. Specifically, it is preferable that the negative electrode active material layer has a rectangular shape (rectangular shape), and the length of the short side of the rectangle is 100 mm or more. Such large batteries can be used in vehicle applications. Here, the length of the short side of the negative electrode active material layer refers to the shortest side among the electrodes. There is no particular upper limit to the length of the short side, but it is usually 400 mm or less.

[0157]

[Volumetric energy density and rated (discharge) capacity]

Considering the driving distance (cruising range) of an electric vehicle on a single charge, the volumetric energy density of the battery is preferably 157 Wh/L or more.

[0158]

Here, from the viewpoint of a large-sized battery, which is different from the viewpoint of the physical size of the electrodes, the increase in size of the battery is regulated from the relationship between the battery volume and the battery capacity (rated capacity). Specifically, the non-aqueous electrolyte rechargeable battery according to this embodiment preferably has a ratio of the battery volume (the product of the projected area and thickness of the battery including the battery casing) to the rated capacity of 10 cm³/Ah or less, and a rated capacity of 3 Ah or more. This large battery is defined as a battery having a large battery capacity per unit volume (10 Ah/cm³ or more), in other words, a battery volume per unit capacity (ratio of battery volume to rated capacity) that is small (10 cm³/Ah or less) and a large battery capacity (rated capacity) that is large (3 Ah or more). This can be said to define a large-capacity battery that has a larger expansion capacity than ever before by using a combination of a silicon material and a carbon material as the negative electrode active material.

[0159]

The upper limit of the ratio of the battery volume (the product of the projected area and thickness of the battery including the battery casing) to the rated capacity is preferably 8 cm³/Ah or less. On the other hand, the lower limit of the ratio of the battery volume (the product of the projected area and thickness of the battery including the battery casing) to the rated capacity is not particularly limited, but it is sufficient if it is 2 cm³/Ah or more, and

preferably 3 cm³/Ah or more. Furthermore, the rated capacity is preferably 5 Ah or more, more preferably 10 Ah or more, even more preferably 15 Ah or more, especially 20 Ah or more, and most preferably 25 Ah or more. Only when a battery with such a large area and large capacity is produced does a deterioration in cycle characteristics become apparent due to the occurrence of local non-uniformity in reactions caused by variations in the dispersion of the Si material and carbon material within the electrode surface. On the other hand, in batteries that do not have a large area and large capacity as described above, such as conventional consumer batteries, even if there is variation in the dispersion of the Si material and the carbon material within the electrode surface, there is no deterioration in cycle characteristics due to the associated non-uniformity of local reactions.

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[0160]

The rated capacity of a battery is calculated as follows:

[0161]

<Measurement of rated capacity>

The rated capacity of the test battery is measured by injecting the electrolyte into the battery and leaving the battery for about 10 hours, then measuring the rated capacity at a temperature of 25 °C. and at a voltage range of 3.0 V to 4.15 V according to the following procedures 1 to 5. Note that, for commercially available batteries (products), since more than 10 hours have passed since the electrolyte was injected, steps 1 to 5 can be carried out to determine the rated capacity.

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[0162]

Step 1: After the voltage reaches 4.15 V with a constant current charge of 0.1 C, pause for 5 minutes.

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[0163]

Step 2: After step 1, charge the battery at a constant voltage for 1.5 hours, then pause for 5 minutes.

[0164]

Step 3: After reaching 3.0 V by constant current discharge at 0.1 C, discharge at constant voltage for 2 hours, and then pause for 10 seconds.

[0165]

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Step 4: After reaching 4.1 V by constant current charging at 0.1 C, charge for 2.5 hours by constant voltage charging, then pause for 10 seconds.

[0166]

Step 5: After reaching 3.0 V with a constant current discharge of 0.1 C, discharge for 2 hours with constant voltage discharge, and then stop for 10 seconds.

[0167]

Rated capacity: The discharge capacity in the discharge from the constant current

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discharge to the constant voltage discharge in step 5 (CCCV discharge capacity) is taken as the rated capacity.

[0168]

The volume of the battery is calculated by multiplying the projected area of the battery, including the battery casing, by the thickness. Of these, with regard to the projected area of the battery including the battery exterior, six projected areas of the battery are obtained: the front, back, right side, left side, flat surface, and bottom surface, among which, the largest projected area of the battery may be used, which is usually the projected area of the flat surface or bottom surface of the battery when the battery is placed in the most stable state on a flat plate. Furthermore, the thickness of the battery, including the battery casing, is measured when the battery is fully charged. In addition, since the thickness of the battery including the battery casing is a large area, measurements are taken at eight or more points to take into consideration variations depending on the measurement location, and the average value is determined.

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[0169]

Furthermore, the aspect ratio of the rectangular electrode is preferably 1 to 3, and more preferably 1 to 2. The aspect ratio of the electrode is defined as the length-to-width ratio of the rectangular positive electrode active material layer. Setting the aspect ratio within this range has the advantage of being able to achieve both the vehicle performance requirements and the mounting space.

