DESCRIPTION

POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY

TECHNICAL FIELD

[0001]

One embodiment of the present invention relates to an object, a method, or a manufacturing method. The present invention relates to a process, a machine, manufacture, or a composition of matter. One embodiment of the present invention relates to a semiconductor device, a display device, a light-emitting device, a power storage device, a lighting device, an electronic device, or a manufacturing method thereof. In particular, one embodiment of the present invention relates to a positive electrode active material that can be used in a secondary battery, a secondary battery, and an electronic device including a secondary battery.

[0002]

In this specification, the power storage device is a collective term describing elements and devices having a power storage function. For example, a storage battery such as a lithium-ion secondary battery (also referred to as secondary battery), a lithium-ion capacitor, and an electric double layer capacitor are included in the category of the power storage device.

[0003]

Note that electronic devices in this specification mean all devices including power storage devices, and electro-optical devices including power storage devices, information terminal devices including power storage devices, and the like are all electronic devices.

BACKGROUND ART

[0004]

In recent years, a variety of power storage devices such as lithium-ion secondary batteries, lithium-ion capacitors, and air batteries have been actively developed. In particular, demand for lithium-ion secondary batteries with high output and high energy density has rapidly grown with the development of the semiconductor industry, for portable information terminals such as mobile phones, smartphones, tablets, and laptop computers; portable music players; digital cameras; medical equipment; next-generation clean energy vehicles such as hybrid electric vehicles (HEV), electric vehicles (EV), and plug-in hybrid electric vehicles (PHEV); and the like. The lithium-ion secondary batteries are essential as rechargeable energy supply sources for today's information society.

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[0005]

The performance required for lithium-ion secondary batteries includes increased energy density, improved cycle performance, safe operation under a variety of environments, and longer-term reliability.

[0006]

Thus, improvement of a positive electrode active material has been studied to increase the cycle performance and the capacity of the lithium ion secondary battery (Patent Document 1 and Patent Document 2).

[Reference]

[Patent Documents]

[0007]

[Patent Document 1] Japanese Published Patent Application No. 2012-018914

[Patent Document 2] Japanese Published Patent Application No. 2015-201432

DISCLOSURE OF INVENTION

[0008]

Development of lithium ion secondary batteries and positive electrode active materials used therein is susceptible to improvement in terms of charge and discharge characteristics, cycle characteristics, reliability, safety, cost, and the like.

[0009]

An object of one embodiment of the present invention is to provide a positive electrode active material which suppresses a reduction in capacity due to charge and discharge cycles when used in a lithium ion secondary battery. Another object of one embodiment of the present invention is to provide a high-capacity secondary battery. Another object of one embodiment of the present invention is to provide a secondary battery with excellent charge and discharge characteristics. Another object of one embodiment of the present invention is to provide a highly safe or highly reliable secondary battery.

[0010]

Another object of one embodiment of the present invention is to provide a novel material, a novel active material particle, a novel secondary battery, or a formation method thereof.

[0011]

Note that the descriptions of these objects do not disturb the existence of other objects. In one embodiment of the present invention, there is no need to achieve all the objects. Other objects can be derived from the description of the specification, the drawings, and the claims.

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[0012]

To achieve the above objects, in one embodiment of the present invention, two kinds of regions which are different from a region inside the positive electrode active material are provided in a superficial portion of the positive electrode active material. It is preferable that the inner region contain a non-stoichiometric compound and the outer region contain a stoichiometric compound.

[0013]

In addition, it is preferable that the inner region contain titanium and the outer region contain magnesium. Furthermore, these two kinds of regions may overlap.

[0014]

In addition, it is preferable that the inner region be formed through a coating process such as a sol-gel method and the outer region be formed by segregation due to heating.

[0015]

One embodiment of the present invention is a positive electrode active material including a first region, a second region, and a third region. The first region is present inside the positive electrode active material. The second region and the third region are present in a superficial portion of the positive electrode active material. The third region is present in a region closer to a surface of the positive electrode active material than the second region is. The first region contains an oxide of lithium and a first transition metal and has a layered rock-salt crystal structure. The second region contains a non-stoichiometric compound containing an oxide of a second transition metal and the non-stoichiometric compound has a rock-salt crystal structure. The third region contains a compound of representative elements and the compound of representative elements has a rock-salt crystal structure.

[0016]

In the above structure, it is preferable that the first transition metal be cobalt, the second transition metal be titanium, and the compound of representative elements be magnesium oxide.

[0017]

In the above structure, the third region may contain fluorine. Furthermore, the second region and the third region may each contain cobalt.

[0018]

In the above structure, it is preferable that crystal orientations of the first region and the second region be partly aligned with each other and crystal orientations of the second region and the third region be partly aligned with each other.

[0019]

In the above structure, a degree of a mismatch between a (1−1−4) plane of the layered

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rock-salt crystal structure in the first region or a plane orthogonal to the (1–1–4) plane and a {100} plane of the rock-salt crystal structure in the second region is preferably less than or equal to 0.12, and a degree of a mismatch between the {100} plane of the rock-salt crystal structure in the second region and a {100} plane of the rock-salt crystal structure in the third region is preferably less than or equal to 0.12.

[0020]

Another embodiment of the present invention is a positive electrode active material containing lithium, titanium, cobalt, magnesium, oxygen, and fluorine. When the concentration of cobalt which is present in a superficial portion of the positive electrode active material and is measured by X-ray photoelectron spectroscopy is 1, the concentration of titanium is greater than or equal to 0.05 and less than or equal to 0.4, the concentration of magnesium is greater than or equal to 0.4 and less than or equal to 1.5, and the concentration of fluorine is greater than or equal to 0.05 and less than or equal to 1.5.

[0021]

Another embodiment of the present invention is a method for forming a positive electrode active material including: a step of mixing a source of lithium, a source of cobalt, a source of magnesium, and a source of fluorine; a step of heating the mixture of the source of lithium, the source of cobalt, the source of magnesium, and the source of fluorine at 800 °C or higher and 1100 °C or lower for 2 hours or longer and 20 hours or shorter to obtain particles containing lithium, cobalt, magnesium, oxygen, and fluorine; a step of dissolving titanium alkoxide into alcohol; a step of mixing the particles containing lithium, cobalt, magnesium, oxygen, and fluorine into the alcohol solution of the titanium alkoxide and stirring the mixed solution in an atmosphere containing water vapor; a step of collecting precipitate from the mixed solution; and a step of heating the collected precipitate at 500°C or higher and 1200 °C or lower in an atmosphere containing oxygen under a condition where a retention time is 50 hours or shorter.

[0022]

In the above formation method, a ratio of the number of atoms of lithium in the source of lithium to the number of atoms of cobalt in the source of cobalt is preferably greater than or equal to 1.00 and less than 1.07.

[0023]

In the above formation method, a ratio between the number of atoms of magnesium in the source of magnesium and the number of atoms of fluorine in the source of fluorine is preferably Mg:F = 1:x ($1.5 \leq x \leq 4$).

[0024]

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In the above formation method, the number of atoms of magnesium in the source of magnesium is preferably greater than or equal to 0.5 atomic% and less than or equal to 1.5 atomic% of the number of atoms of cobalt in the source of cobalt.

[0025]

In the above formation method, lithium carbonate, cobalt oxide, magnesium oxide, and lithium fluoride can be used as a source of lithium, a source of cobalt, a source of magnesium, and a source of fluorine, respectively.

[0026]

When the surface of the positive electrode active material is covered with a coating film to protect the above crystal structure, a decrease in capacity due to charge and discharge cycles can be suppressed. As the coating film covering the surface of the positive electrode active material, a coating film containing carbon (a film containing a graphene compound) or a coating film containing lithium or a decomposition product of an electrolyte solution is used.

[0027]

In particular, powder in which the surface of the positive electrode active material is coated with graphene oxide using a spray dry apparatus is preferably obtained. The spray dry apparatus is a manufacturing apparatus using a spray dry method by which a dispersion medium is removed by supplying a hot wind to a suspension.

[0028]

When charge and discharge cycles are repeated, deformation of the particles of the positive electrode active materials, such as cracking or breaking, might occur. It is said that such deformation makes a new surface of the positive electrode active material exposed, and the surface is in contact with an electrolyte solution to cause a decomposition reaction or the like, so that the cycle characteristics and the charge and discharge characteristics of the secondary battery are degraded.

[0029]

Thus, a coating film is preferably provided to prevent the deformation of the particles of the positive electrode active materials, such as cracking or breaking.

[0030]

However, when suspension is formed and stirred by a rotary and revolutionary mixer to coat the surface of the positive electrode active material whose weight per unit volume is large with graphene oxide whose weight is relatively small, coating is insufficient.

[0031]

Thus, to coat the surfaces of the particles of the positive electrode active materials with the graphene oxide, a method in which the graphene oxide and a polar solvent (such as water)

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are mixed and ultrasonic treatment is performed, the particles of the positive electrode active materials are mixed therein to prepare the suspension, and dried powder is produced with a spray dry apparatus is preferably used. The dried powder produced in this manner is referred to as a composite in some cases.

[0032]

The size of one drop of spray liquid sprayed from a nozzle of the spray dry apparatus depends on a nozzle diameter.

[0033]

When the particle diameter is smaller than the nozzle diameter, there are a plurality of particles in one drop of the spray liquid sprayed from the nozzle. When the surface of the particle after drying under the condition where the largest particle size is smaller than the nozzle diameter is observed, there are some portions where the surface is coated with the graphene oxide; however, the coating is insufficient.

[0034]

The nozzle diameter of the spray dry apparatus is preferably substantially equal to the largest particle size of the active material because the coverage of the active material can be improved. Moreover, the largest particle size of the positive electrode active material is preferably adjusted to be substantially equal to the nozzle diameter in forming the positive electrode active material.

[0035]

Since the graphene oxide is well dispersed into water, the suspension of water and the graphene oxide can be formed by stirring using ultrasonic waves. The positive electrode active material is added to the suspension, and the suspension is sprayed with the spray dry apparatus, whereby powder in which the surface of the positive electrode active material is coated with the graphene oxide can be obtained.

[0036]

Note that the suspension becomes more acidic as the amount of graphene oxide is increased. Thus, part of the surface of the positive electrode active material (e.g., $LiCoO_2$ containing Mg and F) might be etched. Then, a hydrogen ion exponent (pH) of the suspension before being sprayed is preferably adjusted to be close to approximately pH7, that is, close to neutral, or higher than or equal to pH8, that is, alkaline. For the pH adjustment, a LiOH aqueous solution is preferably used. For example, in the case where $LiCoO_2$ is used for the positive electrode active material and only pure water is used as the dispersion medium of the suspension, the surface of the positive electrode active material may be damaged. Thus, a mixed solution of ethanol and water is used as the dispersion medium of the suspension,

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whereby damage to the surface of the active material may be reduced.

[0037]

The suspension is formed in the above manner, whereby the positive electrode active material whose surface is coated with the graphene oxide can be prepared efficiently. When the surface is coated with the graphene oxide, the deformation of the particles of the positive electrode active materials, such as cracking or breaking can be prevented. Moreover, even if the positive electrode active material whose surface is coated with the graphene oxide is exposed to the air after the formation, the change of properties or degradation can be suppressed. Here, "after the formation" refers to a period from the termination of the formation of the positive electrode active material to the start of the fabrication of the secondary battery containing the positive electrode active material and includes the storing, the transporting, and the like of the positive electrode active material. In addition, when the coating film is formed, the positive electrode active material and the electrolyte solution can be prevented from being in direct contact with each other to react; thus, the secondary battery using the coating film has high reliability.

[0038]

For the spray dry method, a known apparatus can be utilized, for example, a countercurrent pressure-nozzle-type spray dry apparatus and a counter-cocurrent pressure-nozzle-type spray dry apparatus can be utilized.

[0039]

Note that the graphene oxide coating the surface of the active material may be reduced when used in the secondary battery. The reduced graphene oxide is referred to as "RGO" in some cases. In RGO, in some cases, part of oxygen atoms remains in a state of oxygen or atomic group containing oxygen that is bonded to carbon. For example, RGO includes a functional group, e.g., an epoxy group, a carbonyl group such as a carboxyl group, or a hydroxyl group.

[0040]

Another embodiment of the present invention is a secondary battery which includes a positive electrode containing the above-described positive electrode active material or the above-described positive electrode active material coated with a coating film and a negative electrode.

[0041]

The secondary battery can have any of a variety of shapes to fit the form of the device to be used, for example, a cylindrical shape, a rectangular shape, a coin-type shape, and a laminated (flat plate) shape.

[0042]

According to one embodiment of the present invention, a positive electrode active material which suppresses a reduction in capacity due to charge and discharge cycles when used in a lithium ion secondary battery is provided. In addition, a secondary battery with excellent charge and discharge characteristics is provided. In addition, a highly safe or highly reliable secondary battery is provided. In addition, a novel material, a novel active material particle, a novel secondary battery, or a formation method thereof is provided.

BRIEF DESCRIPTION OF DRAWINGS

[0043]

In the accompanying drawings:

FIGS. 1A to 1C show examples of a positive electrode active material;

FIGS. 2A and 2B illustrate crystal structures of a positive electrode active material;

FIG. 3 illustrates crystal structures of a positive electrode active material;

FIGS. 4A-1, 4A-2, 4A-3, 4B, 4C, 4D-1, and 4D-2 show a sol-gel method;

FIGS. 5A to 5C illustrate a segregation model of elements contained in a positive electrode active material;

FIGS. 6A to 6D illustrate a segregation model of elements contained in a positive electrode active material;

FIGS. 7A and 7B are cross-sectional views of an active material layer containing a graphene compound as a conductive additive;

FIGS. 8A to 8C illustrate a method for charging a secondary battery;

FIGS. 9A to 9D illustrate a method for charging a secondary battery;

FIG. 10 illustrates a method for discharging a secondary battery;

FIGS. 11A to 11C illustrate a coin-type secondary battery;

FIGS. 12A to 12D illustrate a cylindrical secondary battery;

FIGS. 13A and 13B illustrate an example of a secondary battery;

FIGS. 14A-1, 14A-2, 14B-1, and 14B-2 illustrate examples of secondary batteries;

FIGS. 15A and 15B illustrate examples of secondary batteries;

FIG. 16 illustrates an example of a secondary battery;

FIGS. 17A to 17C illustrate a laminated secondary battery;

FIGS. 18A and 18B illustrate a laminated secondary battery;

FIG. 19 is an external view of a secondary battery;

FIG. 20 is an external view of a secondary battery;

FIGS. 21A to 21C illustrate a formation method of a secondary battery;

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FIGS. 22A, 22B1, 22B2, 22C, and 22D illustrate a bendable secondary battery;

FIGS. 23A and 23B illustrate a bendable secondary battery;

FIGS. 24A to 24H illustrate examples of electronic devices;

FIGS. 25A to 25C illustrate an example of an electronic device;

FIG. 26 illustrates examples of electronic devices;

FIGS. 27A to 27C illustrate examples of electronic devices;

FIG. 28 is a transmission electron microscope image of a positive electrode active material in Example 1;

FIGS. 29A1, 29A2, 29B1, 29B2, 29C1, and 29C2 are FFT images of transmission electron microscope images of a positive electrode active material in Example 1;

FIGS. 30A1, 30A2, 30B1, 30B2, 30C1, and 30C2 are element mapping images of a positive electrode active material in Example 1;

FIGS. 31A1, 31A2, 31B1, 31B2, 31C1, and 31C2 are element mapping images of a positive electrode active material of a comparative example in Example 1;

FIG. 32 is a graph showing TEM-EDX line analysis results of a positive electrode active material in Example 1;

FIG. 33 is a graph showing charge and discharge characteristics of a secondary battery in Example 1;

FIG. 34 is a graph showing charge and discharge characteristics of a secondary battery of a comparative example in Example 1;

FIG. 35 is a graph showing cycle characteristics of a secondary battery in Example 1;

FIG. 36 is a graph showing cycle characteristics of a secondary battery in Example 1;

FIGS. 37A, 37B1, 37B2, 37C1, 37C2, 37D1, 37D2, 37E1, and 37E2 are TEM-EDX plane analysis images of a comparative example in Example 2;

FIGS. 38A, 38B1, 38B2, 38C1, 38C2, 38D1, 38D2, 38E1, and 38E2 are TEM-EDX plane analysis images of a positive electrode active material in Example 2;

FIGS. 39A, 39B1, 39B2, 39C1, 39C2, 39D1, 39D2, 39E1, and 39E2 are TEM-EDX plane analysis images of a comparative example in Example 2;

FIGS. 40A, 40B1, 40B2, 40C1, 40C2, 40D1, 40D2, 40E1, and 40E2 are TEM-EDX plane analysis images of a positive electrode active material in Example 2;

FIGS. 41A and 41B are each a graph showing EDX point analysis results in Example 2;

FIGS. 42A and 42B are each a graph showing EDX point analysis results in Example 2;

FIG. 43 is a graph showing rate characteristics of a secondary battery in Example 2;

FIG. 44 is a graph showing temperature characteristics of a secondary battery in Example 2;

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FIG. 45 is a graph showing cycle characteristics of a secondary battery in Example 2;

FIGS. 46A and 46B are each a graph showing XPS analysis results of a positive electrode active material in Example 3;

FIGS. 47A and 47B are each a graph showing cycle characteristics of a secondary battery containing a positive electrode active material in Example 3;

FIG. 48 is a graph showing cycle characteristics of a secondary battery containing a positive electrode active material in Example 3;

FIG. 49 is a graph showing cycle characteristics of a secondary battery containing a positive electrode active material in Example 3;

FIGS. 50A to 50C are each a graph showing charge and discharge characteristics of a secondary battery containing a positive electrode active material in Example 3;

FIGS. 51A to 51C are SEM images of a positive electrode active material in Example 4;

FIGS. 52A-1, 52A-2, 52B-1, 52B-2, 52C-1, and 52C-2 are SEM-EDX images of a positive electrode active material in Example 4;

FIG. 53 is a process flow chart of Example 5;

FIG. 54 illustrates a spray dry apparatus in Example 5;

FIG. 55 is a TEM image showing one embodiment of the present invention in Example 5;

FIG. 56 is a SEM image showing one embodiment of the present invention in Example 5;

FIG. 57 is a SEM image showing a comparative example in Example 5; and

FIGS. 58A and 58B are cross-sectional views of an active material layer containing a graphene compound as a conductive additive in Example 5.

BEST MODE FOR CARRYING OUT THE INVENTION

[0044]

Embodiments of the present invention will be described below in detail with reference to the drawings. Note that the present invention is not limited to the description below, and it is easily understood by those skilled in the art that modes and details of the present invention can be modified in various ways. In addition, the present invention should not be construed as being limited to the description in the embodiments given below.

[0045]

Note that in drawings used in this specification, the sizes, thicknesses, and the like of components such as a positive electrode, a negative electrode, an active material layer, a separator, and an exterior body are exaggerated for simplicity in some cases. Therefore, the

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sizes of the components are not limited to the sizes in the drawings and relative sizes between the components.

[0046]

Note that in structures of the present invention described in this specification and the like, the same portions or portions having similar functions are denoted by common reference numerals in different drawings, and descriptions thereof are not repeated. Further, the same hatching pattern is applied to portions having similar functions, and the portions are not especially denoted by reference numerals in some cases.

[0047]

In this specification and the like, the Miller index is used for the expression of crystal planes and orientations. In the crystallography, a superscript bar is placed over a number in the expression using the Miller index; however, in this specification and the like, crystal planes and orientations are expressed by placing a minus sign (–) at the front of a number instead of placing the bar over a number because of expression limitations. Furthermore, an individual direction which shows an orientation in crystal is denoted by "[ ]", a set direction which shows all of the equivalent orientations is denoted by "< >", an individual direction which shows a crystal plane is denoted by "( )", and a set plane having equivalent symmetry is denoted by "{ }". In the drawings, the crystal planes and orientations are expressed by a number with a bar placed thereover, which is an original crystallographic expression. Note that 1 Å is 10^{-10} m.

[0048]

In this specification and the like, segregation refers to a phenomenon in which, in a solid made of a plurality of elements (e.g., A, B, and C), a certain element (for example, B) is non-uniformly distributed.

[0049]

In this specification and the like, a layered rock-salt crystal structure included in a composite oxide containing lithium and a transition metal refers to a crystal structure in which a rock-salt ion arrangement where cations and anions are alternately arranged is included and the lithium and the transition metal are regularly arranged to form a two-dimensional plane, so that lithium can be two-dimensionally diffused. Note that a defect such as a cation or anion vacancy can exist. In the layered rock-salt crystal structure, strictly, a lattice of a rock-salt crystal is distorted in some cases.

[0050]

In this specification and the like, a rock-salt crystal structure refers to a structure in which cations and anions are alternately arranged. Note that a cation or anion vacancy may exist.

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[0051]

Anions of a layered rock-salt crystal and anions of a rock-salt crystal each form a cubic closest packed structure (face-centered cubic lattice structure). When a layered rock-salt crystal and a rock-salt crystal are in contact with each other, there is a crystal plane at which directions of cubic closest packed structures formed of anions are aligned with each other. A space group of the layered rock-salt crystal is R−3m, which is different from a space group Fm−3m of a general rock-salt crystal and a space group Fd−3m of a rock-salt crystal having the simplest symmetry; thus, the Miller index of the crystal plane satisfying the above conditions in the layered rock-salt crystal is different from that in the rock-salt crystal. In this specification, in the layered rock-salt crystal and the rock-salt crystal, a state where the directions of the cubic closest packed structures formed of anions are aligned with each other is referred to as a state where crystal orientations are substantially aligned with each other.

[0052]

Whether the crystal orientations in two regions are aligned with each other or not can be judged by a transmission electron microscope (TEM) image, a scanning transmission electron microscope (STEM) image, a high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image, an annular bright-field scan transmission electron microscopy (ABF-STEM) image, and the like. X-ray diffraction, electron diffraction, neutron diffraction, and the like can be used for judging. In the TEM image and the like, alignment of cations and anions can be observed as repetition of bright lines and dark lines. When the orientations of cubic closest packed structures of the layered rock-salt crystal and the rock-salt crystal are aligned with each other, a state where an angle between the repetition of bright lines and dark lines in the layered rock-salt crystal and the repetition of bright lines and dark lines in the rock-salt crystal is less than or equal to 5°, preferably less than or equal to 2.5° is observed. Note that, in the TEM image and the like, a light element such as oxygen or fluorine is not clearly observed in some cases; however, in such a case, alignment of orientations can be judged by arrangement of metal elements.

[0053]

Furthermore, in this specification and the like, a state where structures of two-dimensional interfaces have similarity is referred to as "epitaxy". Crystal growth in which structures of two-dimensional interfaces have similarity is referred to as "epitaxial growth". In addition, a state where three-dimensional structures have similarity or orientations are crystallographically the same is referred to as "topotaxy". Thus, in the case of topotaxy, when part of a cross section is observed, orientations of crystals in two regions (e.g., a region serving as a base and a region formed through growth) are substantially aligned with each other.

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[0054]

(Embodiment 1)

[Structure of positive electrode active material]

First, a positive electrode active material 100, which is one embodiment of the present invention, is described with reference to FIGS. 1A to 1C. The positive electrode active material 100 refers to a substance containing a transition metal which can receive and release lithium ion electrochemically. As illustrated in FIG. 1A, the positive electrode active material 100 includes a first region 101 inside and a second region 102 and a third region 103 in a superficial portion.

[0055]

As illustrated in FIG. 1B, the second region 102 does not necessarily cover the entire first region 101. Similarly, the third region 103 does not necessarily cover the entire second region 102. In addition, the third region 103 may be present in contact with the first region 101.

[0056]

The thicknesses of the second region 102 and the third region 103 may each differ depending on the positions.

[0057]

Furthermore, the third region 103 may be present inside the positive electrode active material 100. For example, in the case where the first region 101 is a polycrystal, the third region 103 may be present in the vicinity of a grain boundary. Furthermore, the third region 103 may be present in a portion which includes crystal defects or a crack portion in the positive electrode active material 100 or in the vicinity thereof. In FIG. 1B, parts of grain boundaries are shown by dotted lines. In this specification and the like, crystal defects refer to defects which can be observed from a TEM image and the like, that is, a structure in which another element enters crystal, a cavity, and the like. In addition, a crack portion refers to a crack or a break formed in a particle like a crack portion 106 illustrated in FIG. 1C, for example.

[0058]

Similarly, as illustrated in FIG. 1B, the second region 102 may be present inside the positive electrode active material 100. For example, in the case where the first region 101 is a polycrystal, the second region 102 may be present in the vicinity of a grain boundary. Furthermore, the second region 102 may be present in a portion which includes crystal defects or a crack portion in the positive electrode active material 100 or in the vicinity thereof. Moreover, the third region 103 and the second region 102 inside the positive electrode active material 100 may overlap.

[0059]

<First region 101>

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The first region 101 contains a composite oxide of lithium and a first transition metal. In other words, the first region 101 contains lithium, a first transition metal, and oxygen.

[0060]

The composite oxide of lithium and a first transition metal preferably has a layered rock-salt crystal structure.

[0061]

As the first transition metal, only cobalt may be used, cobalt and manganese may be used, or cobalt, manganese, and nickel may be used.

[0062]

That is, the first region can include lithium cobalt oxide, lithium manganese oxide, lithium nickel oxide, lithium cobalt oxide in which manganese is substituted for part of cobalt, lithium nickel-manganese-cobalt oxide, or the like. In addition to the transition metal, the first region 101 may include a metal other than the transition metal, such as aluminum.

[0063]

The first region 101 serves as a region which particularly contributes to a charge and discharge reaction in the positive electrode active material 100. To increase capacity of a secondary battery containing the positive electrode active material 100, the volume of the first region 101 is preferably larger than those of the second region and the third region.

[0064]

A material having a layered rock-salt crystal structure has features such as high discharge capacity and low resistance due to lithium that can be diffused two-dimensionally, which is preferably used for the first region 101. In addition, in the case where the first region 101 has a layered rock-salt crystal structure, a segregation of a representative element such as magnesium, which is described later, tends to occur unexpectedly.

[0065]

Note that the first region 101 may be a single crystal or a polycrystal. For example, the first region 101 may be a polycrystal in which an average crystallite size is greater than or equal to 280 nm and less than or equal to 630 nm. In the case of a polycrystal, a grain boundary can be observed from the TEM or the like in some cases. In addition, the average of crystal grain sizes can be calculated from the half width of XRD.

[0066]

The polycrystal has a clear crystal structure; thus, a two-dimensional diffusion path of lithium ions can be sufficiently ensured. In addition, a polycrystal is easily produced as compared with a single crystal; thus, a polycrystal is preferably used for the first region 101.

[0067]

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Furthermore, the entire first region 101 does not necessarily have a layered rock-salt crystal structure. For example, part of the first region 101 may be amorphous or has another crystal structure.

[0068]

<Second region 102>

The second region 102 contains an oxide of a second transition metal. In other words, the second region 102 contains a second transition metal and oxygen.

[0069]

As the second transition metal, a non-stoichiometric metal is preferably used. In other words, the second region 102 preferably includes a non-stoichiometric compound. For example, as the second transition metal, at least one of titanium, vanadium, manganese, iron, chromium, niobium, cobalt, zinc, zirconium, nickel, and the like can be used. Note that the second transition metal is preferably an element different from that of the first transition metal.

[0070]

In this specification and the like, a non-stoichiometric metal refers to a metal that can have a plurality of valences. In addition, a non-stoichiometric compound refers to a compound of a metal that can have a plurality of valences and another element.

[0071]

The second region 102 preferably has a rock-salt crystal structure.

[0072]

The second region 102 serves as a buffer region which connects the first region 101 to the third region 103 which is described later. In the non-stoichiometric compound, an interatomic distance can be changed in accordance with a change in valence of a metal contained in the non-stoichiometric compound. In addition, in the non-stoichiometric compound, a cation or anion vacancy and dislocation (what is called Magneli phase) are often formed. Thus, the second region 102, which serves as a buffer region, can absorb a strain generated between the first region 101 and the third region 103.

[0073]

Furthermore, the second region 102 may contain lithium in addition to the second transition metal and oxygen. For example, lithium titanate or lithium manganite may be contained. Moreover, the second region 102 may contain a representative element contained in the third region 103 which is described later. The second region 102 that contains an element contained in the first region 101, such as lithium, and an element contained in the third region 103 is preferable because the second region 102 serves as a buffer region.

[0074]

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That is, the second region 102 can contain lithium titanate, titanium oxide, vanadium oxide, manganese oxide, iron oxide, copper oxide, chromium oxide, niobium oxide, cobalt oxide, zinc oxide, or the like.

[0075]

In addition, the second region 102 may contain the first transition metal. For example, the second transition metal may be present in part of a first transition metal site of the composite oxide including the first transition metal.

[0076]

For example, in the case where the second transition metal is titanium, titanium may be present as titanium oxide (TiO_2) or lithium titanate ($LiTiO_2$) in the second region 102. Alternatively, in the second region 102, titanium may be substituted for part of the first transition metal site of the composite oxide of lithium and the first transition metal.

[0077]

Moreover, the second region 102 may contain fluorine.

[0078]

The second region 102 preferably has a crystal structure which is the same as that of the third region 103 which is described later. In this case, orientations of crystals of the second region 102 and the third region 103 are likely to be aligned with each other.

[0079]

The second region 102 preferably has a rock-salt crystal structure; however, the entire second region 102 does not necessarily have a rock-salt crystal structure. For example, the second region 102 may have another crystal structure such as a spinel crystal structure, an olivine crystal structure, a corundum crystal structure, or a rutile crystal structure.

[0080]

Furthermore, a crystal structure may have a strain as long as a structure where six oxygen atoms are adjacent to cations is kept. In addition, a cation vacancy may be present in part of the second region 102.

[0081]

Moreover, part of the second region 102 may be amorphous.

[0082]

When the thickness of the second region 102 is too small, the function as the buffer region is degraded; however, when the thickness of the second region 102 is too large, the capacity might be decreased. Thus, the second region 102 is preferably provided in a range from the surface of the positive electrode active material 100 to a depth of 20 nm, preferably a depth of 10 nm, in a depth direction. The second transition metal may have a concentration

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gradient.

[0083]

<Third region 103>

The third region 103 contains a compound of representative elements. A compound of representative elements is a stoichiometric compound. As the compound of representative elements, a compound made of representative elements which are electrochemically stable is preferable, and at least one of magnesium oxide, calcium oxide, beryllium oxide, lithium fluoride, and sodium fluoride can be used, for example.

[0084]

The third region 103 is in contact with an electrolyte solution when the positive electrode active material 100 is used in a secondary battery. Thus, for the third region 103, a material which is hardly changed electrochemically in the process of charging and discharging and is not easily transformed by contact with the electrolyte solution is preferably used. The compound of representative elements which is a stoichiometric compound and electrochemically stable is preferably used for the third region 103. The positive electrode active material 100 includes the third region 103 in a superficial portion to improve stability in charging and discharging of the secondary battery. Here, a state where stability of a secondary battery is high refers to a state where the crystal structure of the composite oxide of lithium and the first transition metal contained in the first region 101 is more stable. Alternatively, it refers to a state where a change in capacity of the secondary battery is small even if charging and discharging are repeated or a state where a change in valence of a metal contained in the positive electrode active material 100 is suppressed even after charging and discharging are repeated.

[0085]

The third region 103 may contain fluorine. In the case where the third region 103 contains fluorine, fluorine may be substituted for some anions in the compound of the representative elements.

[0086]

Fluorine is substituted for some anions in the compound of the representative elements, whereby diffusion properties of lithium can be improved. Thus, the third region 103 is less likely to prevent charging and discharging. In addition, when fluorine is present in a superficial portion of a positive electrode active material particle, corrosion resistance against a hydrofluoric acid generated by decomposition of an electrolyte solution is increased in some cases.

[0087]

Moreover, the third region 103 may include lithium, the first transition metal, and the second transition metal.

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[0088]

The compound of the representative elements contained in the third region 103 preferably has a rock-salt crystal structure. When the third region 103 has a rock-salt crystal structure, orientations of crystals are likely to be aligned with those of the second region 102. The orientations of crystals of the first region 101, the second region 102, and the third region 103 are substantially aligned with each other, whereby the second region 102 and the third region 103 can serve as a more stable coating layer.

[0089]

However, the entire third region 103 does not necessarily have a rock-salt crystal structure. For example, the third region 103 may have another crystal structure such as a spinel crystal structure, an olivine crystal structure, a corundum crystal structure, or a rutile crystal structure.

[0090]

Furthermore, a crystal structure may have a strain as long as a structure where six oxygen atoms are adjacent to cations is kept. In addition, a cation vacancy may be present in part of the third region 103.

[0091]

Moreover, part of the third region 103 may be amorphous.

[0092]

When the thickness of the third region 103 is too small, the function of increasing stability in charging and discharging is degraded; however, when the thickness of the third region 103 is too large, the capacity might be decreased. Thus, the thickness of the third region 103 is preferably greater than or equal to 0.5 nm and less than or equal to 50 nm, further preferably greater than or equal to 0.5 nm and less than or equal to 2 nm.

[0093]

In the case where the third region 103 contains fluorine, fluorine is preferably present in a bonding state other than magnesium fluoride (MgF_2), lithium fluoride (LiF), and cobalt fluoride (CoF_2). Specifically, when an XPS analysis is performed on the vicinity of the surface of the positive electrode active material 100, a peak position of bonding energy with fluorine is preferably higher than or equal to 682 eV and lower than or equal to 685 eV, further preferably approximately 684.3 eV. The bonding energy does not correspond to those of MgF_2, LiF, and CoF_2.

[0094]

In this specification and the like, a peak position of bonding energy with an element in an XPS analysis refers to a value of bonding energy at which the maximum intensity of an

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energy spectrum is obtained in a range corresponding to bonding energy of the element.

[0095]

In general, when charging and discharging are repeated, a side reaction occurs in a positive electrode active material, for example, a first transition metal such as manganese, cobalt, or nickel is dissolved in an electrolyte solution, oxygen is released, and a crystal structure becomes unstable, so that the positive electrode active material deteriorates. However, the positive electrode active material 100 of one embodiment of the present invention includes the second region 102 serving as a buffer region and the third region 103 which is electrochemically stable. Thus, the dissolution of the first transition metal can be effectively suppressed, and the crystal structure of the composite oxide of lithium and the transition metal contained in the first region 101 can be more stable. As a result, the cycle characteristics of the secondary battery including the positive electrode active material 100 can be significantly improved. In addition, in the case where charging and discharging are performed at a voltage higher than 4.3 V (vs. Li/Li^+), in particular, a high voltage of 4.5 V (vs. Li/Li^+) or more, the structure of one embodiment of the present invention is significantly effective.

[0096]

<Heteroepitaxial growth and topotaxy>

The second region 102 is preferably formed by heteroepitaxial growth from the first region 101. Furthermore, the third region 103 is preferably formed by heteroepitaxial growth from the second region 102. A region formed by heteroepitaxial growth becomes topotaxy which has crystal orientations substantially three-dimensionally aligned with those of a region serving as a base. Thus, the first region 101, the second region 102, and the third region 103 can be topotaxy.

[0097]

When the crystal orientations of the first region 101, the second region 102, and the third region 103 are substantially aligned with each other, the second region 102 and the third region 103 serve as a coating layer which has a stable bond with the first region 101. As a result, the positive electrode active material 100 including a strong coating layer can be provided.

[0098]

Since the second region 102 and the third region 103 have a stable bond with the first region 101, when the positive electrode active material 100 is used for the secondary battery, a change of the crystal structure in the first region 101 which is caused by charging and discharging can be effectively suppressed. Even when lithium is released from the first region 101 due to charging, the coating layer having a stable bond can suppress release of cobalt and

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oxygen from the first region 101. Furthermore, a chemically stable material can be used for a region in contact with the electrolyte solution. Thus, a secondary battery having excellent cycle characteristics can be provided.

[0099]

<Degree of mismatch between regions>

To perform heteroepitaxial growth, the degree of a mismatch between crystals in a region serving as a base and crystals on which crystal growth is performed is important.

[0100]

In this specification and the like, the degree of a mismatch f is defined by the following Formula 1. The average of the nearest neighbor distances between oxygen and cations of the crystals in the region serving as a base is represented by a, and the average of the natural nearest neighbor distances between anions and cations of the crystals on which crystal growth is performed is represented by b.

[0101]

[Formula 1]

$$f = \left| \frac{b-a}{a} \right| \qquad \text{(Formula 1)}$$

[0102]

To perform heteroepitaxial growth, the degree of a mismatch f between crystals in a region serving as a base and crystals on which crystal growth is performed needs to be less than or equal to 0.12. To perform more stable heteroepitaxial growth to form a layered shape, the degree of a mismatch f is preferably less than or equal to 0.08, further preferably less than or equal to 0.04.

[0103]

Thus, materials of the first region 101 and the second region 102 are preferably selected so that the degree of a mismatch f between the layered rock-salt crystal structure in the first region 101 and the rock-salt crystal structure in the second region 102 is less than or equal to 0.12.

[0104]

Furthermore, materials of the second region 102 and the third region 103 are preferably selected so that the degree of a mismatch f between the rock-salt crystal structure in the second region 102 and the rock-salt crystal structure in the third region 103 is less than or equal to 0.12.

[0105]

Examples of materials and crystal planes of the first region 101, the second region 102, and the third region 103 are shown below, which satisfy the above-described conditions: the

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degree of a mismatch *f* between the layered rock-salt crystal structure in the first region 101 and the rock-salt crystal structure in the second region 102 is less than or equal to 0.12; and the degree of a mismatch *f* between the rock-salt crystal structure in the second region 102 and the rock-salt crystal structure in the third region 103 is less than or equal to 0.12.

[0106]

<<Example 1: Lithium cobaltate, lithium titanate, and magnesium oxide>>

First, FIGS. 2A and 2B and FIG. 3 show an example in which the first transition metal is cobalt, the first region 101 contains lithium cobaltate having a layered rock-salt crystal structure, the second transition metal is titanium, the second region 102 contains lithium titanate having a rock-salt crystal structure, and the compound of the representative elements in the third region 103 is magnesium oxide having a rock-salt crystal structure.

[0107]

FIG. 2A illustrates a model of a layered rock-salt crystal structure (a space group R−3mH) of lithium cobaltate ($LiCoO_2$), a model of a rock-salt crystal structure (a space group Fd−3mZ) of lithium titanate ($LiTiO_2$), and a model of a rock-salt crystal structure (a space group Fd−3mZ) of magnesium oxide. FIG. 2A illustrates models each of which is seen from the *b*-axis direction.

[0108]

From FIG. 2A, it is not seen that the layered rock-salt crystals and the rock-salt crystals make topotaxy. Then, here, the layered rock-salt crystals are seen from a different direction (e.g., a direction indicated by an arrow in FIG. 2A). FIG. 2B illustrates a model of the layered rock-salt crystals seen from the <1−1−4> plane direction and models of the rock-salt crystals seen from the <100> plane direction.

[0109]

As illustrated in FIG. 2B, when the layered rock-salt crystals are seen from the <1−1−4> plane direction, atomic arrangement of the layered rock-salt crystals is highly similar to those of the rock-salt crystals seen from the <100> plane direction. In addition, the nearest neighbor distances between metal and oxygen have similar values. For example, in the layered rock-salt lithium cobaltate, a distance between Li and O is 2.089 Å and a distance between Co and O is 1.925 Å. In the rock-salt lithium titanate, a distance between Li and O is 2.138 Å and a distance between Ti and O is 2.051 Å. In the rock-salt magnesium oxide, a distance between Mg and O is 2.106 Å.

[0110]

Then, with reference to FIG. 3, the degree of a mismatch between the regions when the (1−1−4) crystal plane of the layered rock-salt crystal and the {100} crystal plane of the rock-salt

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crystal are in contact with each other is described.

[0111]

As illustrated in FIG. 3, a distance between metals through oxygen in a (1−1−4) crystal plane 101p (1−1−4) of lithium cobaltate having the layered rock-salt crystal structure in the first region 101 is 4.01 Å. Furthermore, a distance between metals through oxygen in a {100} crystal plane 102p {100} of lithium titanate having the rock-salt crystal structure in the second region 102 is 4.19 Å. Thus, the degree of a mismatch *f* between the crystal plane 101p (1−1−4) and the crystal plane 102p {100} is 0.04.

[0112]

In addition, a distance between metals through oxygen in a {100} crystal plane 103p {100} of magnesium oxide having the rock-salt crystal structure in the third region 103 is 4.21 Å. Thus, the degree of a mismatch *f* between the crystal plane 102p {100} and the crystal plane 103p {100} is 0.02.

[0113]

In this manner, the degree of a mismatch between the first region 101 and the second region 102 and the degree of a mismatch between the second region 102 and the third region 103 are sufficiently small; thus, the first region 101, the second region 102, and the third region 103 can be topotaxy.

[0114]

Although not illustrated in FIG. 3, if the crystal plane 101p (1−1−4) in the first region 101 and the crystal plane 103p {100} in the third region 103 are in contact with each other, the degree of a mismatch *f* is 0.05. That is, owing to the second region 102, the degree of a mismatch can be small. Moreover, with the second region 102 that is a non-stoichiometric transition metal oxide, the first region 101, the second region 102, and the third region 103 can be more stable topotaxy. Thus, the second region 102 and the third region 103 can serve as a coating layer having a stable bond with the first region 101.

[0115]

In this embodiment, the (1−1−4) plane of the layered rock-salt crystal and the {100} plane of the rock-salt crystal are in contact with each other; however, one embodiment of the present invention is not limited thereto as long as crystal planes which can be topotaxy are in contact with each other.

[0116]

<<Example 2: Lithium cobaltate, manganese oxide, and calcium oxide>>

Next, an example in which the first transition metal is cobalt, the first region 101

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contains lithium cobaltate having a layered rock-salt crystal structure, the second transition metal is manganese, the second region 102 contains manganese oxide having a rock-salt crystal structure, and the compound of the representative elements in the third region 103 is calcium oxide having a rock-salt crystal structure is shown.

[0117]

Also in this case, as in FIGS. 2A and 2B and FIG. 3, when the layered rock-salt crystals are seen from the <1−1−4> plane direction, atomic arrangement of the layered rock-salt crystals in the first region 101 is highly similar to those of the rock-salt crystals in the second region 102 and the third region 103 seen from the <100> plane direction.

[0118]

The degree of a mismatch between the regions when the (1−1−4) crystal plane of the layered rock-salt crystal and the {100} crystal plane of the rock-salt crystal are in contact with each other is described. A distance between metals through oxygen in a crystal plane (1−1−4) of lithium cobaltate having the layered rock-salt crystal structure in the first region 101 is 4.01 Å. Furthermore, a distance between metals through oxygen in a crystal plane {100} of manganese oxide having the rock-salt crystal structure in the second region 102 is 4.45 Å. Thus, the degree of a mismatch *f* between the crystal plane (1−1−4) in the first region 101 and the crystal plane {100} in the second region 102 is 0.11.

[0119]

In addition, a distance between metals through oxygen in a crystal plane {100} of calcium oxide having the rock-salt crystal structure in the third region 103 is 4.82 Å. Thus, the degree of a mismatch *f* between the crystal plane {100} in the second region 102 and the crystal plane {100} in the third region 103 is 0.08.

[0120]

In this manner, the degree of a mismatch between the first region 101 and the second region 102 and the degree of a mismatch between the second region 102 and the third region 103 are sufficiently small; thus, the first region 101, the second region 102, and the third region 103 can be topotaxy.

[0121]

If the crystal plane (1−1−4) in the first region 101 and the crystal plane {100} in the third region 103 are in contact with each other, the degree of a mismatch *f* is 0.20; thus, it is difficult to perform the heteroepitaxial growth. That is, owing to the second region 102, the heteroepitaxial growth from the first region to the third region can be performed. Thus, the second region 102 and the third region 103 can serve as a coating layer having a stable bond with

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the first region 101.

[0122]

<<Example 3: Lithium nickel-manganese-cobalt oxide, manganese oxide, and calcium oxide>>

Next, an example in which the first transition metals are nickel, manganese, and cobalt, the first region 101 contains lithium nickel-manganese-cobalt oxide ($LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$) having a layered rock-salt crystal structure, the second transition metal is manganese, the second region 102 contains manganese oxide having a rock-salt crystal structure, and the compound of the representative elements in the third region 103 is calcium oxide having a rock-salt crystal structure is shown.

[0123]

Also in this case, as illustrated in FIGS. 2A and 2B and FIG. 3, when the layered rock-salt crystals are seen from the <1−1−4> plane direction, atomic arrangement of the layered rock-salt crystals is highly similar to those of the rock-salt crystals seen from the <100> plane direction. The degree of a mismatch between the regions when the (1−1−4) crystal plane of the layered rock-salt crystal and the {100} crystal plane of the rock-salt crystal are in contact with each other is described.

[0124]

A distance between metals through oxygen in a crystal plane (1−1−4) of lithium nickel-manganese-cobalt oxide having the layered rock-salt crystal structure in the first region 101 is 4.07 Å. Furthermore, a distance between metals through oxygen in a crystal plane {100} of manganese oxide having the rock-salt crystal structure in the second region 102 is 4.45 Å. Thus, the degree of a mismatch f between the crystal plane (1−1−4) in the first region 101 and the crystal plane {100} in the second region 102 is 0.09.

[0125]

In addition, a distance between metals through oxygen in a crystal plane {100} of calcium oxide having the rock-salt crystal structure in the third region 103 is 4.82 Å. Thus, the degree of a mismatch f between the crystal plane {100} in the second region 102 and the crystal plane {100} in the third region 103 is 0.08.

[0126]

In this manner, the degree of a mismatch between the first region 101 and the second region 102 and the degree of a mismatch between the second region 102 and the third region 103 are sufficiently small; thus, the first region 101, the second region 102, and the third region 103 can be topotaxy.

[0127]

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If the crystal plane (1−1−4) in the first region 101 and the crystal plane {100} in the third region 103 are in contact with each other, the degree of a mismatch f is 0.18; thus, it is difficult to perform the heteroepitaxial growth. That is, the second region 102 is provided, whereby the heteroepitaxial growth from the first region to the third region can be performed. Thus, the second region 102 and the third region 103 can serve as a coating layer having a stable bond with the first region 101.

[0128]

<Boundaries between regions>

As described above, the first region 101, the second region 102, and the third region 103 have different compositions. The element contained in each region has a concentration gradient in some cases. For example, the second transition metal in the second region 102 may have a concentration gradient. In addition, the third region 103 may have a concentration gradient of a representative element because a representative element preferably segregates in the third region 103 as described later. Thus, the boundaries between the regions are not clear in some cases.

[0129]

The difference of compositions of the first region 101, the second region 102, and the third region 103 can be observed using a TEM image, a STEM image, fast Fourier transform (FFT) analysis, energy dispersive X-ray spectrometry (EDX), an analysis in the depth direction by time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, thermal desorption spectroscopy (TDS), or the like.

[0130]

For example, in the TEM image and the STEM image, difference of constituent elements is observed as difference of brightness; thus, difference of constituent elements of the first region 101, the second region 102, and the third region 103 can be observed. Furthermore, also in plane analysis of EDX (e.g., element mapping), it can be observed that the first region 101, the second region 102, and the third region 103 contain different elements.

[0131]

By line analysis of EDX and analysis in the depth direction using ToF-SIMS, a peak of concentration of each element contained in the first region 101, the second region 102, and the third region 103 can be detected.

[0132]

However, clear boundaries between the first region 101, the second region 102, and the third region 103 are not necessarily observed by the analyses.

[0133]

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In this specification and the like, the third region 103 that is present in a superficial portion of the positive electrode active material 100 refers to a region from the surface of the positive electrode active material 100 to a region where a concentration of a representative element such as magnesium which is detected by analysis in the depth direction is 1/5 of a peak. As the analysis in the depth direction, the line analysis of EDX, analysis in the depth direction using ToF-SIMS, or the like, which is described above, can be used.

[0134]

Furthermore, a peak of a concentration of a representative element is preferably present in a region from the surface of the positive electrode active material 100 to a depth of 3 nm toward the center, further preferably to a depth of 1 nm, and still further preferably to a depth of 0.5 nm.

[0135]

Although the depth at which the concentration of the representative element becomes 1/5 of the peak is different depending on the manufacturing method, in the case of a manufacturing method described later, the depth is approximately 2 nm to 5 nm from the surface of the positive electrode active material.

[0136]

The third region 103 that is present inside the first region 101 in the vicinity of a grain boundary, a crystal defect, or the like also refers to a region where a concentration of a representative element which is detected by analysis in the depth direction is higher than or equal to 1/5 of a peak.

[0137]

A distribution of fluorine in the positive electrode active material 100 preferably overlaps with a distribution of the representative element. Thus, fluorine also has a concentration gradient, and a peak of a concentration of fluorine is preferably present in a region from the surface of the positive electrode active material 100 to a depth of 3 nm toward the center, further preferably to a depth of 1 nm, and still further preferably to a depth of 0.5 nm.

[0138]

In this specification and the like, the second region 102 that is present in a superficial portion of the positive electrode active material 100 refers to a region where a concentration of the second transition metal which is detected by analysis in the depth direction is higher than or equal to 1/2 of a peak. The second region 102 that is present inside the first region 101 in the vicinity of a grain boundary, a crystal defect, or the like also refers to a region where a concentration of the second transition metal which is detected by analysis in the depth direction is higher than or equal to 1/2 of a peak. As the analysis method, the line analysis of EDX,

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analysis in the depth direction using ToF-SIMS, or the like, which is described above, can be used.

[0139]

Thus, the third region 103 and the second region 102 overlap in some cases. Note that the third region 103 is preferably present in a region closer to the surface of the positive electrode active material particle than the second region 102 is. In addition, the peak of the concentration of the representative element is preferably present in a region closer to the surface of the positive electrode active material particle than the peak of the concentration of the second transition metal is.

[0140]

The peak of the second transition metal is preferably present in a region from a depth of 0.2 nm or more to a depth of 10 nm or less from the surface of the positive electrode active material 100 toward the center, further preferably in a region from a depth of 0.5 nm or more to a depth of 3 nm or less.

[0141]

The measurement range of the XPS is from the surface of the particle of the positive electrode active material 100 to a region at a depth of approximately 5 nm. Thus, a concentration of an element present at a depth of approximately 5 nm from the surface can be analyzed quantitatively. Thus, the concentration of elements in the third region 103 and the second region 102 present at a depth of approximately 5 nm from the surface can be analyzed quantitatively.

[0142]

When the surface of the positive electrode active material 100 is subjected to the XPS analysis and the concentration of the first transition metal is defined as 1, a relative value of the concentration of the second transition metal is preferably greater than or equal to 0.05 and less than or equal to 0.4, further preferably greater than or equal to 0.1 and less than or equal to 0.3. In addition, a relative value of the concentration of the representative element is preferably greater than or equal to 0.4 and less than or equal to 1.5, further preferably greater than or equal to 0.45 and less than or equal to 1.00. Furthermore, a relative value of the concentration of fluorine is preferably greater than or equal to 0.05 and less than or equal to 1.5, further preferably greater than or equal to 0.3 and less than or equal to 1.00.

[0143]

Note that, as described above, elements contained in the first region 101, the second region 102, and the third region 103 may each have a concentration gradient; thus, the first region 101 may contain the element in the second region 102 or the third region 103, such as

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fluorine. Similarly, the third region 103 may contain the element in the first region 101 or the second region 102. In addition, the first region 101, the second region 102, and the third region 103 may each contain another element such as carbon, sulfur, silicon, sodium, calcium, chlorine, or zirconium.

[0144]

[Particle diameter]

If the particle diameter of the positive electrode active material 100 is too large, diffusion of lithium is difficult, whereas if the particle diameter is too small, it is difficult to maintain a crystal structure described later. Thus, D50 (also referred to as a median diameter) is preferably 5 μm or more and 100 μm or less, and further preferably 10 μm or more and 70 μm or less. In the case where the coating film is formed on the surface of the positive electrode active material 100 by a spray dry apparatus in a later step, it is preferable that the nozzle diameter and the maximum particle diameter of the positive electrode active material 100 be substantially the same. When the particle diameter is less than 5 μm and a spray dry apparatus having a nozzle diameter of 20 μm is used, secondary particles are covered collectively, which leads to a decrease in coverage.

[0145]

To increase the density of the positive electrode active material layer, it is effective to mix large particles (the longest portion is approximately 20 μm or more and 40 μm or less) and small particles (the longest portion is approximately 1 μm) and embed spaces between the large particles with the small particles. Thus, there may be two peaks of particle size distribution.

[0146]

The particle size of the positive electrode active material is influenced not only by the particle sizes of starting materials but also by a ratio between lithium and the first transition metal (hereinafter expressed as a ratio of Li to the first transition metal) which are contained in the starting material.

[0147]

In the case where the particle size of the starting material is small, the grain growth needs to be performed at the time of baking so that the grain size of the positive electrode active material is in the above-described preferred range.

[0148]

To promote the grain growth at the time of baking, it is effective to make the ratio of Li to the first transition metal of the starting material larger than 1, that is, to make the amount of lithium a little larger. For example, when the ratio of Li to the first transition metal is approximately 1.06, a positive electrode active material in which D50 is larger than or equal to

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15 μm is easily obtained. Note that, as described later, lithium may be lost to the outside of a system in the formation process of the positive electrode active material; thus, the ratio between lithium and the first transition metal of the obtained positive electrode active material does not agree with the ratio between lithium and the first transition metal of the starting material in some cases.

[0149]

However, if the amount of lithium is too large to make the particle size be in the preferred range, the capacity retention rate of a secondary battery containing the positive electrode active material might be decreased.

[0150]

Then, the present inventors found that with the second region 102 containing the second transition metal in the superficial portion, the particle size can be in the preferred range by control of the ratio of Li to the first transition metal and a positive electrode active material having high capacity retention rate can be formed.

[0151]

In the positive electrode active material of one embodiment of the present invention including a region containing the second transition metal in the superficial portion, the ratio of Li to the first transition metal in the starting material is preferably greater than or equal to 1.00 and less than or equal to 1.07, further preferably greater than or equal to 1.03 and less than or equal to 1.06.

[0152]

[Formation of second region]

The second region 102 can be formed by coating particles of the composite oxide of lithium and the first transition metal with a material containing the second transition metal.

[0153]

As the coating method of the material containing the second transition metal, a liquid phase method such as a sol-gel method, a solid phase method, a sputtering method, an evaporation method, a chemical vapor deposition (CVD) method, a pulsed laser deposition (PLD) method, or the like can be used. In this embodiment, the case where the sol-gel method which can be performed with a uniform coverage under an atmospheric pressure is used is described.

[0154]

<Sol-gel method>

A method for forming a material containing the second transition metal using a sol-gel method is described with reference to FIGS. 4A-1, 4A-2, 4A-3, 4B, 4C, 4D-1, and 4D-2.

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[0155]

First, an alkoxide of the second transition metal is dissolved in alcohol.

[0156]

FIG. 4A-1 shows a general formula of the alkoxide of the second transition metal. In the formula of FIG. 4A-1, M2 indicates the alkoxide of the second transition metal. R represents an alkyl group having 1 to 18 carbon atoms or a substituted or unsubstituted aryl group having 6 to 13 carbon atoms. Although FIG. 4A-1 shows the general formula in which the second transition metal has a valence of 4, one embodiment of the present invention is not limited thereto. The second transition metal may have a valence of 2, a valence of 3, a valence of 5, a valence of 6, or a valence of 7. In this case, the alkoxide of the second transition metal includes an alkoxy group corresponding to the valence of the second transition metal.

[0157]

FIG. 4A-2 shows a general formula of the titanium alkoxide used when titanium is used as the second transition metal. R in FIG. 4A-2 represents an alkyl group having 1 to 18 carbon atoms or a substituted or unsubstituted aryl group having 6 to 13 carbon atoms.

[0158]

As the titanium alkoxide, tetramethoxytitanium, tetraethoxytitanium, tetra-*n*-propoxytitanium, tetra-*i*-propoxytitanium (also referred to as tetraisopropyl orthotitanate, titanium (IV) isopropoxide, titanium tetraisopropoxide (IV), TTIP, and the like), tetra-*n*-butoxytitanium, tetra-*i*-butoxytitanium, tetra-*sec*-butoxytitanium, tetra-*t*-butoxytitanium, or the like can be used.

[0159]

FIG. 4A-3 shows a chemical formula of titanium (IV) isopropoxide (TTIP) described in a formation method below, which is a kind of titanium alkoxide.

[0160]

As a solvent in which the alkoxide of the second transition metal is dissolved, an alcohol such as methanol, ethanol, propanol, 2-propanol, butanol, or 2-butanol is preferably used.

[0161]

Next, particles of composite oxide of lithium, a transition metal, magnesium, and fluorine are mixed into the alcohol solution of the alkoxide of the second transition metal and stirred in an atmosphere containing water vapor.

[0162]

When the solution is put in an atmosphere containing H_2O, hydrolysis of water and an alkoxide of the second transition metal occurs as in FIG. 4B. Then, as in FIG. 4C, dehydration

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condensation occurs between the products of FIG. 4B. When the hydrolysis of FIG. 4B and the condensation reaction of FIG. 4C occur repeatedly, a sol of an oxide of the second transition metal is generated. This reaction also occurs on a particle 110 of the composite oxide as in FIGS. 4D-1 and 4D-2, and a layer containing the second transition metal is formed on the surface of the particle 110.

[0163]

After that, the particle 110 is collected, and the alcohol is vaporized. The details of the formation method are described later.

[0164]

Note that in this embodiment, an example in which the particles of the composite oxide of lithium, the first transition metal, the representative element, and fluorine are coated with the material containing the second transition metal before the particles are applied to a positive electrode current collector is described; however, one embodiment of the present invention is not limited thereto. After the positive electrode active material layer including the particles of the composite oxide of lithium, the first transition metal, the representative element, and fluorine is formed on the positive electrode current collector, the positive electrode current collector and the positive electrode active material layer may be both soaked into an alkoxide solution of the second transition metal to be coated with the material containing the second transition metal.

[0165]

[Segregation of third region]

The third region 103 can be formed by a sputtering method, a solid phase method, a liquid phase method such as a sol-gel method, or the like. However, the present inventors found that when a source of a representative element such as magnesium and a source of fluorine are mixed with a material of the first region 101 and then the mixture is heated, the representative element is segregated on a superficial portion of the positive electrode active material particle to form the third region 103. In addition, they found that with the third region 103 formed in this manner, the positive electrode active material 100 has excellent cycle characteristics.

[0166]

In the case where the third region 103 is formed through the heating as described above, the heating is preferably performed after the particle of the composite oxide is coated with the material containing the second transition metal. This is because even after the particle is coated with the material containing the second transition metal, the representative element such as magnesium is unexpectedly segregated on the surface of the particle when the heating is performed.

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[0167]

Segregation models of the representative element are described with reference to FIGS. 5A to 5C and FIGS. 6A to 6D. It is probable that the segregation model of the representative element such as magnesium is slightly different in accordance with the ratio between lithium and the first transition metal contained in a starting material. Then, a segregation model in which the ratio of Li to the first transition metal in the starting material is less than 1.03, that is, the amount of lithium is small, is described with reference to FIGS. 5A to 5C. In addition, a segregation model in which the ratio of Li to the first transition metal in the starting material is greater than or equal to 1.03, that is, the amount of lithium is large, is described with reference to FIGS. 6A to 6D. In these segregation models in FIGS. 5A to 5C and FIGS. 6A to 6D, the first transition metal is cobalt, the second transition metal is titanium, and the representative element is magnesium.

[0168]

FIG. 5A illustrates a model diagram of the vicinity of the surface of the particle 110 of the composite oxide containing lithium, cobalt, magnesium, and fluorine, which is formed at a ratio of Li to Co in the starting material of less than 1.03. A region 111 in the drawings contains lithium, cobalt, magnesium, and fluorine, and lithium cobaltate ($LiCoO_2$) is a main component of the region 111. Lithium cobaltate has a layered rock-salt structure.

[0169]

It is generally known that, at the time of synthesizing particles of the composite oxide containing lithium, cobalt, magnesium, and fluorine, lithium partly moves outside a system (a particle on which lithium is formed). This is because lithium is volatilized at the time of baking, lithium is eluted to a solvent at the time of mixing the starting material, and the like. Thus, the ratio of Li to Co in the particle 110 of the composite oxide containing lithium, cobalt, magnesium, and fluorine becomes smaller than the ratio of Li to Co in the starting material in some cases.

[0170]

When the ratio of Li to Co in the starting material is less than 1.03, on the surface of the particle 110, lithium is released from the lithium cobaltate and cobalt oxide is easily generated. Thus, as illustrated in FIG. 5A, the surface of the particle 110 of the composite oxide is covered with a cobalt oxide (CoO) layer 114 in some cases.

[0171]

The cobalt oxide has a rock-salt crystal structure. Thus, in the particle 110 in FIG. 5A, the cobalt oxide layer 114 having a rock-salt crystal structure is provided over and in contact with the region 111 containing lithium cobaltate having a layered rock-salt crystal structure in

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some cases.

[0172]

The particle 110 is coated with a material containing titanium by a sol-gel method or the like. FIG. 5B illustrates a state where the particle 110 is coated with a layer 112 containing titanium by a sol-gel method. At the stage of FIG. 5B, the layer 112 containing titanium is a gel of titanium oxide; thus, the crystallinity is low.

[0173]

Next, the particle 110 coated with the layer 112 containing titanium is heated. Although the details of the heating conditions are described later, for example, FIG. 5C illustrates a state where the particle 110 is heated in an oxygen atmosphere at 800 °C for two hours to form the positive electrode active material 100, which is one embodiment of the present invention. By heating, titanium in the layer 112 containing titanium is diffused into the inside of the particle 110. At the same time, magnesium and fluorine contained in the region 111 are segregated on the surface of the particle 110.

[0174]

As described above, on the surface of the particle 110, cobalt oxide having a rock-salt structure is present. In addition, magnesium oxide also has a rock-salt crystal structure. Thus, it is probable that magnesium is more stable in the state of being present as magnesium oxide on the surface of the particle 110 as compared with the state of being present inside the particle 110. That could be why magnesium is segregated on the surface of the particle 110 when the particle 110 is heated.

[0175]

Moreover, it is considered that fluorine contained in the starting material promotes the segregation of magnesium.

[0176]

Fluorine has higher electronegativity than oxygen. Thus, it is probable that even in a stable compound such as magnesium oxide, when fluorine is added, uneven charge distribution occurs and a bond between magnesium and oxygen is weakened. Furthermore, it is probable that fluorine is substituted for oxygen in the magnesium oxide, whereby magnesium easily moves around the substituted fluorine.

[0177]

Moreover, this can also be described from a phenomenon in which a melting point of a mixture decreases. When magnesium oxide (melting point: 2852 °C) and lithium fluoride (melting point: 848 °C) are added at the same time, the melting point of the magnesium oxide is lowered. It is considered that the melting point is lowered, whereby magnesium easily moves

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at the time of heating, and the segregation of magnesium easily occurs.

[0178]

Lastly, the third region 103 becomes a solid solution of cobalt oxide and magnesium oxide which has a rock-salt crystal structure. Furthermore, fluorine is probably substituted for part of oxygen contained in the cobalt oxide and the magnesium oxide.

[0179]

Cobalt sites of lithium cobaltate are substituted for part of the diffused titanium and lithium titanate is substituted for another part of the diffused titanium. The second region 102 after the heating contains lithium titanate having a rock-salt crystal structure.

[0180]

The first region 101 after the heating contains lithium cobaltate having a layered rock-salt crystal structure.

[0181]

Next, the case where the ratio of Li to Co in the starting material is larger than or equal to 1.03 is described with reference to FIGS. 6A to 6D. FIG. 6A illustrates a model diagram of the vicinity of the surface of the particle 120 of the composite oxide containing lithium, cobalt, magnesium, and fluorine, which is formed at a ratio of Li to Co in the starting material of greater than or equal to 1.03. A region 121 in the drawings contains lithium, cobalt, magnesium, and fluorine.

[0182]

Since the particle 120 in FIG. 6A contains a sufficient amount of lithium, even when lithium is released from the particle 120 at the time of baking the particle 120 of the composite oxide of lithium, cobalt, magnesium, and fluorine or the like, lithium is diffused from the inside of the particle 120 to the surface thereof to compensate; as a result, a cobalt oxide layer is not easily formed on the surface.

[0183]

FIG. 6B illustrates a state where the particle 120 in FIG. 6A is coated with a layer 122 containing titanium by a sol-gel method. At the stage of FIG. 6B, the layer 122 containing titanium is a gel of titanium oxide; thus, the crystallinity is low.

[0184]

FIG. 6C illustrates the state where the particle 120 coated with the layer 122 containing titanium in FIG. 6B starts to be heated. By heating, titanium in the layer 122 containing titanium is diffused into the inside of the particle 110. The diffused titanium is bonded with lithium contained in the region 121 to become lithium titanate, and a layer 125 containing the lithium titanate is formed.

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[0185]

Since lithium is bonded with titanium to form lithium titanate, the amount of lithium is relatively insufficient at the surface of the particle 120. Thus, it is probable that, as illustrated in FIG. 6C, a cobalt oxide layer 124 is temporarily formed on the surface of the particle 120.

[0186]

FIG. 6D illustrates the state where the state of FIG. 6C is sufficiently heated to form the positive electrode active material 100, which is one embodiment of the present invention. It is considered that, since the cobalt oxide layer 124 having a rock-salt crystal structure is present on the surface, magnesium is more stable in the state of being present as magnesium oxide on the surface of the particle 120 as compared with the state of being present inside the particle 120. As in the case of FIGS. 5A to 5C, fluorine promotes the segregation of magnesium.

[0187]

Thus, as illustrated in FIG. 6D, magnesium and fluorine contained in the region 121 are segregated on the surface to be the third region 103 with the cobalt oxide.

[0188]

In this manner, the positive electrode active material 100, which includes the third region 103 containing magnesium oxide and cobalt oxide, the second region 102 containing lithium titanate, and the first region 101 containing lithium cobaltate, is formed.

[0189]

Note that in the case where the representative element is segregated by heating, when the composite oxide containing lithium and the first transition metal included in the first region 101 is a polycrystal or has crystal defects, the representative element can be segregated not only in the superficial portion but also in the vicinity of a grain boundary of the composite oxide containing lithium and the first transition metal or in the vicinity of crystal defects thereof. The representative element segregated in the vicinity of a grain boundary or in the vicinity of crystal defects can contribute to further improvement in stability of the crystal structure of the composite oxide containing lithium and the first transition metal included in the first region 101.

[0190]

When the composite oxide containing lithium and the first transition metal included in the first region 101 includes a crack portion, the representative element is also segregated in the crack portion by heating. In addition, not only the representative element but also the second transition metal can be segregated. The crack portion is in contact with the electrolyte solution like the surface of the particle. Thus, the representative element and the second transition metal are segregated in the crack portion, and the third region 103 and the second region 102 are generated, whereby a chemically stable material can be used for the region in contact with the

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electrolyte solution. As a result, a secondary battery having excellent cycle characteristics can be provided.

[0191]

The ratio between a representative element (T) and fluorine (F) in a starting material is preferably in a range of T:F = 1:x ($1.5 \leq x \leq 4$) (atomic ratio) because the segregation of the representative element effectively occurs. Further preferably, the ratio between T and F is approximately 1:2 (atomic ratio).

[0192]

Since the third region 103 formed by segregation is formed by epitaxial growth, orientations of crystals in the second region 102 and the third region 103 are partly and substantially aligned with each other in some cases. That is, the second region 102 and the third region 103 become topotaxy in some cases. When the orientations of crystals in the second region 102 and the third region 103 are substantially aligned with each other, these regions can serve as a more favorable coating layer.

[0193]

However, not all of the representative elements such as magnesium which is added as a starting material need not be segregated in the third region 103. For example, the first region 101 may contain a small amount of representative element such as magnesium.

[0194]

<Fourth region 104>

In addition, as illustrated in FIG. 1C, the positive electrode active material 100 may include a fourth region 104 on the third region 103. Furthermore, when the positive electrode active material 100 contains a defect such as a crack portion 106, the fourth region 104 may be present to embed the defect such as the crack portion 106.

[0195]

The fourth region 104 contains some elements contained in the second region 102 and the third region 103. For example, the fourth region 104 contains the second transition metal and the representative element.

[0196]

The fourth region 104 may have a projection, a stripe shape, or a layered shape. The fourth region 104 is formed using the second transition metal and the representative element not contained in the second region 102 or the third region 103 of the second transition metals and the representative elements contained in the starting material and the like. That is, with the fourth region 104, the amount of the second transition metal and the representative element contained in the second region 102 and the third region 103 can be kept in an appropriate range and the

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crystal structures of the second region 102 and the third region 103 can be stabilized in some cases. Moreover, with the fourth region 104, the defect such as the crack portion 106 included in the positive electrode active material 100 can be repaired.

[0197]

The presence of the fourth region 104 and the shape of the fourth region 104 can be observed by a scanning electron microscope (SEM) or the like. Elements contained in the fourth region 104 can be analyzed by SEM-EDX or the like.

[0198]

[Method for forming positive electrode active material]

Next, an example of a method for forming the positive electrode active material 100, which is one embodiment of the present invention, is described.

[0199]

<Step 11: Preparation of starting materials>

First, starting materials are prepared. From the starting materials prepared in this process, the first region 101 and the third region 103 are formed finally.

[0200]

As materials of lithium and the first transition metal contained in the first region 101, a source of lithium and a source of the first transition metal are prepared. In addition, as materials of the compound of the representative elements contained in the third region 103, a source of the representative element is prepared.

[0201]

In addition to these sources, a source of fluorine is preferably prepared. Fluorine used for the materials has an effect of segregating the representative elements contained in the third region 103 on the surface of the positive electrode active material 100 in a later step.

[0202]

As the source of lithium, for example, lithium carbonate and lithium fluoride can be used. As the source of the first transition metal, for example, an oxide of the first transition metal can be used. As the source of the representative element, for example, an oxide of the representative element contained in the third region and fluoride of the representative element contained in the third region can be used.

[0203]

As the source of fluorine, for example, lithium fluoride and fluoride of the representative element contained in the third region can be used. That is, lithium fluoride can be used as either the source of lithium or the source of fluorine.

[0204]

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The amount of fluorine contained in the source of fluorine is preferably 1.0 time to 4 times (atomic ratio), further preferably 1.5 times to 3 times (atomic ratio) the amount of representative element contained in the source of the representative element.

[0205]

<Step 12: Mixing of starting materials>

Next, the source of lithium, the source of the first transition metal, and the source of the representative element are mixed. In addition, the source of fluorine is preferably added. For example, a ball mill and a bead mill can be used for the mixing.

[0206]

<Step 13: First heating>

Next, the materials mixed in Step 12 are heated. In this step, the heating is referred to as baking or first heating in some cases. The heating is preferably performed at higher than or equal to 800 °C and lower than or equal to 1100 °C, further preferably at higher than or equal to 900 °C and lower than or equal to 1000 °C. The heating time is preferably greater than or equal to 2 hours and less than or equal to 20 hours. The baking is preferably performed in a dried atmosphere such as dry air. In the dried atmosphere, for example, the dew point is preferably lower than or equal to −50 °C, further preferably lower than or equal to −100 °C. In this embodiment, the heating is performed at 1000 °C for 10 hours, the temperature rising rate is 200 °C/h, and dry air whose dew point is −109 °C flows at 10 L/min. After that, the heated materials are cooled to room temperature.

[0207]

By the heating in Step 13, the composite oxide of lithium and the first transition metal having a layered rock-salt crystal structure can be synthesized. At this time, the representative element and fluorine contained in the starting materials form a solid solution in the composite oxide. However, some representative elements have been already segregated on the surface of the composite oxide in some cases.

[0208]

In addition, as the starting materials, particles of the composite oxide containing lithium, cobalt, fluorine, and magnesium which are synthesized in advance may be used. In this case, Step 12 and Step 13 can be omitted. For example, lithium cobalt oxide particles (C-20F, produced by NIPPON CHEMICAL INDUSTRIAL CO., LTD.) can be used as one of the starting materials. The lithium cobalt oxide particle has a diameter of approximately 20 μm and contains fluorine, magnesium, calcium, sodium, silicon, sulfur, and phosphorus in a region which can be analyzed by XPS from the surface.

[0209]

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<Step 14: Coating with second transition metal>

Next, the composite oxide of lithium and the first transition metal is cooled to room temperature. Then, the surface of the composite oxide particle of lithium and the first transition metal is coated with a material containing the second transition metal. In the formation method example, a sol-gel method is used.

[0210]

First, the alkoxide of the second transition metal which is dissolved in alcohol and the composite oxide particles of lithium and the first transition metal are mixed.

[0211]

For example, in the case where titanium is used as the second transition metal, TTIP can be used as the alkoxide of the second transition metal. As alcohol, isopropanol can be used, for example.

[0212]

Next, the above mixed solution is stirred in an atmosphere containing water vapor. The stirring can be performed with a magnetic stirrer, for example. The stirring time is not limited as long as water and TTIP in an atmosphere cause hydrolysis and polycondensation reaction. For example, the stirring can be performed at 25 °C and a humidity of 90 %RH (Relative Humidity) for 4 hours.

[0213]

As described above, when water and TTIP in an atmosphere are reacted, a sol-gel reaction can proceed more slowly as compared with the case where liquid water is added. Alternatively, when titanium alkoxide and water are reacted at room temperature, a sol-gel reaction can proceed more slowly as compared with the case where heating is performed at a temperature higher than the boiling point of alcohol which is a solvent, for example. A sol-gel reaction proceeds slowly, whereby a high-quality coating layer containing titanium with a uniform thickness can be formed.

[0214]

After the above process, precipitate is collected from the mixed solution. As the collection method, filtration, centrifugation, evaporation and drying, or the like can be used. In this embodiment, filtration is used. For the filtration, a paper filter is used, and the residue is washed by alcohol which is the same as the solvent in which titanium alkoxide is dissolved.

[0215]

Then, the collected residue is dried. In this embodiment, vacuum drying is performed at 70 °C for one hour.

[0216]

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<Step 15: Second heating>

Next, the composite oxide particle coated with the material containing the second transition metal, which is formed in Step 14, is heated. This step is referred to as second heating in some cases. In the heating, the retention time within a specified temperature range is preferably shorter than or equal to 50 hours, further preferably longer than or equal to 2 hours and shorter than or equal to 10 hours, still further preferably longer than or equal to 1 hour and shorter than or equal to 3 hours. If the heating time is too short, there is concern that the segregation of the representative elements does not occur; however, if the heating time is too long, there is concern that the favorable second region 102 is not formed because diffusion of the second transition metal proceeds too much.

[0217]

The specified temperature is preferably higher than or equal to 500 °C and lower than or equal to 1200 °C, further preferably higher than or equal to 800 °C and lower than or equal to 1000 °C. If the specified temperature is too low, there is concern that the segregation of the representative elements and the second transition metal does not occur. However, if the specified temperature is too high, there is concern that the first transition metal in the composite oxide particle is reduced to decompose the composite oxide particle, that a layered structure of lithium and the first transition metal in the composite oxide particle cannot be kept, and the like.

[0218]

In this embodiment, the specified temperature is 800 °C and kept for 2 hours, the temperature rising rate is 200 °C/h, and the flow rate of dry air is 10 L/min.

[0219]

By the heating in Step 15, the composite oxide of lithium and the first transition metal and the oxide of the second transition metal covering the composite oxide become topotaxy. In other words, the first region 101 and the second region 102 become topotaxy.

[0220]

By the heating in Step 15, the representative elements which form a solid solution inside the composite oxide particle of lithium and the first transition metal are unevenly distributed on the surface to form a solid solution, that is, the representative elements are segregated, the compound of the representative elements is formed, and the third region 103 is formed. At this time, the compound of the representative elements is formed by heteroepitaxial growth from the second region 102. That is, the second region 102 and the third region 103 become topotaxy.

[0221]

Since the second region 102 and the third region 103 contain crystals whose orientations are substantially aligned with each other and have a stable bond with the first region 101, when

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the positive electrode active material 100 is used for the secondary battery, a change of the crystal structure in the first region 101 which is caused by charging and discharging can be effectively suppressed. Even when lithium is released from the first region 101 due to charging, the superficial portion having a stable bond can suppress release of oxygen and the first transition metal such as cobalt from the first region 101. Furthermore, a chemically stable material can be used for a region in contact with the electrolyte solution. Thus, a secondary battery having excellent cycle characteristics can be provided.

[0222]

Note that the entire first region 101 and second region 102 does not need to become topotaxy as long as part of the first region 101 and second region 102 becomes topotaxy. Furthermore, the entire second region 102 and third region 103 does not need to become topotaxy as long as part of the second region 102 and third region 103 becomes topotaxy.

[0223]

In the case where the compound of the representative elements contained in the third region contains oxygen, the heating in Step 15 is preferably performed in an atmosphere containing oxygen. Heating in an atmosphere containing oxygen promotes the formation of the third region 103.

[0224]

Furthermore, fluorine contained in the starting materials promotes the segregation of the representative elements.

[0225]

In this manner, in the method for forming the positive electrode active material of one embodiment of the present invention, after the elements forming the second region 102 are coated, heating is performed to form the third region 103, and two kinds of regions can be formed on the surface of the positive electrode active material 100. That is, in general, two coating steps are necessary for providing two kinds of regions in a superficial portion; however, in the method for forming the positive electrode active material of one embodiment of the present invention, only one coating step (sol-gel process) is needed, which is a formation method with high productivity.

[0226]

<Step 16: Cooling>

Next, the particles heated in Step 15 are cooled to room temperature. The time of decreasing temperature is preferably long because topotaxy is easily generated. For example, the time of decreasing temperature from retention temperature to room temperature is preferably the same as the time of increasing temperature or longer, specifically longer than or equal to 10

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hours and shorter than or equal to 50 hours.

[0227]

<Step 17: Collecting>

Next, the cooled particles are collected. Moreover, the particles are preferably made to pass through a sieve. Through the above process, the positive electrode active material 100 including the first region 101, the second region 102, and the third region 103 can be formed.

[0228]

This embodiment can be implemented in appropriate combination with any of the other embodiments.

[0229]

(Embodiment 2)

In this embodiment, examples of materials which can be used for a secondary battery containing the positive electrode active material 100 described in the above embodiment are described. In this embodiment, a secondary battery in which a positive electrode, a negative electrode, and an electrolyte solution are wrapped in an exterior body is described as an example.

[0230]

[Positive electrode]

The positive electrode includes a positive electrode active material layer and a positive electrode current collector.

[0231]

<Positive electrode active material layer>

The positive electrode active material layer contains at least a positive electrode active material. The positive electrode active material layer may contain, in addition to the positive electrode active material, other materials such as a coating film of the active material surface, a conductive additive, and a binder.

[0232]

As the positive electrode active material, the positive electrode active material 100 described in the above embodiment can be used. When the above-described positive electrode active material 100 is used, a secondary battery with high capacity and excellent cycle characteristics can be obtained.

[0233]

Examples of the conductive additive include a carbon material, a metal material, and a conductive ceramic material. Alternatively, a fiber material may be used as the conductive additive. The content of the conductive additive with respect to the total amount of the active material layer is preferably greater than or equal to 1 wt% and less than or equal to 10 wt%,

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more preferably greater than or equal to 1 wt% and less than or equal to 5 wt%.

[0234]

A network for electric conduction can be formed in the active material layer by the conductive additive. The conductive additive also allows maintaining of a path for electric conduction between the positive electrode active material particles. The addition of the conductive additive to the active material layer increases the electric conductivity of the active material layer.

[0235]

Examples of the conductive additive include natural graphite, artificial graphite such as mesocarbon microbeads, and carbon fiber. Examples of carbon fiber include mesophase pitch-based carbon fiber, isotropic pitch-based carbon fiber, carbon nanofiber, and carbon nanotube. Carbon nanotube can be formed by, for example, a vapor deposition method. Other examples of the conductive additive include carbon materials such as carbon black (e.g., acetylene black (AB)), graphite (black lead) particles, graphene, and fullerene. Alternatively, metal powder or metal fibers of copper, nickel, aluminum, silver, gold, or the like, a conductive ceramic material, or the like can be used.

[0236]

Alternatively, a graphene compound may be used as the conductive additive.

[0237]

A graphene compound has excellent electrical characteristics of high conductivity and excellent physical properties of high flexibility and high mechanical strength. Furthermore, a graphene compound has a planar shape. A graphene compound enables low-resistance surface contact. Furthermore, a graphene compound has extremely high conductivity even with a small thickness in some cases and thus allows a conductive path to be formed in an active material layer efficiently even with a small amount. For this reason, it is preferable to use a graphene compound as the conductive additive because the area where the active material and the conductive additive are in contact with each other can be increased. It is preferable to form the graphene compound serving as a conductive additive as a coating film to cover the entire surface of the active material with a spray dry apparatus, in which case the electrical resistance may be reduced. Here, it is particularly preferable to use, for example, graphene, multilayer graphene, or RGO as a graphene compound. Note that RGO refers to a compound obtained by reducing graphene oxide (GO), for example.

[0238]

In the case where an active material with a small particle diameter (e.g., 1 μm or less) is used, the specific surface area of the active material is large and thus more conductive paths for

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the active material particles are needed. Thus, the amount of conductive additive tends to increase and the supported amount of active material tends to decrease relatively. When the supported amount of active material decreases, the capacity of the secondary battery also decreases. In such a case, a graphene compound that can efficiently form a conductive path even in a small amount is particularly preferably used as the conductive additive because the supported amount of active material does not decrease.

[0239]

A cross-sectional structure example of an active material layer 200 containing a graphene compound as a conductive additive is described below.

[0240]

FIG. 7A shows a longitudinal cross-sectional view of the active material layer 200. The active material layer 200 includes positive electrode active material particles 100, a graphene compound 201 serving as a conductive additive, and a binder (not illustrated). Here, graphene or multilayer graphene may be used as the graphene compound 201, for example. The graphene compound 201 preferably has a sheet-like shape. The graphene compound 201 may have a sheet-like shape formed of a plurality of sheets of multilayer graphene and/or a plurality of sheets of graphene that partly overlap with each other.

[0241]

The longitudinal cross section of the active material layer 200 in FIG. 7B shows substantially uniform dispersion of the sheet-like graphene compounds 201 in the active material layer 200. The graphene compounds 201 are schematically shown by thick lines in FIG. 7B but are actually thin films each having a thickness corresponding to the thickness of a single layer or a multi-layer of carbon molecules. The plurality of graphene compounds 201 are formed in such a way as to partly coat or adhere to the surfaces of the plurality of positive electrode active material particles 100, so that the graphene compounds 201 make surface contact with the positive electrode active material particles 100.

[0242]

Here, the plurality of graphene compounds are bonded to each other to form a net-like graphene compound sheet (hereinafter referred to as a graphene compound net or a graphene net). The graphene net covering the active material can function as a binder for bonding active materials. The amount of a binder can thus be reduced, or the binder does not have to be used. This can increase the proportion of the active material in the electrode volume or weight. That is to say, the capacity of the secondary battery can be increased.

[0243]

Here, it is preferable to perform reduction after a layer to be the active material layer

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200 is formed in such a manner that graphene oxide is used as the graphene compound 201 and mixed with an active material. When graphene oxide with extremely high dispersibility in a polar solvent is used for the formation of the graphene compounds 201, the graphene compounds 201 can be substantially uniformly dispersed in the active material layer 200. The solvent is removed by volatilization from a dispersion medium in which graphene oxide is uniformly dispersed, and the graphene oxide is reduced; hence, the graphene compounds 201 remaining in the active material layer 200 partly overlap with each other and are dispersed such that surface contact is made, thereby forming a three-dimensional conduction path. Note that graphene oxide can be reduced either by heat treatment or with the use of a reducing agent, for example.

[0244]

Unlike a conductive additive in the form of particles, such as acetylene black, which makes point contact with an active material, the graphene compound 201 is capable of making low-resistance surface contact; accordingly, the electrical conduction between the positive electrode active material particles 100 and the graphene compounds 201 can be improved with a smaller amount of the graphene compound 201 than that of a normal conductive additive. This increases the proportion of the positive electrode active material particles 100 in the active material layer 200, resulting in increased discharge capacity of the secondary battery.

[0245]

Alternatively, the graphene compound may cover the entire surface of the active material in advance with a spray dry apparatus. After that, at the time of forming the positive electrode active material layer, a graphene compound can be further added to make the conductive path between the active materials more favorable.

[0246]

As the binder, a rubber material such as styrene-butadiene rubber (SBR), styrene-isoprene-styrene rubber, acrylonitrile-butadiene rubber, butadiene rubber, or ethylene-propylene-diene copolymer can be used, for example. Alternatively, fluororubber can be used as the binder.

[0247]

For the binder, for example, water-soluble polymers are preferably used. As the water-soluble polymers, a polysaccharide and the like can be used. As the polysaccharide, a cellulose derivative such as carboxymethyl cellulose (CMC), methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, diacetyl cellulose, or regenerated cellulose, starch, or the like can be used. It is more preferred that such water-soluble polymers be used in combination with any of the above rubber materials.

[0248]

Alternatively, as the binder, a material such as polystyrene, poly(methyl acrylate), poly(methyl methacrylate) (PMMA), sodium polyacrylate, polyvinyl alcohol (PVA), polyethylene oxide (PEO), polypropylene oxide, polyimide, polyvinyl chloride, polytetrafluoroethylene, polyethylene, polypropylene, polyisobutylene, polyethylene terephthalate, nylon, polyvinylidene fluoride (PVdF), polyacrylonitrile (PAN), ethylene-propylene-diene polymer, polyvinyl acetate, or nitrocellulose is preferably used.

[0249]

A plurality of the above materials may be used in combination for the binder.

[0250]

For example, a material having a significant viscosity modifying effect and another material may be used in combination. For example, a rubber material or the like has high adhesion or high elasticity but may have difficulty in viscosity modification when mixed in a solvent. In such a case, a rubber material or the like is preferably mixed with a material having a significant viscosity modifying effect, for example. As a material having a significant viscosity modifying effect, for example, a water-soluble polymer is preferably used. An example of a water-soluble polymer having an especially significant viscosity modifying effect is the above-mentioned polysaccharide; for example, a cellulose derivative such as carboxymethyl cellulose (CMC), methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, diacetyl cellulose, or regenerated cellulose, or starch can be used.

[0251]

Note that a cellulose derivative such as carboxymethyl cellulose obtains a higher solubility when converted into a salt such as a sodium salt or an ammonium salt of carboxymethyl cellulose, and accordingly, easily exerts an effect as a viscosity modifier. The high solubility can also increase the dispersibility of an active material and other components in the formation of slurry for an electrode. In this specification, cellulose and a cellulose derivative used as a binder of an electrode include salts thereof.

[0252]

The water-soluble polymers stabilize viscosity by being dissolved in water and allow stable dispersion of the active material and another material combined as a binder such as styrene-butadiene rubber in an aqueous solution. Furthermore, a water-soluble polymer is expected to be easily and stably adsorbed to an active material surface because it has a functional group. Many cellulose derivatives such as carboxymethyl cellulose have functional groups such as a hydroxyl group and a carboxyl group. Because of functional groups, polymers are expected to interact with each other and cover an active material surface in a large area.

[0253]

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In the case where the binder covering or being in contact with the active material surface forms a film, the film is expected to serve as a passivation film to suppress the decomposition of the electrolyte solution. Here, the passivation film refers to a film without electric conductivity or a film with extremely low electric conductivity, and can inhibit the decomposition of an electrolyte solution at a potential at which a battery reaction occurs in the case where the passivation film is formed on the active material surface, for example. It is preferred that the passivation film can conduct lithium ions while suppressing electric conduction.

[0254]

<Positive electrode current collector>

The positive electrode current collector can be formed using a material that has high conductivity, such as a metal like stainless steel, gold, platinum, aluminum, or titanium, or an alloy thereof. It is preferred that a material used for the positive electrode current collector not dissolve at the potential of the positive electrode. Alternatively, the positive electrode current collector can be formed using an aluminum alloy to which an element that improves heat resistance, such as silicon, titanium, neodymium, scandium, or molybdenum, is added. Still alternatively, a metal element that forms silicide by reacting with silicon can be used. Examples of the metal element that forms silicide by reacting with silicon include zirconium, titanium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, cobalt, and nickel. The current collector can have any of various shapes including a foil-like shape, a plate-like shape (sheet-like shape), a net-like shape, a punching-metal shape, and an expanded-metal shape. The current collector preferably has a thickness of 5 μm to 30 μm.

[0255]

[Negative electrode]

The negative electrode includes a negative electrode active material layer and a negative electrode current collector. The negative electrode active material layer may contain a conductive additive and a binder.

[0256]

<Negative electrode active material>

As a negative electrode active material, for example, an alloy-based material or a carbon-based material can be used.

[0257]

For the negative electrode active material, an element which enables charge-discharge reactions by an alloying reaction and a dealloying reaction with lithium can be used. For example, a material containing at least one of silicon, tin, gallium, aluminum, germanium, lead,

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antimony, bismuth, silver, zinc, cadmium, indium, and the like can be used. Such elements have higher capacity than carbon. In particular, silicon has a significantly high theoretical capacity of 4200 mAh/g. For this reason, silicon is preferably used as the negative electrode active material. Alternatively, a compound containing any of the above elements may be used. Examples of the compound include SiO, Mg_2Si, Mg_2Ge, SnO, SnO_2, Mg_2Sn, SnS_2, V_2Sn_3, $FeSn_2$, $CoSn_2$, Ni_3Sn_2, Cu_6Sn_5, Ag_3Sn, Ag_3Sb, Ni_2MnSb, $CeSb_3$, $LaSn_3$, $La_3Co_2Sn_7$, $CoSb_3$, InSb, and SbSn. Here, an element that enables charge-discharge reactions by an alloying reaction and a dealloying reaction with lithium, a compound containing the element, and the like may be referred to as an alloy-based material.

[0258]

In this specification and the like, SiO refers, for example, to silicon monoxide. SiO can alternatively be expressed as SiO_x. Here, x preferably has an approximate value of 1. For example, x is preferably 0.2 or more and 1.5 or less, more preferably 0.3 or more and 1.2 or less.

[0259]

As the carbon-based material, graphite, graphitizing carbon (soft carbon), non-graphitizing carbon (hard carbon), a carbon nanotube, graphene, carbon black, and the like can be used.

[0260]

Examples of graphite include artificial graphite and natural graphite. Examples of artificial graphite include meso-carbon microbeads (MCMB), coke-based artificial graphite, and pitch-based artificial graphite. As artificial graphite, spherical graphite having a spherical shape can be used. For example, MCMB is preferably used because it may have a spherical shape. Moreover, MCMB may preferably be used because it can relatively easily have a small surface area. Examples of natural graphite include flake graphite and spherical natural graphite.

[0261]

Graphite has a low potential substantially equal to that of a lithium metal (higher than or equal to 0.05 V and lower than or equal to 0.3 V vs. Li/Li^+) when lithium ions are intercalated into the graphite (while a lithium-graphite intercalation compound is formed). For this reason, a lithium-ion secondary battery can have a high operating voltage. In addition, graphite is preferred because of its advantages such as a relatively high capacity per unit volume, relatively small volume expansion, low cost, and higher level of safety than that of a lithium metal.

[0262]

Alternatively, for the negative electrode active material, an oxide such as titanium dioxide (TiO_2), lithium titanium oxide ($Li_4Ti_5O_{12}$), lithium-graphite intercalation compound (Li_xC_6), niobium pentoxide (Nb_2O_5), tungsten oxide (WO_2), or molybdenum oxide (MoO_2) can

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be used.

[0263]

Still alternatively, for the negative electrode active material, $Li_{3-x}M_xN$ (M = Co, Ni, or Cu) with a Li_3N structure, which is a nitride containing lithium and a transition metal, can be used. For example, $Li_{2.6}Co_{0.4}N_3$ is preferable because of high charge and discharge capacity (900 mAh/g and 1890 mAh/cm^3).

[0264]

A nitride containing lithium and a transition metal is preferably used, in which case lithium ions are contained in the negative electrode active material and thus the negative electrode active material can be used in combination with a material for a positive electrode active material which does not contain lithium ions, such as V_2O_5 or Cr_3O_8. In the case of using a material containing lithium ions as a positive electrode active material, the nitride containing lithium and a transition metal can be used for the negative electrode active material by extracting the lithium ions contained in the positive electrode active material in advance.

[0265]

Alternatively, a material which causes a conversion reaction can be used for the negative electrode active material; for example, a transition metal oxide which does not form an alloy with lithium, such as cobalt oxide (CoO), nickel oxide (NiO), and iron oxide (FeO), may be used. Other examples of the material which causes a conversion reaction include oxides such as Fe_2O_3, CuO, Cu_2O, RuO_2, and Cr_2O_3, sulfides such as $CoS_{0.89}$, NiS, and CuS, nitrides such as Zn_3N_2, Cu_3N, and Ge_3N_4, phosphides such as NiP_2, FeP_2, and CoP_3, and fluorides such as FeF_3 and BiF_3.

[0266]

For the conductive additive and the binder that can be included in the negative electrode active material layer, materials similar to those of the conductive additive and the binder that can be included in the positive electrode active material layer can be used.

[0267]

<Negative electrode current collector>

For the negative electrode current collector, a material similar to that of the positive electrode current collector can be used. Note that a material which is not alloyed with a carrier ion such as lithium is preferably used for the negative electrode current collector.

[0268]

[Electrolyte solution]

The electrolyte solution contains a solvent and an electrolyte. As a solvent of the electrolyte solution, an aprotic organic solvent is preferably used. For example, one of ethylene

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carbonate (EC), propylene carbonate (PC), butylene carbonate, chloroethylene carbonate, vinylene carbonate, γ-butyrolactone, γ-valerolactone, dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), methyl formate, methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, propyl propionate, methyl butyrate, 1,3-dioxane, 1,4-dioxane, dimethoxyethane (DME), dimethyl sulfoxide, diethyl ether, methyl diglyme, acetonitrile, benzonitrile, tetrahydrofuran, sulfolane, and sultone can be used, or two or more of these solvents can be used in an appropriate combination in an appropriate ratio.

[0269]

Alternatively, when one or more kinds of ionic liquids (room temperature molten salts) which have features of non-flammability and non-volatility is used as a solvent of the electrolyte solution, a secondary battery can be prevented from exploding or catching fire even when the secondary battery internally shorts out or the internal temperature increases owing to overcharging or the like. An ionic liquid contains a cation and an anion. The ionic liquid contains an organic cation and an anion. Examples of the organic cation used for the electrolyte solution include aliphatic onium cations such as a quaternary ammonium cation, a tertiary sulfonium cation, and a quaternary phosphonium cation, and aromatic cations such as an imidazolium cation and a pyridinium cation. Examples of the anion used for the electrolyte solution include a monovalent amide-based anion, a monovalent methide-based anion, a fluorosulfonate anion, a perfluoroalkylsulfonate anion, a tetrafluoroborate anion, a perfluoroalkylborate anion, a hexafluorophosphate anion, and a perfluoroalkylphosphate anion.

[0270]

As an electrolyte dissolved in the above-described solvent, one of lithium salts such as $LiPF_6$, $LiClO_4$, $LiAsF_6$, $LiBF_4$, $LiAlCl_4$, LiSCN, LiBr, LiI, Li_2SO_4, $Li_2B_{10}Cl_{10}$, $Li_2B_{12}Cl_{12}$, $LiCF_3SO_3$, $LiC_4F_9SO_3$, $LiC(CF_3SO_2)_3$, $LiC(C_2F_5SO_2)_3$, $LiN(CF_3SO_2)_2$, $LiN(C_4F_9SO_2)(CF_3SO_2)$, and $LiN(C_2F_5SO_2)_2$ can be used, or two or more of these lithium salts can be used in an appropriate combination in an appropriate ratio.

[0271]

The electrolyte solution used for a secondary battery is preferably highly purified and contains a small amount of dust particles and elements other than the constituent elements of the electrolyte solution (hereinafter also simply referred to as impurities). Specifically, the weight ratio of impurities to the electrolyte solution is less than or equal to 1 %, preferably less than or equal to 0.1 %, and further preferably less than or equal to 0.01 %.

[0272]

Furthermore, an additive agent such as vinylene carbonate, propane sultone (PS), *tert*-butylbenzene (TBB), fluoroethylene carbonate (FEC), LiBOB, or a dinitrile compound such

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as succinonitrile or adiponitrile may be added to the electrolyte solution. The concentration of a material to be added with respect to the whole solvent is, for example, higher than or equal to 0.1 wt% and lower than or equal to 5 wt%.

[0273]

Alternatively, a gelled electrolyte obtained in such a manner that a polymer is swelled with an electrolyte solution may be used.

[0274]

When a polymer gel electrolyte is used, safety against liquid leakage and the like is improved. Furthermore, a secondary battery can be thinner and more lightweight.

[0275]

As a polymer that undergoes gelation, a silicone gel, an acrylic gel, an acrylonitrile gel, a polyethylene oxide-based gel, a polypropylene oxide-based gel, a fluorine-based polymer gel, or the like can be used.

[0276]

Examples of the polymer include a polymer having a polyalkylene oxide structure, such as polyethylene oxide (PEO); PVDF; polyacrylonitrile; and a copolymer containing any of them. For example, PVDF-HFP, which is a copolymer of PVDF and hexafluoropropylene (HFP) can be used. The formed polymer may be porous.

[0277]

Instead of the electrolyte solution, a solid electrolyte including an inorganic material such as a sulfide-based inorganic material or an oxide-based inorganic material, or a solid electrolyte including a high-molecular material such as a polyethylene oxide (PEO)-based high-molecular material may alternatively be used. When the solid electrolyte is used, a separator and a spacer are not necessary. Furthermore, since the battery can be entirely solidified, there is no possibility of liquid leakage to increase the safety of the battery dramatically.

[0278]

[Separator]

The secondary battery preferably includes a separator. As the separator, for example, paper; nonwoven fabric; glass fiber; ceramics; or synthetic fiber using nylon (polyamide), vinylon (polyvinyl alcohol-based fiber), polyester, acrylic, polyolefin, or polyurethane can be used. The separator is preferably formed to have an envelope-like shape to wrap one of the positive electrode and the negative electrode.

[0279]

The separator may have a multilayer structure. For example, an organic material film

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such as polypropylene or polyethylene can be coated with a ceramic-based material, a fluorine-based material, a polyamide-based material, a mixture thereof, or the like. Examples of the ceramic-based material include aluminum oxide particles and silicon oxide particles. Examples of the fluorine-based material include PVDF and a polytetrafluoroethylene. Examples of the polyamide-based material include nylon and aramid (meta-based aramid and para-based aramid).

[0280]

Deterioration of the separator in charging and discharging at high voltage can be suppressed and thus the reliability of the secondary battery can be improved because oxidation resistance is improved when the separator is coated with the ceramic-based material. In addition, when the separator is coated with the fluorine-based material, the separator is easily brought into close contact with an electrode, resulting in high output characteristics. When the separator is coated with the polyamide-based material, in particular, aramid, the safety of the secondary battery is improved because heat resistance is improved.

[0281]

For example, both surfaces of a polypropylene film may be coated with a mixed material of aluminum oxide and aramid. Alternatively, a surface of the polypropylene film in contact with the positive electrode may be coated with the mixed material of aluminum oxide and aramid, and a surface of the polypropylene film in contact with the negative electrode may be coated with the fluorine-based material.

[0282]

With the use of a separator having a multilayer structure, the capacity of the secondary battery per volume can be increased because the safety of the secondary battery can be maintained even when the total thickness of the separator is small.

[0283]

[Exterior body]

For an exterior body included in the secondary battery, a metal material such as aluminum and a resin material can be used, for example. An exterior body in the form of a film can also be used. As the film, for example, a film having a three-layer structure in which a highly flexible metal thin film of aluminum, stainless steel, copper, nickel, or the like is provided over a film formed of a material such as polyethylene, polypropylene, polycarbonate, ionomer, or polyamide, and an insulating synthetic resin film of a polyamide-based resin, a polyester-based resin, or the like is provided as the outer surface of the exterior body over the metal thin film can be used.

[0284]

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[Charging and discharging methods]

The secondary battery can be charged and discharged in the following manner, for example.

[0285]

<<CC charge>>

First, CC charge, which is one of charging methods, is described. CC charge is a charging method in which a constant current is made to flow to a secondary battery in the whole charging period and charge is terminated when the voltage reaches a predetermined voltage. The secondary battery is assumed to be an equivalent circuit with internal resistance R and secondary battery capacitance C as illustrated in FIG. 8A. In that case, a secondary battery voltage V_B is the sum of a voltage V_R applied to the internal resistance R and a voltage V_C applied to the secondary battery capacitance C.

[0286]

While the CC charge is performed, a switch is on as illustrated in FIG. 8A, so that a constant current I flows to the secondary battery. During the period, the current I is constant; thus, according to the Ohm's law ($V_R = R \times I$), the voltage V_R applied to the internal resistance R is also constant. In contrast, the voltage V_C applied to the secondary battery capacitance C increases over time. Accordingly, the secondary battery voltage V_B increases over time.

[0287]

When the secondary battery voltage V_B reaches a predetermined voltage, e.g., 4.3 V, the charge is terminated. On termination of the CC charge, the switch is turned off as illustrated in FIG. 8B, and the current I becomes 0. Thus, the voltage V_R applied to the internal resistance R becomes 0 V. Consequently, the secondary battery voltage V_B is decreased by the lost voltage drop in the internal resistance R.

[0288]

FIG. 8C shows an example of the secondary battery voltage V_B and charging current during a period in which the CC charge is performed and after the CC charge is terminated. The secondary battery voltage V_B increases while the CC charge is performed, and slightly decreases after the CC charge is terminated.

[0289]

<<CCCV charge>>

Next, CCCV charge, which is a charging method different from the above-described method, is described. CCCV charge is a charging method in which CC charge is performed until the voltage reaches a predetermined voltage and then constant voltage (CV) charge is performed until the amount of current flow becomes small, specifically, a termination current

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value.

[0290]

While the CC charge is performed, a switch of a constant current power source is on and a switch of a constant voltage power source is off as illustrated in FIG. 9A, so that the constant current I flows to the secondary battery. During the period, the current I is constant; thus, according to the Ohm's law ($V_R = R \times I$), the voltage V_R applied to the internal resistance R is also constant. In contrast, the voltage V_C applied to the secondary battery capacitance C increases over time. Accordingly, the secondary battery voltage V_B increases over time.

[0291]

When the secondary battery voltage V_B reaches a predetermined voltage, e.g., 4.3 V, switching is performed from the CC charge to the CV charge. While the CV charge is performed, the switch of the constant voltage power source is on and the switch of the constant current power source is off as illustrated in FIG. 9B; thus, the secondary battery voltage V_B is constant. In contrast, the voltage V_C applied to the secondary battery capacitance C increases over time. Since $V_B = V_R + V_C$ is satisfied, the voltage V_R applied to the internal resistance R decreases over time. As the voltage V_R applied to the internal resistance R decreases, the current I flowing to the secondary battery also decreases according to the Ohm's law ($V_R = R \times I$).

[0292]

When the current I flowing to the secondary battery becomes a predetermined current, e.g., approximately 0.01 C, charge is terminated. On termination of the CCCV charge, all the switches are turned off as illustrated in FIG. 9C, so that the current I becomes 0. Thus, the voltage V_R applied to the internal resistance R becomes 0 V. However, the voltage V_R applied to the internal resistance R becomes sufficiently small by the CV charge; thus, even when a voltage drop no longer occurs in the internal resistance R, the secondary battery voltage V_B hardly decreases.

[0293]

FIG. 9D shows an example of the secondary battery voltage V_B and charging current while the CCCV charge is performed and after the CCCV charge is terminated. Even after the CCCV charge is terminated, the secondary battery voltage V_B hardly decreases.

[0294]

<<CC discharge>>

Next, CC discharge, which is one of discharging methods, is described. CC discharge is a discharging method in which a constant current is made to flow from the secondary battery in the whole discharging period, and discharge is terminated when the secondary battery voltage

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V_B reaches a predetermined voltage, e.g., 2.5 V.

[0295]

FIG. 10 shows an example of the secondary battery voltage V_B and discharging current while the CC discharge is performed. As discharge proceeds, the secondary battery voltage V_B decreases.

[0296]

Next, a discharge rate and a charge rate will be described. The discharge rate refers to the relative ratio of discharging current to battery capacity and is expressed in a unit C. A current of approximately 1 C in a battery with a rated capacity X (Ah) is X A. The case where discharge is performed at a current of $2X$ A is rephrased as follows: discharge is performed at 2 C. The case where discharge is performed at a current of $X/5$ A is rephrased as follows: discharge is performed at 0.2 C. Similarly, the case where charging is performed at a current of $2X$ A is rephrased as follows: charging is performed at 2 C, and the case where charging is performed at a current of $X/5$ A is rephrased as follows: charging is performed at 0.2 C.

[0297]

(Embodiment 3)

In this embodiment, examples of a shape of a secondary battery containing the positive electrode active material 100 described in the above embodiment are described. For the materials used for the secondary battery described in this embodiment, the description of the above embodiment can be referred to.

[0298]

[Coin-type secondary battery]

First, an example of a coin-type secondary battery is described. FIG. 11A is an external view of a coin-type (single-layer flat type) secondary battery, and FIG. 11B is a cross-sectional view thereof.

[0299]

In a coin-type secondary battery 300, a positive electrode can 301 doubling as a positive electrode terminal and a negative electrode can 302 doubling as a negative electrode terminal are insulated from each other and sealed by a gasket 303 made of polypropylene or the like. A positive electrode 304 includes a positive electrode current collector 305 and a positive electrode active material layer 306 provided in contact with the positive electrode current collector 305. A negative electrode 307 includes a negative electrode current collector 308 and a negative electrode active material layer 309 provided in contact with the negative electrode current collector 308.

[0300]

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Note that only one surface of each of the positive electrode 304 and the negative electrode 307 used for the coin-type secondary battery 300 is provided with an active material layer.

[0301]

For the positive electrode can 301 and the negative electrode can 302, a metal having a corrosion-resistant property to an electrolyte solution, such as nickel, aluminum, or titanium, an alloy of such a metal, or an alloy of such a metal and another metal (e.g., stainless steel) can be used. Alternatively, the positive electrode can 301 and the negative electrode can 302 are preferably covered with nickel, aluminum, or the like in order to prevent corrosion due to the electrolyte solution. The positive electrode can 301 and the negative electrode can 302 are electrically connected to the positive electrode 304 and the negative electrode 307, respectively.

[0302]

The negative electrode 307, the positive electrode 304, and the separator 310 are immersed in the electrolyte solution. Then, as illustrated in FIG. 11B, the positive electrode 304, the separator 310, the negative electrode 307, and the negative electrode can 302 are stacked in this order with the positive electrode can 301 positioned at the bottom, and the positive electrode can 301 and the negative electrode can 302 are subjected to pressure bonding with the gasket 303 located therebetween. In such a manner, the coin-type secondary battery 300 can be manufactured.

[0303]

When the positive electrode active material described in the above embodiment is used in the positive electrode 304, the coin-type secondary battery 300 with high capacity and excellent cycle characteristics can be obtained.

[0304]

Here, a current flow in charging a secondary battery is described with reference to FIG. 11C. When a secondary battery using lithium is regarded as a closed circuit, lithium ions transfer and a current flows in the same direction. Note that in the secondary battery using lithium, an anode and a cathode change places in charge and discharge, and an oxidation reaction and a reduction reaction occur on the corresponding sides; hence, an electrode with a high reaction potential is called a positive electrode and an electrode with a low reaction potential is called a negative electrode. For this reason, in this specification, the positive electrode is referred to as a "positive electrode" or a "plus electrode" and the negative electrode is referred to as a "negative electrode" or a "minus electrode" in all the cases where charge is performed, discharge is performed, a reverse pulse current is supplied, and a charging current is supplied. The use of the terms "anode" and "cathode" related to an oxidation reaction and a reduction

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reaction might cause confusion because the anode and the cathode change places at the time of charging and discharging. Thus, the terms "anode" and "cathode" are not used in this specification. If the term "anode" or "cathode" is used, it should be mentioned that the anode or the cathode is which of the one at the time of charging or the one at the time of discharging and corresponds to which of a positive (plus) electrode or a negative (minus) electrode.

[0305]

Two terminals in FIG. 11C are connected to a charger, and the secondary battery 300 is charged. As the charge of the secondary battery 300 proceeds, a potential difference between electrodes increases.

[0306]

[Cylindrical secondary battery]

Next, an example of a cylindrical secondary battery will be described with reference to FIGS. 12A to 12D. A cylindrical secondary battery 600 includes, as illustrated in FIG. 12A, a positive electrode cap (battery lid) 601 on the top surface and a battery can (outer can) 602 on the side and bottom surfaces. The positive electrode cap and the battery can (outer can) 602 are insulated from each other by a gasket (insulating packing) 610.

[0307]

FIG. 12B is a schematic cross-sectional view of the cylindrical secondary battery. Inside the battery can 602 having a hollow cylindrical shape, a battery element in which a strip-like positive electrode 604 and a strip-like negative electrode 606 are wound with a strip-like separator 605 located therebetween is provided. Although not illustrated, the battery element is wound around a center pin. One end of the battery can 602 is close and the other end thereof is open. For the battery can 602, a metal having a corrosion-resistant property to an electrolyte solution, such as nickel, aluminum, or titanium, an alloy of such a metal, or an alloy of such a metal and another metal (e.g., stainless steel) can be used. Alternatively, the battery can 602 is preferably covered with nickel, aluminum, or the like in order to prevent corrosion due to the electrolyte solution. Inside the battery can 602, the battery element in which the positive electrode, the negative electrode, and the separator are wound is provided between a pair of insulating plates 608 and 609 that face each other. Furthermore, a nonaqueous electrolyte solution (not illustrated) is injected inside the battery can 602 provided with the battery element. As the nonaqueous electrolyte solution, a nonaqueous electrolyte solution that is similar to that of the coin-type secondary battery can be used.

[0308]

Since the positive electrode and the negative electrode of the cylindrical secondary battery are wound, active materials are preferably formed on both sides of the current collectors.

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A positive electrode terminal (positive electrode current collecting lead) 603 is connected to the positive electrode 604, and a negative electrode terminal (negative electrode current collecting lead) 607 is connected to the negative electrode 606. Both the positive electrode terminal 603 and the negative electrode terminal 607 can be formed using a metal material such as aluminum. The positive electrode terminal 603 and the negative electrode terminal 607 are resistance-welded to a safety valve mechanism 612 and the bottom of the battery can 602, respectively. The safety valve mechanism 612 is electrically connected to the positive electrode cap 601 through a positive temperature coefficient (PTC) element 611. The safety valve mechanism 612 cuts off electrical connection between the positive electrode cap 601 and the positive electrode 604 when the internal pressure of the battery exceeds a predetermined threshold value. The PTC element 611, which serves as a thermally sensitive resistor whose resistance increases as temperature rises, limits the amount of current by increasing the resistance, in order to prevent abnormal heat generation. Barium titanate ($BaTiO_3$)-based semiconductor ceramic can be used for the PTC element.

[0309]

Alternatively, as illustrated in FIG. 12C, a plurality of secondary batteries 600 may be sandwiched between a conductive plate 613 and a conductive plate 614 to form a module 615. The plurality of secondary batteries 600 may be connected in parallel, connected in series, or connected in series after being connected in parallel. With the module 615 including the plurality of secondary batteries 600, large electric power can be extracted.

[0310]

FIG. 12D is a top view of the module 615. The conductive plate 613 is shown by a dotted line for clarity of the drawing. As illustrated in FIG. 12D, the module 615 may include a wiring 616 which electrically connects the plurality of secondary batteries 600 to each other. It is possible to provide the conductive plate 613 over the wiring 616 to overlap with each other. In addition, a temperature control device 617 may be provided between the plurality of secondary batteries 600. When the secondary batteries 600 are overheated, the temperature control device 617 can cool them, and when the secondary batteries 600 are cooled too much, the temperature control device 617 can heat them. Thus, the performance of the module 615 is not easily influenced by the outside air temperature.

[0311]

When the positive electrode active material described in the above embodiment is used in the positive electrode 604, the cylindrical secondary battery 600 with high capacity and excellent cycle characteristics can be obtained.

[0312]

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[Structural examples of secondary battery]

Other structural examples of secondary batteries will be described with reference to FIGS. 13A and 13B, FIGS. 14A-1, 14A-2, 14B-1, and 14B-2, FIGS. 15A and 15B, and FIG. 16.

[0313]

FIGS. 13A and 13B are external views of a secondary battery. The secondary battery includes a circuit board 900 and a secondary battery 913. A label 910 is attached to the secondary battery 913. As shown in FIG. 13B, the secondary battery further includes a terminal 951, a terminal 952, an antenna 914, and an antenna 915.

[0314]

The circuit board 900 includes terminals 911 and a circuit 912. The terminals 911 are connected to the terminals 951 and 952, the antennas 914 and 915, and the circuit 912. Note that a plurality of terminals 911 serving as a control signal input terminal, a power supply terminal, and the like may be provided.

[0315]

The circuit 912 may be provided on the rear surface of the circuit board 900. The shape of each of the antennas 914 and 915 is not limited to a coil shape and may be a linear shape or a plate shape. Furthermore, a planar antenna, an aperture antenna, a traveling-wave antenna, an EH antenna, a magnetic-field antenna, a dielectric antenna, or the like may be used. Alternatively, the antenna 914 or the antenna 915 may be a flat-plate conductor. The flat-plate conductor can serve as one of conductors for electric field coupling. That is, the antenna 914 or the antenna 915 can serve as one of two conductors of a capacitor. Thus, electric power can be transmitted and received not only by an electromagnetic field or a magnetic field but also by an electric field.

[0316]

The line width of the antenna 914 is preferably larger than that of the antenna 915. This makes it possible to increase the amount of electric power received by the antenna 914.

[0317]

The secondary battery includes a layer 916 between the secondary battery 913 and the antennas 914 and 915. The layer 916 has a function of blocking an electromagnetic field from the secondary battery 913, for example. As the layer 916, for example, a magnetic body can be used.

[0318]

Note that the structure of the secondary battery is not limited to that shown in FIGS. 13A and 13B.

[0319]

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For example, as shown in FIGS. 14A-1 and 14A-2, two opposite surfaces of the secondary battery 913 in FIGS. 13A and 13B may be provided with respective antennas. FIG. 14A-1 is an external view showing one side of the opposite surfaces, and FIG. 14A-2 is an external view showing the other side of the opposite surfaces. For portions similar to those in FIGS. 13A and 13B, a description of the secondary battery illustrated in FIGS. 13A and 13B can be referred to as appropriate.

[0320]

As illustrated in FIG. 14A-1, the antenna 914 is provided on one of the opposite surfaces of the secondary battery 913 with the layer 916 located therebetween, and as illustrated in FIG. 14A-2, an antenna 918 is provided on the other of the opposite surfaces of the secondary battery 913 with a layer 917 located therebetween. The layer 917 has a function of blocking an electromagnetic field from the secondary battery 913, for example. As the layer 917, for example, a magnetic body can be used.

[0321]

With the above structure, both of the antennas 914 and 918 can be increased in size. The antenna 918 has a function of communicating data with an external device, for example. An antenna with a shape that can be applied to the antenna 914, for example, can be used as the antenna 918. As a system for communication using the antenna 918 between the secondary battery and another device, a response method that can be used between the secondary battery and another device, such as NFC, can be employed.

[0322]

Alternatively, as illustrated in FIG. 14B-1, the secondary battery 913 in FIGS. 13A and 13B may be provided with a display device 920. The display device 920 is electrically connected to the terminal 911. It is possible that the label 910 is not provided in a portion where the display device 920 is provided. For portions similar to those in FIGS. 13A and 13B, a description of the secondary battery illustrated in FIGS. 13A and 13B can be referred to as appropriate.

[0323]

The display device 920 can display, for example, an image showing whether charge is being carried out, an image showing the amount of stored power, or the like. As the display device 920, electronic paper, a liquid crystal display device, an electroluminescent (EL) display device, or the like can be used. For example, the use of electronic paper can reduce power consumption of the display device 920.

[0324]

Alternatively, as illustrated in FIG. 14B-2, the secondary battery 913 illustrated in FIGS.

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13A and 13B may be provided with a sensor 921. The sensor 921 is electrically connected to the terminal 911 via a terminal 922. For portions similar to those in FIGS. 13A and 13B, a description of the secondary battery illustrated in FIGS. 13A and 13B can be referred to as appropriate.

[0325]

The sensor 921 has a function of measuring, for example, displacement, position, speed, acceleration, angular velocity, rotational frequency, distance, light, liquid, magnetism, temperature, chemical substance, sound, time, hardness, electric field, electric current, voltage, electric power, radiation, flow rate, humidity, gradient, oscillation, odor, or infrared rays. With the sensor 921, for example, data on an environment (e.g., temperature) where the secondary battery is placed can be determined and stored in a memory inside the circuit 912.

[0326]

Furthermore, structural examples of the secondary battery 913 will be described with reference to FIGS. 15A and 15B and FIG. 16.

[0327]

The secondary battery 913 illustrated in FIG. 15A includes a wound body 950 provided with the terminals 951 and 952 inside a housing 930. The wound body 950 is soaked in an electrolyte solution inside the housing 930. The terminal 952 is in contact with the housing 930. An insulator or the like inhibits contact between the terminal 951 and the housing 930. Note that in FIG. 15A, the housing 930 divided into two pieces is illustrated for convenience; however, in the actual structure, the wound body 950 is covered with the housing 930 and the terminals 951 and 952 extend to the outside of the housing 930. For the housing 930, a metal material (such as aluminum) or a resin material can be used.

[0328]

Note that as illustrated in FIG. 15B, the housing 930 in FIG. 15A may be formed using a plurality of materials. For example, in the secondary battery 913 in FIG. 15B, a housing 930a and a housing 930b are bonded to each other, and the wound body 950 is provided in a region surrounded by the housing 930a and the housing 930b.

[0329]

For the housing 930a, an insulating material such as an organic resin can be used. In particular, when a material such as an organic resin is used for the side on which an antenna is formed, blocking of an electric field from the secondary battery 913 can be inhibited. When an electric field is not significantly blocked by the housing 930a, an antenna such as the antennas 914 and 915 may be provided inside the housing 930a. For the housing 930b, a metal material can be used, for example.

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[0330]

FIG. 16 illustrates the structure of the wound body 950. The wound body 950 includes a negative electrode 931, a positive electrode 932, and separators 933. The wound body 950 is obtained by winding a sheet of a stack in which the negative electrode 931 overlaps with the positive electrode 932 with the separator 933 provided therebetween. Note that a plurality of stacks each including the negative electrode 931, the positive electrode 932, and the separator 933 may be stacked.

[0331]

The negative electrode 931 is connected to the terminal 911 in FIGS. 13A and 13B via one of the terminals 951 and 952. The positive electrode 932 is connected to the terminal 911 in FIGS. 13A and 13B via the other of the terminals 951 and 952.

[0332]

When the positive electrode active material described in the above embodiment is used in the positive electrode 932, the secondary battery 913 with high capacity and excellent cycle characteristics can be obtained.

[0333]

[Laminated secondary battery]

Next, an example of a laminated secondary battery will be described with reference to FIGS. 17A to 17C, FIG. 18A and 18B, FIG. 19, FIG. 20, FIGS. 21A to 21C, FIGS. 22A, 22B1, 22B2, 22C, and 22D, and FIGS. 23A and 23B. When the laminated secondary battery has flexibility and is used in an electronic device at least part of which is flexible, the secondary battery can be bent as the electronic device is bent.

[0334]

A laminated secondary battery 980 is described with reference to FIGS. 17A to 17C. The laminated secondary battery 980 includes a wound body 993 illustrated in FIG. 17A. The wound body 993 includes a negative electrode 994, a positive electrode 995, and a separator 996. The wound body 993 is, like the wound body 950 illustrated in FIG. 16, obtained by winding a sheet of a stack in which the negative electrode 994 overlaps with the positive electrode 995 with the separator 996 therebetween.

[0335]

Note that the number of stacks each including the negative electrode 994, the positive electrode 995, and the separator 996 may be determined as appropriate depending on capacity and an element volume which are required. The negative electrode 994 is connected to a negative electrode current collector (not illustrated) via one of a lead electrode 997 and a lead electrode 998. The positive electrode 995 is connected to a positive electrode current collector

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(not illustrated) via the other of the lead electrode 997 and the lead electrode 998.

[0336]

As illustrated in FIG. 17B, the wound body 993 is packed in a space formed by bonding a film 981 and a film 982 having a depressed portion that serve as exterior bodies by thermocompression bonding or the like, whereby the secondary battery 980 can be formed as illustrated in FIG. 17C. The wound body 993 includes the lead electrode 997 and the lead electrode 998, and is soaked in an electrolyte solution inside a space surrounded by the film 981 and the film 982 having a depressed portion.

[0337]

For the film 981 and the film 982 having a depressed portion, a metal material such as aluminum or a resin material can be used, for example. With the use of a resin material for the film 981 and the film 982 having a depressed portion, the film 981 and the film 982 having a depressed portion can be changed in their forms when external force is applied; thus, a flexible secondary battery can be fabricated.

[0338]

Although FIGS. 17B and 17C illustrate an example where a space is formed by two films, the wound body 993 may be placed in a space formed by bending one film.

[0339]

When the positive electrode active material described in the above embodiment is used in the positive electrode 995, the secondary battery 980 with high capacity and excellent cycle characteristics can be obtained.

[0340]

In FIGS. 17A to 17C, an example in which the secondary battery 980 includes a wound body in a space formed by films serving as exterior bodies is described; however, as illustrated in FIGS. 18A and 18B, a secondary battery may include a plurality of strip-shaped positive electrodes, a plurality of strip-shaped separators, and a plurality of strip-shaped negative electrodes in a space formed by films serving as exterior bodies, for example.

[0341]

A laminated secondary battery 500 illustrated in FIG. 18A includes a positive electrode 503 including a positive electrode current collector 501 and a positive electrode active material layer 502, a negative electrode 506 including a negative electrode current collector 504 and a negative electrode active material layer 505, a separator 507, an electrolyte solution 508, and an exterior body 509. The separator 507 is provided between the positive electrode 503 and the negative electrode 506 in the exterior body 509. The exterior body 509 is filled with the electrolyte solution 508. The electrolyte solution described in Embodiment 2 can be used for

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the electrolyte solution 508.

[0342]

In the laminated secondary battery 500 illustrated in FIG. 18A, the positive electrode current collector 501 and the negative electrode current collector 504 also serve as terminals for an electrical contact with an external portion. For this reason, the positive electrode current collector 501 and the negative electrode current collector 504 may be arranged so as to be partly exposed to the outside of the exterior body 509. Alternatively, a lead electrode and the positive electrode current collector 501 or the negative electrode current collector 504 may be bonded to each other by ultrasonic welding, and instead of the positive electrode current collector 501 and the negative electrode current collector 504, the lead electrode may be exposed to the outside of the exterior body 509.

[0343]

As the exterior body 509 of the laminated secondary battery 500, for example, a laminate film having a three-layer structure can be employed in which a highly flexible metal thin film of aluminum, stainless steel, copper, nickel, or the like is provided over a film formed of a material such as polyethylene, polypropylene, polycarbonate, ionomer, or polyamide, and an insulating synthetic resin film of a polyamide-based resin, a polyester-based resin, or the like is provided over the metal thin film as the outer surface of the exterior body.

[0344]

FIG. 18B illustrates an example of a cross-sectional structure of the laminated secondary battery 500. Although FIG. 18A illustrates an example including only two current collectors for simplicity, an actual battery includes a plurality of electrode layers.

[0345]

The example in FIG. 18B includes 16 electrode layers. The laminated secondary battery 500 has flexibility even though including 16 electrode layers. FIG. 18B illustrates a structure including 8 layers of negative electrode current collectors 504 and 8 layers of positive electrode current collectors 501, i.e., 16 layers in total. Note that FIG. 18B illustrates a cross section of the lead portion of the negative electrode, and the 8 negative electrode current collectors 504 are bonded to each other by ultrasonic welding. It is needless to say that the number of electrode layers is not limited to 16, and may be more than 16 or less than 16. With a large number of electrode layers, the secondary battery can have high capacity. In contrast, with a small number of electrode layers, the secondary battery can have small thickness and high flexibility.

[0346]

FIGS. 19 and 20 each illustrate an example of the external view of the laminated

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secondary battery 500. In FIGS. 19 and 20, the positive electrode 503, the negative electrode 506, the separator 507, the exterior body 509, a positive electrode lead electrode 510, and a negative electrode lead electrode 511 are included.

[0347]

FIG. 21A illustrates external views of the positive electrode 503 and the negative electrode 506. The positive electrode 503 includes the positive electrode current collector 501, and the positive electrode active material layer 502 is formed on a surface of the positive electrode current collector 501. The positive electrode 503 also includes a region where the positive electrode current collector 501 is partly exposed (hereinafter referred to as a tab region). The negative electrode 506 includes the negative electrode current collector 504, and the negative electrode active material layer 505 is formed on a surface of the negative electrode current collector 504. The negative electrode 506 also includes a region where the negative electrode current collector 504 is partly exposed, that is, a tab region. The areas and the shapes of the tab regions included in the positive electrode and the negative electrode are not limited to those illustrated in FIG. 21A.

[0348]

[Method for manufacturing laminated secondary battery]

Here, an example of a method for manufacturing the laminated secondary battery whose external view is illustrated in FIG. 19 will be described with reference to FIGS. 21B and 21C.

[0349]

First, the negative electrode 506, the separator 507, and the positive electrode 503 are stacked. FIG. 21B illustrates a stack including the negative electrode 506, the separator 507, and the positive electrode 503. The secondary battery described here as an example includes 5 negative electrodes and 4 positive electrodes. Next, the tab regions of the positive electrodes 503 are bonded to each other, and the tab region of the positive electrode on the outermost surface and the positive electrode lead electrode 510 are bonded to each other. The bonding can be performed by ultrasonic welding, for example. In a similar manner, the tab regions of the negative electrodes 506 are bonded to each other, and the negative electrode lead electrode 511 is bonded to the tab region of the negative electrode on the outermost surface.

[0350]

After that, the negative electrode 506, the separator 507, and the positive electrode 503 are placed over the exterior body 509.

[0351]

Subsequently, the exterior body 509 is folded along a dashed line as illustrated in FIG. 21C. Then, the outer edge of the exterior body 509 is bonded. The bonding can be performed

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by thermocompression bonding, for example. At this time, a part (or one side) of the exterior body 509 is left unbonded (to provide an inlet) so that the electrolyte solution 508 can be introduced later.

[0352]

Next, the electrolyte solution 508 is introduced into the exterior body 509 from the inlet of the exterior body 509. The electrolyte solution 508 is preferably introduced in a reduced pressure atmosphere or in an inert gas atmosphere. Lastly, the inlet is bonded. In the above manner, the laminated secondary battery 500 can be manufactured.

[0353]

When the positive electrode active material described in the above embodiment is used in the positive electrode 503, the secondary battery 500 with high capacity and excellent cycle characteristics can be obtained.

[0354]

[Bendable secondary battery]

Next, an example of a bendable secondary battery is described with reference to FIGS. 22A, 22B1, 22B2, 22C and 22D and FIGS. 23A and 23B.

[0355]

FIG. 22A is a schematic top view of a bendable secondary battery 50. FIGS. 22B1, 22B2, and 22C are schematic cross-sectional views taken along cutting line C1-C2, cutting line C3-C4, and cutting line A1-A2, respectively, in FIG. 22A. The battery 50 includes an exterior body 51 and a positive electrode 11a, and a negative electrode 11b held in the exterior body 51. A lead 12a electrically connected to the positive electrode 11a and a lead 12b electrically connected to the negative electrode 11b are extended to the outside of the exterior body 51. In addition to the positive electrode 11a and the negative electrode 11b, an electrolyte solution (not illustrated) is enclosed in a region surrounded by the exterior body 51.

[0356]

FIGS. 23A and 23B illustrate the positive electrode 11a and the negative electrode 11b included in the battery 50. FIG. 23A is a perspective view illustrating the stacking order of the positive electrode 11a, the negative electrode 11b, and the separator 14. FIG. 23B is a perspective view illustrating the lead 12a and the lead 12b in addition to the positive electrode 11a and the negative electrode 11b.

[0357]

As illustrated in FIG. 23A, the battery 50 includes a plurality of strip-shaped positive electrodes 11a, a plurality of strip-shaped negative electrodes 11b, and a plurality of separators 14. The positive electrode 11a and the negative electrode 11b each include a projected tab

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portion and a portion other than the tab. A positive electrode active material layer is formed on one surface of the positive electrode 11a other than the tab portion, and a negative electrode active material layer is formed on one surface of the negative electrode 11b other than the tab portion.

[0358]

The positive electrodes 11a and the negative electrodes 11b are stacked so that surfaces of the positive electrodes 11a on each of which the positive electrode active material layer is not formed are in contact with each other and that surfaces of the negative electrodes 11b on each of which the negative electrode active material layer is not formed are in contact with each other.

[0359]

Furthermore, the separator 14 is provided between the surface of the positive electrode 11a on which the positive electrode active material is formed and the surface of the negative electrode 11b on which the negative electrode active material is formed. In FIG. 23A, the separator 14 is shown by a dotted line for easy viewing.

[0360]

In addition, as illustrated in FIG. 23B, the plurality of positive electrodes 11a are electrically connected to the lead 12a in a bonding portion 15a. The plurality of negative electrodes 11b are electrically connected to the lead 12b in a bonding portion 15b.

[0361]

Next, the exterior body 51 is described with reference to FIGS. 22B1, 22B2, 22C, and 22D.

[0362]

The exterior body 51 has a film-like shape and is folded in half with the positive electrodes 11a and the negative electrodes 11b between facing portions of the exterior body 51. The exterior body 51 includes a folded portion 61, a pair of seal portions 62, and a seal portion 63. The pair of seal portions 62 is provided with the positive electrodes 11a and the negative electrodes 11b positioned therebetween and thus can also be referred to as side seals. The seal portion 63 has portions overlapping with the lead 12a and the lead 12b and can also be referred to as a top seal.

[0363]

Part of the exterior body 51 that overlaps with the positive electrodes 11a and the negative electrodes 11b preferably has a wave shape in which crest lines 71 and trough lines 72 are alternately arranged. The seal portions 62 and the seal portion 63 of the exterior body 51 are preferably flat.

[0364]

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FIG. 22B1 shows a cross section cut along the part overlapping with the crest line 71. FIG. 22B2 shows a cross section cut along the part overlapping with the trough line 72. FIGS. 22B1 and 22B2 correspond to cross sections of the battery 50, the positive electrodes 11a, and the negative electrodes 11b in the width direction.

[0365]

The distance between an end portion of the negative electrode 11b in the width direction and the seal portion 62 is referred to as a distance La. When the battery 50 changes in shape, for example, is bent, the positive electrode 11a and the negative electrode 11b change in shape such that the positions thereof are shifted from each other in the length direction as described later. At the time, if the distance La is too short, the exterior body 51 and the positive electrode 11a and the negative electrode 11b are rubbed hard against each other, so that the exterior body 51 is damaged in some cases. In particular, when a metal film of the exterior body 51 is exposed, there is concern that the metal film is corroded by the electrolyte solution. Thus, the distance La is preferably set as long as possible. However, if the distance La is too long, the volume of the battery 50 is increased.

[0366]

The distance La between the end portion of the negative electrode 11b and the seal portion 62 is preferably increased as the total thickness of the stacked positive electrodes 11a and negative electrodes 11b is increased.

[0367]

Specifically, when the total thickness of the stacked positive electrodes 11a and negative electrodes 11b and the separators 214 (not illustrated) is referred to as a thickness t, the distance La is preferably 0.8 times or more and 3.0 times or less, further preferably 0.9 times or more and 2.5 times or less, still further preferably 1.0 times or more and 2.0 times or less as large as the thickness t. When the distance La is in the above-described range, a compact battery which is highly reliable for bending can be obtained.

[0368]

Furthermore, when a distance between the pair of seal portions 62 is referred to as a distance Lb, it is preferable that the distance Lb be sufficiently longer than a width Wb of the negative electrode 11b. In this case, even when the positive electrode 11a and the negative electrode 11b come into contact with the exterior body 51 by change in the shape of the battery 50 such as repeated bending, the position of part of the positive electrode 11a and the negative electrode 11b can be shifted in the width direction; thus, the positive and negative electrodes 11a and 11b and the exterior body 51 can be effectively prevented from being rubbed against each other.

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[0369]

For example, the difference between the distance Lb (i.e., the distance between the pair of seal portions 62) and the width Wb of the negative electrode 11b is preferably 1.6 times or more and 6.0 times or less, further preferably 1.8 times or more and 5.0 times or less, still further preferably 2.0 times or more and 4.0 times or less as large as the total thickness t of the positive electrode 11a and the negative electrode 11b.

[0370]

In other words, the distance Lb, the width Wb, and the thickness t preferably satisfy the relation of the following Formula 2.

[0371]

[Formula 2]

$$\frac{Lb - Wb}{2t} \geq \alpha \qquad \text{(Formula 2)}$$

[0372]

In the formula, α is 0.8 or more and 3.0 or less, preferably 0.9 or more and 2.5 or less, further preferably 1.0 or more and 2.0 or less.

[0373]

FIG. 22C illustrates a cross section including the lead 12a and corresponds to a cross section of the battery 50, the positive electrode 11a, and the negative electrode 11b in the length direction. As illustrated in FIG. 22C, a space 73 is preferably provided between end portions of the positive electrode 11a and the negative electrode 11b in the length direction and the exterior body 51 in the folded portion 61.

[0374]

FIG. 22D is a schematic cross-sectional view of the battery 50 in a state of being bent. FIG. 22D corresponds to a cross section along cutting line B1-B2 in FIG. 22A.

[0375]

When the battery 50 is bent, a part of the exterior body 51 positioned on the outer side in bending is unbent and the other part positioned on the inner side changes its shape as it shrinks. More specifically, the part of the exterior body 51 positioned on the outer side in bending changes its shape such that the wave amplitude becomes smaller and the length of the wave period becomes larger. In contrast, the part of the exterior body 51 positioned on the inner side in bending changes its shape such that the wave amplitude becomes larger and the length of the wave period becomes smaller. When the exterior body 51 changes its shape in this manner, stress applied to the exterior body 51 due to bending is relieved, so that a material itself that

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forms the exterior body 51 does not need to expand and contract. As a result, the battery 50 can be bent with weak force without damage to the exterior body 51.

[0376]

Furthermore, as illustrated in FIG. 22D, when the battery 50 is bent, the positions of the positive electrode 11a and the negative electrode 11b are shifted relatively. At this time, ends of the stacked positive electrodes 11a and negative electrodes 11b on the seal portion 63 side are fixed by the fixing member 17. Thus, the plurality of positive electrodes 11a and the plurality of negative electrodes 11b are more shifted at a position closer to the folded portion 61. Therefore, stress applied to the positive electrode 11a and the negative electrode 11b is relieved, and the positive electrode 11a and the negative electrode 11b themselves do not need to expand and contract. As a result, the battery 50 can be bent without damage to the positive electrode 11a and the negative electrode 11b.

[0377]

Furthermore, the space 73 is provided between the end portions of the positive and negative electrodes 11a and 11b and the exterior body 51, whereby the relative positions of the positive electrode 11a and the negative electrode 11b can be shifted while the end portions of the positive electrode 11a and the negative electrode 11b located on an inner side when the battery 50 is bent do not contact the exterior body 51.

[0378]

In the battery 50 illustrated in FIGS. 22A, 22B1, 22B2, 22C and 22D and FIGS. 23A and 23B, the exterior body, the positive electrode 11a, and the negative electrode 11b are less likely to be damaged and the battery characteristics are less likely to deteriorate even when the battery 50 is repeatedly bent and unbent. When the positive electrode active material described in the above embodiment is used for the positive electrode 11a included in the battery 50, a battery with more excellent cycle characteristics can be obtained.

[0379]

(Embodiment 4)

In this embodiment, examples of electronic devices including the secondary battery of one embodiment of the present invention are described.

[0380]

First, FIGS. 24A to 24G show examples of electronic devices including the bendable secondary battery described in Embodiment 3. Examples of an electronic device including a flexible secondary battery include television sets (also referred to as televisions or television receivers), monitors of computers or the like, digital cameras or digital video cameras, digital photo frames, mobile phones (also referred to as cellular phones or mobile phone devices),

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portable game machines, portable information terminals, audio reproducing devices, and large game machines such as pachinko machines.

[0381]

In addition, a flexible secondary battery can be incorporated along a curved inside/outside wall surface of a house or a building or a curved interior/exterior surface of an automobile.

[0382]

FIG. 24A illustrates an example of a mobile phone. A mobile phone 7400 is provided with a display portion 7402 incorporated in a housing 7401, an operation button 7403, an external connection port 7404, a speaker 7405, a microphone 7406, and the like. Note that the mobile phone 7400 includes a secondary battery 7407. When the secondary battery of one embodiment of the present invention is used as the secondary battery 7407, a lightweight mobile phone with a long lifetime can be provided.

[0383]

FIG. 24B illustrates the mobile phone 7400 that is bent. When the whole mobile phone 7400 is curved by external force, the secondary battery 7407 included in the mobile phone 7400 is also curved. FIG. 24C illustrates the curved secondary battery 7407. The secondary battery 7407 is a thin storage battery. The secondary battery 7407 is curved and fixed. Note that the secondary battery 7407 includes a lead electrode 7408 electrically connected to a current collector 7409. The current collector 7409 is, for example, copper foil, and partly alloyed with gallium; thus, adhesion between the current collector 7409 and an active material layer in contact with the current collector 7409 is improved and the secondary battery 7407 can have high reliability even in a state of being bent.

[0384]

FIG. 24D illustrates an example of a bangle display device. A portable display device 7100 includes a housing 7101, a display portion 7102, an operation button 7103, and a secondary battery 7104. FIG. 24E illustrates the bent secondary battery 7104. When the curved secondary battery 7104 is on a user's arm, the housing changes its form and the curvature of a part or the whole of the secondary battery 7104 is changed. Note that the radius of curvature of a curve at a point refers to the radius of the circular arc that best approximates the curve at that point. The reciprocal of the radius of curvature is curvature. Specifically, part or the whole of the housing or the main surface of the secondary battery 7104 is changed in the range of radius of curvature from 40 mm to 150 mm. When the radius of curvature at the main surface of the secondary battery 7104 is greater than or equal to 40 mm and less than or equal to 150 mm, the reliability can be kept high. When the secondary battery of one embodiment of the present

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invention is used as the secondary battery 7104, a lightweight portable display device with a long lifetime can be provided.

[0385]

FIG. 24F illustrates an example of a watch-type portable information terminal. A portable information terminal 7200 includes a housing 7201, a display portion 7202, a band 7203, a buckle 7204, an operation button 7205, an input output terminal 7206, and the like.

[0386]

The portable information terminal 7200 is capable of executing a variety of applications such as mobile phone calls, e-mailing, viewing and editing texts, music reproduction, Internet communication, and a computer game.

[0387]

The display surface of the display portion 7202 is curved, and images can be displayed on the curved display surface. In addition, the display portion 7202 includes a touch sensor, and operation can be performed by touching the screen with a finger, a stylus, or the like. For example, by touching an icon 7207 displayed on the display portion 7202, application can be started.

[0388]

With the operation button 7205, a variety of functions such as time setting, power on/off, on/off of wireless communication, setting and cancellation of a silent mode, and setting and cancellation of a power saving mode can be performed. For example, the functions of the operation button 7205 can be set freely by setting the operation system incorporated in the portable information terminal 7200.

[0389]

The portable information terminal 7200 can employ near field communication that is a communication method based on an existing communication standard. For example, mutual communication between the portable information terminal 7200 and a headset capable of wireless communication can be performed, and thus hands-free calling is possible.

[0390]

Moreover, the portable information terminal 7200 includes the input output terminal 7206, and data can be directly transmitted to and received from another information terminal via a connector. In addition, charging via the input output terminal 7206 is possible. Note that the charging operation may be performed by wireless power feeding without using the input output terminal 7206.

[0391]

The display portion 7202 of the portable information terminal 7200 includes the

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secondary battery of one embodiment of the present invention. When the secondary battery of one embodiment of the present invention is used, a lightweight portable information terminal with a long lifetime can be provided. For example, the secondary battery 7104 illustrated in FIG. 24E that is in the state of being curved can be provided in the housing 7201. Alternatively, the secondary battery 7104 illustrated in FIG. 24E can be provided in the band 7203 such that it can be curved.

[0392]

A portable information terminal 7200 preferably includes a sensor. As the sensor, for example a human body sensor such as a fingerprint sensor, a pulse sensor, or a temperature sensor, a touch sensor, a pressure sensitive sensor, an acceleration sensor, or the like is preferably mounted.

[0393]

FIG. 24G illustrates an example of an armband display device. A display device 7300 includes a display portion 7304 and the secondary battery of one embodiment of the present invention. The display device 7300 can include a touch sensor in the display portion 7304 and can serve as a portable information terminal.

[0394]

The display surface of the display portion 7304 is bent, and images can be displayed on the bent display surface. A display state of the display device 7300 can be changed by, for example, near field communication, which is a communication method based on an existing communication standard.

[0395]

The display device 7300 includes an input output terminal, and data can be directly transmitted to and received from another information terminal via a connector. In addition, charging via the input output terminal is possible. Note that the charging operation may be performed by wireless power feeding without using the input output terminal.

[0396]

When the secondary battery of one embodiment of the present invention is used as the secondary battery included in the display device 7300, a lightweight display device with a long lifetime can be provided.

[0397]

In addition, FIG. 24H, FIGS. 25A to 25C, and FIG. 26 show examples of electronic devices including the secondary battery with excellent cycle characteristics described in the above embodiment.

[0398]

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When the secondary battery of one embodiment of the present invention is used as a secondary battery of a daily electronic device, a lightweight product with a long lifetime can be provided. As the daily electronic devices, an electric toothbrush, an electric shaver, electric beauty equipment, and the like are given. As secondary batteries of these products, in consideration of handling ease for users, small and lightweight stick type secondary batteries with high capacity are desired.

[0399]

FIG. 24H is a perspective view of a device which is called a vaporizer. In FIG. 24H, a vaporizer 7500 includes an atomizer 7501 including a heating element, a secondary battery 7504 supplying power to the atomizer, and a cartridge 7502 including a liquid supply bottle, a sensor, and the like. To improve safety, a protection circuit which prevents overcharge and overdischarge of the secondary battery 7504 may be electrically connected to the secondary battery 7504. The secondary battery 7504 in FIG. 24H includes an output terminal for connecting to a charger. When the vaporizer 7500 is held by a user, the secondary battery 7504 becomes a tip portion; thus, it is preferable that the secondary battery 7504 have a short total length and be lightweight. With the secondary battery of one embodiment of the present invention which has high capacity and excellent cycle characteristics, the small and lightweight vaporizer 7500 which can be used for a long time for a long period can be provided.

[0400]

Next, FIGS. 25A and 25B illustrate an example of a foldable tablet terminal. A tablet terminal 9600 illustrated in FIGS. 25A and 25B includes a housing 9630a, a housing 9630b, a movable portion 9640 connecting the housings 9630a and 9630b, a display portion 9631 including a display portion 9631a and a display portion 9631b, a display mode changing switch 9626, a power switch 9627, a power saving mode changing switch 9625, a fastener 9629, and an operation switch 9628. A flexible panel is used for the display portion 9631, whereby a tablet terminal with a larger display portion can be provided. FIG. 25A illustrates the tablet terminal 9600 that is opened, and FIG. 25B illustrates the tablet terminal 9600 that is closed.

[0401]

The tablet terminal 9600 includes a power storage unit 9635 inside the housings 9630a and 9630b. The power storage unit 9635 is provided across the housings 9630a and 9630b, passing through the movable portion 9640.

[0402]

Part of the display portion 9631a can be a touch panel region 9632a and data can be input when a displayed operation key 9638 is touched. Although a structure in which a half region in the display portion 9631a has only a display function and the other half region has a

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touch panel function is shown as an example, the display portion 9631a is not limited to the structure. The whole region in the display portion 9631a may have a touch panel function. For example, the display portion 9631a can display keyboard buttons in the whole region to be a touch panel, and the display portion 9631b can be used as a display screen.

[0403]

Like the display portion 9631a, part of the display portion 9631b can be a touch panel region 9632b. A switching button 9639 for showing/hiding a keyboard of the touch panel is touched with a finger, a stylus, or the like, so that keyboard buttons can be displayed on the display portion 9631b.

[0404]

Touch input can be performed in the touch panel region 9632a and the touch panel region 9632b at the same time.

[0405]

The display mode switch 9626 can switch the display between a portrait mode and a landscape mode, and between monochrome display and color display, for example. The power saving mode changing switch 9625 can control display luminance in accordance with the amount of external light in use of the tablet terminal 9600, which is measured with an optical sensor incorporated in the tablet terminal 9600. Another detection device including a sensor for detecting inclination, such as a gyroscope sensor or an acceleration sensor, may be incorporated in the tablet terminal, in addition to the optical sensor.

[0406]

Although the display portion 9631a and the display portion 9631b have the same area in FIG. 25A, one embodiment of the present invention is not limited to this example. The display portion 9631a and the display portion 9631b may have different areas or different display quality. For example, one display panel may be capable of higher-definition display than the other display panel.

[0407]

The tablet terminal is closed in FIG. 25B. The tablet terminal includes the housing 9630, a solar cell 9633, and a charge and discharge control circuit 9634 including a DCDC converter 9636. The power storage unit of one embodiment of the present invention is used as the power storage unit 9635.

[0408]

The tablet terminal 9600 can be folded such that the housings 9630a and 9630b overlap with each other when not in use. Thus, the display portions 9631a and 9631b can be protected, which increases the durability of the tablet terminal 9600. With the power storage unit 9635

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including the secondary battery of one embodiment of the present invention which has high capacity and excellent cycle characteristics, the tablet terminal 9600 which can be used for a long time for a long period can be provided.

[0409]

The tablet terminal illustrated in FIGS. 25A and 25B can also have a function of displaying various kinds of data (e.g., a still image, a moving image, and a text image), a function of displaying a calendar, a date, or the time on the display portion, a touch-input function of operating or editing data displayed on the display portion by touch input, a function of controlling processing by various kinds of software (programs), and the like.

[0410]

The solar cell 9633, which is attached on the surface of the tablet terminal, supplies electric power to a touch panel, a display portion, an image signal processor, and the like. Note that the solar cell 9633 can be provided on one or both surfaces of the housing 9630 and the power storage unit 9635 can be charged efficiently. The use of a lithium-ion battery as the power storage unit 9635 brings an advantage such as reduction in size.

[0411]

The structure and operation of the charge and discharge control circuit 9634 illustrated in FIG. 25B will be described with reference to a block diagram in FIG. 25C. The solar cell 9633, the power storage unit 9635, the DC-DC converter 9636, a converter 9637, switches SW1 to SW3, and the display portion 9631 are illustrated in FIG. 25C, and the power storage unit 9635, the DC-DC converter 9636, the converter 9637, and the switches SW1 to SW3 correspond to the charge and discharge control circuit 9634 in FIG. 25B.

[0412]

First, an example of the operation in the case where power is generated by the solar cell 9633 using external light is described. The voltage of electric power generated by the solar cell is raised or lowered by the DCDC converter 9636 to a voltage for charging the power storage unit 9635. When the power from the solar cell 9633 is used for the operation of the display portion 9631, the switch SW1 is turned on and the voltage of the power is raised or lowered by the converter 9637 to a voltage needed for operating the display portion 9631. When display on the display portion 9631 is not performed, the switch SW1 is turned off and the switch SW2 is turned on, so that the power storage unit 9635 can be charged.

[0413]

Note that the solar cell 9633 is described as an example of a power generation means; however, one embodiment of the present invention is not limited to this example. The power storage unit 9635 may be charged using another power generation means such as a piezoelectric

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element or a thermoelectric conversion element (Peltier element). For example, the power storage unit 9635 may be charged with a non-contact power transmission module that transmits and receives power wirelessly (without contact) to charge the battery or with a combination of other charging means.

[0414]

FIG. 26 illustrates other examples of electronic devices. In FIG. 26, a display device 8000 is an example of an electronic device including a secondary battery 8004 of one embodiment of the present invention. Specifically, the display device 8000 corresponds to a display device for TV broadcast reception and includes a housing 8001, a display portion 8002, speaker portions 8003, the secondary battery 8004, and the like. The secondary battery 8004 of one embodiment of the present invention is provided in the housing 8001. The display device 8000 can receive electric power from a commercial power supply. Alternatively, the display device 8000 can use electric power stored in the secondary battery 8004. Thus, the display device 8000 can operate with the use of the secondary battery 8004 of one embodiment of the present invention as an uninterruptible power supply even when electric power cannot be supplied from a commercial power supply due to power failure or the like.

[0415]

A semiconductor display device such as a liquid crystal display device, a light-emitting device in which a light-emitting element such as an organic EL element is provided in each pixel, an electrophoretic display device, a digital micromirror device (DMD), a plasma display panel (PDP), or a field emission display (FED) can be used for the display portion 8002.

[0416]

Note that the display device includes, in its category, all of information display devices for personal computers, advertisement displays, and the like other than TV broadcast reception.

[0417]

In FIG. 26, an installation lighting device 8100 is an example of an electronic device using a secondary battery 8103 of one embodiment of the present invention. Specifically, the lighting device 8100 includes a housing 8101, a light source 8102, the secondary battery 8103, and the like. Although FIG. 26 illustrates the case where the secondary battery 8103 is provided in a ceiling 8104 on which the housing 8101 and the light source 8102 are installed, the secondary battery 8103 may be provided in the housing 8101. The lighting device 8100 can receive electric power from a commercial power supply. Alternatively, the lighting device 8100 can use electric power stored in the secondary battery 8103. Thus, the lighting device 8100 can operate with the use of the secondary battery 8103 of one embodiment of the present invention as an uninterruptible power supply even when electric power cannot be supplied from a

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commercial power supply due to power failure or the like.

[0418]

Note that although the installation lighting device 8100 provided in the ceiling 8104 is illustrated in FIG. 26 as an example, the secondary battery of one embodiment of the present invention can be used as an installation lighting device provided in, for example, a wall 8105, a floor 8106, a window 8107, or the like other than the ceiling 8104. Alternatively, the secondary battery can be used in a tabletop lighting device or the like.

[0419]

As the light source 8102, an artificial light source which emits light artificially by using power can be used. Specifically, an incandescent lamp, a discharge lamp such as a fluorescent lamp, and a light-emitting element such as an LED or an organic EL element are given as examples of the artificial light source.

[0420]

In FIG. 26, an air conditioner including an indoor unit 8200 and an outdoor unit 8204 is an example of an electronic device including a secondary battery 8203 of one embodiment of the present invention. Specifically, the indoor unit 8200 includes a housing 8201, an air outlet 8202, the secondary battery 8203, and the like. Although FIG. 26 illustrates the case where the secondary battery 8203 is provided in the indoor unit 8200, the secondary battery 8203 may be provided in the outdoor unit 8204. Alternatively, the secondary batteries 8203 may be provided in both the indoor unit 8200 and the outdoor unit 8204. The air conditioner can receive electric power from a commercial power supply. Alternatively, the air conditioner can use electric power stored in the secondary battery 8203. Particularly in the case where the secondary batteries 8203 are provided in both the indoor unit 8200 and the outdoor unit 8204, the air conditioner can operate with the use of the secondary battery 8203 of one embodiment of the present invention as an uninterruptible power supply even when electric power cannot be supplied from a commercial power supply due to power failure or the like.

[0421]

Note that although the split-type air conditioner including the indoor unit and the outdoor unit is illustrated in FIG. 26 as an example, the secondary battery of one embodiment of the present invention can be used in an air conditioner in which the functions of an indoor unit and an outdoor unit are integrated in one housing.

[0422]

In FIG. 26, an electric refrigerator-freezer 8300 is an example of an electronic device using a secondary battery 8304 of one embodiment of the present invention. Specifically, the electric refrigerator-freezer 8300 includes a housing 8301, a refrigerator door 8302, a freezer

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door 8303, the secondary battery 8304, and the like. The secondary battery 8304 is provided in the housing 8301 in FIG. 26. The electric refrigerator-freezer 8300 can receive electric power from a commercial power supply. Alternatively, the electric refrigerator-freezer 8300 can use electric power stored in the secondary battery 8304. Thus, the electric refrigerator-freezer 8300 can operate with the use of the secondary battery 8304 of one embodiment of the present invention as an uninterruptible power supply even when electric power cannot be supplied from a commercial power supply due to power failure or the like.

[0423]

Note that among the electronic devices described above, a high-frequency heating apparatus such as a microwave oven and an electronic device such as an electric rice cooker require high power in a short time. The tripping of a circuit breaker of a commercial power source in use of electronic devices can be prevented by using the secondary battery of one embodiment of the present invention as an auxiliary power source for supplying power which cannot be supplied enough by a commercial power source.

[0424]

In addition, in a time period when electronic devices are not used, particularly when the proportion of the amount of power which is actually used to the total amount of power which can be supplied from a commercial power source (such a proportion referred to as a usage rate of power) is low, power can be stored in the secondary battery, whereby the usage rate of power can be reduced in a time period when the electronic devices are used. For example, in the case of the electric refrigerator-freezer 8300, power can be stored in the secondary battery 8304 in night time when the temperature is low and the refrigerator door 8302 and the freezer door 8303 are not often opened and closed. On the other hand, in daytime when the temperature is high and the refrigerator door 8302 and the freezer door 8303 are frequently opened and closed, the secondary battery 8304 is used as an auxiliary power source; thus, the usage rate of power in daytime can be reduced.

[0425]

According to one embodiment of the present invention, the secondary battery can have excellent cycle characteristics and improve reliability. Furthermore, in accordance with one embodiment of the present invention, a secondary battery with high capacity can be obtained; thus, the secondary battery itself can be made more compact and lightweight as a result of improved characteristics of the secondary battery. Thus, the secondary battery of one embodiment of the present invention is used in the electronic device described in this embodiment, whereby a more lightweight electronic device with a longer lifetime can be obtained. This embodiment can be implemented in appropriate combination with any of the

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other embodiments.

[0426]

(Embodiment 5)

In this embodiment, examples of vehicles including the secondary battery of one embodiment of the present invention are described.

[0427]

The use of secondary batteries in vehicles enables production of next-generation clean energy vehicles such as hybrid electric vehicles (HEVs), electric vehicles (EVs), and plug-in hybrid electric vehicles (PHEVs).

[0428]

FIGS. 27A to 27C each illustrate an example of a vehicle using the secondary battery of one embodiment of the present invention. An automobile 8400 illustrated in FIG. 27A is an electric vehicle that runs on the power of an electric motor. Alternatively, the automobile 8400 is a hybrid electric vehicle capable of driving appropriately using either an electric motor or an engine. One embodiment of the present invention can provide a high-mileage vehicle. The automobile 8400 includes the secondary battery. As the secondary battery, the modules of the secondary batteries illustrated in FIGS. 12C and 12D may be arranged to be used in a floor portion in the automobile. Alternatively, a battery pack in which a plurality of secondary batteries each of which is illustrated in FIGS. 17A to 17C are combined may be placed in a floor portion in the automobile. The secondary battery is used not only for driving an electric motor 8406, but also for supplying electric power to a light-emitting device such as a headlight 8401 or a room light (not illustrated).

[0429]

The secondary battery can also supply electric power to a display device of a speedometer, a tachometer, or the like included in the automobile 8400. Furthermore, the secondary battery can supply electric power to a semiconductor device included in the automobile 8400, such as a navigation system.

[0430]

FIG. 27B illustrates an automobile 8500 including the secondary battery. The automobile 8500 can be charged when the secondary battery is supplied with electric power through external charging equipment by a plug-in system, a contactless power feeding system, or the like. In FIG. 27B, a secondary battery 8024 included in the automobile 8500 is charged with the use of a ground-based charging apparatus 8021 through a cable 8022. In charging, a given method such as CHAdeMO (registered trademark) or Combined Charging System may be employed as a charging method, the standard of a connector, or the like as appropriate. The

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ground-based charging apparatus 8021 may be a charging station provided in a commerce facility or a power source in a house. With the use of a plug-in technique, the secondary battery 8024 included in the automobile 8500 can be charged by being supplied with electric power from the outside, for example. The charging can be performed by converting AC electric power into DC electric power through a converter such as an AC-DC converter.

[0431]

Furthermore, although not illustrated, the vehicle may include a power receiving device so that it can be charged by being supplied with electric power from an above-ground power transmitting device in a contactless manner. In the case of the contactless power feeding system, by fitting a power transmitting device in a road or an exterior wall, charging can be performed not only when the electric vehicle is stopped but also when driven. In addition, the contactless power feeding system may be utilized to perform transmission and reception of electric power between vehicles. A solar cell may be provided in the exterior of the automobile to charge the secondary battery when the automobile stops or moves. To supply electric power in such a contactless manner, an electromagnetic induction method or a magnetic resonance method can be used.

[0432]

FIG. 27C shows an example of a motorcycle using the secondary battery of one embodiment of the present invention. A motor scooter 8600 illustrated in FIG. 27C includes a secondary battery 8602, side mirrors 8601, and indicators 8603. The secondary battery 8602 can supply electric power to the indicators 8603.

[0433]

Furthermore, in the motor scooter 8600 illustrated in FIG. 27C, the secondary battery 8602 can be held in a storage unit under seat 8604. The secondary battery 8602 can be held in the storage unit under seat 8604 even with a small size. The secondary battery 8602 is detachable; thus, the secondary battery 8602 is carried indoors when it is charged, and is stored before the motorcycle is driven.

[0434]

In accordance with one embodiment of the present invention, the secondary battery can have improved cycle characteristics and the capacity of the secondary battery can be increased. Thus, the secondary battery itself can be made more compact and lightweight. The compact and lightweight secondary battery contributes to a reduction in the weight of a vehicle, and thus increases the driving radius. Furthermore, the secondary battery included in the vehicle can be used as a power source for supplying electric power to products other than the vehicle. In such a case, the use of a commercial power source can be avoided at peak time of electric power

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demand, for example. If the use of a commercial power source can be avoided at peak time of electric power demand, the avoidance can contribute to energy saving and a reduction in carbon dioxide emissions. Moreover, if the cycle characteristics are excellent, the secondary battery can be used for a long period; thus, the use amount of rare metals such as cobalt can be reduced.

[0435]

This embodiment can be implemented in appropriate combination with the other embodiments.

[Example 1]

[0436]

In this example, the positive electrode active materials which are embodiments of the present invention are formed, and the observation results of the positive electrode active materials by STEM, the results of TEM images subjected to fast Fourier transform, and the analysis results obtained by energy dispersive X-ray spectroscopy (EDX) are described. In addition, the evaluation results of characteristics of secondary batteries containing the positive electrode active materials are described.

[0437]

[Formation of positive electrode active material]

<<Sample 01>>

In this example, a positive electrode active material of Sample 01, which contains lithium cobaltate as a composite oxide of lithium and a first transition metal contained in a first region, lithium titanate as an oxide of a second transition metal contained in a second region, and magnesium oxide as an oxide of a representative element contained in a third region, was formed.

[0438]

In this example, lithium cobalt oxide particles (C-20F, produced by NIPPON CHEMICAL INDUSTRIAL CO., LTD.) were used as a starting material. Thus, in this example, Step 12 and Step 13 described in Embodiment 1 were omitted. Note that the above-described lithium cobalt oxide particles each have a particle diameter of approximately 20 μm, and contain fluorine, magnesium, calcium, sodium, silicon, sulfur, and phosphorus in a region which can be analyzed by XPS.

[0439]

Next, as Step 14, the lithium cobalt oxide particles containing magnesium and fluorine were coated with a material containing titanium by a sol-gel method. Specifically, TTIP was dissolved in isopropanol, and an isopropanol solution of TTIP was formed. Then, the lithium cobalt oxide particles were mixed into the solution so that TTIP to lithium cobalt oxide

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containing magnesium and fluorine was 0.01 ml/g.

[0440]

The above mixed solution was stirred with a magnetic stirrer for four hours, at 25 °C, and at a humidity of 90 %RH. Through the process, water in an atmosphere and TTIP caused hydrolysis and polycondensation reaction, and a layer containing titanium was formed on the surface of the lithium cobalt oxide particle containing magnesium and fluorine.

[0441]

The mixed solution which had been subjected to the above process was filtered to collect the residue. As a filter for filtration, Kiriyama filter paper (No. 4) was used.

[0442]

The collected residue was dried in a vacuum at 70 °C for one hour.

[0443]

Next, the lithium cobalt oxide particles coated with the material containing titanium was heated. With a muffle furnace, the heating was performed under the following conditions: the flow rate of dry air was 10 L/min; the temperature was 800 °C (the temperature rising rate was 200 °C/h); and the retention time was two hours. The dew point of the dry air is preferably lower than or equal to −109 °C.

[0444]

Then, the heated particles were cooled to room temperature. The time of decreasing temperature from the retention temperature to room temperature was 10 hours to 15 hours. After that, crushing treatment was performed. In the crushing treatment, the particles were made to pass through a sieve. The sieve has an aperture width of 53 μm.

[0445]

Lastly, the cooled particles were collected, and the positive electrode active material of Sample 01 was obtained.

[0446]

<<Sample 02>>

Sample 02 was formed as a comparative example by heating lithium cobalt oxide particles containing magnesium and fluorine without being coated with a material containing titanium.

[0447]

Lithium cobalt oxide particles produced by NIPPON CHEMICAL INDUSTRIAL CO., LTD. (product name: C-20F) were used as the lithium cobalt oxide particles containing magnesium and fluorine.

[0448]

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The lithium cobalt oxide particles containing magnesium and fluorine were heated. The heating was performed under the following conditions: the temperature was 800 °C (the temperature rising rate was 200 °C/h); the retention time was two hours; and the flow rate of oxygen was 10 L/min.

[0449]

The heated particles were cooled and made to pass through a sieve like Sample 01 to obtain a positive electrode active material of Sample 02.

[0450]

It is probable that Sample 02 is a positive electrode active material which contains lithium cobalt oxide inside and includes a region containing magnesium in a superficial portion.

[0451]

<<Sample 03>>

Sample 03 was formed as a comparative example in the following manner: a region containing titanium was formed in lithium cobalt oxide particles which do not contain magnesium by a sol-gel method and then the lithium cobalt oxide particles were heated.

[0452]

Lithium cobalt oxide particles produced by NIPPON CHEMICAL INDUSTRIAL CO., LTD. (product name: C-10N) were used. In the lithium cobalt oxide particles, magnesium is not detected and fluorine is detected at approximately 1 atomic% by XPS.

[0453]

A region containing titanium was formed by a sol-gel method in the lithium cobalt oxide particles, and the lithium cobalt oxide particles were dried, heated, cooled, and made to pass through a sieve, like Sample 01. The obtained lithium cobalt oxide particles were used as a positive electrode active material of Sample 03.

[0454]

It is probable that Sample 03 is a positive electrode active material which contains lithium cobalt oxide inside and includes a region containing titanium in a superficial portion.

[0455]

<<Sample 04>>

For Sample 04, as a comparative example, lithium cobalt oxide particles were used as it is without being heated.

[0456]

Lithium cobalt oxide particles produced by NIPPON CHEMICAL INDUSTRIAL CO., LTD. (product name: C-10N) were used.

[0457]

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Sample 04 is a positive electrode active material which does not have a coating layer.

[0458]

<<Sample 05>>

For Sample 05, as a comparative example, lithium cobalt oxide particles containing magnesium and fluorine were used as it is without being heated.

[0459]

Lithium cobalt oxide particles produced by NIPPON CHEMICAL INDUSTRIAL CO., LTD. (product name: C-20F) were used as the lithium cobalt oxide particles containing magnesium and fluorine. That is, Sample 05 was used as the same as the starting material of Sample 01.

[0460]

Table 1 shows the conditions of Sample 01 to Sample 05.

[0461]

[Table 1]

	Conditions
Sample 01	$LiCoO_2$+Mg+F, coated with a material containing Ti, heated
Sample 02	$LiCoO_2$+Mg+F, heated
Sample 03	$LiCoO_2$, coated with a material containing Ti, heated
Sample 04	$LiCoO_2$, not heated
Sample 05	$LiCoO_2$+Mg+F, not heated

[0462]

[STEM]

The obtained positive electrode active material of Sample 01 was observed by an electron microscope (JEM-ARM200F, manufactured by JEOL Ltd.) under the condition where the acceleration voltage was 200 kV. FIG. 28 shows the obtained electron microscope image. As shown in FIG. 28, the positive electrode active material probably includes three different regions: the first region 101; the second region 102; and the third region 103. The third region 103 is observed as a region brighter than the first region 101 and the second region 102. Furthermore, crystal orientations of the first region 101 and the second region 102 are partly aligned with each other, and crystal orientations of the second region 102 and the third region 103 are partly aligned with each other.

[0463]

[STEM-FFT]

FIG. 29A1 shows a fast Fourier transform (FFT) image of a region 103FFT in the

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STEM image of FIG. 28. In FIG. 29A2, a center point O of FIG. 29A1 is shown by a cross, and bright points A, B, and C are each surrounded by a circle. Similarly, FIG. 29B1 shows an FFT image of a region 102FFT. In FIG. 29B2, a center point O of FIG. 29B1 is shown by a cross, and bright points A, B, and C are each surrounded by a circle. In addition, FIG. 29C1 shows an FFT image of a region 101FFT. In FIG. 29C2, a center point O of FIG. 29C1 is shown by a cross, and bright points A, B, and C are each surrounded by a circle.

[0464]

In FIG. 29A2, a distance d between the bright point A and the center point O is 0.256 nm, a distance d between the bright point B and the center point O is 0.241 nm, and a distance d between the bright point C and the center point O is 0.209 nm. In addition, $\angle$COA is 121°, $\angle$COB is 52°, and $\angle$AOB is 69°. From these results, the region 103FFT probably contains magnesium oxide (MgO, cubic crystal).

[0465]

Similarly, in FIG. 29B2, the distance d between the bright point A and the center point O is 0.238 nm, the distance d between the bright point B and the center point O is 0.225 nm, and the distance d between the bright point C and the center point O is 0.198 nm. In addition, $\angle$COA is 123°, $\angle$COB is 52°, and $\angle$AOB is 71°. From these results, the region 102FFT probably contains lithium titanate ($LiTiO_2$, cubic crystal).

[0466]

In FIG. 29C2, the distance d between the bright point A and the center point O is 0.240 nm, the distance d between the bright point B and the center point O is 0.235 nm, and the distance d between the bright point C and the center point O is 0.196 nm. In addition, $\angle$COA is 126°, $\angle$COB is 52°, and $\angle$AOB is 74°. From these results, the region 101FFT probably contains lithium cobaltate ($LiCoO_2$, rhombohedral).

[0467]

[EDX]

FIGS. 30A1, 30A2, 30B1, 30B2, 30C1, and 30C2 show a high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and element mapping images with EDX of the positive electrode active material of Sample 01. FIG. 30A1 shows a HAADF-STEM image, FIG. 30A2 shows a mapping image of oxygen atoms, FIG. 30B1 shows a mapping image of cobalt atoms, FIG. 30B2 shows a mapping image of fluorine atoms, FIG. 30C1 shows a mapping image of titanium atoms, and FIG. 30C2 shows a mapping image of magnesium atoms. Note that in EDX element mapping images in FIGS. 30A2, 30B1, 30B2, 30C1, and 30C2 and FIGS. 31A2, 31B1, 31B2, 31C1, and 31C2, a region where the number of elements is less than or equal to a lower limit of the detection is indicated in white, and as the

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number of elements is increased, the white region becomes black.

[0468]

As shown in FIGS. 30A2 and 30B1, it is found that the oxygen atoms and the cobalt atoms are distributed in the whole of the positive electrode active material particle. In contrast, as shown in FIGS. 30B2, 30C1, and 30C2, it is found that the fluorine atoms, the titanium atoms, and the magnesium atoms are unevenly distributed in a region close to the surface of the positive electrode active material.

[0469]

Next, FIGS. 31A1, 31A2, 31B1, 31B2, 31C1, and 31C2 show a HAADF-STEM image and element mapping images with EDX of the positive electrode active material of Sample 05, which is a comparative example. FIG. 31A1 shows a HAADF-STEM image, FIG. 31A2 shows a mapping image of oxygen atoms, FIG. 31B1 shows a mapping image of cobalt atoms, FIG. 31B2 shows a mapping image of fluorine atoms, FIG. 31C1 shows a mapping image of titanium atoms, and FIG. 31C2 shows a mapping image of magnesium atoms.

[0470]

As shown in FIGS. 31B2 and 31C2, it is found that, even in Sample 05 which is not heated, a certain amount of magnesium and fluorine is unevenly distributed in the vicinity of the surface.

[0471]

[EDX line analysis]

FIG. 32 shows results of line analysis with TEM-EDX performed on a cross section of the vicinity of the surface of the positive electrode active material of Sample 01. FIG. 32 is a graph showing data detected on a line connecting the outside of the positive electrode active material of Sample 01 to the inside of the positive electrode active material, and a distance of 0 nm indicates the outside of the positive electrode active material and a distance of 14 nm indicates the inside of the particle. With EDX, the analysis region tends to be large, so that elements not only at a center of an electron beam irradiation region but also in a region around the center may be detected.

[0472]

As shown in FIG. 32, it is found that there are peaks of magnesium and titanium in the vicinity of the surface of the positive electrode active material of Sample 01, the distribution of magnesium is closer to the surface than the distribution of titanium is. It is also found that the peak of magnesium is closer to the surface than the peak of titanium is. In addition, it is probable that cobalt and oxygen are present from the outermost surface of the positive electrode active material particle.

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[0473]

As shown in FIG. 32, fluorine is hardly detected. This is probably because fluorine, which is a light element, is difficult to detect with EDX.

[0474]

From the above STEM images, FFT images, element mapping images with EDX, and EDX line analysis, it is found that Sample 01 is a positive electrode active material of one embodiment of the present invention, which includes the first region containing lithium cobaltate, the second region containing lithium, titanium, cobalt, and oxygen, and the third region containing magnesium and oxygen. It is found that, in Sample 01, part of the second region and part of the third region overlap.

[0475]

In the graph of FIG. 32, the amount of detected oxygen is stable at a distance of 4 nm or more. Thus, in this example, the average value O_{ave} of the amount of detected oxygen in the stable region is obtained, and a distance x of the measurement point at which the measurement value closest to 0.5 O_{ave}, the value of 50 % of the average value O_{ave}, is obtained is assumed to be the surface of the positive electrode active material particle.

[0476]

In this example, the average value O_{ave} of the amount of detected oxygen in a range from a distance of 4 nm to a distance of 14 nm is 674.2. The x axis of the measurement point at which the measurement value closest to 337.1, which is 50 % of 674.2, is obtained indicates a distance of 1.71 nm. Thus, in this example, a distance of 1.71 nm in the graph of FIG. 32 is assumed to be the surface of the positive electrode active material particle.

[0477]

When the surface of the positive electrode active material particle is set at a distance of 1.71 nm in FIG. 32, the peak of magnesium and the peak of titanium are present at 0.72 nm and 1.00 nm, respectively, from the surface of the positive electrode active material particle.

[0478]

The concentration of magnesium is higher than or equal to 1/5 of the peak from the surface of the positive electrode active material particle to a distance of 4.42 nm, that is, to a region at 2.71 nm from the surface. The measurement value of magnesium is less than 1/5 of the peak at a distance of 4.57 nm or more, that is, at a depth of 2.86 nm or more from the surface of the positive electrode active material particle. Thus, it is found that in Sample 01, a region from the surface to a depth of 2.71 nm is the third region.

[0479]

Furthermore, the concentration of titanium is higher than or equal to 1/2 of the peak

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from a distance of 2.14 nm to a distance of 3.42 nm. Thus, it is found that a region from a depth of 0.43 nm to a depth of 1.71 nm from the surface of the positive electrode active material particle is the second region.

[0480]

Next, evaluation results of charge and discharge characteristics of secondary batteries which are fabricated using the positive electrode active materials of Sample 01 to Sample 05 formed in the above manner are described.

[0481]

[Fabrication of secondary batteries]

CR2032 coin-type secondary batteries (with a diameter of 20 mm and a height of 3.2 mm) were fabricated using the positive electrode active materials of Sample 01 to Sample 05 formed in the above manner.

[0482]

A positive electrode formed by applying slurry in which a positive electrode active material (LCO), acetylene black (AB), and polyvinylidene fluoride (PVDF) were mixed at a weight ratio of 95:2.5:2.5 to a current collector was used.

[0483]

A lithium metal was used for the counter electrode.

[0484]

As an electrolyte contained in an electrolyte solution, 1 mol/L lithium hexafluorophosphate ($LiPF_6$) was used, and as the electrolyte solution, a solution in which ethylene carbonate (EC) and diethyl carbonate (DEC) at a volume ratio of 3:7 and vinylene carbonate (VC) at a 2 weight% were mixed was used.

[0485]

A positive electrode can and a negative electrode can were formed of stainless steel (SUS).

[0486]

[Evaluation of charge and discharge characteristics]

Next, charge and discharge characteristics of the secondary batteries of Sample 01 and Sample 05 formed in the above manner were evaluated. The measurement temperature was 25 °C. Twenty cycles of charging and discharging were performed at 4.6 V (CCCV, 0.5 C, a cutoff current of 0.01 C) and 2.5 V (CC, 0.5 C), respectively. Here, 1C was set to 137 mA/g, which was a current value per weight of the positive electrode active material.

[0487]

FIG. 33 is a graph showing charge and discharge characteristics of the secondary battery

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using the positive electrode active material of Sample 01. FIG. 33 shows excellent charge and discharge characteristics with a wide plateau. In addition, results of 20 cycles of charging and discharging almost overlap, which means that the cycle characteristics are excellent.

[0488]

FIG. 34 is a graph showing charge and discharge characteristics of the secondary battery of Sample 05, which is a comparative example. In the initial cycles, excellent charge and discharge characteristics are shown; however, as indicated by arrows in FIG. 34, charge capacity and discharge capacity decrease with an increase in cycles.

[0489]

[Evaluation of cycle characteristics]

<<Charging at 4.4 V>>

The cycle characteristics of the secondary batteries of Sample 01 and Sample 05 charged at 4.4 V were evaluated. The measurement temperature was 25 °C. The charging was performed at 4.4 V (CCCV, 0.5 C, a cutoff current of 0.01 C), and the discharging was performed at 2.5 V (CC, 0.5 C).

[0490]

FIG. 35 is a graph showing the cycle characteristics of the secondary batteries charged at 4.4 V. In FIG. 35, a solid line and a dotted line indicate secondary batteries containing the positive electrode active materials of Sample 01 and Sample 05, respectively. As shown in FIG. 35, in the secondary battery containing Sample 01, an energy density retention rate is 99.5 % even after 50 cycles of charging and discharging were performed, which shows extremely excellent cycle characteristics. In the secondary battery containing Sample 05, an energy density retention rate is 94.3 % after 50 cycles were performed.

[0491]

<<Charging at 4.6 V>>

The cycle characteristics of the secondary batteries of Sample 01 to Sample 04 charged at 4.6 V were evaluated. The measurement temperature was 25 °C. The charging was performed to 4.6 V (CCCV, 0.5 C, a cutoff current of 0.01 C), and the discharging was performed to 2.5 V (CC, 0.5 C).

[0492]

FIG. 36 is a graph showing the cycle characteristics charged at 4.6 V. As shown in FIG. 36, in the secondary battery containing Sample 01, which is the positive electrode active material of one embodiment of the present invention, an energy density retention rate is 94.1 % even after 50 cycles of charging and discharging were performed at a high voltage of 4.6 V, which shows extremely excellent cycle characteristics. On the other hand, the secondary

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batteries containing the positive electrode active materials of Sample 02, Sample 03, and Sample 04, which are comparative examples, are inferior to that of Sample 01, and in Sample 04, for example, energy density retention rate is 33.2 % after 50 cycles were performed.

[0493]

As described above, it is found that the positive electrode active material with the structure of one embodiment of the present invention can achieve an advantageous effect when charging and discharging is performed at a voltage higher than 4.4 V.

[Example 2]

[0494]

In this example, the positive electrode active materials which are embodiments of the present invention are formed, and results of analysis which is different from that in Example 1 are described. In addition, evaluation results of characteristics of secondary batteries containing the positive electrode active materials under conditions different from those in Example 1 are described.

[0495]

In this example, a positive electrode active material which contains lithium cobaltate as a composite oxide of lithium and a first transition metal contained in a first region, lithium titanate as an oxide of a second transition metal contained in a second region, and magnesium oxide as an oxide of a representative element contained in a third region, was formed.

[0496]

[Formation of positive electrode active material and fabrication of secondary battery]

<<Sample 06 and Sample 07>>

In this example, lithium cobalt oxide particles (C-20F, produced by NIPPON CHEMICAL INDUSTRIAL CO., LTD.) were used as a starting material.

[0497]

Next, as Step 14, the lithium cobalt oxide particles were coated with titanium oxide by a sol-gel method and dried. Step 14 was performed in a manner similar to that in Example 1 except that mixture was performed so that TTIP to lithium cobalt oxide was 0.004 ml/g. The lithium cobalt oxide particles which are coated with the titanium oxide and are not heated yet are referred to as Sample 06.

[0498]

Next, Sample 06, which is the lithium cobalt oxide particles coated with the titanium oxide, was heated. With a muffle furnace, the heating was performed at 800 °C in an oxygen atmosphere under the following conditions: the retention time was two hours; and the flow rate of oxygen was 10 L/min.

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[0499]

Then, as in Example 1, the particles were cooled and collected to obtain the positive electrode active material. The heated positive electrode active material is referred to as Sample 07.

[0500]

[TEM-EDX]

Sample 06 and Sample 07, in particular, cracks generated in the particles and the vicinity of the cracks were subjected to analysis with TEM-EDX.

[0501]

First, results of TEM-EDX plane analysis of titanium are shown in FIGS. 37A, 37B1, 37B2, 37C1, 37C2, 37D1, 37D2, 37E1, and 37E2 and FIGS. 38A, 38B1, 38B2, 38C1, 38C2, 38D1, 38D2, 38E1, and 38E2.

[0502]

FIGS. 37A, 37B1, 37B2, 37C1, 37C2, 37D1, 37D2, 37E1, and 37E2 show TEM-EDX analysis results of Sample 06 before heating. FIG. 37A is a cross-sectional TEM image showing the surfaces of the particles and the crack portions. FIG. 37B1 and FIG. 37B2 show a HAADF-STEM image and a Ti mapping image of a region including the surface of the particle that is denoted by a circle marked with "1" in FIG. 37A, respectively. Similarly, FIG. 37C1 and FIG. 37C2 show a HAADF-STEM image and a Ti mapping image of a region at a depth of approximately 20 nm from the surface in the crack portion that is denoted by a circle marked with "2" in FIG. 37A, respectively. FIG. 37D1 and FIG. 37D2 show a HAADF-STEM image and a Ti mapping image of a region at a depth of approximately 500 nm from the surface in the crack portion that is denoted by a circle marked with "3" in FIG. 37A, respectively. FIG. 37E1 and FIG. 37E2 show a HAADF-STEM image and a Ti mapping image of a region at a depth of approximately 1000 nm from the surface in the crack portion that is denoted by a circle marked with "4" in FIG. 37A, respectively. Note that in EDX element mapping images in FIGS. 37A, 37B1, 37B2, 37C1, 37C2, 37D1, 37D2, 37E1, and 37E2, FIGS. 38A, 38B1, 38B2, 38C1, 38C2, 38D1, 38D2, 38E1, and 38E2, FIGS. 39A, 39B1, 39B2, 39C1, 39C2, 39D1, 39D2, 39E1, and 39E2, and FIGS. 40A, 40B1, 40B2, 40C1, 40C2, 40D1, 40D2, 40E1, and 40E2, a region where the number of elements is less than or equal to a lower limit of the detection is indicated in white, and as the number of elements is increased, the white region becomes black.

[0503]

FIGS. 38A, 38B1, 38B2, 38C1, 38C2, 38D1, 38D2, 38E1, and 38E2 show TEM-EDX analysis results of Sample 07 after heating. FIG. 38A is a cross-sectional TEM image showing the surfaces of the particles and the crack portions. FIG. 38B1 and FIG. 38B2 show a

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HAADF-STEM image and a Ti mapping image of a region including the surface of the particle that is denoted by a circle marked with "1" in FIG. 38A, respectively. Similarly, FIG. 38C1 and FIG. 38C2 show a HAADF-STEM image and a Ti mapping image of a region at a depth of approximately 20 nm from the surface in the crack portion that is denoted by a circle marked with "2" in FIG. 38A, respectively. FIG. 38D1 and FIG. 38D2 show a HAADF-STEM image and a Ti mapping image of a region at a depth of approximately 500 nm from the surface in the crack portion that is denoted by a circle marked with "3" in FIG. 38A, respectively. FIG. 38E1 and FIG. 38E2 show a HAADF-STEM image and a Ti mapping image of a region at a depth of approximately 1000 nm from the surface in the crack portion that is denoted by a circle marked with "4" in FIG. 38A, respectively.

[0504]

As shown in FIGS. 37A, 37B1, 37B2, 37C1, 37C2, 37D1, 37D2, 37E1, and 37E2 and FIGS. 38A, 38B1, 38B2, 38C1, 38C2, 38D1, 38D2, 38E1, and 38E2, in Sample 06 before heating, segregation of titanium on the surfaces of the particles is observed; however, no segregation is observed in the crack portion. In contrast, in Sample 07 after heating, segregation of titanium is observed both on the surfaces of the particles and in the crack portion. That is, it is found that titanium is segregated at the surface of the crack portion by heating.

[0505]

Next, results of TEM-EDX plane analysis of magnesium are shown in FIGS. 39A, 39B1, 39B2, 39C1, 39C2, 39D1, 39D2, 39E1, and 39E2, and FIGS. 40A, 40B1, 40B2, 40C1, 40C2, 40D1, 40D2, 40E1, and 40E2.

[0506]

FIG. 39A is a cross-sectional TEM image of Sample 06, which is the same as FIG. 37A. FIGS. 39B1, 39C1, 39D1, and 39E1 are HAADF-STEM images, which are the same as FIGS. 37B1, 37C1, 37D1, and 37E1. FIG. 39B2 shows a Mg mapping image of a region which is the same as FIG. 39B1. FIG. 39C2 shows a Mg mapping image of a region which is the same as FIG. 39C1. FIG. 39D2 shows a Mg mapping image of a region which is the same as FIG. 39D1. FIG. 39E2 shows a Mg mapping image of a region which is the same as FIG. 39E1.

[0507]

FIG. 40A is a cross-sectional TEM image of Sample 07, which is the same as FIG. 38A. FIGS. 40B1, 40C1, 40D1, and 40E1 are HAADF-STEM images, which are the same as FIGS. 38B1, 38C1, 38D1, and 38E1. FIG. 40B2 shows a Mg mapping image of a region which is the same as FIG. 40B1. FIG. 40C2 shows a Mg mapping image of a region which is the same as FIG. 40C1. FIG. 40D2 shows a Mg mapping image of a region which is the same as FIG. 40D1. FIG. 40E2 shows a Mg mapping image of a region which is the same as FIG. 40E1.

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[0508]

As shown in FIGS. 39A, 39B1, 39B2, 39C1, 39C2, 39D1, 39D2, 39E1, and 39E2, and FIGS. 40A, 40B1, 40B2, 40C1, 40C2, 40D1, 40D2, 40E1, and 40E2, in Sample 06 before heating, segregation of magnesium is not observed on the surfaces of the particles or in the crack portion. In contrast, in Sample 07 after heating, segregation of magnesium is observed both on the surfaces of the particles and in the crack portion.

[0509]

Next, to quantify titanium and magnesium, EDX point analysis was performed on the regions indicated by circles marked with 1 to 6 in FIG. 37A and the regions indicated by circles marked with 1 to 6 in FIG. 38A. In each region, two points were measured.

[0510]

FIGS. 41A and 41B show results of EDX point analysis in an atomic ratio of titanium to cobalt. FIG. 41A shows results of Sample 06 before heating. Detection points 1 to 6 in FIG. 41A correspond to the regions indicated by circles marked with 1 to 6 in FIG. 37A. FIG. 41B shows results of Sample 07 after heating. Detection points 1 to 6 in FIG. 41B correspond to the regions indicated by circles marked with 1 to 6 in FIG. 38A.

[0511]

As shown in FIGS. 41A and 41B, in the crack portion of Sample 06, Ti/Co is less than or equal to 0.01 in each measurement point; in contrast, in the crack portion of Sample 07, the amount of titanium is increased in many points, and there are measurement points where Ti/Co is greater than or equal to 0.05. Furthermore, Ti/Co on the surfaces of the particles of Sample 07 is between 0.10 and 0.18.

[0512]

Next, FIGS. 42A and 42B show results of EDX point analysis in an atomic ratio of magnesium to cobalt. The detection points are the same as those in FIGS. 41A and 41B.

[0513]

As shown in FIGS. 42A and 42B, in Sample 06, Mg/Co is less than or equal to 0.03 both on the surfaces of the particles and in the crack portion; in contrast, in Sample 07, there are many points where the amount of magnesium is increased both on the surfaces of the particles and in the crack portion. Furthermore, Mg/Co on the surfaces of the particles is between 0.15 and 0.50, and that in the crack portion is between 0 and 0.22.

[0514]

Next, CR2032 coin-type secondary batteries were fabricated using the positive electrode active material of Sample 07 after heating. A positive electrode formed by applying slurry in which a positive electrode active material (LCO) of Sample 02, AB, and polyvinylidene fluoride

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(PVDF) were mixed at a weight ratio of 95:3:2 to a positive electrode current collector was used. As the positive electrode current collector, 20-μm-thick aluminum foil was used. The amount of positive electrode active material layer containing the positive electrode active material, AB, and PVDF was 7.6 mg/cm^2.

[0515]

A lithium metal was used for the counter electrode.

[0516]

An electrolyte solution formed in such a manner that 1 mol/L $LiPF_6$ was dissolved in a solution in which ethylene carbonate (EC) and diethyl carbonate (DEC) were mixed at a volume ratio of 3:7, and vinylene carbonate (VC) was added to the solution at a 2 wt% was used.