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[0170]

<Method for manufacturing lithium-ion rechargeable battery>

The method for producing the lithium ion rechargeable battery is not particularly limited, and the battery can be produced by a known method. Specifically, this includes (1) preparation of electrodes, (2) preparation of single cell layers, (3) preparation of power generating elements, and (4) manufacturing of stacked batteries. An example of a method for producing a lithium ion rechargeable battery will be described below, but the method is not limited to this.

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[0171]

(1) Preparation of electrodes (positive and negative electrodes)

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An electrode (positive electrode or negative electrode) can be produced, for example, by preparing an active material slurry (positive electrode active material slurry or negative electrode active material slurry), applying the active material slurry onto a current collector, drying, and then pressing. The active material slurry contains the above active material (positive electrode active material or negative electrode active material), a binder (when an aqueous binder is used on the negative electrode side, it is desirable to use a thickener in combination), a conductive agent, and a solvent.

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[0172]

The solvent is not particularly limited, and examples of the solvent that can be used include N-methyl-2-pyrrolidone (NMP), dimethylformamide, dimethylacetamide, methylformamide, cyclohexane, hexane, and water.

[0173]

The aqueous solvent used in preparing the negative electrode active material (aqueous) slurry is not particularly limited, and any conventionally known aqueous solvent may be used. For example, water (pure water, ultrapure water, distilled water, deionized water, groundwater, well water, clean water (tap water), and the like), a mixed solvent of water and alcohol (for example, ethyl alcohol, methyl alcohol, isopropyl alcohol, and the like), and the like may be used. However, the present embodiment is not limited to these, and any conventionally known aqueous solvent can be appropriately selected and used as long as it does not impair the effects of the present embodiment. These may be used alone or in a combination of two or more types.

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[0174]

The method for applying the active material slurry to the current collector is not particularly limited, and examples of the method include screen printing, spray coating, electrostatic spray coating, inkjet printing, doctor blade printing, and the like.

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[0175]

The method for drying the coating film formed on the surface of the current collector is not particularly limited, and it is sufficient that at least a portion of the solvent in the coating film is removed. The drying method includes heating. The drying conditions (drying time, drying temperature, and the like) can be appropriately set depending on the evaporation rate of the solvent contained in the active material slurry to be applied, the application amount of the active material slurry, and the like. Note that the solvent may partially remain. The remaining solvent can be removed by a pressing step or the like, which will be described later.

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[0176]

The pressing means is not particularly limited, and for example, a calendar roll, a flat plate press, or the like can be used.

[0177]

(2) Preparation of a single cell layer

The single cell layer can be produced by stacking the electrodes (positive electrode and negative electrode) produced in (1) with a separator (electrolyte layer) interposed therebetween.

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[0178]

(3) Preparation of power generating element

The power generating element can be produced by stacking the single cell layers, taking

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into account the output and capacity of the single cell layers, the output and capacity required as a battery, and the like.

[0179]

(4) Manufacturing of stacked batteries

In the laminated battery, leads are joined to the current collectors of the power generating elements obtained above, and the positive electrode lead or negative electrode lead is joined to a positive electrode tab or negative electrode tab. Then, the power generating element is placed in a laminate sheet so that the positive and negative electrode tabs are exposed to the outside of the battery, and the electrolyte is poured in using a liquid pouring machine, followed by vacuum sealing to produce a stacked battery.

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[0180]

(5) Activation process, and the like

In this embodiment, from the viewpoint of improving the performance and durability of the stacked battery obtained as described above, an initial charging process, a gas removal process, an activation process, and the like may be further carried out as necessary under the following conditions. In this case, in order to enable gas removal processing in the manufacturing of the stacked battery of (4) above, when sealing, three sides of the laminate sheet (casing) in a rectangular shape are completely sealed (mainly sealed) by thermocompression bonding, and the remaining side is temporarily sealed by thermocompression bonding. The remaining side may be made openable and closable by, for example, clipping, but from the standpoint of mass production (production efficiency), it is preferable to temporarily seal it by thermocompression bonding. In this case, it is only necessary to adjust the temperature and pressure for compression bonding. When the container is temporarily sealed by thermocompression, it can be opened by applying a light force, and after degassing, it may be temporarily sealed again by thermocompression, or finally, it may be completely sealed (mainly sealed) by thermocompression.

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[0181]

(Initial charging process)

The aging process of the battery is preferably carried out as follows. The battery is charged at 25 °C for 4 hours at a constant current of 0.05 C (SOC about 20%). Next, the battery is charged at 25° C at a rate of 0.1 C up to 4.45 V, after which the charging is stopped and the battery is kept in this state (SOC about 70%) for about 2 days (48 hours).

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[0182]

(Initial (first) gas removal process)

Next, the following process is carried out as the initial (first) gas removal process. First, the side that has been temporarily sealed by thermocompression is opened, and gas is removed for 5 minutes at 10±3 hPa, after which thermocompression is again performed to temporarily

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seal. Furthermore, the electrode and the separator are pressed with a roller (surface pressure 0.5 ± 0.1 MPa) to be shaped so as to be sufficiently adhered to each other.

[0183]

(Activation process)

Next, as an activation process method, the following electrochemical preprocess method is performed.