[0517]

[Initial characteristics, rate characteristics]

Initial characteristics and rate characteristics of the secondary battery using the positive electrode active material of Sample 07 formed in the above manner were measured.

[0518]

In the measurement of the initial characteristics, charging was performed at CCCV, 0.2 C, 4.6 V, and a cutoff current of 0.05 C, and discharging was performed at CC, 0.2 C, and a cutoff voltage of 3.0 V. Here, 1C was set to 160 mA/g, which was a current value per weight of the positive electrode active material. The measurement temperature was 25 °C. Table 2 shows measurement results of initial characteristics.

[0519]

[Table 2]

Initial charge capacity [mAh/g]	Initial discharge capacity [mAh/g]	Initial charge and discharge efficiency [%]
221.2	217.5	98.3

[0520]

The rate characteristics were measured after the initial characteristics were measured. The measurement was performed by changing a discharge rate in the following order: 0.2 C charge/0.2 C discharge; 0.2 C charge/0.5 C discharge; 0.2 C charge/1.0 C discharge; 0.2 C charge/2.0 C discharge; 0.2 C charge/3.0 C discharge; 0.2 C charge/4.0 C discharge; and 0.2 C charge/5.0 C discharge. Note that the conditions other than the discharge rate are the same as those of the measurement of the initial characteristics. The measurement temperature was 25 °C.

[0521]

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Table 3 shows the measurement results of the initial characteristics and the rate characteristics. In addition, FIG. 43 shows discharge curves of the rates.

[0522]

[Table 3]

Rate [C]	Discharge capacity [mAh/g]	Discharge capacity retention rate [%]
0.2	218.2	100.0
0.5	215.8	98.9
1.0	213.1	97.7
2.0	207.9	95.3
3.0	204.0	93.5
4.0	198.8	91.1
5.0	184.3	84.5

[0523]

[Temperature characteristics]

Next, a cell was fabricated under conditions similar to those of a cell for evaluating the rate characteristics except that the amount of positive electrode active material layer was 8.2 mg/cm^2, and the temperature characteristics were measured. Charging was performed at 25 °C, CCCV, 0.2 C, 4.6 V, and a cutoff current of 0.05 C. Discharging was performed at 25 °C, 0 °C, −10 °C, −20 °C, and 45 °C in this order, CC, 0.2 C, and a cutoff voltage of 3.0 V. FIG. 44 shows measurement results of temperature characteristics.

[0524]

[Cycle characteristics]

Next, a cell was fabricated under conditions similar to those of the cell for measuring the temperature characteristics, and the cycle characteristics were measured. In the measurement of the cycle characteristics, charging was performed at CCCV, 1.0 C, 4.55 V, and a cutoff current of 0.05 C, and discharging was performed at CC, 1.0 C, and a cutoff voltage of 3.0 V. The measurement temperature of the cycle characteristics was 45 °C and 100 cycles were measured. The discharge capacity retention rate after 100 cycles was 86 %. FIG. 45 is a graph showing the discharge capacity retention rate of the measured cycle characteristics.

[0525]

From the measurement results, the specific surface area of the positive electrode active material of Sample 07 was 0.13 m^2/g.

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[0526]

Furthermore, from the measurement results of particle size distribution of the positive electrode active material of Sample 07, the average particle diameter was 21.5 μm, 10 %D was 13.1 μm, 50 %D was 22.0 μm, and 90 %D was 34.4 μm.

[0527]

The tap density of the positive electrode active material of Sample 07 is 2.21 g/cm^3. The tap density was measured with MULTI TESTER MT-1000 (manufactured by SEISHIN ENTERPRISE Co., Ltd.).

[0528]

As described above, it is found that the positive electrode active material of Sample 07 which is one embodiment of the present invention shows excellent initial charge and discharge capacity, rate characteristics, and cycle characteristics. In particular, the initial charge and discharge capacity is high, which is 98 % or higher; thus, it is probable that a side reaction is inhibited. In addition, even at a high discharge rate of 2 C, an excellent capacity of 96.1 % is shown using 0.2 C as a reference.

[Example 3]

[0529]

In this example, a positive electrode active material including a region containing titanium and magnesium in a superficial portion was formed by changing the ratio of Li to the first transition metal of starting materials, and evaluation results of characteristics are shown.

[0530]

[Formation of positive electrode active material]

In this example, positive electrode active materials of Samples 11 to 17, Samples 21 to 28, and Samples 31 to 40 in which cobalt was used as the first transition metal were prepared. Formation methods and conditions of these samples are as follows.

[0531]

<<Samples 11 to 17>>

First, a source of lithium, a source of cobalt, a source of magnesium, and a source of fluorine, which are to be starting materials, were individually weighed. In this example, lithium carbonate, cobalt oxide, magnesium oxide, and lithium fluoride were used as the source of lithium, the source of cobalt, the source of magnesium, and the source of fluorine, respectively.

[0532]

At that time, the starting materials of Sample 11 were weighed so that the ratio of Li to Co was 1.00. The starting materials of Sample 12 were weighed so that the ratio of Li to Co was 1.03. The starting materials of Sample 13 were weighed so that the ratio of Li to Co was

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1.05. The starting materials of Sample 14 were weighed so that the ratio of Li to Co was 1.06. The starting materials of Sample 15 were weighed so that the ratio of Li to Co was 1.07. The starting materials of Sample 16 were weighed so that the ratio of Li to Co was 1.08. The starting materials of Sample 17 were weighed so that the ratio of Li to Co was 1.13.

[0533]

In addition, the starting materials of each of Samples 11 to 17 were weighed so that, when the number of atoms of cobalt contained in the starting materials was set to 1, the number of atoms of magnesium was 0.01 and the number of atoms of fluorine was 0.02.

[0534]

Next, the weighed starting materials were separately mixed with a ball mill for each sample.

[0535]

Then, the mixed starting materials were baked. The baking was performed at 1000 °C for 10 hours under the following conditions: the temperature rising rate was 200 °C/h; and the flow rate of dry air was 10 L/min.

[0536]

Through the above process, particles of a composite oxide containing lithium, cobalt, fluorine, and magnesium were synthesized.

[0537]

Next, TTIP was added to 2-propanol so that the amount of TTIP per weight of the positive electrode active material was 0.01 ml/g and then mixing was performed, so that a 2-propanol solution of tetra-i-propoxy titanium was formed.

[0538]

To the 2-propanol solution of TTIP, the particles of a composite oxide containing lithium, cobalt, fluorine, and magnesium were added and then mixing was performed.

[0539]

The above-described mixed solution was stirred with a magnetic stirrer for four hours, at 25 °C, and at a humidity of 90 %RH. Through the process, water in an atmosphere and TTIP caused hydrolysis and polycondensation reaction, and a layer containing titanium was formed on the surface of the lithium cobalt oxide particle containing magnesium and fluorine.

[0540]

The mixed solution which had been subjected to the above process was filtered to collect the residue. As a filter for filtration, Kiriyama filter paper (No. 4) was used.

[0541]

The collected residue was dried in a vacuum at 70 °C for one hour.

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[0542]

The dried particles were heated. The heating was performed in an oxygen atmosphere under the following conditions: the temperature was 800 °C (the temperature rising rate was 200 °C/h); and the retention time was two hours.

[0543]

The heated particles were cooled and subjected to crushing treatment. In the crushing treatment, the particles were made to pass through a sieve. The sieve has an aperture width of 53 μm.

[0544]

The particles which were subjected to crushing treatment were used as the positive electrode active materials of Samples 11 to 17.

[0545]

<<Samples 21 to 27>>

The starting materials of Samples 21 to 27 were the same as those of Samples 11 to 16. At that time, the starting materials of Sample 21 were weighed so that the ratio of Li to Co was 1.00. The starting materials of Sample 22 were weighed so that the ratio of Li to Co was 1.03. The starting materials of Sample 23 were weighed so that the ratio of Li to Co was 1.05. The starting materials of Sample 24 were weighed so that the ratio of Li to Co was 1.06. The starting materials of Sample 25 were weighed so that the ratio of Li to Co was 1.07. The starting materials of Sample 26 were weighed so that the ratio of Li to Co was 1.08. The starting materials of Sample 27 were weighed so that the ratio of Li to Co was 1.13.

[0546]

Samples 21 to 27 were formed in manners similar to those of Samples 11 to 17 except that the concentration of TTIP in the 2-propanol solution was adjusted so that the amount of TTIP per weight of the positive electrode active material was 0.02 ml/g.

[0547]

<<Sample 28>>

The ratio of Li to Co of the starting materials and the amount of TTIP of Sample 28 were the same as the ratio of Li to Co of the starting materials and the amount of TTIP of Sample 23. That is, in Sample 28, the starting materials were weighed so that the ratio of Li to Co was 1.05, and the amount of TTIP per weight of the positive electrode active material was 0.02 ml/g.

[0548]

Note that in Sample 28, after the starting materials were mixed, baking was performed at 950 °C.

[0549]

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Sample 28 was formed in a manner similar to that of Sample 23 except for the baking temperature.

[0550]

It is probable that Samples 11 to 17 and Samples 21 to 28 are each a positive electrode active material which contains lithium cobaltate inside and includes a region containing titanium and magnesium in a superficial portion.

[0551]

<<Samples 31 to 40>>

Samples 31 to 40 were formed as comparative examples, each of which did not include a region containing titanium.

[0552]

The starting materials of Sample 31 were weighed so that the ratio of Li to Co was 1.00. The starting materials of Sample 32 were weighed so that the ratio of Li to Co was 1.01. The starting materials of Sample 33 were weighed so that the ratio of Li to Co was 1.02. The starting materials of Sample 34 were weighed so that the ratio of Li to Co was 1.03. The starting materials of Sample 35 were weighed so that the ratio of Li to Co was 1.035. The starting materials of Sample 36 were weighed so that the ratio of Li to Co was 1.04. The starting materials of Sample 37 were weighed so that the ratio of Li to Co was 1.051. The starting materials of Sample 38 were weighed so that the ratio of Li to Co was 1.061. The starting materials of Sample 39 were weighed so that the ratio of Li to Co was 1.081. The starting materials of Sample 40 were weighed so that the ratio of Li to Co was 1.130.

[0553]

In addition, the starting materials of each of Samples 31 to 40 were weighed so that, when the number of atoms of cobalt contained in the starting materials was set to 1, the number of atoms of magnesium was 0.01 and the number of atoms of fluorine was 0.02.

[0554]

Next, the weighed starting materials were separately mixed with a ball mill for each sample.

[0555]

Then, the mixed starting materials were baked. The baking was performed at 1000 °C for 10 hours under the following conditions: the temperature rising rate was 200 °C/h; and the flow rate of dry air was 10 L/min.

[0556]

Through the above process, particles of a composite oxide containing lithium, cobalt, fluorine, and magnesium were synthesized.

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[0557]

The synthesized particles were cooled and then heated. The heating was performed in an oxygen atmosphere under the following conditions: the temperature was 800 °C (the temperature rising rate was 200 °C/h); and the retention time was two hours.

[0558]

The heated particles were cooled and subjected to crushing treatment. In the crushing treatment, the particles were made to pass through a sieve. The sieve has an aperture width of 53 μm.

[0559]

The particles which were subjected to crushing treatment were used as the positive electrode active materials of Samples 31 to 40.

[0560]

Table 4 shows the formation conditions of Samples 11 to 17, Samples 21 to 28, and Samples 31 to 40.

[0561]

[Table 4]

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	Li/Co	TTIP	Baking temperature
Sample 11	1.00	0.01 ml/g	1000 °C
Sample 12	1.03		
Sample 13	1.05		
Sample 14	1.06		
Sample 15	1.07		
Sample 16	1.08		
Sample 17	1.13		
Sample 21	1.00	0.02 ml/g	1000 °C
Sample 22	1.03		
Sample 23	1.05		
Sample 24	1.06		
Sample 25	1.07		
Sample 26	1.08		
Sample 27	1.13		
Sample 28	1.05	0.02 ml/g	950 °C
Sample 31	1.00	-	1000 °C
Sample 32	1.01		
Sample 33	1.02		
Sample 34	1.03		
Sample 35	1.035		
Sample 36	1.04		
Sample 37	1.051		
Sample 38	1.061		
Sample 39	1.081		
Sample 40	1.130		

[0562]

[XPS]

The positive electrode active materials of Samples 11 to 17, Samples 21 to 28, and Samples 31 to 40 were subjected to an XPS analysis. Table 5 shows results of the XPS analysis of Samples 11 to 17, Table 6 shows results of the XPS analysis of Samples 21 to 28, and Table 7 shows results of the XPS analysis of Samples 31 to 40. Tables 5 to 7 show a relative value of the concentration of each element under the condition where the concentration of cobalt is 1.

[0563]

[Table 5]

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		Relative value under condition where concentration of Co is 1										
	Li/Co	Li	Co	O	C	F	Mg	Ti	Si	Ca	Na	S
Sample 11	1.00	0.82	1.00	2.87	0.25	0.37	0.57	0.15	0.00	0.04	0.27	0.01
Sample 12	1.03	0.69	1.00	2.84	0.93	0.63	0.63	0.14	0.00	0.05	0.04	0.00
Sample 13	1.05	0.96	1.00	3.22	0.66	0.47	0.61	0.14	0.00	0.03	0.09	0.03
Sample 14	1.06	1.04	1.00	3.13	0.34	0.77	0.77	0.15	0.00	0.05	0.34	0.04
Sample 15	1.07	0.84	1.00	3.42	0.58	0.60	0.23	0.18	0.00	0.08	0.27	0.00
Sample 16	1.08	1.08	1.00	3.10	0.66	0.59	0.04	0.16	0.00	0.03	0.16	0.02
Sample 17	1.13	1.29	1.00	3.70	0.83	0.87	0.00	0.19	0.00	0.04	0.20	0.02

[0564]

[Table 6]

		Relative value under condition where concentration of Co is 1										
	Li/Co	Li	Co	O	C	F	Mg	Ti	Si	Ca	Na	S
Sample 21	1.00	1.08	1.00	3.23	0.47	0.45	0.49	0.20	0.00	0.06	0.35	0.01
Sample 22	1.03	0.73	1.00	3.05	1.06	0.70	0.59	0.17	0.00	0.03	0.09	0.00
Sample 23	1.05	1.19	1.00	3.40	0.73	0.48	0.58	0.23	0.00	0.05	0.10	0.04
Sample 24	1.06	1.10	1.00	3.44	0.33	0.92	0.91	0.25	0.00	0.05	0.30	0.04
Sample 25	1.07	1.05	1.00	4.26	0.74	0.20	0.25	0.29	0.00	0.07	0.30	0.02
Sample 26	1.08	1.12	1.00	3.32	0.74	0.52	0.14	0.21	0.00	0.05	0.15	0.00
Sample 27	1.13	1.49	1.00	3.80	0.60	0.41	0.00	0.12	0.00	0.00	0.16	0.02
Sample 28	1.05	0.99	1.00	3.11	0.72	0.86	0.56	0.18	0.00	0.05	0.12	0.02

[0565]

[Table 7]

		Relative value under condition where concentration of Co is 1							
	Li/Co	Li	Co	O	C	F	Mg	Ca	Na
Sample 31	1.00	0.51	1.00	2.45	0.69	0.08	0.27	0.03	0.08
Sample 32	1.01	0.67	1.00	2.65	0.77	0.08	0.28	0.03	0.08
Sample 33	1.02	0.53	1.00	2.51	0.66	0.09	0.27	0.02	0.06
Sample 34	1.03	0.79	1.00	2.93	0.92	0.09	0.35	0.04	0.14
Sample 35	1.04	0.65	1.00	2.33	0.48	0.11	0.32	0.03	0.11
Sample 36	1.04	0.69	1.00	2.73	0.56	0.11	0.38	0.05	0.16
Sample 37	1.05	0.67	1.00	3.04	0.64	0.09	0.35	0.04	0.21
Sample 38	1.06	0.83	1.00	2.65	1.03	0.29	0.10	0.05	0.11
Sample 39	1.08	0.80	1.00	2.79	1.04	0.26	0.03	0.08	0.10
Sample 40	1.13	0.77	1.00	2.72	0.22	0.99	0.00	0.01	0.26

[0566]

FIGS. 46A and 46B are graphs in which the relative valueof magnesium and the relative valueof titanium are extracted from the analysis results of Tables 5 to 7. FIG. 46A is a graph showing the ratio of Li to Co and the relative valueof magnesium. FIG. 46B is a graph showing

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the ratio of Li to Co and the relative valueof titanium.

[0567]

From the analysis results of Samples 31 to 40 in FIG. 46A, it is found that, in the case where a coating layer containing titanium is not included, the concentration of magnesium is high in samples where the ratio of Li to Co is greater than or equal to 1.00 and less than or equal to 1.05. This is probably because magnesium contained in the starting materials is segregated in a range where the element concentration can be detected by XPS by heating. In contrast, in samples where the ratio of Li to Co is greater than or equal to 1.06, the concentration of magnesium is low; thus, it is probable that the segregation of magnesium does not easily occur when the amount of lithium is too large.

[0568]

From the analysis results of Samples 11 to 16 and Samples 21 to 26 in FIG. 46A, it is found that the concentration of magnesium in a range where the element concentration can be detected by XPS is higher in the case where a region containing titanium is included in a superficial portion than in the case where the region containing titanium is not included.

[0569]

Moreover, in the case where the ratio of Li to Co is 1.06, in samples where the region containing titanium is not included, the concentration of magnesium in a range where the element concentration can be detected by XPS is low; in contrast, in samples where the region containing titanium is included, the concentration of magnesium in a range where the element concentration can be detected by XPS is high. That is, when the region containing titanium is formed in the superficial portion, magnesium is sufficiently segregated even in the case where the ratio of Li to Co is high.

[0570]

Note that even if the region containing titanium is included, the concentration of magnesium is lower in the case where the ratio of Li to Co is 1.07 than in the case where the ratio of Li to Co is 1.06. Furthermore, it is probable that, in the case where the ratio of Li to Co is greater than or equal to 1.08, the segregation of magnesium does not easily occur even if the region containing titanium is included.

[0571]

[Evaluation of cycle characteristics]

<<Energy density retention rate>>

Next, cycle characteristics were evaluated in a manner similar to that of Example 1 using positive electrode active materials of Samples 11 to 14, Sample 16, Samples 21 to 24, and Sample 26.

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[0572]

The shape of the secondary battery, the materials and the mixture ratios of the positive electrode active material, the conductive additive, and the binder in the positive electrode, the counter electrode, the electrolyte solution, the exterior body, the conditions of the cycle characteristics test, and the like are the same as those in Example 1.

[0573]

FIG. 47A is a graph showing the energy density retention rates and the number of charge and discharge cycles at the time of charging at 4.6 V of secondary batteries using the positive electrode active materials of Samples 11 to 14 and Sample 16 which were formed so that the amount of TTIP per weight of the positive electrode active material was 0.01 ml/g. FIG. 47B is a graph showing the energy density retention rates and the number of charge and discharge cycles at the time of charging at 4.6 V of secondary batteries using the positive electrode active materials of Samples 21 to 24 and Sample 26 which were formed so that the amount of TTIP per weight of the positive electrode active material was 0.02 ml/g.

[0574]

As shown in FIG. 47A, in the case where TTIP is 0.01 ml/g, Samples 11 to 14, that is, the positive electrode active materials in which the ratio of Li to Co is greater than or equal to 1.00 and less than or equal to 1.06 have excellent cycle characteristics. In particular, Samples 11 and 12, that is, the positive electrode active materials in which the ratio of Li to Co is greater than or equal to 1.00 and less than or equal to 1.03 have extremely excellent cycle characteristics. In contrast, in Sample 16 in which the ratio of Li to Co is 1.08, the energy density retention rate decreases at a relatively early stage.

[0575]

As shown in FIG. 47B, in the case where TTIP is 0.02 ml/g, Samples 21 to 24, that is, the positive electrode active materials in which the ratio of Li to Co is greater than or equal to 1.00 and less than or equal to 1.06 have excellent cycle characteristics. In particular, Samples 23 and 24, that is, the positive electrode active materials in which the ratio of Li to Co is greater than or equal to 1.05 and less than or equal to 1.06 have extremely excellent cycle characteristics.

[0576]

FIG. 48 is a graph showing comparison between Sample 11 having the most excellent cycle characteristics in Samples 11 to 15 and Sample 23 having the most excellent cycle characteristics in Samples 21 to 25.

[0577]

As shown in FIG. 48, both Sample 11 and Sample 23 have excellent cycle

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characteristics; however, Sample 23 in which TTIP is 0.02 ml/g has more excellent cycle characteristics.

[0578]

<<Discharge capacity retention rate>>

Next, FIG. 49 shows evaluation results of a discharge capacity retention rate, which is one of the cycle characteristics of each of Samples 21 to 26 and Sample 28.

[0579]

The shape of the secondary battery, the material and the mixture ratio of the positive electrode active material, the conductive additive, and the binder in the positive electrode, the counter electrode, the electrolyte solution, the exterior body, the conditions of the cycle characteristics test, and the like of Samples 21 to 26 are the same as those in Example 1.

[0580]

The secondary battery using Sample 28 was formed in a manner similar to those of the secondary batteries using Samples 21 to 26 except that PVDF was used as a binder and the positive electrode active material (LCO), AB, and PVDF were mixed such that the weight ratio of LCO to AB and PVDF was 95:3:2, and evaluated.

[0581]

As shown in FIG. 49, Samples 21 to 24 and Sample 28 have excellent cycle characteristics. In particular, Sample 28 has extremely excellent cycle characteristics. In Sample 28, the discharge capacity retention rate after 50 cycles was higher than or equal to 85 %.

[0582]

In contrast, in Sample 25 and Sample 26 in which the ratios of Li to Co are 1.07 and 1.08, respectively, the discharge capacity retention rates decrease at a relatively early stage.

[0583]

From the above results, it is found that in the case where TTIP per weight of the positive electrode active material is 0.02 ml/g, the ratio of Li to Co preferably has a range of greater than or equal to 1.00 and less than 1.07. Moreover, it is found that a sample in which the ratio of Li to Co has a range of greater than or equal to 1.05 and less than or equal to 1.06 has extremely excellent cycle characteristics.

[0584]

FIGS. 50A to 50C show charge and discharge curves of the secondary batteries using Sample 28, which has extremely excellent cycle characteristics in FIG. 49, Sample 24, and Sample 25, in which the degradation occurs at a relatively early stage.

[0585]

FIG. 50A, FIG. 50B, and FIG. 50C show charge and discharge curves of the secondary

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batteries using Sample 28, Sample 24, and Sample 25, respectively. Each of the figures shows overlap of results of 50 cycles of charge and discharge. As indicated by an arrow in each figure, the charge and discharge capacity decreases from the first cycle to the fiftieth cycle.

[0586]

As shown in FIGS. 50A and 50B, Sample 28 and Sample 24, which are positive electrode active materials of one embodiment of the present invention, have high charge and discharge capacity and excellent charge and discharge characteristics. In addition, it is found that a decrease in charge and discharge capacity of each of Sample 28 and Sample 24 in FIGS. 50A and 50B is significantly suppressed as compared with Sample 25 in FIG. 50C.

[Example 4]

[0587]

In this example, SEM observation results and SEM-EDX analysis results of the positive electrode active material of Sample 24 formed in Example 2 are described.

[0588]

Sample 24 was formed so that Li/Co was 1.06 and TTIP per weight of the positive electrode active material was 0.02 ml/g. FIG. 51A shows a SEM image of Sample 24. FIGS. 51B and 51C each show an enlarged image of a part in FIG. 51A.

[0589]

As shown in FIGS. 51A to 51C, there are a large number of projected regions in a superficial portion of the positive electrode active material.

[0590]

Next, FIGS. 52A-1, 52A-2, 52B-1, 52B-2, 52C-1, and 52C-2 show analysis results of the positive electrode active material of Sample 24 using SEM-EDX. FIG. 52A-1 shows a SEM image of a superficial portion of the positive electrode active material, FIG. 52A-2 shows a mapping image of titanium, FIG. 52B-1 shows a mapping image of magnesium, FIG. 52B-2 shows a mapping image of oxygen, FIG. 52C-1 shows a mapping image of aluminum, and FIG. 52C-2 shows a mapping image of cobalt. Note that in EDX element mapping images in FIGS. 52A-2, 52B-1, 52B-2, 52C-1, and 52C-2, a region where the number of elements is less than or equal to a lower limit of the detection is indicated in black, and as the number of elements is increased, the black region becomes white.

[0591]

The same regions in FIGS. 52A-1, 52A-2, and 52B-1 are surrounded by dotted lines. When the regions surrounded by dotted lines are compared with each other, it is found that in the projected regions in the superficial portion of the positive electrode active material, titanium and magnesium are distributed.

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[0592]

Thus, it is found that Sample 24 is a positive electrode active material including the projected fourth region 104 containing titanium and magnesium over the third region 103.

[0593]

As shown in Example 2, Sample 24 is one of the samples which show extremely excellent cycle characteristics. Thus, it is found that, even if the fourth region is provided in the superficial portion or when the fourth region is provided, the positive electrode active material with excellent cycle characteristics can be obtained.

[0594]

From the above results of Examples 1 to 3, it is found that when the region containing titanium is formed in the superficial portion, the positive electrode active material with excellent cycle characteristics can be obtained. In addition, it is found that, when the ratio of Li to Co is increased to increase the particle diameter of the positive electrode active material, the cycle characteristics might be degraded; however, the region containing titanium is formed in the superficial portion, whereby the range of the ratio of Li to Co in which excellent cycle characteristics is obtained can be widened. Furthermore, it is found that even when the fourth region containing titanium and magnesium is provided in the superficial portion of the positive electrode active material, excellent cycle characteristics is obtained.

[Example 5]

[0595]

In this example, an example of a method for producing a positive electrode active material coated with graphene oxide is shown, and observation results of the positive electrode active material produced by the method with an electron microscope are described.

[0596]

As shown in a process flow chart in FIG. 53, a process for forming a coating film on a positive electrode active material includes the steps of: weighing graphene oxide (S11); mixing and stirring the graphene oxide and pure water (S12); controlling pH (S13); adding an active material (S14); completing a suspension (S15); spraying the suspension using a spray dry apparatus (S16); and collecting particles in a container (S17).

[0597]

Note that in (S12), pure water is used as a dispersion medium; however, a dispersion medium is not particularly limited and ethanol or the like may be used. In addition, in (S14), the active material is a positive electrode active material.

[0598]

FIG. 54 is a schematic view of a spray dry apparatus 280. The spray dry apparatus 280

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includes a chamber 281 and a nozzle 282. A suspension 284 is supplied to the nozzle 282 through a tube 283. The suspension 284 is supplied from the nozzle 282 to the chamber 281 in the form of mist and dried in the chamber 281. The nozzle 282 may be heated with a heater 285. Here, a region of the chamber 281 which is close to the nozzle 282, for example, a region surrounded by dashed-two dotted line in FIG. 54, is also heated with the heater 285.

[0599]

In the case of using a suspension containing a positive electrode active material and graphene oxide as the suspension 284, powder of the positive electrode active material coated with the graphene oxide is collected in a collection container 286 through the chamber 281.

[0600]

The air in the chamber 281 may be suctioned by an aspirator or the like through a path indicated by an arrow 288.

[0601]

An example of conditions for forming the coating film is shown below.

[0602]

First, a suspension was formed by dispersing graphene oxide into a solvent.

[0603]

Although in pure water, graphene oxide is highly dispersible, pure water might react with an active material added later, so that Li might be dissolved or an active material might be damaged to change the surface structure. Thus, the graphene oxide was dispersed into a solution such that the ratio between ethanol and pure water was 4:6.

[0604]

Stirring to disperse the graphene oxide into a solution was performed under the following conditions: a stirrer and an ultrasonic wave generator were used; a rotation rate was 750 rpm; and irradiation time with ultrasonic waves was 2 minutes.

[0605]

Then, a LiOH aqueous solution was dropped to adjust pH to be pH7 (25 °C).

[0606]

The positive electrode active materials (in this example, lithium cobalt oxide particles produced by NIPPON CHEMICAL INDUSTRIAL CO., LTD. (product name: C-20F)) were added, and stirring was performed using a stirrer and an ultrasonic wave generator under the following conditions: a rotation rate was 750 rpm; and irradiation time with ultrasonic waves was 1 minute. Through the above process, the suspension was prepared. The above lithium cobalt oxide particles produced by NIPPON CHEMICAL INDUSTRIAL CO., LTD. (product name: C-20F) contain at least fluorine, magnesium, calcium, sodium, silicon, sulfur, and

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phosphorus, and each have a diameter of approximately 20 μm.

[0607]

Next, the suspension was sprayed uniformly with a spray nozzle (having a nozzle diameter of 20 μm) of the spray dry apparatus to obtain powder. The inlet temperature was 160 °C and the outlet temperature was 40 °C as the hot-air temperature of the spray dry apparatus, and the N_2 gas flow rate was 10 L/min.

[0608]

FIG. 55 shows a cross-sectional TEM image of the obtained powder. In addition, FIG. 56 shows a SEM image of the obtained powder. When a positive electrode active material which was the same as the sprayed positive electrode active material (C-20F, produced by NIPPON CHEMICAL INDUSTRIAL CO., LTD.) was mixed with the graphene oxide with a planetary centrifugal mixer as a comparative example, coating was insufficient. FIG. 57 shows a SEM image of the comparative example.

[0609]

It is found that, as compared with FIG. 57, the coating film is uniformly formed on the surface of the powder in FIG. 56.

[0610]

FIGS. 58A and 58B illustrate a cross-sectional structure example of an active material layer 200 which is coated with graphene oxide with a spray dry apparatus and includes a graphene compound as a conductive additive.

[0611]

FIG. 58A is a longitudinal sectional view of the active material layer 200. The active material layer 200 includes positive electrode active material particles 100 coated with graphene oxide, a graphene compound 201 as a conductive additive, and a binder (not illustrated). Here, graphene or multilayer graphene may be used as the graphene compound 201, for example. The graphene compound 201 preferably has a sheet-like shape. The graphene compound 201 may have a sheet-like shape formed of a plurality of sheets of multilayer graphene and/or a plurality of sheets of graphene that partly overlap with each other.

[0612]

In the longitudinal section of the active material layer 200, as illustrated in FIG. 58B, the positive electrode active material 100 coated with a coating film 105 formed of graphene oxide is in contact with the graphene compound 201. A plurality of graphene compounds 201 are formed in such a way as to be partly in contact with the positive electrode active material 100 coated with the coating film 105 and adhere to the coating film 105 of the adjacent positive electrode active material 100, so that the graphene compounds 201 are in contact with each of

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the positive electrode active material 100.

[0613]

The graphene compound 201 and the coating film 105 are formed using carbon-based materials; thus, an excellent conductive path can be formed.

[0614]

The coating film 105 is effective in protecting the crystal structure of the positive electrode active material 100 so as not to be in contact with the electrolyte solution and in forming the excellent conductive path.

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[0615]

11a: positive electrode, 11b: negative electrode, 12a: lead, 12b: lead, 14: separator, 15a: bonding portion, 15b: bonding portion, 17: fixing member, 50: secondary battery, 51: exterior body, 61: folded portion, 62: seal portion, 63: seal portion, 71: crest line, 72: trough line, 73: space, 100: positive electrode active material, 101: region, 101p: crystal plane, 102: region, 102p: crystal plane, 103: region, 103p: crystal plane, 104: region, 105: coating film, 106: crack portion, 110: particle, 111: region, 112: layer, 114: cobalt oxide layer, 120: particle, 121: region, 122: layer, 124: cobalt oxide layer, 125: layer, 200: active material layer, 201: graphene compound, 214: separator, 280: spray dry apparatus, 281: chamber, 282: nozzle, 283: tube, 284: suspension, 285: heater, 286: collection container, 288: arrow, 300: secondary battery, 301: positive electrode can, 302: negative electrode can, 303: gasket, 304: positive electrode, 305: positive electrode current collector, 306: positive electrode active material layer, 307: negative electrode, 308: negative electrode current collector, 309: negative electrode active material layer, 310: separator, 500: secondary battery, 501: positive electrode current collector, 502: positive electrode active material layer, 503: positive electrode, 504: negative electrode current collector, 505: negative electrode active material layer, 506: negative electrode, 507: separator, 508: electrolyte solution, 509: exterior body, 510: positive electrode lead electrode, 511: negative electrode lead electrode, 600: secondary battery, 601: positive electrode cap, 602: battery can, 603: positive electrode terminal, 604: positive electrode, 605: separator, 606: negative electrode, 607: negative electrode terminal, 608: insulating plate, 609: insulating plate, 611: PTC element, 612: safety valve mechanism, 613: conductive plate, 614: conductive plate, 615: module, 616: wiring, 617: temperature control device, 900: circuit board, 910: label, 911: terminal, 912: circuit, 913: secondary battery, 914: antenna, 915: antenna, 916: layer, 917: layer, 918: antenna, 920: display device, 921: sensor, 922: terminal, 930: housing, 930a: housing, 930b: housing, 931: negative electrode, 932: positive electrode, 933: separator, 950: wound body, 951: terminal, 952: terminal,

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980: secondary battery, 981: film, 982: film, 993: wound body, 994: negative electrode, 995: positive electrode, 996: separator, 997: lead electrode, 998: lead electrode, 7100: portable display device, 7101: housing, 7102: display portion, 7103: operation button, 7104: secondary battery, 7200: portable information terminal, 7201: housing, 7202: display portion, 7203: band, 7204: buckle, 7205: operation button, 7206: input output terminal, 7207: icon, 7300: display device, 7304: display portion, 7400: mobile phone, 7401: housing, 7402: display portion, 7403: operation button, 7404: external connection port, 7405: speaker, 7406: microphone, 7407: secondary battery, 7408: lead electrode, 7409: current collector, 7500: vaporizer, 7501: atomizer, 7502: cartridge, 7504: secondary battery, 8000: display device, 8001: housing, 8002: display portion, 8003: speaker portion, 8004: secondary battery, 8021: charging apparatus, 8022: cable, 8024: secondary battery, 8100: lighting device, 8101: housing, 8102: light source, 8103: secondary battery, 8104: ceiling, 8105: wall, 8106: floor, 8107: window, 8200: indoor unit, 8201: housing, 8202: air outlet, 8203: secondary battery, 8204: outdoor unit, 8300: electric refrigerator-freezer, 8301: housing, 8302: refrigerator door, 8303: freezer door, 8304: secondary battery, 8400: automobile, 8401: headlight, 8406: electric motor, 8500: automobile, 8600: motor scooter, 8601: side mirror, 8602: secondary battery, 8603: indicator, 8604: storage unit under seat, 9600: tablet terminal, 9625: switch, 9626: switch, 9627: power switch, 9628: operation switch, 9629: fastener, 9630: housing, 9630a: housing, 9630b: housing, 9631: display portion, 9631a: display portion, 9631b: display portion, 9632a: region, 9632b: region, 9633: solar cell, 9634: charge and discharge control circuit, 9635: power storage unit, 9636: DCDC converter, 9637: converter, 9638: operation key, 9639: button, 9640: movable portion.

This application is based on Japanese Patent Application Serial No. 2016-133997 filed with Japan Patent Office on July 6, 2016, Japanese Patent Application Serial No. 2016-133143 filed with Japan Patent Office on July 5, 2016, Japanese Patent Application Serial No. 2017-002831 filed with Japan Patent Office on January 11, 2017, Japanese Patent Application Serial No. 2017-030693 filed with Japan Patent Office on February 22, 2017, Japanese Patent Application Serial No. 2017-084321 filed with Japan Patent Office on April 21, 2017,and Japanese Patent Application Serial No. 2017-119272 filed with Japan Patent Office on June 19, 2017 the entire contents of which are hereby incorporated by reference.

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CLAIMS

1. A positive electrode active material comprising:

a first region positioned inside the positive electrode active material; and

a second region and a third region positioned in a superficial portion of the positive electrode active material,

wherein the third region is positioned closer to a surface of the positive electrode active material than the second region is,

wherein the first region comprises a first compound comprising an oxide of lithium and a first transition metal,

wherein a type of a crystal structure of the first compound is a layered rock-salt crystal structure,

wherein the second region comprises a second compound comprising an oxide of a second transition metal,

wherein a type of a crystal structure of the second compound is a rock-salt crystal structure,

wherein the second compound is a non-stoichiometric compound,

wherein the third region comprises a third compound comprising representative elements, and

wherein a type of a crystal structure of the third compound is the rock-salt crystal structure.

2. The positive electrode active material according to claim 1,

wherein a degree of a mismatch between the crystal structure of the first compound and the crystal structure of the second compound is less than or equal to 0.12, and

wherein a degree of a mismatch between the crystal structure of the second compound and the crystal structure of the third compound is less than or equal to 0.12.

3. The positive electrode active material according to claim 1,

wherein a degree of a mismatch between a (1−1−4) plane of the crystal structure of the first compound or a plane orthogonal to the (1−1−4) plane and a {100} plane of the crystal structure of the second compound is less than or equal to 0.12, and

wherein a degree of a mismatch between the {100} plane of the crystal structure of the second compound and a {100} plane of the crystal structure of the third compound is less than or equal to 0.12.

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4. The positive electrode active material according to claim 1,

wherein the first compound is a polycrystal.

5. The positive electrode active material according to claim 4,

wherein an average crystallite size of the oxide of lithium and the first compound is greater than or equal to 280 nm and less than or equal to 630 nm.

6. The positive electrode active material according to claim 1,

wherein the third compound essentially consists of the representative elements.

7. The positive electrode active material according to claim 1,

wherein the third compound comprises at least one of magnesium oxide, calcium oxide, beryllium oxide, lithium fluoride, and sodium fluoride.

8. A secondary battery comprising:

a positive electrode comprising the positive electrode active material according to claim 1; and

a negative electrode.

9. A positive electrode active material comprising:

a first region positioned inside the positive electrode active material; and

a second region and a third region positioned in a superficial portion of the positive electrode active material,

wherein the third region is positioned closer to a surface of the positive electrode active material than the second region is,

wherein the first region comprises lithium cobaltate,

wherein the second region comprises lithium titanate, and

wherein the third region comprises magnesium oxide.

10. The positive electrode active material according to claim 9,

wherein a crystal orientation of a part of the lithium cobaltate of the first region and a crystal orientation of a part of the lithium titanate of the second region are substantially aligned with each other.

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11. The positive electrode active material according to claim 9,

wherein a crystal orientation of a part of the lithium titanate of the second region and a crystal orientation of a part of the magnesium oxide of the third region are substantially aligned with each other.

12. The positive electrode active material according to claim 9,

wherein a degree of a mismatch between a crystal structure of the lithium cobaltate of the first region and a crystal structure of the lithium titanate of the second region is less than or equal to 0.12, and

wherein a degree of a mismatch between the crystal structure of the lithium titanate of the second region and a crystal structure of the magnesium oxide of the third region is less than or equal to 0.12.

13. A positive electrode active material particle comprising lithium, titanium, cobalt, magnesium, oxygen, and fluorine,

wherein when a concentration of cobalt in a superficial portion of the positive electrode active material particle measured by X-ray photoelectron spectroscopy is 1, a concentration of titanium is greater than or equal to 0.05 and less than or equal to 0.4, a concentration of magnesium is greater than or equal to 0.4 and less than or equal to 1.5, and a concentration of fluorine is greater than or equal to 0.05 and less than or equal to 1.5.

14. The positive electrode active material particle according to claim 13, further comprising:

a first region positioned inside the positive electrode active material particle; and

a second region and a third region positioned in the superficial portion of the positive electrode active material particle,

wherein the third region is positioned closer to a surface of the positive electrode active material particle than the second region is,

wherein the first region comprises a first compound comprising lithium and cobalt,

wherein the second region comprises a second compound comprising titanium,

wherein the second compound is a non-stoichiometric compound, and

wherein the third region comprises a third compound comprising magnesium and fluorine.

15. The positive electrode active material particle according to claim 14,

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wherein a type of a crystal structure of the first compound is a layered rock-salt crystal structure,

wherein a type of a crystal structure of the second compound is a rock-salt crystal structure, and

wherein a type of a crystal structure of the third compound is the rock-salt crystal structure.

16. A secondary battery comprising:

a positive electrode comprising the positive electrode active material particle according to claim 13; and

a negative electrode.

17. A method for forming a positive electrode active material comprising the steps of:

mixing a source of lithium, a source of cobalt, a source of magnesium, and a source of fluorine;

heating the mixture of the source of lithium, the source of cobalt, the source of magnesium, and the source of fluorine at 800 °C or higher and 1100 °C or lower for 2 hours or longer and 20 hours or shorter to obtain particles comprising lithium, cobalt, magnesium, oxygen, and fluorine;

dissolving an alkoxide of a second transition metal into alcohol;

mixing the particles comprising lithium, cobalt, magnesium, oxygen, and fluorine into an alcohol solution of the alkoxide of the second transition metal to form a mixed solution,

stirring the mixed solution in an atmosphere comprising water vapor;

collecting precipitate from the mixed solution after stirring; and

heating the collected precipitate at 500°C or higher and 1200 °C or lower in an atmosphere comprising oxygen for a retention time of 50 hours or shorter.

18. The method for forming a positive electrode active material according to claim 17,

wherein a ratio of a number of atoms of lithium in the source of lithium to a number of atoms of cobalt in the source of cobalt is greater than or equal to 1.00 and less than 1.07.

19. The method for forming a positive electrode active material according to claim 17,

wherein a ratio between a number of atoms of magnesium in the source of magnesium and a number of atoms of fluorine in the source of fluorine is Mg:F = 1:x ($1.5 \leq x \leq 4$).

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20. The method for forming a positive electrode active material according to claim 17,

wherein a number of atoms of magnesium in the source of magnesium is greater than or equal to 0.5 atomic% and less than or equal to 1.5 atomic% of a number of atoms of cobalt in the source of cobalt.

21. The method for forming a positive electrode active material according to claim 17,

wherein the positive electrode active material and a graphene compound are mixed, and are subjected to treatment by a spray dry method.

22. The method for forming a positive electrode active material according to claim 21,

wherein the graphene compound is a conductive additive.

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ABSTRACT

A positive electrode active material which can improve cycle characteristics of a secondary battery is provided. Two kinds of regions are provided in a superficial portion of a positive electrode active material such as lithium cobaltate which has a layered rock-salt crystal structure. The inner region is a non-stoichiometric compound containing a transition metal such as titanium, and the outer region is a compound of representative elements such as magnesium oxide. The two kinds of regions each have a rock-salt crystal structure. The inner layered rock-salt crystal structure and the two kinds of regions in the superficial portion are topotaxy; thus, a change of the crystal structure of the positive electrode active material generated by charging and discharging can be effectively suppressed. In addition, since the outer coating layer in contact with an electrolyte solution is the compound of representative elements which is chemically stable, the secondary battery having excellent cycle characteristics can be obtained.

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FIG. 1A

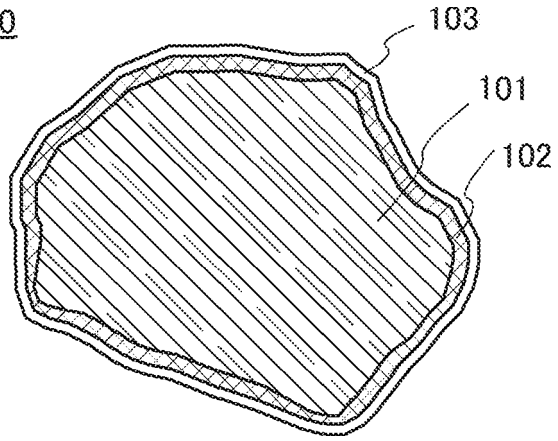


FIG. 1B

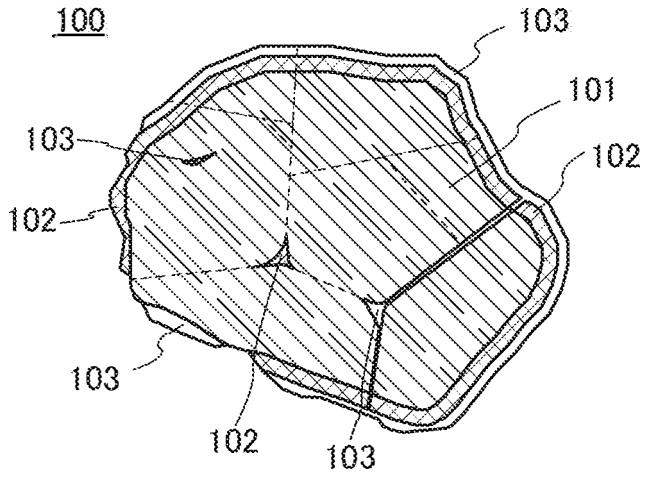


FIG. 1C

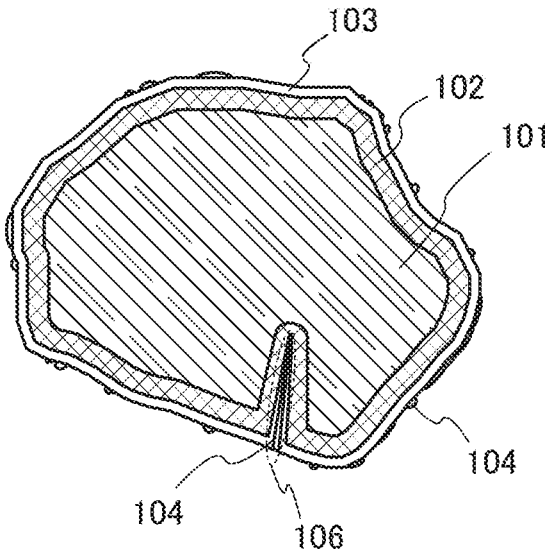


FIG. 2A

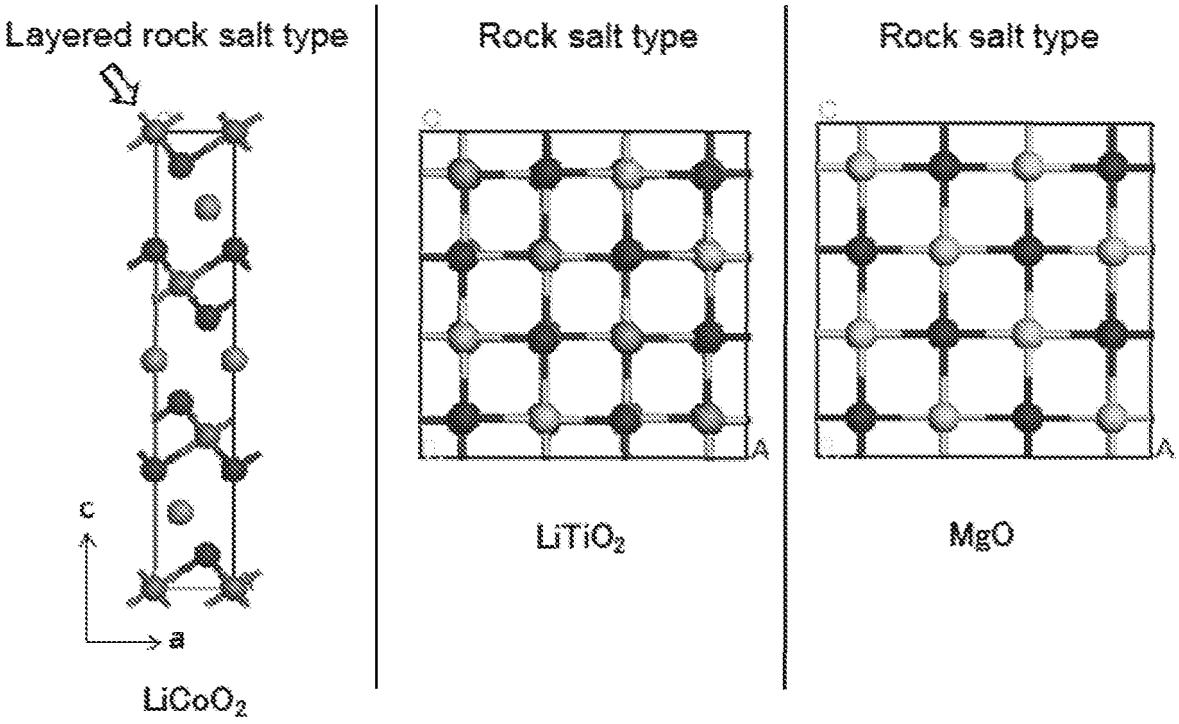

Layered rock salt type
Rock salt type
Rock salt type
c
a
c
a
c
a
$LiCoO_2$
$LiTiO_2$
MgO

FIG. 2B

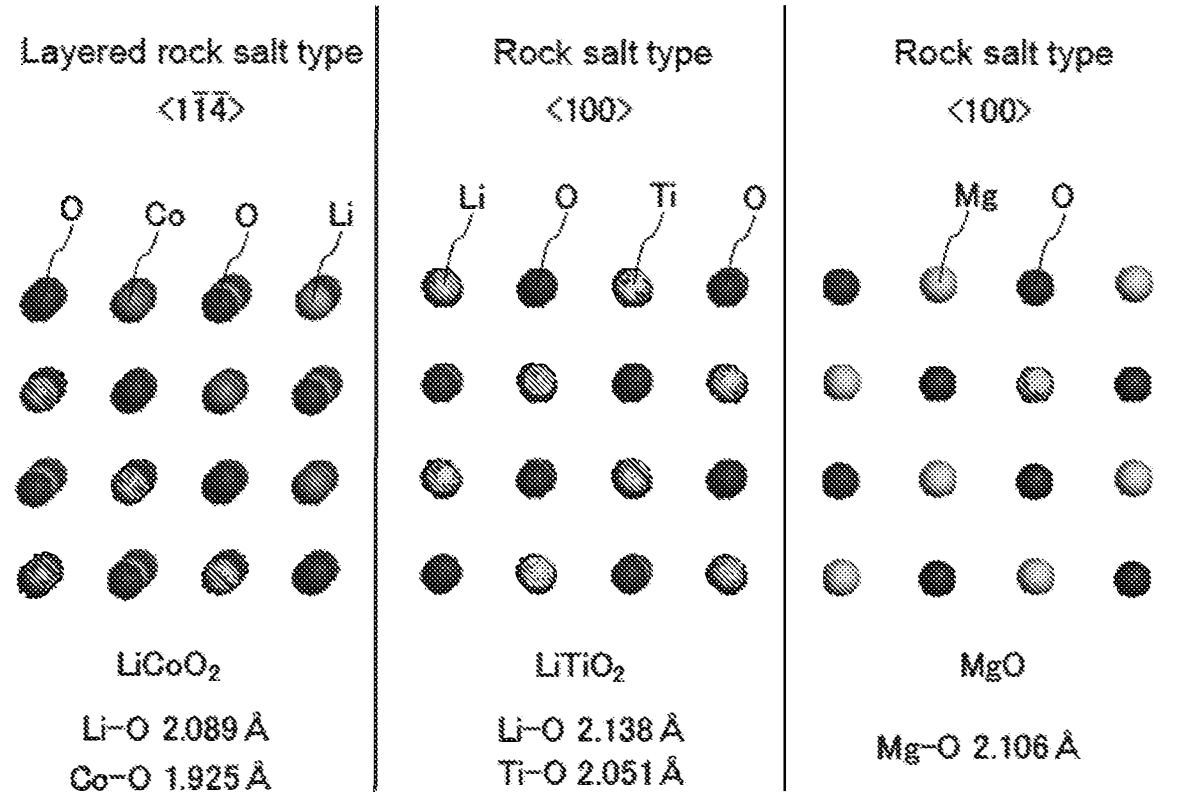

Layered rock salt type
<1$\bar{1}$4>
Rock salt type
<100>
Rock salt type
<100>
O
Co
O
Li
Li
O
Ti
O
Mg
O
$LiCoO_2$
Li–O 2.089 Å
Co–O 1.925 Å
$LiTiO_2$
Li–O 2.138 Å
Ti–O 2.051 Å
MgO
Mg–O 2.106 Å

FIG. 3

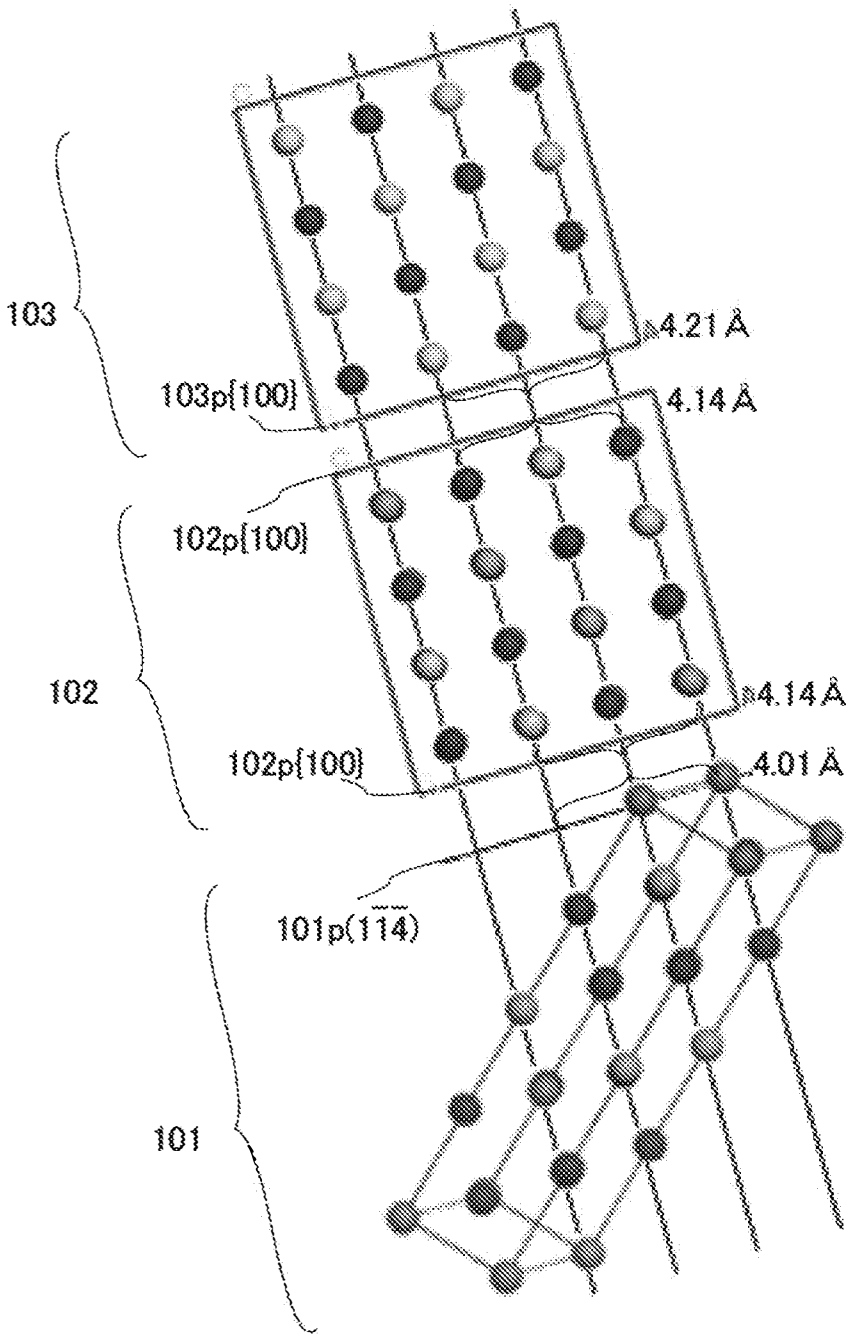
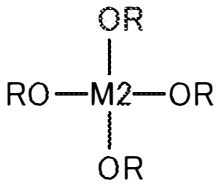
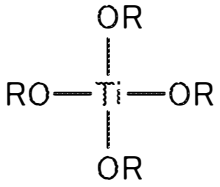

103
103p[100]
102p[100]
102
102p[100]
101p(1$\bar{1}\bar{1}$4)
101
4.21 Å
4.14 Å
4.14 Å
4.01 Å

FIG. 4A-1



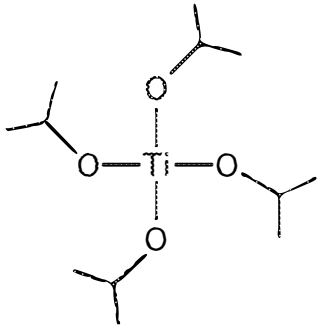
$M2(OR)_4$

FIG. 4A-2



$Ti(OR)_4$

FIG. 4A-3



TTIP

FIG. 4B

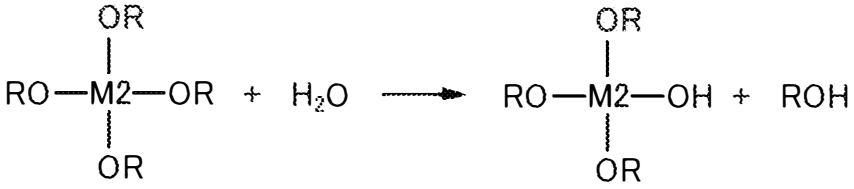


FIG. 4C

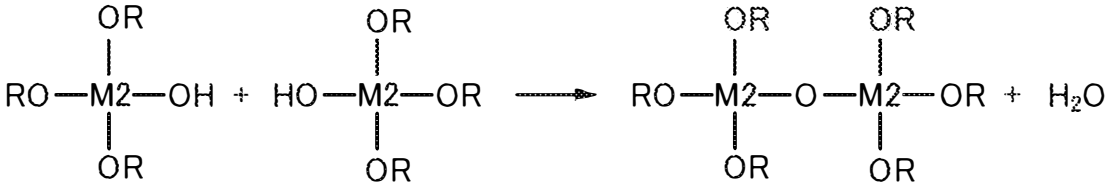


FIG. 4D-1

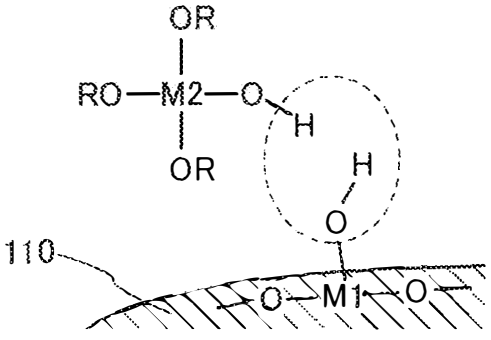


FIG. 4D-2

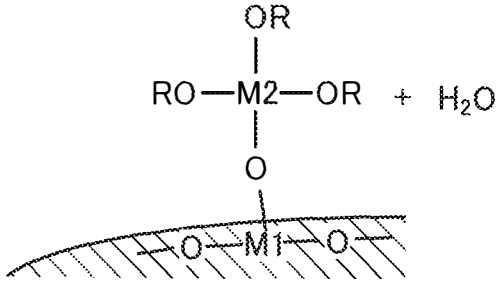


FIG. 5A

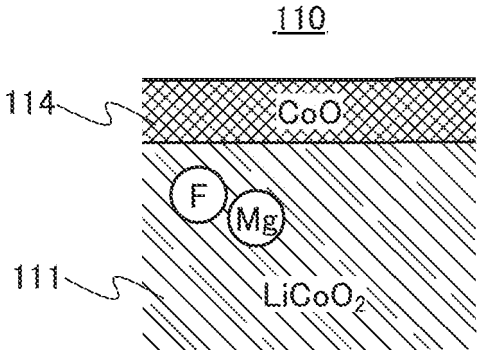


FIG. 5B

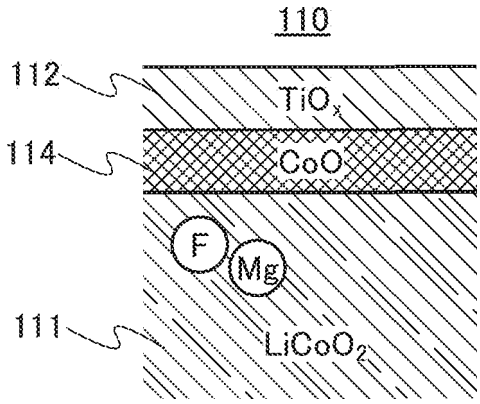


FIG. 5C

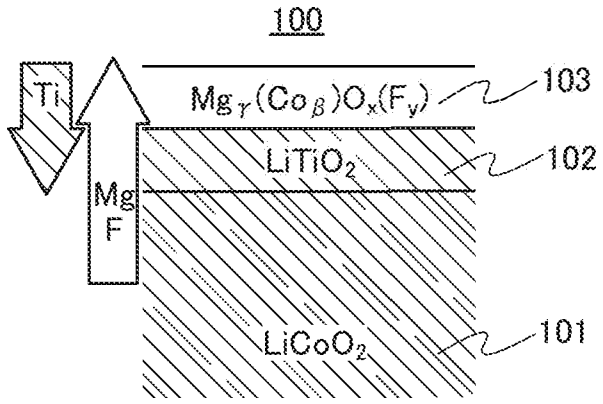


FIG. 6A

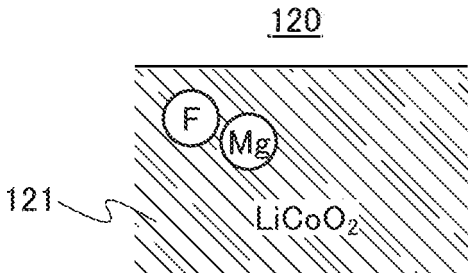


FIG. 6B

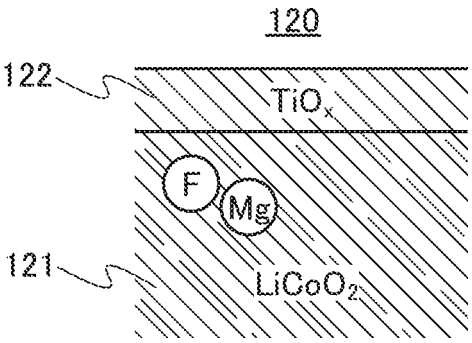


FIG. 6C

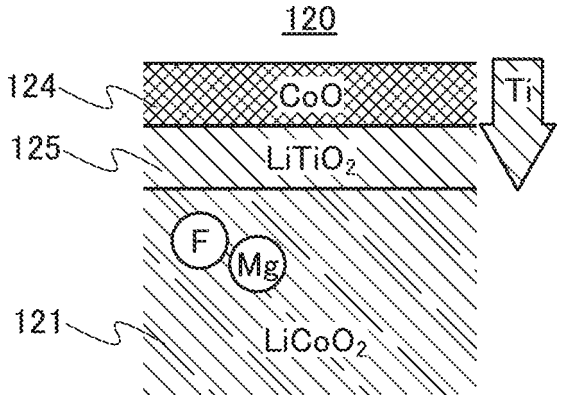


FIG. 6D

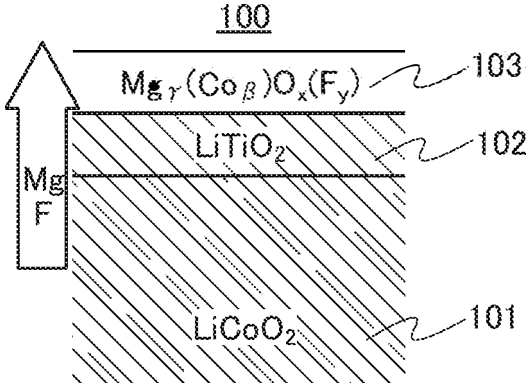


FIG. 7A

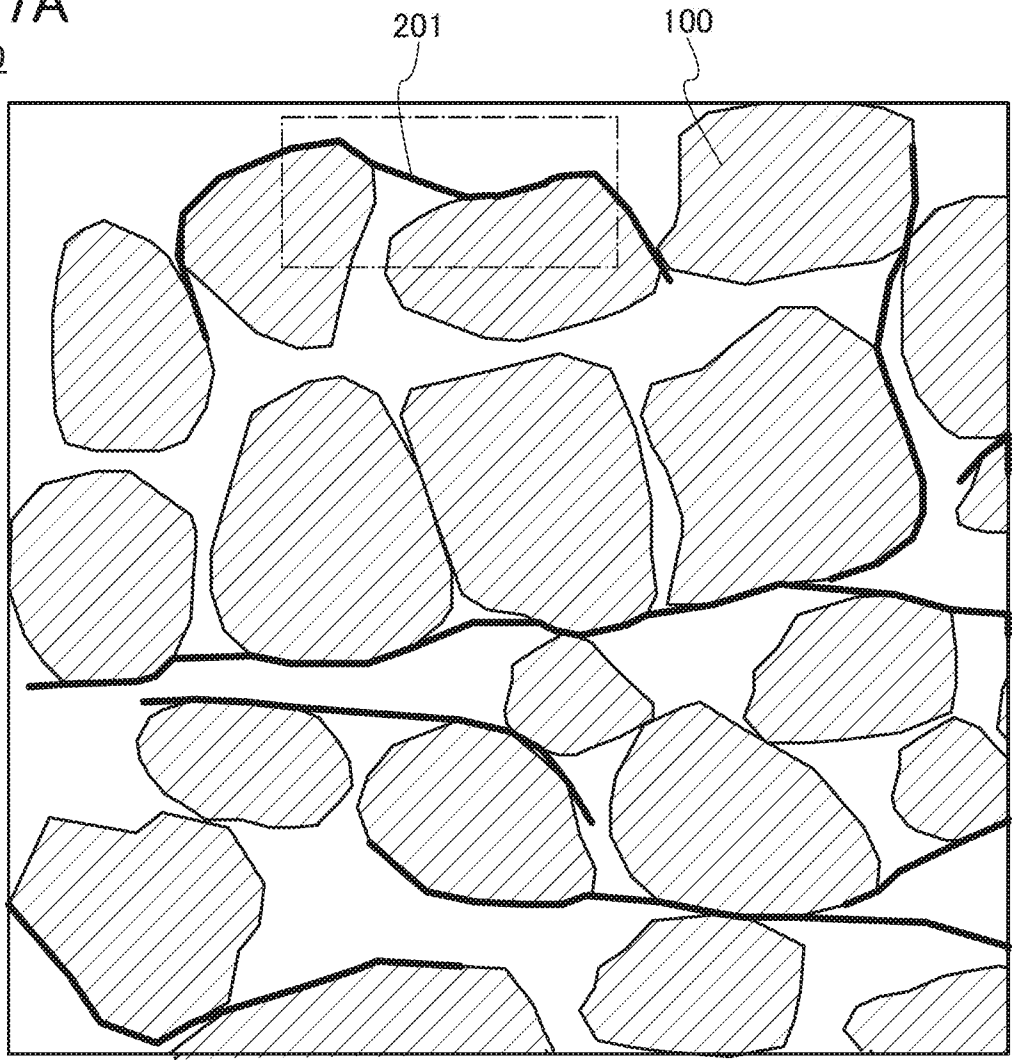


FIG. 7B

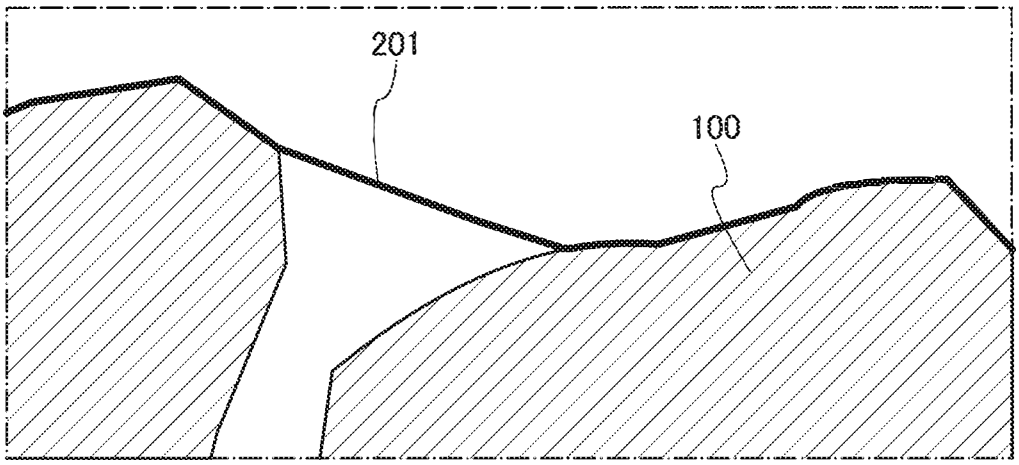


FIG. 8A

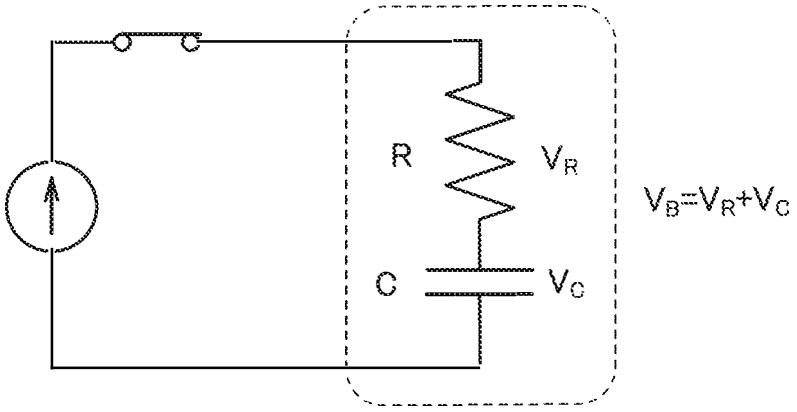


FIG. 8B

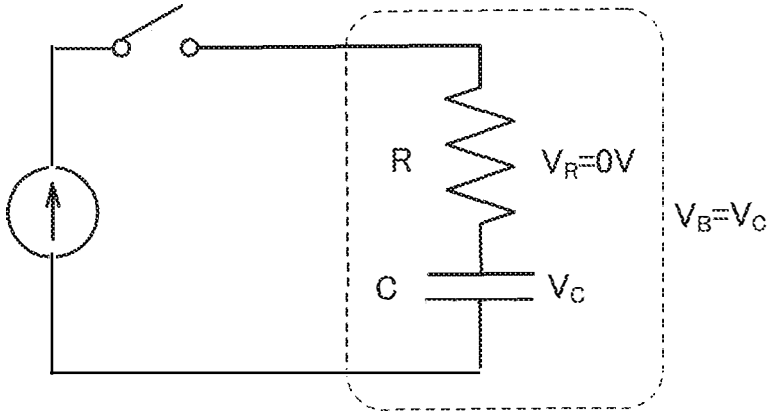


FIG. 8C

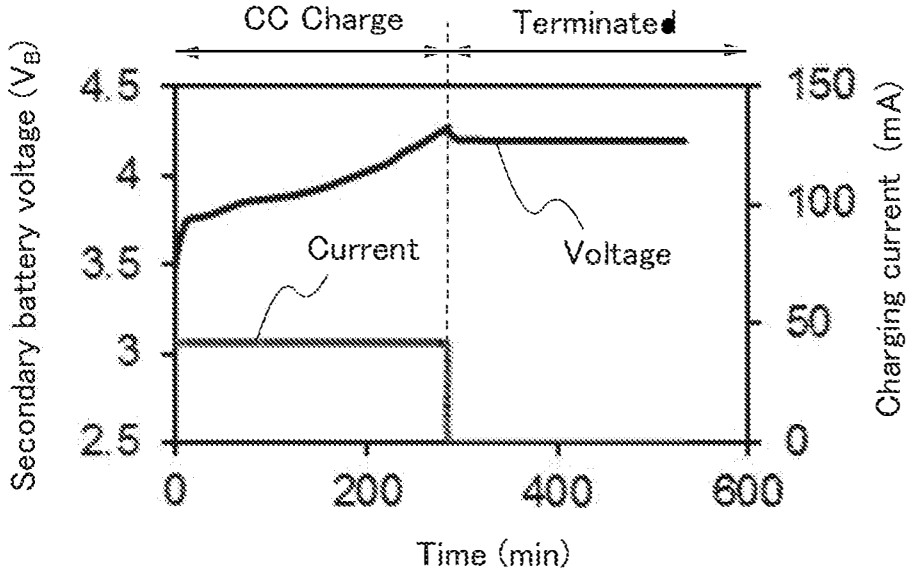


FIG. 9A

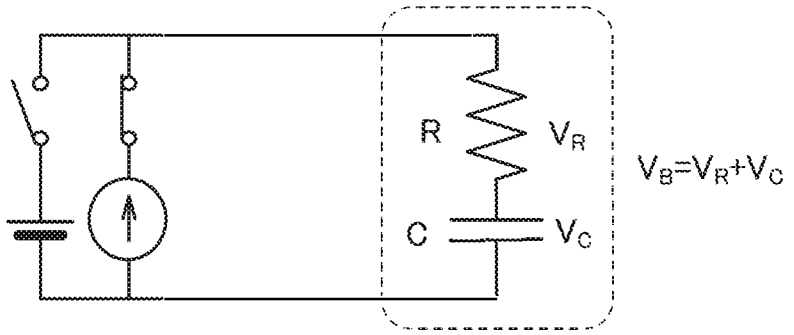


FIG. 9B

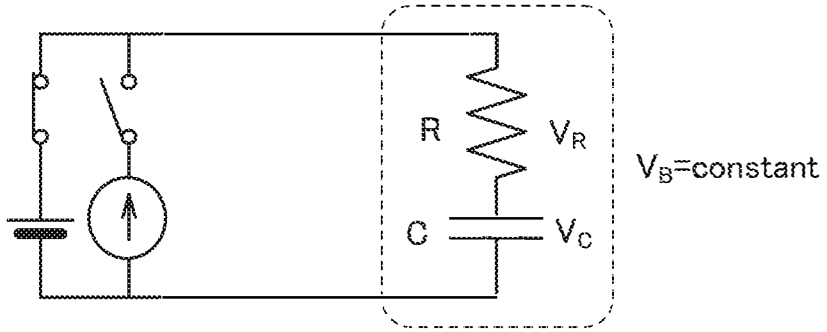


FIG. 9C

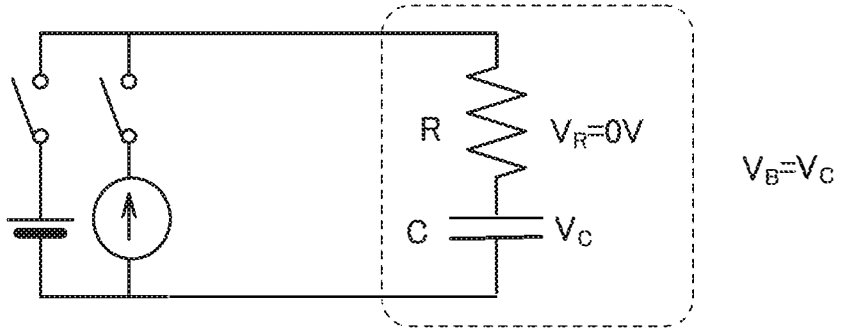


FIG. 9D

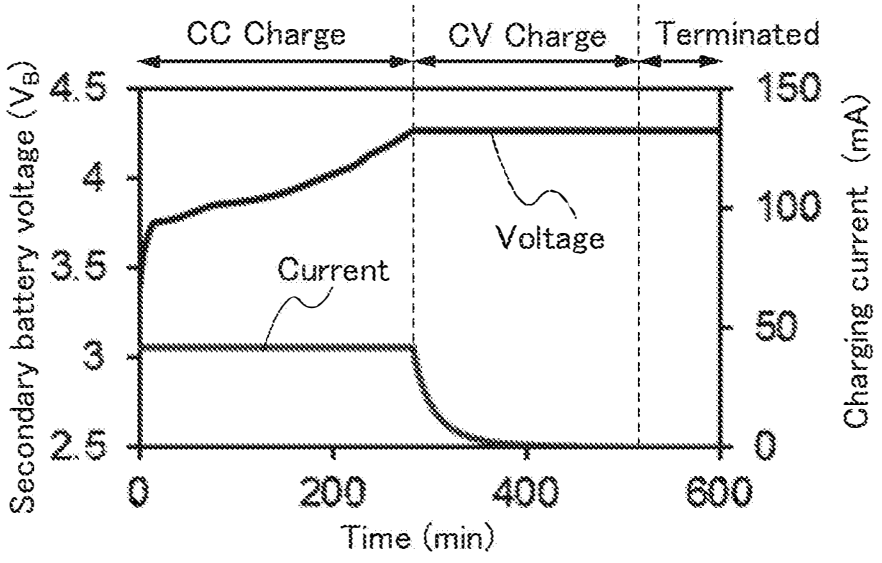


FIG. 10

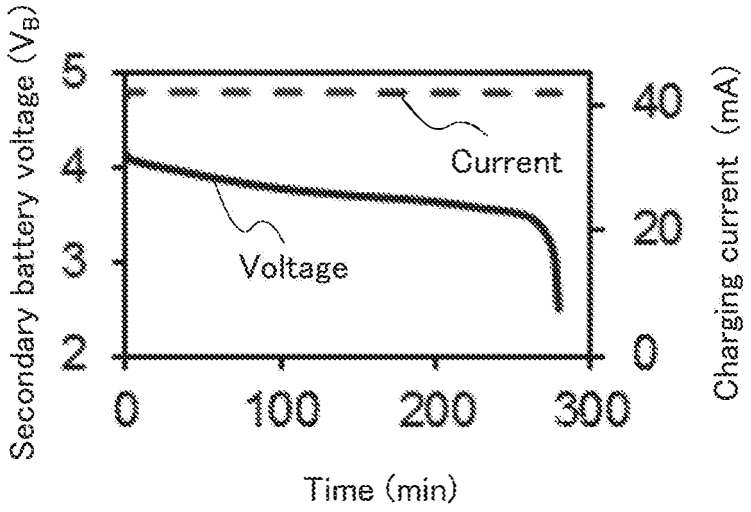

Secondary battery voltage (V_B)
5
4
3
2
0
100
200
300
Time (min)
Current
Voltage
40
20
0
Charging current (mA)