[0184]

First, the battery was charged at 25 °C by a constant current charging method at 0.1 C until the voltage reached 4.45 V, and then discharged at 0.1 C until the voltage reached 2.0 V. This cycle was repeated twice. Similarly, at 25 °C, the battery was charged at 0.1 C using a constant current charging method until the voltage reached 4.55 V, and then discharged at 0.1 C until the voltage reached 2.0 V. This cycle was repeated once, and the battery was charged at 0.1 C until the voltage reached 4.65 V, and then discharged at 0.1 C until the voltage reached 2.0 V. Furthermore, one cycle of charging at 0.1 C until 4.75 V at 0.1 C and discharging to 2.0 V at 0.1 C should be performed at 25°C using the constant-current charging method.

[0185]

In this example, an electrochemical preprocess method is described as an activation process method using a constant current charging method with voltage as the termination condition, but the charging method may also be a constant current/constant voltage charging method. Moreover, the termination condition may be determined not only by the voltage but also by the charge amount or time.

[0186]

(Final (second) gas removal process)

Next, the following process is carried out as the initial (first) gas removal process. First, the side temporarily sealed by thermocompression is opened, gas removal is performed at 10 ± 3 hPa for 5 minutes, and then thermocompression is performed again for main sealing. Furthermore, the electrode and the separator are pressed with a roller (surface pressure 0.5 ± 0.1 MPa) to be shaped so as to be sufficiently adhered to each other.

[0187]

In this embodiment, by carrying out the above initial charging process, gas removal process, and activation process, the performance and durability of the obtained battery can be improved.

[0188]

[Battery pack]

A battery pack is made up of multiple connected batteries. More specifically, at least two or more of them are used, and are configured in a serial or parallel manner, or both. By

connecting them in series or parallel, it becomes possible to freely adjust the capacity and voltage.

[0189]

A plurality of batteries can be connected in series or parallel to form a small, detachable battery pack. Furthermore, by connecting multiple such small, detachable assembled batteries in series or in parallel, it is possible to form an assembled battery with large capacity and high output suitable for use as a power source for driving a vehicle or an auxiliary power source, which require high volumetric energy density and high volumetric output density. The number of batteries to be connected to make a battery pack, and the number of stages of small battery packs to be stacked to make a large-capacity battery pack, can be determined based on the battery capacity and output of the vehicle (electric vehicle) in which the battery pack will be installed.

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[0190]

[Vehicle]

The non-aqueous electrolyte rechargeable battery of this embodiment has excellent rate characteristics, maintains its discharge capacity even after long-term use, and has good cycle characteristics. In vehicle applications such as electric vehicles, hybrid electric vehicles, fuel cell vehicles, and hybrid fuel cell vehicles, higher capacity, larger size, and longer life are required compared to electrical and portable electronic device applications. Therefore, the non-aqueous electrolyte rechargeable battery can be suitably used as a power source for a vehicle, for example, as a power source for driving a vehicle or an auxiliary power source.

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[0191]

Specifically, a battery or a battery pack formed by combining a plurality of batteries can be mounted on a vehicle. In this embodiment, a long-life battery with excellent long-term reliability and output characteristics can be constructed, and by installing such a battery, a plug-in hybrid electric vehicle with a long EV driving distance or an electric vehicle with a long driving distance on a single charge can be constructed. This is because the use of batteries or assembled batteries composed of a combination of multiple batteries in, for example, hybrid vehicles, fuel cell vehicles, and electric vehicles (all of which include four-wheeled vehicles (commercial vehicles such as passenger cars, trucks, and buses, and light vehicles, as well as two-wheeled vehicles (motorcycles) and three-wheeled vehicles)) can result in automobiles with long life and high reliability. However, the uses are not limited to automobiles, and the present invention can be applied to various power sources for other vehicles, for example, mobile bodies such as trains, and can also be used as an on-board power source for uninterruptible power supplies, and the like.

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[Examples]

[0192]

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The present invention will be described in more detail below with reference to examples and comparative examples, but the present invention is not limited to the following examples as long as it does not depart from the essence of the present invention.

[0193]

[Effect of Si composition ratio and thickness of negative electrode active material layer on rate characteristics]

1. Preparation of positive electrode

Solid content composed of 94 mass% NMC composite oxide (average particle size 15 μm) having a composition of $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ as a positive electrode active material, 3 mass% acetylene black as a conductive additive, and 3 mass% polyvinylidene fluoride (PVdF) as a binder was prepared. As the PVdF, Kureha KF Polymer, powder type, grade No. W#7200 manufactured by Kureha Battery Materials Japan Co., Ltd. was used. A suitable amount of N-methyl-2-pyrrolidone (NMP), a slurry viscosity adjusting solvent, was mixed with this solid content to prepare a positive electrode active material slurry. The obtained positive electrode active material slurry was applied to the surface of an aluminum foil (thickness: 20 μm) serving as a positive electrode current collector, dried at 120 °C for 3 minutes, and then compression molded with a roll press to prepare a positive electrode active material layer having a rectangular planar shape. The positive electrode active material layer was formed on the back side in the same manner, and a positive electrode active material layer with a thickness of 65 μm was formed on each side of the positive electrode current collector (aluminum foil). Note that the capacity per unit weight of the positive electrode active material used was 180 mAh/g. The coating amount of the positive electrode active material layer on one side was 22 mg/cm² (not including foil). Furthermore, the density was 3.4 g/cm³ (not including foil).