FIG. 11A

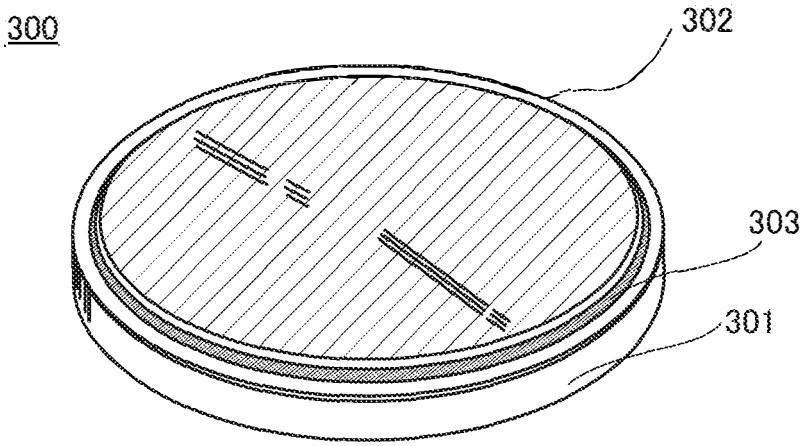


FIG. 11B

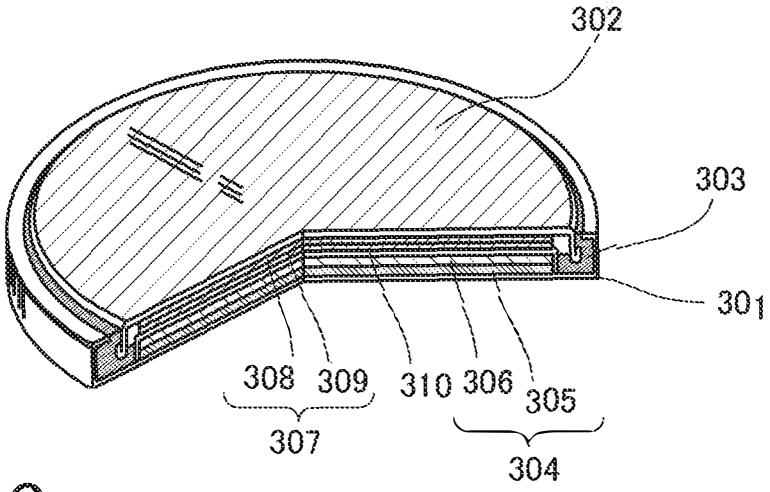


FIG. 11C

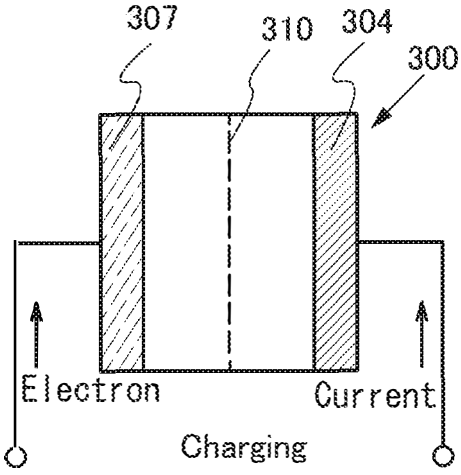


FIG. 12A

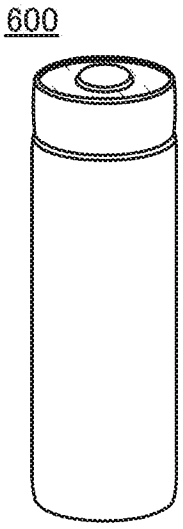


FIG. 12B

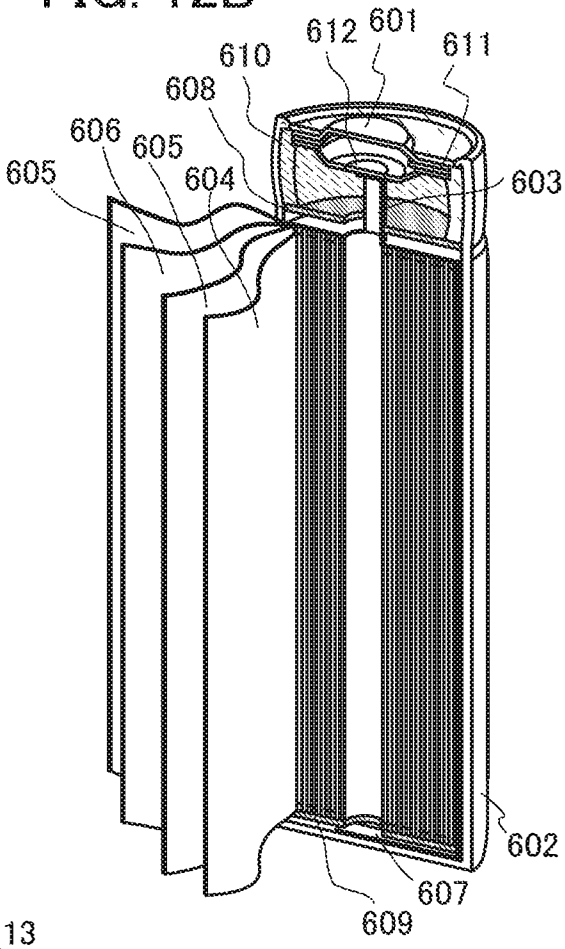


FIG. 12C

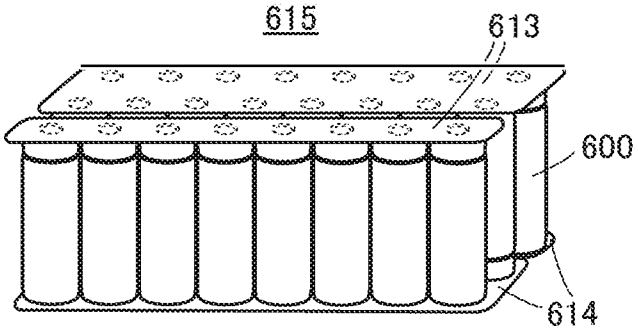


FIG. 12D

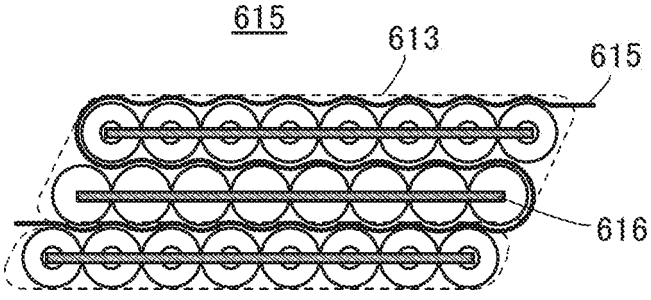


FIG. 13A

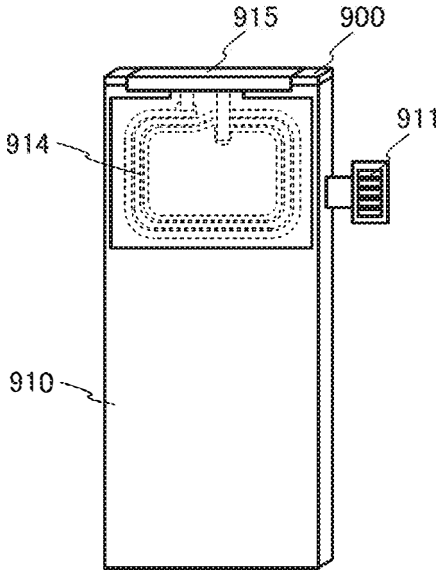


FIG. 13B

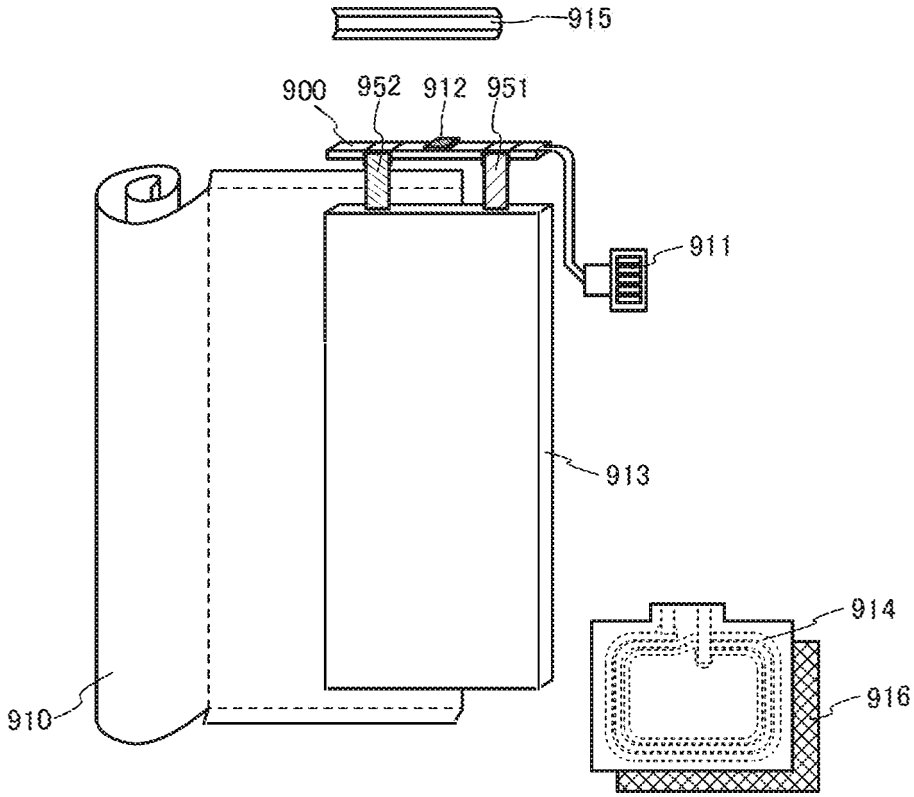


FIG. 14A-1

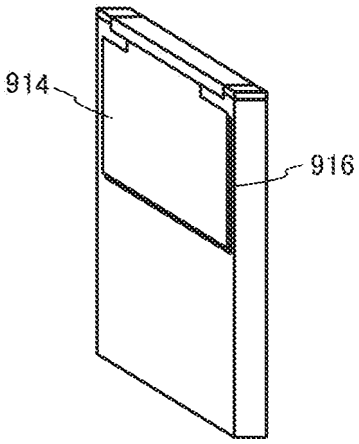


FIG. 14A-2

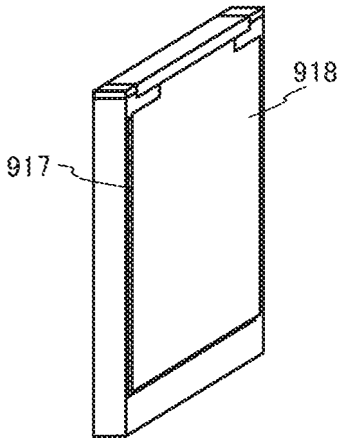


FIG. 14B-1

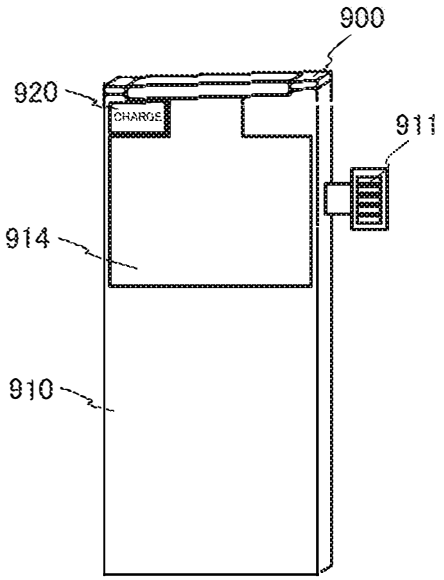


FIG. 14B-2

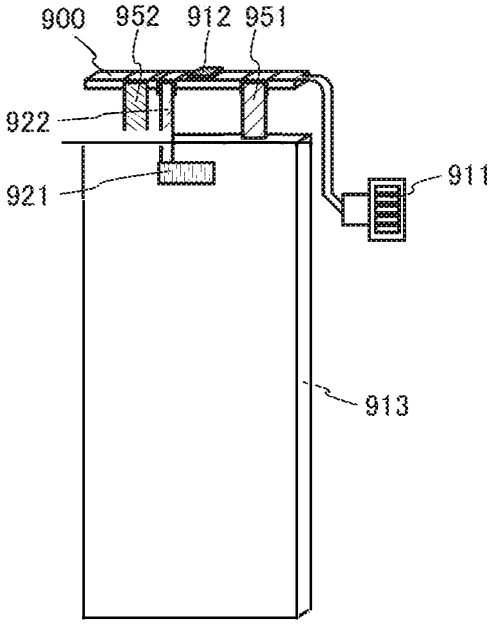


FIG. 15A

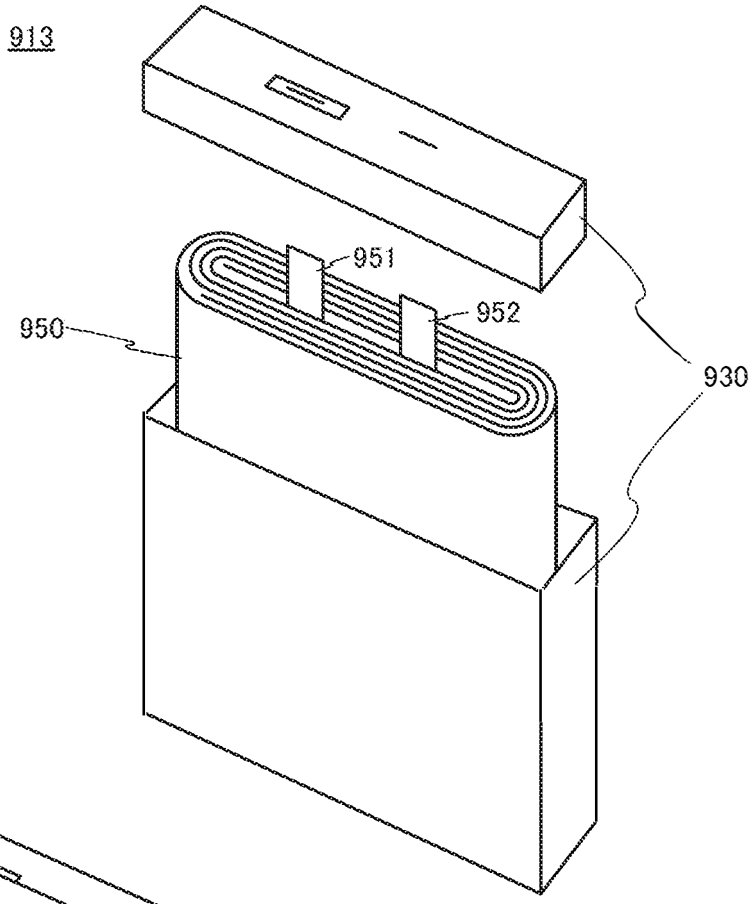


FIG. 15B

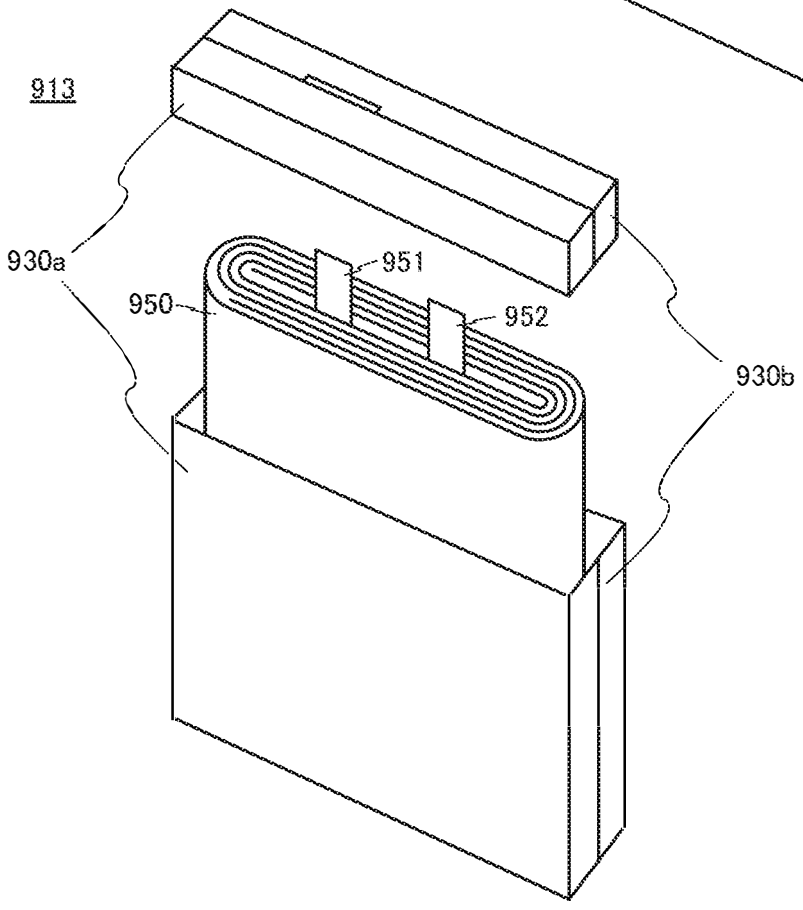


FIG. 16

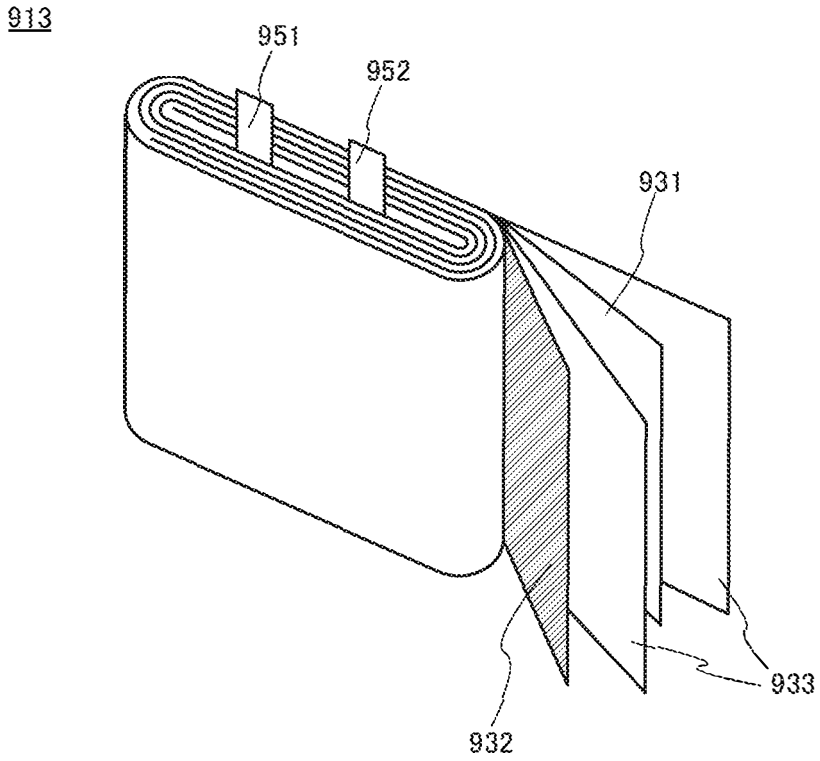


FIG. 17A

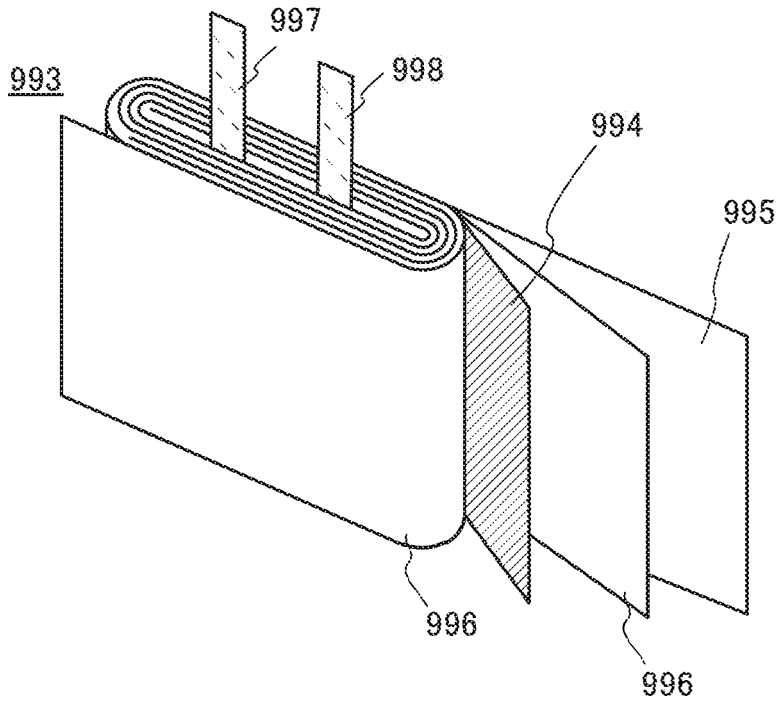


FIG. 17B

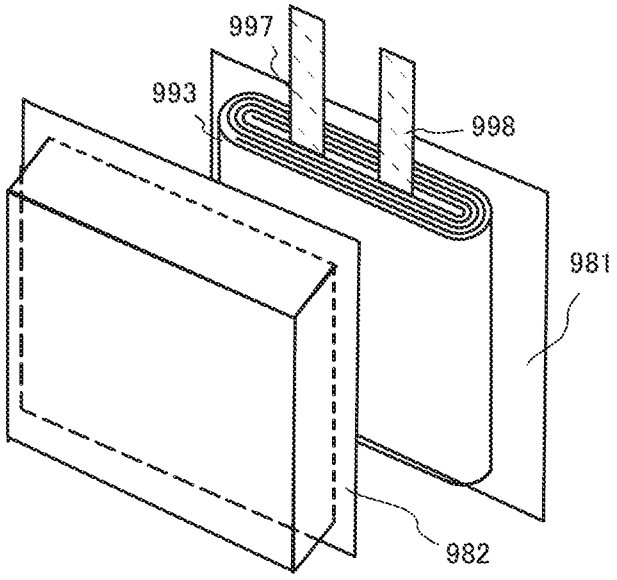


FIG. 17C

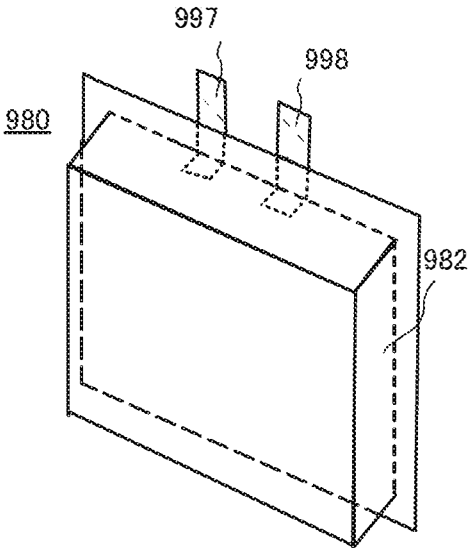


FIG. 18A

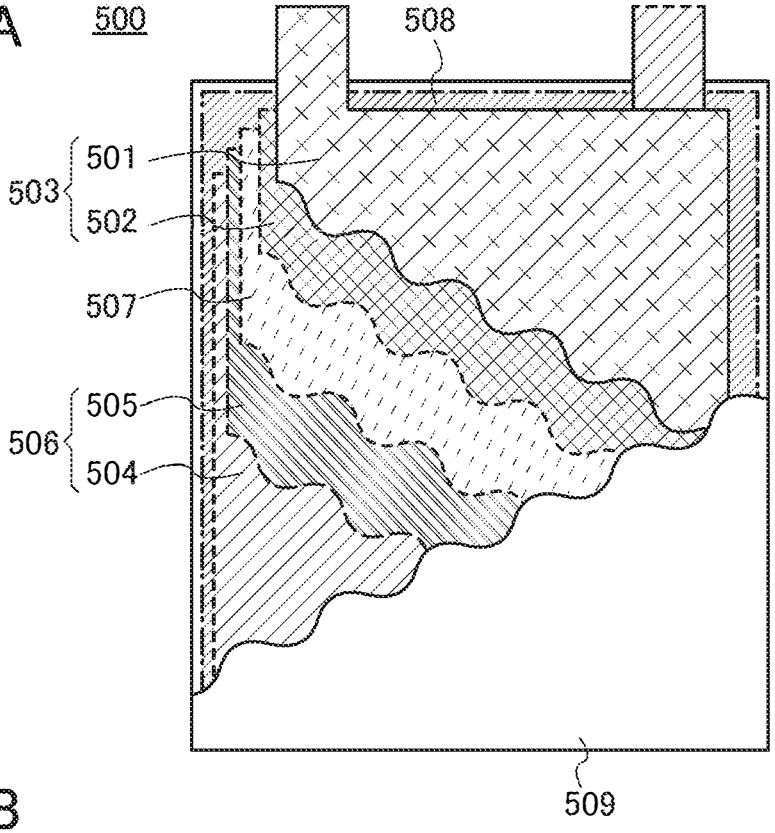


FIG. 18B

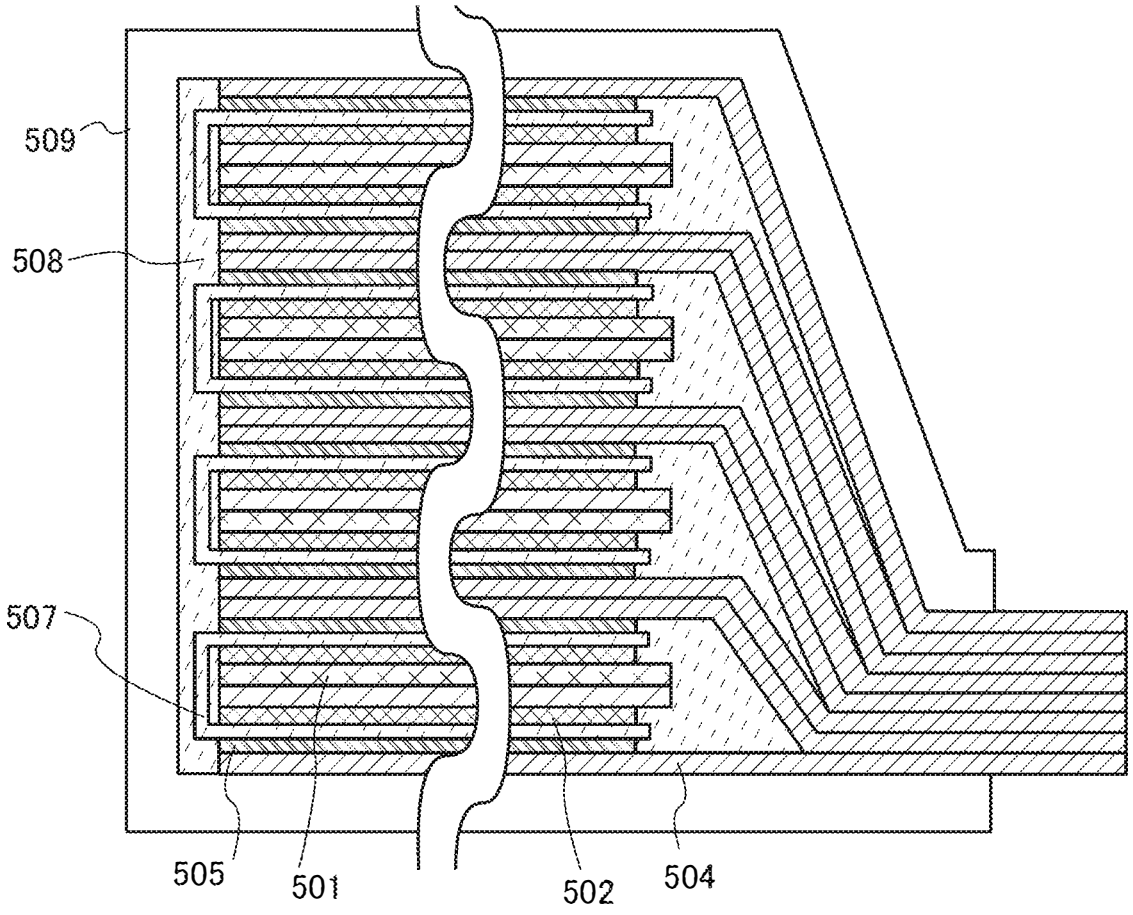


FIG. 19

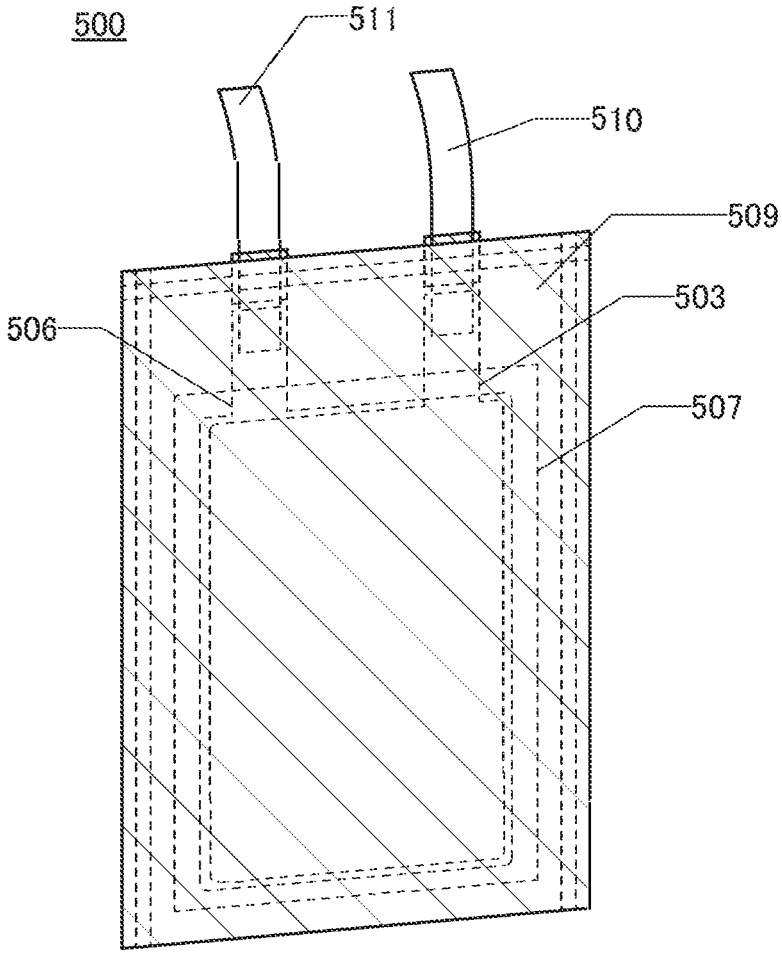


FIG. 20

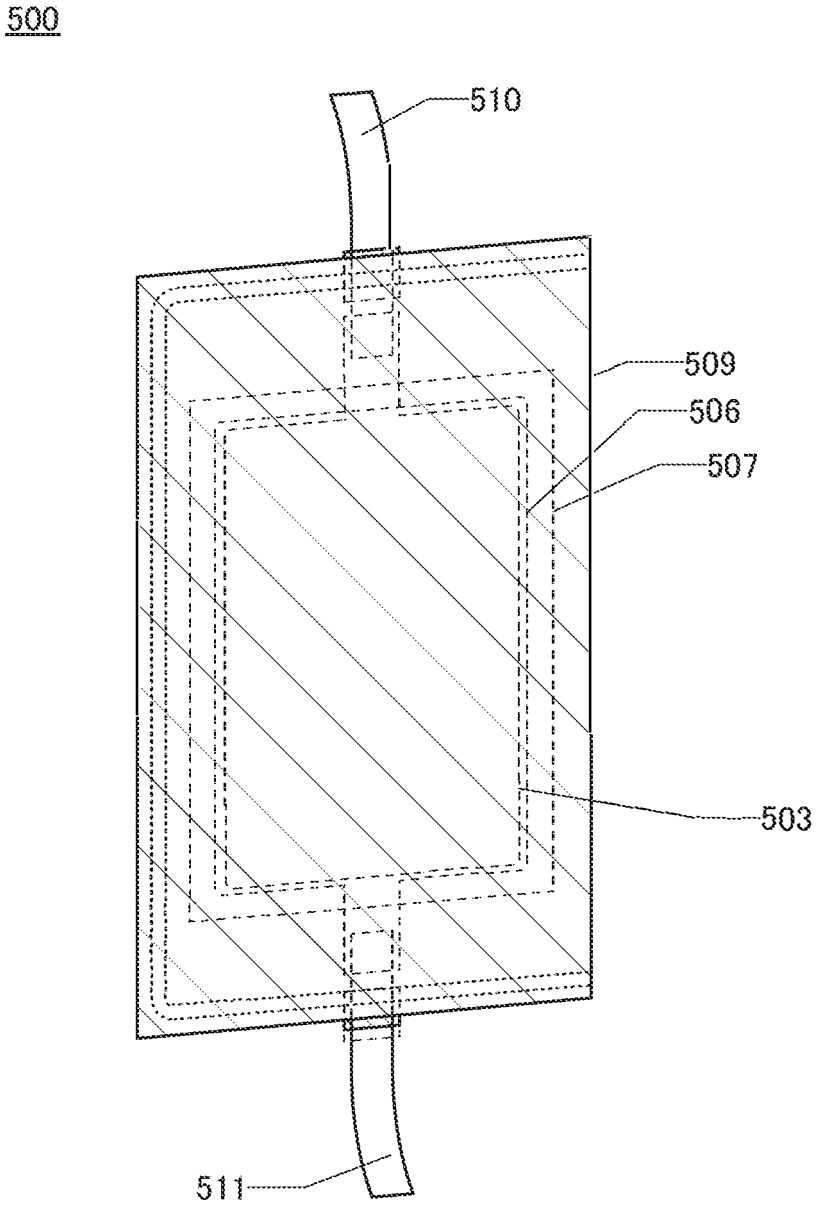


FIG. 21A

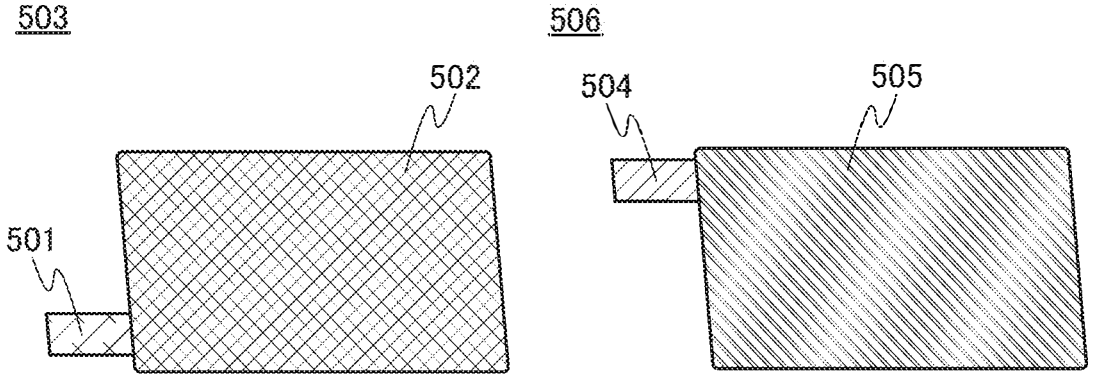


FIG. 21B

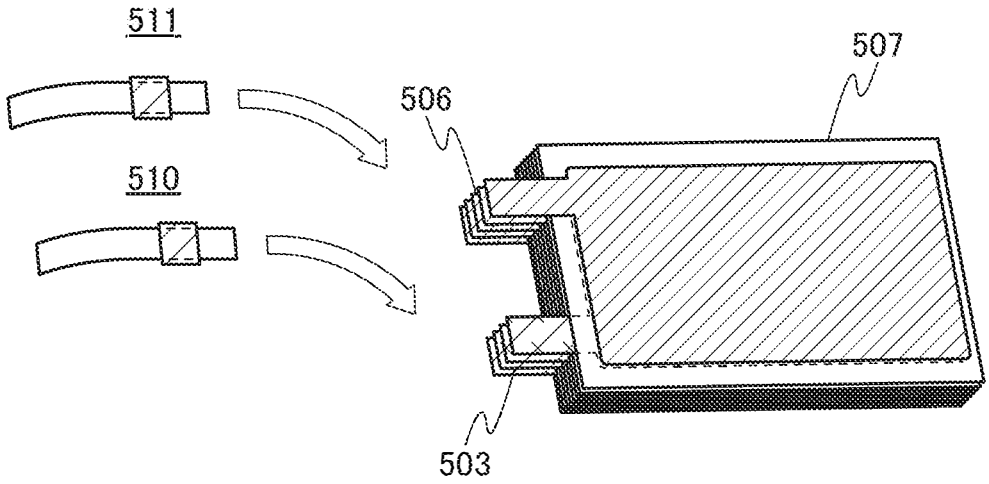


FIG. 21C

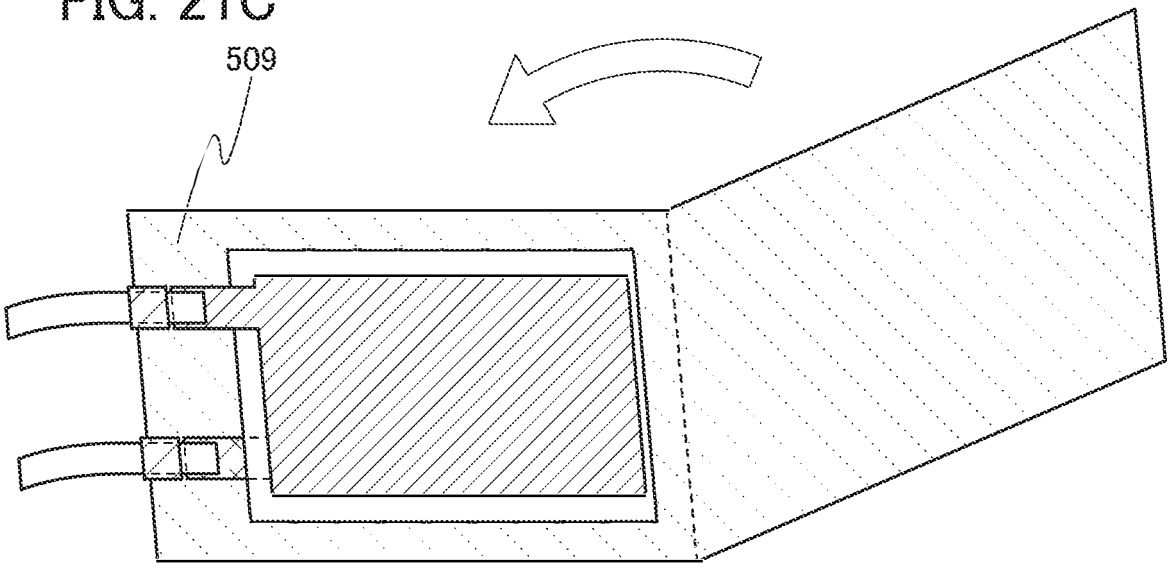


FIG. 22A

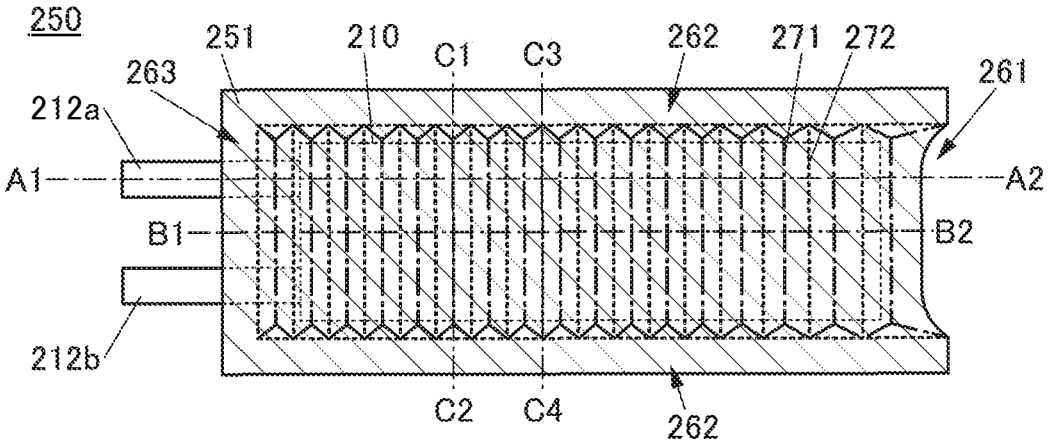


FIG. 22B1

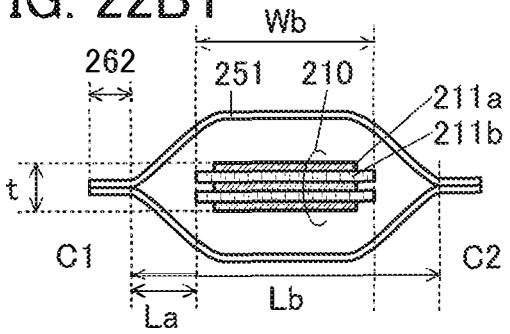


FIG. 22B2

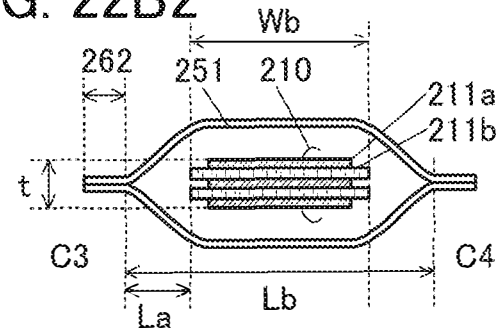


FIG. 22C

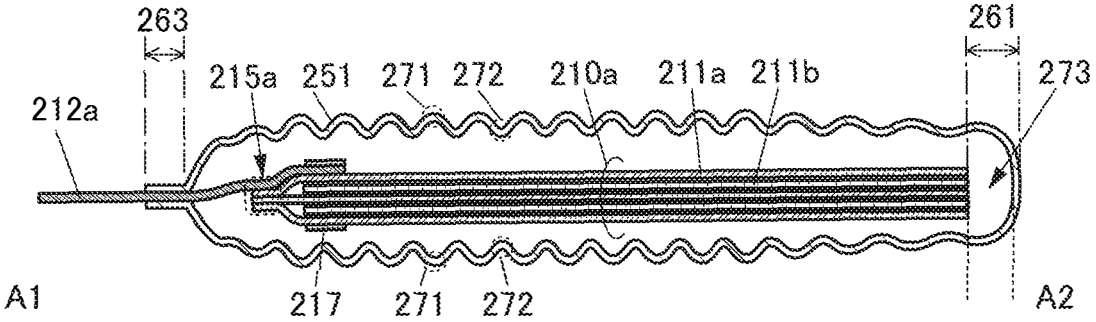


FIG. 22D

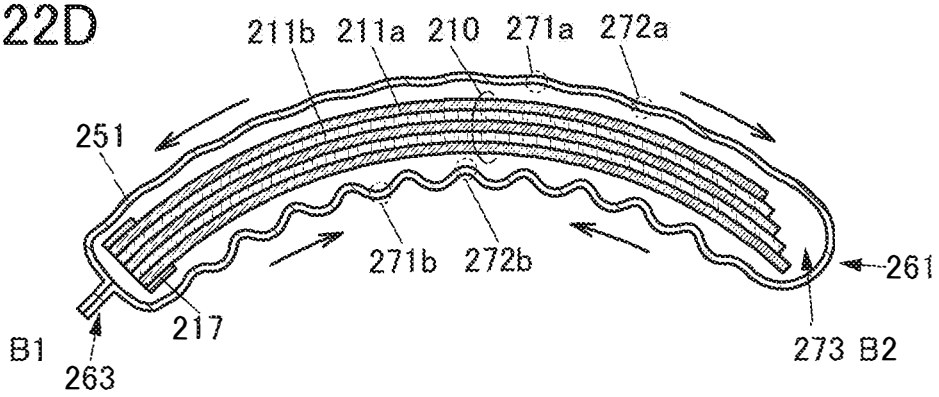


FIG. 23A

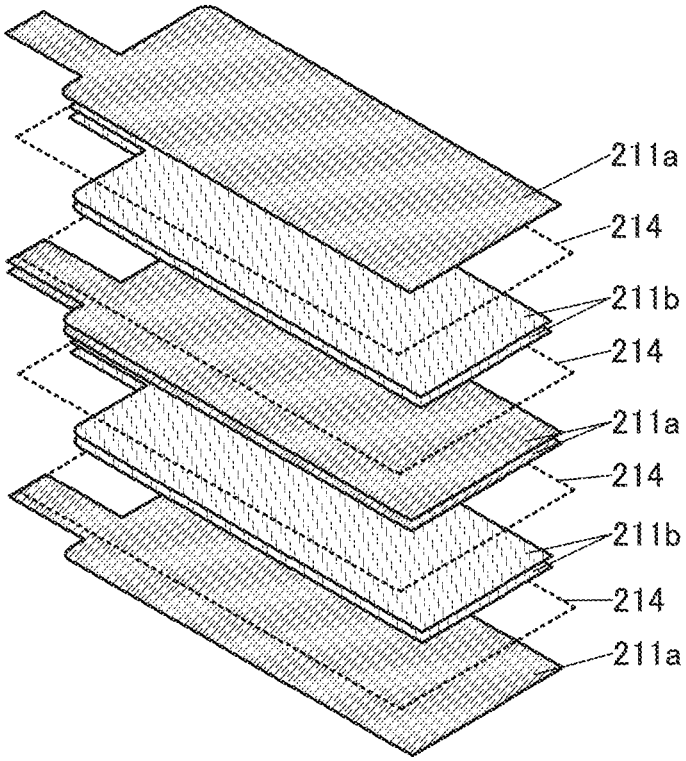


FIG. 23B

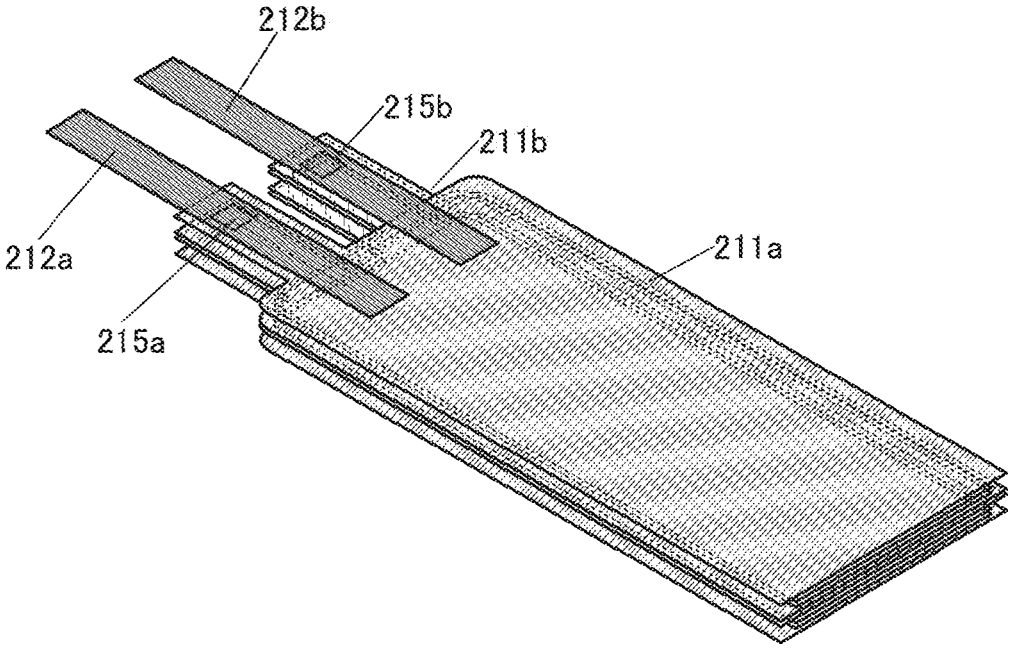


FIG. 24A

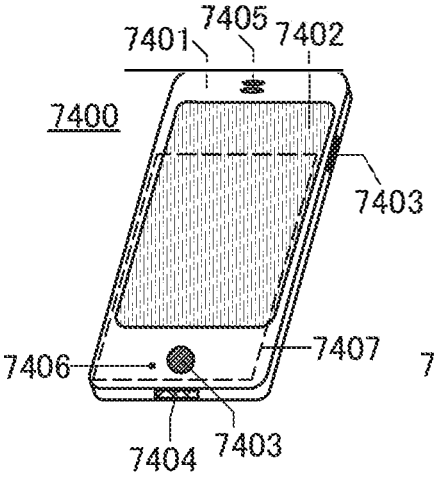


FIG. 24B

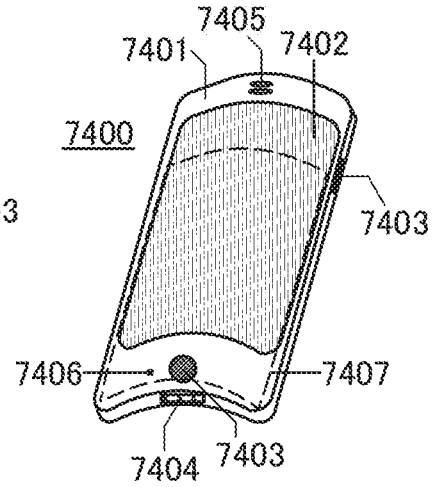


FIG. 24C

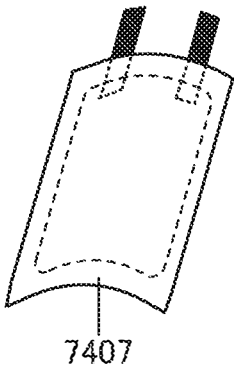


FIG. 24D

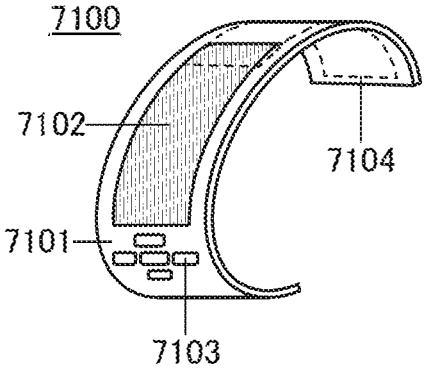


FIG. 24E

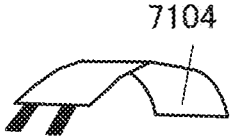


FIG. 24F

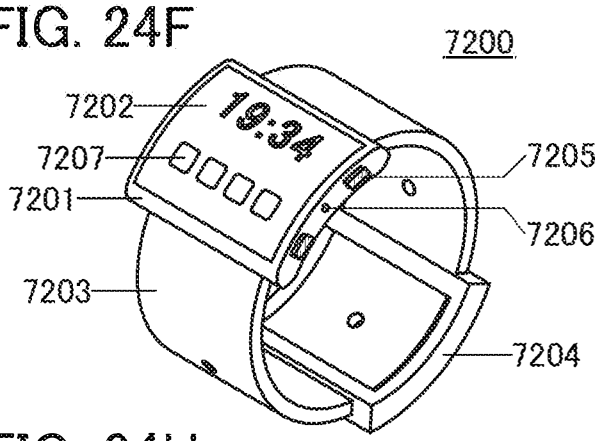


FIG. 24G

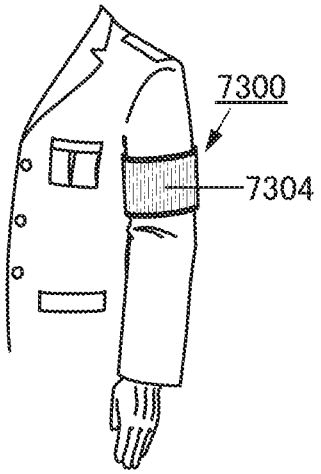


FIG. 24H

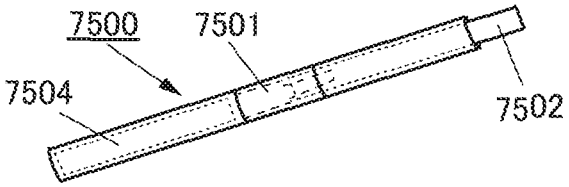


FIG. 25A

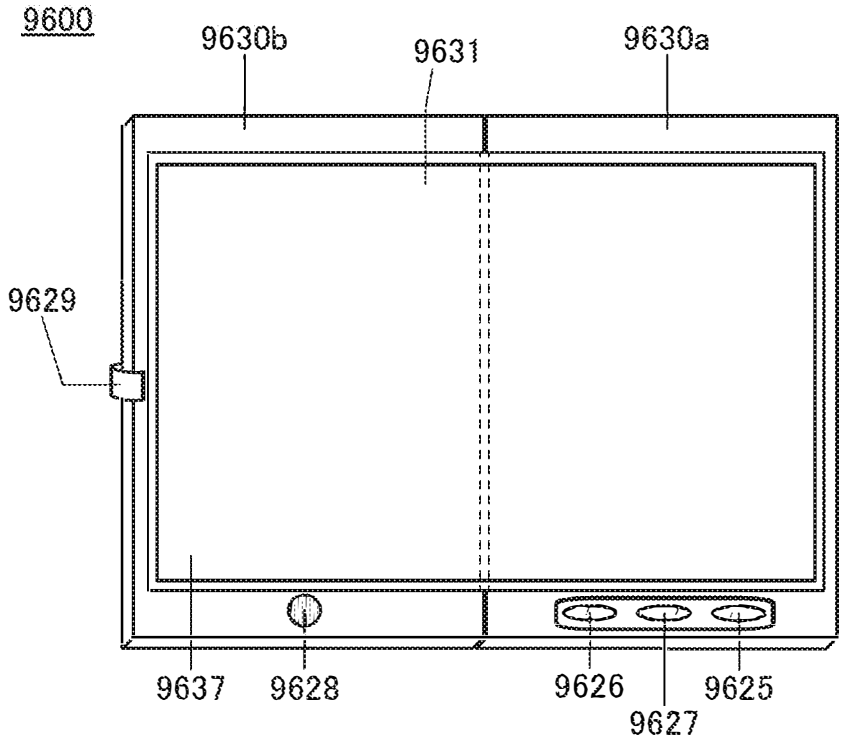


FIG. 25B

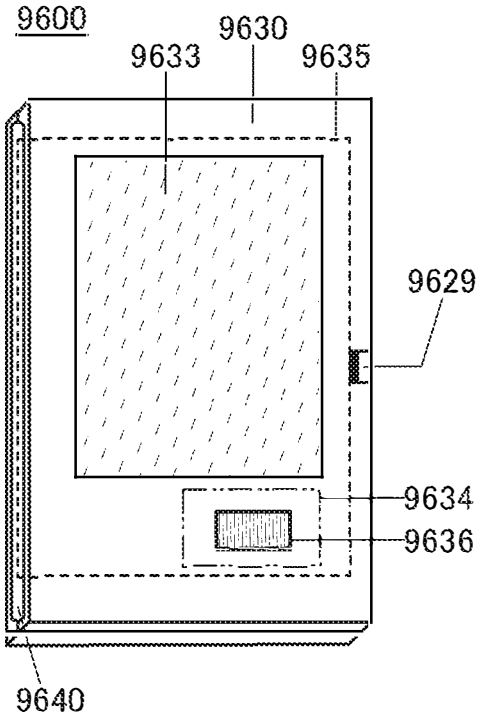


FIG. 25C

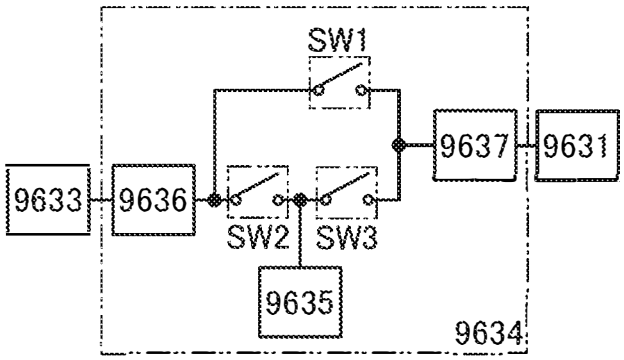


FIG. 26

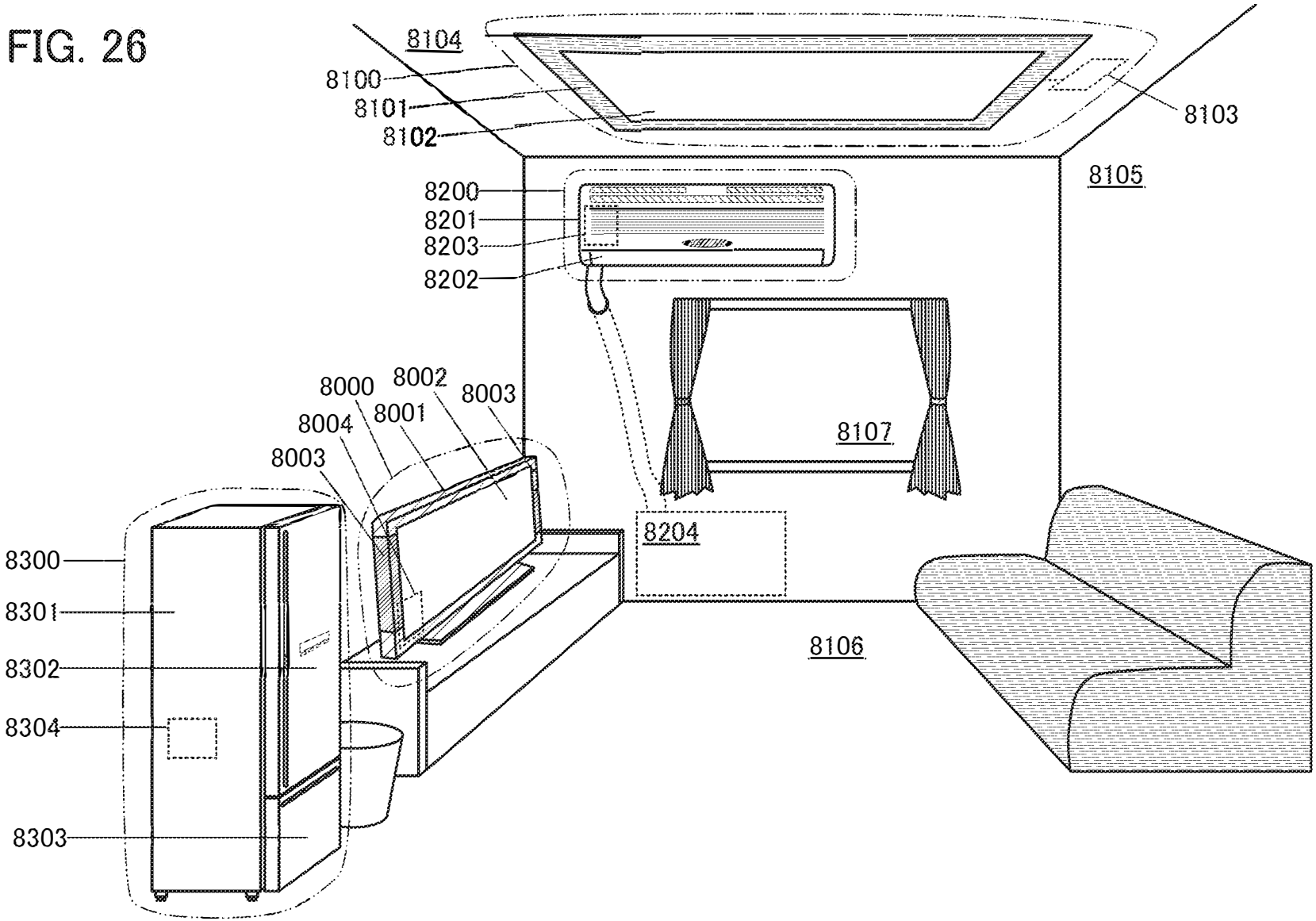

8104
8100
8101
8102
8103
8105
8200
8201
8203
8202
8000
8002
8003
8004
8001
8003
8107
8204
8300
8301
8302
8304
8303
8106

FIG. 27A

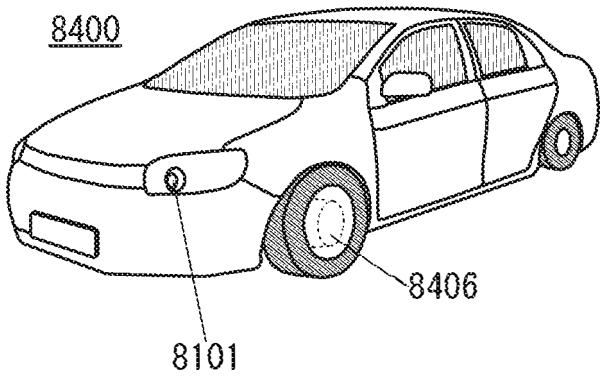


FIG. 27B

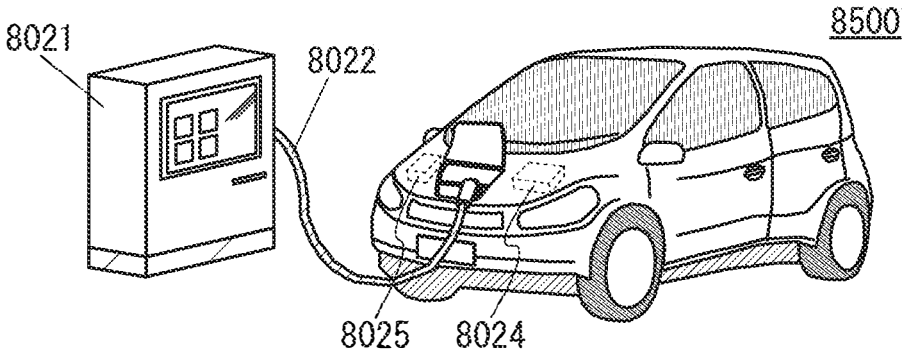


FIG. 27C

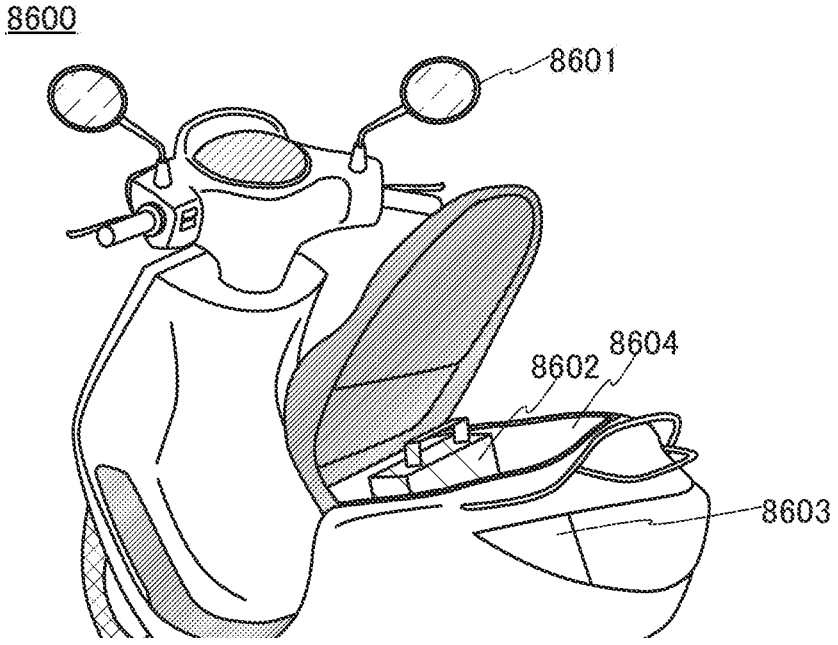


FIG. 28

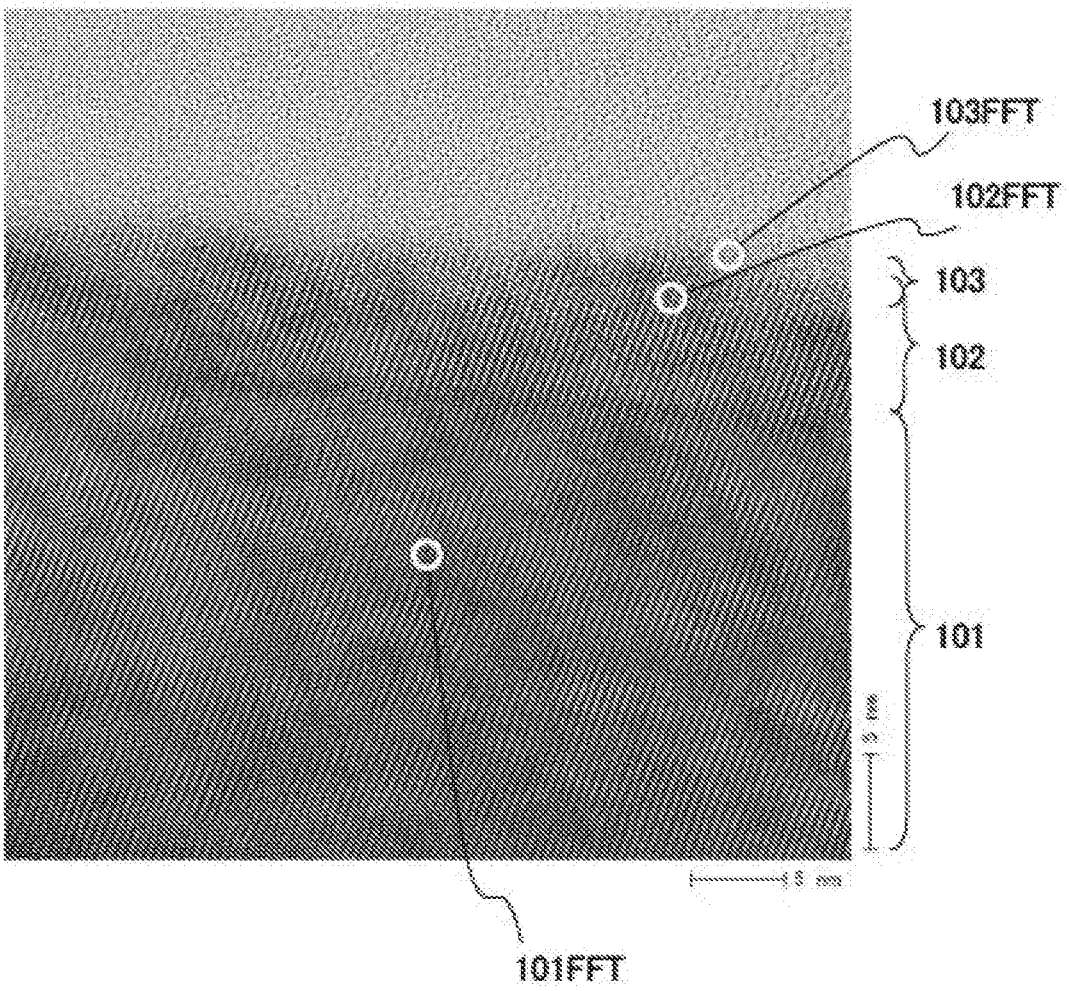


FIG. 29A1

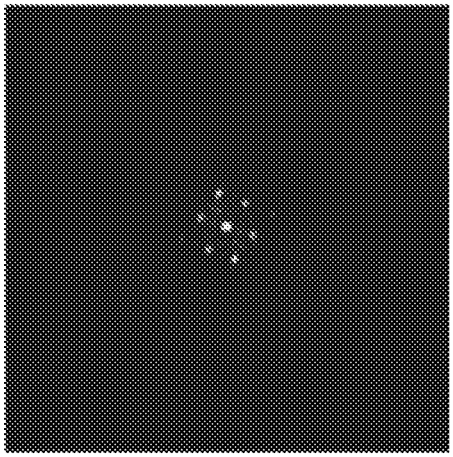


FIG. 29A2

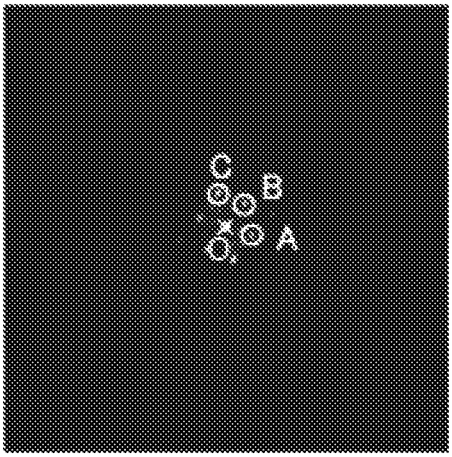


FIG. 29B1

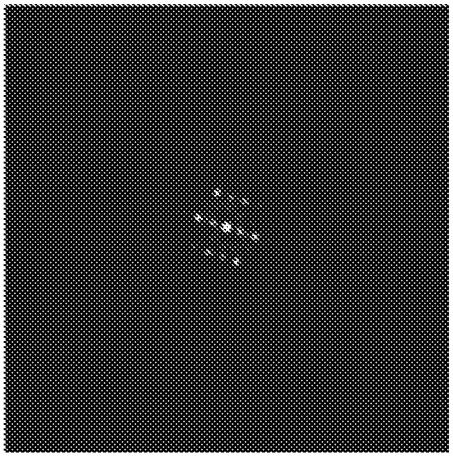


FIG. 29B2



FIG. 29C1

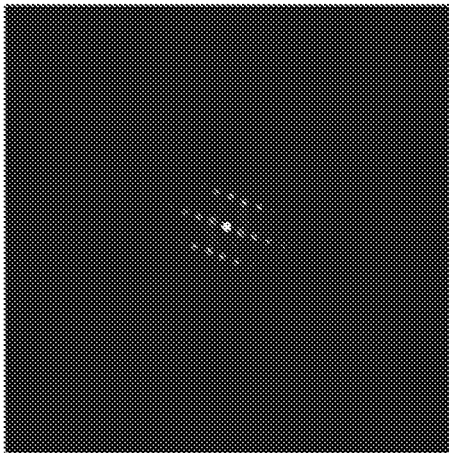


FIG. 29C2

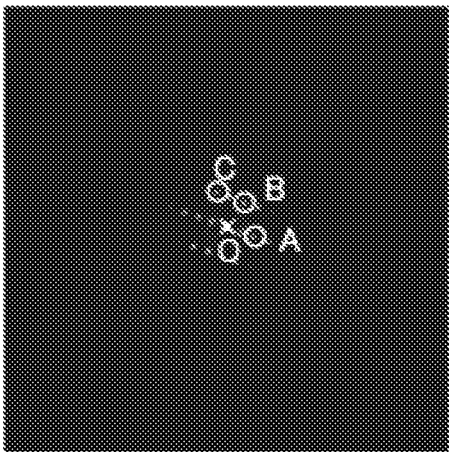


FIG. 30A1

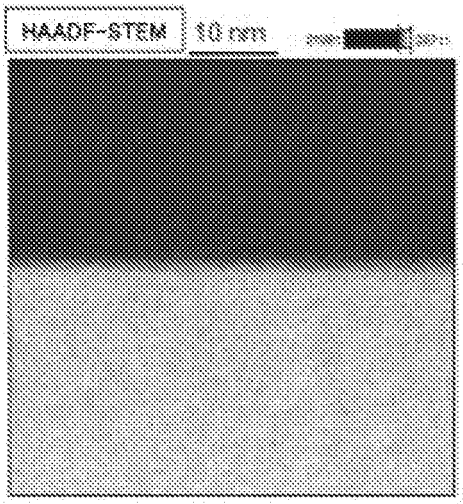


FIG. 30A2

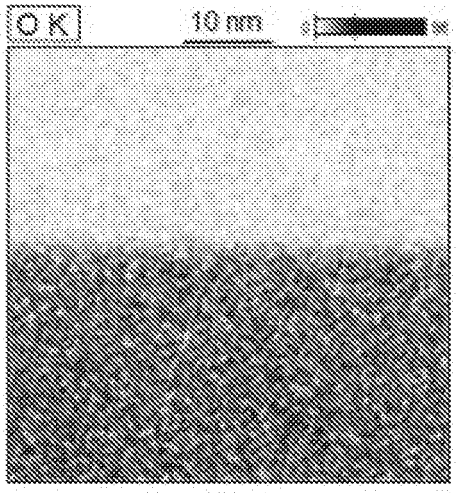


FIG. 30B1

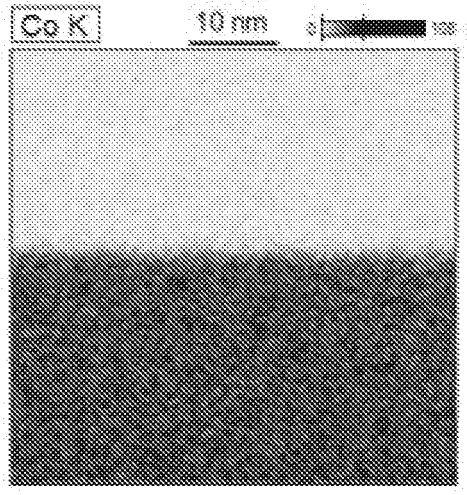


FIG. 30B2

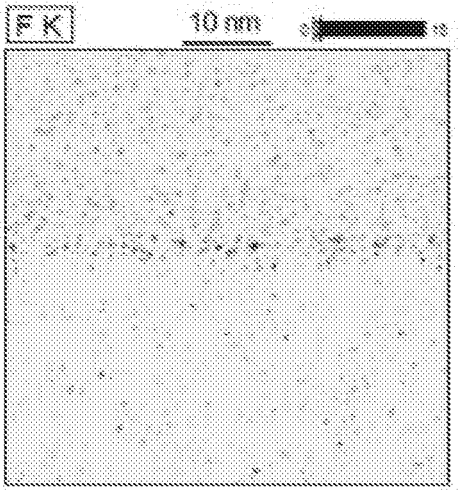


FIG. 30C1

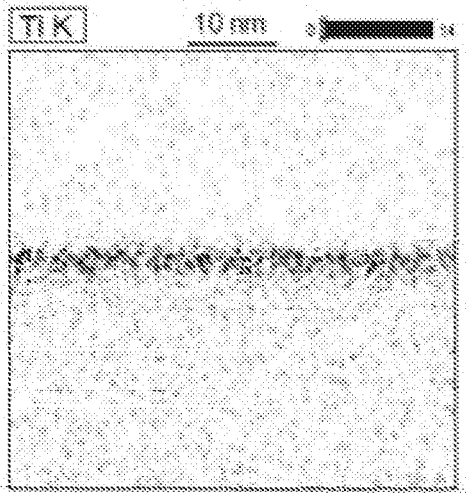


FIG. 30C2

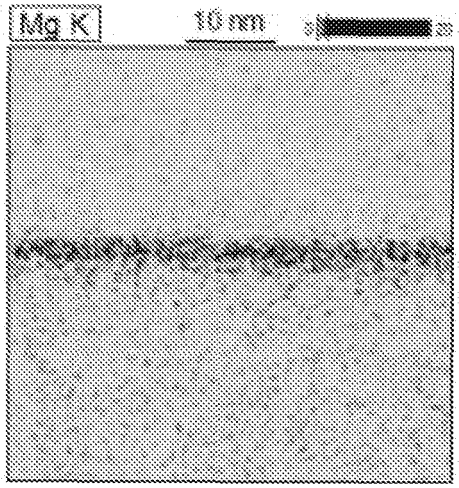


FIG. 31A1

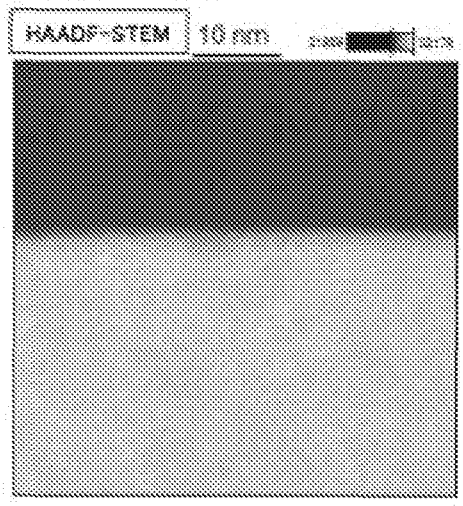


FIG. 31A2

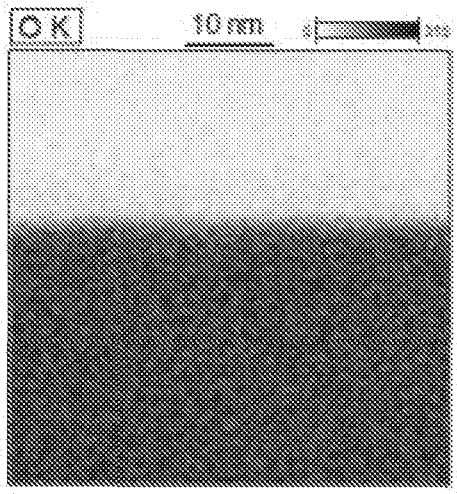


FIG. 31B1

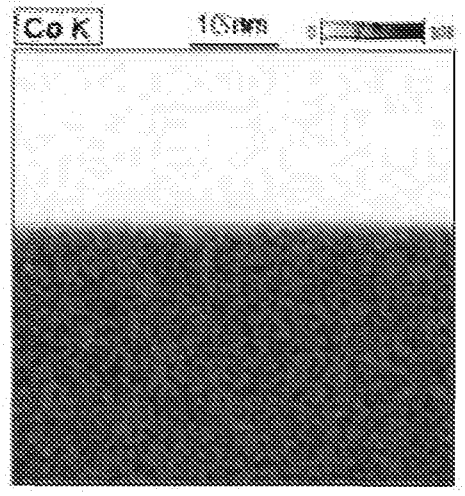


FIG. 31B2

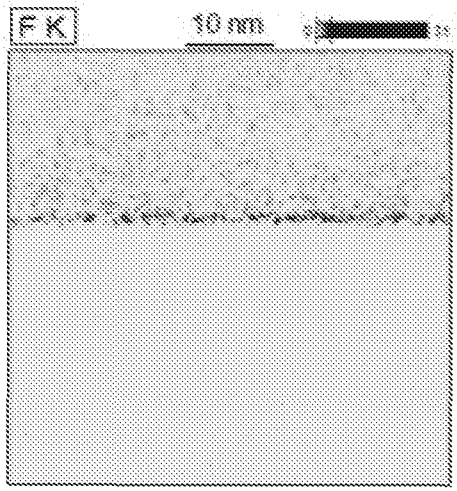


FIG. 31C1

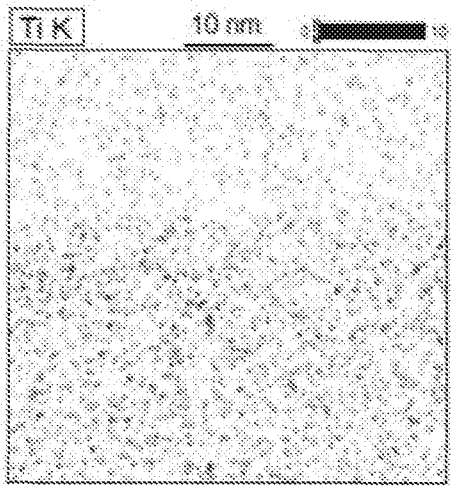


FIG. 31C2

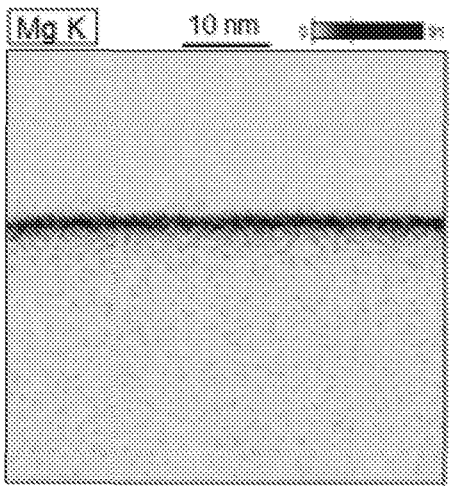


FIG. 32

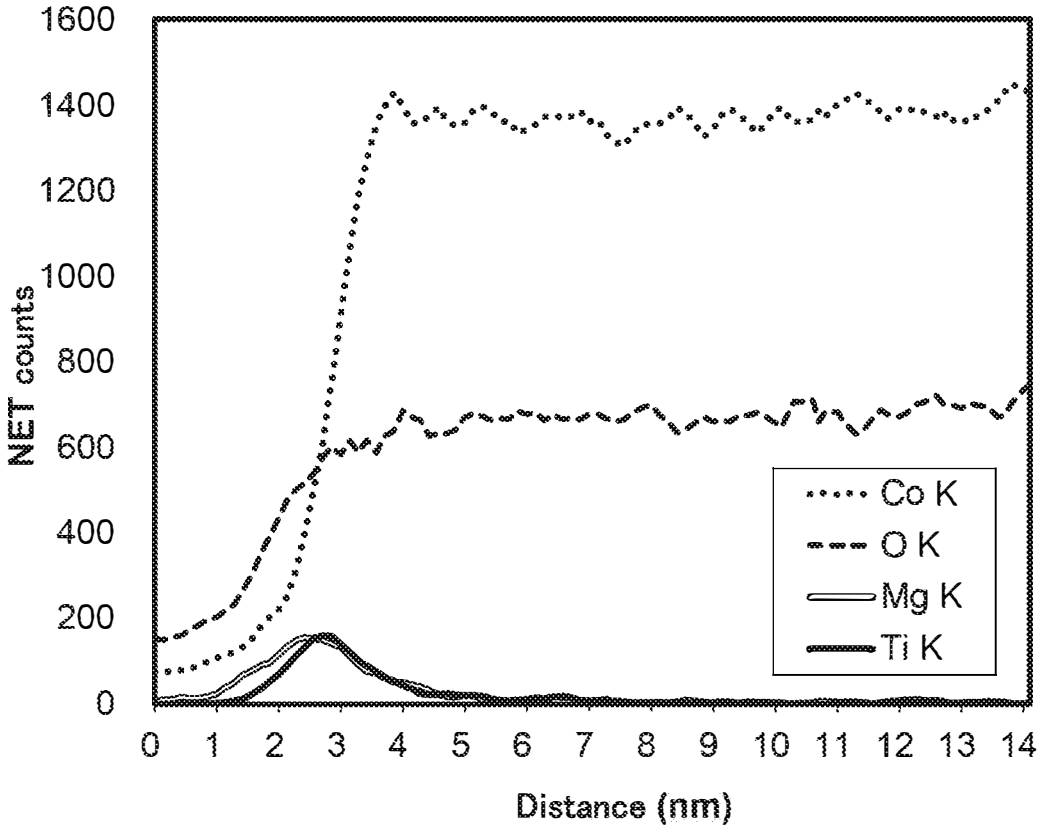

1600
1400
1200
1000
800
600
400
200
0
NET counts
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
Distance (nm)
Co K
O K
Mg K
Ti K

FIG. 33

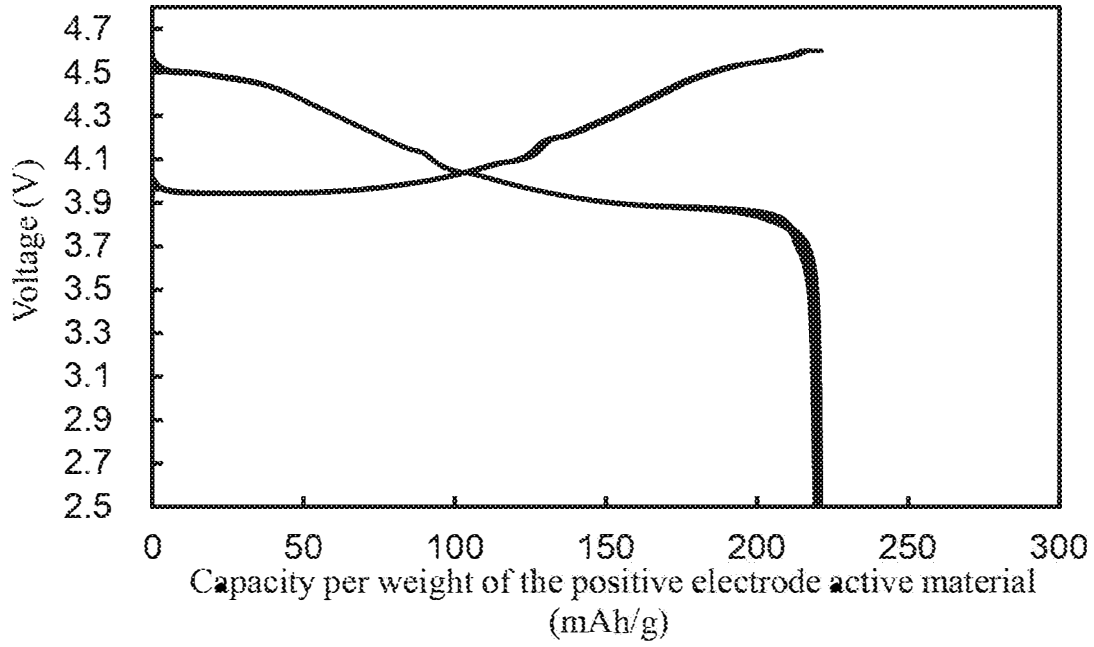

4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
Voltage (V)
0
50
100
150
200
250
300
Capacity per weight of the positive electrode active material (mAh/g)

FIG. 34

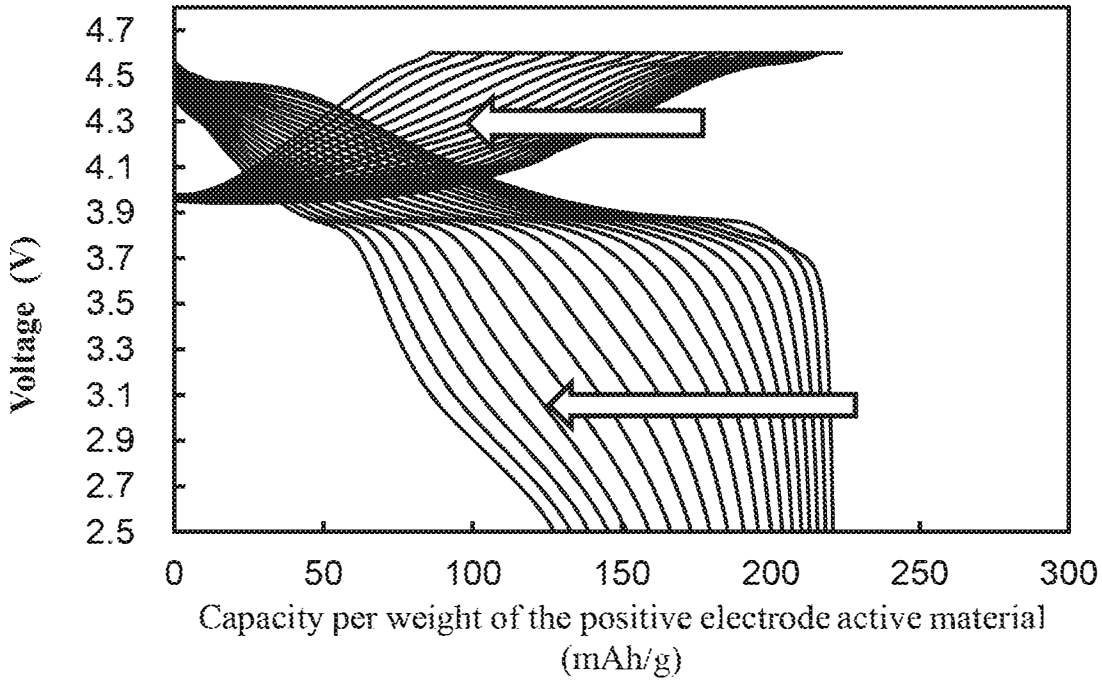

4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
Voltage (V)
0
50
100
150
200
250
300
Capacity per weight of the positive electrode active material
(mAh/g)

FIG. 35

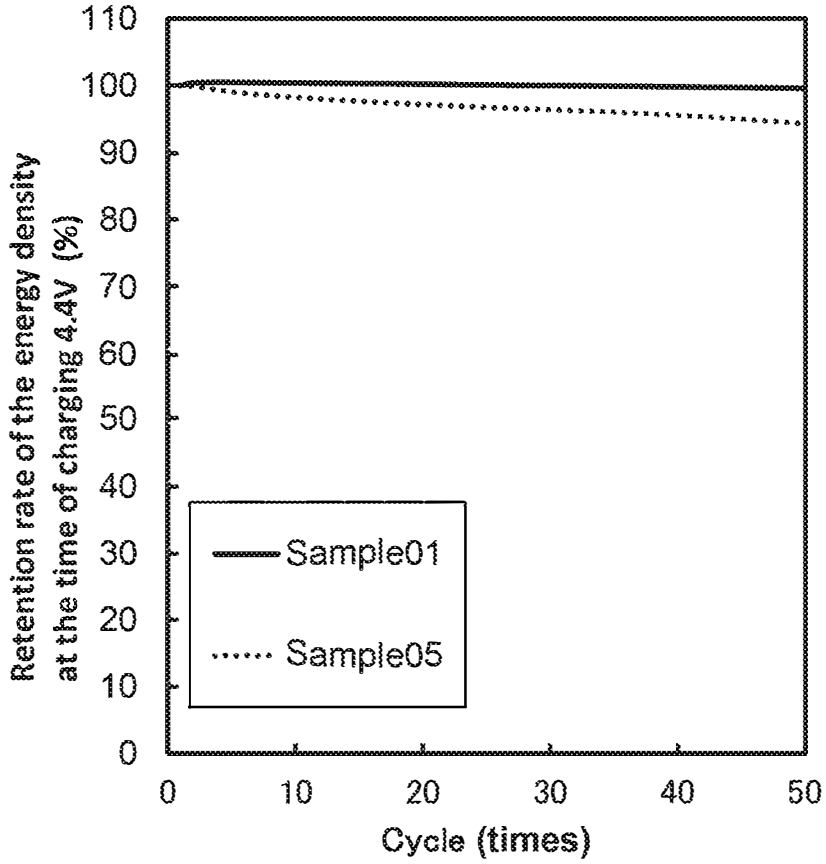
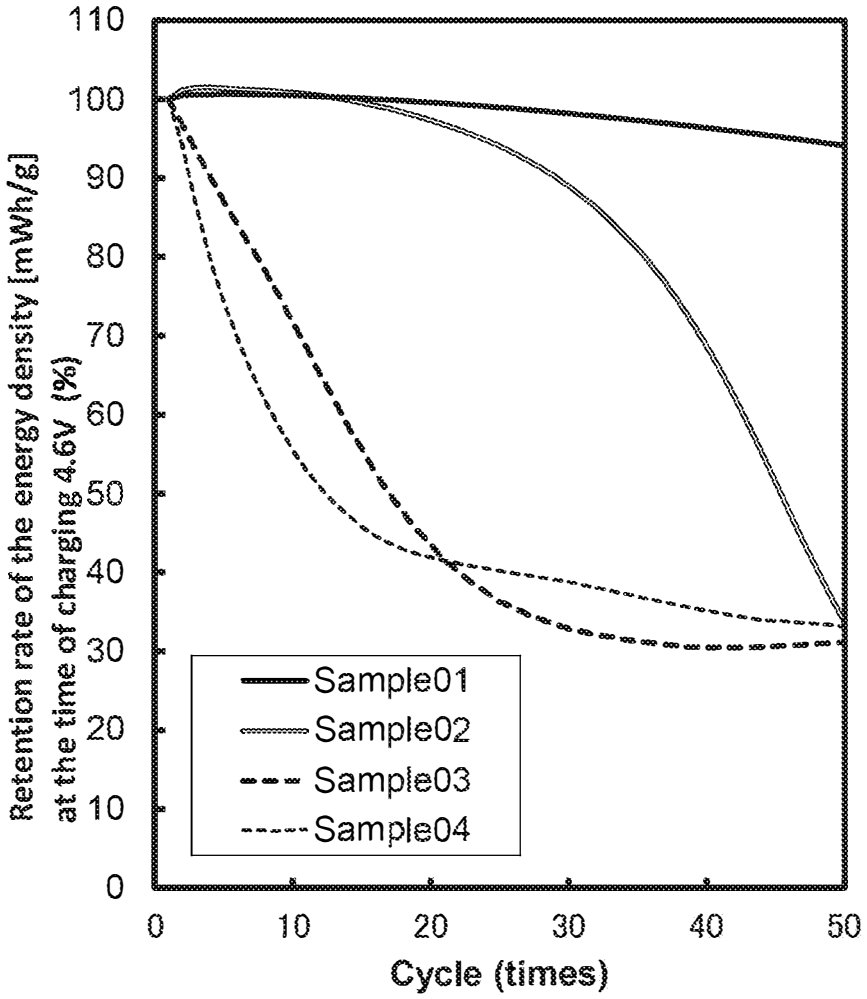

110
100
90
80
70
60
50
40
30
20
10
0
Retention rate of the energy density at the time of charging 4.4V (%)
Sample01
Sample05
0
10
20
30
40
50
Cycle (times)

FIG. 36


Retention rate of the energy density [mWh/g] at the time of charging 4.6V (%)
110
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
Cycle (times)
Sample01
Sample02
Sample03
Sample04

before Ti heating (Sample06)

FIG. 37A

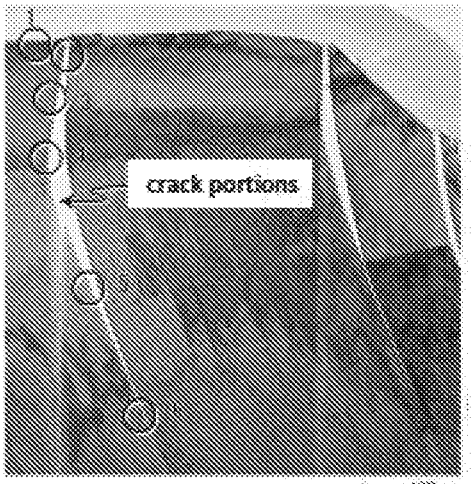
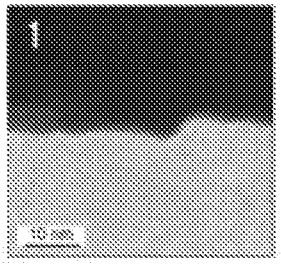


FIG. 37B1



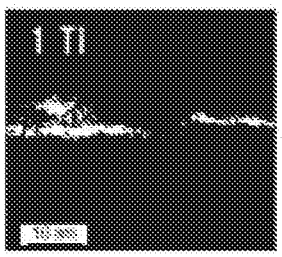
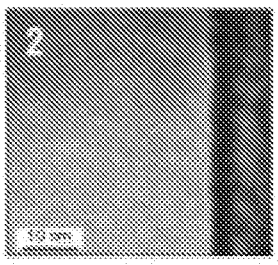


FIG. 37B2

FIG. 37C1



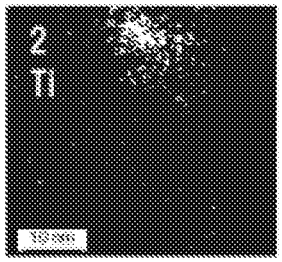
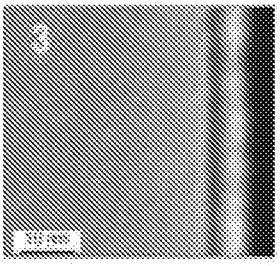


FIG. 37C2

FIG. 37D1



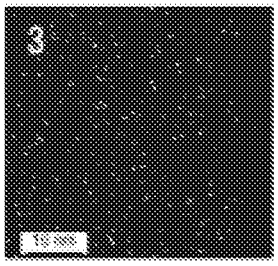
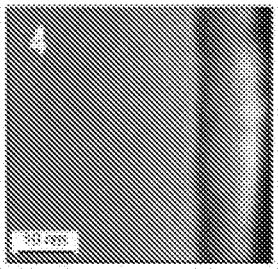


FIG. 37D2

FIG. 37E1



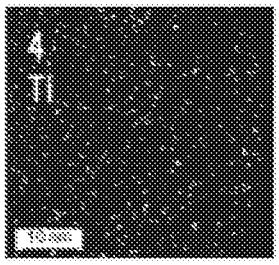


FIG. 37E2

after Ti heating (Sample07)

FIG. 38A

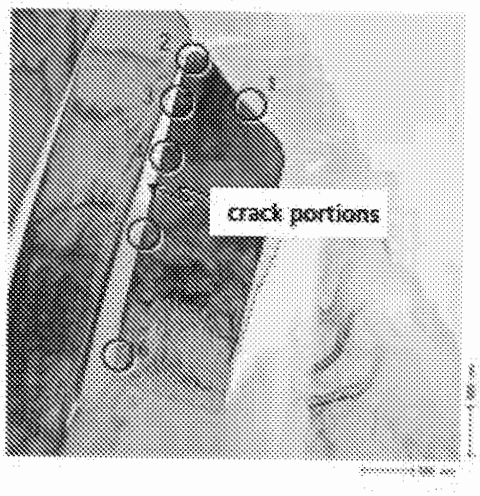
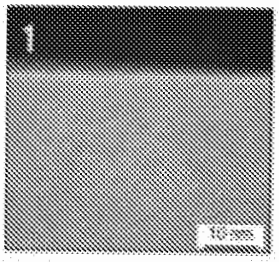


FIG. 38B1



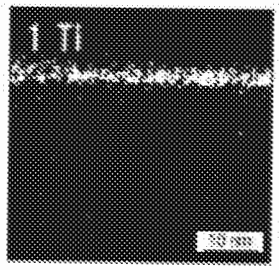
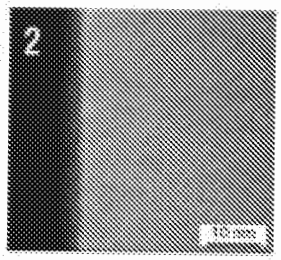


FIG. 38B2

FIG. 38C1



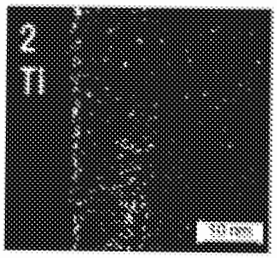
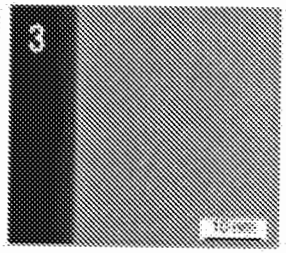


FIG. 38C2

FIG. 38D1



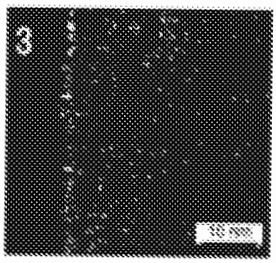
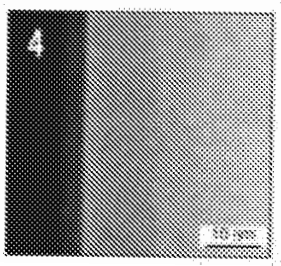


FIG. 38D2

FIG. 38E1



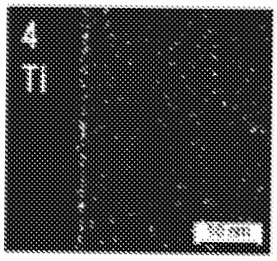


FIG. 38E2

before Mg heating (Sample06)

FIG. 39A

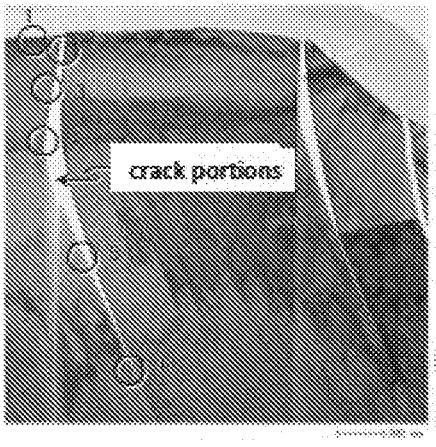


FIG. 39B1

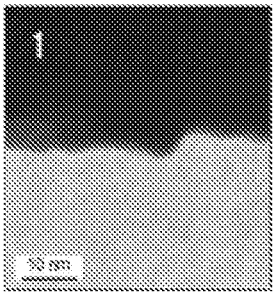


FIG. 39B2

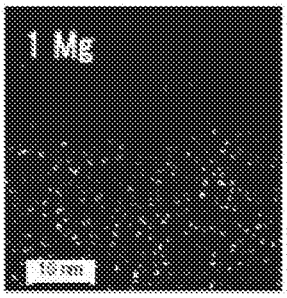


FIG. 39C1

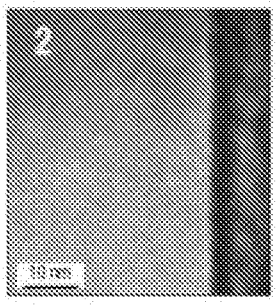


FIG. 39C2

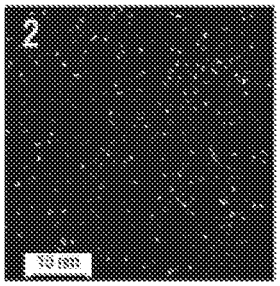


FIG. 39D1

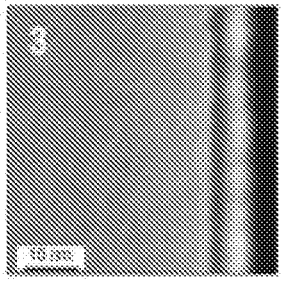


FIG. 39D2

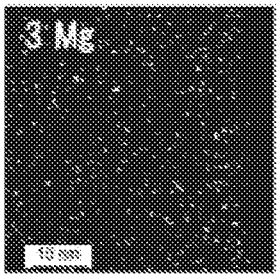


FIG. 39E1

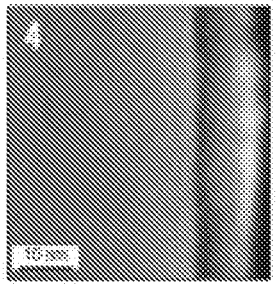
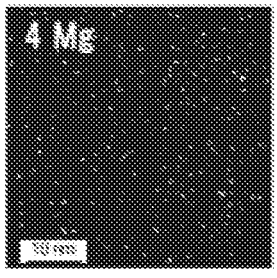


FIG. 39E2



after Mg heating (Sample07)

FIG. 40A

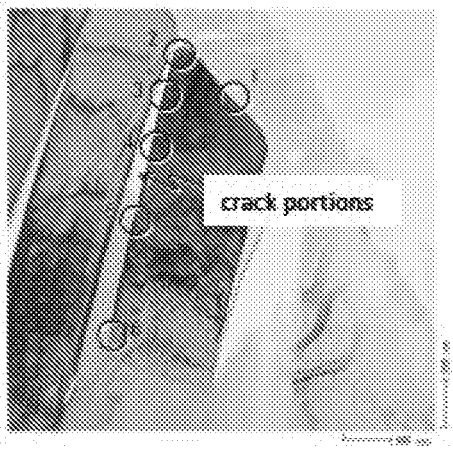


FIG. 40B1

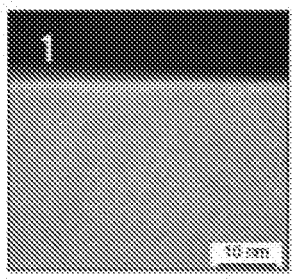


FIG. 40B2

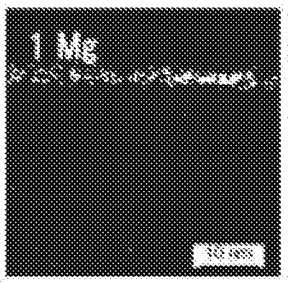


FIG. 40C1

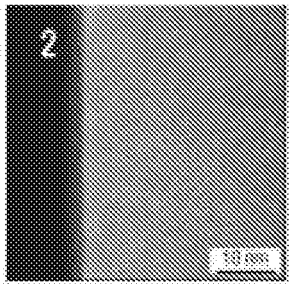


FIG. 40C2

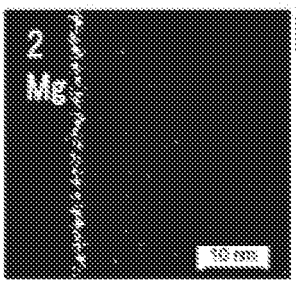


FIG. 40D1

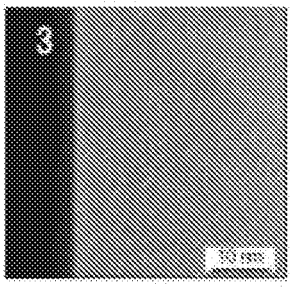


FIG. 40D2

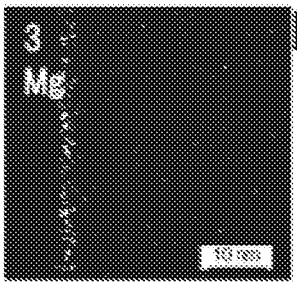


FIG. 40E1

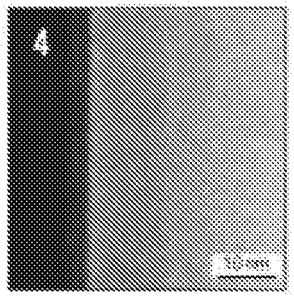
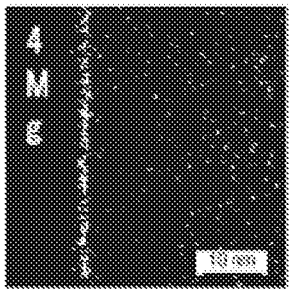


FIG. 40E2



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FIG. 41A

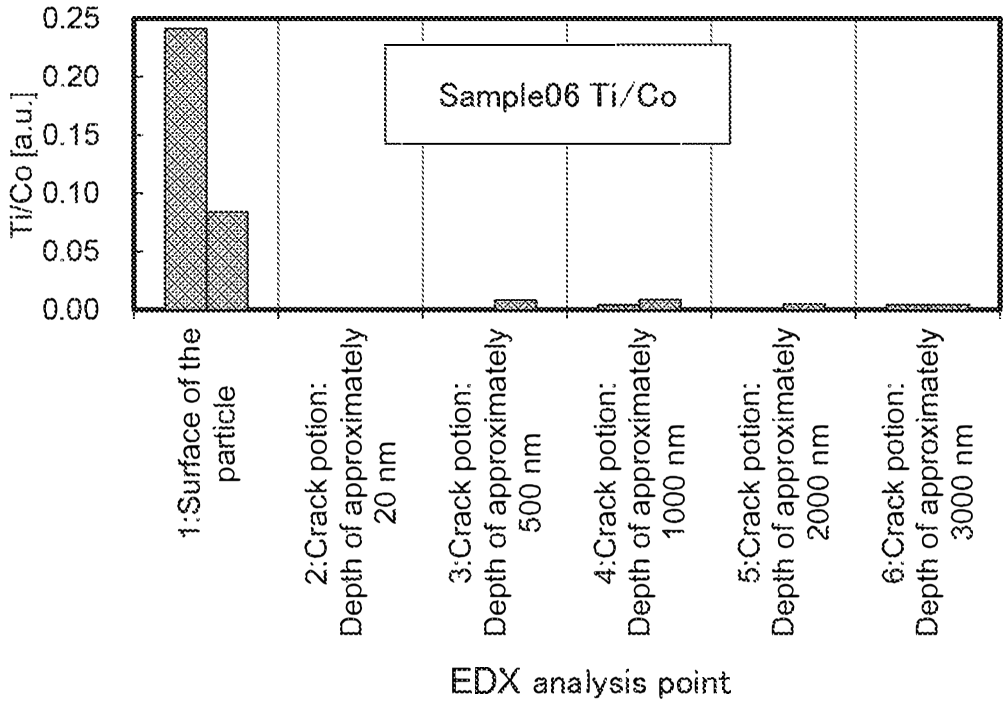
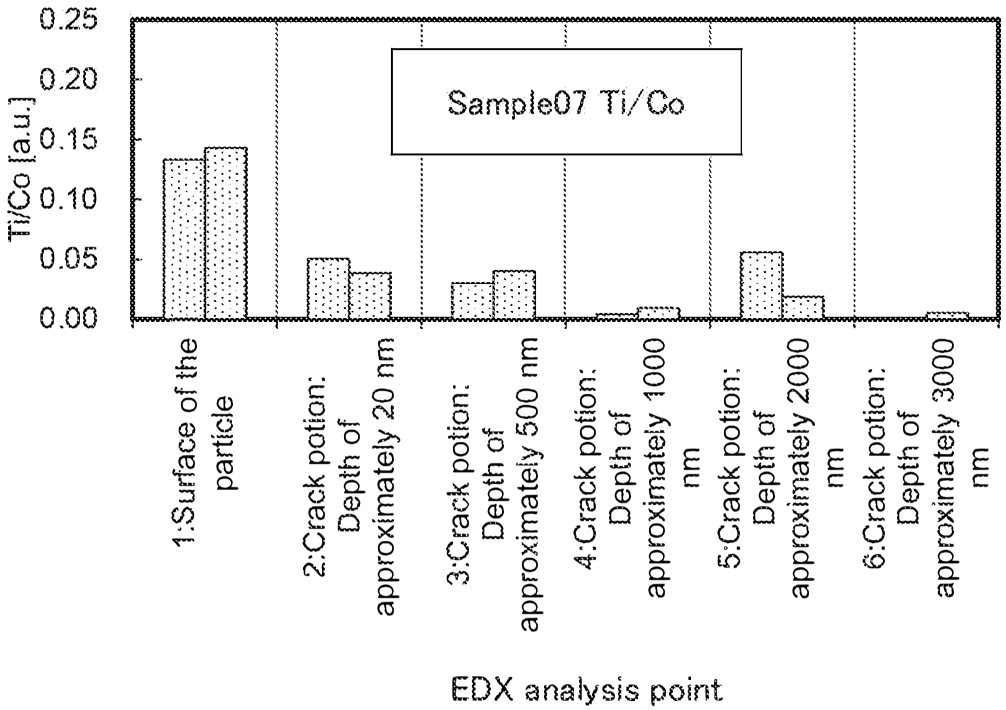


FIG. 41B



AMPEREX Ex. 1002
Page 160

FIG. 42A

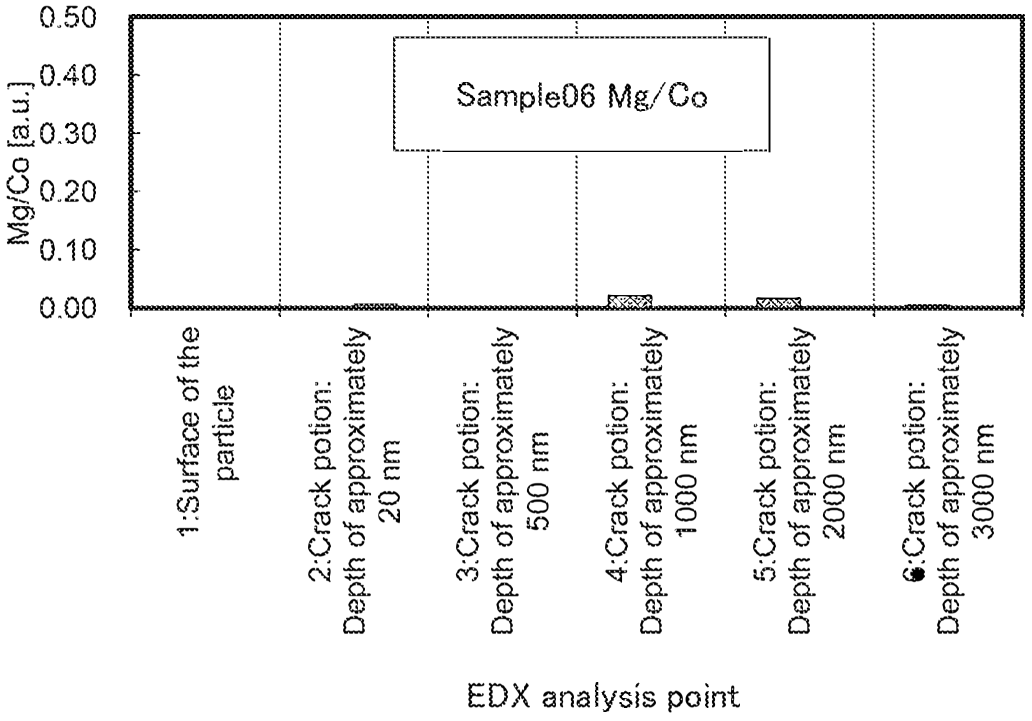


FIG. 42B

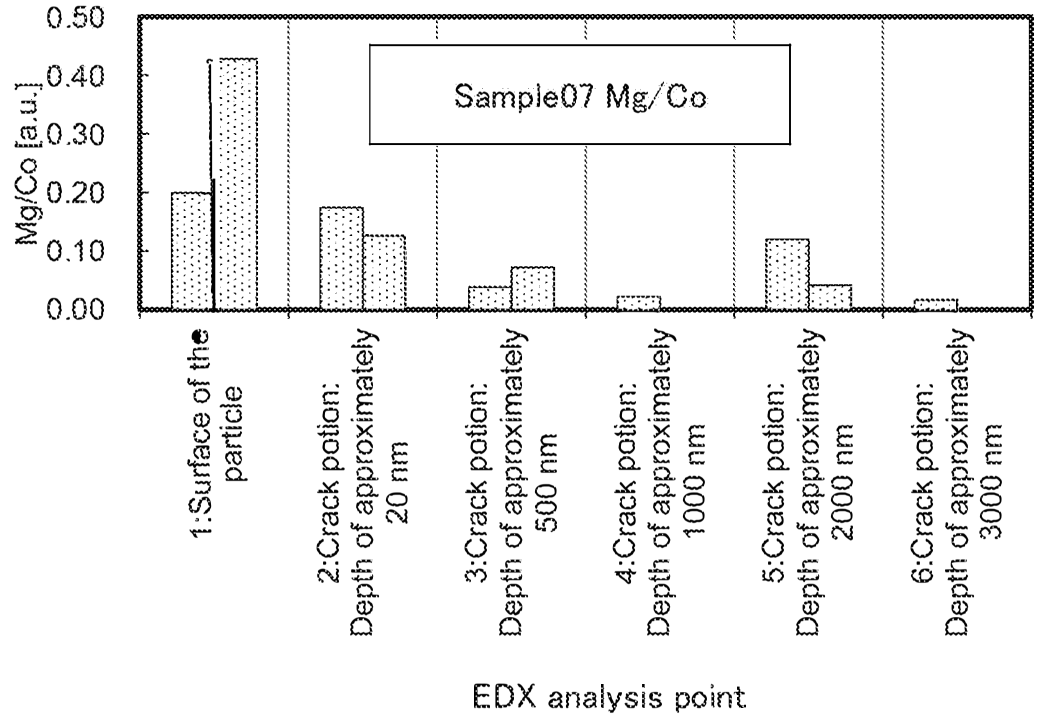


FIG. 43

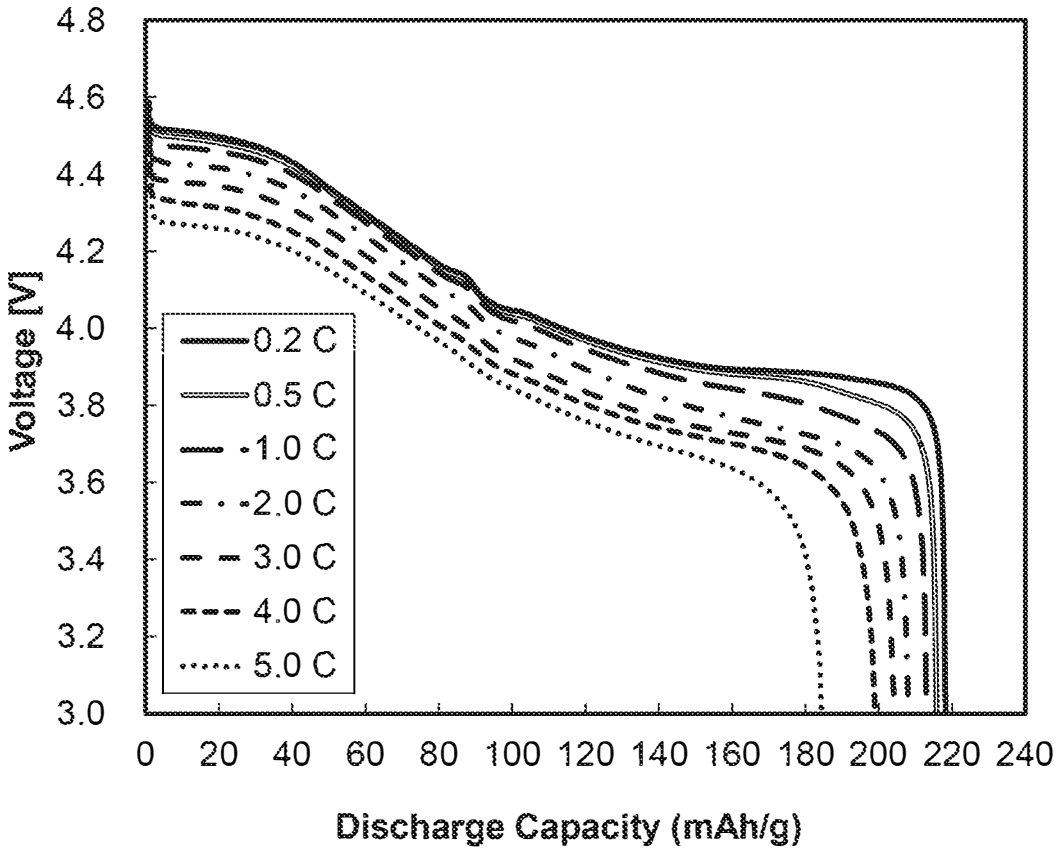

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
Voltage [V]
0.2 C
0.5 C
1.0 C
2.0 C
3.0 C
4.0 C
5.0 C
0
20
40
60
80
100
120
140
160
180
200
220
240
Discharge Capacity (mAh/g)

FIG. 44

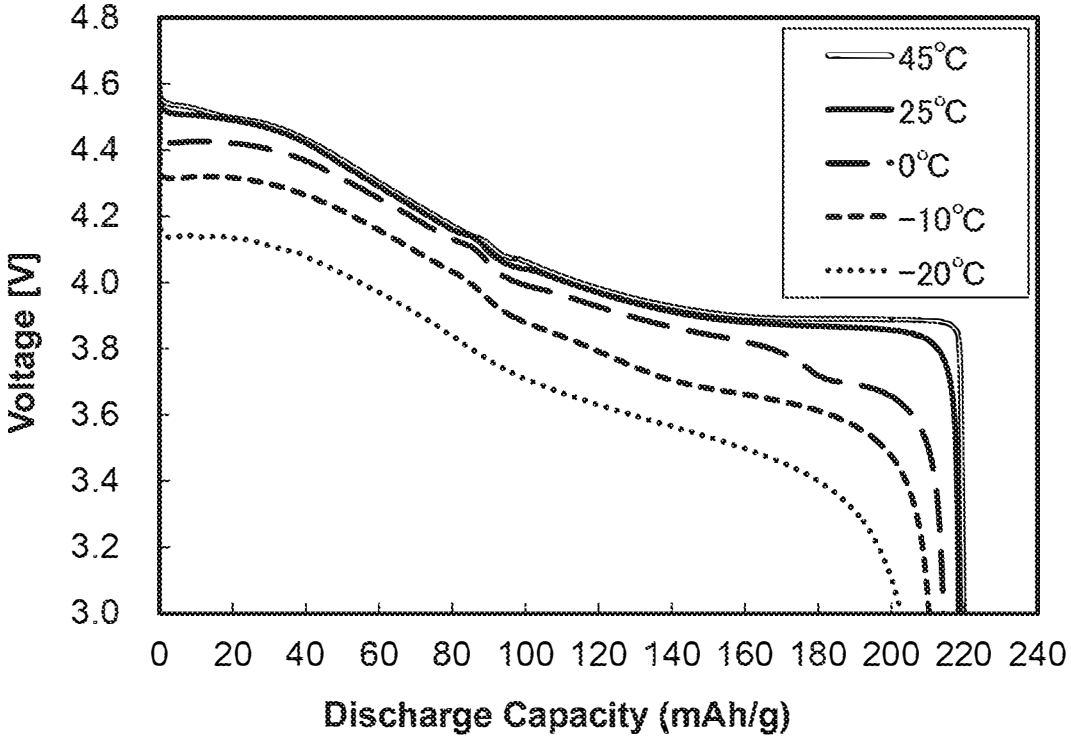
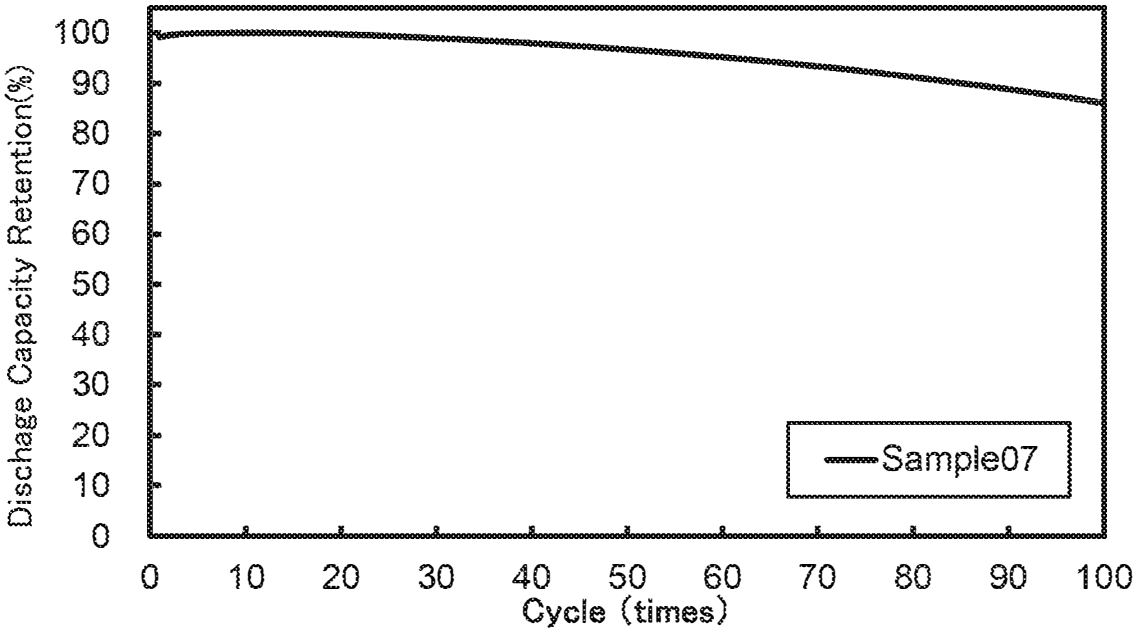

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
Voltage [V]
0
20
40
60
80
100
120
140
160
180
200
220
240
Discharge Capacity (mAh/g)
45°C
25°C
0°C
-10°C
-20°C

FIG. 45


Dischage Capacity Retention(%)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
Cycle (times)
Sample07

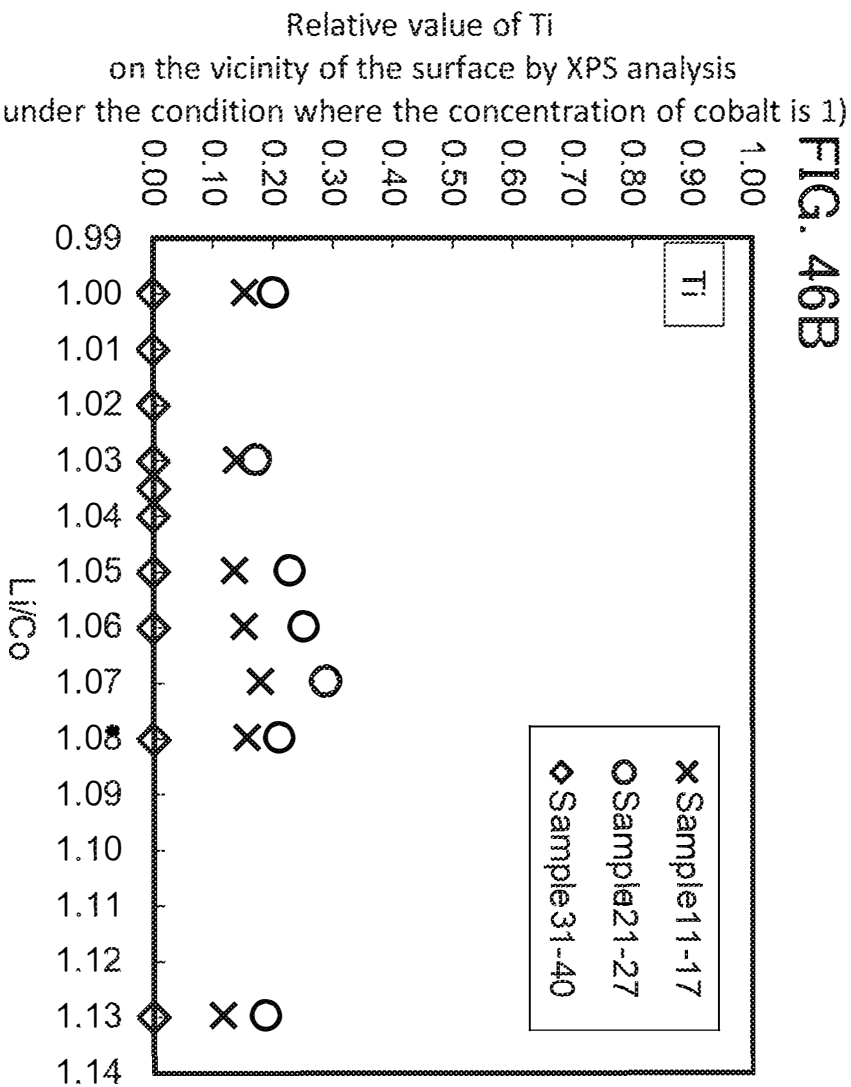


FIG. 46B

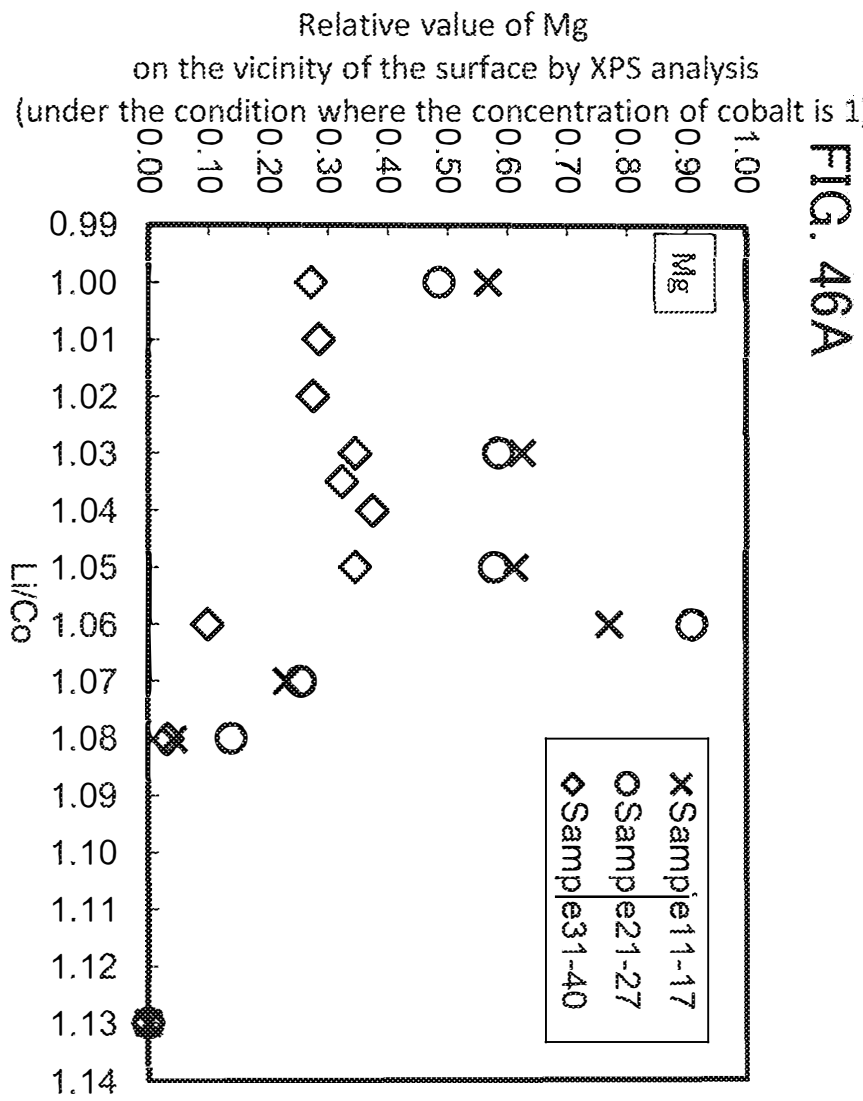


FIG. 46A

FIG. 47A

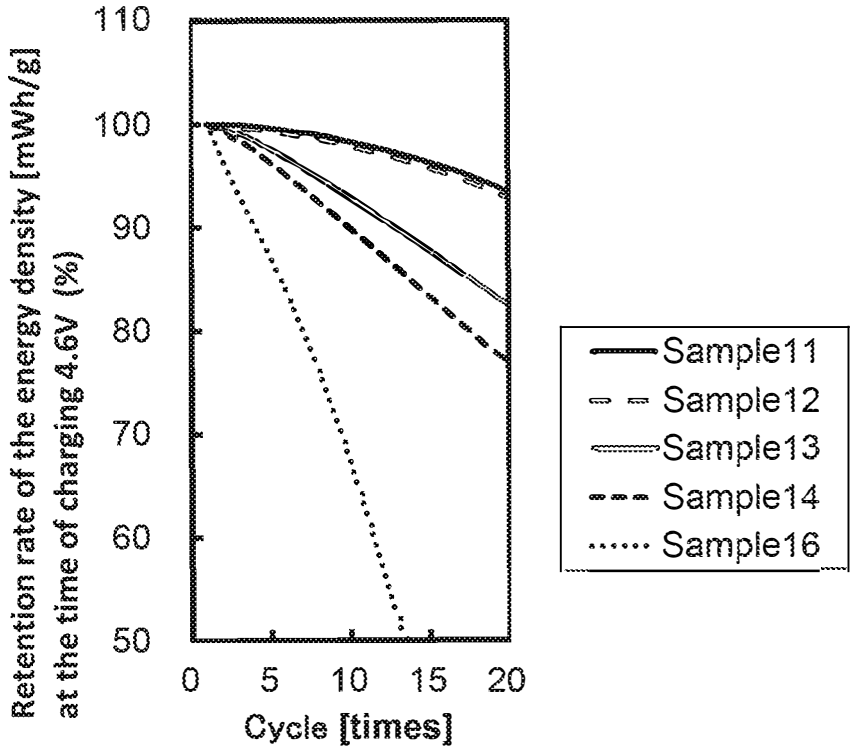


FIG. 47B

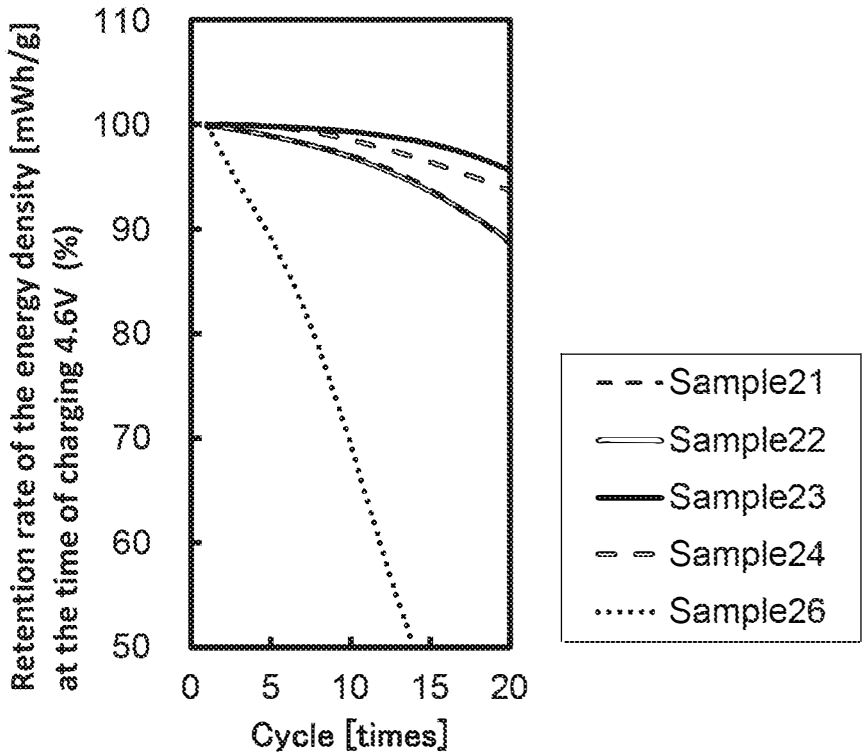


FIG. 48

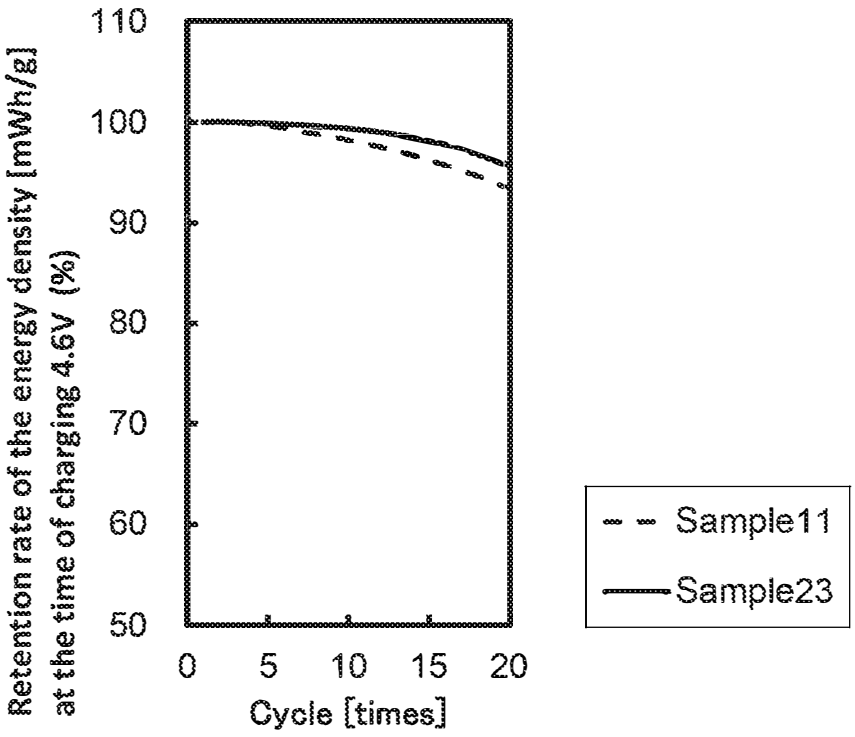

110
100
90
80
70
60
50
Retention rate of the energy density [mWh/g] at the time of charging 4.6V (%)
0
5
10
15
20
Cycle [times]
Sample11
Sample23

FIG. 49

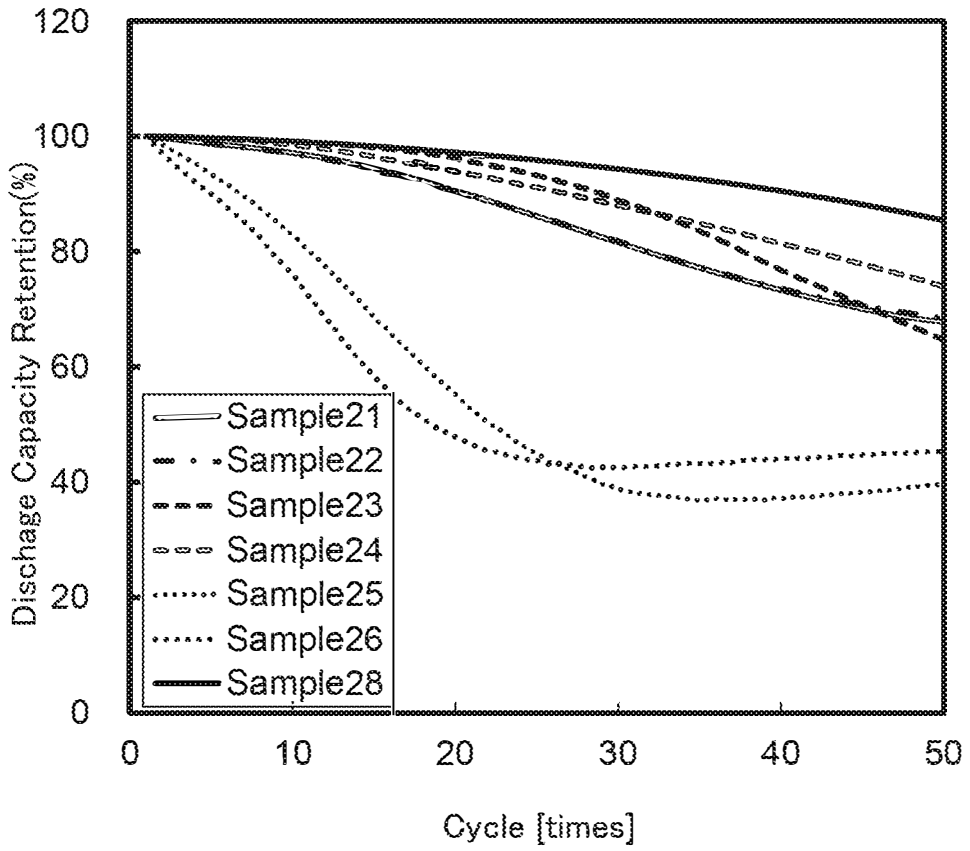

120
100
80
60
40
20
0
Dischage Capacity Retention(%)
0
10
20
30
40
50
Cycle [times]
Sample21
Sample22
Sample23
Sample24
Sample25
Sample26
Sample28

FIG. 50A

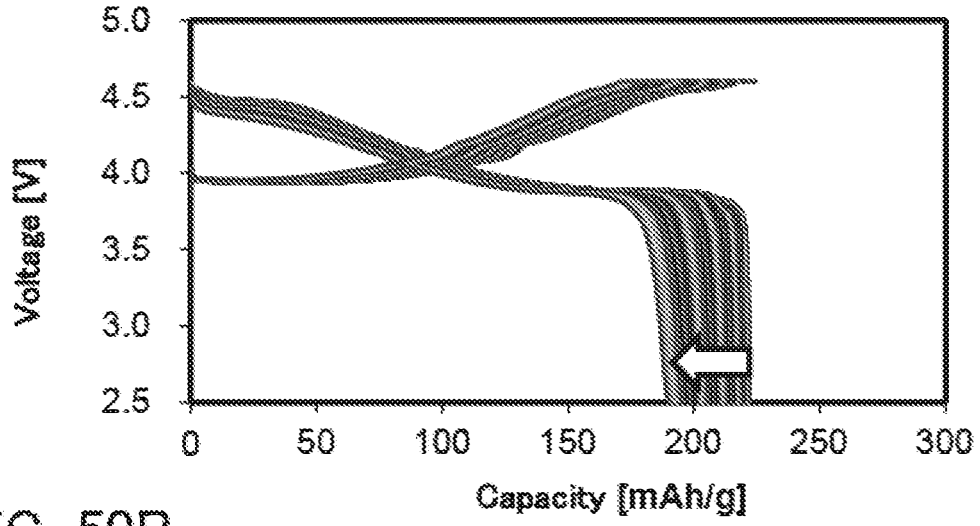


FIG. 50B

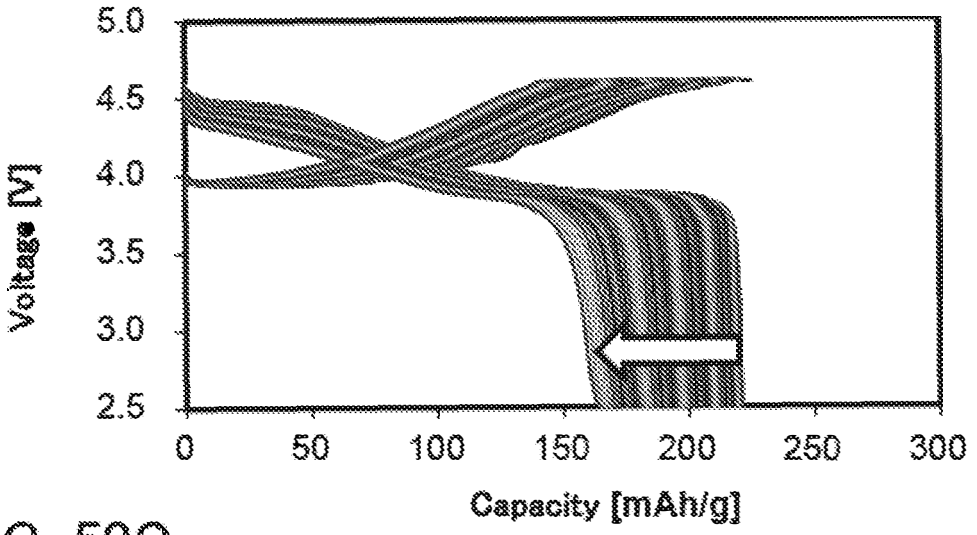


FIG. 50C

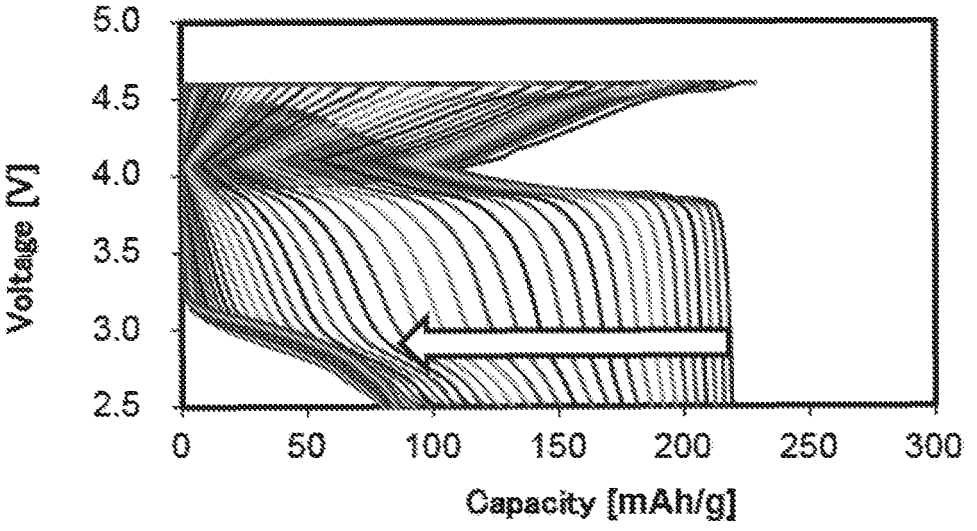


FIG. 51A

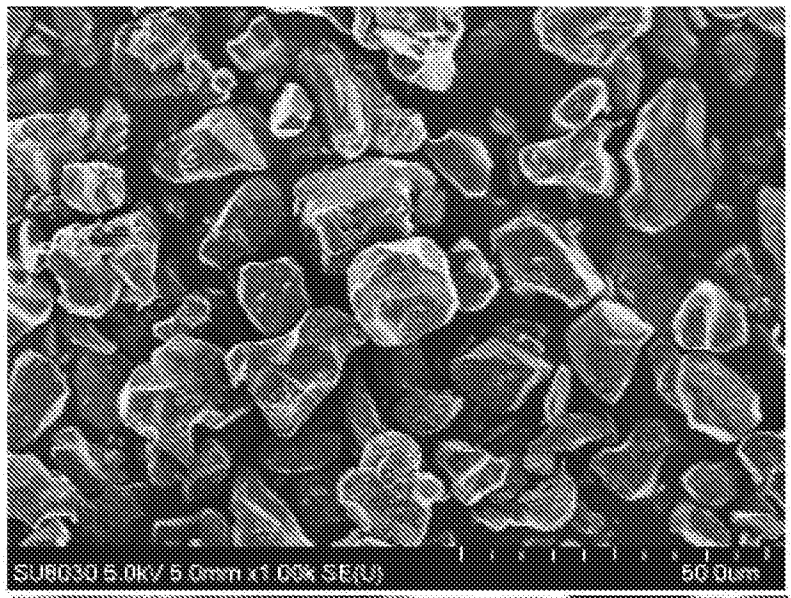


FIG. 51B

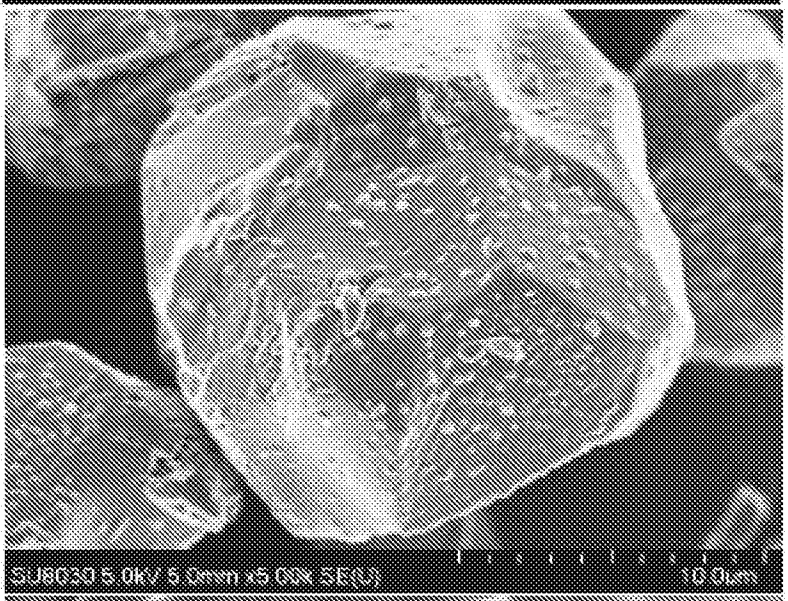


FIG. 51C

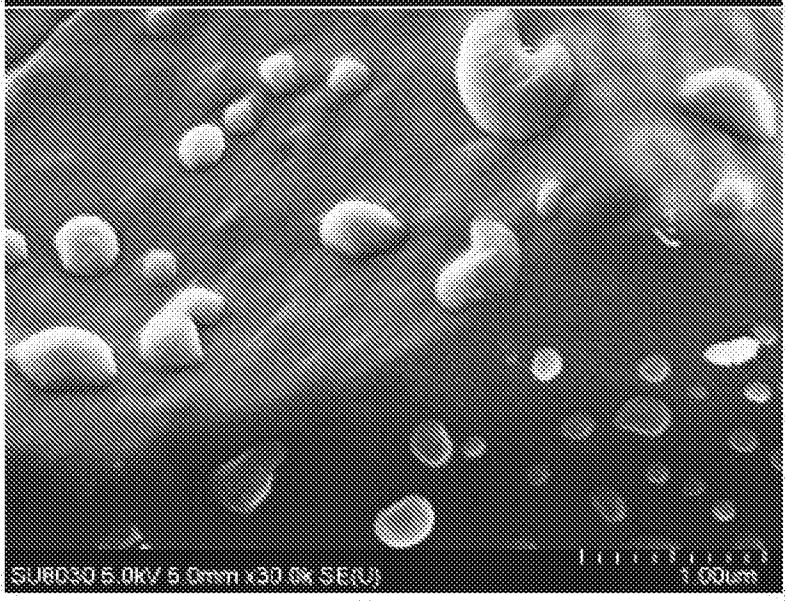


FIG. 52A-1

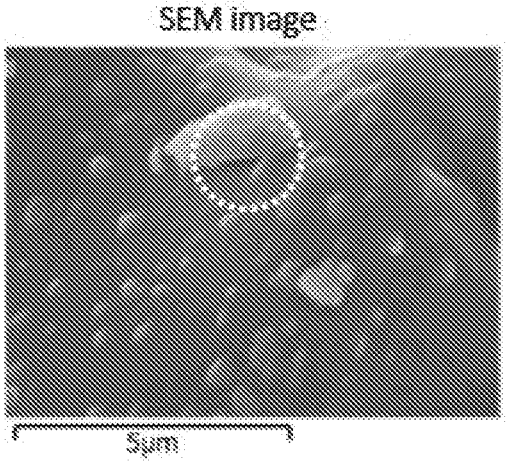


FIG. 52A-2

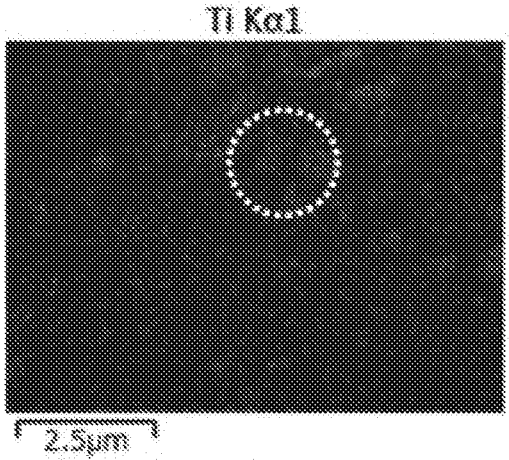


FIG. 52B-1

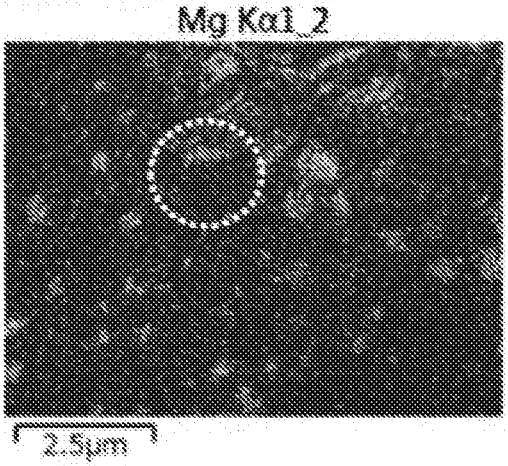


FIG. 52B-2

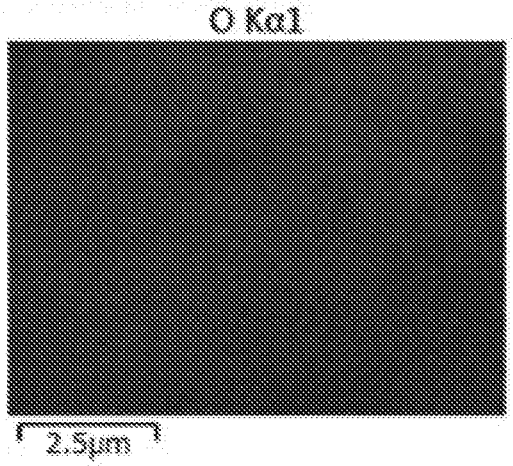


FIG. 52C-1

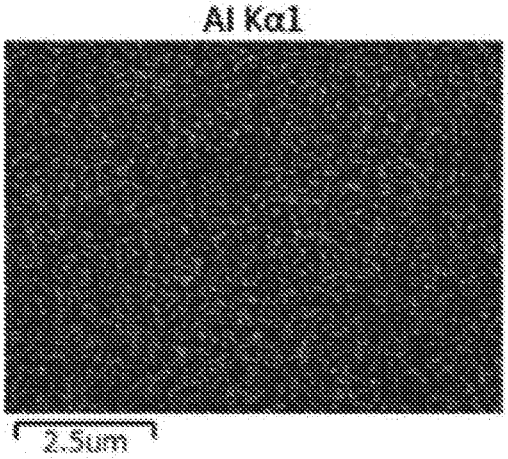


FIG. 52C-2

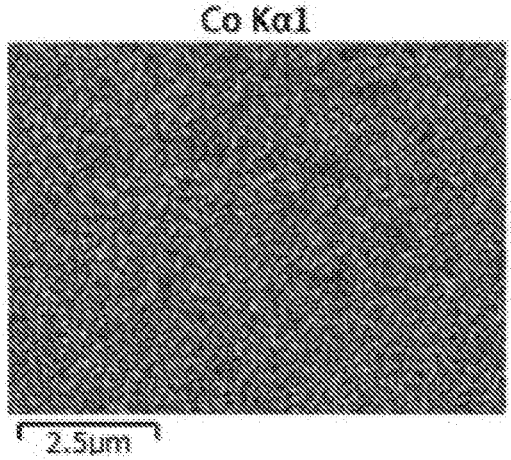


FIG. 53

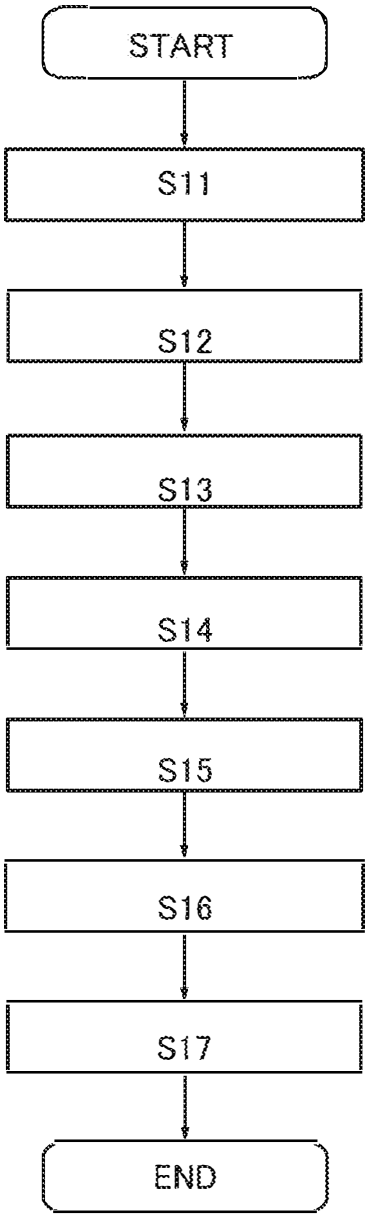


FIG. 54

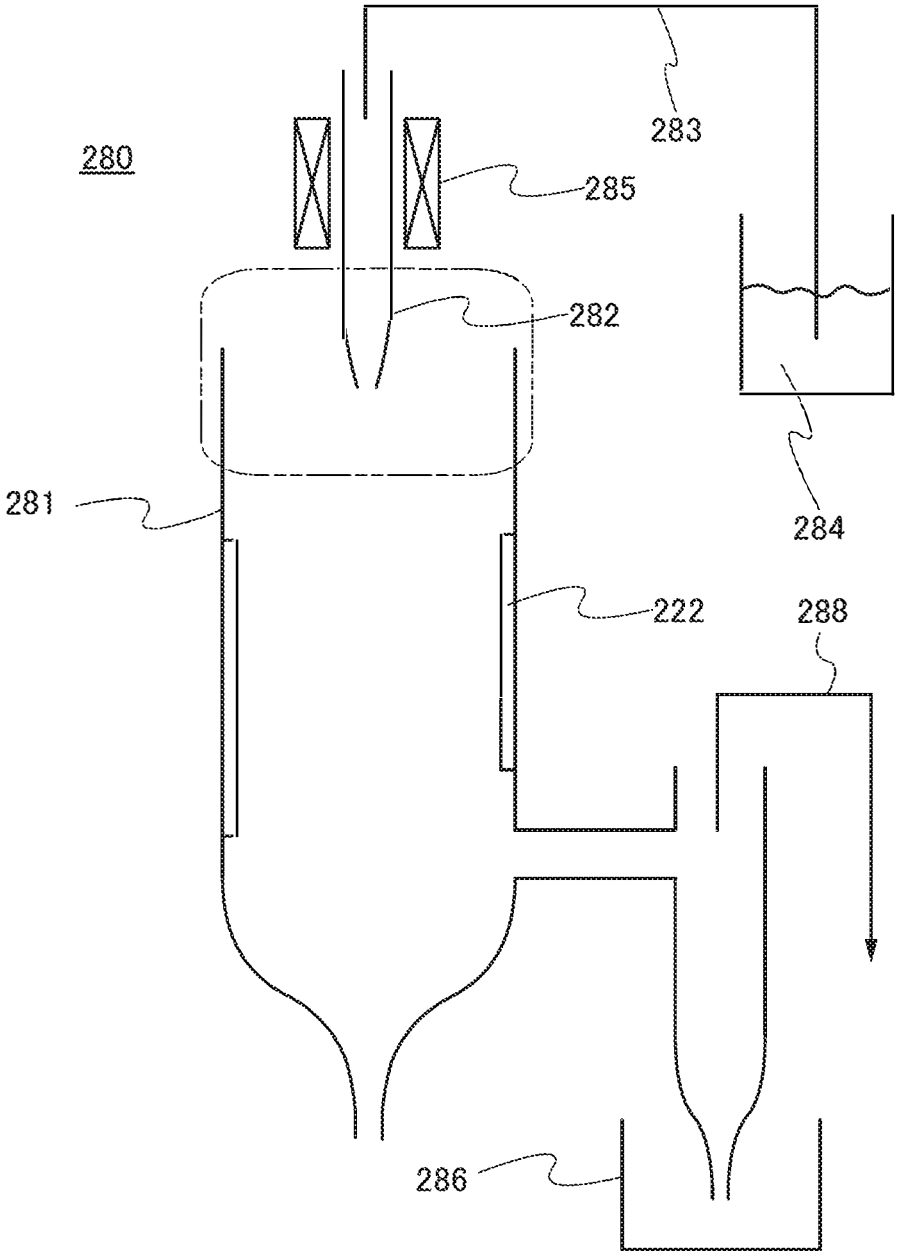


FIG. 55

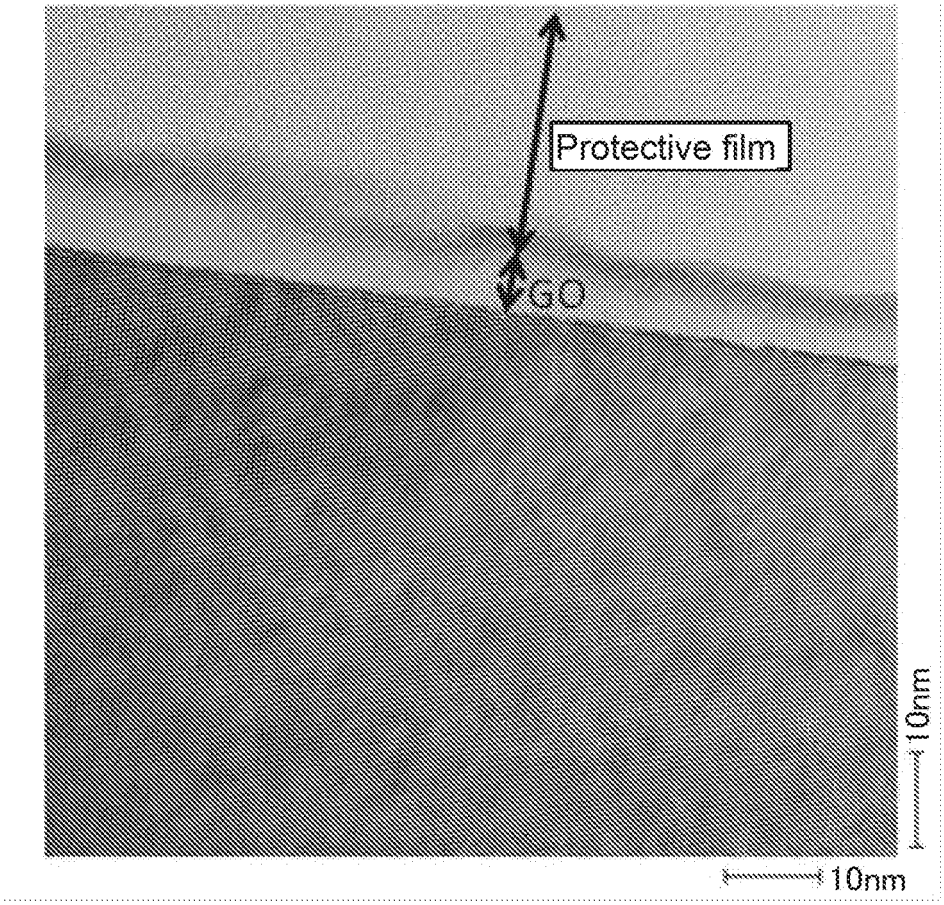


FIG. 56

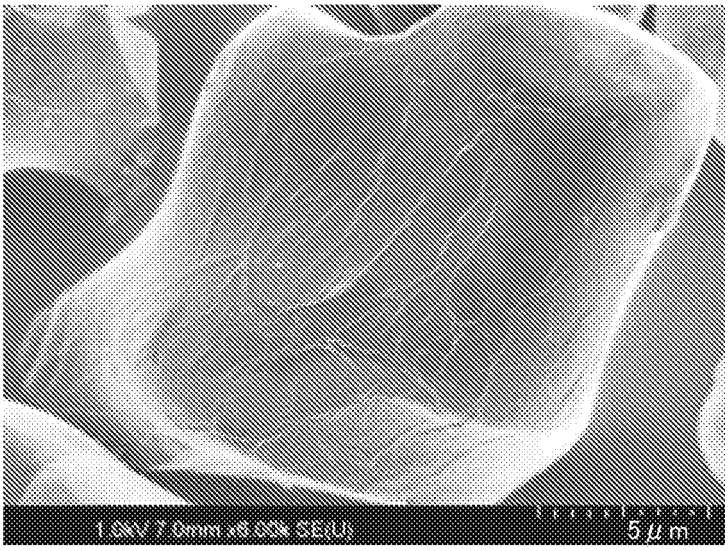


FIG. 57

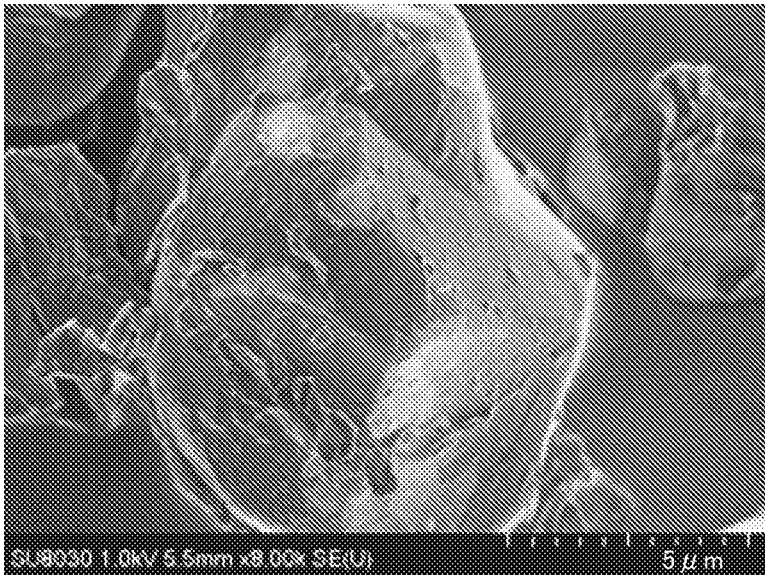


FIG. 58A

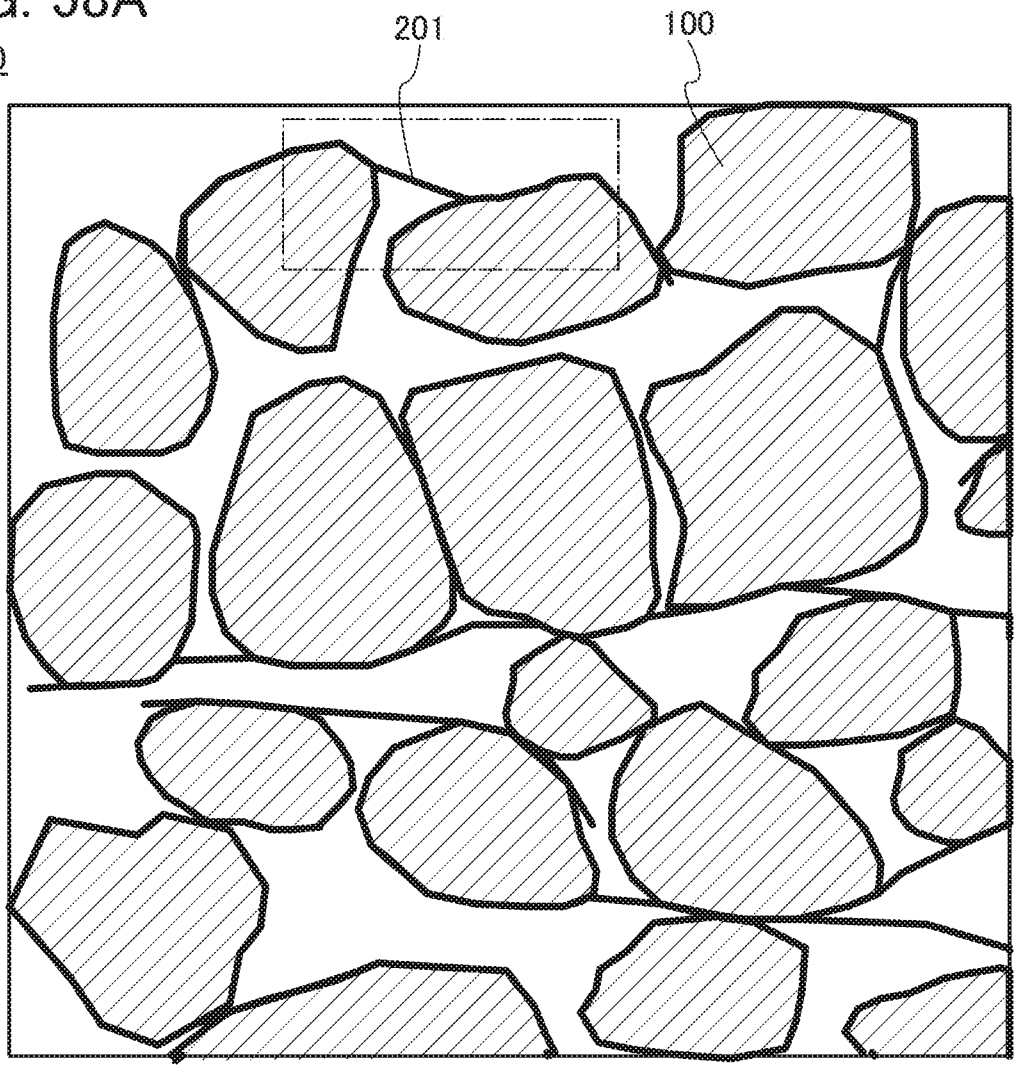
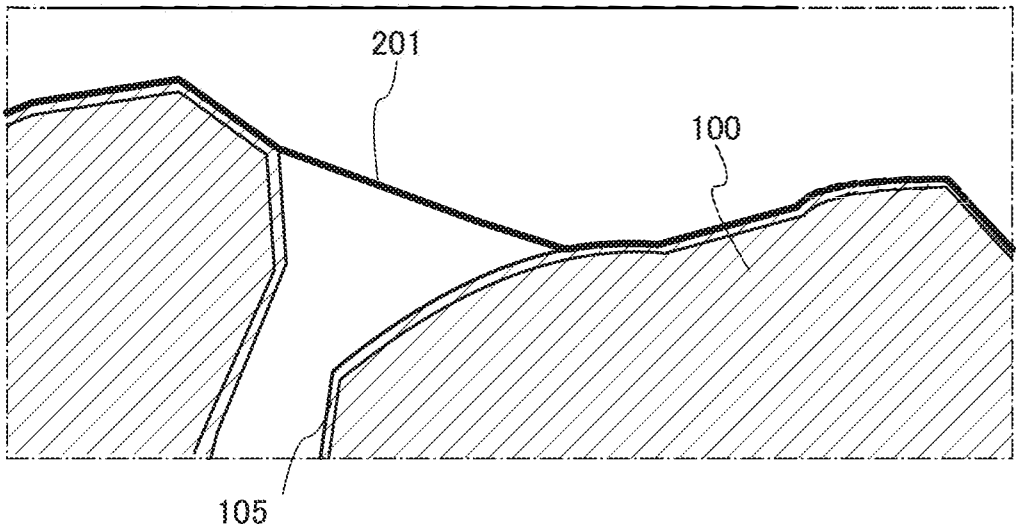


FIG. 58B



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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	740756-004563
	Application Number	
Title of Invention	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Teruaki		OCHIAI	

Residence Information (Select One) US Residency ● Non US Residency Active US Military Service

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Mailing Address of Inventor:

Address 1	c/o Semiconductor Energy Laboratory Co., Ltd.
Address 2	398, Hase
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State/Province	
Postal Code	243-0036
Country i	JP

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Takahiro		KAWAKAMI	

Residence Information (Select One) US Residency ◉ Non US Residency Active US Military Service

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Mailing Address of Inventor:

Address 1	1-28-13, Nurumizunishi
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City	Atsugi-shi, Kanagawa-ken
State/Province	
Postal Code	243-0039
Country i	JP

Inventor 3 Remove

Legal Name

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	740756-004563
	Application Number	
Title of Invention	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY	

Prefix	Given Name	Middle Name	Family Name	Suffix
	Mayumi		MIKAMI	

Residence Information (Select One) US Residency ◉ Non US Residency Active US Military Service

City	Atsugi, Kanagawa	Country of Residence i	JP

Mailing Address of Inventor:

Address 1	c/o Semiconductor Energy Laboratory Co., Ltd.		
Address 2	398, Hase		
City	Atsugi-shi, Kanagawa-ken	State/Province	
Postal Code	243-0036	Country i	JP

Inventor 4 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Yohei		MOMMA	

Residence Information (Select One) US Residency ◉ Non US Residency Active US Military Service

City	Isehara, Kanagawa	Country of Residence i	JP

Mailing Address of Inventor:

Address 1	c/o Semiconductor Energy Laboratory Co., Ltd.		
Address 2	398, Hase		
City	Atsugi-shi, Kanagawa-ken	State/Province	
Postal Code	243-0036	Country i	JP

Inventor 5 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Masahiro		TAKAHASHI	

Residence Information (Select One) US Residency ◉ Non US Residency Active US Military Service

City	Atsugi, Kanagawa	Country of Residence i	JP

Mailing Address of Inventor:

Address 1	c/o Semiconductor Energy Laboratory Co., Ltd.		
Address 2	398, Hase		
City	Atsugi-shi, Kanagawa-ken	State/Province	
Postal Code	243-0036	Country i	JP

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	740756-004563
	Application Number	
Title of Invention	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY	

Inventor 6 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Ayae		TSURUTA	

Residence Information (Select One) US Residency ◉ Non US Residency Active US Military Service

City	Atsugi, Kanagawa	Country of Residence i	JP

Mailing Address of Inventor:

Address 1	c/o Semiconductor Energy Laboratory Co., Ltd.		
Address 2	398, Hase		
City	Atsugi-shi, Kanagawa-ken	**State/Province**	
Postal Code	243-0036	**Country** i	JP

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	22204		
Email Address		Add Email	Remove Email

Application Information:

Title of the Invention	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY		
Attorney Docket Number	740756-004563	**Small Entity Status Claimed**	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)		**Suggested Figure for Publication (if any)**	

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	740756-004563
	Application Number	
Title of Invention	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY	

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	● Customer Number	US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)
Customer Number	22204		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the "Application Number" field blank.

Prior Application Status			Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button. Add

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	740756-004563
	Application Number	
Title of Invention	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY	

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
2016-133997	JP	2016-07-06	

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
2016-133143	JP	2016-07-05	

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
2017-002831	JP	2017-01-11	

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
2017-030693	JP	2017-02-22	

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
2017-084321	JP	2017-04-21	

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
2017-119272	JP	2017-06-19	

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button. Add

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	740756-004563
	Application Number	
Title of Invention	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY	

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	740756-004563
	Application Number	
Title of Invention	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY	

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1 Remove

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

● Assignee	Legal Representative under 35 U.S.C. 117	Joint Inventor
Person to whom the inventor is obligated to assign.	Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor:

If the Applicant is an Organization check here. ☒

Organization Name	SEMICONDUCTOR ENERGY LABORATORY CO., LTD.		
Mailing Address Information For Applicant:			
Address 1	398, Hase		
Address 2			
City	Atsugi-shi, Kanagawa-ken	**State/Province**	
Country	JP	Postal Code	243-0036
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button. Add

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	740756-004563
	Application Number	
Title of Invention	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY	

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

Remove

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		**State/Province**	
Country i		Postal Code	
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button. Add

Signature:

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NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is a **juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	/Jeffrey L. Costellia, Reg. No. 35,483/			Date (YYYY-MM-DD)	2017-06-30
First Name	Jeffrey L.	Last Name	Costellia	Registration Number	35483

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	740756-004563
	Application Number	
Title of Invention	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY	

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The information provided by you in this form will be subject to the following routine uses:

1 The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3 A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the PatentCooperationTreaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY
First Named Inventor/Applicant Name:	Teruaki OCHIAI
Filer:	Jeffrey Costellia/donald sias
Attorney Docket Number:	740756-004563

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
UTILITY APPLICATION FILING	1011	1	280	280
UTILITY SEARCH FEE	1111	1	600	600
UTILITY EXAMINATION FEE	1311	1	720	720
Pages:				
UTILITY APPL SIZE FEE PER 50 SHEETS >100	1081	1	400	400
Claims:				
CLAIMS IN EXCESS OF 20	1202	2	80	160
INDEPENDENT CLAIMS IN EXCESS OF 3	1201	1	420	420

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous-Filing:				
LATE FILING FEE FOR OATH OR DECLARATION	1051	1	140	140
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**2720**

Electronic Acknowledgement Receipt

EFS ID:	29649048
Application Number:	15638449
International Application Number:	
Confirmation Number:	1074
Title of Invention:	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY
First Named Inventor/Applicant Name:	Teruaki OCHIAI
Customer Number:	22204
Filer:	Jeffrey Costellia/donald sias
Filer Authorized By:	Jeffrey Costellia
Attorney Docket Number:	740756-004563
Receipt Date:	30-JUN-2017
Filing Date:	
Time Stamp:	09:13:15
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$2720
RAM confirmation Number	063017INTEFSW00009350192380
Deposit Account	
Authorized User	

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		740756_004563_Specification.pdf	824796 8469fd871cf7bb01a87f1d4d2ed6dec6afebd298	yes	118
	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	
	Specification		1	112	
	Claims		113	117	
	Abstract		118	118	
Warnings:					
Information:					
2	Drawings-only black and white line drawings	740756_004563_Drawings.pdf	19980840 8d3dd96e52270c8b4708cb5c85f3967e8d15f18d	no	58
Warnings:					
Information:					
3	Application Data Sheet	740756_004563_Application_Data_Sheet.pdf	1830031 ee83a21d98f0012214fedeb6c7577244b5981382	no	10
Warnings:					
Information:					
4	Fee Worksheet (SB06)	fee-info.pdf	41406 998b2b0f9bed55d810bb337a6195399fe1def8e9	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	22677073		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

SCORE Placeholder Sheet for IFW Content

Application Number: 15638449 Document Date: 06/30/2017

The presence of this form in the IFW record indicates that the following document type was received in electronic format on the date identified above. This content is stored in the SCORE database.

- Drawings – Other than Black and White Line Drawings

Since this was an electronic submission, there is no physical artifact folder, no artifact folder is recorded in PALM, and no paper documents or physical media exist. The TIFF images in the IFW record were created from the original documents that are stored in SCORE.

To access the documents in the SCORE database, refer to instructions below.

At the time of document entry (noted above):

- Examiners may access SCORE content via the eDAN interface.
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- External customers may access SCORE content via the Public and Private PAIR interfaces.

Form Revision Date: September 30, 2013

UNITED STATES PATENT AND TRADEMARK OFFICE

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United States Patent and Trademark Office
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www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
15/638,449	06/30/2017	Teruaki OCHIAI	740756-004563

CONFIRMATION NO. 1074

22204
NIXON PEABODY, LLP
799 Ninth Street, NW
SUITE 500
WASHINGTON, DC 20001

INFORMAL NOTICE

OC000000092845243

Date Mailed: 07/19/2017

INFORMATIONAL NOTICE TO APPLICANT

Applicant is notified that the above-identified application contains the deficiencies noted below. No period for reply is set forth in this notice for correction of these deficiencies. However, if a deficiency relates to the inventor's oath or declaration, the applicant must file an oath or declaration in compliance with 37 CFR 1.63, or a substitute statement in compliance with 37 CFR 1.64, executed by or with respect to each actual inventor no later than the expiration of the time period set in the "Notice of Allowability" to avoid abandonment. See 37 CFR 1.53(f).

The item(s) indicated below are also required and should be submitted with any reply to this notice to avoid further processing delays.

- A properly executed inventor's oath or declaration has not been received for the following inventor(s):
  Teruaki OCHIAI
  Takahiro KAWAKAMI
  Mayumi MIKAMI
  Yohei MOMMA
  Masahiro TAKAHASHI
  Ayae TSURUTA

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/kung/

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 15/638,449

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	280
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	600
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	720
TOTAL CLAIMS (37 CFR 1.16(i))	22 minus 20 =	* 2			OR	x 80 =	160
INDEPENDENT CLAIMS (37 CFR 1.16(h))	4 minus 3 =	* 1				x 420 =	420
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						400
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	2580

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
15/638,449	06/30/2017	2811	2720	740756-004563	22	4

CONFIRMATION NO. 1074

22204
NIXON PEABODY, LLP
799 Ninth Street, NW
SUITE 500
WASHINGTON, DC 20001

FILING RECEIPT



Date Mailed: 07/19/2017

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

Teruaki OCHIAI, Atsugi, JAPAN;
Takahiro KAWAKAMI, Atsugi, JAPAN;
Mayumi MIKAMI, Atsugi, JAPAN;
Yohei MOMMA, Isehara, JAPAN;
Masahiro TAKAHASHI, Atsugi, JAPAN;
Ayae TSURUTA, Atsugi, JAPAN;

Applicant(s)

SEMICONDUCTOR ENERGY LABORATORY CO., LTD., Atsugi-shi, JAPAN;

Power of Attorney: None

Domestic Applications for which benefit is claimed - None.
A proper domestic benefit claim must be provided in an Application Data Sheet in order to constitute a claim for domestic benefit. See 37 CFR 1.76 and 1.78.

Foreign Applications (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.)
JAPAN 2016-133997 07/06/2016
JAPAN 2016-133143 07/05/2016
JAPAN 2017-002831 01/11/2017
JAPAN 2017-030693 02/22/2017
JAPAN 2017-084321 04/21/2017
JAPAN 2017-119272 06/19/2017

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

Request to Retrieve - This application either claims priority to one or more applications filed in an intellectual property Office that participates in the Priority Document Exchange (PDX) program or contains a proper **Request to Retrieve Electronic Priority Application(s)** (PTO/SB/38 or its equivalent). Consequently, the USPTO will attempt to electronically retrieve these priority documents.

If Required, Foreign Filing License Granted: 07/18/2017

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 15/638,449**

Projected Publication Date: 01/11/2018

Non-Publication Request: No

Early Publication Request: No

Title

POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY

Preliminary Class

257

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign

patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

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No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

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日 本 国 特 許 庁
JAPAN PATENT OFFICE

別紙添付の書類に記載されている事項は下記の出願書類に記載されている事項と同一であることを証明する。

This is to certify that the annexed is a true copy of the following application as filed with this Office.

出願年月日 Date of Application:	２０１６年　７月　６日
出願番号 Application Number:	特願２０１６－１３３９９７
パリ条約による外国への出願に用いる優先権の主張の基礎となる出願の国コードと出願番号 The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is	ＪＰ２０１６－１３３９９７
出願人 Applicant(s):	株式会社半導体エネルギー研究所

２０１７年　８月１５日

特許庁長官
Commissioner,
Japan Patent Office　宗像直

【書類名】　特許願
【整理番号】　P024652
【提出日】　平成28年 7月 6日
【あて先】　特許庁長官　殿
【発明者】
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　【識別番号】　000153878
　【氏名又は名称】　株式会社半導体エネルギー研究所
　【代表者】　山崎　舜平
【手数料の表示】
　【振替番号】　00003528
　【納付金額】　14,000円
【提出物件の目録】
　【物件名】　明細書　1
　【物件名】　特許請求の範囲　1
　【物件名】　要約書　1
　【物件名】　図面　1

【書類名】明細書
【発明の名称】正極活物質、正極活物質の作製方法、および二次電池
【技術分野】
【０００１】
本発明の一様態は、物、方法、又は、製造方法に関する。または、本発明は、プロセス、マシン、マニュファクチャ、又は、組成物（コンポジション・オブ・マター）に関する。本発明の一態様は、半導体装置、表示装置、発光装置、蓄電装置、照明装置または電子機器の製造方法に関する。特に、電子機器およびそのオペレーティングシステムに関する。
【０００２】
なお、本明細書中において、蓄電装置とは、蓄電機能を有する素子及び装置全般を指すものである。例えば、リチウムイオン二次電池などの蓄電池（二次電池ともいう）、リチウムイオンキャパシタ、及び電気二重層キャパシタなどを含む。
【０００３】
また、本明細書中において電子機器とは、蓄電装置を有する装置全般を指し、蓄電装置を有する電気光学装置、蓄電装置を有する情報端末装置などは全て電子機器である。
【背景技術】
【０００４】
近年、リチウムイオン二次電池、リチウムイオンキャパシタ、空気電池等、種々の蓄電装置の開発が盛んに行われている。特に高出力、高エネルギー密度であるリチウムイオン二次電池は、携帯電話、スマートフォン、もしくはノート型コンピュータ等の携帯情報端末、携帯音楽プレーヤ、デジタルカメラ、医療機器、又は、ハイブリッド車（ＨＥＶ）、電気自動車（ＥＶ）、もしくはプラグインハイブリッド車（ＰＨＥＶ）等の次世代クリーンエネルギー自動車など、半導体産業の発展と併せて急速にその需要が拡大し、充電可能なエネルギーの供給源として現代の情報化社会に不可欠なものとなっている。
【０００５】
リチウムイオン二次電池に要求されている特性としては、さらなる高エネルギー密度化、サイクル特性の向上及び様々な動作環境での安全性、長期信頼性の向上などがある。たとえばサイクル特性の向上のためには、正極活物質の改良、負極活物質の改良、電解液の劣化抑制など、様々な面からのアプローチがありうる。正極活物質の改良としては、たとえば、特許文献１のように、正極活物質上に被覆層を設けることが行われている。
【先行技術文献】
【特許文献】
【０００６】
【特許文献１】特開２０１２―０１８９１４号公報
【発明の概要】
【発明が解決しようとする課題】
【０００７】
しかしリチウムイオン二次電池およびそれに用いられる正極活物質には、充放電特性、サイクル特性、信頼性、安全性、又はコストといった様々な面で改善の余地が残されている。
【０００８】
本発明の一態様は、リチウムイオン二次電池に用いることで、充放電サイクルにおける容量の低下が抑制される正極活物質を提供することを課題の一とする。本発明の一態様は、充放電特性の優れた二次電池を提供することを課題の一とする。または、本発明の一態様は、充放電サイクルにおける容量の低下が抑制された二次電池を提供することを課題の一とする。または、本発明の一態様は、安全性又は信頼性の高い二次電池を提供することを課題の一とする。
【０００９】
または、本発明の一態様は、新規な物質、活物質粒子、蓄電装置、又はそれらの作製方法を提供することを課題の一とする。

【００１０】
なお、これらの課題の記載は、他の課題の存在を妨げるものではない。なお、本発明の一態様は、これらの課題の全てを解決する必要はないものとする。なお、明細書、図面、請求項の記載から、これら以外の課題を抽出することが可能である。
【課題を解決するための手段】
【００１１】
上記目的を達成するために、本発明の一態様は、正極活物質表面に２種の被覆層を設け、内側の被覆層はゾルゲル法等の被覆工程を経て形成し、外側の被覆層は加熱に伴う析出によって形成することを特徴とする。
【００１２】
本発明の一態様は、第１の領域と、第１の領域の少なくとも一部を被覆する第２の領域と、第２の領域の少なくとも一部を被覆する第３の領域と、を有し、第１の領域はコバルト酸リチウムを有し、第２の領域はチタン酸リチウムを有し、第３の領域は酸化マグネシウムを有する正極活物質である。
【００１３】
上記において、第１の領域と、第２の領域の結晶の配向が一部で一致し、第２の領域と、第３の領域の結晶の配向が一部で一致することが好ましい。
【００１４】
また、本発明の一態様は、リチウム源、第１の遷移金属源、マグネシウム源およびフッ素源を混合する工程と、８００℃以上１１００℃以下で２時間以上２０時間以下加熱する工程と、第２の遷移金属アルコキシドを加えて混合する工程と、酸素を有する雰囲気で５００℃以上１２００℃以下、保持時間５０時間以下で加熱する工程と、室温まで冷却する工程と、を有する正極活物質の作製方法である。
【００１５】
上記において、フッ素源に含まれるフッ素と、マグネシウム源に含まれるマグネシウムの比は、Ｍｇ：Ｆ＝１：ｘ（１．５≦ｘ≦４）であることが好ましい。
【００１６】
また、上記においてマグネシウム源に含まれるマグネシウムは、コバルト源に含まれるコバルトの０．５ｍｏｌ％以上１．５ｍｏｌ％以下であることが好ましい。
【００１７】
また上記において、第１の遷移金属は、ニッケル、マンガン、コバルトの少なくとも一とすることができる。
【００１８】
また上記において、第２の遷移金属アルコキシドは、チタンイソプロポキシドとすることができる。
【００１９】
また上記において、リチウム源には炭酸リチウムを用い、コバルト源には酸化コバルトを用い、マグネシウム源には酸化マグネシウムを用い、フッ素源にはフッ化リチウムを用いることができる。
【発明の効果】
【００２０】
本発明の一態様により、リチウムイオン二次電池に用いることで、充放電サイクルにおける容量の低下が抑制される正極活物質を提供することができる。また、充放電特性の優れた二次電池を提供することができる。また、充放電サイクルにおける容量の低下が抑制された二次電池を提供することができる。また、安全性又は信頼性の高い二次電池を提供することができる。また、新規な物質、活物質粒子、蓄電装置、又はそれらの作製方法を提供することができる。
【図面の簡単な説明】
【００２１】
【図１】正極活物質の一例を説明する図。

【図２】正極活物質の作製方法の一例を説明する図。
【図３】導電助剤としてグラフェン化合物を用いた場合の活物質層の断面図。
【図４】コイン型二次電池を説明する図。
【図５】円筒型二次電池を説明する図。
【図６】曲げることのできる二次電池を説明する図。
【図７】曲げることのできる二次電池を説明する図。
【図８】電子機器の一例を説明する図。
【図９】電子機器の一例を説明する図。
【図１０】電子機器の一例を説明する図。
【図１１】電子機器の一例を説明する図。
【図１２】正極活物質の透過型電子顕微鏡像。
【図１３】正極活物質の透過型電子顕微鏡像のＦＦＴ像。
【図１４】正極活物質の元素マッピング像。
【図１５】比較例の正極活物質の元素マッピング像。
【図１６】二次電池の充放電特性のグラフ。
【図１７】比較例の充放電特性のグラフ。
【図１８】二次電池のサイクル特性のグラフ。
【図１９】二次電池のサイクル特性のグラフ。

【発明を実施するための形態】

【００２２】

以下では、本発明の実施の形態について図面を用いて詳細に説明する。ただし、本発明は以下の説明に限定されず、その形態および詳細を様々に変更し得ることは、当業者であれば容易に理解される。また、本発明は以下に示す実施の形態の記載内容に限定して解釈されるものではない。

【００２３】

本明細書等において、二次元界面の構造に類似性があることをエピタキシという。また二次元界面の構造に類似性を有する結晶成長を、エピタキシャル成長という。また三次元的な構造上の類似性を有すること、または結晶学的に同じ配向であることをトポタキシという。そのためトポタキシである場合、断面の一部を観察すると、二つの領域（たとえば下地となった領域と成長して形成された領域）の結晶の配向が一致する。

【００２４】

また本明細書等において、結晶の配向が一致するとは、陽イオンと陰イオンが交互に配列している場合の、列の方向の差が１０度以下であることをいう。

【００２５】

また、二つの領域の結晶の配向が一致すること、つまりトポタキシであることは、ＴＥＭ（透過電子顕微鏡）像、ＳＴＥＭ（走査透過電子顕微鏡）像、ＨＡＡＤＦ－ＳＴＥＭ（高角散乱環状暗視野走査透過電子顕微鏡）像、ＡＢＦ－ＳＴＥＭ（環状明視野走査透過電子顕微鏡）像等から判断することができる。Ｘ線回折、電子線回折、中性子線回折等も判断の材料にすることができる。

【００２６】

（実施の形態１）

［正極活物質の構造］

まず図１を用いて、本発明の一態様である正極活物質１００について説明する。図１（Ａ）に示すように、正極活物質１００は、第１の領域１０１、第２の領域１０２および第３の領域１０３を有する。第２の領域１０２は、第１の領域１０１の少なくとも一部を被覆する。第３の領域１０３は、第２の領域の少なくとも一部を被覆する。

【００２７】

＜第１の領域１０１＞

第１の領域１０１は、リチウムと第１の遷移金属の複合酸化物を有する。リチウムと第１の遷移金属の複合酸化物としては、たとえばコバルト酸リチウム、マンガン酸リチウム、

ニッケル酸リチウム、コバルトの一部がマンガンまたはニッケルで置換されたコバルト酸リチウム、ニッケル―マンガン―コバルト酸リチウム（三元系とも呼ばれる）等を用いることができる。

【００２８】

第１の領域１０１に用いるリチウムと第１の遷移金属の複合酸化物は、層状岩塩型の結晶構造を有することが好ましい。層状岩塩型の結晶構造を持つ正極活物質は、放電容量が高い、リチウムが二次元的に拡散可能であるため抵抗が低いといった利点がある。

【００２９】

本明細書等において、リチウムと第１の遷移金属の複合酸化物が有する層状岩塩型の結晶構造とは、陽イオンと陰イオンが交互に配列する岩塩型のイオン配列を有し、第１の遷移金属とリチウムが規則配列して二次元平面を形成するため、リチウムの二次元的拡散が可能である結晶構造をいう。なお陽イオンまたは陰イオンの欠損があってもよい。

【００３０】

また、層状岩塩型の結晶構造は、面心立方格子構造から一部の陽イオンを置換し歪ませた構造であるともいえる。このとき、面心立方格子構造のａ軸，ｂ軸，ｃ軸に相当する軸は長さが異なっていてもよい。また面心立方格子構造の軸角α、β、γに相当する角度は９０°に限定されず、その他の角度であってもよい。

【００３１】

第１の領域１０１は、正極活物質１００の中でも特に充放電反応に寄与する領域として機能する。二次電池の容量を大きくするために、第１の領域１０１は、第２の領域および第３の領域よりも体積が大きいことが好ましい。

【００３２】

＜第２の領域１０２＞

第２の領域１０２は、第２の遷移金属の酸化物を有する。第２の遷移金属の酸化物としては、たとえば酸化チタン、チタン酸リチウム、酸化ジルコニウム、酸化ニッケル、ニッケル酸リチウム、酸化バナジウム、酸化マンガン、マンガン酸リチウム、酸化鉄、酸化クロム、酸化ニオブ、酸化コバルト、の少なくとも一を用いることができる。

【００３３】

第２の領域１０２は、第１の領域１０１と、後述する第３の領域１０３を繋ぐバッファ領域として機能する。遷移金属は、金属の価数によって原子間距離が変化しうる。そのため、遷移金属の酸化物は、第２の領域１０２に用いる材料として好ましい。

【００３４】

また第２の領域１０２は、第２の遷移金属の酸化物に加えて、リチウムを有していてもよい。たとえば、チタン酸リチウム、マンガン酸リチウムなどを有してもよい。また、第２の領域１０２は、後述する第３の領域が有する元素を有していてもよい。第２の領域１０２が、第１の領域１０１または第３の領域１０３に有する元素を含むことは、バッファ領域として好ましい。

【００３５】

また第２の領域１０２が有する第２の遷移金属の酸化物は、岩塩型の結晶構造を有することが好ましい。本明細書等において、岩塩型の結晶構造とは、陽イオンと陰イオンが交互に配列している構造をいう。なお陽イオンまたは陰イオンの欠損があってもよい。また結晶のａ軸，ｂ軸，ｃ軸は長さが異なっていてもよい。また軸角α、β、γは９０°に限定されず、その他の角度であってもよい。

【００３６】

＜第３の領域１０３＞

第３の領域１０３は、典型元素の酸化物を有する。典型元素の酸化物としては、たとえば酸化マグネシウム、酸化カルシウム、酸化ベリリウムの少なくとも一を用いることができる。

【００３７】

第３の領域１０３は、正極活物質１００を二次電池に用いた際に、電解液と接触する領域

である。そのため、第３の領域１０３に用いる材料は、充放電の過程で変化が少なく、電解液との接触で変質しにくい材料であることが好ましい。化学的に安定な典型元素の酸化物は、第３の領域として好ましい。

【００３８】

なお、第３の領域は化学的に安定な材料であれば、典型元素の酸化物以外を有していてもよい。たとえば第３の領域は、酸化ジルコニウム、酸化ニッケル、酸化チタン等を有していてもよい。

【００３９】

また第３の領域１０３が有する典型元素の酸化物は、岩塩型の結晶構造を有することが好ましい。

【００４０】

なお、これまで図１（Ａ）のように第１の領域１０１上に第２の領域１０２が接し、かつ第２の領域１０２上に第３の領域１０３が接する例について説明したが、本発明の一態様はこれに限らない。

【００４１】

たとえば、図１（Ｂ）に示すように、第３の領域１０３は正極活物質１００のすべてを覆っていなくてもよい。第１の領域１０１上に第２の領域１０２が接しているが、第３の領域１０３がない部分があってもよい。

【００４２】

また、第２の領域１０２も正極活物質１００のすべてを覆っていなくてもよい。第１の領域１０１上に第３の領域が接し、第２の領域がない部分があってもよい。

【００４３】

さらに、第２の領域１０２および第３の領域１０３は、厚さが場所により異なっていてもよい。

【００４４】

また、第１の領域１０１の内部に、第２の領域１０２が有する材料が存在してもよい。また第１の領域１０１の内部に、第３の領域１０３が有する材料が存在してもよい。たとえば図１（Ｂ）に示す正極活物質１００は、第１の領域１０１の内部に第２の領域１０２が有する材料が存在している。

【００４５】

また、これまで正極活物質１００が第１の領域１０１、第２の領域１０２および第３の領域１０３を有する例について説明したが、本発明の一態様はこれに限らない。たとえば、図１（Ｃ）に示すように、第４の領域１０４を有していてもよい。たとえば第３の領域１０３上に第４の領域１０４が接するように設けることができる。第４の領域は、たとえば炭素を有する被膜であってもよいし、リチウムまたは電解液の分解生成物を有する被膜であってもよい。第４の領域が炭素を有する被膜である場合、正極活物質１００同士の導電性を高めることができる。また第４の領域がリチウムまたは電解液の分解生成物を有する被膜である場合、電解液との過剰な反応を抑制し、二次電池に用いた際サイクル特性を向上させることができる。

【００４６】

［正極活物質の作製方法］

次に図２を用いて、正極活物質１００の作製方法について説明する。

【００４７】

＜ステップＳ１１：出発原料の準備＞

はじめに、出発原料を準備する。この工程で用意する原料から、最終的に第１の領域１０１および第３の領域１０３が形成される。

【００４８】

第１の領域１０１が有するリチウムと第１の遷移金属の原料として、リチウム源と、第１の遷移金属源を用意する。また第３の領域１０３が有する典型元素の酸化物の原料として、典型元素源を用意する。

【００４９】
これらに加えて、フッ素源を用意することが好ましい。フッ素は、原料に加えることで、後の工程で第３の領域１０３を正極活物質１００の表面に析出させる効果がある。
【００５０】
リチウム源としては、例えば炭酸リチウムを用いることができる。第１の遷移金属源としては、例えば第１の遷移金属の酸化物を用いることができる。典型元素源としては、例えば第３の領域が有する典型元素の酸化物、第３の領域が有する典型元素のフッ化物等を用いることができる。フッ素源としては、例えばフッ化リチウム、第３の領域が有する典型元素のフッ化物等を用いることができる。
【００５１】
フッ素源に含まれるフッ素は、典型元素源に含まれる典型元素の、１．０モル倍以上４モル倍以下であることが好ましく、１．５モル倍以上３モル倍以下であることがさらに好ましい。
【００５２】
＜ステップＳ１２：出発材料の混合＞
次に、リチウム源、第１の遷移金属源、典型元素源、フッ素源を混合する。混合には例えばボールミルを用いることができる。
【００５３】
＜ステップＳ１３：加熱＞
次に、ステップＳ１２で混合した材料を加熱する。加熱は８００℃以上１１００℃以下で行うことが好ましく、９００℃以上１０００℃以下で行うことがより好ましい。加熱時間は、２時間以上２０時間以下とすることが好ましい。その後加熱した材料を室温まで冷却する。
【００５４】
ステップＳ１３の加熱により、第１の領域が有する、リチウムと第１の遷移金属の複合酸化物を合成することができる。この時点では、出発材料に含まれた典型元素とフッ素は、リチウムと第１の遷移金属の複合酸化物中に固溶している。ただし、これらの元素の一部が、リチウムと第１の遷移金属の複合酸化物の表面に偏在している場合もある。
【００５５】
また、出発原料としてあらかじめ合成されたリチウムと第１の遷移金属の複合酸化物の粒子を用いてもよい。この場合、ステップＳ１２およびステップＳ１３を省略することができる。たとえば、日本化学工業株式会社製の、コバルト酸リチウム粒子（商品名：Ｃ―２０Ｆ）を出発原料の一として用いることができる。これは粒径が約２０μｍであり、表面にフッ素、マグネシウム、カルシウム、ナトリウム、シリコン、硫黄、リンを含むコバルト酸リチウム粒子である。
【００５６】
＜ステップＳ１４：第２の遷移金属で被覆＞
次に、リチウムと第１の遷移金属の複合酸化物粒子の表面を、第２の遷移金属の酸化物で被覆する。
【００５７】
被覆の方法としては、例えばゾルゲル法、スパッタリング法、ＣＶＤ法等を用いることができる。
【００５８】
なお本明細書等において、ゾルゲル法とは、金属の有機化合物溶液を出発原料として、溶液中の化合物の加水分解・重合によって溶液を金属の酸化物あるいは、水酸化物の微粒子が溶解したゾルとし、さらに反応を進ませてゲル化して出来た非晶質である多孔質ゲルを加熱して膜または結晶体をつくる方法をいう。
【００５９】
ゾルゲル法を用いる場合は、第２の遷移金属のアルコキシドと、リチウムと第１の遷移金属の複合酸化物粒子と、アルコールを混合する。すると第２の遷移金属のアルコキシドは

、大気中の水分と反応して加水分解し、第２の遷移金属の水酸化物となる。さらに、第２の遷移金属の水酸化物と、リチウムと第１の遷移金属の複合酸化物粒子表面の官能基が反応して、第２の遷移金属の酸化物となり、第１の遷移金属の複合酸化物粒子表面を被覆する。また第２の遷移金属の水酸化物の分子同士も脱水縮合反応して第２の遷移金属の酸化物となる。

【００６０】

たとえば第２の遷移金属としてチタンを用い、ゾルゲル法で被覆する場合、第２の遷移金属のアルコキシドとしてはたとえばチタンイソプロポキシドを用いることができる。またアルコールとしては、たとえばイソプロパノールを用いることができる。つまりリチウムと第１の遷移金属の複合酸化物粒子と、チタンイソプロポキシドと、イソプロパノールと、を混合し、反応させることで、リチウムと第１の遷移金属の複合酸化物粒子の表面にチタン酸化物を被覆することができる。

【００６１】

ゾルゲル法を用いると、常温で簡便に、リチウムと第１の遷移金属の複合酸化物粒子を、第２の遷移金属の酸化物で被覆することができ好ましい。

【００６２】

＜ステップＳ１５：加熱＞

次に、ステップＳ１４で合成した、第２の遷移金属の酸化物で被覆された、リチウムと第１の遷移金属の複合酸化物粒子を加熱する。加熱時間は、規定温度での保持時間を５０時間以下で行うことが好ましく、２時間以上１０時間以下で行うことがより好ましい。該規定温度としては５００℃以上１２００℃以下が好ましく、８００℃以上１０００℃以下がより好ましい。また、酸素を含む雰囲気で加熱することが好ましい。

【００６３】

ステップＳ１５の加熱によって、リチウムと第１の遷移金属の複合酸化物と、その上に被覆された第２の遷移金属の酸化物が、結晶の配向が三次元的に一致するトポタキシとなる。つまり第１の領域１０１と第２の領域１０２がトポタキシとなる。

【００６４】

さらにステップＳ１５の加熱によって、リチウムと第１の遷移金属の複合酸化物粒子の内部に固溶していた典型元素が表面に偏在して固溶、または析出し、典型元素の酸化物となり、第３の領域を形成する。このとき、酸素を含む雰囲気で加熱することで、第３の領域の形成が促進される。また、出発原料に含まれたフッ素により、典型元素の析出が促進される。

【００６５】

典型元素は、通常リチウムと第１の遷移金属の複合酸化物中のリチウムのサイトに置換されるのが最も安定である。しかし、出発原料にフッ素を加えてリチウムと第１の遷移金属の複合酸化物を作製することで、典型元素が第１の遷移金属のサイトに置換されうる。その後、ステップＳ１５の加熱によって、比較的不安定な第１の遷移金属のサイト中の典型元素が、雰囲気中の酸素に引き寄せられ、結果的に典型元素の酸化として析出すると考えられる。