[0194]

2. Preparation of negative electrode

The following Si materials 1 to 5 were prepared.

[0195]

(Si material 1)

A Si-containing alloy expressed as $\text{Si}_{60}\text{Ti}_{40}$ (units are mass percentages) was used as the Si material 1. Note that the Si-containing alloy was produced by a mechanical alloying method. Specifically, using a planetary ball mill P-6 manufactured by Fritsch AG of Germany, zirconia milling balls and alloy raw material powder were placed in a zirconia milling pot, and alloying was carried out at 600 rpm for 48 hours. Then, the mixture was ground at 400 rpm for 1 hour. Metal powders of Si and Ti were used as raw material powders for the alloy. Here, the alloying process involves imparting high energy to the alloy raw material powder at a high speed (600 rpm) to cause alloying. On the other hand, the crushing process involves breaking down

secondary particles at a low rotation speed (400 rpm) (no alloying is performed in this process). The secondary particle size D50 of the obtained Si material 1 was 3.0 μm , and the capacity per unit weight was 660 mAh/g.

[0196]

(Si material 2)

A Si-containing alloy expressed as $\text{Si}_{55}\text{Ti}_{45}$ (units are mass percentages) was used as the Si material 2. Note that the Si-containing alloy was produced by a mechanical alloying method. Specifically, using a planetary ball mill P-6 manufactured by Fritsch AG of Germany, zirconia milling balls and alloy raw material powder were placed in a zirconia milling pot, and alloying was carried out at 600 rpm for 48 hours. Then, the mixture was ground at 400 rpm for 1 hour. Metal powders of Si and Ti were used as raw material powders for the alloy. Here, the alloying process involves imparting high energy to the alloy raw material powder at a high speed (600 rpm) to cause alloying. On the other hand, the crushing process involves breaking down secondary particles at a low rotation speed (400 rpm) (no alloying is performed in this process). The D50 of the secondary particle size of the resulting Si material 2 was 2.5 μm , and the capacity per unit weight was 670 mAh/g.

[0197]

(Si material 3)

A Si-containing alloy expressed as $\text{Si}_{65}\text{Ti}_{35}$ (units are mass percentages) was used as the Si material 3. Note that the Si-containing alloy was produced by a mechanical alloying method. Specifically, using a planetary ball mill P-6 manufactured by Fritsch AG of Germany, zirconia milling balls and alloy raw material powder were placed in a zirconia milling pot, and alloying was carried out at 600 rpm for 48 hours. Then, the mixture was ground at 400 rpm for 1 hour. Metal powders of Si and Ti were used as raw material powders for the alloy. Here, the alloying process involves imparting high energy to the alloy raw material powder at a high speed (600 rpm) to cause alloying. On the other hand, the crushing process involves breaking down secondary particles at a low rotation speed (400 rpm) (no alloying is performed in this process). The D50 of the secondary particle size of the resulting Si material 3 was 2.3 μm , and the capacity per unit weight was 860 mAh/g.

[0198]

(Si material 4)

A Si-containing alloy expressed as $\text{Si}_{62}\text{Ti}_{38}$ (units are mass percentages) was used as the Si material 4. Note that the Si-containing alloy was produced by a mechanical alloying method. Specifically, using a planetary ball mill P-6 manufactured by Fritsch AG of Germany, zirconia milling balls and alloy raw material powder were placed in a zirconia milling pot, and alloying was carried out at 600 rpm for 48 hours. Then, the mixture was ground at 400 rpm for 1 hour. Metal powders of Si and Ti were used as raw material powders for the alloy. Here, the alloying

process involves imparting high energy to the alloy raw material powder at a high speed (600 rpm) to cause alloying. On the other hand, the crushing process involves breaking down secondary particles at a low rotation speed (400 rpm) (no alloying is performed in this process). The D50 of the secondary particle size of the resulting Si material 4 was 2.3 μm , and the capacity per unit weight was 1100 mAh/g.

[0199]

(Si material 5)

A Si-containing alloy expressed as $\text{Si}_{72}\text{Ti}_{28}$ (units are mass percentages) was used as the Si material 5. Note that the Si-containing alloy was produced by a mechanical alloying method. Specifically, using a planetary ball mill P-6 manufactured by Fritsch AG of Germany, zirconia milling balls and alloy raw material powder were placed in a zirconia milling pot, and alloying was carried out at 600 rpm for 48 hours. Then, the mixture was ground at 400 rpm for 1 hour. Metal powders of Si and Ti were used as raw material powders for the alloy. Here, the alloying process involves imparting high energy to the alloy raw material powder at a high speed (600 rpm) to cause alloying. On the other hand, the crushing process involves breaking down secondary particles at a low rotation speed (400 rpm) (no alloying is performed in this process). The D50 of the secondary particle size of the resulting Si material 5 was 2.5 μm , and the capacity per unit weight was 1300 mAh/g.

[0200]

Note that the capacity (charging capacity) per unit weight of each of the above Si materials can be determined by using Li metal as the counter electrode in a coin cell and evaluating the capacity of only the Si material.