【００６６】

このように、本発明の一態様である正極活物質の作製方法では、第２の領域を形成した後、加熱を行うことで第３の領域を形成し、正極活物質１００に２種の被覆層を形成することが可能となる。つまり通常、２種の被覆層を設けるためには２回の被覆工程が必要であるところ、本発明の一態様である正極活物質の作製方法は１回の被覆工程のみでよいため、生産性のよい作製方法である。

【００６７】

さらに、第３の領域を析出によって形成するため、第２の領域からエピタキシャル成長により第３の領域を形成させることができる。そのため第２の領域と第３の領域はトポタキシとすることができる。第２の領域と第３の領域の結晶の配向が一致すると、第２の領域１０２および第３の領域１０３は安定した被覆層として機能する。そのため強固な被覆層

を有する正極活物質１００とすることができる。
【００６８】
第２の領域１０２および第３の領域１０３が、第１の領域１０１と安定した結合を有するため、正極活物質１００を二次電池に用いた際、充放電によって生じる第１の領域１０１の結晶構造の変化を効果的に抑制できる。また、充電によって第１の領域１０１からリチウムが抜けた状態となっても、安定した結合を有する被覆層によって第１の領域１０１からコバルトや酸素が離脱するのを抑制することができる。さらに、電解液と接触する領域を、化学的に安定した材料とすることができる。そのため、サイクル特性の優れた二次電池とすることができる。
【００６９】
なお、第１の領域１０１と第２の領域１０２は一部がトポタキシであればよく、第１の領域１０１と第２の領域１０２のすべてがトポタキシである必要はない。また、第２の領域と第３の領域は一部がトポタキシであればよく、第２の領域と第３の領域のすべてがトポタキシである必要はない。さらに、たとえば第１の領域１０１の一部は非晶質であってもよい。また第２の領域の一部は非晶質であってもよい。また第３の領域の一部は非晶質であってもよい。
【００７０】
＜ステップＳ１６：冷却＞
次に、ステップＳ１５で加熱した粒子を、室温まで冷却する。降温時間は長くとると、トポタキシとさせやすく好ましい。たとえば、保持温度から室温までの降温時間は、１０時間以上５０時間以下とすることが好ましい。
【００７１】
＜ステップＳ１７：回収＞
最後に、冷却された粒子を回収する。上記の工程で、第１の領域、第２の領域および第３の領域を有する正極活物質１００を作製することができる。
【００７２】
（実施の形態２）
本実施の形態では、先の実施の形態で説明した正極活物質１００を有する二次電池に用いることのできる材料の例について説明する。本実施の形態では、正極、負極および電解液が、外装体に包まれている二次電池を例にとって説明する。
【００７３】
［正極］
正極は、正極活物質層および正極集電体を有する。
【００７４】
＜正極活物質層＞
正極活物質層は、正極活物質を有する。また、正極活物質層は、導電助剤およびバインダを有していてもよい。
【００７５】
正極活物質としては、先の実施の形態で説明した正極活物質１００を用いることができる。先の実施の形態で説明した正極活物質１００を用いることで、サイクル特性に優れた二次電池とすることができる。
【００７６】
導電助剤としては、炭素材料、金属材料、又は導電性セラミックス材料等を用いることができる。また、導電助剤として繊維状の材料を用いてもよい。活物質層の総量に対する導電助剤の含有量は、１ｗｔ％以上１０ｗｔ％以下が好ましく、１ｗｔ％以上５ｗｔ％以下がより好ましい。
【００７７】
導電助剤により、電極中に電気伝導のネットワークを形成することができる。導電助剤により、正極活物質どうしの電気伝導の経路を維持することができる。活物質層中に導電助剤を添加することにより、高い電気伝導性を有する活物質層を実現することができる。

【００７８】
導電助剤としては、例えば天然黒鉛、メソカーボンマイクロビーズ等の人造黒鉛、炭素繊維などを用いることができる。炭素繊維としては、例えばメソフェーズピッチ系炭素繊維、等方性ピッチ系炭素繊維等の炭素繊維を用いることができる。また炭素繊維として、カーボンナノファイバーやカーボンナノチューブなどを用いることができる。カーボンナノチューブは、例えば気相成長法などで作製することができる。また、導電助剤として、例えばカーボンブラック（アセチレンブラック（ＡＢ）など）、グラファイト（黒鉛）粒子、グラフェン、フラーレンなどの炭素材料を用いることができる。また、例えば、銅、ニッケル、アルミニウム、銀、金などの金属粉末や金属繊維、導電性セラミックス材料等を用いることができる。
【００７９】
また、導電助剤としてグラフェン化合物を用いてもよい。
【００８０】
グラフェン化合物は、高い導電性を有するという優れた電気特性と、高い柔軟性および高い機械的強度を有するという優れた物理特性と、を有する場合がある。また、グラフェン化合物は平面的な形状を有する。グラフェン化合物は、接触抵抗の低い面接触を可能とする。また、薄くても導電性が非常に高い場合があり、少ない量で効率よく活物質層内で導電パスを形成することができる。そのため、グラフェン化合物を導電助剤として用いることにより、活物質と導電助剤との接触面積を増大させることができるため好ましい。また、電気的な抵抗を減少できる場合があるため好ましい。ここでグラフェン化合物として例えば、グラフェンまたはマルチグラフェンまたはｒｅｄｕｃｅｄ　Ｇｒａｐｈｅｎｅ　Ｏｘｉｄｅ（以下、ＲＧＯ）を用いることが特に好ましい。ここで、ＲＧＯは例えば、酸化グラフェン（ｇｒａｐｈｅｎｅ　ｏｘｉｄｅ：ＧＯ）を還元して得られる化合物を指す。
【００８１】
粒径の小さい活物質、例えば１μｍ以下の活物質を用いる場合には、活物質の比表面積が大きく、活物質同士を繋ぐ導電パスがより多く必要となる。このような場合には、少ない量でも効率よく導電パスを形成することができるグラフェン化合物を用いることが、特に好ましい。
【００８２】
以下では一例として、活物質層２００に、導電助剤としてグラフェン化合物を用いる場合の断面構成例を説明する。
【００８３】
図３（Ａ）に、活物質層２００の縦断面図を示す。活物質層２００は、粒状の正極活物質１００と、導電助剤としてのグラフェン化合物２０１と、バインダ（図示せず）と、を含む。ここで、グラフェン化合物２０１として例えばグラフェンまたはマルチグラフェンを用いればよい。ここで、グラフェン化合物２０１はシート状の形状を有することが好ましい。また、グラフェン化合物２０１は、複数のマルチグラフェン、または（および）複数のグラフェンが部分的に重なりシート状となっていてもよい。
【００８４】
活物質層２００の縦断面においては、図３（Ａ）に示すように、活物質層２００の内部において概略均一にシート状のグラフェン化合物２０１が分散する。図３（Ａ）においてはグラフェン化合物２０１を模式的に太線で表しているが、実際には炭素分子の単層又は多層の厚みを有する薄膜である。複数のグラフェン化合物２０１は、複数の粒状の正極活物質１００を包むように、覆うように、あるいは複数の粒状の正極活物質１００の表面上に張り付くように形成されているため、互いに面接触している。
【００８５】
ここで、複数のグラフェン化合物同士が結合することにより、網目状のグラフェン化合物シート（以下グラフェン化合物ネットまたはグラフェンネットと呼ぶ）を形成することができる。活物質をグラフェンネットが被覆する場合に、グラフェンネットは活物質同士を結合するバインダとしても機能することができる。よって、バインダの量を少なくするこ

とができる、又は使用しないことができるため、電極体積や電極重量に占める活物質の比率を向上させることができる。すなわち、蓄電装置の容量を増加させることができる。

【００８６】

ここで、グラフェン化合物２０１として酸化グラフェンを用い、活物質と混合して活物質層２００となる層を形成後、還元することが好ましい。グラフェン化合物２０１の形成に、極性溶媒中での分散性が極めて高い酸化グラフェンを用いることにより、グラフェン化合物２０１を活物質層２００の内部において概略均一に分散させることができる。均一に分散した酸化グラフェンを含有する分散媒から溶媒を揮発除去し、酸化グラフェンを還元するため、活物質層２００に残留するグラフェン化合物２０１は部分的に重なり合い、互いに面接触する程度に分散していることで三次元的な導電パスを形成することができる。なお、酸化グラフェンの還元は、例えば熱処理により行ってもよいし、還元剤を用いて行ってもよい。

【００８７】

従って、活物質と点接触するアセチレンブラック等の粒状の導電助剤と異なり、グラフェン化合物２０１は接触抵抗の低い面接触を可能とするものであるから、通常の導電助剤よりも少量で粒状の正極活物質１００とグラフェン化合物２０１との電気伝導性を向上させることができる。よって、正極活物質１００の活物質層２００における比率を増加させることができる。これにより、蓄電装置の放電容量を増加させることができる。

【００８８】

バインダとしては、例えば、スチレン―ブタジエンゴム（ＳＢＲ）、スチレン―イソプレン―スチレンゴム、アクリロニトリル―ブタジエンゴム、ブタジエンゴム、エチレン―プロピレン―ジエン共重合体などのゴム材料を用いることが好ましい。またバインダとして、フッ素ゴムを用いることができる。

【００８９】

また、バインダとしては、例えば水溶性の高分子を用いることが好ましい。水溶性の高分子としては、例えば多糖類などを用いることができる。多糖類としては、カルボキシメチルセルロース（ＣＭＣ）、メチルセルロース、エチルセルロース、ヒドロキシプロピルセルロース、ジアセチルセルロース、再生セルロースなどのセルロース誘導体や、澱粉などを用いることができる。また、これらの水溶性の高分子を、前述のゴム材料と併用して用いると、さらに好ましい。

【００９０】

または、バインダとしては、ポリスチレン、ポリアクリル酸メチル、ポリメタクリル酸メチル（ＰＭＭＡ）、ポリアクリル酸ナトリウム、ポリビニルアルコール（ＰＶＡ）、ポリエチレンオキシド（ＰＥＯ）、ポリプロピレンオキシド、ポリイミド、ポリ塩化ビニル、ポリテトラフルオロエチレン、ポリエチレン、ポリプロピレン、イソブチレン、ポリエチレンテレフタレート、ナイロン、ポリフッ化ビニリデン（ＰＶＤＦ）、ポリアクリロニトリル（ＰＡＮ）、ポリビニルクロライド、エチレンプロピレンジエンポリマー、ポリ酢酸ビニル、ポリメチルメタクリレート、ニトロセルロース等の材料を用いることが好ましい。

【００９１】

バインダは上記のうち複数を組み合わせて使用してもよい。

【００９２】

例えば粘度調整効果の特に優れた材料と、他の材料とを組み合わせて使用してもよい。例えばゴム材料等は接着力や弾性力に優れる反面、溶媒に混合した場合に粘度調整が難しい場合がある。このような場合には例えば、粘度調整効果の特に優れた材料と混合することが好ましい。粘度調整効果の特に優れた材料としては、例えば水溶性高分子を用いるとよい。また、粘度調整効果に特に優れた水溶性高分子としては、前述の多糖類、例えばカルボキシメチルセルロース（ＣＭＣ）、メチルセルロース、エチルセルロース、ヒドロキシプロピルセルロースおよびジアセチルセルロース、再生セルロースなどのセルロース誘導体や、澱粉を用いることができる。

【００９３】
なお、カルボキシメチルセルロースなどのセルロース誘導体は、例えばカルボキシメチルセルロースのナトリウム塩やアンモニウム塩などの塩とすることにより溶解度が上がり、粘度調整剤としての効果を発揮しやすくなる。溶解度が高くなることにより電極のスラリーを作製する際に活物質や他の構成要素との分散性を高めることもできる。本明細書においては、電極のバインダとして使用するセルロースおよびセルロース誘導体としては、それらの塩も含むものとする。
【００９４】
水溶性高分子は水に溶解することにより粘度を安定化させ、また活物質や、バインダとして組み合わせる他の材料、例えばスチレンブタジエンゴムなどを、水溶液中に安定して分散させることができる。また、官能基を有するために活物質表面に安定に吸着しやすいことが期待される。また、例えばカルボキシメチルセルロースなどのセルロース誘導体は、例えば水酸基やカルボキシル基などの官能基を有する材料が多く、官能基を有するために高分子同士が相互作用し、活物質表面を広く覆って存在することが期待される。
【００９５】
活物質表面を覆う、または表面に接するバインダが膜を形成する場合には、不動態膜としての役割を果たして電解液の分解を抑える効果も期待される。ここで、不動態膜とは、電子の伝導性のない膜、または電気伝導性の極めて低い膜であり、例えば活物質の表面に不動態膜が形成された場合には、電池反応電位において、電解液の分解を抑制することができる。また、不動態膜は、電気の伝導性を抑えるとともに、リチウムイオンは伝導できるとさらに望ましい。
【００９６】
＜正極集電体＞
正極集電体としては、ステンレス、金、白金、アルミニウム、チタン等の金属、及びこれらの合金など、導電性が高い材料をもちいることができる。また正極集電体に用いる材料は、正極の電位で溶出しないことが好ましい。また、シリコン、チタン、ネオジム、スカンジウム、モリブデンなどの耐熱性を向上させる元素が添加されたアルミニウム合金を用いることができる。また、シリコンと反応してシリサイドを形成する金属元素で形成してもよい。シリコンと反応してシリサイドを形成する金属元素としては、ジルコニウム、チタン、ハフニウム、バナジウム、ニオブ、タンタル、クロム、モリブデン、タングステン、コバルト、ニッケル等がある。集電体は、箔状、板状（シート状）、網状、パンチングメタル状、エキスパンドメタル状等の形状を適宜用いることができる。集電体は、厚みが５μｍ以上３０μｍ以下のものを用いるとよい。
【００９７】
［負極］
負極は、負極活物質層および負極集電体を有する。また、負極活物質層は、導電助剤およびバインダを有していてもよい。
【００９８】
＜負極活物質＞
負極活物質としては、例えば合金系材料や炭素系材料等を用いることができる。
【００９９】
負極活物質として、リチウムとの合金化・脱合金化反応により充放電反応を行うことが可能な元素を用いることができる。例えば、シリコン、スズ、ガリウム、アルミニウム、ゲルマニウム、鉛、アンチモン、ビスマス、銀、亜鉛、カドミウム、インジウム等のうち少なくとも一つを含む材料を用いることができる。このような元素は炭素と比べて容量が大きく、特にシリコンは理論容量が４２００ｍＡｈ／ｇと高い。このため、負極活物質にシリコンを用いることが好ましい。また、これらの元素を有する化合物を用いてもよい。例えば、ＳｉＯ、Mg_2Si、Mg_2Ge、ＳｎＯ、SnO_2、Mg_2Sn、SnS_2、V_2Sn_3、$FeSn_2$、$CoSn_2$、Ni_3Sn_2、Cu_6Sn_5、Ag_3Sn、Ag_3Sb、Ni_2MnSb、$CeSb_3$、$LaSn_3$、$La_3Co_2Sn_7$、$CoSb_3$、Ｉ

ｎＳｂ、ＳｂＳｎ等がある。ここで、リチウムとの合金化・脱合金化反応により充放電反応を行うことが可能な元素、および該元素を有する化合物等を合金系材料と呼ぶ場合がある。

【０１００】

本明細書等において、ＳｉＯは例えば一酸化シリコンを指す。あるいはＳｉＯは、SiO_xと表すこともできる。ここでｘは１近傍の値を有することが好ましい。例えばｘは、０．２以上１．５以下が好ましく、０．３以上１．２以下が好ましい。

【０１０１】

炭素系材料としては、黒鉛、易黒鉛化性炭素（ソフトカーボン）、難黒鉛化性炭素（ハードカーボン）、カーボンナノチューブ、グラフェン、カーボンブラック等を用いればよい。

【０１０２】

黒鉛としては、人造黒鉛や、天然黒鉛等が挙げられる。人造黒鉛としては例えば、メソカーボンマイクロビーズ（ＭＣＭＢ）、コークス系人造黒鉛、ピッチ系人造黒鉛等が挙げられる。ここで人造黒鉛として、球状の形状を有する球状黒鉛を用いることができる。例えば、ＭＣＭＢは球状の形状を有する場合があり、好ましい。また、ＭＣＭＢはその表面積を小さくすることが比較的容易であり、好ましい場合がある。天然黒鉛としては例えば、鱗片状黒鉛、球状化天然黒鉛等が挙げられる。

【０１０３】

黒鉛はリチウムイオンが黒鉛に挿入されたとき（リチウム―黒鉛層間化合物の生成時）にリチウム金属と同程度に低い電位を示す（０．０５Ｖ以上０．３Ｖ以下　ｖｓ．Li/Li^+）。これにより、リチウムイオン二次電池は高い作動電圧を示すことができる。さらに、黒鉛は、単位体積当たりの容量が比較的高い、体積膨張が比較的小さい、安価である、リチウム金属に比べて安全性が高い等の利点を有するため、好ましい。

【０１０４】

また、負極活物質として、二酸化チタン（TiO_2）、リチウムチタン酸化物（$Li_4Ti_5O_{12}$）、リチウム―黒鉛層間化合物（Li_xC_6）、五酸化ニオブ（Nb_2O_5）、酸化タングステン（WO_2）、酸化モリブデン（MoO_2）等の酸化物を用いることができる。

【０１０５】

また、負極活物質として、リチウムと遷移金属の複窒化物である、Li_3N型構造をもつ$Li_{3-x}M_xN$（Ｍ＝Ｃｏ、Ｎｉ、Ｃｕ）を用いることができる。例えば、$Li_{2.6}Co_{0.4}N_3$は大きな充放電容量（９００ｍＡｈ／ｇ、１８９０ｍＡｈ／ｃｍ^3）を示し好ましい。

【０１０６】

リチウムと遷移金属の複窒化物を用いると、負極活物質中にリチウムイオンを含むため、正極活物質としてリチウムイオンを含まないV_2O_5、Cr_3O_8等の材料と組み合わせることができ好ましい。なお、正極活物質にリチウムイオンを含む材料を用いる場合でも、あらかじめ正極活物質に含まれるリチウムイオンを脱離させることで、負極活物質としてリチウムと遷移金属の複窒化物を用いることができる。

【０１０７】

また、コンバージョン反応が生じる材料を負極活物質として用いることもできる。例えば、酸化コバルト（ＣｏＯ）、酸化ニッケル（ＮｉＯ）、酸化鉄（ＦｅＯ）等の、リチウムとの合金を作らない遷移金属酸化物を負極活物質に用いてもよい。コンバージョン反応が生じる材料としては、さらに、Fe_2O_3、ＣｕＯ、Cu_2O、RuO_2、Cr_2O_3等の酸化物、$CoS_{0.89}$、ＮｉＳ、ＣｕＳ等の硫化物、Zn_3N_2、Cu_3N、Ge_3N_4等の窒化物、NiP_2、FeP_2、CoP_3等のリン化物、FeF_3、BiF_3等のフッ化物でも起こる。

【０１０８】

負極活物質層が有することのできる導電助剤およびバインダとしては、正極活物質層が有

することのできる導電助剤およびバインダと同様の材料を用いることができる。
【０１０９】
＜負極集電体＞
負極集電体には、正極集電体と同様の材料を用いることができる。なお負極集電体は、リチウム等のキャリアイオンと合金化しない材料を用いることが好ましい。
【０１１０】
［電解液］
電解液は、溶媒と電解質を有する。電解液の溶媒としては、非プロトン性有機溶媒が好ましく、例えば、エチレンカーボネート（ＥＣ）、プロピレンカーボネート（ＰＣ）、ブチレンカーボネート、クロロエチレンカーボネート、ビニレンカーボネート、γ―ブチロラクトン、γ―バレロラクトン、ジメチルカーボネート（ＤＭＣ）、ジエチルカーボネート（ＤＥＣ）、エチルメチルカーボネート（ＥＭＣ）、ギ酸メチル、酢酸メチル、酪酸メチル、１，３―ジオキサン、１，４―ジオキサン、ジメトキシエタン（ＤＭＥ）、ジメチルスルホキシド、ジエチルエーテル、メチルジグライム、アセトニトリル、ベンゾニトリル、テトラヒドロフラン、スルホラン、スルトン等の１種、又はこれらのうちの２種以上を任意の組み合わせおよび比率で用いることができる。
【０１１１】
また、電解液の溶媒としてゲル化される高分子材料を用いることで、漏液性等に対する安全性が高まる。また、二次電池の薄型化および軽量化が可能である。ゲル化される高分子材料の代表例としては、シリコーンゲル、アクリルゲル、アクリロニトリルゲル、ポリエチレンオキサイド系ゲル、ポリプロピレンオキサイド系ゲル、フッ素系ポリマーのゲル等がある。
【０１１２】
また、電解液の溶媒として、難燃性および難揮発性であるイオン液体（常温溶融塩）を一つ又は複数用いることで、蓄電装置の内部短絡や、過充電等によって内部温度が上昇しても、蓄電装置の破裂や発火などを防ぐことができる。イオン液体は、カチオンとアニオンからなり、有機カチオンとアニオンとを含む。電解液に用いる有機カチオンとして、四級アンモニウムカチオン、三級スルホニウムカチオン、および四級ホスホニウムカチオン等の脂肪族オニウムカチオンや、イミダゾリウムカチオンおよびピリジニウムカチオン等の芳香族カチオンが挙げられる。また、電解液に用いるアニオンとして、１価のアミド系アニオン、１価のメチド系アニオン、フルオロスルホン酸アニオン、パーフルオロアルキルスルホン酸アニオン、テトラフルオロボレートアニオン、パーフルオロアルキルボレートアニオン、ヘキサフルオロホスフェートアニオン、またはパーフルオロアルキルホスフェートアニオン等が挙げられる。
【０１１３】
また、上記の溶媒に溶解させる電解質としては、例えば$LiPF_6$、$LiClO_4$、$LiAsF_6$、$LiBF_4$、$LiAlCl_4$、ＬｉＳＣＮ、ＬｉＢｒ、ＬｉＩ、Li_2SO_4、$Li_2B_{10}Cl_{10}$、$Li_2B_{12}Cl_{12}$、$LiCF_3SO_3$、$LiC_4F_9SO_3$、$LiC(CF_3SO_2)_3$、$LiC(C_2F_5SO_2)_3$、$LiN(CF_3SO_2)_2$、$LiN(C_4F_9SO_2)(CF_3SO_2)$、$LiN(C_2F_5SO_2)_2$等のリチウム塩を一種、又はこれらのうちの二種以上を任意の組み合わせおよび比率で用いることができる。
【０１１４】
蓄電装置に用いる電解液は、粒状のごみや電解液の構成元素以外の元素（以下、単に「不純物」ともいう。）の含有量が少ない高純度化された電解液を用いることが好ましい。具体的には、電解液に対する不純物の重量比を１％以下、好ましくは０．１％以下、より好ましくは０．０１％以下とすることが好ましい。
【０１１５】
また、電解液にビニレンカーボネート、プロパンスルトン（ＰＳ）、ｔｅｒｔ―ブチルベンゼン（ＴＢＢ）、フルオロエチレンカーボネート（ＦＥＣ）、ＬｉＢＯＢなどの添加剤

を添加してもよい。添加剤の濃度は、例えば溶媒全体に対して０．１ｗｅｉｇｈｔ％以上５ｗｅｉｇｈｔ％以下とすればよい。

【０１１６】

また、ポリマーを電解液で膨潤させたポリマーゲル電解質を用いてもよい。

【０１１７】

ポリマーとしては、例えばポリエチレンオキシド（ＰＥＯ）などのポリアルキレンオキシド構造を有するポリマーや、ＰＶＤＦ、およびポリアクリロニトリル等、およびそれらを含む共重合体等を用いることができる。例えばＰＶＤＦとヘキサフルオロプロピレン（ＨＦＰ）の共重合体であるＰＶＤＦ―ＨＦＰを用いることができる。また、形成されるポリマーは、多孔質形状を有してもよい。

【０１１８】

また、電解液の代わりに、硫化物系や酸化物系等の無機物材料を有する固体電解質や、ＰＥＯ（ポリエチレンオキシド）系等の高分子材料を有する固体電解質を用いることができる。固体電解質を用いる場合には、セパレータやスペーサの設置が不要となる。また、電池全体を固体化できるため、漏液のおそれがなくなり安全性が飛躍的に向上する。

【０１１９】

［セパレータ］

また二次電池は、セパレータを有することが好ましい。セパレータとしては、例えば、紙、不織布、ガラス繊維、セラミックス、或いはナイロン（ポリアミド）、ビニロン（ポリビニルアルコール系繊維）、ポリエステル、アクリル、ポリオレフィン、ポリウレタンを用いた合成繊維等で形成されたものを用いることができる。セパレータは袋状に加工し、正極または負極のいずれか一方を包むように配置することが好ましい。

【０１２０】

［外装体］

二次電池が有する外装体としては、例えばアルミニウムなどの金属材料や樹脂材料を用いることができる。また、フィルム状の外装体を用いることもできる。フィルムとしては、例えばポリエチレン、ポリプロピレン、ポリカーボネート、アイオノマー、ポリアミド等の材料からなる膜上に、アルミニウム、ステンレス、銅、ニッケル等の可撓性に優れた金属薄膜を設け、さらに該金属薄膜上に外装体の外面としてポリアミド系樹脂、ポリエステル系樹脂等の絶縁性合成樹脂膜を設けた三層構造のフィルムを用いることができる。

【０１２１】

（実施の形態３）

本実施の形態では、先の実施の形態で説明した正極活物質１００を有する二次電池の形状の例について説明する。本実施の形態で説明する二次電池に用いる材料は、先の実施の形態の記載を参酌することができる。

【０１２２】

［コイン型二次電池］

まずコイン型の二次電池の一例について説明する。図４（Ａ）はコイン型（単層偏平型）の二次電池の外観図であり、図４（Ｂ）は、その断面図である。

【０１２３】

コイン型の二次電池３００は、正極端子を兼ねた正極缶３０１と負極端子を兼ねた負極缶３０２とが、ポリプロピレン等で形成されたガスケット３０３で絶縁シールされている。正極３０４は、正極集電体３０５と、これと接するように設けられた正極活物質層３０６により形成される。また、負極３０７は、負極集電体３０８と、これに接するように設けられた負極活物質層３０９により形成される。

【０１２４】

なお、コイン型の二次電池３００に用いる正極３０４および負極３０７は、それぞれ活物質層は片面のみに形成すればよい。

【０１２５】

正極缶３０１、負極缶３０２には、電解液に対して耐食性のあるニッケル、アルミニウム

、チタン等の金属、又はこれらの合金やこれらと他の金属との合金（例えばステンレス鋼等）を用いることができる。また、電解液による腐食を防ぐため、ニッケルやアルミニウム等を被覆することが好ましい。正極缶３０１は正極３０４と、負極缶３０２は負極３０７とそれぞれ電気的に接続する。

【０１２６】

これら負極３０７、正極３０４およびセパレータ３１０を電解質に含浸させ、図４（Ｂ）に示すように、正極缶３０１を下にして正極３０４、セパレータ３１０、負極３０７、負極缶３０２をこの順で積層し、正極缶３０１と負極缶３０２とをガスケット３０３を介して圧着してコイン形の二次電池３００を製造する。

【０１２７】

正極３０４に、先の実施の形態で説明した正極活物質を用いることで、サイクル特性に優れたコイン型の二次電池３００とすることができる。

【０１２８】

［円筒型二次電池］

次に円筒型の二次電池の例について図５を参照して説明する。円筒型の二次電池６００は、図５（Ａ）に示すように、上面に正極キャップ（電池蓋）６０１を有し、側面および底面に電池缶（外装缶）６０２を有している。これら正極キャップと電池缶（外装缶）６０２とは、ガスケット（絶縁パッキン）６１０によって絶縁されている。

【０１２９】

図５（Ｂ）は、円筒型の二次電池の断面を模式的に示した図である。中空円柱状の電池缶６０２の内側には、帯状の正極６０４と負極６０６とがセパレータ６０５を間に挟んで捲回された電池素子が設けられている。図示しないが、電池素子はセンターピンを中心に捲回されている。電池缶６０２は、一端が閉じられ、他端が開いている。電池缶６０２には、電解液に対して耐腐食性のあるニッケル、アルミニウム、チタン等の金属、又はこれらの合金やこれらと他の金属との合金（例えば、ステンレス鋼等）を用いることができる。また、電解液による腐食を防ぐため、ニッケルやアルミニウム等を被覆することが好ましい。電池缶６０２の内側において、正極、負極およびセパレータが捲回された電池素子は、対向する一対の絶縁板６０８、６０９により挟まれている。また、電池素子が設けられた電池缶６０２の内部は、非水電解液（図示せず）が注入されている。非水電解液は、コイン型の二次電池と同様のものを用いることができる。

【０１３０】

円筒型の蓄電池に用いる正極および負極は捲回するため、集電体の両面に活物質を形成することが好ましい。正極６０４には正極端子（正極集電リード）６０３が接続され、負極６０６には負極端子（負極集電リード）６０７が接続される。正極端子６０３および負極端子６０７は、ともにアルミニウムなどの金属材料を用いることができる。正極端子６０３は安全弁機構６１２に、負極端子６０７は電池缶６０２の底にそれぞれ抵抗溶接される。安全弁機構６１２は、ＰＴＣ素子（Ｐｏｓｉｔｉｖｅ　Ｔｅｍｐｅｒａｔｕｒｅ　Ｃｏｅｆｆｉｃｉｅｎｔ）６１１を介して正極キャップ６０１と電気的に接続されている。安全弁機構６１２は電池の内圧の上昇が所定の閾値を超えた場合に、正極キャップ６０１と正極６０４との電気的な接続を切断するものである。また、ＰＴＣ素子６１１は温度が上昇した場合に抵抗が増大する熱感抵抗素子であり、抵抗の増大により電流量を制限して異常発熱を防止するものである。ＰＴＣ素子には、チタン酸バリウム（ＢａＴｉＯ$_3$）系半導体セラミックス等を用いることができる。

【０１３１】

正極６０４に、先の実施の形態で説明した正極活物質を用いることで、サイクル特性に優れた円筒型の二次電池６００とすることができる。

【０１３２】

［曲げることのできる二次電池］

次に、曲げることのできる二次電池の例について図６および図７を参照して説明する。

【０１３３】

図６（Ａ）に、曲げることのできる二次電池５０の上面概略図を示す。図６（Ｂ１）、（Ｂ２）、（Ｃ）にはそれぞれ、図６（Ａ）中の切断線Ｃ１―Ｃ２、切断線Ｃ３―Ｃ４、切断線Ａ１―Ａ２における断面概略図である。電池５０は、外装体５１と、外装体５１の内部に収容された正極１１ａおよび負極１１ｂを有する。正極１１ａと電気的に接続されたリード１２ａ、および負極１１ｂと電気的に接続されたリード１２ｂは、外装体５１の外側に延在している。また外装体５１で囲まれた領域には、正極１１ａおよび負極１１ｂに加えて電解液（図示しない）が封入されている。

【０１３４】

電池５０が有する正極１１ａおよび負極１１ｂについて、図７を用いて説明する。図７（Ａ）は、正極１１ａ、負極１１ｂおよびセパレータ１４の積層順を説明する斜視図である。図７（Ｂ）は正極１１ａおよび負極１１ｂに加えて、リード１２ａおよびリード１２ｂを示す斜視図である。

【０１３５】

図７（Ａ）に示すように、電池５０は、複数の短冊状の正極１１ａ、複数の短冊状の負極１１ｂおよび複数のセパレータ１４を有する。正極１１ａおよび負極１１ｂはそれぞれ突出したタブ部分と、タブ以外の部分を有する。正極１１ａの一方の面のタブ以外の部分に正極活物質層が形成され、負極１１ｂの一方の面のタブ以外の部分に負極活物質層が形成される。

【０１３６】

正極１１ａの正極活物質層の形成されていない面同士、および負極１１ｂの負極活物質の形成されていない面同士が接するように、正極１１ａおよび負極１１ｂは積層される。

【０１３７】

また、正極１１ａの正極活物質が形成された面と、負極１１ｂの負極活物質が形成された面の間にはセパレータ１４が設けられる。図７では見やすくするためセパレータ１４を点線で示す。

【０１３８】

また図７（Ｂ）に示すように、複数の正極１１ａとリード１２ａは、接合部１５ａにおいて電気的に接続される。また複数の負極１１ｂとリード１２ｂは、接合部１５ｂにおいて電気的に接続される。

【０１３９】

次に、外装体５１について図６（Ｂ１）、（Ｂ２）、（Ｃ）、（◗）を用いて説明する。

【０１４０】

外装体５１は、フィルム状の形状を有し、正極１１ａおよび負極１１ｂを挟むように２つに折り曲げられている。外装体５１は、折り曲げ部６１と、一対のシール部６２と、シール部６３と、を有する。一対のシール部６２は、正極１１ａおよび負極１１ｂを挟んで設けられ、サイドシールとも呼ぶことができる。また、シール部６３は、リード１２ａ及びリード１２ｂと重なる部分を有し、トップシールとも呼ぶことができる。

【０１４１】

外装体５１は、正極１１ａおよび負極１１ｂと重なる部分に、稜線７１と谷線７２が交互に並んだ波形状を有することが好ましい。また、外装体５１のシール部６２及びシール部６３は、平坦であることが好ましい。

【０１４２】

図６（Ｂ１）は、稜線７１と重なる部分で切断した断面であり、図６（Ｂ２）は、谷線７２と重なる部分で切断した断面である。図６（Ｂ１）、（Ｂ２）は共に、電池５０及び正極１１ａおよび負極１１ｂの幅方向の断面に対応する。

【０１４３】

ここで、正極１１ａおよび負極１１ｂの幅方向の端部、すなわち正極１１ａおよび負極１１ｂの端部と、シール部６２との間の距離を距離Ｌａとする。電池５０に曲げるなどの変形を加えたとき、後述するように正極１１ａおよび負極１１ｂが長さ方向に互いにずれるように変形する。その際、距離Ｌａが短すぎると、外装体５１と正極１１ａおよび負極１

１ｂとが強く擦れ、外装体５１が破損してしまう場合がある。特に外装体５１の金属フィルムが露出すると、当該金属フィルムが電解液により腐食されてしまう恐れがある。したがって、距離Ｌａを出来るだけ長く設定することが好ましい。一方で、距離Ｌａを大きくしすぎると、電池５０の体積が増大してしまう。

【０１４４】

また、積層された正極１１ａおよび負極１１ｂの合計の厚さが厚いほど、正極１１ａおよび負極１１ｂと、シール部６２との間の距離Ｌａを大きくすることが好ましい。

【０１４５】

より具体的には、積層された正極１１ａおよび負極１１ｂの合計の厚さを厚さｔとしたとき、距離Ｌａは、厚さｔの０．８倍以上３．０倍以下、好ましくは０．９倍以上２．５倍以下、より好ましくは１．０倍以上２．０倍以下であることが好ましい。距離Ｌａをこの範囲とすることで、コンパクトで、且つ曲げに対する信頼性の高い電池を実現できる。

【０１４６】

また、一対のシール部６２の間の距離を距離Ｌｂとしたとき、距離Ｌｂを正極１１ａおよび負極１１ｂの幅（ここでは、負極１１ｂの幅Ｗｂ）よりも十分大きくすることが好ましい。これにより、電池５０に繰り返し曲げるなどの変形を加えたときに、正極１１ａおよび負極１１ｂと外装体５１とが接触しても、正極１１ａおよび負極１１ｂの一部が幅方向にずれることができるため、正極１１ａおよび負極１１ｂと外装体５１とが擦れてしまうことを効果的に防ぐことができる。

【０１４７】

例えば、一対のシール部６２の間の距離Ｌａと、負極１１ｂの幅Ｗｂとの差が、正極１１ａおよび負極１１ｂの厚さｔの１．６倍以上６．０倍以下、好ましくは１．８倍以上５．０倍以下、より好ましくは、２．０倍以上４．０倍以下を満たすことが好ましい。

【０１４８】

言い換えると、距離Ｌｂ、幅Ｗｂ、及び厚さｔが、下記数式１の関係を満たすことが好ましい。

【０１４９】

【数１】

$$\frac{Lb-Wb}{2t} \geq a \qquad \text{（数式１）}$$

【０１５０】

ここで、ａは、０．８以上３．０以下、好ましくは０．９以上２．５以下、より好ましくは１．０以上２．０以下を満たす。

【０１５１】

また、図６（Ｃ）はリード１２ａを含む断面であり、電池５０、正極１１ａおよび負極１１ｂの長さ方向の断面に対応する。図６（Ｃ）に示すように、折り曲げ部６１において、正極１１ａおよび負極１１ｂの長さ方向の端部と、外装体５１との間に空間７３を有することが好ましい。

【０１５２】

図６（Ｄ）に、電池５０を曲げたときの断面概略図を示している。図６（Ｄ）は、図６（Ａ）中の切断線Ｂ１―Ｂ２における断面に相当する。

【０１５３】

電池５０を曲げると、曲げの外側に位置する外装体５１の一部は伸び、内側に位置する他の一部は縮むように変形する。より具体的には、外装体５１の外側に位置する部分は、波の振幅が小さく、且つ波の周期が大きくなるように変形する。一方、外装体５１の内側に位置する部分は、波の振幅が大きく、且つ波の周期が小さくなるように変形する。このように、外装体５１が変形することにより、曲げに伴って外装体５１にかかる応力が緩和されるため、外装体５１を構成する材料自体が伸縮する必要がない。その結果、外装体５１

は破損することなく、小さな力で電池５０を曲げることができる。
【０１５４】
また、図６（Ｄ）に示すように、電池５０を曲げると、正極１１ａおよび負極１１ｂとがそれぞれ相対的にずれる。このとき、複数の積層された正極１１ａおよび負極１１ｂは、シール部６３側の一端が固定部材１７で固定されているため、折り曲げ部６１に近いほどずれ量が大きくなるように、それぞれずれる。これにより、正極１１ａおよび負極１１ｂにかかる応力が緩和され、正極１１ａおよび負極１１ｂ自体が伸縮する必要がない。その結果、正極１１ａおよび負極１１ｂが破損することなく電池５０を曲げることができる。
【０１５５】
また、正極１１ａおよび負極１１ｂと外装体５１との間に空間７３を有していることにより、曲げた時内側に位置する正極１１ａおよび負極１１ｂが、外装体５１に接触することなく、相対的にずれることができる。
【０１５６】
図６および図７で例示した電池５０は、繰り返し曲げ伸ばしを行っても、外装体の破損、正極１１ａおよび負極１１ｂの破損などが生じにくく、電池特性も劣化しにくい電池である。電池５０が有する正極１１ａに、先の実施の形態で説明した正極活物質を用いることで、さらにサイクル特性に優れた電池とすることができる。
【０１５７】
（実施の形態４）
本実施の形態では、本発明の一態様である二次電池を電子機器に実装する例について説明する。
【０１５８】
まず実施の形態３で説明した、曲げることのできる二次電池を電子機器に実装する例を図８に示す。フレキシブルな形状を備える二次電池を適用した電子機器として、例えば、テレビジョン装置（テレビ、又はテレビジョン受信機ともいう）、コンピュータ用などのモニタ、デジタルカメラ、デジタルビデオカメラ、デジタルフォトフレーム、携帯電話機（携帯電話、携帯電話装置ともいう）、携帯型ゲーム機、携帯情報端末、音響再生装置、パチンコ機などの大型ゲーム機などが挙げられる。
【０１５９】
また、フレキシブルな形状を備える二次電池を、家屋やビルの内壁または外壁や、自動車の内装または外装の曲面に沿って組み込むことも可能である。
【０１６０】
図８（Ａ）は、携帯電話機の一例を示している。携帯電話機７４００は、筐体７４０１に組み込まれた表示部７４０２の他、操作ボタン７４０３、外部接続ポート７４０４、スピーカ７４０５、マイク７４０６などを備えている。なお、携帯電話機７４００は、二次電池７４０７を有している。
【０１６１】
図８（Ｂ）は、携帯電話機７４００を湾曲させた状態を示している。携帯電話機７４００を外部の力により変形させて全体を湾曲させると、その内部に設けられている二次電池７４０７も湾曲される。また、その時、曲げられた二次電池７４０７の状態を図８（Ｃ）に示す。二次電池７４０７は薄型の蓄電池である。二次電池７４０７は曲げられた状態で固定されている。なお、二次電池７４０７は集電体７４０９と電気的に接続されたリード電極７４０８を有している。例えば、集電体７４０９は銅箔であり、一部ガリウムと合金化させて、集電体７４０９と接する活物質層との密着性を向上し、二次電池７４０７が曲げられた状態での信頼性が高い構成となっている。
【０１６２】
図８（Ｄ）は、バングル型の表示装置の一例を示している。携帯表示装置７１００は、筐体７１０１、表示部７１０２、操作ボタン７１０３、及び二次電池７１０４を備える。また、図８（Ｅ）に曲げられた二次電池７１０４の状態を示す。二次電池７１０４は曲げられた状態で使用者の腕への装着時に、筐体が変形して二次電池７１０４の一部または全部

の曲率が変化する。なお、曲線の任意の点における曲がり具合を相当する円の半径の値で表したものを曲率半径であり、曲率半径の逆数を曲率と呼ぶ。具体的には、曲率半径が４０ｍｍ以上１５０ｍｍ以下の範囲内で筐体または二次電池７１０４の主表面の一部または全部が変化する。二次電池７１０４の主表面における曲率半径が４０ｍｍ以上１５０ｍｍ以下の範囲であれば、高い信頼性を維持できる。

【０１６３】

図８（Ｆ）は、腕時計型の携帯情報端末の一例を示している。携帯情報端末７２００は、筐体７２０１、表示部７２０２、バンド７２０３、バックル７２０４、操作ボタン７２０５、入出力端子７２０６などを備える。

【０１６４】

携帯情報端末７２００は、移動電話、電子メール、文章閲覧及び作成、音楽再生、インターネット通信、コンピュータゲームなどの種々のアプリケーションを実行することができる。

【０１６５】

表示部７２０２はその表示面が湾曲して設けられ、湾曲した表示面に沿って表示を行うことができる。また、表示部７２０２はタッチセンサを備え、指やスタイラスなどで画面に触れることで操作することができる。例えば、表示部７２０２に表示されたアイコン７２０７に触れることで、アプリケーションを起動することができる。

【０１６６】

操作ボタン７２０５は、時刻設定のほか、電源のオン、オフ動作、無線通信のオン、オフ動作、マナーモードの実行及び解除、省電力モードの実行及び解除など、様々な機能を持たせることができる。例えば、携帯情報端末７２００に組み込まれたオペレーティングシステムにより、操作ボタン７２０５の機能を自由に設定することもできる。

【０１６７】

また、携帯情報端末７２００は、通信規格された近距離無線通信を実行することが可能である。例えば無線通信可能なヘッドセットと相互通信することによって、ハンズフリーで通話することもできる。

【０１６８】

また、携帯情報端末７２００は入出力端子７２０６を備え、他の情報端末とコネクターを介して直接データのやりとりを行うことができる。また入出力端子７２０６を介して充電を行うこともできる。なお、充電動作は入出力端子７２０６を介さずに無線給電により行ってもよい。

【０１６９】

携帯情報端末７２００の表示部７２０２には、本発明の一態様の二次電池を有している。例えば、図８（Ｅ）に示した二次電池７１０４を、筐体７２０１の内部に湾曲した状態で、またはバンド７２０３の内部に湾曲可能な状態で組み込むことができる。

【０１７０】

携帯情報端末７２００はセンサを有することが好ましい。センサとして例えば、指紋センサ、脈拍センサ、体温センサ等の人体センサや、タッチセンサ、加圧センサ、加速度センサ、等が搭載されることが好ましい。

【０１７１】

図８（Ｇ）は、腕章型の表示装置の一例を示している。表示装置７３００は、表示部７３０４を有し、本発明の一態様の二次電池を有している。また、表示装置７３００は、表示部７３０４にタッチセンサを備えることもでき、また、携帯情報端末として機能させることもできる。

【０１７２】

表示部７３０４はその表示面が湾曲しており、湾曲した表示面に沿って表示を行うことができる。また、表示装置７３００は、通信規格された近距離無線通信などにより、表示状況を変更することができる。

【０１７３】

また、表示装置７３００は入出力端子を備え、他の情報端末とコネクターを介して直接データのやりとりを行うことができる。また入出力端子を介して充電を行うこともできる。なお、充電動作は入出力端子を介さずに無線給電により行ってもよい。

【０１７４】

次に、図９（Ａ）および図９（Ｂ）に、２つ折り可能なタブレット型端末の一例を示す。図９（Ａ）および図９（Ｂ）に示すタブレット型端末９６００は、筐体９６３０ａ、筐体９６３０ｂ、筐体９６３０ａと筐体９６３０ｂを接続する可動部９６４０、表示部９６３１ａと表示部９６３１ｂを有する表示部９６３１、表示モード切り替えスイッチ９６２６、電源スイッチ９６２７、省電力モード切り替えスイッチ９６２５、留め具９６２９、操作スイッチ９６２８、を有する。図９（Ａ）は、タブレット型端末９６００を開いた状態を示し、図９（Ｂ）は、タブレット型端末９６００を閉じた状態を示している。

【０１７５】

また、タブレット型端末９６００は、筐体９６３０ａおよび筐体９６３０ｂの内部に蓄電体９６３５を有する。蓄電体９６３５は、可動部９６４０を通り、筐体９６３０ａと筐体９６３０ｂに渡って設けられている。

【０１７６】

表示部９６３１ａは、一部をタッチパネルの領域９６３２ａとすることができ、表示された操作キー９６３８にふれることでデータ入力をすることができる。なお、表示部９６３１ａにおいては、一例として半分の領域が表示のみの機能を有する構成、もう半分の領域がタッチパネルの機能を有する構成を示しているが該構成に限定されない。表示部９６３１ａの全ての領域がタッチパネルの機能を有する構成としても良い。例えば、表示部９６３１ａの全面をキーボードボタン表示させてタッチパネルとし、表示部９６３１ｂを表示画面として用いることができる。

【０１７７】

また、表示部９６３１ｂにおいても表示部９６３１ａと同様に、表示部９６３１ｂの一部をタッチパネルの領域９６３２ｂとすることができる。また、タッチパネルのキーボード表示切り替えボタン９６３９が表示されている位置に指やスタイラスなどでふれることで表示部９６３１ｂにキーボードボタン表示することができる。

【０１７８】

また、タッチパネルの領域９６３２ａとタッチパネルの領域９６３２ｂに対して同時にタッチ入力することもできる。

【０１７９】

また、表示モード切り替えスイッチ９６２６は、縦表示又は横表示などの表示の向きを切り替え、白黒表示やカラー表示の切り替えなどを選択できる。省電力モード切り替えスイッチ９６２５は、タブレット型端末９６００に内蔵している光センサで検出される使用時の外光の光量に応じて表示の輝度を最適なものとすることができる。タブレット型端末は光センサだけでなく、ジャイロ、加速度センサ等の傾きを検出するセンサなどの他の検出装置を内蔵させてもよい。

【０１８０】

また、図９（Ａ）では表示部９６３１ｂと表示部９６３１ａの表示面積が同じ例を示しているが特に限定されず、一方のサイズともう一方のサイズが異なっていてもよく、表示の品質も異なっていてもよい。例えば一方が他方よりも高精細な表示を行える表示パネルとしてもよい。

【０１８１】

図９（Ｂ）は、閉じた状態であり、タブレット型端末は、筐体９６３０、太陽電池９６３３、ＤＣ－ＤＣコンバータ９６３６を含む充放電制御回路９６３４有する。また、蓄電体９６３５として、本発明の一態様に係る蓄電体を用いる。

【０１８２】

なお、タブレット型端末９６００は２つ折り可能なため、未使用時に筐体９６３０ａおよび筐体９６３０ｂを重ね合せるように折りたたむことができる。折りたたむことにより、

表示部９６３１ａ、表示部９６３１ｂを保護できるため、タブレット型端末９６００の耐久性を高めることができる。また、本発明の一態様の蓄電体を用いた蓄電体９６３５は可撓性を有し、曲げ伸ばしを繰り返しても充放電容量が低下しにくい。よって、信頼性の優れたタブレット型端末を提供できる。

【０１８３】

また、この他にも図９（Ａ）および図９（Ｂ）に示したタブレット型端末は、様々な情報（静止画、動画、テキスト画像など）を表示する機能、カレンダー、日付又は時刻などを表示部に表示する機能、表示部に表示した情報をタッチ入力操作又は編集するタッチ入力機能、様々なソフトウェア（プログラム）によって処理を制御する機能、等を有することができる。

【０１８４】

タブレット型端末の表面に装着された太陽電池９６３３によって、電力をタッチパネル、表示部、又は映像信号処理部等に供給することができる。なお、太陽電池９６３３は、筐体９６３０の片面又は両面に設けることができ、蓄電体９６３５の充電を効率的に行う構成とすることができる。なお蓄電体９６３５としては、リチウムイオン電池を用いると、小型化を図れる等の利点がある。

【０１８５】

また、図９（Ｂ）に示す充放電制御回路９６３４の構成、および動作について図９（Ｃ）にブロック図を示し説明する。図９（Ｃ）には、太陽電池９６３３、蓄電体９６３５、ＤＣＤＣコンバータ９６３６、コンバータ９６３７、スイッチＳＷ１乃至ＳＷ３、表示部９６３１について示しており、蓄電体９６３５、ＤＣＤＣコンバータ９６３６、コンバータ９６３７、スイッチＳＷ１乃至ＳＷ３が、図９（Ｂ）に示す充放電制御回路９６３４に対応する箇所となる。

【０１８６】

まず外光により太陽電池９６３３により発電がされる場合の動作の例について説明する。太陽電池で発電した電力は、蓄電体９６３５を充電するための電圧となるようＤＣＤＣコンバータ９６３６で昇圧又は降圧がなされる。そして、表示部９６３１の動作に太陽電池９６３３からの電力が用いられる際にはスイッチＳＷ１をオンにし、コンバータ９６３７で表示部９６３１に必要な電圧に昇圧又は降圧をすることとなる。また、表示部９６３１での表示を行わない際には、ＳＷ１をオフにし、ＳＷ２をオンにして蓄電体９６３５の充電を行う構成とすればよい。

【０１８７】

なお太陽電池９６３３については、発電手段の一例として示したが、特に限定されず、圧電素子（ピエゾ素子）や熱電変換素子（ペルティエ素子）などの他の発電手段による蓄電体９６３５の充電を行う構成であってもよい。例えば、無線（非接触）で電力を送受信して充電する無接点電力伝送モジュールや、また他の充電手段を組み合わせて行う構成としてもよい。

【０１８８】

図１０に、他の電子機器の例を示す。図１０において、表示装置８０００は、本発明の一態様に係る二次電池８００４を用いた電子機器の一例である。具体的に、表示装置８０００は、ＴＶ放送受信用の表示装置に相当し、筐体８００１、表示部８００２、スピーカ部８００３、二次電池８００４等を有する。本発明の一態様に係る二次電池８００４は、筐体８００１の内部に設けられている。表示装置８０００は、商用電源から電力の供給を受けることもできるし、二次電池８００４に蓄積された電力を用いることもできる。よって、停電などにより商用電源から電力の供給が受けられない時でも、本発明の一態様に係る二次電池８００４を無停電電源として用いることで、表示装置８０００の利用が可能となる。

【０１８９】

表示部８００２には、液晶表示装置、有機ＥＬ素子などの発光素子を各画素に備えた発光装置、電気泳動表示装置、ＤＭＤ（Ｄｉｇｉｔａｌ　Ｍｉｃｒｏｍｉｒｒｏｒ　Ｄｅｖｉ

ｃｅ）、ＰＤＰ（Ｐｌａｓｍａ　Ｄｉｓｐｌａｙ　Ｐａｎｅｌ）、ＦＥＤ（Ｆｉｅｌｄ Ｅｍｉｓｓｉｏｎ　Ｄｉｓｐｌａｙ）などの、半導体表示装置を用いることができる。

【０１９０】

なお、表示装置には、ＴＶ放送受信用の他、パーソナルコンピュータ用、広告表示用など、全ての情報表示用表示装置が含まれる。

【０１９１】

図１０において、据え付け型の照明装置８１００は、本発明の一態様に係る二次電池８１０３を用いた電子機器の一例である。具体的に、照明装置８１００は、筐体８１０１、光源８１０２、二次電池８１０３等を有する。図１０では、二次電池８１０３が、筐体８１０１及び光源８１０２が据え付けられた天井８１０４の内部に設けられている場合を例示しているが、二次電池８１０３は、筐体８１０１の内部に設けられていても良い。照明装置８１００は、商用電源から電力の供給を受けることもできるし、二次電池８１０３に蓄積された電力を用いることもできる。よって、停電などにより商用電源から電力の供給が受けられない時でも、本発明の一態様に係る二次電池８１０３を無停電電源として用いることで、照明装置８１００の利用が可能となる。

【０１９２】

なお、図１０では天井８１０４に設けられた据え付け型の照明装置８１００を例示しているが、本発明の一態様に係る二次電池は、天井８１０４以外、例えば側壁８１０５、床８１０６、窓８１０７等に設けられた据え付け型の照明装置に用いることもできるし、卓上型の照明装置などに用いることもできる。

【０１９３】

また、光源８１０２には、電力を利用して人工的に光を得る人工光源を用いることができる。具体的には、白熱電球、蛍光灯などの放電ランプ、ＬＥＤや有機ＥＬ素子などの発光素子が、上記人工光源の一例として挙げられる。

【０１９４】

図１０において、室内機８２００及び室外機８２０４を有するエアコンディショナーは、本発明の一態様に係る二次電池８２０３を用いた電子機器の一例である。具体的に、室内機８２００は、筐体８２０１、送風口８２０２、二次電池８２０３等を有する。図１０では、二次電池８２０３が、室内機８２００に設けられている場合を例示しているが、二次電池８２０３は室外機８２０４に設けられていても良い。或いは、室内機８２００と室外機８２０４の両方に、二次電池８２０３が設けられていても良い。エアコンディショナーは、商用電源から電力の供給を受けることもできるし、二次電池８２０３に蓄積された電力を用いることもできる。特に、室内機８２００と室外機８２０４の両方に二次電池８２０３が設けられている場合、停電などにより商用電源から電力の供給が受けられない時でも、本発明の一態様に係る二次電池８２０３を無停電電源として用いることで、エアコンディショナーの利用が可能となる。

【０１９５】

なお、図１０では、室内機と室外機で構成されるセパレート型のエアコンディショナーを例示しているが、室内機の機能と室外機の機能とを１つの筐体に有する一体型のエアコンディショナーに、本発明の一態様に係る二次電池を用いることもできる。

【０１９６】

図１０において、電気冷凍冷蔵庫８３００は、本発明の一態様に係る二次電池８３０４を用いた電子機器の一例である。具体的に、電気冷凍冷蔵庫８３００は、筐体８３０１、冷蔵室用扉８３０２、冷凍室用扉８３０３、二次電池８３０４等を有する。図１０では、二次電池８３０４が、筐体８３０１の内部に設けられている。電気冷凍冷蔵庫８３００は、商用電源から電力の供給を受けることもできるし、二次電池８３０４に蓄積された電力を用いることもできる。よって、停電などにより商用電源から電力の供給が受けられない時でも、本発明の一態様に係る二次電池８３０４を無停電電源として用いることで、電気冷凍冷蔵庫８３００の利用が可能となる。

【０１９７】

なお、上述した電子機器のうち、電子レンジ等の高周波加熱装置、電気炊飯器などの電子機器は、短時間で高い電力を必要とする。よって、商用電源では賄いきれない電力を補助するための補助電源として、本発明の一態様に係る二次電池を用いることで、電子機器の使用時に商用電源のブレーカーが落ちるのを防ぐことができる。

【０１９８】

また、電子機器が使用されない時間帯、特に、商用電源の供給元が供給可能な総電力量のうち、実際に使用される電力量の割合（電力使用率と呼ぶ）が低い時間帯において、二次電池に電力を蓄えておくことで、上記時間帯以外において電力使用率が高まるのを抑えることができる。例えば、電気冷凍冷蔵庫８３００の場合、気温が低く、冷蔵室用扉８３０２、冷凍室用扉８３０３の開閉が行われない夜間において、二次電池８３０４に電力を蓄える。そして、気温が高くなり、冷蔵室用扉８３０２、冷凍室用扉８３０３の開閉が行われる昼間において、二次電池８３０４を補助電源として用いることで、昼間の電力使用率を低く抑えることができる。

【０１９９】

本発明の一態様により、二次電池のサイクル特性が良好となり、信頼性を向上させることができる。また、本発明の一態様によれば、二次電池の特性を向上することができ、よって、二次電池自体を小型軽量化することができる。そのため本発明の一態様である二次電池を、本実施の形態で説明した電子機器に搭載することで、より長寿命で、より軽量な電子機器とすることができる。本実施の形態は、他の実施の形態と適宜組み合わせて実施することが可能である。

【０２００】

（実施の形態５）

本実施の形態では、車両に本発明の一態様である二次電池を搭載する例を示す。

【０２０１】

二次電池を車両に搭載すると、ハイブリッド車（ＨＥＶ）、電気自動車（ＥＶ）、又はプラグインハイブリッド車（ＰＨＥＶ）等の次世代クリーンエネルギー自動車を実現できる。

【０２０２】

図１１において、本発明の一態様である二次電池を用いた車両を例示する。図１１（Ａ）に示す自動車８４００は、走行のための動力源として電気モーターを用いる電気自動車である。または、走行のための動力源として電気モーターとエンジンを適宜選択して用いることが可能なハイブリッド自動車である。本発明の一態様を用いることで、航続距離の長い車両を実現することができる。また、自動車８４００は二次電池を有する。二次電池は電気モター８４０６を駆動するだけでなく、ヘッドライト８４０１やルームライト（図示せず）などの発光装置に電力を供給することができる。

【０２０３】

また、二次電池は、自動車８４００が有するスピードメーター、タコメーターなどの表示装置に電力を供給することができる。また、二次電池は、自動車８４００が有するナビゲーションシステムなどの半導体装置に電力を供給することができる。

【０２０４】

図１１（Ｂ）に示す自動車８５００は、自動車８５００が有する二次電池にプラグイン方式や非接触給電方式等により外部の充電設備から電力供給を受けて、充電することができる。図１１（Ｂ）に、地上設置型の充電装置８０２１から自動車８５００に搭載された二次電池８０２４に、ケーブル８０２２を介して充電を行っている状態を示す。充電に際しては、充電方法やコネクターの規格等はＣＨＡｄｅＭＯ（登録商標）やコンボ等の所定の方式で適宜行えばよい。充電装置８０２１は、商用施設に設けられた充電ステーションでもよく、また家庭の電源であってもよい。例えば、プラグイン技術によって、外部からの電力供給により自動車８５００に搭載された二次電池８０２４を充電することができる。充電は、ＡＣＤＣコンバータ等の変換装置を介して、交流電力を直流電力に変換して行うことができる。

【０２０５】
また、図示しないが、受電装置を車両に搭載し、地上の送電装置から電力を非接触で供給して充電することもできる。この非接触給電方式の場合には、道路や外壁に送電装置を組み込むことで、停車中に限らず走行中に充電を行うこともできる。また、この非接触給電の方式を利用して、車両どうしで電力の送受信を行ってもよい。さらに、車両の外装部に太陽電池を設け、停車時や走行時に二次電池の充電を行ってもよい。このような非接触での電力の供給には、電磁誘導方式や磁界共鳴方式を用いることができる。
【０２０６】
また、図１１（Ｃ）は、本発明の一態様の二次電池を用いた二輪車の一例である。図１１（Ｃ）に示すスクータ８６００は、二次電池８６０２、サイドミラー８６０１、方向指示灯８６０３を備える。二次電池８６０２は、方向指示灯８６０３に電気を供給することができる。
【０２０７】
また、図１１（Ｃ）に示すスクータ８６００は、座席下収納８６０４に、二次電池８６０２を収納することができる。二次電池８６０２は、座席下収納８６０４が小型であっても、座席下収納８６０４に収納することができる。
【０２０８】
本発明の一態様によれば、二次電池のサイクル特性が良好となり、信頼性を向上させることができる。また、本発明の一態様によれば、二次電池の特性を向上することができ、よって、二次電池自体を小型軽量化することができる。二次電池自体を小型軽量化できれば、車両の軽量化に寄与するため、航続距離を向上させることができる。また、車両に搭載した二次電池を車両以外の電力供給源として用いることもできる。この場合、電力需要のピーク時に商用電源を用いることを回避することができる。
【０２０９】
本実施の形態は、他の実施の形態と適宜組み合わせて実施することが可能である。
【実施例１】
【０２１０】
本実施例では、本発明の一態様である正極活物質を作製し、該正極活物質についてＳＴＥＭで観察した結果、ＴＥＭ像を高速フーリエ変換した結果、およびエネルギー分散型Ｘ線解析（ＥＤＸ）した結果について説明する。
【０２１１】
本実施例では、正極活物質として、第１の領域が有するリチウムと第１の遷移金属の複合酸化物として、コバルト酸リチウムを有し、第２の領域が有する、第２の遷移金属の酸化物として、チタン酸リチウムを有し、第３の領域が有する、典型元素の酸化物として、酸化マグネシウムを有するものを作製した。
【０２１２】
［正極活物質の作製］
本実施例では、出発原料としてコバルト酸リチウム粒子（日本化学工業株式会社製、商品名：Ｃ―２０Ｆ）を用いた。そのため本実施例では、実施の形態１で説明したステップＳ１２およびステップＳ１３を省略した。なお上記コバルト酸リチウム粒子は、粒径が約２０μｍであり、表面にフッ素、マグネシウム、カルシウム、ナトリウム、シリコン、硫黄、リンを含むコバルト酸リチウム粒子である。
【０２１３】
次に、ステップＳ１４としてコバルト酸リチウム粒子にゾルゲル法によりチタン酸化物を被覆した。具体的には、コバルト酸リチウム粒子に、チタンイソプロポキシドをコバルト酸リチウムに対して０．０１ｍｌ／ｇの割合で混合し、イソプロパノールをその混合物に対して４ｍｌ／ｇとなるように混合した。そして大気中の水分と反応させることで、コバルト酸リチウム粒子の表面をチタン酸化物で被覆した。
【０２１４】
次に、チタン酸化物で被覆されたコバルト酸リチウム粒子を加熱した。マッフル炉を用い

て、流量１０Ｌ＼ｍｉｎのＡｉｒガス雰囲気にて８００℃、保持時間２時間で加熱した。
【０２１５】
次に、加熱された粒子を室温まで冷却した。保持温度から室温までの降温時間は１０～１５時間とした。
【０２１６】
最後に冷却された粒子を回収し、正極活物質を得た。
【０２１７】
［ＳＴＥＭ］
得られた正極活物質を、ＳＴＥＭ（日本電子株式会社製ＪＥＭ―ＡＲＭ２００Ｆ、加速電圧２００ｋＶ）で観察した。得られたＴＥＭ像を図１２に示す。図１２に示すように、正極活物質は、第１の領域１０１と、第２の領域１０２と、第３の領域１０３を有した。第３の領域１０３は酸化マグネシウムであり、第１の領域と第２の領域よりも明るい領域として観察された。また第１の領域と第２の領域の結晶の配向が一部で一致し、第２の領域と第３の領域の結晶の配向が一部で一致した。
【０２１８】
［ＦＦＴ］
図１２に示すＳＴＥＭ像中の１０３ＦＦＴで示す領域の、ＦＦＴ（高速フーリエ変換）像を図１３（Ａ１）に示した。図１３（Ａ２）は、図１３（Ａ１）の中心点Ｏを十字で示し、輝点Ａ、Ｂ、Ｃを丸で囲って示した図である。同様に、１０２ＦＦＴで示す領域のＦＦＴ像を図１３（Ｂ１）に示した。図１３（Ｂ２）は、図１３（Ｂ１）の中心点Ｏを十字で示し、輝点Ａ、Ｂ、Ｃを丸で囲って示した図である。また１０３ＦＦＴで示す領域のＦＦＴ像を図１３（Ｃ１）に示した。図１３（Ｃ２）は、図１３（Ｃ１）の中心点Ｏを十字で示し、輝点Ａ、Ｂ、Ｃを丸で囲って示した図である。
【０２１９】
図１３（Ａ２）に示した輝点Ａと中心点Ｏ間の距離は、ｄ　＝　０．２５６ｎｍであった。輝点Ｂと中心点Ｏ間の距離は、ｄ　＝　０．２４１ｎｍであった。輝点Ｃと中心点Ｏ間の距離は、ｄ　＝　０．２０９ｎｍであった。また、∠ＣＯＡ＝１２１°、∠ＣＯＢ＝５２°、∠ＡＯＢ＝６９°であった。これらの結果から、１０３ＦＦＴで示す領域は酸化マグネシウム（ＭｇＯ、立方晶）であることが推察された。
【０２２０】
同様に、図１３（Ｂ２）に示した輝点Ａと中心点Ｏ間の距離は、ｄ＝　０．２３８ｎｍであった。輝点Ｂと中心点Ｏ間の距離は、ｄ＝０．２２５ｎｍであった。輝点Ｃと中心点Ｏ間の距離は、ｄ＝０．１９８ｎｍであった。また、∠ＣＯＡ＝１２３°、∠ＣＯＢ＝５２°、∠ＡＯＢ＝７１°であった。これらの結果から、１０２ＦＦＴで示す領域はチタン酸リチウム（$LiTiO_2$、立方晶）であることが推察された。
【０２２１】
図１３（Ｃ２）に示した輝点Ａと中心点Ｏ間の距離は、ｄ＝０．２４０ｎｍであった。輝点Ｂと中心点Ｏ間の距離は、ｄ＝０．２３５ｎｍであった。輝点Ｃと中心点Ｏ間の距離は、ｄ＝０．１９６ｎｍであった。また、∠ＣＯＡ＝１２６°、∠ＣＯＢ＝５２°、∠ＡＯＢ＝７４°であった。これらの結果から、１０３ＦＦＴで示す領域はコバルト酸リチウム（$LiCoO_2$、Ｒｈｏｍｂｏｈｅｄｒａｌ）であることが推察された。
【０２２２】
［ＥＤＸ］
また得られた正極活物質の、高角散乱環状暗視野走査透過顕微鏡法（ＨＡＡＤＦ―ＳＴＥＭ）像およびＥＤＸを用いた元素マッピング像を図１４に示す。図１４（Ａ１）はＨＡＡＤＦ―ＳＴＥＭ像、図１４（Ａ２）は酸素原子マッピング像、図１４（Ｂ１）はコバルト原子マッピング像、図１４（Ｂ２）はフッ素原子マッピング像、図１４（Ｃ１）はチタン原子マッピング像、図１４（Ｃ２）はマグネシウム原子マッピング像である。
【０２２３】
図１４に示すように、酸素原子、コバルト原子およびフッ素原子は正極活物質粒子全体に

分布していることが明らかとなった。一方、図１４（Ｃ１）および図１４（Ｃ２）に示すようにチタン原子およびマグネシウム原子は、正極活物質の表面に近い、第２の領域および第３の領域に偏在していることが明らかとなった。

【０２２４】

上記のＳＴＥＭ像、ＦＦＴ像およびＥＤＸを用いた元素マッピング像から、第１の領域がコバルト酸リチウムを有し、第２の領域がチタン酸リチウムを有し、第３の領域が酸化マグネシウムを有する正極活物質を作製できたことを確認できた。

【実施例２】

【０２２５】

本実施例では、実施例１で作製した正極活物質を用いた二次電池を作製し、該二次電池の充放電特性について評価した結果について説明する。

【０２２６】

［実施例１で作製した正極活物質を用いた二次電池の作製］

実施例１で作製した正極活物質を用いた、ＣＲ２０３２タイプ（直径２０ｍｍ高さ３．２ｍｍ）のコイン型の二次電池を作製した。

【０２２７】

正極には、実施例１で作製した正極活物質（ＬＣＯ）と、アセチレンブラック（ＡＢ）と、ポリフッ化ビニリデン（ＰＶＤＦ）をＬＣＯ：ＡＢ：ＰＶＤＦ＝９５：２．５：２．５（重量比）で混合したスラリーを集電体に塗工したものを用いた。

【０２２８】

対極にはリチウム金属を用いた。

【０２２９】

電解液が有する電解質には、１ｍｏｌ／Ｌの六フッ化リン酸リチウム（ＬｉＰＦ$_6$）を用い、電解液には、エチレンカーボネート（ＥＣ）とジエチルカーボネート（ＤＥＣ）がＥＣ：ＤＥＣ＝３：７（体積比）、ビニレンカーボネート（ＶＣ）が２重量％で混合されたものを用いた。

【０２３０】

正極缶及び負極缶には、ステンレス（ＳＵＳ）で形成されているものを用いた。

【０２３１】

［比較例の二次電池の作製］

次に、比較例の二次電池を作製した。比較例の二次電池が有する正極活物質としては、コバルト酸リチウム粒子（日本化学工業株式会社製、商品名：Ｃ―２０Ｆ）を用いた。該コバルト酸リチウム粒子は、実施例１で出発原料として用いたものであり、実施例１で作製した正極活物質と異なり実施の形態１で説明したステップＳ１４からステップＳ１７を行っていない正極活物質である。

【０２３２】

比較例の正極活物質の、ＥＤＸを用いた元素マッピング像を図１５に示す。図１５（Ａ１）はＨＡＡＤＦ―ＳＴＥＭ像、図１５（Ａ２）は酸素原子マッピング像、図１５（Ｂ１）はコバルト原子マッピング像、図１５（Ｂ２）はフッ素原子マッピング像、図１５（Ｃ１）はチタン原子マッピング像、図１５（Ｃ２）はマグネシウム原子マッピング像である。

【０２３３】

図１５に示すように、酸素原子、コバルト原子およびフッ素原子は、実施例１で作製した正極活物質粒子と同様に、全体に分布していることが明らかとなった。

【０２３４】

一方、図１５（Ｃ１）に示す輝点はバックグラウンドのノイズと考えられ、比較例の正極活物質中にチタン原子はほとんど存在しなかった。

【０２３５】

また、図１５（Ｃ２）に示すようにマグネシウム原子は、正極活物質の表面に近い領域に偏在していることが明らかとなった。

【０２３６】

［充放電特性の評価］
次に、上記で作製した２種の二次電池の充放電特性の評価を行った。測定温度は２５℃とした。充電は４．６Ｖ（ＣＣＣＶ，０．５Ｃ―０．０１Ｃ）、放電は２．５Ｖ（ＣＣ，０．５Ｃ）で、それぞれ２０サイクル充放電を行った。
【０２３７】
図１６に、実施例１で作製した正極活物質を用いた二次電池の充放電特性のグラフを示す。図１６に示すように、広いプラトーを有する良好な充放電特性を示した。また２０サイクルの充放電のグラフはほぼ重なり、サイクル特性は良好であった。
【０２３８】
図１７に、比較例の二次電池の充放電特性のグラフを示す。初期のサイクルでは良好な充放電特性を示したが、図中の矢印で示すように、サイクルを経るにつれて充放電容量が減少した。
【実施例３】
【０２３９】
本実施例では、実施例１で作製した正極活物質を用いた二次電池を作製し、該二次電池のサイクル特性について評価した結果について説明する。
【０２４０】
［サイクル特性の評価］
実施例２と同様に、実施例１で作製した正極活物質を用いた二次電池と、比較例の二次電池を作製した。そして、４．４Ｖ充電の場合と、４．６Ｖ充電の場合のサイクル特性をそれぞれ評価した。
【０２４１】
［充電４．４Ｖ］
充電４．４Ｖの場合のサイクル特性測定温度は２５℃とした。充電は４．４Ｖ（ＣＣＣＶ，０．５Ｃ―０．０１Ｃ）、放電は２．５Ｖ（ＣＣ，０．５Ｃ）で行った。
【０２４２】
図１８に、充電４．４Ｖの場合のサイクル特性のグラフを示す。図中の実線は実施例１で作製した正極活物質を有する二次電池、点線は比較例の正極活物質を有する二次電池のグラフである。図１８に示すように、実施例１で作製した正極活物質を有する二次電池は、５０サイクルを経てもエネルギー密度の維持率は９９．５％であり、極めて良好なサイクル特性を示した。一方、比較例の正極活物質を有する二次電池は、５０サイクルを経た時点のエネルギー密度の維持率は９４．３％であった。
【０２４３】
［充電４．６Ｖ］
充電４．６Ｖの場合の測定温度は２５℃とした。充電は４．６Ｖ（ＣＣＣＶ，０．５Ｃ―０．０１Ｃ）、放電は２．５Ｖ（ＣＣ，０．５Ｃ）で行った。
【０２４４】
図１９に、充電４．６Ｖの場合のサイクル特性のグラフを示す。図中の実線は実施例１で作製した正極活物質を有する二次電池、点線は比較例の正極活物質を有する二次電池のグラフである。図１９に示すように、本発明の一態様の正極活物質を有する二次電池は、４．６Ｖという高い電圧の充電で５０サイクルを経てもエネルギー密度の維持率は９４．１％であり、良好なサイクル特性を示した。一方、比較例の正極活物質を有する二次電池は、５０サイクルを経た時点のエネルギー密度の維持率は３３．２％であった。
【符号の説明】
【０２４５】
１１ａ　正極
１１ｂ　負極
１２ａ　リード
１２ｂ　リード
１４　セパレータ

１５ａ　接合部
１５ｂ　接合部
１７　固定部材
５０　電池
５１　外装体
６１　折り曲げ部
６２　シール部
６３　シール部
７１　稜線
７２　谷線
７３　空間
１００　正極活物質
１０１　第１の領域
１０２　第２の領域
１０３　第３の領域
１０４　第４の領域
２００　活物質層
２０１　グラフェン化合物
３００　二次電池
３０１　正極缶
３０２　負極缶
３０３　ガスケット
３０４　正極
３０５　正極集電体
３０６　正極活物質層
３０７　負極
３０８　負極集電体
３０９　負極活物質層
３１０　セパレータ
６００　二次電池
６０１　正極キャップ
６０２　電池缶
６０３　正極端子
６０４　正極
６０５　セパレータ
６０６　負極
６０７　負極端子
６０８　絶縁板
６０９　絶縁板
６１１　ＰＴＣ素子
６１２　安全弁機構
７１００　携帯表示装置
７１０１　筐体
７１０２　表示部
７１０３　操作ボタン
７１０４　二次電池
７２００　携帯情報端末
７２０１　筐体
７２０２　表示部
７２０３　バンド

７２０４　バックル
７２０５　操作ボタン
７２０６　入出力端子
７２０７　アイコン
７３００　表示装置
７３０４　表示部
７４００　携帯電話機
７４０１　筐体
７４０２　表示部
７４０３　操作ボタン
７４０４　外部接続ポート
７４０５　スピーカ
７４０６　マイク
７４０７　二次電池
７４０８　リード電極
７４０９　集電体
８０００　表示装置
８００１　筐体
８００２　表示部
８００３　スピーカ部
８００４　二次電池
８０２１　充電装置
８０２２　ケーブル
８０２４　二次電池
８１００　照明装置
８１０１　筐体
８１０２　光源
８１０３　二次電池
８１０４　天井
８１０５　側壁
８１０６　床
８１０７　窓
８２００　室内機
８２０１　筐体
８２０２　送風口
８２０３　二次電池
８２０４　室外機
８３００　電気冷凍冷蔵庫
８３０１　筐体
８３０２　冷蔵室用扉
８３０３　冷凍室用扉
８３０４　二次電池
８４００　自動車
８４０１　ヘッドライト
８４０６　電気モーター
８５００　自動車
８６００　スクータ
８６０１　サイドミラー
８６０２　二次電池
８６０３　方向指示灯

８６０４　　座席下収納
９６００　　タブレット型端末
９６２５　　スイッチ
９６２６　　スイッチ
９６２７　　電源スイッチ
９６２８　　操作スイッチ
９６２９　　留め具
９６３０　　筐体
９６３０ａ　　筐体
９６３０ｂ　　筐体
９６３１　　表示部
９６３１ａ　　表示部
９６３１ｂ　　表示部
９６３２ａ　　領域
９６３２ｂ　　領域
９６３３　　太陽電池
９６３４　　充放電制御回路
９６３５　　蓄電体
９６３６　　ＤＣＤＣコンバータ
９６３７　　コンバータ
９６３８　　操作キー
９６３９　　ボタン
９６４０　　可動部

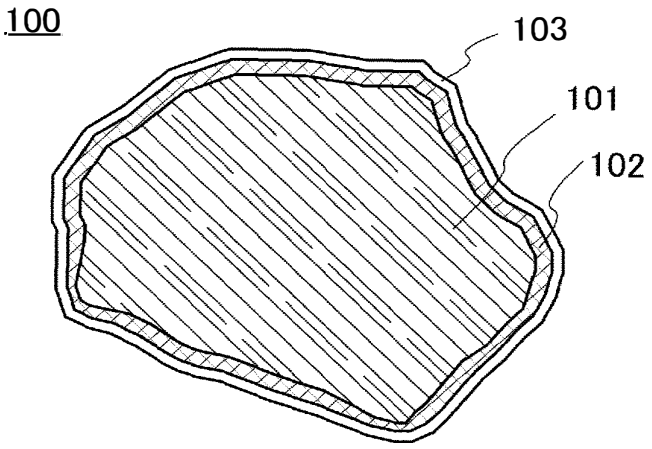
【書類名】特許請求の範囲
【請求項１】
第１の領域と、
前記第１の領域の少なくとも一部を被覆する第２の領域と、
前記第２の領域の少なくとも一部を被覆する第３の領域と、を有し、
前記第１の領域はコバルト酸リチウムを有し、
前記第２の領域はチタン酸リチウムを有し、
前記第３の領域は酸化マグネシウムを有する正極活物質。
【請求項２】
請求項１において、
前記第１の領域と、前記第２の領域の結晶の配向が一部で一致し、
前記第２の領域と、前記第３の領域の結晶の配向が一部で一致する正極活物質。
【請求項３】
請求項２において、
前記第１の領域は、層状岩塩型の結晶構造を有し、
前記第２の領域は、岩塩型の結晶構造を有し、
前記第３の領域は、岩塩型の結晶構造を有する正極活物質。
【請求項４】
請求項１乃至請求項３のいずれか一に記載の正極活物質を有する正極と、
負極と、を有する二次電池。
【請求項５】
リチウム源、第１の遷移金属源、マグネシウム源およびフッ素源を混合する工程と、
８００℃以上１１００℃以下で２時間以上２０時間以下加熱する工程と、
第２の遷移金属アルコキシドを加えて混合する工程と、
酸素を有する雰囲気で５００℃以上１２００℃以下、保持時間５０時間以下で加熱する工程と、
室温まで冷却する工程と、
を有する正極活物質の作製方法。
【請求項６】
請求項５において、
前記フッ素源に含まれるフッ素と、前記マグネシウム源に含まれるマグネシウムの比は、
Ｍｇ：Ｆ＝１：ｘ（１．５≦ｘ≦４）
である、正極活物質の作製方法。
【請求項７】
請求項５または請求項６において、
前記マグネシウム源に含まれるマグネシウムは、
前記コバルト源に含まれるコバルトの０．５ｍｏｌ％以上１．５ｍｏｌ％以下である正極活物質の作製方法。
【請求項８】
請求項５乃至請求項７のいずれか一において、
前記第１の遷移金属は、ニッケル、マンガン、コバルトの少なくとも一である正極活物質の作製方法。
【請求項９】
請求項５乃至請求項８のいずれか一において、
前記第２の遷移金属アルコキシドは、チタンイソプロポキシドである正極活物質の作製方法。
【請求項１０】
請求項５乃至請求項９のいずれか一において
前記リチウム源には炭酸リチウムを用い、

前記コバルト源には酸化コバルトを用い、
前記マグネシウム源には酸化マグネシウムを用い、
前記フッ素源にはフッ化リチウムを用いる、正極活物質の作製方法。
【請求項１１】
請求項５乃至請求項１０のいずれか一に記載の作製方法により作製される正極活物質。

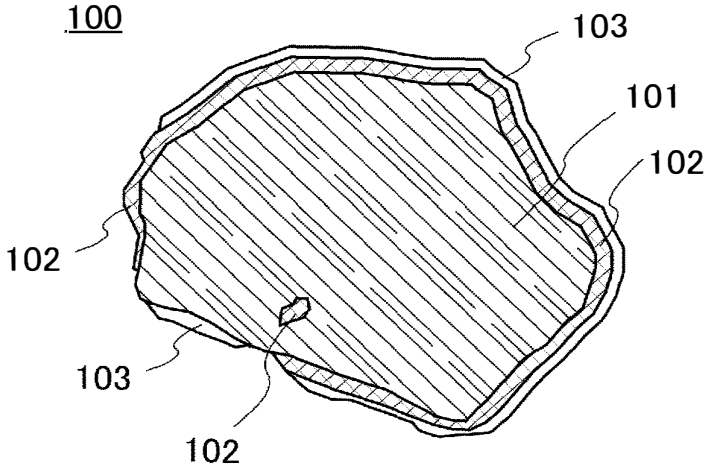
【書類名】要約書
【要約】
【課題】二次電池のサイクル特性を向上できる正極活物質、および該正極活物質の作製方法を提供する。
【解決手段】層状岩塩型の結晶構造を有する正極活物質の表面に、２種の被覆層を設ける。内側の被覆層はゾルゲル法等の被覆工程を経て形成し、外側の被覆層は加熱に伴う析出によって形成する。２種の被覆層を１回の被覆工程で形成できるため、生産性のよい作製方法とすることができる。またエピタキシャル成長により外側の被覆層を形成させることができるため、結晶の配向が一致した、安定した被覆層を有する正極活物質とすることができる。
【選択図】図１

【書類名】図面
【図１】

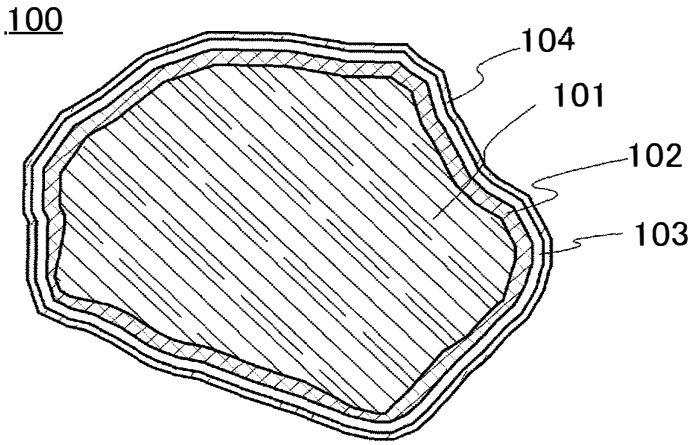
(A)



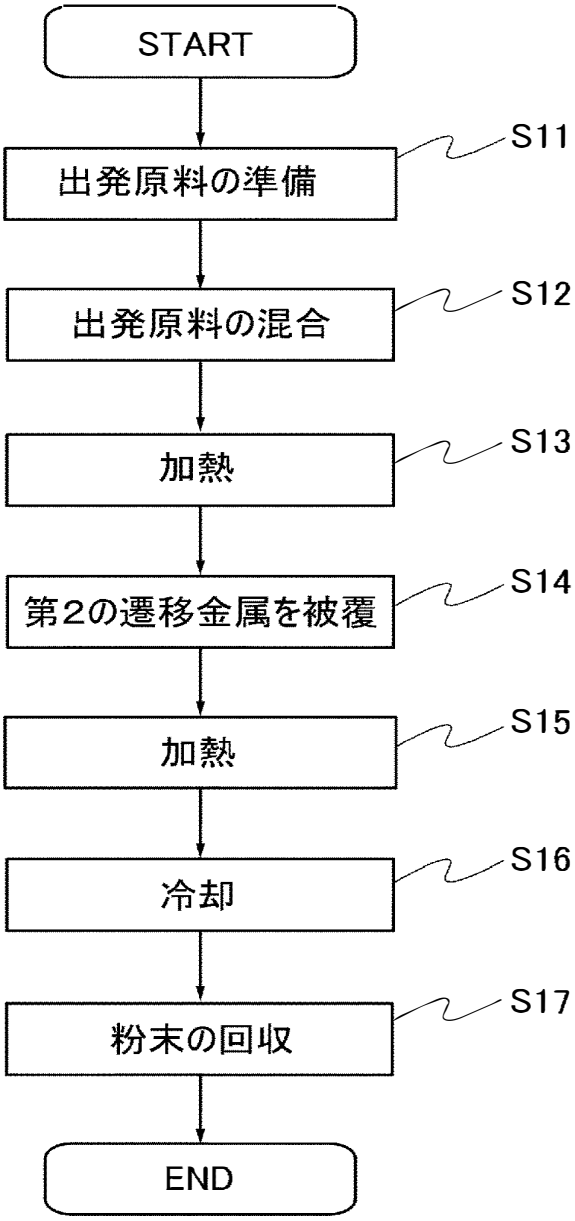
(B)



(C)

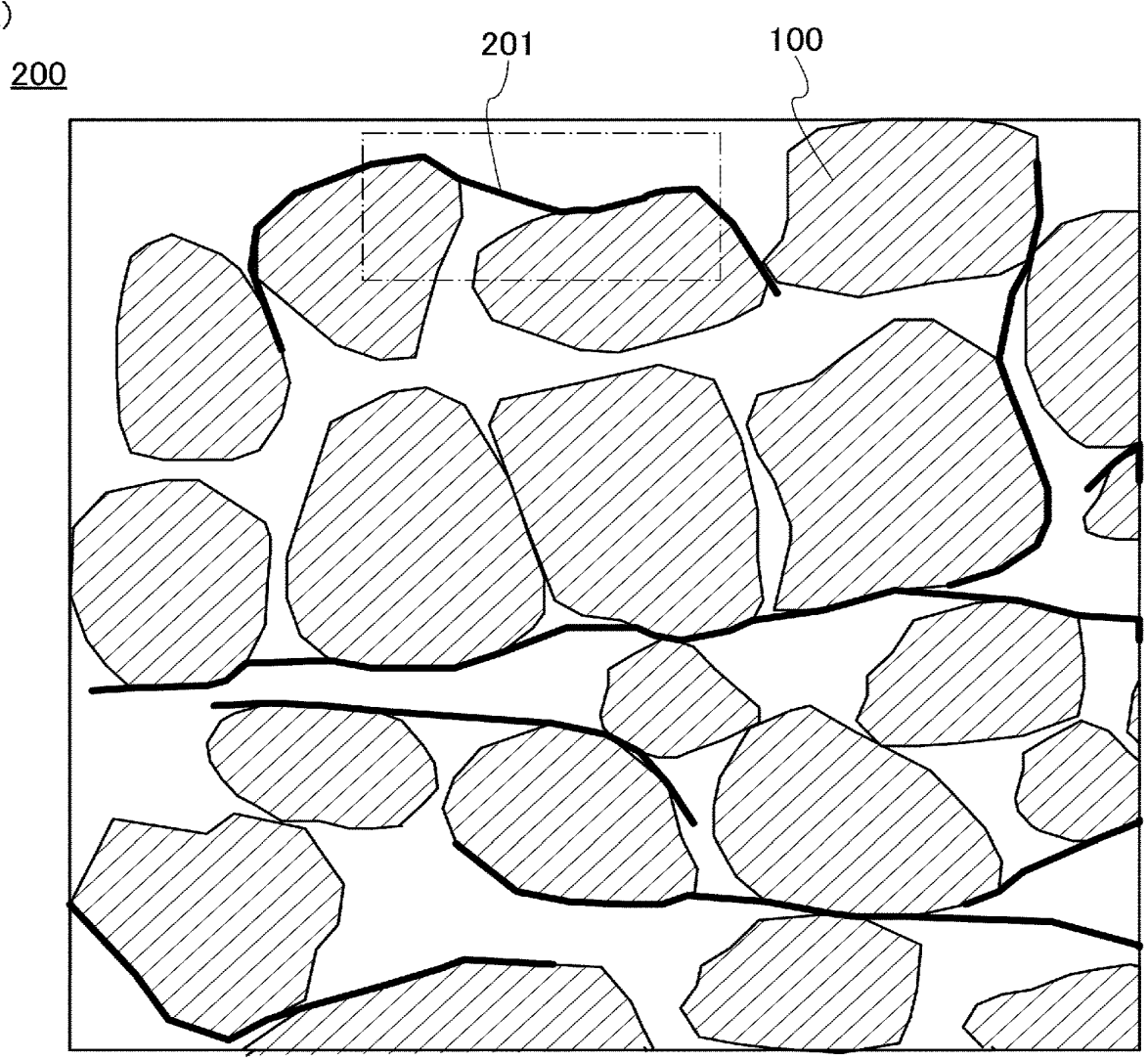


【図２】

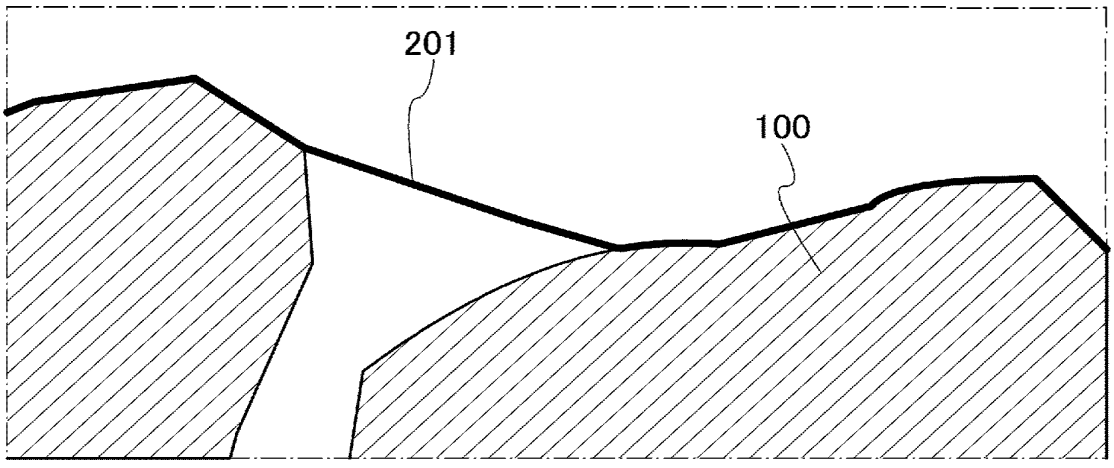

START
S11
出発原料の準備
S12
出発原料の混合
S13
加熱
S14
第2の遷移金属を被覆
S15
加熱
S16
冷却
S17
粉末の回収
END

【図３】

(A)

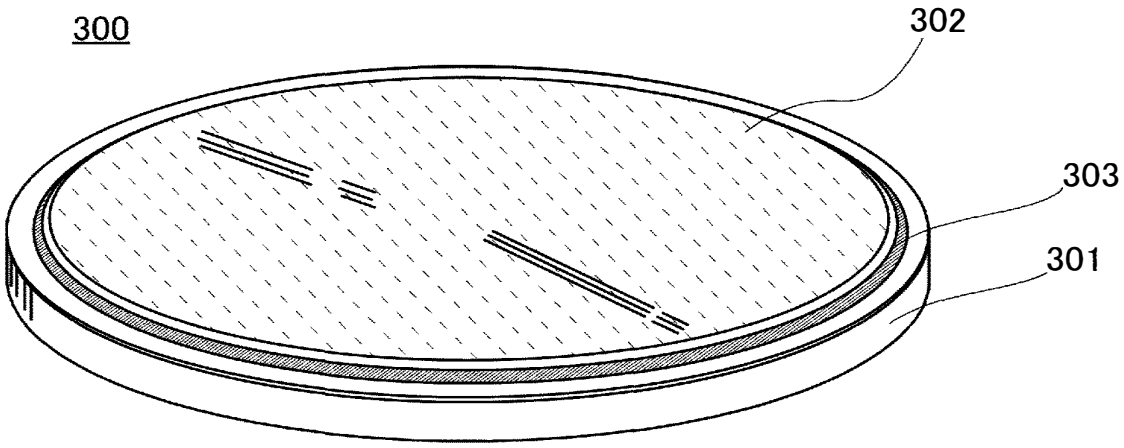


(B)