[0201]

(Preparation of a negative electrode with a Si material mixing ratio of 6.5 mass%)

Using the above Si materials 1 to 5 as the negative electrode active material, negative electrodes were fabricated with a Si material mixing ratio of 6.5 mass%. Specifically, 6.27 mass% of Si material, 90.23 mass% of natural graphite (secondary particle size D50: 2.0 μm), 0.5 mass% of carbon black (Super-P, manufactured by TIMCAL) as a conductive agent, 2.0 mass% of styrene-butadiene rubber as a binder, and 1.0 mass% of sodium salt of carboxymethyl cellulose as a thickener were dispersed in deionized water to prepare a negative electrode active material slurry.

[0202]

This negative electrode active material slurry was applied to a copper foil (thickness: 10 μm) serving as a negative electrode current collector, dried at 120 °C for 3 minutes, and then compression molded with a roll press to prepare a negative electrode. The negative electrode active material layer was formed on the back side in the same manner to produce a negative electrode composed of a negative electrode active material layer on each side of the negative

electrode current collector (copper foil). The amount of coating on one side of the negative electrode active material layer was 10.52 to 11.58 mg/cm² (not including foil). Furthermore, the density of the negative electrode active material layer was 1.55 to 1.60 g/cm³(not including foil).

[0203]

(Preparation of negative electrode with 15 mass% Si material mixture)

In the above (production of a negative electrode having a Si material mixing ratio of 6.5 mass%), the Si material was changed to 14.5 mass% and the natural graphite (secondary particle size D50: 2.0 μm) was changed to 82.0 mass%, and similar procedures were used to produce negative electrodes having a Si material mixing ratio of 15 mass%. Negative electrode 2 was prepared. The amount of coating on one side of the negative electrode active material layer ranged from 9.00 to 10.98 mg/cm² (not including foil). Furthermore, the density of the negative electrode active material layer was 1.60 to 1.65 g/cm³ (not including foil).

[0204]

3. Preparation of battery

The positive electrode obtained in 1 above and the negative electrode obtained in 2 above were cut out to have an active material layer area of 42 mm length×31 mm width, and stacked (one positive electrode, one negative electrode) between porous polypropylene separators (thickness 25 μm, porosity 55%) to prepare a power generating element. A positive electrode lead and a negative electrode lead were joined to each current collector of the obtained power generating element, and these positive electrode leads or negative electrode leads were joined to a positive electrode current collector plate or a negative electrode current collector plate. The power generating element was then inserted into an aluminum laminated sheet bag (length 70 mm×width 70 mm) serving as the battery casing so that the positive and negative current collector plates were exposed to the outside of the battery, and an electrolyte was poured into it. This aluminum laminate bag is made by stacking two aluminum laminate sheets (film sheets in which aluminum is laminated with a PP film) together, with three of the four outer edges sealed by thermocompression bonding, and the remaining edge left unsealed (opening). The electrolyte used was a 100 mass% solution of 1.0M LiPF₆ dissolved in a 3:7 (volume ratio of EC:DEC) mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC), to which 1 mass% of vinylene carbonate as an additive was added. Next, under vacuum conditions, the opening of the aluminum laminate sheet bag was sealed by thermocompression bonding so that the positive electrode current collector and the negative electrode current collector connected to both electrodes (current collectors) via leads were exposed, completing the battery.

[0205]

Thereafter, the battery was sandwiched between urethane rubber sheets (thickness 3 mm)

larger than the area of the electrodes and further between Al plates (thickness 5 mm), and the battery was appropriately pressed from both sides in the stacking direction. The thus obtained battery was initially charged for 5 hours (upper limit voltage 4.15 V), and then aged at 45 °C for 5 days, degassed, and discharged to complete the battery.

[0206]

4. Measurement of discharge rate characteristics

The battery prepared above was charged at a constant current of 1 C ampere, and when the voltage reached 4.15 V, charging was continued at a constant voltage of 4.15 V. Charging was completed (cut off) when the current value reached 0.02 C ampere, and the charge capacity at 1 C ampere was measured. Next, discharge was started at a constant current of 0.1 C ampere and 1 C ampere, and the discharge was completed (cut off) when the voltage reached 3.0 V, and the discharge capacity at 0.1 C ampere and 1 C ampere was measured. Note that a fully charged state of 4.15 V was defined as SOC 100%.

[0207]

Then, the ratio % of the discharge capacity obtained at each discharge rate (abbreviated as "1C/0.1C") was calculated. The results are illustrated in FIG. 4.

[0208]

FIG. 4 is a graph illustrating the relationship between the thickness of the negative electrode active material layer and the discharge rate properties (1C/0.1C) of a battery in which a mixture of Si and carbon materials is used as the negative electrode active material, when the capacity per unit area of the negative electrode active material layer is kept at an approximate constant. As illustrated in FIG. 4, it was found that the rate characteristics were hardly affected by the type or mixture ratio of the Si material, but were mainly dependent on the thickness of the negative electrode active material layer. Therefore, in a battery having a stacked structure of three or more layers, the reactivity can be increased by making the thickness of the negative electrode active material layer of the outer cell layer relatively thin, thereby reducing the difference in reactivity with the inner cell layer.