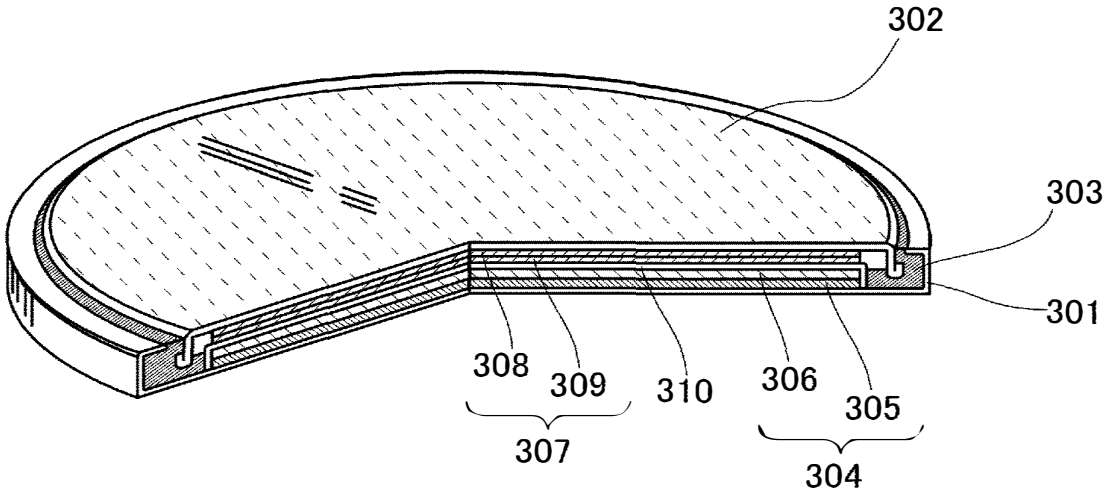


【図４】

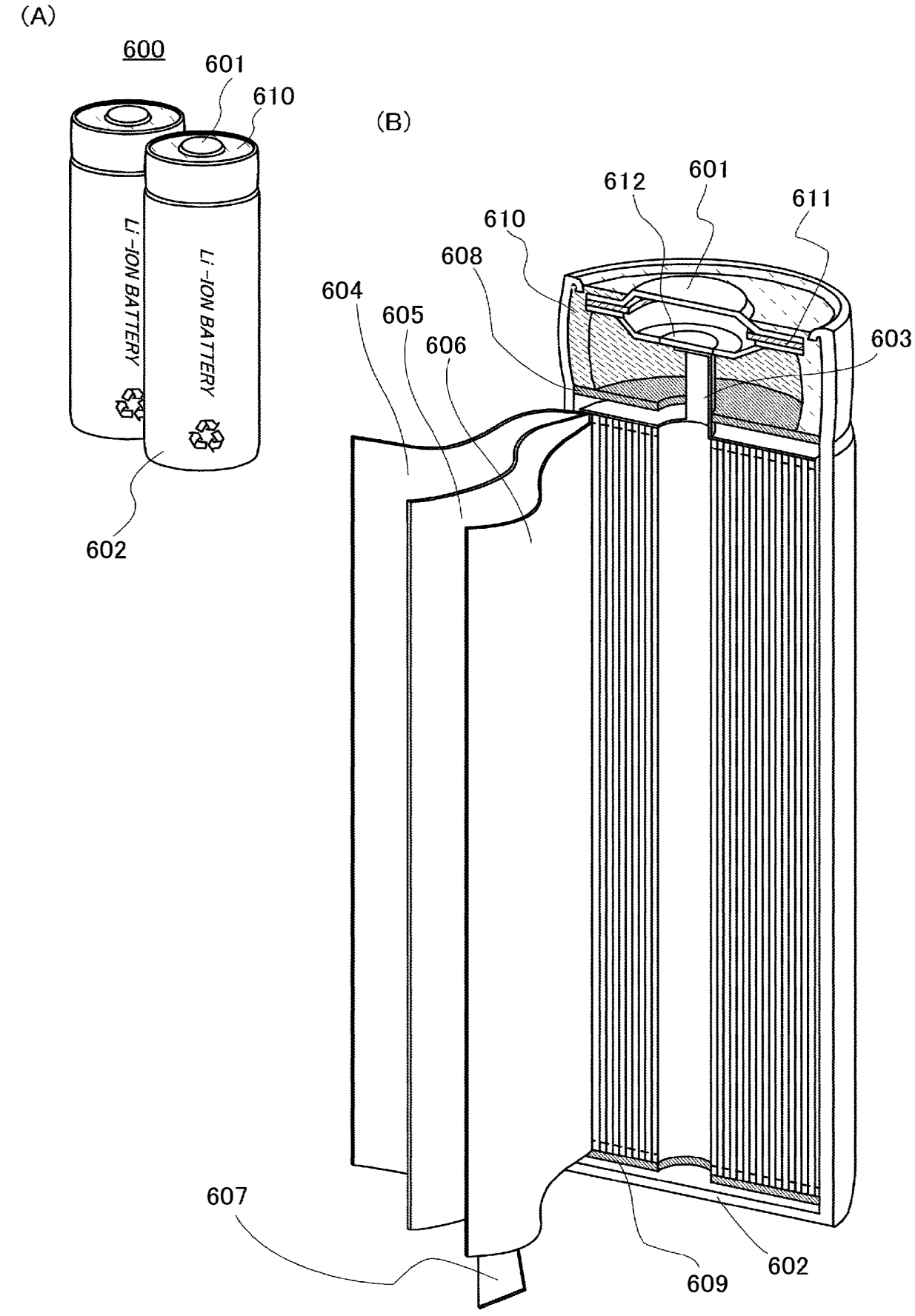
(A)



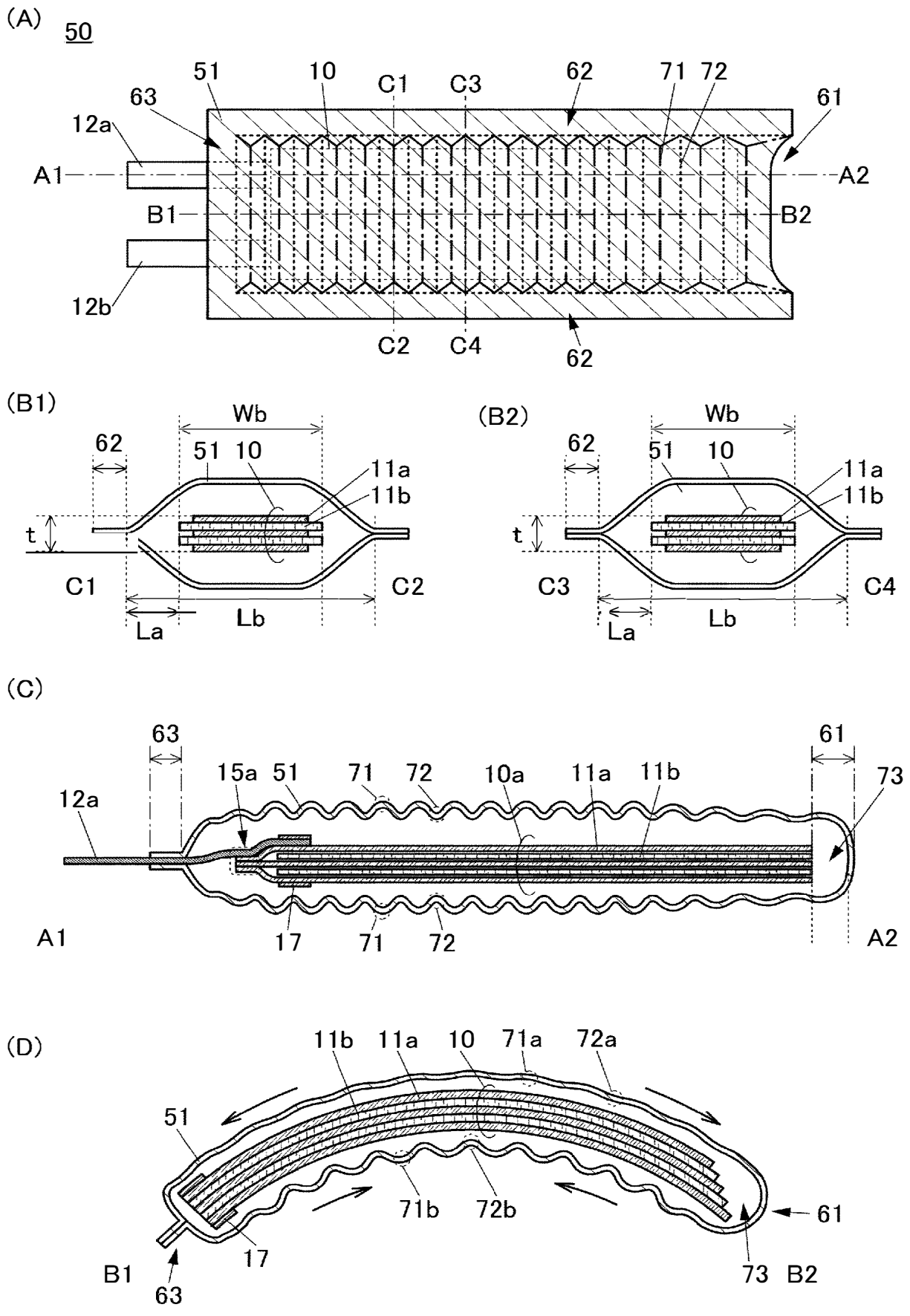
(B)



【図５】

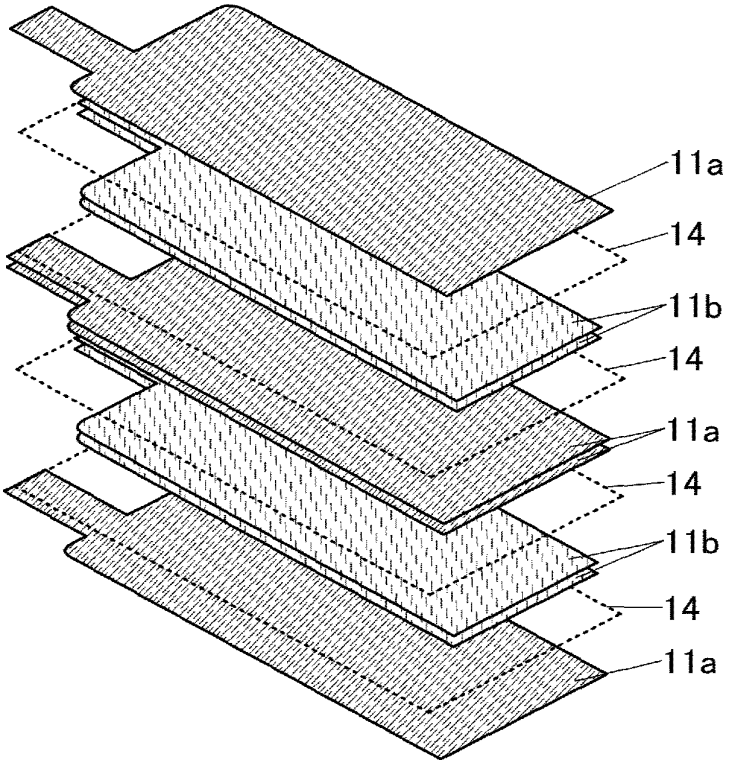

(A)
600
601
610
Li-ION BATTERY
Li-ION BATTERY
602
(B)
612
601
611
610
608
604
605
606
603
607
609
602

【図６】

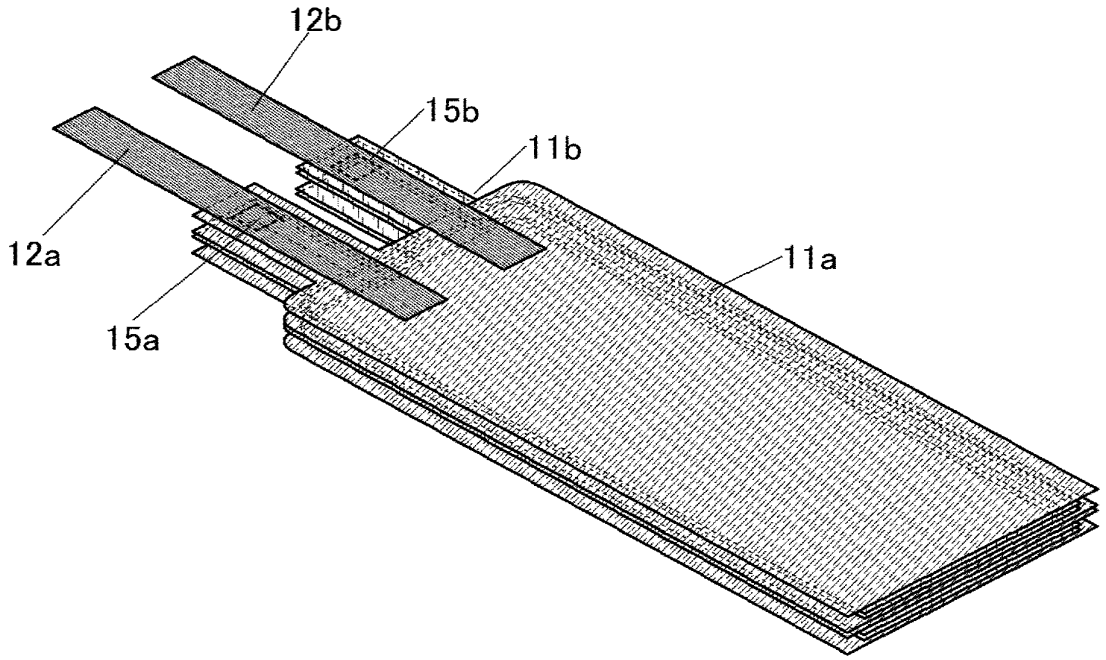

(A)
50
51
10
C1
C3
62
71
72
63
61
12a
A1
A2
B1
B2
12b
C2
C4
62
(B1)
Wb
62
51
10
11a
11b
t
C1
C2
La
Lb
(B2)
Wb
62
51
10
11a
11b
t
C3
C4
La
Lb
(C)
63
61
15a
51
71
72
10a
11a
11b
73
12a
A1
17
71
72
A2
(D)
11b
11a
10
71a
72a
51
71b
72b
61
17
B1
63
73
B2

【図７】

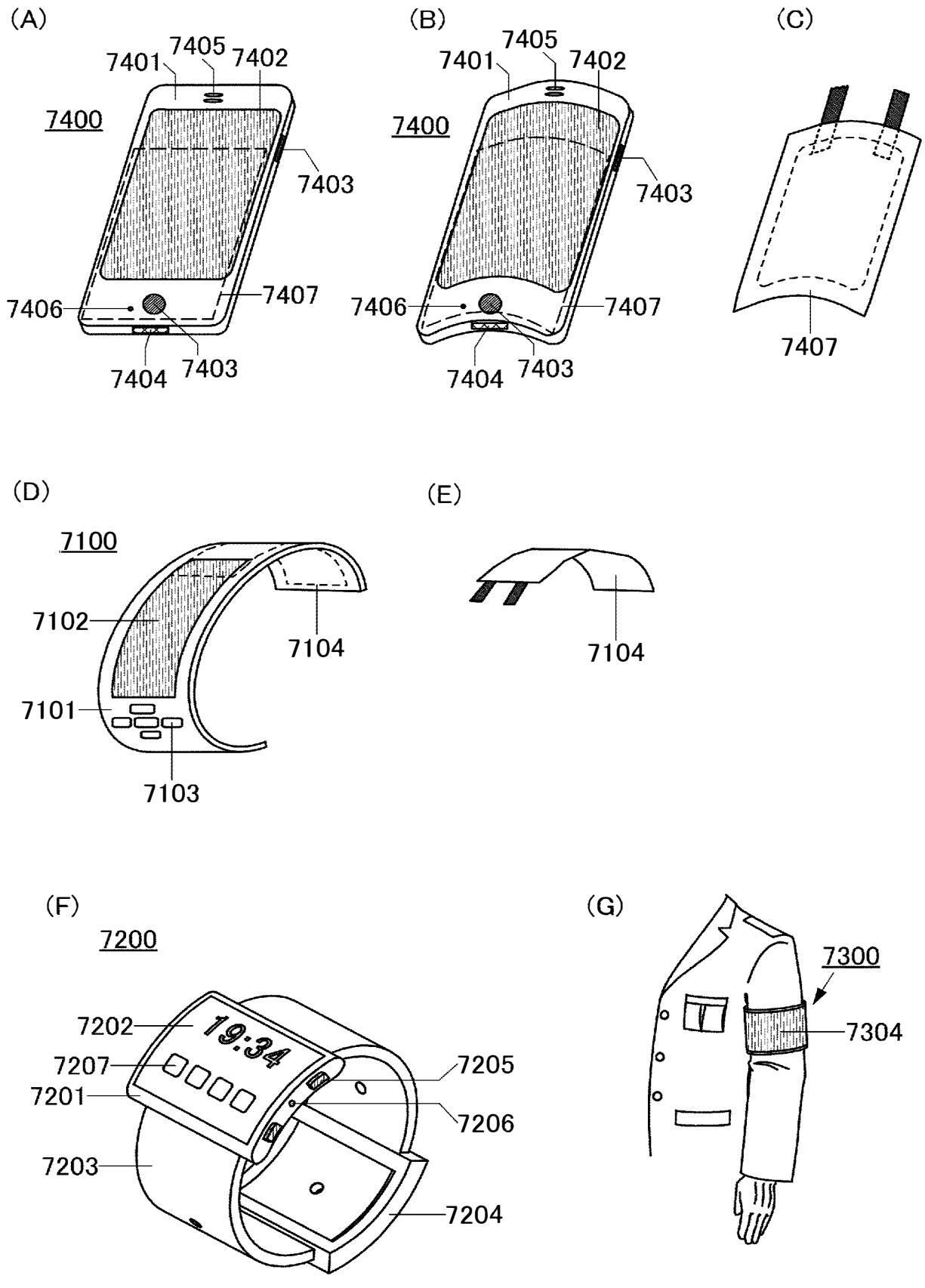
(A)



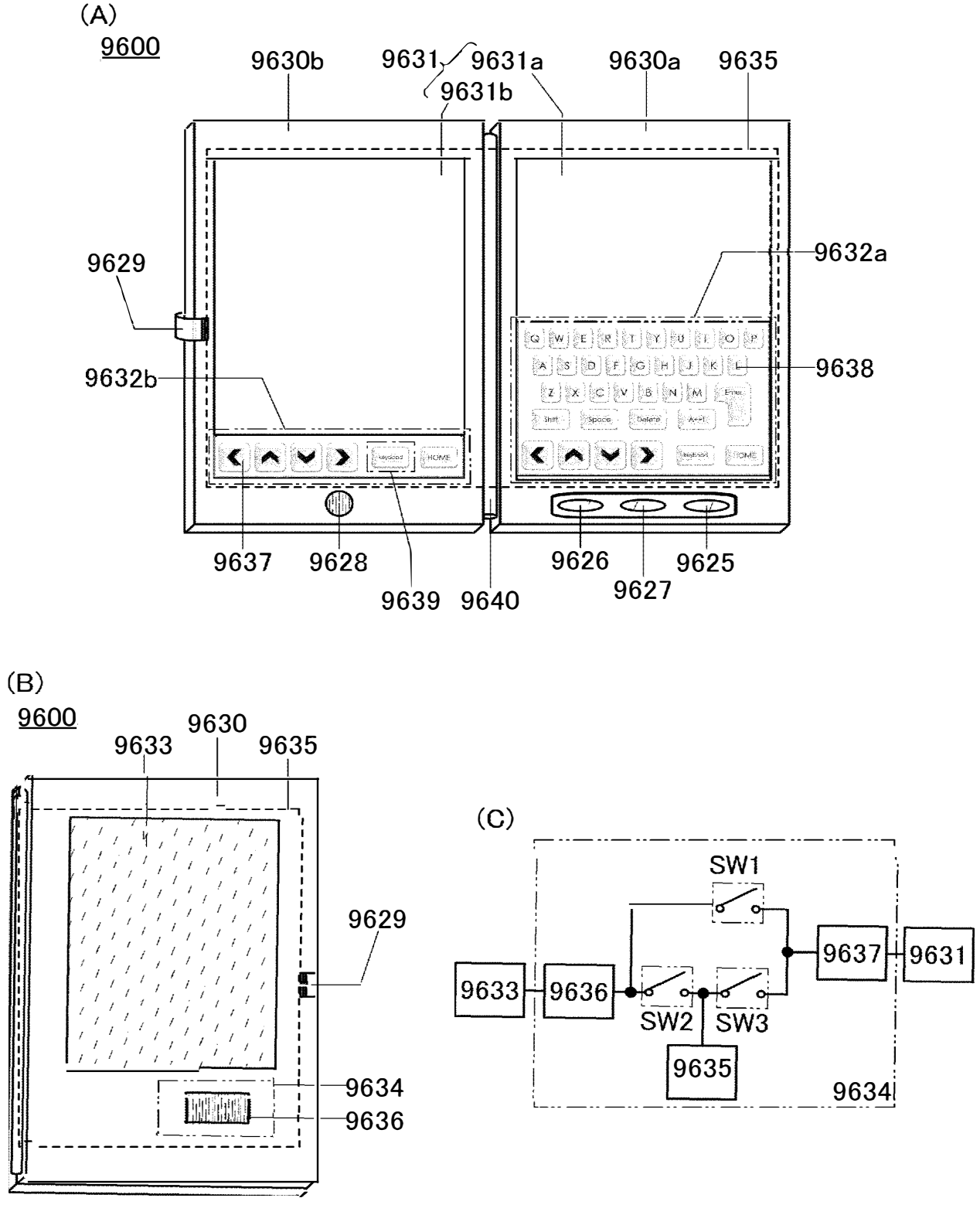
(B)



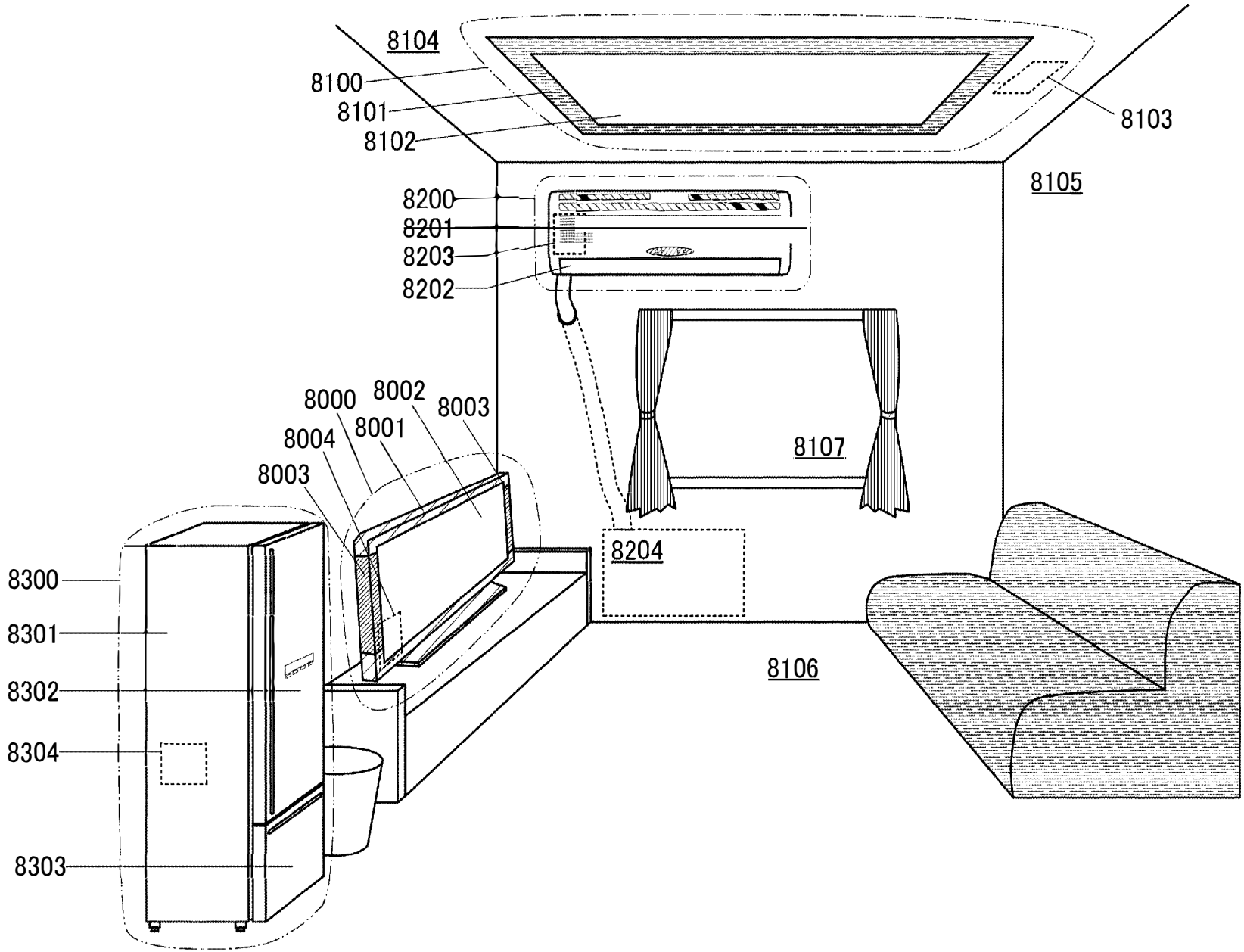
【図８】


(A)
7401
7405
7402
7400
7403
7406
7407
7404
7403
(B)
7401
7405
7402
7400
7403
7406
7407
7404
7403
(C)
7407
(D)
7100
7102
7104
7101
7103
(E)
7104
(F)
7200
7202
19:34
7207
7201
7205
7206
7203
7204
(G)
7300
7304

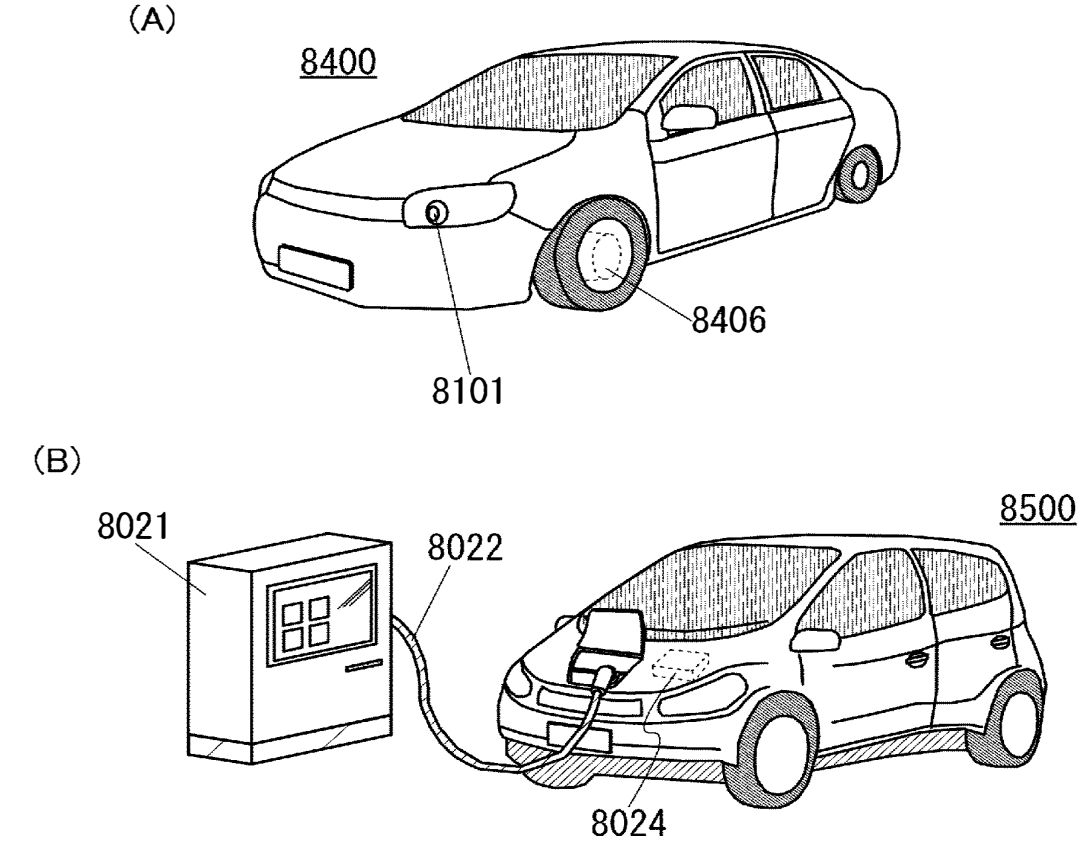
【図９】


(A)
9600
9630b
9631
9631a
9630a
9635
9631b
9629
9632a
9632b
9638
9637
9628
9639
9640
9626
9627
9625
(B)
9600
9633
9630
9635
9629
9634
9636
(C)
SW1
9637
9631
9633
9636
SW2
SW3
9635
9634

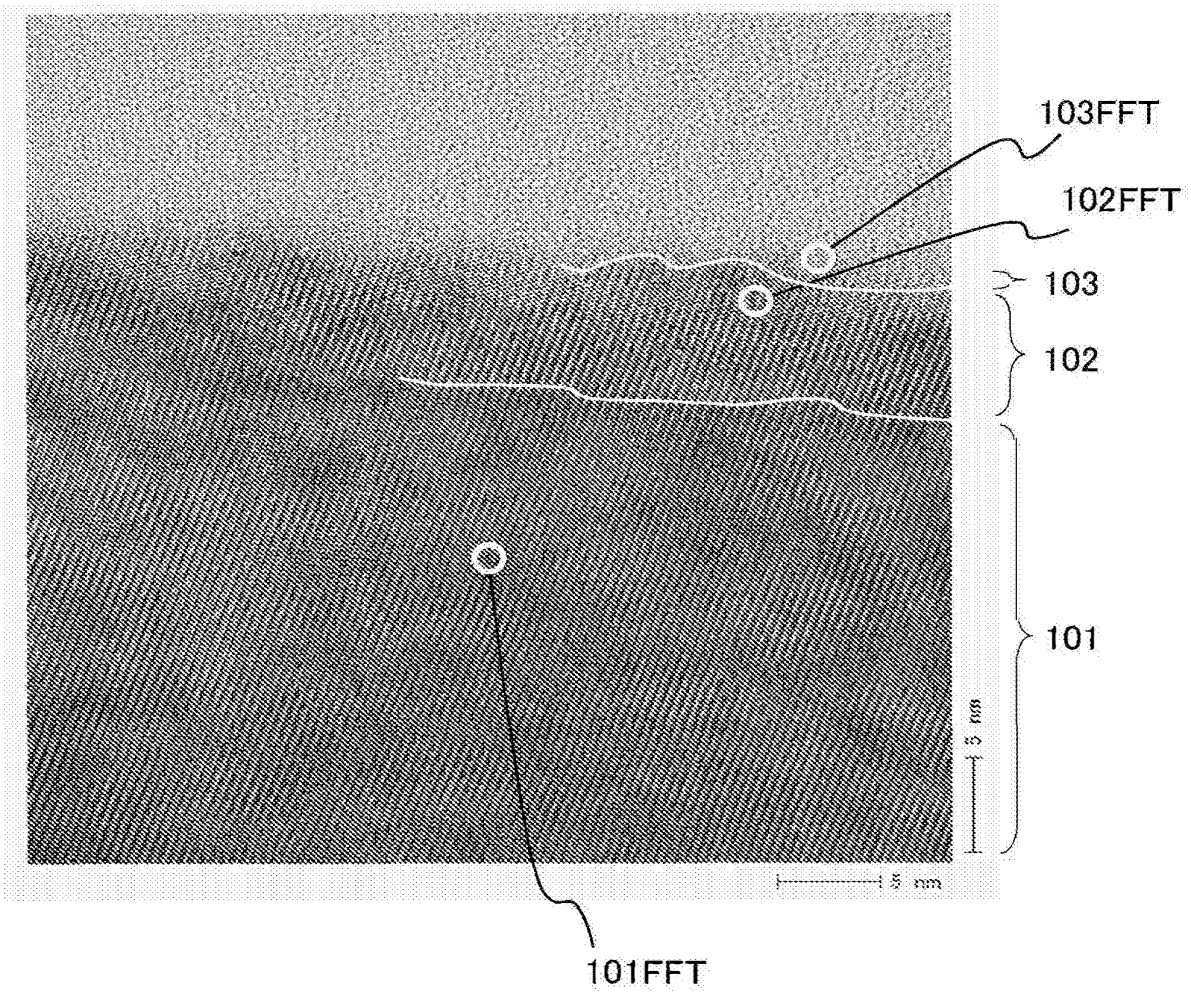
【図１０】


8104
8100
8101
8102
8103
8105
8200
8201
8203
8202
8000
8002
8003
8001
8004
8003
8107
8204
8300
8301
8302
8304
8303
8106

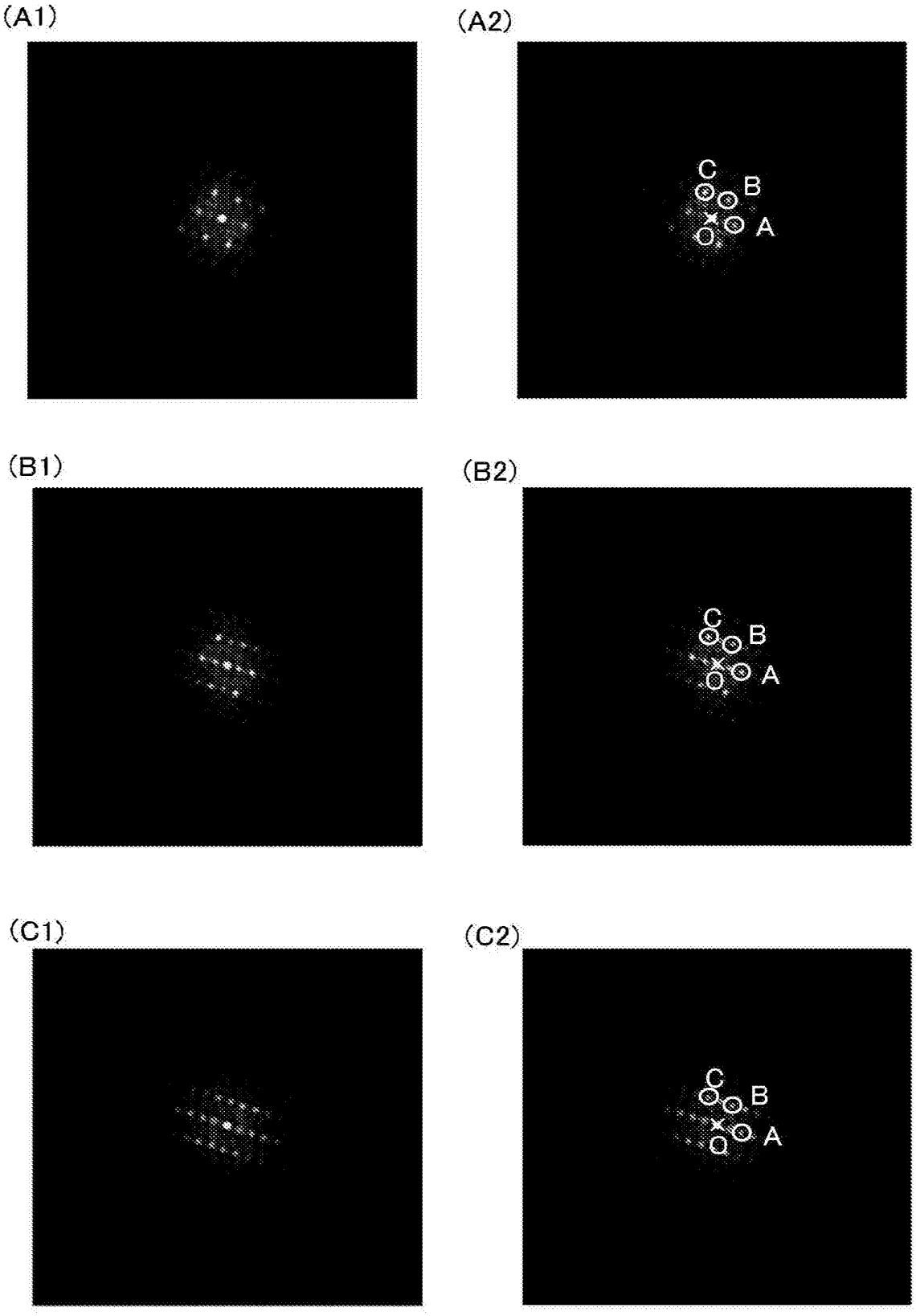
【図１１】


(A)
8400
8406
8101
(B)
8021
8022
8500
8024
(C)
8600
8601
8604
8602
8603

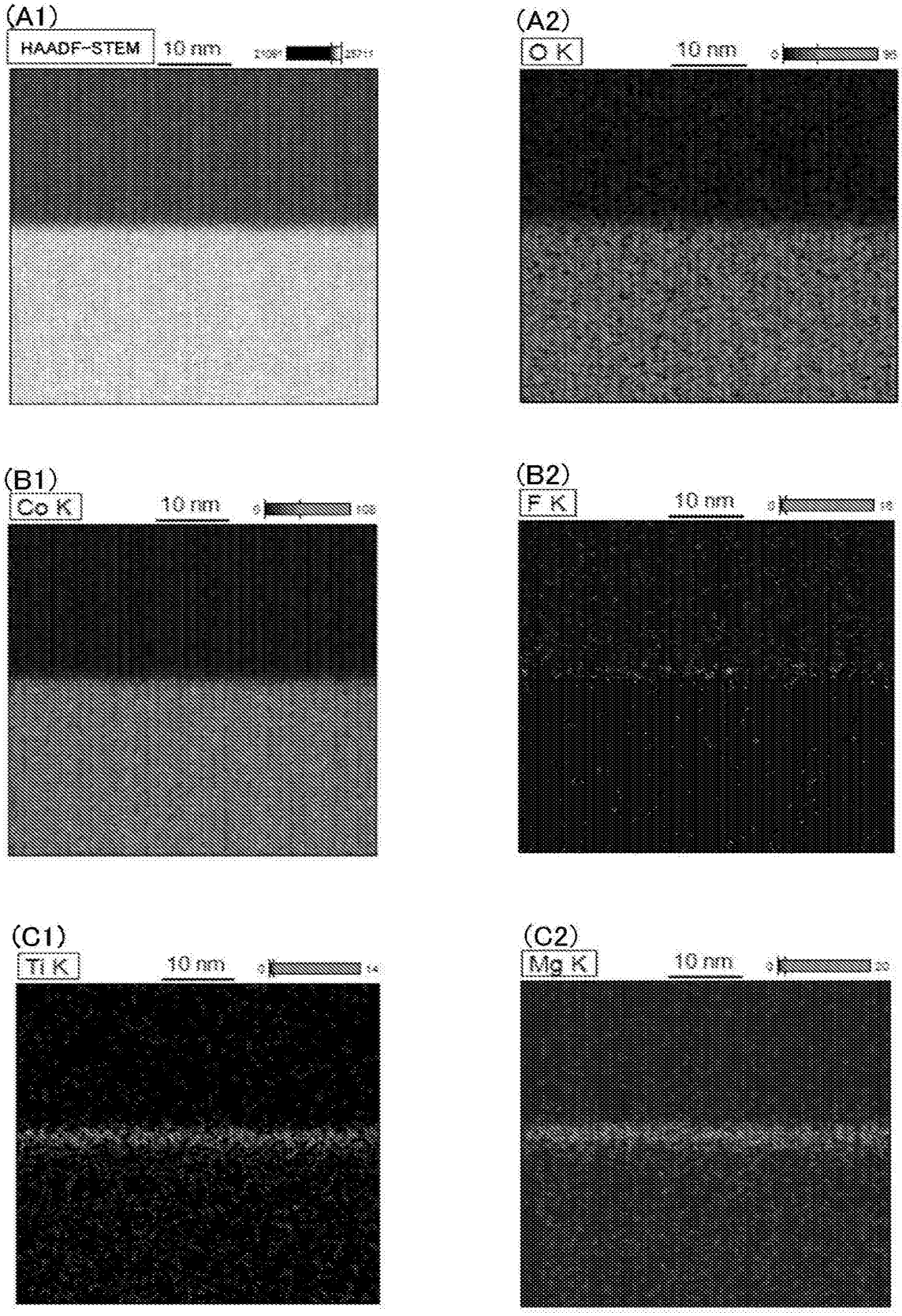
【図１２】



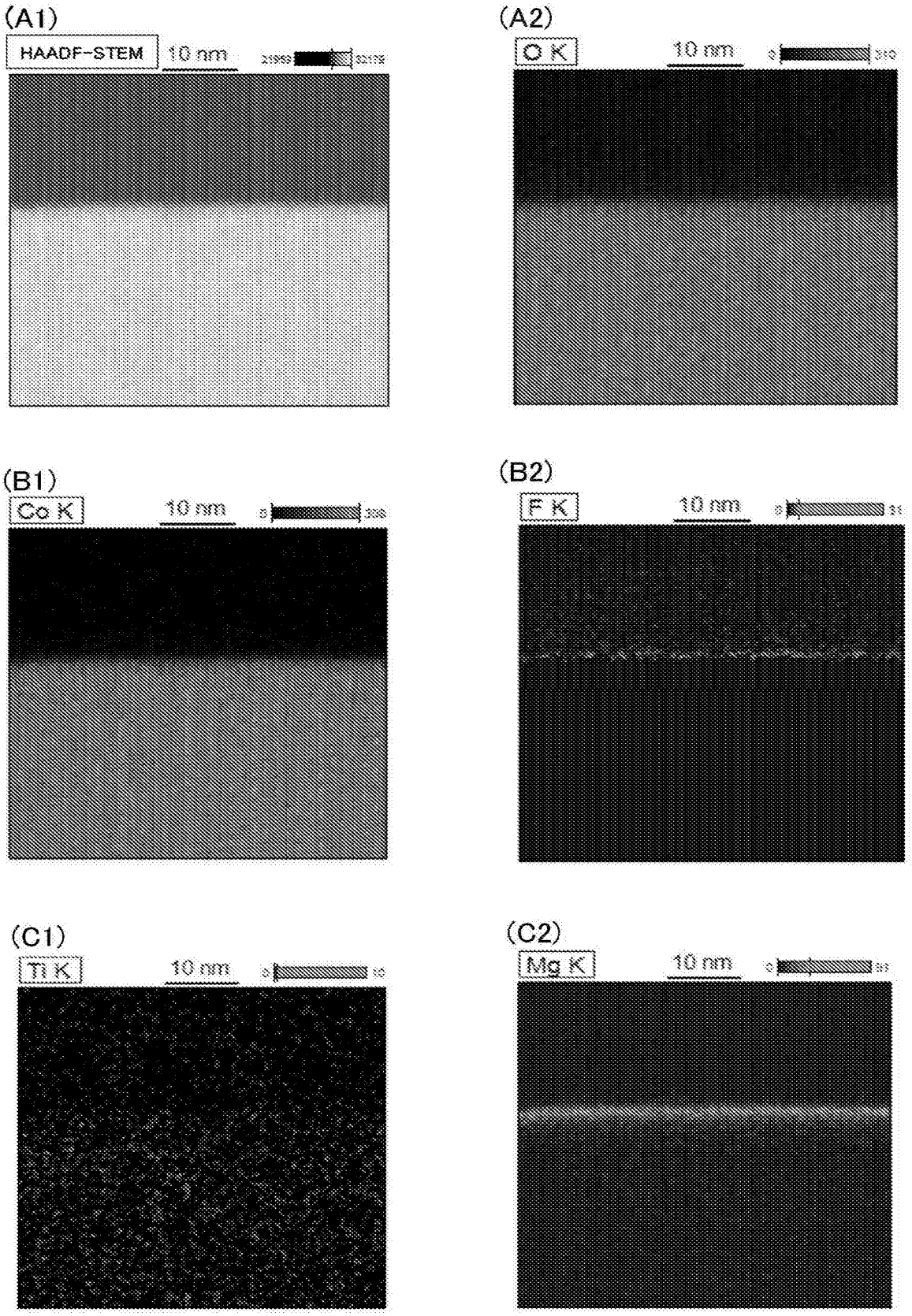
【図１３】



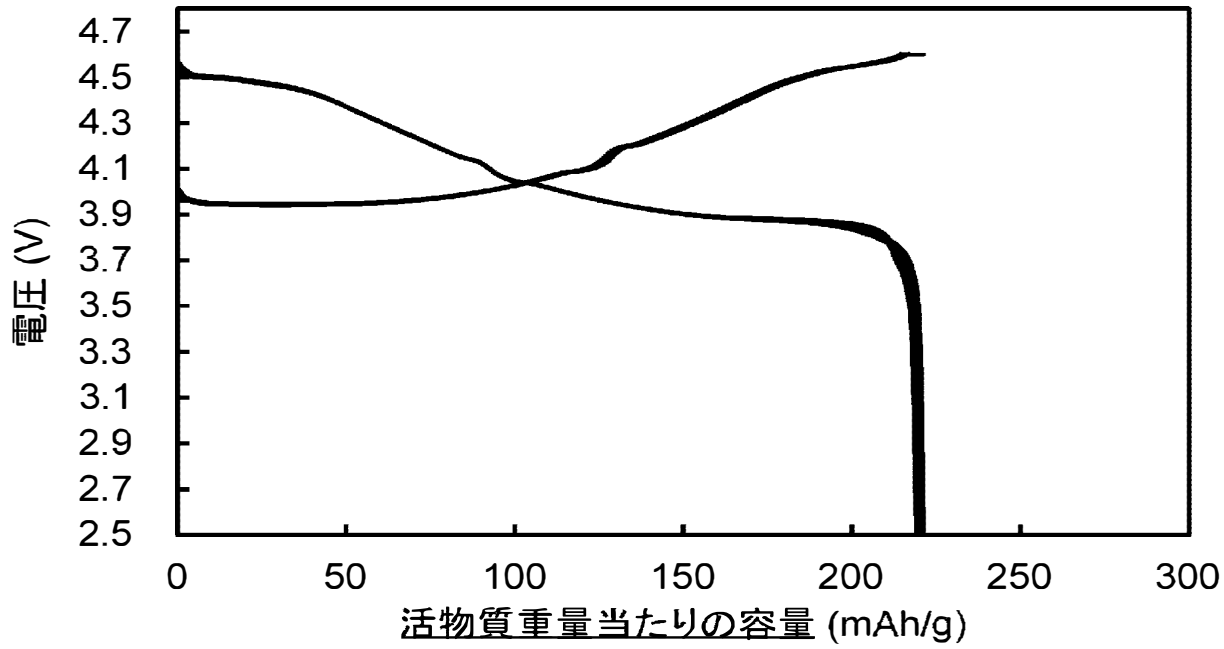
【図１４】


(A1)
HAADF-STEM
10 nm
(A2)
O K
10 nm
(B1)
Co K
10 nm
(B2)
F K
10 nm
(C1)
Ti K
10 nm
(C2)
Mg K
10 nm

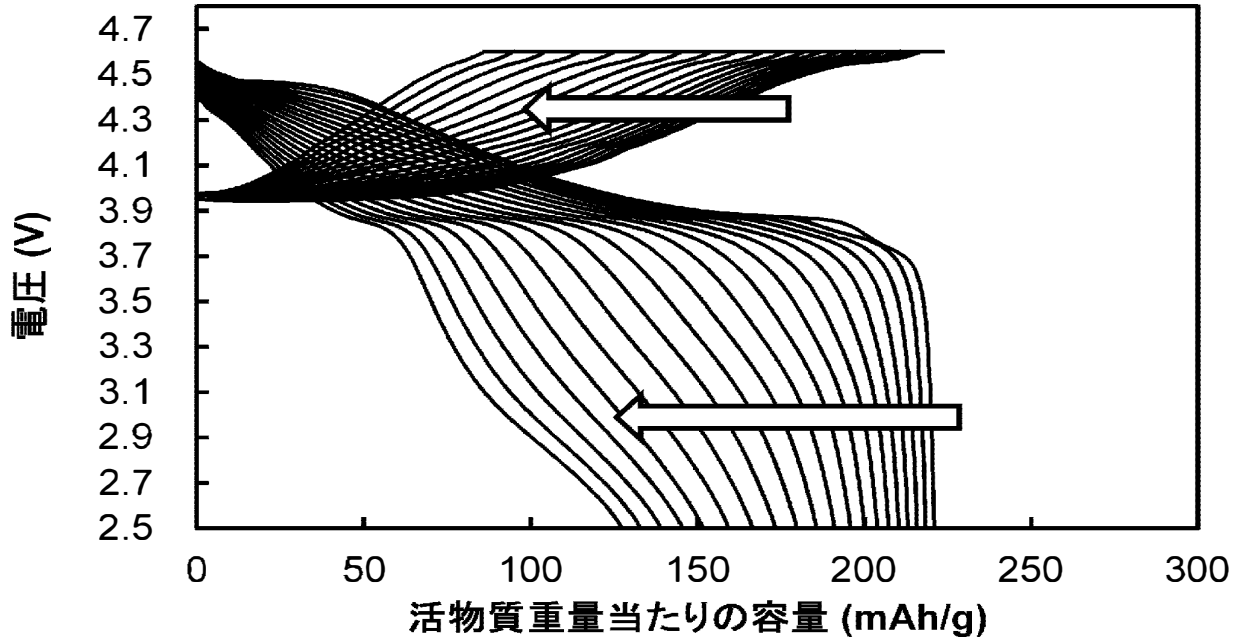
【図１５】


(A1)
HAADF-STEM
10 nm
(A2)
O K
10 nm
(B1)
Co K
10 nm
(B2)
F K
10 nm
(C1)
Ti K
10 nm
(C2)
Mg K
10 nm

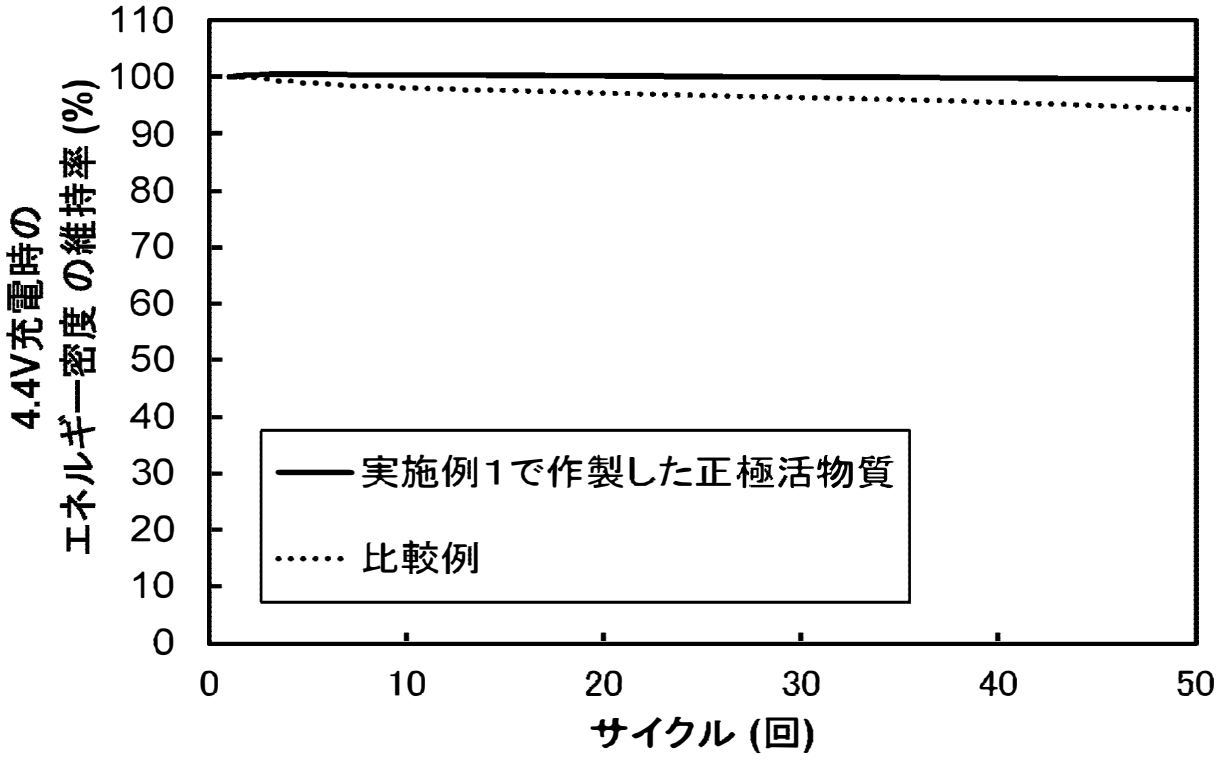
【図１６】


4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
電圧 (V)
0
50
100
150
200
250
300
活物質重量当たりの容量 (mAh/g)

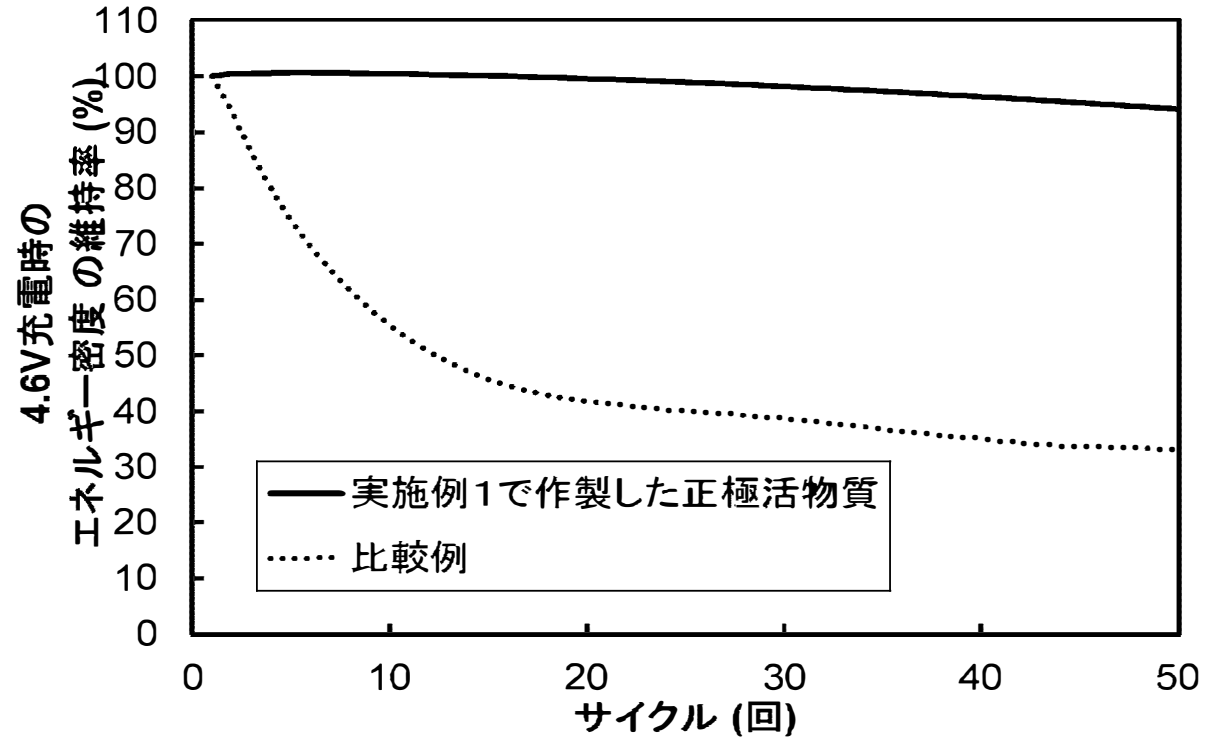
【図１７】


4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
電圧 (V)
0
50
100
150
200
250
300
活物質重量当たりの容量 (mAh/g)

【図１８】


4.4V充電時の
エネルギー密度の維持率 (%)
110
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
サイクル (回)
実施例１で作製した正極活物質
比較例

【図１９】


4.6V充電時の
エネルギー密度の維持率 (%)
110
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
サイクル (回)
実施例１で作製した正極活物質
比較例

出願人履歴

０００１５３８７８

19900817

新規登録

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株式会社半導体エネルギー研究所

日 本 国 特 許 庁
JAPAN PATENT OFFICE

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This is to certify that the annexed is a true copy of the following application as filed with this Office.

出願年月日 Date of Application:	２０１６年　７月　５日
出願番号 Application Number:	特願２０１６－１３３１４３
パリ条約による外国への出願に用いる優先権の主張の基礎となる出願の国コードと出願番号 The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is	ＪＰ２０１６－１３３１４３
出願人 Applicant(s):	株式会社半導体エネルギー研究所

２０１７年　８月１５日

特許庁長官
Commissioner,
Japan Patent Office　宗像直

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【整理番号】　P024681
【提出日】　平成28年 7月 5日
【あて先】　特許庁長官　殿
【発明者】
　【住所又は居所】　神奈川県厚木市長谷３９８番地　株式会社半導体エネルギー研究所内
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【書類名】明細書
【発明の名称】正極活物質、二次電池および正極活物質の作製方法
【技術分野】
【０００１】
本発明の一様態は、物、方法、又は、製造方法に関する。または、本発明は、プロセス、マシン、マニュファクチャ、又は、組成物（コンポジション・オブ・マター）に関する。本発明の一態様は、半導体装置、表示装置、発光装置、蓄電装置、照明装置または電子機器の製造方法に関する。特に、電子機器およびそのオペレーティングシステムに関する。
【０００２】
なお、本明細書中において、蓄電装置とは、蓄電機能を有する素子及び装置全般を指すものである。例えば、リチウムイオン二次電池などの蓄電池（二次電池ともいう）、リチウムイオンキャパシタ、及び電気二重層キャパシタなどを含む。
【０００３】
また、本明細書中において電子機器とは、蓄電装置を有する装置全般を指し、蓄電装置を有する電気光学装置、蓄電装置を有する情報端末装置などは全て電子機器である。
【背景技術】
【０００４】
近年、リチウムイオン二次電池、リチウムイオンキャパシタ、空気電池等、種々の蓄電装置の開発が盛んに行われている。特に高出力、高エネルギー密度であるリチウムイオン二次電池は、携帯電話、スマートフォン、タブレット、もしくはノート型コンピュータ等の携帯情報端末、携帯音楽プレーヤ、デジタルカメラ、医療機器、又は、ハイブリッド車（ＨＥＶ）、電気自動車（ＥＶ）、もしくはプラグインハイブリッド車（ＰＨＥＶ）等の次世代クリーンエネルギー自動車など、半導体産業の発展と併せて急速にその需要が拡大し、充電可能なエネルギーの供給源として現代の情報化社会に不可欠なものとなっている。
【０００５】
リチウムイオン二次電池に要求されている特性としては、さらなる高エネルギー密度化、サイクル特性の向上及び様々な動作環境での安全性、長期信頼性の向上などがある。これらの特性の向上のために、正極活物質の改良、負極活物質の改良、電解液の劣化抑制など、様々な面からのアプローチが行われている。中でも正極活物質の改良としては、特許文献１のように、正極活物質上に被覆層を設けることが行われている。
【先行技術文献】
【特許文献】
【０００６】
【特許文献１】特開２０１２―０１８９１４
【発明の概要】
【発明が解決しようとする課題】
【０００７】
リチウムイオン二次電池およびそれに用いられる正極活物質には、充放電特性、サイクル特性、信頼性、安全性、又はコストといった様々な面で改善の余地が残されている。
【０００８】
本発明の一態様は、リチウムイオン二次電池に用いることで、充放電サイクルにおける容量の低下が抑制される正極活物質を提供することを課題の一とする。本発明の一態様は、充放電特性の優れた二次電池を提供することを課題の一とする。または、本発明の一態様は、充放電サイクルにおける容量の低下が抑制された二次電池を提供することを課題の一とする。または、本発明の一態様は、安全性又は信頼性の高い二次電池を提供することを課題の一とする。
【０００９】
または、本発明の一態様は、新規な物質、活物質粒子、二次電池、又はそれらの作製方法を提供することを課題の一とする。
【００１０】

なお、これらの課題の記載は、他の課題の存在を妨げるものではない。なお、本発明の一態様は、これらの課題の全てを解決する必要はないものとする。なお、明細書、図面、請求項の記載から、これら以外の課題を抽出することが可能である。

【課題を解決するための手段】

【００１１】

上記目的を達成するために、本発明の一態様は、正極活物質表面に２種の被覆層を設け、内側の被覆層は不定比化合物であり、外側の被覆層は定比化合物であることを特徴とする。

【００１２】

本発明の一態様は、第１の領域と、第１の領域の少なくとも一部を被覆する第２の領域と、第２の領域の少なくとも一部を被覆する第３の領域と、を有し、第１の領域はリチウムと第１の遷移金属の酸化物を有し、層状岩塩型の結晶構造を有し、第２の領域は第２の遷移金属の酸化物を有する不定比化合物を有し、不定比化合物は岩塩型の結晶構造を有し、第３の領域は典型元素の化合物を有し、典型元素の化合物は岩塩型の結晶構造を有する正極活物質である。

【００１３】

上記において、第１の領域が有する層状岩塩型の結晶構造の（１―１―４）面、または（１―１―４）面と直交する面と、第２の領域が有する岩塩型の結晶構造の｛１００｝面の不整合度が０．１２以下であり、第２の領域が有する岩塩型の結晶構造の｛１００｝面と、第３の領域が有する岩塩型の結晶構造の｛１００｝面の不整合度が０．１２以下であることが好ましい。

【００１４】

また上記において、第１の遷移金属はコバルト、第２の遷移金属はチタン、典型元素の化合物は酸化マグネシウムであることが好ましい。

【００１５】

また、本発明の一態様は、上記の正極活物質を有する正極と、負極と、を有する二次電池である。

【発明の効果】

【００１６】

本発明の一態様により、リチウムイオン二次電池に用いることで、充放電サイクルにおける容量の低下が抑制される正極活物質を提供することができる。また、充放電特性の優れた二次電池を提供することができる。また、充放電サイクルにおける容量の低下が抑制された二次電池を提供することができる。また、安全性又は信頼性の高い二次電池を提供することができる。また、新規な物質、活物質粒子、蓄電装置、又はそれらの作製方法を提供することができる。

【図面の簡単な説明】

【００１７】

【図１】正極活物質の一例を説明する図。
【図２】正極活物質の結晶構造を説明する図。
【図３】正極活物質の結晶構造を説明する図。
【図４】導電助剤としてグラフェン化合物を用いた場合の活物質層の断面図。
【図５】コイン型二次電池を説明する図。
【図６】円筒型二次電池を説明する図。
【図７】曲げることのできる二次電池を説明する図。
【図８】曲げることのできる二次電池を説明する図。
【図９】電子機器の一例を説明する図。
【図１０】電子機器の一例を説明する図。
【図１１】電子機器の一例を説明する図。
【図１２】電子機器の一例を説明する図。

【発明を実施するための形態】

【００１８】
以下では、本発明の実施の形態について図面を用いて詳細に説明する。ただし、本発明は以下の説明に限定されず、その形態および詳細を様々に変更し得ることは、当業者であれば容易に理解される。また、本発明は以下に示す実施の形態の記載内容に限定して解釈されるものではない。
【００１９】
なお、結晶面および方向の表記は、結晶学上、数字に上付きのバーを付すが、本明細書等における結晶面および方向の表記は、出願表記の制約上、数字の上にバーを付す代わりに、数字の前に―（マイナス符号）を付して表現する。また、結晶内の方向を示す個別方位は［　］で、等価な方向すべてを示す集合方位は＜　＞で、結晶面を示す個別面は（　）で、等価な対称性を有する集合面は｛　｝でそれぞれ表現する。なお、図面における結晶面および方向の表記は、結晶学上の数字の上にバーを付した本来の表記で行う。また、１Åは１０－１０ｍである。
【００２０】
（実施の形態１）
［正極活物質の構造］
まず図１を用いて、本発明の一態様である正極活物質１００について説明する。図１（Ａ）に示すように、正極活物質１００は、第１の領域１０１、第２の領域１０２および第３の領域１０３を有する。第２の領域１０２は、第１の領域１０１の少なくとも一部を被覆する。第３の領域１０３は、第２の領域の少なくとも一部を被覆する。
【００２１】
なお正極活物質１００の粒径は、大きすぎるとリチウムの拡散が難しくなり、小さすぎると後述する結晶構造を維持することが難しくなる。そのため、Ｄ５０（メディアン径ともいう）が、５μｍ以上１００μｍ以下が好ましく、１０μｍ以上７０μｍ以下であることがより好ましい。
【００２２】
＜第１の領域１０１＞
第１の領域１０１は、リチウムと第１の遷移金属の酸化物を有し、該酸化物は、層状岩塩型の結晶構造を有する。該酸化物は、リチウムと第１の遷移金属の複合酸化物ということができる。
【００２３】
本明細書等において、リチウムと第１の遷移金属の複合酸化物が有する層状岩塩型の結晶構造とは、陽イオンと陰イオンが交互に配列する岩塩型のイオン配列を有し、第１の遷移金属とリチウムが規則配列して二次元平面を形成するため、リチウムの二次元的拡散が可能である結晶構造をいう。なお陽イオンまたは陰イオンの欠損があってもよい。
【００２４】
また、層状岩塩型の結晶構造は、面心立方格子構造から一部の陽イオンを置換し歪ませた構造であるともいえる。このとき、面心立方格子構造のａ軸，ｂ軸，ｃ軸に相当する軸は長さが異なっていてもよい。また面心立方格子構造の軸角α、β、γに相当する角度は９０°に限定されず、その他の角度であってもよい。
【００２５】
第１の遷移金属としては、リチウムとともに層状岩塩型の複合酸化物を形成する金属を用いる。たとえば第１の遷移金属としてマンガン、コバルト、ニッケルの少なくとも一を用いることができる。つまり第１の遷移金属としてコバルトのみを用いてもよいし、第１の遷移金属としてコバルトとマンガンの２種を用いてもよいし、コバルト、マンガン、ニッケルの３種を用いてもよい。
【００２６】
つまり、第１の領域は、マンガン酸リチウム、コバルト酸リチウム、ニッケル酸リチウム、コバルトの一部がマンガンで置換されたコバルト酸リチウム、ニッケル―マンガン―コバルト酸リチウム（三元系とも呼ばれる）等を有することができる。

【００２７】
第１の領域１０１は、正極活物質１００の中でも特に充放電反応に寄与する領域として機能する。正極活物質１００を二次電池に用いた際の容量を大きくするために、第１の領域１０１は、第２の領域および第３の領域よりも体積が大きいことが好ましい。
【００２８】
層状岩塩型の結晶構造を持つ正極活物質は、放電容量が高い、リチウムが二次元的に拡散可能であるため抵抗が低い、などの特長があり、第１の領域として好ましい。
【００２９】
なお、第１の領域１０１は層状岩塩型の結晶構造を有するが、第１の領域１０１が単結晶である必要はなく、多結晶であってもよい。たとえば第１の領域１０１は、結晶粒径の平均が２８０μｍ以上６３０μｍ以下の多結晶であってもよい。多結晶である場合、ＴＥＭ等で結晶粒界が観察できることがある。また結晶粒径の平均は、ＸＲＤの半値幅から計算することができる。
【００３０】
多結晶は明瞭な結晶構造を有するため、リチウムイオンの二次元的な拡散のパスは十分に確保される。加えて単結晶よりも生産が容易であるため、第１の領域１０１として好ましい。
【００３１】
また第１の領域１０１のすべてが層状岩塩型の結晶構造でなくともよい。たとえば、第１の領域１０１の一部は非晶質であってもよいし、その他の結晶構造を有していてもよい。
【００３２】
＜第２の領域１０２＞
第２の領域１０２は、第２の遷移金属の酸化物を有する不定比化合物を有し、該不定比化合物は、岩塩型の結晶構造を有する。第２の遷移金属としては、不定比性のある金属を用いる。たとえば、第２の遷移金属としてチタン、バナジウム、マンガン、鉄、クロム、ニオブ、コバルト、亜鉛などの少なくとも一を用いることができる。
【００３３】
本明細書等において、不定比性のある金属とは、複数の原子価を取りうる金属をいう。また不定比化合物とは、複数の原子価を取りうる金属と他の元素との化合物をいう。
【００３４】
また本明細書等において、岩塩型の結晶構造とは、陽イオンと陰イオンが交互に配列している構造をいう。なお陽イオンまたは陰イオンの欠損があってもよい。また結晶のａ軸，ｂ軸，ｃ軸は長さが異なっていてもよい。また軸角α、β、γは９０°に限定されず、その他の角度であってもよい。
【００３５】
第２の領域１０２は、第１の領域１０１と、後述する第３の領域１０３を繋ぐバッファ領域として機能する。不定比化合物は、不定比化合物が有する金属の価数の変化によって、原子間距離が変化しうる。また、不定比化合物はしばしば陽イオンまたは陰イオンの欠損や、転位（いわゆるマグネリ相）を形成し、マクロに第１の領域と第２の領域に生じたひずみ、および第２の領域と第３の領域に生じたひずみをキャンセルできる。そのため、バッファ領域である第２の領域として好ましい。
【００３６】
また、第２の領域１０２は、リチウムと第２の遷移金属の複合酸化物を有してもよい。たとえば、チタン酸リチウム、マンガン酸リチウムなどを有してもよい。また、第２の領域１０２は、後述する第３の領域が有する典型元素を有していてもよい。第２の領域１０２が、第１の領域１０１または第３の領域１０３に有する元素を含むことは、バッファ領域として好ましい。
【００３７】
つまり第２の領域１０２は、酸化チタン、チタン酸リチウム、酸化バナジウム、酸化マンガン、酸化鉄、酸化銅、酸化クロム、酸化ニオブ、酸化コバルト、酸化亜鉛等を有するこ

とができる。
【００３８】
また、第２の領域は後述する第３の領域と同じ型の結晶構造を有するため、結晶格子の整合がとりやすく好ましい。
【００３９】
なお、第２の領域１０２は岩塩型の結晶構造を有するが、第２の領域１０２のすべてが岩塩型の結晶構造でなくともよい。たとえば、第２の領域１０２の一部は非晶質であってもよいし、その他の結晶構造を有していてもよい。
【００４０】
＜第３の領域１０３＞
第３の領域１０３は、典型元素の化合物を有し、該典型元素の化合物は、岩塩型の結晶構造を有する。原型元素の化合物は定比性のある化合物である。典型元素の化合物としては、たとえば酸化マグネシウム、酸化カルシウム、酸化ベリリウム、フッ化リチウム、フッ化ナトリウムの少なくとも一を用いることができる。
【００４１】
第３の領域１０３は、正極活物質１００を二次電池に用いた際に、電解液と接触する領域である。そのため、第３の領域１０３に用いる材料は、充放電の過程で変化が少なく、電解液との接触で変質しにくい材料であることが好ましい。定比化合物であるため化学的に安定な典型元素の化合物は、第３の領域として好ましい。
【００４２】
なお、第３の領域１０３は岩塩型の結晶構造を有するが、第３の領域１０３のすべてが岩塩型の結晶構造でなくともよい。たとえば、第３の領域１０３の一部は非晶質であってもよいし、その他の結晶構造を有していてもよい。
【００４３】
また、本発明の一態様では第２の領域１０２および第３の領域１０３が岩塩型の結晶構造を有する例について説明したが、本発明の一態様はこれに限らない。バッファ領域として機能する第２の領域１０２が、第３の領域１０３と同じ結晶構造を有していればよい。たとえば、第２の領域１０２および第３の領域１０３がスピネル型結晶構造を有していてもよい。また第２の領域１０２および第３の領域１０３がコランダム型結晶構造を有していてもよい。また第２の領域１０２および第３の領域１０３がルチル型結晶構造を有していてもよい。
【００４４】
＜ヘテロエピタキシャル成長と、トポタキシ＞
第２の領域１０２は、第１の領域１０１からヘテロエピタキシャル成長して形成されることが好ましい。また、第３の領域１０３は、第２の領域１０２からヘテロエピタキシャル成長して形成されることが好ましい。ヘテロエピタキシャル成長により形成された領域は、下地となった領域と結晶配向が三次元的に一致する、トポタキシとなる。そのため、第１の領域１０１、第２の領域１０２および第３の領域１０３をトポタキシとすることができる。
【００４５】
なお本明細書等において、二次元界面の構造に類似性があることをエピタキシという。また二次元界面の構造に類似性を有する結晶成長を、エピタキシャル成長という。また三次元的な構造上の類似性を有すること、または結晶学的に同じ配向であることをトポタキシという。そのためトポタキシである場合、断面の一部を観察すると、二つの領域（たとえば下地となった領域と成長して形成された領域）の結晶の配向が一致する。
【００４６】
また本明細書等において、結晶の配向が一致するとは、陽イオンと陰イオンが交互に配列している場合の、列の方向の差が１０度以下であることをいう。
【００４７】
また、二つの領域の結晶の配向が一致すること、つまりトポタキシであることは、ＴＥＭ

（透過電子顕微鏡）像、ＳＴＥＭ（走査透過電子顕微鏡）像、ＨＡＡＤＦ―ＳＴＥＭ（高角散乱環状暗視野走査透過電子顕微鏡）像、ＡＢＦ―ＳＴＥＭ（環状明視野走査透過電子顕微鏡）像等から判断することができる。Ｘ線回折、電子線回折、中性子線回折等も判断の材料にすることができる。

【００４８】

第１の領域１０１から第３の領域１０３までの結晶の配向が一致すると、第２の領域１０２および第３の領域１０３は、第１の領域１０１と安定した結合を有する被覆層として機能する。そのため強固な被覆層を有する正極活物質１００とすることができる。

【００４９】

第２の領域１０２および第３の領域１０３が、第１の領域１０１と安定した結合を有するため、正極活物質１００を二次電池に用いた際、充放電によって生じる第１の領域１０１の結晶構造の変化を効果的に抑制できる。また、充電によって第１の領域１０１からリチウムが抜けた状態となっても、安定した結合を有する被覆層によって第１の領域１０１からコバルトや酸素が離脱するのを抑制することができる。さらに、電解液と接触する領域を、化学的に安定した材料とすることができる。そのため、サイクル特性の優れた二次電池とすることができる。

【００５０】

＜領域間の不整合度＞

ヘテロエピタキシャル成長させるためには、下地となる領域の結晶と、成長させたい結晶の不整合度が重要である。

【００５１】

本明細書等において、不整合度ｆは下記数式１で定義される。下地となる領域の結晶における酸素と陽イオンの最近接距離の平均をａ、成長させたい結晶の自然な陰イオンと陽イオンの最近接距離の平均をｂとする。

【００５２】

【数１】

$$f = \frac{b - a}{a} \qquad \text{（数式１）}$$

【００５３】

テロエピタキシャル成長するためには、下地となる領域の結晶と成長させたい結晶の不整合度ｆが０．１２以下である必要がある。層状のより安定したヘテロエピタキシャル成長のためには、不整合度ｆは０．０８以下が好ましく、０．０４以下であればさらに好ましい。

【００５４】

そのため、第１の領域１０１が有する層状岩塩型の結晶構造と、第２の領域１０２が有する岩塩型の結晶構造の不整合度ｆが０．１２以下となるように、第１の領域と第２の領域の材料および接する結晶面を選定することが好ましい。

【００５５】

また、第２の領域が有する岩塩型の結晶構造と、第３の領域１０３が有する岩塩型の結晶構造の不整合度ｆが０．１２以下となるように、第２の領域と第３の領域の材料および接する結晶面を選定することが好ましい。

【００５６】

上述のような、第１の領域１０１が有する層状岩塩型の結晶構造と、第２の領域１０２が有する岩塩型の結晶構造の不整合度ｆが０．１２以下であり、かつ第２の領域が有する岩塩型の結晶構造と、第３の領域１０３が有する岩塩型の結晶構造の不整合度ｆが０．１２以下であるという条件を満たす、第１の領域、第２の領域、第３の領域の材料および結晶面を以下に例示する。

【００５７】

＜例１：コバルト酸リチウム、チタン酸リチウム、および酸化マグネシウム＞
まず図２および図３を用いて、第１の遷移金属がコバルトであり、第１の領域１０１が層状岩塩型の結晶構造を有するコバルト酸リチウムを有し、第２の遷移金属がチタンであり、第２の領域１０２が岩塩型の結晶構造を有するチタン酸リチウムを有し、第３の領域１０３が有する典型元素の化合物が、岩塩型の結晶構造を有する酸化マグネシウムである例について説明する。

【００５８】

図２（Ａ）に、コバルト酸リチウム（ＬｉＣｏＯ$_2$）の層状岩塩型（空間群Ｒ－３ｍＨ）の結晶構造のモデル、チタン酸リチウム（ＬｉＴｉＯ$_2$）の岩塩型（空間群Ｆｄ－３ｍＺ）の結晶構造のモデル、および酸化マグネシウムの岩塩型（空間群Ｆｄ－３ｍＺ）の結晶構造のモデルを示す。図２（Ａ）は全てｂ軸方向から見た場合のモデルである。

【００５９】

図２（Ａ）の図だけでは、層状岩塩型の結晶と岩塩型の結晶がトポタキシになるようには見えない。しかしここで、発想を変えて層状岩塩型の結晶を異なる方位（たとえば図２（Ａ）中の矢印が含む方位）から見ることとする。図２（Ｂ）に層状岩塩型の結晶を＜１－１－４＞の面方位から見たモデル、岩塩型の結晶を＜１００＞の面方位から見たモデルを示す。

【００６０】

図２（Ｂ）に示すように、層状岩塩型の結晶を＜１－１－４＞の面方位から見ると、岩塩型の結晶を＜１００＞の面方位から見た場合とよく似た原子配置となる。また、金属と酸素の最近接距離も似たような値をとる。たとえば層状岩塩型のコバルト酸リチウムにおけるＬｉ－Ｏ間は２．０８９Å、Ｃｏ－Ｏ間は１．９２５Åである。また岩塩型のチタン酸リチウムにおけるＬｉ－Ｏ間は２．１３８Å、Ｔｉ－Ｏ間は２．０５１Åである。また岩塩型の酸化マグネシウムにおけるＭｇ－Ｏ間は２．１０６Åである。

【００６１】

そこで図３を用いて、層状岩塩型の結晶の（１－１－４）の結晶面と、岩塩型結晶の｛１００｝の結晶面が接する場合の、各領域間の不整合度について説明する。

【００６２】

図３に示すように、第１の領域１０１の層状岩塩型の結晶構造を有するコバルト酸リチウムの（１－１－４）の結晶面１０１ｐ（１－１－４）の金属－酸素－金属間の距離は４．０１Åである。また第２の領域１０２の岩塩型の結晶構造を有するチタン酸リチウムの｛１００｝の結晶面１０２ｐ｛１００｝の金属－酸素－金属間の距離は４．１９Åである。そのため、結晶面１０１ｐ（１－１－４）と結晶面１０２ｐ｛１００｝の不整合度ｆは０．０４である。

【００６３】

また、第３の領域１０３の岩塩型の結晶構造を有する酸化マグネシウムの｛１００｝の結晶面１０３ｐ｛１００｝の金属－酸素－金属間の距離は４．２１Åである。そのため結晶面１０２ｐ｛１００｝と結晶面１０３ｐ｛１００｝の不整合度ｆは０．０２である。

【００６４】

このように、第１の領域１０１と第２の領域１０２間の不整合度、および第２の領域１０２と第３の領域１０３間の不整合度は十分に小さいため、第１の領域１０１から第３の領域１０３までトポタキシとすることができる。

【００６５】

一方、図３では接していないが、仮に第１の領域の結晶面１０１ｐ（１－１－４）と第３の領域の結晶面１０３ｐ｛１００｝が接した場合の不整合度ｆは０．０５となる。すなわち、第２の領域１０２が存在することで、不整合度を小さくすることができている。つまり第２の領域が不定比性を有する遷移金属酸化物であるため、第２の領域１０２が存在することで、第１の領域から第３の領域まではより安定したトポタキシとなる。そのため第２の領域１０２および第３の領域１０３を、第１の領域１０１と安定した結合を有する被覆層として機能させることができる。

【００６６】
なお本実施の形態では、層状岩塩型の（１―１―４）面と岩塩型の｛１００｝面が接する例について説明したが、本発明の一態様はこれに限らない。トポタキシとなりうる結晶面同士の組み合わせであればよい。
【００６７】
ただし、ＳＴＥＭ像などで観察できる、第１の領域１０１に含まれる酸素原子の最密充填構造と、第２の領域１０２に含まれる酸素原子の最密充填構造は連続的であることが好ましい。酸素原子の最密充填構造が第１の領域１０１と第２の領域１０２で連続であることで、安定したトポタキシとすることができる。なお本明細書等において酸素原子の最密充填構造が連続的であるとは、ＳＴＥＭ像などで酸素原子と推定される原子の列の方向が、２つの領域で平行である、または列の方向の差が１０度以下であることをいう。
【００６８】
＜例２：コバルト酸リチウム、酸化マンガンおよび酸化カルシウム＞
次に、第１の遷移金属がコバルトであり、第１の領域１０１が層状岩塩型の結晶構造を有するコバルト酸リチウムを有し、第２の遷移金属がマンガンであり、第２の領域１０２が酸化マンガンを有し、第３の領域１０３が有する典型元素の化合物が、岩塩型の結晶構造を有する酸化カルシウムである例について説明する。
【００６９】
この場合も、図２および図３と同様に、第１の領域１０１の層状岩塩型の結晶を＜１―１―４＞の面方位から見ると、第２の領域１０２および第３の領域１０３の岩塩型の結晶を＜１００＞の面方位から見た場合とよく似た原子配置となる。
【００７０】
層状岩塩型の結晶の（１―１―４）の結晶面と、岩塩型結晶の｛１００｝の結晶面が接する場合の、各領域間の不整合度について説明する。第１の領域１０１の層状岩塩型の結晶構造を有するコバルト酸リチウムの結晶面（１―１―４）の金属―酸素―金属間の距離は４．０１Åである。また第２の領域１０２の岩塩型の結晶構造を有する酸化マンガンの結晶面｛１００｝の金属―酸素―金属間の距離は４．４５Åである。そのため、第１の領域１０１の結晶面（１―１―４）と第２の領域１０２の結晶面｛１００｝の不整合度ｆは０．１１である。
【００７１】
また、第３の領域１０３の岩塩型の結晶構造を有する酸化カルシウムの結晶面｛１００｝の金属―酸素―金属間の距離は４．８２である。そのため第２の領域１０２の結晶面｛１００｝と第３の領域の結晶面｛１００｝の不整合度ｆは０．０８である。
【００７２】
このように、第１の領域１０１と第２の領域１０２間の不整合度、および第２の領域１０２と第３の領域１０３間の不整合度は十分に小さいため、第１の領域１０１から第３の領域１０３までトポタキシとすることができる。
【００７３】
一方、仮に第１の領域の結晶面（１―１―４）と第３の領域の結晶面｛１００｝が接した場合、不整合度ｆは０．２０となるため、ヘテロエピタキシャル成長は難しい。つまり第２の領域１０２が存在することで、第１の領域から第３の領域までのヘテロエピタキシャル成長が可能となる。そのため第２の領域１０２および第３の領域１０３を、第１の領域１０１と安定した結合を有する被覆層として機能させることができる。
【００７４】
＜例３：ニッケル―マンガン―コバルト酸リチウム、酸化マンガン、酸化カルシウム＞
次に、第１の遷移金属がニッケル、マンガンおよびコバルトであり、第１の領域１０１が層状岩塩型の結晶構造を有するニッケル―マンガン―コバルト酸リチウム（$LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$、三元系ともいう）を有し、第２の遷移金属がマンガンであり、第２の領域１０２が酸化マンガンを有し、第３の領域１０３が有する典型元素の化合物が、岩塩型の結晶構造を有する酸化カルシウムである例について説明する。

【００７５】
この場合も、図２および図３に示したように、層状岩塩型の結晶を＜１－１－４＞の面方位から見ると、岩塩型の結晶を＜１００＞の面方位から見た場合とよく似た原子配置となる。層状岩塩型の結晶の（１－１－４）の結晶面と、岩塩型結晶の｛１００｝の結晶面が接する場合の、各領域間の不整合度について説明する。
【００７６】
第１の領域１０１の層状岩塩型の結晶構造を有するニッケル―マンガン―コバルト酸リチウムの結晶面（１－１－４）の金属―酸素―金属間の距離は４．０７Åである。また第２の領域１０２の岩塩型の結晶構造を有する酸化マンガンの結晶面｛１００｝の金属―酸素―金属間の距離は４．４５Åである。そのため、第１の領域１０１の結晶面（１－１－４）と第２の領域１０２の結晶面｛１００｝の不整合度ｆは０．０９である。
【００７７】
また、第３の領域１０３の岩塩型の結晶構造を有する酸化カルシウムの結晶面｛１００｝の金属―酸素―金属間の距離は４．８２である。そのため第２の領域１０２の結晶面｛１００｝と第３の領域の結晶面｛１００｝の不整合度ｆは０．０８である。
【００７８】
このように、第１の領域１０１と第２の領域１０２間の不整合度、および第２の領域１０２と第３の領域１０３間の不整合度は十分に小さいため、第１の領域１０１から第３の領域１０３までトポタキシとすることができる。
【００７９】
一方、仮に第１の領域の結晶面（１－１－４）と第３の領域の結晶面｛１００｝が接した場合、不整合度ｆは０．１８となるため、ヘテロエピタキシャル成長は難しい。つまり第２の領域１０２が存在することで、第１の領域から第３の領域までのヘテロエピタキシャル成長が可能となる。そのため第２の領域１０２および第３の領域１０３を、第１の領域１０１と安定した結合を有する被覆層として機能させることができる。
【００８０】
なお、これまで図１（Ａ）のように第１の領域１０１上に第２の領域１０２が接し、かつ第２の領域１０２上に第３の領域１０３が接する例について説明したが、本発明の一態様はこれに限らない。
【００８１】
たとえば、図１（Ｂ）に示すように、第３の領域１０３は正極活物質１００のすべてを覆っていなくてもよい。第１の領域１０１上に第２の領域１０２が接しているが、第３の領域１０３がない部分があってもよい。
【００８２】
また、第２の領域１０２も正極活物質１００のすべてを覆っていなくてもよい。第１の領域１０１上に第３の領域が接し、第２の領域がない部分があってもよい。この場合、第１の領域と第３の領域がトポタキシであってもよいし、トポタキシでなくてもよい。
【００８３】
さらに、第２の領域１０２および第３の領域１０３は、厚さが場所により異なっていてもよい。また、第２の領域１０２および第３の領域１０３は、エピタキシャル成長の際、島状に成長していてもよいし、膜状成長の後に島状に成長していてもよい。
【００８４】
また、これまで正極活物質１００が第１の領域１０１、第２の領域１０２および第３の領域１０３を有する例について説明したが、本発明の一態様はこれに限らない。たとえば、図１（Ｃ）に示すように、第４の領域１０４を有していてもよい。たとえば第３の領域１０３上に第４の領域１０４が接するように設けることができる。第４の領域は、たとえば炭素を有する被膜であってもよいし、リチウムまたは電解液の分解生成物を有する被膜であってもよい。第４の領域が炭素を有する被膜である場合、正極活物質１００同士の導電性を高めることができる。また第４の領域がリチウムまたは電解液の分解生成物を有する被膜である場合、電解液との過剰な反応を抑制し、二次電池に用いた際サイクル特性を向

上させることができる。
【００８５】
［正極活物質の作製方法］
次に、本発明の一態様である正極活物質１００の作製方法の一例について説明する。
【００８６】
＜ステップ１１：出発原料の準備＞
はじめに、出発原料を準備する。この工程で用意する原料から、最終的に第１の領域１０１および第３の領域１０３が形成される。
【００８７】
第１の領域１０１が有するリチウムと第１の遷移金属の原料として、リチウム源と、第１の遷移金属源を用意する。また第３の領域１０３が有する典型元素の化合物の原料として、典型元素源を用意する。
【００８８】
リチウム源としては、例えば炭酸リチウムを用いることができる。第１の遷移金属源としては、例えば第１の遷移金属の酸化物を用いることができる。典型元素源としては、例えば第３の領域が有する典型元素の酸化物、第３の領域が有する典型元素のフッ化物等を用いることができる。
【００８９】
＜ステップ１２：出発材料の混合＞
次に、リチウム源、第１の遷移金属源、典型元素源を混合する。混合には例えばボールミルを用いることができる。
【００９０】
＜ステップ１３：加熱＞
次に、ステップ１２で混合した材料を加熱する。加熱は８００℃以上１１００℃以下で行うことが好ましく、９００℃以上１０００℃以下で行うことがより好ましい。加熱時間は、２時間以上２０時間以下とすることが好ましい。
【００９１】
ステップ１３の加熱により、層状岩塩型の結晶構造を有する、リチウムと第１の遷移金属の複合酸化物を合成することができる。
【００９２】
＜ステップ１４：第２の遷移金属で被覆＞
次に、ステップ１３で合成したリチウムと第１の遷移金属の複合酸化物を室温まで冷却する。そしてリチウムと第１の遷移金属の複合酸化物粒子の表面を、第２の遷移金属を有する材料で被覆する。
【００９３】
被覆の方法としては、例えばゾルゲル法、スパッタリング法、ＣＶＤ法等を用いることができる。
【００９４】
なお本明細書等において、ゾルゲル法とは、金属の有機化合物溶液を出発原料として、溶液中の化合物の加水分解・重合によって溶液を金属の酸化物あるいは、水酸化物の微粒子が溶解したゾルとし、さらに反応を進ませてゲル化して出来た非晶質である多孔質ゲルを加熱して膜または結晶体をつくる方法をいう。
【００９５】
ゾルゲル法を用いる場合は、第２の遷移金属のアルコキシドと、リチウムと第１の遷移金属の複合酸化物粒子と、アルコールを混合する。すると第２の遷移金属のアルコキシドは、大気中の水分と反応して加水分解し、第２の遷移金属の水酸化物となる。さらに、第２の遷移金属の水酸化物と、リチウムと第１の遷移金属の複合酸化物粒子表面の官能基が反応して、第２の遷移金属の酸化物となり、第１の遷移金属の複合酸化物粒子表面を被覆する。また第２の遷移金属の水酸化物の分子同士も脱水縮合反応して第２の遷移金属の酸化物となる。

【００９６】
ゾルゲル法を用いると、常温で簡便に、リチウムと第１の遷移金属の複合酸化物粒子を、第２の遷移金属を有する材料で被覆することができ好ましい。
【００９７】
＜ステップ１５：加熱＞
次に、ステップ１４で合成した、第２の遷移金属を有する材料で被覆された、リチウムと第１の遷移金属の複合酸化物粒子を加熱する。加熱は５００℃以上１２００℃以下で行うことが好ましく、８００℃以上１０００℃以下で行うことがより好ましい。加熱時間は、上述の温度の範囲内での保持時間を５０時間以下とすることが好ましく、２時間以上１０時間以下とすることがより好ましい。また、酸素を含む雰囲気で加熱することが好ましい。
【００９８】
ステップ１５の加熱によって、第２の遷移金属を有する材料は酸化され、第２の遷移金属の酸化物となる。さらに、リチウムと第１の遷移金属の複合酸化物と、その上に被覆された第２の遷移金属の酸化物がトポタキシとなる。つまり第１の領域１０１と第２の領域１０２がトポタキシとなる。
【００９９】
またステップ１５の加熱によって、リチウムと第１の遷移金属の複合酸化物粒子の内部に混合されていた典型元素が、典型元素の化合物となり最表面に析出し、第３の領域を形成する。このとき典型元素の化合物は、第２の領域１０２からヘテロエピタキシャル成長する。つまり第２の領域１０２と第３の領域１０３がトポタキシとなる。
【０１００】
＜ステップ１６：冷却＞
次に、ステップ１５で加熱した粒子を、室温まで冷却する。
【０１０１】
＜ステップ１７：回収＞
最後に、冷却された粒子を回収する。上記の工程で、第１の領域、第２の領域および第３の領域を有する正極活物質１００を作製することができる。
【０１０２】
（実施の形態２）
本実施の形態では、先の実施の形態で説明した正極活物質１００を有する二次電池に用いることのできる材料の例について説明する。本実施の形態では、正極、負極および電解液が、外装体に包まれている二次電池を例にとって説明する。
【０１０３】
［正極］
正極は、正極活物質層および正極集電体を有する。
【０１０４】
＜正極活物質層＞
正極活物質層は、正極活物質を有する。また、正極活物質層は、導電助剤およびバインダを有していてもよい。
【０１０５】
正極活物質としては、先の実施の形態で説明した正極活物質１００を用いることができる。先の実施の形態で説明した正極活物質１００を用いることで、サイクル特性に優れた二次電池とすることができる。
【０１０６】
導電助剤としては、炭素材料、金属材料、又は導電性セラミックス材料等を用いることができる。また、導電助剤として繊維状の材料を用いてもよい。活物質層の総量に対する導電助剤の含有量は、１ｗｔ％以上１０ｗｔ％以下が好ましく、１ｗｔ％以上５ｗｔ％以下がより好ましい。
【０１０７】

導電助剤により、電極中に電気伝導のネットワークを形成することができる。導電助剤により、正極活物質どうしの電気伝導の経路を維持することができる。活物質層中に導電助剤を添加することにより、高い電気伝導性を有する活物質層を実現することができる。

【０１０８】

導電助剤としては、例えば天然黒鉛、メソカーボンマイクロビーズ等の人造黒鉛、炭素繊維などを用いることができる。炭素繊維としては、例えばメソフェーズピッチ系炭素繊維、等方性ピッチ系炭素繊維等の炭素繊維を用いることができる。また炭素繊維として、カーボンナノファイバーやカーボンナノチューブなどを用いることができる。カーボンナノチューブは、例えば気相成長法などで作製することができる。また、導電助剤として、例えばカーボンブラック（アセチレンブラック（ＡＢ）など）、グラファイト（黒鉛）粒子、グラフェン、フラーレンなどの炭素材料を用いることができる。また、例えば、銅、ニッケル、アルミニウム、銀、金などの金属粉末や金属繊維、導電性セラミックス材料等を用いることができる。