[0209]

[Table 1]

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Table 1

Type	Si Material			Negative electrode active material layer				Rate characteristics (1C/0.1C) (%)
	Composition Formula	Charging capacity per unit weight (mAh/g)	Content (mass%)	Appraisal (mg/cm ²)	Density (g/cm ³)	Thickness (μm)	Charge capacity per unit area (mAh/cm ²)	
1	Si ₆₀ Ti ₄₀	660	6.5	10.98	1.60	70.2	4.62	56.7
2	Si ₅₅ Ti ₄₅	670	6.5	11.58	1.55	74.6	4.62	56.9
3	Si ₆₅ Ti ₃₅	860	6.5	11.24	1.55	72.5	4.62	57.2
4	Si ₆₂ Ti ₃₈	1100	6.5	10.86	1.55	70.0	4.62	59.6
5	Si ₇₂ Ti ₂₈	1300	6.5	10.52	1.55	67.8	4.62	60.3
1	Si ₆₀ Ti ₄₀	660	15	10.98	1.65	60.3	4.62	70.4
2	Si ₅₅ Ti ₄₅	670	15	10.98	1.60	68.7	4.62	61.1
3	Si ₆₅ Ti ₃₅	860	15	10.30	1.60	64.4	4.62	63.8
4	Si ₆₂ Ti ₃₈	1100	15	9.59	1.60	60.0	4.62	65.5
5	Si ₇₂ Ti ₂₈	1300	15	9.00	1.60	56.3	4.62	71.3

[0210]

[Example 1]

1. Preparation of positive electrode

Solid content composed of 94 mass% NMC composite oxide (average particle size 15 μm) with a composition of LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ as the positive electrode active material, 3 mass% acetylene black as conductivity aid, and 3 mass% polyvinylidene fluoride (PVdF) as a binder

was prepared. As the PVdF, Kureha KF Polymer, powder type, grade No. W#7200 manufactured by Kureha Battery Materials Japan Co., Ltd. was used. A suitable amount of N-methyl-2-pyrrolidone (NMP), a slurry viscosity adjusting solvent, was mixed with this solid content to prepare a positive electrode active material slurry. The obtained positive electrode active material slurry was applied to the surface of an aluminum foil (thickness: 20 μm) serving as a positive electrode current collector, dried at 120 $^{\circ}\text{C}$ for 3 minutes, and then compression molded with a roll press to prepare a positive electrode active material layer having a rectangular planar shape. The positive electrode active material layer was formed on the back side in the same manner, and a positive electrode active material layer with a thickness of 62.2 μm was formed on each side of the positive electrode current collector (aluminum foil). Note that the capacity per unit weight of the positive electrode active material used was 3.14 mAh/g. The amount of positive electrode active material layer coated on one side was 21.3 mg/cm² (not including foil). Furthermore, the density was 3.43 g/cm³ (not including foil).

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[0211]

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2. Preparation of negative electrode

(Preparation of negative electrode 1 (0 mass% of Si material mixed))

The negative electrode active material slurry was prepared by dispersing 96.50 mass% of natural graphite (D50 of secondary particle size: 2 μm) as the negative electrode active material, 0.50 mass% of carbon black (Super-P, manufactured by TIMCAL) as a conductivity aid, 1.00 mass% of sodium salt of carboxymethyl cellulose as a thickener, and 2.00 mass% of styrene-butadiene rubber as a binder, then 2.00 mass% of styrene-butadiene rubber, which is a binder, was dispersed in deionized water.

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[0212]

This negative electrode active material slurry was applied to a copper foil (thickness: 10 μm) serving as a negative electrode current collector, dried at 120 $^{\circ}\text{C}$ for 3 minutes, and then compression molded with a roll press to prepare a negative electrode. The negative electrode active material layer was formed on the back side in the same manner to produce a negative electrode composed of a negative electrode active material layer 80 μm thick on each side of the negative electrode current collector (copper foil). The amount of coating on one side of the negative electrode active material layer was 10.8 mg/cm² (not including foil). Furthermore, the density of the negative electrode active material layer was 1.52 g/cm³ (not including foil).

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[0213]

(Preparation of negative electrode 2 (mixing ratio of Si material: 6.5 mass%))

A Si-containing alloy expressed as Si₉₀Ti₁₀ (units are mass percentages) was used as the Si material. Note that the Si-containing alloy was produced by a mechanical alloying method. Specifically, using a planetary ball mill P-6 manufactured by Fritsch AG of Germany, zirconia

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milling balls and alloy raw material powder were placed in a zirconia milling pot, and alloying was carried out at 600 rpm for 48 hours. Then, the mixture was ground at 400 rpm for 1 hour. Metal powders of Si and Ti were used as raw material powders for the alloy. Here, the alloying process involves imparting high energy to the alloy raw material powder at a high speed (600 rpm) to cause alloying. On the other hand, the crushing process involves breaking down secondary particles at a low rotation speed (400 rpm) (no alloying is performed in this process). The secondary particle size D50 of the obtained Si-containing alloy was 2.0 μm .

[0214]

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In the preparation of the above negative electrode 1, 96.50 mass% of natural graphite was changed to 90.23 mass% of natural graphite and 6.27 mass% of the above prepared Si-containing alloy. Moreover, negative electrode 2 was produced in the same manner as negative electrode 1 above, except that the thickness of one side of the negative electrode active material layer was changed to 70 μm . The amount of one-sided coating of the negative electrode active material layer of negative electrode 2 was 11.1 mg/cm^2 (not including foil). The density of the negative electrode active material layer was 1.51 g/cm^3 (not including foil).

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[0215]

(Preparation of negative electrode 3 (mixture ratio of Si material: 15 mass%))

In the preparation of the above negative electrode 1, 96.50 mass% of natural graphite was changed to 82.0 mass% of natural graphite and 14.5 mass% of the above prepared Si-containing alloy. Moreover, negative electrode 3 was produced in the same manner as negative electrode 1 above, except that the thickness of one side of the negative electrode active material layer was changed to 62 μm . The amount of one-sided coating of the negative electrode active material layer of negative electrode 3 was 11.58 mg/cm^2 (not including foil). The density of the negative electrode active material layer was 1.51 g/cm^3 (not including foil).

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[0216]

(Preparation of negative electrode 4 (mixture ratio of Si material: 20 mass%))

In the preparation of the above negative electrode 1, 96.50 mass% of natural graphite was changed to 77.2 mass% of natural graphite and 19.3 mass% of the above prepared Si-containing alloy. Moreover, negative electrode 4 was produced in the same manner as negative electrode 1 above, except that the thickness of one side of the negative electrode active material layer was changed to 55 μm . The amount of one-sided coating of the negative electrode active material layer of negative electrode 4 was 11.94 mg/cm^2 (not including foil). The density of the negative electrode active material layer was 1.50 g/cm^3 (not including foil).

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[0217]

Table 2

	Si material content	Appraisal (mg/cm^2)	Density (g/cm^3)	Capacity per unit area	Thickness (μm)
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	(mass%)			(mAh/cm ²)	
Negative electrode 1	0	10.8	1.52	4.14	80
Negative electrode 2	6.5	11.1	1.51	4.14	70
Negative electrode 3	15	11.58	1.51	4.14	62
Negative electrode 4	20	11.94	1.50	4.14	55

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[Table 2]

[0218]

3. Preparation of battery

(Preparation of Battery of Comparative Example 1)

The positive electrode obtained in 1 above and the negative electrode 1 obtained in 2 above were cut out to have an active material layer area of 42 mm length×31 mm width, and stacked (two positive electrodes, three negative electrode) between porous polypropylene separators (thickness 25 μm, porosity 55%) to prepare a power generating element. A positive electrode lead and a negative electrode lead were joined to each current collector of the obtained power generating element, and these positive electrode leads or negative electrode leads were joined to a positive electrode current collector plate or a negative electrode current collector plate. The power generating element was then inserted into an aluminum laminated sheet bag (length 70 mm×width 70 mm) serving as the battery casing so that the positive and negative current collector plates were exposed to the outside of the battery, and an electrolyte was poured into it. This aluminum laminate bag is made by stacking two aluminum laminate sheets (film sheets in which aluminum is laminated with a PP film) together, with three of the four outer edges sealed by thermocompression bonding, and the remaining edge left unsealed (opening). The electrolyte used was a 100 mass% solution of 1.0M LiPF₆ dissolved in a 3:7 (volume ratio of EC:DEC) mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC), to which 1 mass% of vinylene carbonate as an additive was added. Next, under vacuum conditions, the opening of the aluminum laminate sheet bag was sealed by thermocompression bonding so that the positive electrode current collector and the negative electrode current collector connected to both electrodes (current collectors) via leads were exposed, completing the battery.

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[0219]

Thereafter, the battery was sandwiched between urethane rubber sheets (thickness 3 mm) larger than the area of the electrodes and further between Al plates (thickness 5 mm), and

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the battery was appropriately pressed from both sides in the stacking direction. The thus obtained battery was initially charged for 5 hours (upper limit voltage 4.15 V), and then aged at 45 °C for 5 days, degassed, and discharged to complete the battery of Comparative Example 1.

[0220]

(Preparation of Battery of Example 1)

The battery of Example 1 was obtained in the same manner as in the battery of Comparative Example 1, except that, of the three negative electrodes, the negative electrode 3 prepared above was used as the outer layer (first and third layers) and the negative electrode 2 prepared above was used as the inner layer (second layer).

[0221]

(Preparation of Battery of Example 2)

The battery of Example 1 was obtained in the same manner as in the battery of Comparative Example 1, except that, of the three negative electrodes, the negative electrode 4 prepared above was used as the outer layer (first and third layers) and the negative electrode 2 prepared above was used as the inner layer (second layer).

[0222]

4. Measurement of maximum output characteristics

For each battery (test cell) obtained above, a constant current was applied for 10 seconds at each C-rate of 0.2 C, 0.4 C, 1 C, 2 C, 4 C, and 8 C, and the average voltage at each C-rate (current value) was measured. From the relationship between the current value and the average voltage obtained above, the current value (I) at 2.5 V was extrapolated, and the output value at 2.5 V was taken as the maximum output (Wmax). The maximum output value was determined as a relative value when the maximum output of the battery of Comparative Example 1 was taken as 100%. The results are illustrated in Table 3 below.

[0223]

[Table 3]

Table 3

	Negative electrode active material layer of the inner (second) single cell layer			Negative electrode active material layer of the outer (first and third) single cell layers			Maximum output (Relative value) (%)
	Si material content (mass%)	Thickness (μm)	Capacity per unit area (mAh/cm ²)	Si material content (mass%)	Thickness (μm)	Capacity per unit area (mAh/cm ²)	
Comparative Example	0	80	4.14	0	80	4.14	100

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Example 1	6.5	70	4.14	15	62	4.14	120
Example 2	6.5	70	4.14	20	55	4.14	130

[0224]

As illustrated in Table 3 above, in the non-aqueous electrolyte rechargeable batteries using a mixture of a Si material and a carbon material as the negative electrode active material layer, the batteries of Examples 1 and 2 in which the thickness of the negative electrode active material layer is outside < inside in the stacking direction, were found to exhibit higher output characteristics than the battery of Comparative Example 1.

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[Description of Reference Numerals]

[0225]

10, 50 Lithium-ion rechargeable batteries,
 11 Negative electrode current collector,
 12 Positive electrode current collector,
 13 Negative electrode active material layer,
 15 Positive electrode active material layer,
 17 Electrolyte layer (separator),
 19 single-cell layer,
 21, 57 Power generating element,
 25 Negative electrode current collector,
 27 Positive electrode current collector,
 29, 52 Battery casing materials,
 58 Positive electrode tab,
 59 Negative electrode tab.

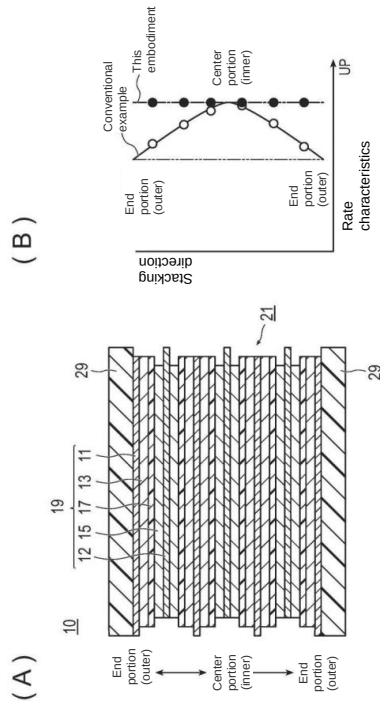
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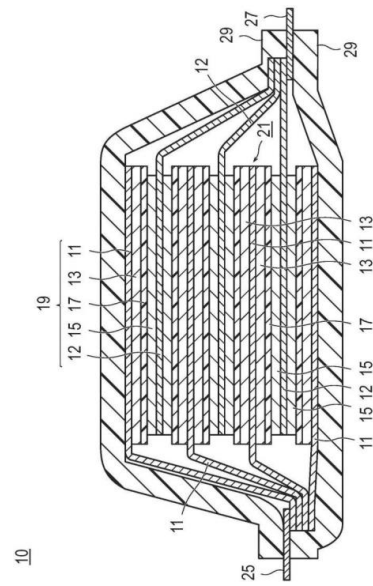
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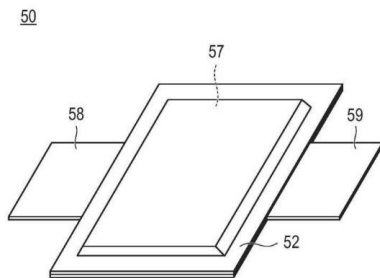
[FIG. 1]



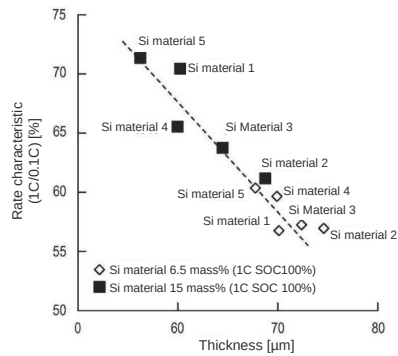
[FIG. 2]



[FIG. 3]



[FIG. 4]



Continued from front page

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<i>H01M</i>	<i>4/133</i>	<i>(2010.01)</i>	<i>H01M</i>	<i>4/133</i>		
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AM05 AM07 AM16 BJ04 DJ12 DJ16 HJ01 HJ02						
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5H050 AA02 BA16 BA17 CA08 CA09 CB02 CB08 CB09						
CB11 DA03 FA08 FA17 HA01 HA02 HA04 HA19						



DECLARATION OF TRANSLATOR

I, Eric Vance, hereby declare as follows:

1. I personally performed the attached translation from Japanese into English of the patent number JP2018-078052 that is entitled “非水電解質二次電池” in Japanese and “NON-AQUEOUS ELECTROLYTE RECHARGEABLE BATTERY” in English (also attached).

2. The attached translation is, to the best of my knowledge, a true, full and accurate translation of the attached Japanese document.

3. I am competent to perform this translation, because I have a baccalaureate degree in Japanese and 7 years of experience as a patent translator.

4. I declare under the penalty of perjury under the laws of the United States that the foregoing is true and correct; and further declare that I am aware that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 1001 of Title 18 of the United States Code.

Dated: March 4, 2024


Eric Vance

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