【０１０９】

また、導電助剤としてグラフェン化合物を用いてもよい。

【０１１０】

グラフェン化合物は、高い導電性を有するという優れた電気特性と、高い柔軟性および高い機械的強度を有するという優れた物理特性と、を有する場合がある。また、グラフェン化合物は平面的な形状を有する。グラフェン化合物は、接触抵抗の低い面接触を可能とする。また、薄くても導電性が非常に高い場合があり、少ない量で効率よく活物質層内で導電パスを形成することができる。そのため、グラフェン化合物を導電助剤として用いることにより、活物質と導電助剤との接触面積を増大させることができるため好ましい。また、電気的な抵抗を減少できる場合があるため好ましい。ここでグラフェン化合物として例えば、グラフェンまたはマルチグラフェンまたはｒｅｄｕｃｅｄ　Ｇｒａｐｈｅｎｅ　Ｏｘｉｄｅ（以下、ＲＧＯ）を用いることが特に好ましい。ここで、ＲＧＯは例えば、酸化グラフェン（ｇｒａｐｈｅｎｅ　ｏｘｉｄｅ：ＧＯ）を還元して得られる化合物を指す。

【０１１１】

粒径の小さい活物質、例えば１μｍ以下の活物質を用いる場合には、活物質の比表面積が大きく、活物質同士を繋ぐ導電パスがより多く必要となる。このような場合には、少ない量でも効率よく導電パスを形成することができるグラフェン化合物を用いることが、特に好ましい。

【０１１２】

以下では一例として、活物質層２００に、導電助剤としてグラフェン化合物を用いる場合の断面構成例を説明する。

【０１１３】

図４（Ａ）に、活物質層２００の縦断面図を示す。活物質層２００は、粒状の正極活物質１００と、導電助剤としてのグラフェン化合物２０１と、バインダ（図示せず）と、を含む。ここで、グラフェン化合物２０１として例えばグラフェンまたはマルチグラフェンを用いればよい。ここで、グラフェン化合物２０１はシート状の形状を有することが好ましい。また、グラフェン化合物２０１は、複数のマルチグラフェン、または（および）複数のグラフェンが部分的に重なりシート状となっていてもよい。

【０１１４】

活物質層２００の縦断面においては、図４（Ａ）に示すように、活物質層２００の内部において概略均一にシート状のグラフェン化合物２０１が分散する。図４（Ａ）においてはグラフェン化合物２０１を模式的に太線で表しているが、実際には炭素分子の単層又は多層の厚みを有する薄膜である。複数のグラフェン化合物２０１は、複数の粒状の正極活物質１００を包むように、覆うように、あるいは複数の粒状の正極活物質１００の表面上に張り付くように形成されているため、互いに面接触している。

【０１１５】

ここで、複数のグラフェン化合物同士が結合することにより、網目状のグラフェン化合物

シート（以下グラフェン化合物ネットまたはグラフェンネットと呼ぶ）を形成することができる。活物質をグラフェンネットが被覆する場合に、グラフェンネットは活物質同士を結合するバインダとしても機能することができる。よって、バインダの量を少なくすることができる、又は使用しないことができるため、電極体積や電極重量に占める活物質の比率を向上させることができる。すなわち、蓄電装置の容量を増加させることができる。

【０１１６】

ここで、グラフェン化合物２０１として酸化グラフェンを用い、活物質と混合して活物質層２００となる層を形成後、還元することが好ましい。グラフェン化合物２０１の形成に、極性溶媒中での分散性が極めて高い酸化グラフェンを用いることにより、グラフェン化合物２０１を活物質層２００の内部において概略均一に分散させることができる。均一に分散した酸化グラフェンを含有する分散媒から溶媒を揮発除去し、酸化グラフェンを還元するため、活物質層２００に残留するグラフェン化合物２０１は部分的に重なり合い、互いに面接触する程度に分散していることで三次元的な導電パスを形成することができる。なお、酸化グラフェンの還元は、例えば熱処理により行ってもよいし、還元剤を用いて行ってもよい。

【０１１７】

従って、活物質と点接触するアセチレンブラック等の粒状の導電助剤と異なり、グラフェン化合物２０１は接触抵抗の低い面接触を可能とするものであるから、通常の導電助剤よりも少量で粒状の正極活物質１００とグラフェン化合物２０１との電気伝導性を向上させることができる。よって、正極活物質１００の活物質層２００における比率を増加させることができる。これにより、蓄電装置の放電容量を増加させることができる。

【０１１８】

バインダとしては、例えば、スチレン―ブタジエンゴム（ＳＢＲ）、スチレン―イソプレン―スチレンゴム、アクリロニトリル―ブタジエンゴム、ブタジエンゴム、エチレン―プロピレン―ジエン共重合体などのゴム材料を用いることが好ましい。またバインダとして、フッ素ゴムを用いることができる。

【０１１９】

また、バインダとしては、例えば水溶性の高分子を用いることが好ましい。水溶性の高分子としては、例えば多糖類などを用いることができる。多糖類としては、カルボキシメチルセルロース（ＣＭＣ）、メチルセルロース、エチルセルロース、ヒドロキシプロピルセルロース、ジアセチルセルロース、再生セルロースなどのセルロース誘導体や、澱粉などを用いることができる。また、これらの水溶性の高分子を、前述のゴム材料と併用して用いると、さらに好ましい。

【０１２０】

または、バインダとしては、ポリスチレン、ポリアクリル酸メチル、ポリメタクリル酸メチル（ＰＭＭＡ）、ポリアクリル酸ナトリウム、ポリビニルアルコール（ＰＶＡ）、ポリエチレンオキシド（ＰＥＯ）、ポリプロピレンオキシド、ポリイミド、ポリ塩化ビニル、ポリテトラフルオロエチレン、ポリエチレン、ポリプロピレン、イソブチレン、ポリエチレンテレフタレート、ナイロン、ポリフッ化ビニリデン（ＰＶｄＦ）、ポリアクリロニトリル（ＰＡＮ）、ポリビニルクロライド、エチレンプロピレンジエンポリマー、ポリ酢酸ビニル、ポリメチルメタクリレート、ニトロセルロース等の材料を用いることが好ましい。

【０１２１】

バインダは上記のうち複数を組み合わせて使用してもよい。

【０１２２】

例えば粘度調整効果の特に優れた材料と、他の材料とを組み合わせて使用してもよい。例えばゴム材料等は接着力や弾性力に優れる反面、溶媒に混合した場合に粘度調整が難しい場合がある。このような場合には例えば、粘度調整効果の特に優れた材料と混合することが好ましい。粘度調整効果の特に優れた材料としては、例えば水溶性高分子を用いるとよい。また、粘度調整効果に特に優れた水溶性高分子としては、前述の多糖類、例えばカル

ボキシメチルセルロース（ＣＭＣ）、メチルセルロース、エチルセルロース、ヒドロキシプロピルセルロースおよびジアセチルセルロース、再生セルロースなどのセルロース誘導体や、澱粉を用いることができる。

【０１２３】

なお、カルボキシメチルセルロースなどのセルロース誘導体は、例えばカルボキシメチルセルロースのナトリウム塩やアンモニウム塩などの塩とすることにより溶解度が上がり、粘度調整剤としての効果を発揮しやすくなる。溶解度が高くなることにより電極のスラリーを作製する際に活物質や他の構成要素との分散性を高めることもできる。本明細書においては、電極のバインダとして使用するセルロースおよびセルロース誘導体としては、それらの塩も含むものとする。

【０１２４】

水溶性高分子は水に溶解することにより粘度を安定化させ、また活物質や、バインダとして組み合わせる他の材料、例えばスチレンブタジエンゴムなどを、水溶液中に安定して分散させることができる。また、官能基を有するために活物質表面に安定に吸着しやすいことが期待される。また、例えばカルボキシメチルセルロースなどのセルロース誘導体は、例えば水酸基やカルボキシル基などの官能基を有する材料が多く、官能基を有するために高分子同士が相互作用し、活物質表面を広く覆って存在することが期待される。

【０１２５】

活物質表面を覆う、または表面に接するバインダが膜を形成する場合には、不動態膜としての役割を果たして電解液の分解を抑える効果も期待される。ここで、不動態膜とは、電子の伝導性のない膜、または電気伝導性の極めて低い膜であり、例えば活物質の表面に不動態膜が形成された場合には、電池反応電位において、電解液の分解を抑制することができる。また、不動態膜は、電気の伝導性を抑えるとともに、リチウムイオンは伝導できるとさらに望ましい。

【０１２６】

＜正極集電体＞

正極集電体としては、ステンレス、金、白金、アルミニウム、チタン等の金属、及びこれらの合金など、導電性が高い材料をもちいることができる。また正極集電体に用いる材料は、正極の電位で溶出しないことが好ましい。また、シリコン、チタン、ネオジム、スカンジウム、モリブデンなどの耐熱性を向上させる元素が添加されたアルミニウム合金を用いることができる。また、シリコンと反応してシリサイドを形成する金属元素で形成してもよい。シリコンと反応してシリサイドを形成する金属元素としては、ジルコニウム、チタン、ハフニウム、バナジウム、ニオブ、タンタル、クロム、モリブデン、タングステン、コバルト、ニッケル等がある。集電体は、箔状、板状（シート状）、網状、パンチングメタル状、エキスパンドメタル状等の形状を適宜用いることができる。集電体は、厚みが５μｍ以上３０μｍ以下のものを用いるとよい。

【０１２７】

［負極］

負極は、負極活物質層および負極集電体を有する。また、負極活物質層は、導電助剤およびバインダを有していてもよい。

【０１２８】

＜負極活物質＞

負極活物質としては、例えば合金系材料や炭素系材料等を用いることができる。

【０１２９】

負極活物質として、リチウムとの合金化・脱合金化反応により充放電反応を行うことが可能な元素を用いることができる。例えば、シリコン、スズ、ガリウム、アルミニウム、ゲルマニウム、鉛、アンチモン、ビスマス、銀、亜鉛、カドミウム、インジウム等のうち少なくとも一つを含む材料を用いることができる。このような元素は炭素と比べて容量が大きく、特にシリコンは理論容量が４２００ｍＡｈ／ｇと高い。このため、負極活物質にシリコンを用いることが好ましい。また、これらの元素を有する化合物を用いてもよい。例

えば、ＳｉＯ、Mg_2Si、Mg_2Ge、ＳｎＯ、SnO_2、Mg_2Sn、SnS_2、V_2Sn_3、$FeSn_2$、$CoSn_2$、Ni_3Sn_2、Cu_6Sn_5、Ag_3Sn、Ag_3Sb、Ni_2MnSb、$CeSb_3$、$LaSn_3$、$La_3Co_2Sn_7$、$CoSb_3$、ＩｎＳｂ、ＳｂＳｎ等がある。ここで、リチウムとの合金化・脱合金化反応により充放電反応を行うことが可能な元素、および該元素を有する化合物等を合金系材料と呼ぶ場合がある。

【０１３０】

本明細書等において、ＳｉＯは例えば一酸化シリコンを指す。あるいはＳｉＯは、SiO_xと表すこともできる。ここでｘは１近傍の値を有することが好ましい。例えばｘは、０．２以上１．５以下が好ましく、０．３以上１．２以下が好ましい。

【０１３１】

炭素系材料としては、黒鉛、易黒鉛化性炭素（ソフトカーボン）、難黒鉛化性炭素（ハードカーボン）、カーボンナノチューブ、グラフェン、カーボンブラック等を用いればよい。

【０１３２】

黒鉛としては、人造黒鉛や、天然黒鉛等が挙げられる。人造黒鉛としては例えば、メソカーボンマイクロビーズ（ＭＣＭＢ）、コークス系人造黒鉛、ピッチ系人造黒鉛等が挙げられる。ここで人造黒鉛として、球状の形状を有する球状黒鉛を用いることができる。例えば、ＭＣＭＢは球状の形状を有する場合があり、好ましい。また、ＭＣＭＢはその表面積を小さくすることが比較的容易であり、好ましい場合がある。天然黒鉛としては例えば、鱗片状黒鉛、球状化天然黒鉛等が挙げられる。

【０１３３】

黒鉛はリチウムイオンが黒鉛に挿入されたとき（リチウム―黒鉛層間化合物の生成時）にリチウム金属と同程度に低い電位を示す（０．０５Ｖ以上０．３Ｖ以下　ｖｓ．Li/Li^+）。これにより、リチウムイオン二次電池は高い作動電圧を示すことができる。さらに、黒鉛は、単位体積当たりの容量が比較的高い、体積膨張が比較的小さい、安価である、リチウム金属に比べて安全性が高い等の利点を有するため、好ましい。

【０１３４】

また、負極活物質として、二酸化チタン（TiO_2）、リチウムチタン酸化物（$Li_4Ti_5O_{12}$）、リチウム―黒鉛層間化合物（Li_xC_6）、五酸化ニオブ（Nb_2O_5）、酸化タングステン（WO_2）、酸化モリブデン（MoO_2）等の酸化物を用いることができる。

【０１３５】

また、負極活物質として、リチウムと遷移金属の複窒化物である、Li_3N型構造をもつ$Li_{3-x}M_xN$（Ｍ＝Ｃｏ、Ｎｉ、Ｃｕ）を用いることができる。例えば、$Li_{2.6}Co_{0.4}N_3$は大きな充放電容量（９００ｍＡｈ／ｇ、１８９０ｍＡｈ／ｃｍ^3）を示し好ましい。

【０１３６】

リチウムと遷移金属の複窒化物を用いると、負極活物質中にリチウムイオンを含むため、正極活物質としてリチウムイオンを含まないV_2O_5、Cr_3O_8等の材料と組み合わせることができ好ましい。なお、正極活物質にリチウムイオンを含む材料を用いる場合でも、あらかじめ正極活物質に含まれるリチウムイオンを脱離させることで、負極活物質としてリチウムと遷移金属の複窒化物を用いることができる。

【０１３７】

また、コンバージョン反応が生じる材料を負極活物質として用いることもできる。例えば、酸化コバルト（ＣｏＯ）、酸化ニッケル（ＮｉＯ）、酸化鉄（ＦｅＯ）等の、リチウムとの合金を作らない遷移金属酸化物を負極活物質に用いてもよい。コンバージョン反応が生じる材料としては、さらに、Fe_2O_3、ＣｕＯ、Cu_2O、RuO_2、Cr_2O_3等の酸化物、$CoS_{0.89}$、ＮｉＳ、ＣｕＳ等の硫化物、Zn_3N_2、Cu_3N、Ge_3N_4等の窒化物、NiP_2、FeP_2、CoP_3等のリン化物、FeF_3、BiF_3等の

フッ化物でも起こる。
【０１３８】
負極活物質層が有することのできる導電助剤およびバインダとしては、正極活物質層が有することのできる導電助剤およびバインダと同様の材料を用いることができる。
【０１３９】
＜負極集電体＞
負極集電体には、正極集電体と同様の材料を用いることができる。なお負極集電体は、リチウム等のキャリアイオンと合金化しない材料を用いることが好ましい。
【０１４０】
［電解液］
電解液は、溶媒と電解質を有する。電解液の溶媒としては、非プロトン性有機溶媒が好ましく、例えば、エチレンカーボネート（ＥＣ）、プロピレンカーボネート（ＰＣ）、ブチレンカーボネート、クロロエチレンカーボネート、ビニレンカーボネート、γ―ブチロラクトン、γ―バレロラクトン、ジメチルカーボネート（ＤＭＣ）、ジエチルカーボネート（ＤＥＣ）、エチルメチルカーボネート（ＥＭＣ）、ギ酸メチル、酢酸メチル、酪酸メチル、１，３―ジオキサン、１，４―ジオキサン、ジメトキシエタン（ＤＭＥ）、ジメチルスルホキシド、ジエチルエーテル、メチルジグライム、アセトニトリル、ベンゾニトリル、テトラヒドロフラン、スルホラン、スルトン等の１種、又はこれらのうちの２種以上を任意の組み合わせおよび比率で用いることができる。
【０１４１】
また、電解液の溶媒としてゲル化される高分子材料を用いることで、漏液性等に対する安全性が高まる。また、二次電池の薄型化および軽量化が可能である。ゲル化される高分子材料の代表例としては、シリコーンゲル、アクリルゲル、アクリロニトリルゲル、ポリエチレンオキサイド系ゲル、ポリプロピレンオキサイド系ゲル、フッ素系ポリマーのゲル等がある。
【０１４２】
また、電解液の溶媒として、難燃性および難揮発性であるイオン液体（常温溶融塩）を一つ又は複数用いることで、蓄電装置の内部短絡や、過充電等によって内部温度が上昇しても、蓄電装置の破裂や発火などを防ぐことができる。イオン液体は、カチオンとアニオンからなり、有機カチオンとアニオンとを含む。電解液に用いる有機カチオンとして、四級アンモニウムカチオン、三級スルホニウムカチオン、および四級ホスホニウムカチオン等の脂肪族オニウムカチオンや、イミダゾリウムカチオンおよびピリジニウムカチオン等の芳香族カチオンが挙げられる。また、電解液に用いるアニオンとして、１価のアミド系アニオン、１価のメチド系アニオン、フルオロスルホン酸アニオン、パーフルオロアルキルスルホン酸アニオン、テトラフルオロボレートアニオン、パーフルオロアルキルボレートアニオン、ヘキサフルオロホスフェートアニオン、またはパーフルオロアルキルホスフェートアニオン等が挙げられる。
【０１４３】
また、上記の溶媒に溶解させる電解質としては、例えば$LiPF_6$、$LiClO_4$、$LiAsF_6$、$LiBF_4$、$LiAlCl_4$、ＬｉＳＣＮ、ＬｉＢｒ、ＬｉＩ、Li_2SO_4、$Li_2B_{10}Cl_{10}$、$Li_2B_{12}Cl_{12}$、$LiCF_3SO_3$、$LiC_4F_9SO_3$、$LiC(CF_3SO_2)_3$、$LiC(C_2F_5SO_2)_3$、$LiN(CF_3SO_2)_2$、$LiN(C_4F_9SO_2)(CF_3SO_2)$、$LiN(C_2F_5SO_2)_2$等のリチウム塩を一種、又はこれらのうちの二種以上を任意の組み合わせおよび比率で用いることができる。
【０１４４】
蓄電装置に用いる電解液は、粒状のごみや電解液の構成元素以外の元素（以下、単に「不純物」ともいう。）の含有量が少ない高純度化された電解液を用いることが好ましい。具体的には、電解液に対する不純物の重量比を１％以下、好ましくは０．１％以下、より好ましくは０．０１％以下とすることが好ましい。

【０１４５】
また、電解液にビニレンカーボネート、プロパンスルトン（ＰＳ）、ｔｅｒｔ―ブチルベンゼン（ＴＢＢ）、フルオロエチレンカーボネート（ＦＥＣ）、ＬｉＢＯＢなどの添加剤を添加してもよい。添加剤の濃度は、例えば溶媒全体に対して０．１ｗｅｉｇｈｔ％以上５ｗｅｉｇｈｔ％以下とすればよい。
【０１４６】
また、ポリマーを電解液で膨潤させたポリマーゲル電解質を用いてもよい。
【０１４７】
ポリマーとしては、例えばポリエチレンオキシド（ＰＥＯ）などのポリアルキレンオキシド構造を有するポリマーや、ＰＶＤＦ、およびポリアクリロニトリル等、およびそれらを含む共重合体等を用いることができる。例えばＰＶＤＦとヘキサフルオロプロピレン（ＨＦＰ）の共重合体であるＰＶＤＦ―ＨＦＰを用いることができる。また、形成されるポリマーは、多孔質形状を有してもよい。
【０１４８】
また、電解液の代わりに、硫化物系や酸化物系等の無機物材料を有する固体電解質や、ＰＥＯ（ポリエチレンオキシド）系等の高分子材料を有する固体電解質を用いることができる。固体電解質を用いる場合には、セパレータやスペーサの設置が不要となる。また、電池全体を固体化できるため、漏液のおそれがなくなり安全性が飛躍的に向上する。
【０１４９】
［セパレータ］
また二次電池は、セパレータを有することが好ましい。セパレータとしては、例えば、紙、不織布、ガラス繊維、セラミックス、或いはナイロン（ポリアミド）、ビニロン（ポリビニルアルコール系繊維）、ポリエステル、アクリル、ポリオレフィン、ポリウレタンを用いた合成繊維等で形成されたものを用いることができる。セパレータは袋状に加工し、正極または負極のいずれか一方を包むように配置することが好ましい。
【０１５０】
［外装体］
二次電池が有する外装体としては、例えばアルミニウムなどの金属材料や樹脂材料を用いることができる。また、フィルム状の外装体を用いることもできる。フィルムとしては、例えばポリエチレン、ポリプロピレン、ポリカーボネート、アイオノマー、ポリアミド等の材料からなる膜上に、アルミニウム、ステンレス、銅、ニッケル等の可撓性に優れた金属薄膜を設け、さらに該金属薄膜上に外装体の外面としてポリアミド系樹脂、ポリエステル系樹脂等の絶縁性合成樹脂膜を設けた三層構造のフィルムを用いることができる。
【０１５１】
（実施の形態３）
本実施の形態では、先の実施の形態で説明した正極活物質１００を有する二次電池の形状の例について説明する。本実施の形態で説明する二次電池に用いる材料は、先の実施の形態の記載を参酌することができる。
【０１５２】
［コイン型二次電池］
まずコイン型の二次電池の一例について説明する。図５（Ａ）はコイン型（単層偏平型）の二次電池の外観図であり、図５（Ｂ）は、その断面図である。
【０１５３】
コイン型の二次電池３００は、正極端子を兼ねた正極缶３０１と負極端子を兼ねた負極缶３０２とが、ポリプロピレン等で形成されたガスケット３０３で絶縁シールされている。正極３０４は、正極集電体３０５と、これと接するように設けられた正極活物質層３０６により形成される。また、負極３０７は、負極集電体３０８と、これに接するように設けられた負極活物質層３０９により形成される。
【０１５４】
なお、コイン型の二次電池３００に用いる正極３０４および負極３０７は、それぞれ活物

質層は片面のみに形成すればよい。
【０１５５】
正極缶３０１、負極缶３０２には、電解液に対して耐食性のあるニッケル、アルミニウム、チタン等の金属、又はこれらの合金やこれらと他の金属との合金（例えばステンレス鋼等）を用いることができる。また、電解液による腐食を防ぐため、ニッケルやアルミニウム等を被覆することが好ましい。正極缶３０１は正極３０４と、負極缶３０２は負極３０７とそれぞれ電気的に接続する。
【０１５６】
これら負極３０７、正極３０４およびセパレータ３１０を電解質に含浸させ、図５（Ｂ）に示すように、正極缶３０１を下にして正極３０４、セパレータ３１０、負極３０７、負極缶３０２をこの順で積層し、正極缶３０１と負極缶３０２とをガスケット３０３を介して圧着してコイン形の二次電池３００を製造する。
【０１５７】
正極３０４に、先の実施の形態で説明した正極活物質を用いることで、サイクル特性に優れたコイン型の二次電池３００とすることができる。
【０１５８】
［円筒型二次電池］
次に円筒型の二次電池の例について図６を参照して説明する。円筒型の二次電池６００は、図６（Ａ）に示すように、上面に正極キャップ（電池蓋）６０１を有し、側面および底面に電池缶（外装缶）６０２を有している。これら正極キャップと電池缶（外装缶）６０２とは、ガスケット（絶縁パッキン）６１０によって絶縁されている。
【０１５９】
図６（Ｂ）は、円筒型の二次電池の断面を模式的に示した図である。中空円柱状の電池缶６０２の内側には、帯状の正極６０４と負極６０６とがセパレータ６０５を間に挟んで捲回された電池素子が設けられている。図示しないが、電池素子はセンターピンを中心に捲回されている。電池缶６０２は、一端が閉じられ、他端が開いている。電池缶６０２には、電解液に対して耐腐食性のあるニッケル、アルミニウム、チタン等の金属、又はこれらの合金やこれらと他の金属との合金（例えば、ステンレス鋼等）を用いることができる。また、電解液による腐食を防ぐため、ニッケルやアルミニウム等を被覆することが好ましい。電池缶６０２の内側において、正極、負極およびセパレータが捲回された電池素子は、対向する一対の絶縁板６０８、６０９により挟まれている。また、電池素子が設けられた電池缶６０２の内部は、非水電解液（図示せず）が注入されている。非水電解液は、コイン型の二次電池と同様のものを用いることができる。
【０１６０】
円筒型の蓄電池に用いる正極および負極は捲回するため、集電体の両面に活物質を形成することが好ましい。正極６０４には正極端子（正極集電リード）６０３が接続され、負極６０６には負極端子（負極集電リード）６０７が接続される。正極端子６０３および負極端子６０７は、ともにアルミニウムなどの金属材料を用いることができる。正極端子６０３は安全弁機構６１２に、負極端子６０７は電池缶６０２の底にそれぞれ抵抗溶接される。安全弁機構６１２は、ＰＴＣ素子（Ｐｏｓｉｔｉｖｅ　Ｔｅｍｐｅｒａｔｕｒｅ　Ｃｏｅｆｆｉｃｉｅｎｔ）６１１を介して正極キャップ６０１と電気的に接続されている。安全弁機構６１２は電池の内圧の上昇が所定の閾値を超えた場合に、正極キャップ６０１と正極６０４との電気的な接続を切断するものである。また、ＰＴＣ素子６１１は温度が上昇した場合に抵抗が増大する熱感抵抗素子であり、抵抗の増大により電流量を制限して異常発熱を防止するものである。ＰＴＣ素子には、チタン酸バリウム（$BaTiO_3$）系半導体セラミックス等を用いることができる。
【０１６１】
正極６０４に、先の実施の形態で説明した正極活物質を用いることで、サイクル特性に優れた円筒型の二次電池６００とすることができる。
【０１６２】

［曲げることのできる二次電池］
次に、曲げることのできる二次電池の例について図７および図８を参照して説明する。
【０１６３】
図７（Ａ）に、曲げることのできる二次電池５０の上面概略図を示す。図７（Ｂ１）、（Ｂ２）、（Ｃ）にはそれぞれ、図７（Ａ）中の切断線Ｃ１―Ｃ２、切断線Ｃ３―Ｃ４、切断線Ａ１―Ａ２における断面概略図である。電池５０は、外装体５１と、外装体５１の内部に収容された正極１１ａおよび負極１１ｂを有する。正極１１ａと電気的に接続されたリード１２ａ、および負極１１ｂと電気的に接続されたリード１２ｂは、外装体５１の外側に延在している。また外装体５１で囲まれた領域には、正極１１ａおよび負極１１ｂに加えて電解液（図示しない）が封入されている。
【０１６４】
電池５０が有する正極１１ａおよび負極１１ｂについて、図８を用いて説明する。図８（Ａ）は、正極１１ａ、負極１１ｂおよびセパレータ１４の積層順を説明する斜視図である。図８（Ｂ）は正極１１ａおよび負極１１ｂに加えて、リード１２ａおよびリード１２ｂを示す斜視図である。
【０１６５】
図８（Ａ）に示すように、電池５０は、複数の短冊状の正極１１ａ、複数の短冊状の負極１１ｂおよび複数のセパレータ１４を有する。正極１１ａおよび負極１１ｂはそれぞれ突出したタブ部分と、タブ以外の部分を有する。正極１１ａの一方の面のタブ以外の部分に正極活物質層が形成され、負極１１ｂの一方の面のタブ以外の部分に負極活物質層が形成される。
【０１６６】
正極１１ａの正極活物質層の形成されていない面同士、および負極１１ｂの負極活物質の形成されていない面同士が接するように、正極１１ａおよび負極１１ｂは積層される。
【０１６７】
また、正極１１ａの正極活物質が形成された面と、負極１１ｂの負極活物質が形成された面の間にはセパレータ１４が設けられる。図８では見やすくするためセパレータ１４を点線で示す。
【０１６８】
また図８（Ｂ）に示すように、複数の正極１１ａとリード１２ａは、接合部１５ａにおいて電気的に接続される。また複数の負極１１ｂとリード１２ｂは、接合部１５ｂにおいて電気的に接続される。
【０１６９】
次に、外装体５１について図７（Ｂ１）、（Ｂ２）、（Ｃ）、（◗）を用いて説明する。
【０１７０】
外装体５１は、フィルム状の形状を有し、正極１１ａおよび負極１１ｂを挟むように２つに折り曲げられている。外装体５１は、折り曲げ部６１と、一対のシール部６２と、シール部６３と、を有する。一対のシール部６２は、正極１１ａおよび負極１１ｂを挟んで設けられ、サイドシールとも呼ぶことができる。また、シール部６３は、リード１２ａ及びリード１２ｂと重なる部分を有し、トップシールとも呼ぶことができる。
【０１７１】
外装体５１は、正極１１ａおよび負極１１ｂと重なる部分に、稜線７１と谷線７２が交互に並んだ波形状を有することが好ましい。また、外装体５１のシール部６２及びシール部６３は、平坦であることが好ましい。
【０１７２】
図７（Ｂ１）は、稜線７１と重なる部分で切断した断面であり、図７（Ｂ２）は、谷線７２と重なる部分で切断した断面である。図７（Ｂ１）、（Ｂ２）は共に、電池５０及び正極１１ａおよび負極１１ｂの幅方向の断面に対応する。
【０１７３】
ここで、正極１１ａおよび負極１１ｂの幅方向の端部、すなわち正極１１ａおよび負極１

１ｂの端部と、シール部６２との間の距離を距離Ｌａとする。電池５０に曲げるなどの変形を加えたとき、後述するように正極１１ａおよび負極１１ｂが長さ方向に互いにずれるように変形する。その際、距離Ｌａが短すぎると、外装体５１と正極１１ａおよび負極１１ｂとが強く擦れ、外装体５１が破損してしまう場合がある。特に外装体５１の金属フィルムが露出すると、当該金属フィルムが電解液により腐食されてしまう恐れがある。したがって、距離Ｌａを出来るだけ長く設定することが好ましい。一方で、距離Ｌａを大きくしすぎると、電池５０の体積が増大してしまう。

【０１７４】

また、積層された正極１１ａおよび負極１１ｂの合計の厚さが厚いほど、正極１１ａおよび負極１１ｂと、シール部６２との間の距離Ｌａを大きくすることが好ましい。

【０１７５】

より具体的には、積層された正極１１ａおよび負極１１ｂの合計の厚さを厚さｔとしたとき、距離Ｌａは、厚さｔの０．８倍以上３．０倍以下、好ましくは０．９倍以上２．５倍以下、より好ましくは１．０倍以上２．０倍以下であることが好ましい。距離Ｌａをこの範囲とすることで、コンパクトで、且つ曲げに対する信頼性の高い電池を実現できる。

【０１７６】

また、一対のシール部６２の間の距離を距離Ｌｂとしたとき、距離Ｌｂを正極１１ａおよび負極１１ｂの幅（ここでは、負極１１ｂの幅Ｗｂ）よりも十分大きくすることが好ましい。これにより、電池５０に繰り返し曲げるなどの変形を加えたときに、正極１１ａおよび負極１１ｂと外装体５１とが接触しても、正極１１ａおよび負極１１ｂの一部が幅方向にずれることができるため、正極１１ａおよび負極１１ｂと外装体５１とが擦れてしまうことを効果的に防ぐことができる。

【０１７７】

例えば、一対のシール部６２の間の距離Ｌａと、負極１１ｂの幅Ｗｂとの差が、正極１１ａおよび負極１１ｂの厚さｔの１．６倍以上６．０倍以下、好ましくは１．８倍以上５．０倍以下、より好ましくは、２．０倍以上４．０倍以下を満たすことが好ましい。

【０１７８】

言い換えると、距離Ｌｂ、幅Ｗｂ、及び厚さｔが、下記数式２の関係を満たすことが好ましい。

【０１７９】

【数２】

$$\frac{Lb-Wb}{2t} \geq a \qquad \text{（数式２）}$$

【０１８０】

ここで、ａは、０．８以上３．０以下、好ましくは０．９以上２．５以下、より好ましくは１．０以上２．０以下を満たす。

【０１８１】

また、図７（Ｃ）はリード１２ａを含む断面であり、電池５０、正極１１ａおよび負極１１ｂの長さ方向の断面に対応する。図７（Ｃ）に示すように、折り曲げ部６１において、正極１１ａおよび負極１１ｂの長さ方向の端部と、外装体５１との間に空間７３を有することが好ましい。

【０１８２】

図７（Ｄ）に、電池５０を曲げたときの断面概略図を示している。図７（Ｄ）は、図７（Ａ）中の切断線Ｂ１―Ｂ２における断面に相当する。

【０１８３】

電池５０を曲げると、曲げの外側に位置する外装体５１の一部は伸び、内側に位置する他の一部は縮むように変形する。より具体的には、外装体５１の外側に位置する部分は、波の振幅が小さく、且つ波の周期が大きくなるように変形する。一方、外装体５１の内側に

位置する部分は、波の振幅が大きく、且つ波の周期が小さくなるように変形する。このように、外装体５１が変形することにより、曲げに伴って外装体５１にかかる応力が緩和されるため、外装体５１を構成する材料自体が伸縮する必要がない。その結果、外装体５１は破損することなく、小さな力で電池５０を曲げることができる。

【０１８４】

また、図７（Ｄ）に示すように、電池５０を曲げると、正極１１ａおよび負極１１ｂとがそれぞれ相対的にずれる。このとき、複数の積層された正極１１ａおよび負極１１ｂは、シール部６３側の一端が固定部材１７で固定されているため、折り曲げ部６１に近いほどずれ量が大きくなるように、それぞれずれる。これにより、正極１１ａおよび負極１１ｂにかかる応力が緩和され、正極１１ａおよび負極１１ｂ自体が伸縮する必要がない。その結果、正極１１ａおよび負極１１ｂが破損することなく電池５０を曲げることができる。

【０１８５】

また、正極１１ａおよび負極１１ｂと外装体５１との間に空間７３を有していることにより、曲げた時内側に位置する正極１１ａおよび負極１１ｂが、外装体５１に接触することなく、相対的にずれることができる。

【０１８６】

図７および図８で例示した電池５０は、繰り返し曲げ伸ばしを行っても、外装体の破損、正極１１ａおよび負極１１ｂの破損などが生じにくく、電池特性も劣化しにくい電池である。電池５０が有する正極１１ａに、先の実施の形態で説明した正極活物質を用いることで、さらにサイクル特性に優れた電池とすることができる。

【０１８７】

（実施の形態４）

本実施の形態では、本発明の一態様である二次電池を電子機器に実装する例について説明する。

【０１８８】

まず実施の形態３で説明した、曲げることのできる二次電池を電子機器に実装する例を図９に示す。フレキシブルな形状を備える二次電池を適用した電子機器として、例えば、テレビジョン装置（テレビ、又はテレビジョン受信機ともいう）、コンピュータ用などのモニタ、デジタルカメラ、デジタルビデオカメラ、デジタルフォトフレーム、携帯電話機（携帯電話、携帯電話装置ともいう）、携帯型ゲーム機、携帯情報端末、音響再生装置、パチンコ機などの大型ゲーム機などが挙げられる。

【０１８９】

また、フレキシブルな形状を備える二次電池を、家屋やビルの内壁または外壁や、自動車の内装または外装の曲面に沿って組み込むことも可能である。

【０１９０】

図９（Ａ）は、携帯電話機の一例を示している。携帯電話機７４００は、筐体７４０１に組み込まれた表示部７４０２の他、操作ボタン７４０３、外部接続ポート７４０４、スピーカ７４０５、マイク７４０６などを備えている。なお、携帯電話機７４００は、二次電池７４０７を有している。

【０１９１】

図９（Ｂ）は、携帯電話機７４００を湾曲させた状態を示している。携帯電話機７４００を外部の力により変形させて全体を湾曲させると、その内部に設けられている二次電池７４０７も湾曲される。また、その時、曲げられた二次電池７４０７の状態を図９（Ｃ）に示す。二次電池７４０７は薄型の蓄電池である。二次電池７４０７は曲げられた状態で固定されている。なお、二次電池７４０７は集電体７４０９と電気的に接続されたリード電極７４０８を有している。例えば、集電体７４０９は銅箔であり、一部ガリウムと合金化させて、集電体７４０９と接する活物質層との密着性を向上し、二次電池７４０７が曲げられた状態での信頼性が高い構成となっている。

【０１９２】

図９（Ｄ）は、バングル型の表示装置の一例を示している。携帯表示装置７１００は、筐

体７１０１、表示部７１０２、操作ボタン７１０３、及び二次電池７１０４を備える。また、図９（Ｅ）に曲げられた二次電池７１０４の状態を示す。二次電池７１０４は曲げられた状態で使用者の腕への装着時に、筐体が変形して二次電池７１０４の一部または全部の曲率が変化する。なお、曲線の任意の点における曲がり具合を相当する円の半径の値で表したものを曲率半径であり、曲率半径の逆数を曲率と呼ぶ。具体的には、曲率半径が４０ｍｍ以上１５０ｍｍ以下の範囲内で筐体または二次電池７１０４の主表面の一部または全部が変化する。二次電池７１０４の主表面における曲率半径が４０ｍｍ以上１５０ｍｍ以下の範囲であれば、高い信頼性を維持できる。

【０１９３】

図９（Ｆ）は、腕時計型の携帯情報端末の一例を示している。携帯情報端末７２００は、筐体７２０１、表示部７２０２、バンド７２０３、バックル７２０４、操作ボタン７２０５、入出力端子７２０６などを備える。

【０１９４】

携帯情報端末７２００は、移動電話、電子メール、文章閲覧及び作成、音楽再生、インターネット通信、コンピュータゲームなどの種々のアプリケーションを実行することができる。

【０１９５】

表示部７２０２はその表示面が湾曲して設けられ、湾曲した表示面に沿って表示を行うことができる。また、表示部７２０２はタッチセンサを備え、指やスタイラスなどで画面に触れることで操作することができる。例えば、表示部７２０２に表示されたアイコン７２０７に触れることで、アプリケーションを起動することができる。

【０１９６】

操作ボタン７２０５は、時刻設定のほか、電源のオン、オフ動作、無線通信のオン、オフ動作、マナーモードの実行及び解除、省電力モードの実行及び解除など、様々な機能を持たせることができる。例えば、携帯情報端末７２００に組み込まれたオペレーティングシステムにより、操作ボタン７２０５の機能を自由に設定することもできる。

【０１９７】

また、携帯情報端末７２００は、通信規格された近距離無線通信を実行することが可能である。例えば無線通信可能なヘッドセットと相互通信することによって、ハンズフリーで通話することもできる。

【０１９８】

また、携帯情報端末７２００は入出力端子７２０６を備え、他の情報端末とコネクターを介して直接データのやりとりを行うことができる。また入出力端子７２０６を介して充電を行うこともできる。なお、充電動作は入出力端子７２０６を介さずに無線給電により行ってもよい。

【０１９９】

携帯情報端末７２００の表示部７２０２には、本発明の一態様の二次電池を有している。例えば、図９（Ｅ）に示した二次電池７１０４を、筐体７２０１の内部に湾曲した状態で、またはバンド７２０３の内部に湾曲可能な状態で組み込むことができる。

【０２００】

携帯情報端末７２００はセンサを有することが好ましい。センサとして例えば、指紋センサ、脈拍センサ、体温センサ等の人体センサや、タッチセンサ、加圧センサ、加速度センサ、等が搭載されることが好ましい。

【０２０１】

図９（Ｇ）は、腕章型の表示装置の一例を示している。表示装置７３００は、表示部７３０４を有し、本発明の一態様の二次電池を有している。また、表示装置７３００は、表示部７３０４にタッチセンサを備えることもでき、また、携帯情報端末として機能させることもできる。

【０２０２】

表示部７３０４はその表示面が湾曲しており、湾曲した表示面に沿って表示を行うことが

できる。また、表示装置７３００は、通信規格された近距離無線通信などにより、表示状況を変更することができる。

【０２０３】

また、表示装置７３００は入出力端子を備え、他の情報端末とコネクターを介して直接データのやりとりを行うことができる。また入出力端子を介して充電を行うこともできる。なお、充電動作は入出力端子を介さずに無線給電により行ってもよい。

【０２０４】

次に、図１０（Ａ）および図１０（Ｂ）に、２つ折り可能なタブレット型端末の一例を示す。図１０（Ａ）および図１０（Ｂ）に示すタブレット型端末９６００は、筐体９６３０ａ、筐体９６３０ｂ、筐体９６３０ａと筐体９６３０ｂを接続する可動部９６４０、表示部９６３１ａと表示部９６３１ｂを有する表示部９６３１、表示モード切り替えスイッチ９６２６、電源スイッチ９６２７、省電力モード切り替えスイッチ９６２５、留め具９６２９、操作スイッチ９６２８、を有する。図１０（Ａ）は、タブレット型端末９６００を開いた状態を示し、図１０（Ｂ）は、タブレット型端末９６００を閉じた状態を示している。

【０２０５】

また、タブレット型端末９６００は、筐体９６３０ａおよび筐体９６３０ｂの内部に蓄電体９６３５を有する。蓄電体９６３５は、可動部９６４０を通り、筐体９６３０ａと筐体９６３０ｂに渡って設けられている。

【０２０６】

表示部９６３１ａは、一部をタッチパネルの領域９６３２ａとすることができ、表示された操作キー９６３８にふれることでデータ入力をすることができる。なお、表示部９６３１ａにおいては、一例として半分の領域が表示のみの機能を有する構成、もう半分の領域がタッチパネルの機能を有する構成を示しているが該構成に限定されない。表示部９６３１ａの全ての領域がタッチパネルの機能を有する構成としても良い。例えば、表示部９６３１ａの全面をキーボードボタン表示させてタッチパネルとし、表示部９６３１ｂを表示画面として用いることができる。

【０２０７】

また、表示部９６３１ｂにおいても表示部９６３１ａと同様に、表示部９６３１ｂの一部をタッチパネルの領域９６３２ｂとすることができる。また、タッチパネルのキーボード表示切り替えボタン９６３９が表示されている位置に指やスタイラスなどでふれることで表示部９６３１ｂにキーボードボタン表示することができる。

【０２０８】

また、タッチパネルの領域９６３２ａとタッチパネルの領域９６３２ｂに対して同時にタッチ入力することもできる。

【０２０９】

また、表示モード切り替えスイッチ９６２６は、縦表示又は横表示などの表示の向きを切り替え、白黒表示やカラー表示の切り替えなどを選択できる。省電力モード切り替えスイッチ９６２５は、タブレット型端末９６００に内蔵している光センサで検出される使用時の外光の光量に応じて表示の輝度を最適なものとすることができる。タブレット型端末は光センサだけでなく、ジャイロ、加速度センサ等の傾きを検出するセンサなどの他の検出装置を内蔵させてもよい。

【０２１０】

また、図１０（Ａ）では表示部９６３１ｂと表示部９６３１ａの表示面積が同じ例を示しているが特に限定されず、一方のサイズともう一方のサイズが異なっていてもよく、表示の品質も異なっていてもよい。例えば一方が他方よりも高精細な表示を行える表示パネルとしてもよい。

【０２１１】

図１０（Ｂ）は、閉じた状態であり、タブレット型端末は、筐体９６３０、太陽電池９６３３、ＤＣＤＣコンバータ９６３６を含む充放電制御回路９６３４有する。また、蓄電体

９６３５として、本発明の一態様に係る蓄電体を用いる。
【０２１２】
なお、タブレット型端末９６００は２つ折り可能なため、未使用時に筐体９６３０ａおよび筐体９６３０ｂを重ね合せるように折りたたむことができる。折りたたむことにより、表示部９６３１ａ、表示部９６３１ｂを保護できるため、タブレット型端末９６００の耐久性を高めることができる。また、本発明の一態様の蓄電体を用いた蓄電体９６３５は可撓性を有し、曲げ伸ばしを繰り返しても充放電容量が低下しにくい。よって、信頼性の優れたタブレット型端末を提供できる。
【０２１３】
また、この他にも図１０（Ａ）および図１０（Ｂ）に示したタブレット型端末は、様々な情報（静止画、動画、テキスト画像など）を表示する機能、カレンダー、日付又は時刻などを表示部に表示する機能、表示部に表示した情報をタッチ入力操作又は編集するタッチ入力機能、様々なソフトウェア（プログラム）によって処理を制御する機能、等を有することができる。
【０２１４】
タブレット型端末の表面に装着された太陽電池９６３３によって、電力をタッチパネル、表示部、又は映像信号処理部等に供給することができる。なお、太陽電池９６３３は、筐体９６３０の片面又は両面に設けることができ、蓄電体９６３５の充電を効率的に行う構成とすることができる。なお蓄電体９６３５としては、リチウムイオン電池を用いると、小型化を図れる等の利点がある。
【０２１５】
また、図１０（Ｂ）に示す充放電制御回路９６３４の構成、および動作について図１０（Ｃ）にブロック図を示し説明する。図１０（Ｃ）には、太陽電池９６３３、蓄電体９６３５、ＤＣＤＣコンバータ９６３６、コンバータ９６３７、スイッチＳＷ１乃至ＳＷ３、表示部９６３１について示しており、蓄電体９６３５、ＤＣＤＣコンバータ９６３６、コンバータ９６３７、スイッチＳＷ１乃至ＳＷ３が、図１０（Ｂ）に示す充放電制御回路９６３４に対応する箇所となる。
【０２１６】
まず外光により太陽電池９６３３により発電がされる場合の動作の例について説明する。太陽電池で発電した電力は、蓄電体９６３５を充電するための電圧となるようＤＣＤＣコンバータ９６３６で昇圧又は降圧がなされる。そして、表示部９６３１の動作に太陽電池９６３３からの電力が用いられる際にはスイッチＳＷ１をオンにし、コンバータ９６３７で表示部９６３１に必要な電圧に昇圧又は降圧をすることとなる。また、表示部９６３１での表示を行わない際には、ＳＷ１をオフにし、ＳＷ２をオンにして蓄電体９６３５の充電を行う構成とすればよい。
【０２１７】
なお太陽電池９６３３については、発電手段の一例として示したが、特に限定されず、圧電素子（ピエゾ素子）や熱電変換素子（ペルティエ素子）などの他の発電手段による蓄電体９６３５の充電を行う構成であってもよい。例えば、無線（非接触）で電力を送受信して充電する無接点電力伝送モジュールや、また他の充電手段を組み合わせて行う構成としてもよい。
【０２１８】
図１１に、他の電子機器の例を示す。図１１において、表示装置８０００は、本発明の一態様に係る二次電池８００４を用いた電子機器の一例である。具体的に、表示装置８０００は、ＴＶ放送受信用の表示装置に相当し、筐体８００１、表示部８００２、スピーカ部８００３、二次電池８００４等を有する。本発明の一態様に係る二次電池８００４は、筐体８００１の内部に設けられている。表示装置８０００は、商用電源から電力の供給を受けることもできるし、二次電池８００４に蓄積された電力を用いることもできる。よって、停電などにより商用電源から電力の供給が受けられない時でも、本発明の一態様に係る二次電池８００４を無停電電源として用いることで、表示装置８０００の利用が可能とな

る。
【０２１９】
表示部８００２には、液晶表示装置、有機ＥＬ素子などの発光素子を各画素に備えた発光装置、電気泳動表示装置、ＤＭＤ（Ｄｉｇｉｔａｌ　Ｍｉｃｒｏｍｉｒｒｏｒ　Ｄｅｖｉｃｅ）、ＰＤＰ（Ｐｌａｓｍａ　Ｄｉｓｐｌａｙ　Ｐａｎｅｌ）、ＦＥＤ（Ｆｉｅｌｄ　Ｅｍｉｓｓｉｏｎ　Ｄｉｓｐｌａｙ）などの、半導体表示装置を用いることができる。
【０２２０】
なお、表示装置には、ＴＶ放送受信用の他、パーソナルコンピュータ用、広告表示用など、全ての情報表示用表示装置が含まれる。
【０２２１】
図１１において、据え付け型の照明装置８１００は、本発明の一態様に係る二次電池８１０３を用いた電子機器の一例である。具体的に、照明装置８１００は、筐体８１０１、光源８１０２、二次電池８１０３等を有する。図１１では、二次電池８１０３が、筐体８１０１及び光源８１０２が据え付けられた天井８１０４の内部に設けられている場合を例示しているが、二次電池８１０３は、筐体８１０１の内部に設けられていても良い。照明装置８１００は、商用電源から電力の供給を受けることもできるし、二次電池８１０３に蓄積された電力を用いることもできる。よって、停電などにより商用電源から電力の供給が受けられない時でも、本発明の一態様に係る二次電池８１０３を無停電電源として用いることで、照明装置８１００の利用が可能となる。
【０２２２】
なお、図１１では天井８１０４に設けられた据え付け型の照明装置８１００を例示しているが、本発明の一態様に係る二次電池は、天井８１０４以外、例えば側壁８１０５、床８１０６、窓８１０７等に設けられた据え付け型の照明装置に用いることもできるし、卓上型の照明装置などに用いることもできる。
【０２２３】
また、光源８１０２には、電力を利用して人工的に光を得る人工光源を用いることができる。具体的には、白熱電球、蛍光灯などの放電ランプ、ＬＥＤや有機ＥＬ素子などの発光素子が、上記人工光源の一例として挙げられる。
【０２２４】
図１１において、室内機８２００及び室外機８２０４を有するエアコンディショナーは、本発明の一態様に係る二次電池８２０３を用いた電子機器の一例である。具体的に、室内機８２００は、筐体８２０１、送風口８２０２、二次電池８２０３等を有する。図１１では、二次電池８２０３が、室内機８２００に設けられている場合を例示しているが、二次電池８２０３は室外機８２０４に設けられていても良い。或いは、室内機８２００と室外機８２０４の両方に、二次電池８２０３が設けられていても良い。エアコンディショナーは、商用電源から電力の供給を受けることもできるし、二次電池８２０３に蓄積された電力を用いることもできる。特に、室内機８２００と室外機８２０４の両方に二次電池８２０３が設けられている場合、停電などにより商用電源から電力の供給が受けられない時でも、本発明の一態様に係る二次電池８２０３を無停電電源として用いることで、エアコンディショナーの利用が可能となる。
【０２２５】
なお、図１１では、室内機と室外機で構成されるセパレート型のエアコンディショナーを例示しているが、室内機の機能と室外機の機能とを１つの筐体に有する一体型のエアコンディショナーに、本発明の一態様に係る二次電池を用いることもできる。
【０２２６】
図１１において、電気冷凍冷蔵庫８３００は、本発明の一態様に係る二次電池８３０４を用いた電子機器の一例である。具体的に、電気冷凍冷蔵庫８３００は、筐体８３０１、冷蔵室用扉８３０２、冷凍室用扉８３０３、二次電池８３０４等を有する。図１１では、二次電池８３０４が、筐体８３０１の内部に設けられている。電気冷凍冷蔵庫８３００は、商用電源から電力の供給を受けることもできるし、二次電池８３０４に蓄積された電力を

用いることもできる。よって、停電などにより商用電源から電力の供給が受けられない時でも、本発明の一態様に係る二次電池８３０４を無停電電源として用いることで、電気冷凍冷蔵庫８３００の利用が可能となる。

【０２２７】

なお、上述した電子機器のうち、電子レンジ等の高周波加熱装置、電気炊飯器などの電子機器は、短時間で高い電力を必要とする。よって、商用電源では賄いきれない電力を補助するための補助電源として、本発明の一態様に係る二次電池を用いることで、電子機器の使用時に商用電源のブレーカーが落ちるのを防ぐことができる。

【０２２８】

また、電子機器が使用されない時間帯、特に、商用電源の供給元が供給可能な総電力量のうち、実際に使用される電力量の割合（電力使用率と呼ぶ）が低い時間帯において、二次電池に電力を蓄えておくことで、上記時間帯以外において電力使用率が高まるのを抑えることができる。例えば、電気冷凍冷蔵庫８３００の場合、気温が低く、冷蔵室用扉８３０２、冷凍室用扉８３０３の開閉が行われない夜間において、二次電池８３０４に電力を蓄える。そして、気温が高くなり、冷蔵室用扉８３０２、冷凍室用扉８３０３の開閉が行われる昼間において、二次電池８３０４を補助電源として用いることで、昼間の電力使用率を低く抑えることができる。

【０２２９】

本発明の一態様により、二次電池のサイクル特性が良好となり、信頼性を向上させることができる。また、本発明の一態様によれば、二次電池の特性を向上することができ、よって、二次電池自体を小型軽量化することができる。そのため本発明の一態様である二次電池を、本実施の形態で説明した電子機器に搭載することで、より長寿命で、より軽量な電子機器とすることができる。本実施の形態は、他の実施の形態と適宜組み合わせて実施することが可能である。

【０２３０】

（実施の形態５）

本実施の形態では、車両に本発明の一態様である二次電池を搭載する例を示す。

【０２３１】

二次電池を車両に搭載すると、ハイブリッド車（ＨＥＶ）、電気自動車（ＥＶ）、又はプラグインハイブリッド車（ＰＨＥＶ）等の次世代クリーンエネルギー自動車を実現できる。

【０２３２】

図１２において、本発明の一態様である二次電池を用いた車両を例示する。図１２（Ａ）に示す自動車８４００は、走行のための動力源として電気モーターを用いる電気自動車である。または、走行のための動力源として電気モーターとエンジンを適宜選択して用いることが可能なハイブリッド自動車である。本発明の一態様を用いることで、航続距離の長い車両を実現することができる。また、自動車８４００は二次電池を有する。二次電池は電気モーター８４０６を駆動するだけでなく、ヘッドライト８４０１やルームライト（図示せず）などの発光装置に電力を供給することができる。

【０２３３】

また、二次電池は、自動車８４００が有するスピードメーター、タコメーターなどの表示装置に電力を供給することができる。また、二次電池は、自動車８４００が有するナビゲーションシステムなどの半導体装置に電力を供給することができる。

【０２３４】

図１２（Ｂ）に示す自動車８５００は、自動車８５００が有する二次電池にプラグイン方式や非接触給電方式等により外部の充電設備から電力供給を受けて、充電することができる。図１２（Ｂ）に、地上設置型の充電装置８０２１から自動車８５００に搭載された二次電池８０２４に、ケーブル８０２２を介して充電を行っている状態を示す。充電に際しては、充電方法やコネクターの規格等はＣＨＡｄｅＭＯ（登録商標）やコンボ等の所定の方式で適宜行えばよい。充電装置８０２１は、商用施設に設けられた充電ステーションで

もよく、また家庭の電源であってもよい。例えば、プラグイン技術によって、外部からの電力供給により自動車８５００に搭載された二次電池８０２４を充電することができる。充電は、ＡＣＤＣコンバータ等の変換装置を介して、交流電力を直流電力に変換して行うことができる。

【０２３５】

また、図示しないが、受電装置を車両に搭載し、地上の送電装置から電力を非接触で供給して充電することもできる。この非接触給電方式の場合には、道路や外壁に送電装置を組み込むことで、停車中に限らず走行中に充電を行うこともできる。また、この非接触給電の方式を利用して、車両どうしで電力の送受信を行ってもよい。さらに、車両の外装部に太陽電池を設け、停車時や走行時に二次電池の充電を行ってもよい。このような非接触での電力の供給には、電磁誘導方式や磁界共鳴方式を用いることができる。

【０２３６】

また、図１２（Ｃ）は、本発明の一態様の二次電池を用いた二輪車の一例である。図１２（Ｃ）に示すスクータ８６００は、二次電池８６０２、サイドミラー８６０１、方向指示灯８６０３を備える。二次電池８６０２は、方向指示灯８６０３に電気を供給することができる。

【０２３７】

また、図１２（Ｃ）に示すスクータ８６００は、座席下収納８６０４に、二次電池８６０２を収納することができる。二次電池８６０２は、座席下収納８６０４が小型であっても、座席下収納８６０４に収納することができる。

【０２３８】

本発明の一態様によれば、二次電池のサイクル特性が良好となり、信頼性を向上させることができる。また、本発明の一態様によれば、二次電池の特性を向上することができ、よって、二次電池自体を小型軽量化することができる。二次電池自体を小型軽量化できれば、車両の軽量化に寄与するため、航続距離を向上させることができる。また、車両に搭載した二次電池を車両以外の電力供給源として用いることもできる。この場合、電力需要のピーク時に商用電源を用いることを回避することができる。

【０２３９】

本実施の形態は、他の実施の形態と適宜組み合わせて実施することが可能である。

【符号の説明】

【０２４０】

１１ａ　正極
１１ｂ　負極
１２ａ　リード
１２ｂ　リード
１４　セパレータ
１５ａ　接合部
１５ｂ　接合部
１７　固定部材
５０　電池
５１　外装体
６１　折り曲げ部
６２　シール部
６３　シール部
７１　稜線
７２　谷線
７３　空間
１００　正極活物質
１０１　第１の領域
１０１ｐ　結晶面

１０２　第２の領域
１０２ｐ　結晶面
１０３　第３の領域
１０３ｐ　結晶面
１０４　第４の領域
２００　活物質層
２０１　グラフェン化合物
３００　二次電池
３０１　正極缶
３０２　負極缶
３０３　ガスケット
３０４　正極
３０５　正極集電体
３０６　正極活物質層
３０７　負極
３０８　負極集電体
３０９　負極活物質層
３１０　セパレータ
６００　二次電池
６０１　正極キャップ
６０２　電池缶
６０３　正極端子
６０４　正極
６０５　セパレータ
６０６　負極
６０７　負極端子
６０８　絶縁板
６０９　絶縁板
６１１　ＰＴＣ素子
６１２　安全弁機構
７１００　携帯表示装置
７１０１　筐体
７１０２　表示部
７１０３　操作ボタン
７１０４　二次電池
７２００　携帯情報端末
７２０１　筐体
７２０２　表示部
７２０３　バンド
７２０４　バックル
７２０５　操作ボタン
７２０６　入出力端子
７２０７　アイコン
７３００　表示装置
７３０４　表示部
７４００　携帯電話機
７４０１　筐体
７４０２　表示部
７４０３　操作ボタン
７４０４　外部接続ポート

７４０５　スピーカ
７４０６　マイク
７４０７　二次電池
７４０８　リード電極
７４０９　集電体
８０００　表示装置
８００１　筐体
８００２　表示部
８００３　スピーカ部
８００４　二次電池
８０２１　充電装置
８０２２　ケーブル
８０２４　二次電池
８１００　照明装置
８１０１　筐体
８１０２　光源
８１０３　二次電池
８１０４　天井
８１０５　側壁
８１０６　床
８１０７　窓
８２００　室内機
８２０１　筐体
８２０２　送風口
８２０３　二次電池
８２０４　室外機
８３００　電気冷凍冷蔵庫
８３０１　筐体
８３０２　冷蔵室用扉
８３０３　冷凍室用扉
８３０４　二次電池
８４００　自動車
８４０１　ヘッドライト
８４０６　電気モーター
８５００　自動車
８６００　スクータ
８６０１　サイドミラー
８６０２　二次電池
８６０３　方向指示灯
８６０４　座席下収納
９６００　タブレット型端末
９６２５　スイッチ
９６２６　スイッチ
９６２７　電源スイッチ
９６２８　操作スイッチ
９６２９　留め具
９６３０　筐体
９６３０ａ　筐体
９６３０ｂ　筐体
９６３１　表示部

９６３１ａ　　表示部
９６３１ｂ　　表示部
９６３２ａ　　領域
９６３２ｂ　　領域
９６３３　　太陽電池
９６３４　　充放電制御回路
９６３５　　蓄電体
９６３６　　ＤＣＤＣコンバータ
９６３７　　コンバータ
９６３８　　操作キー
９６３９　　ボタン
９６４０　　可動部

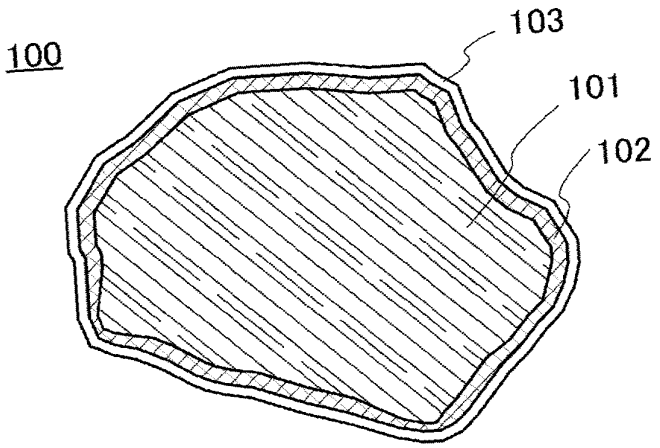
【書類名】特許請求の範囲
【請求項１】
第１の領域と、
前記第１の領域の少なくとも一部を被覆する第２の領域と、
前記第２の領域の少なくとも一部を被覆する第３の領域と、を有し、
前記第１の領域はリチウムと第１の遷移金属の酸化物を有し、層状岩塩型の結晶構造を有し、
前記第２の領域は第２の遷移金属の酸化物を有する不定比化合物を有し、前記不定比化合物は岩塩型の結晶構造を有し、
前記第３の領域は典型元素の化合物を有し、前記典型元素の化合物は岩塩型の結晶構造を有する正極活物質。
【請求項２】
請求項１において、
前記第１の領域が有する前記層状岩塩型の結晶構造と、前記第２の領域が有する前記岩塩型の結晶構造の不整合度が０．１２以下、
前記第２の領域が有する前記岩塩型の結晶構造と、前記第３の領域が有する前記岩塩型の結晶構造の不整合度が０．１２以下である正極活物質。
【請求項３】
請求項２において、
前記第１の領域が有する前記層状岩塩型の結晶構造と、前記第２の領域が有する前記岩塩型の結晶構造の不整合度が０．０４以下、
前記第２の領域が有する前記岩塩型の結晶構造と、前記第３の領域が有する前記岩塩型の結晶構造の不整合度が０．０４以下である正極活物質。
【請求項４】
請求項１乃至請求項３のいずれか一において、
前記第１の領域が有する前記層状岩塩型の結晶構造の（１―１―４）面、または前記（１―１―４）面と直交する面と、前記第２の領域が有する前記岩塩型の結晶構造の｛１００｝面の不整合度が０．１２以下であり、
前記第２の領域が有する前記岩塩型の結晶構造の｛１００｝面と、前記第３の領域が有する前記岩塩型の結晶構造の｛１００｝面の不整合度が０．１２以下である正極活物質。
【請求項５】
請求項４において、
前記第１の領域が有する前記層状岩塩型の結晶構造の（１―１―４）面、または前記（１―１―４）面と直交する面と、前記第２の領域が有する前記岩塩型の結晶構造の｛１００｝面の不整合度が０．０４以下であり、
前記第２の領域が有する前記岩塩型の結晶構造の｛１００｝面と、前記第３の領域が有する前記岩塩型の結晶構造の｛１００｝面の不整合度が０．０４以下である正極活物質。
【請求項６】
請求項１乃至請求項５のいずれか一において、
前記第１の領域が有するリチウムと第１の遷移金属の酸化物は多結晶である正極活物質。
【請求項７】
請求項６において、
前記第１の領域が有するリチウムと第１の遷移金属の酸化物の、結晶粒径の平均は２８０μｍ以上６３０μｍ以下である正極活物質。
【請求項８】
請求項１乃至請求項７のいずれか一において、
前記第１の遷移金属はコバルトであり、
前記第２の遷移金属はチタンであり、
前記典型元素の化合物は酸化マグネシウムである正極活物質。

【請求項９】
請求項１乃至請求項８のいずれか一において、
正極活物質は第４の領域を有し、
前記第４の領域は前記第３の領域の少なくとも一部を被覆し、
前記第４の領域は炭素を有する正極活物質。
【請求項１０】
請求項９において、
前記第４の領域が有する前記炭素は、グラフェン化合物である正極活物質。
【請求項１１】
請求項１乃至請求項１０のいずれか一に記載の正極活物質を有する正極と、
負極と、を有する二次電池。

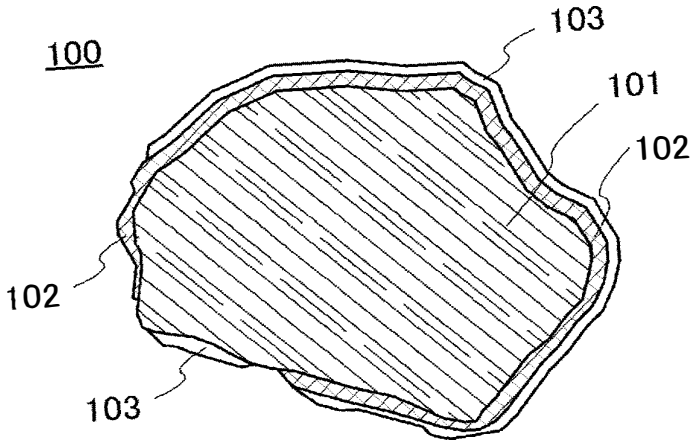
【書類名】要約書
【要約】
【課題】二次電池のサイクル特性を向上できる正極活物質を提供する。
【解決手段】層状岩塩型の結晶構造を有する正極活物質の表面に、２種の被覆層を設ける。内側の被覆層は遷移金属を有する不定比化合物、外側の被覆層は典型元素の化合物とする。２種の被覆層はどちらも岩塩型の結晶構造を有する。また層状岩塩型の結晶構造と、２種の被覆層はトポタキシである。２種の被覆層が正極活物質とトポタキシであるため、充放電によって生じる正極活物質の結晶構造の変化を効果的に抑制できる。また電解液と接触する外側の被覆層が、化学的に安定した典型元素の化合物であるため、サイクル特性の優れた二次電池とすることができる。
【選択図】図１

【書類名】図面
【図１】

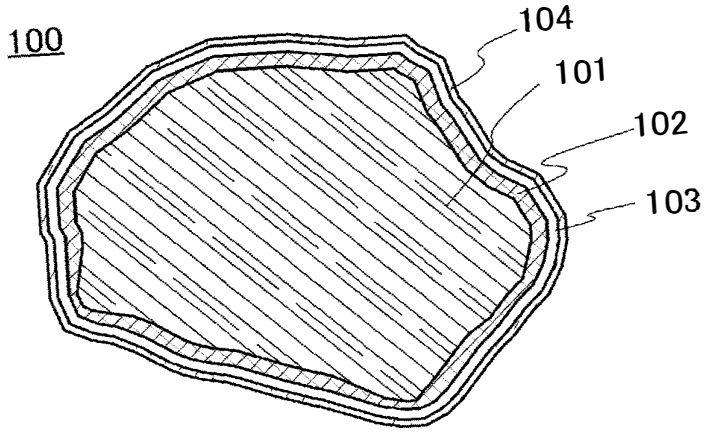
(A)



(B)

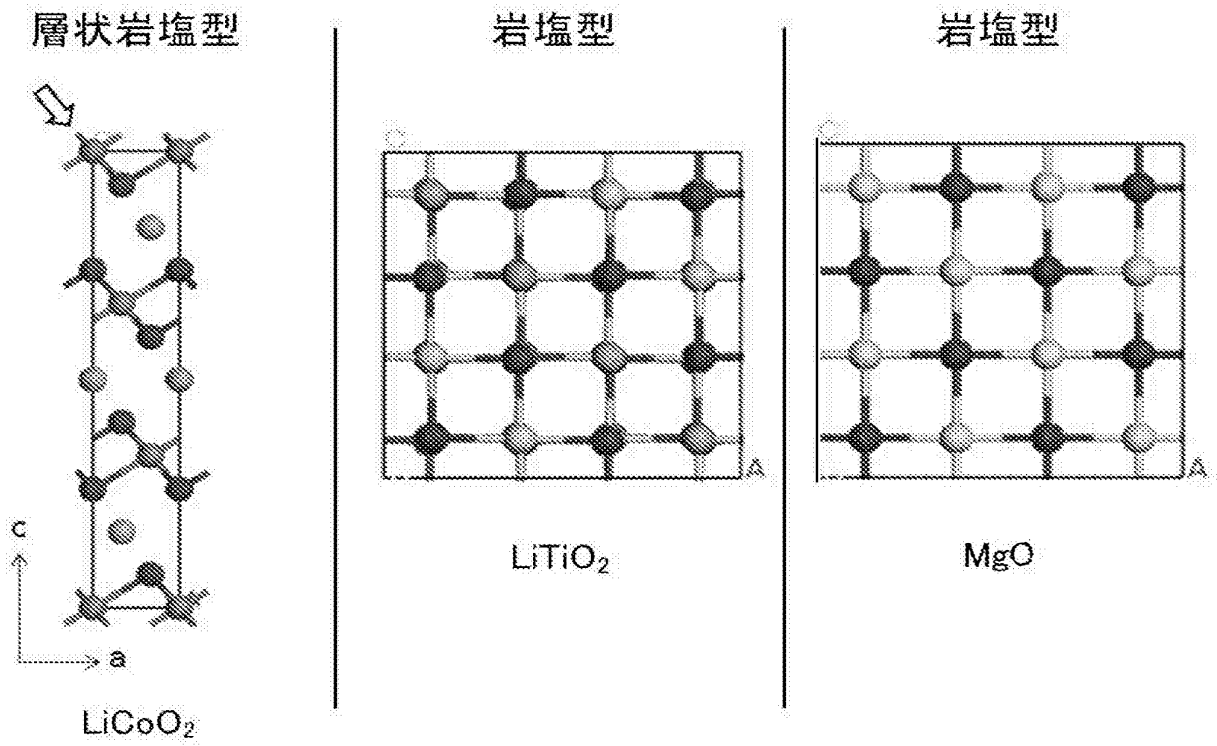


(C)

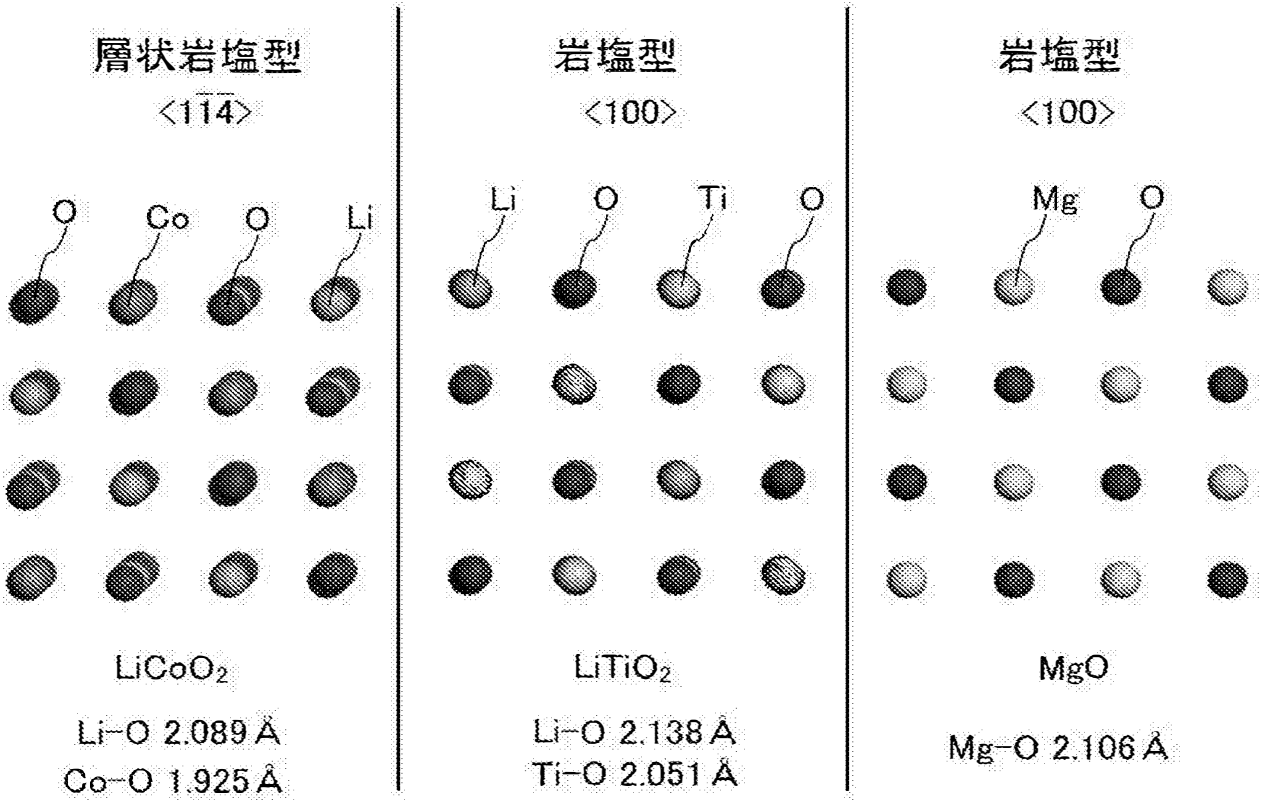


【図２】

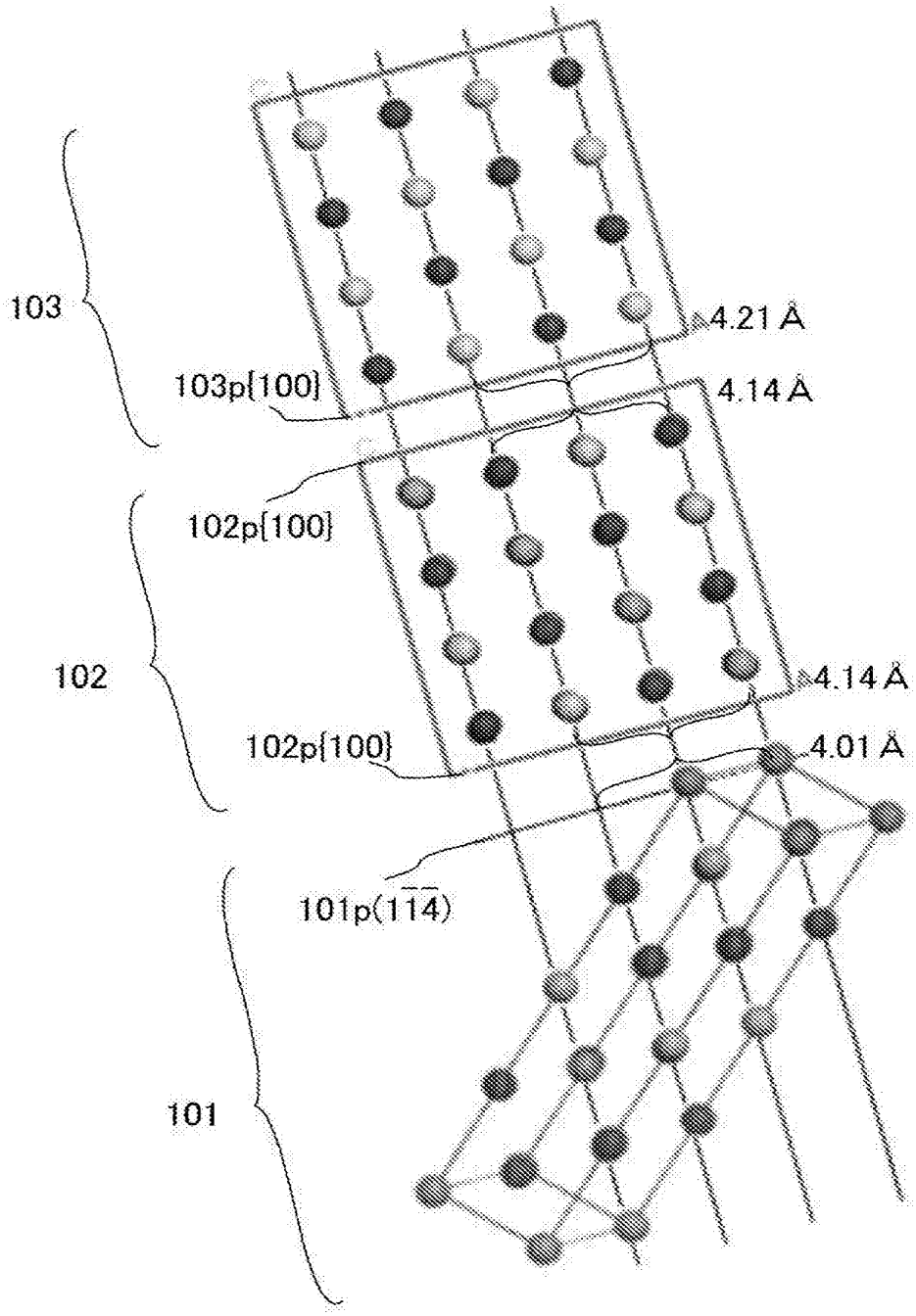
(A)


層状岩塩型
岩塩型
岩塩型
c
a
$LiCoO_2$
$LiTiO_2$
MgO

(B)

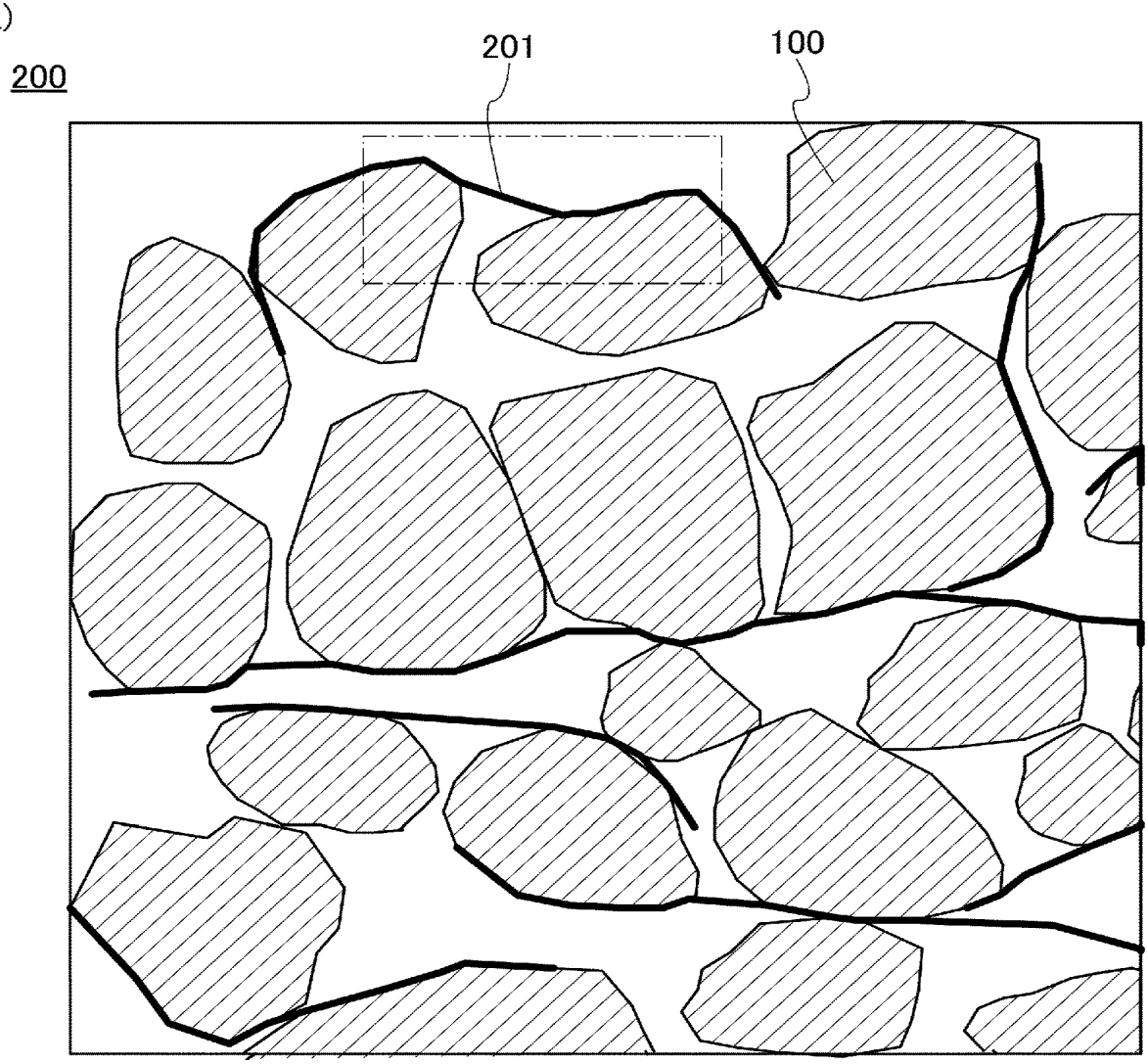

層状岩塩型
<1$\bar{1}$4>
岩塩型
<100>
岩塩型
<100>
O
Co
O
Li
Li
O
Ti
O
Mg
O
$LiCoO_2$
Li–O 2.089 Å
Co–O 1.925 Å
$LiTiO_2$
Li–O 2.138 Å
Ti–O 2.051 Å
MgO
Mg–O 2.106 Å

【図３】

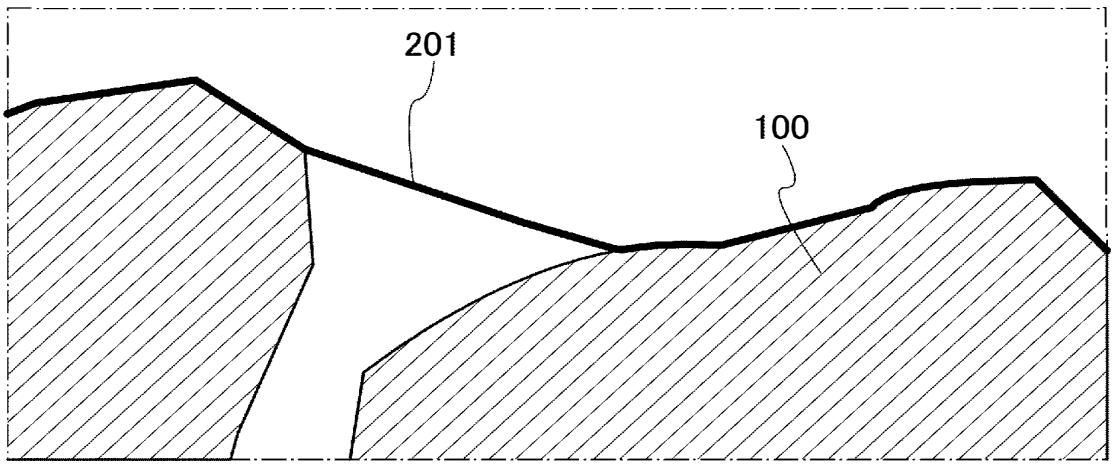

103
4.21 Å
103p{100}
4.14 Å
102p{100}
102
4.14 Å
102p{100}
4.01 Å
101p(1$\bar{1}\bar{4}$)
101

【図４】

(A)

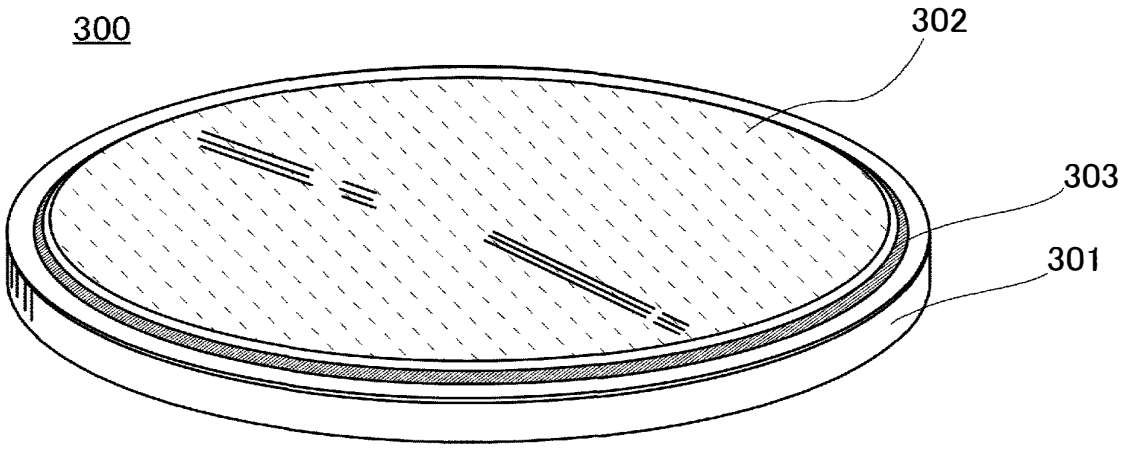


(B)

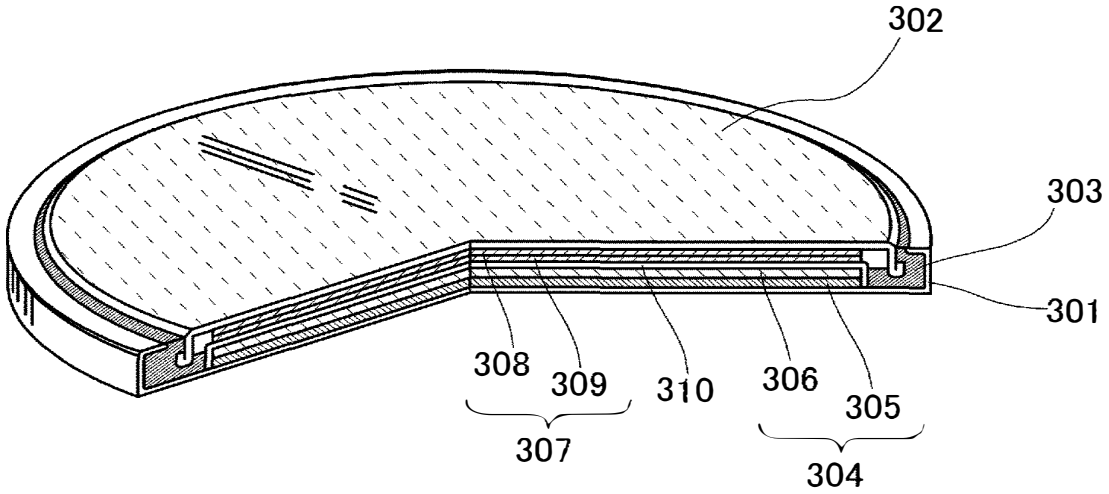


【図５】

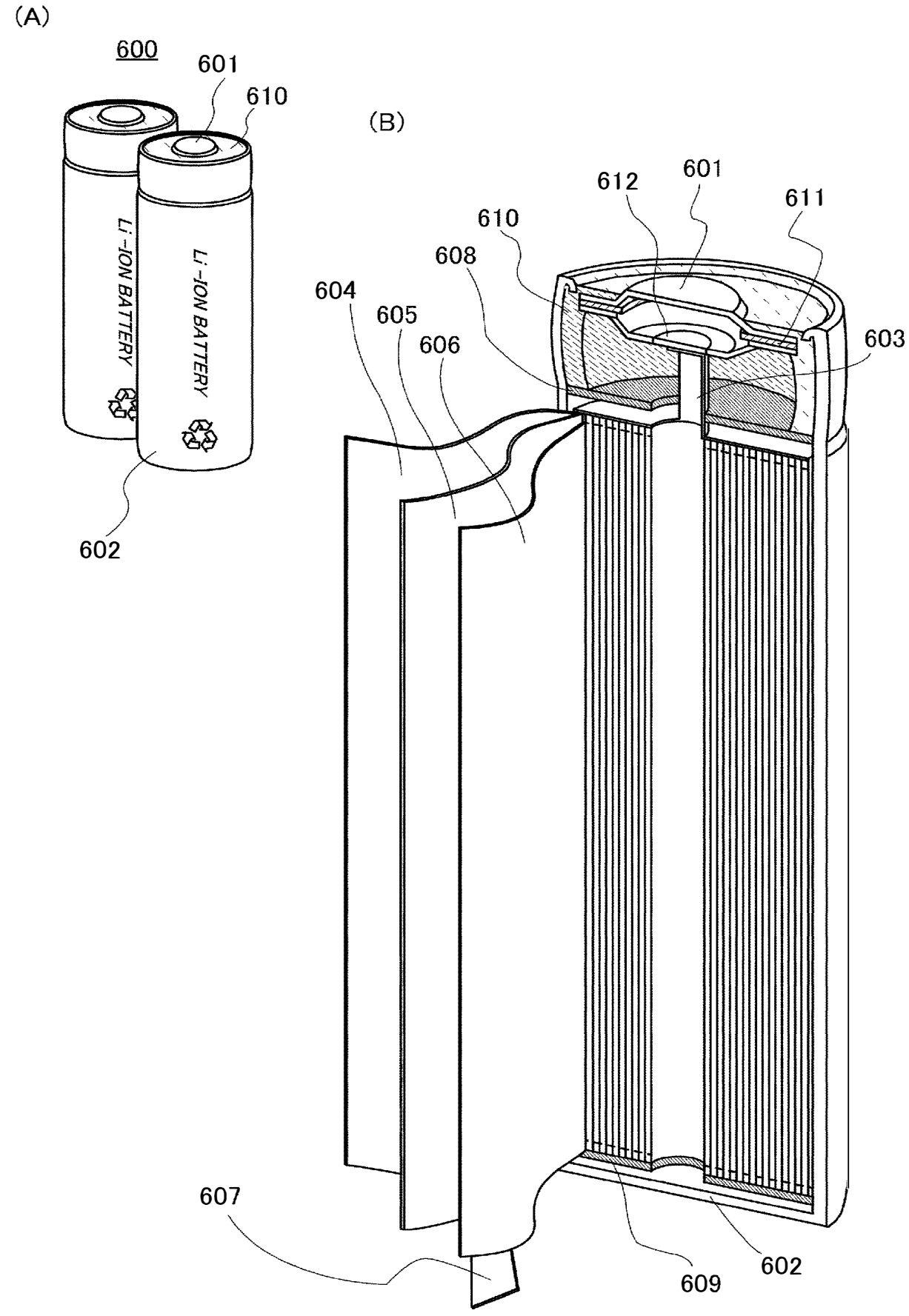
(A)



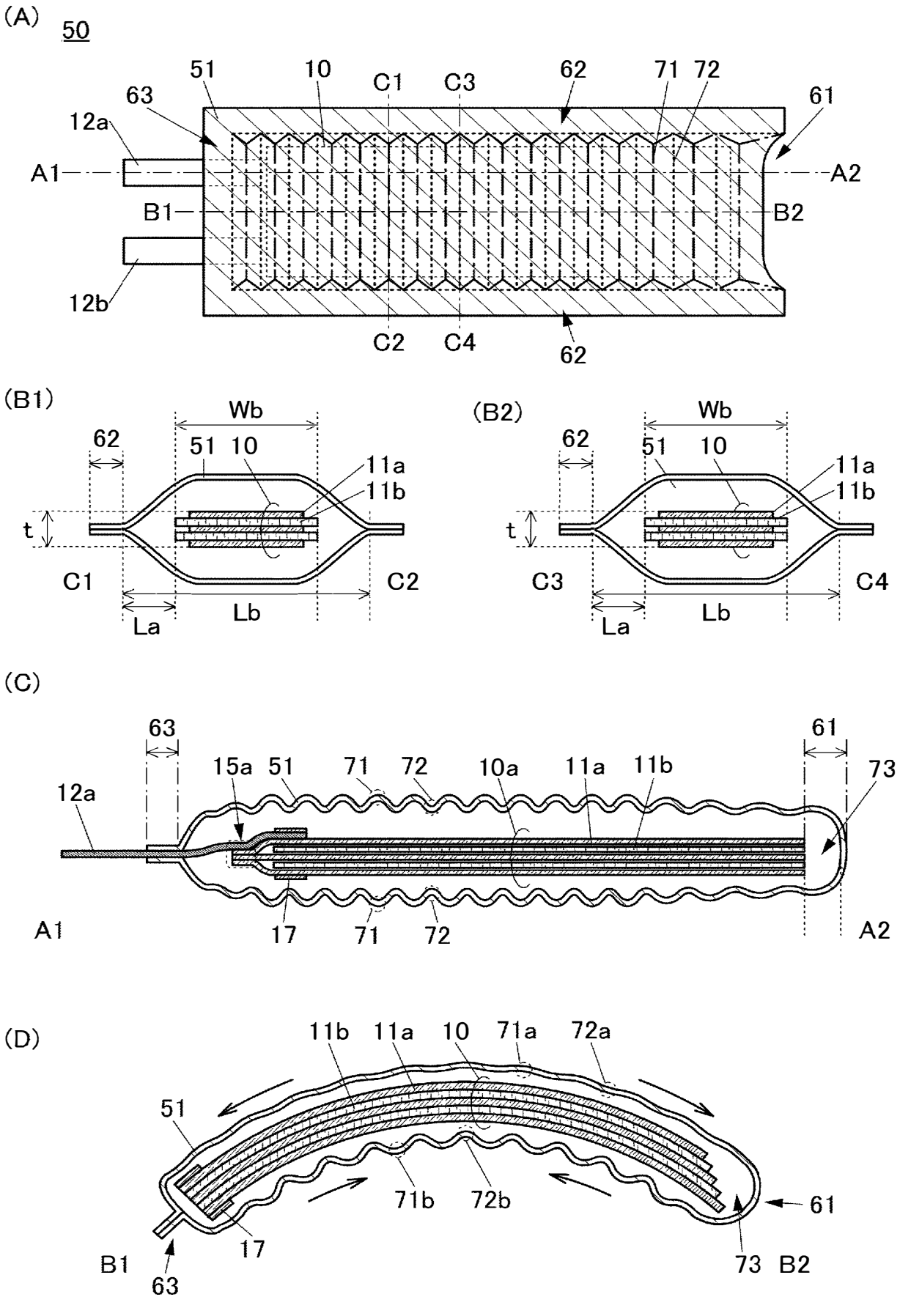
(B)



【図６】

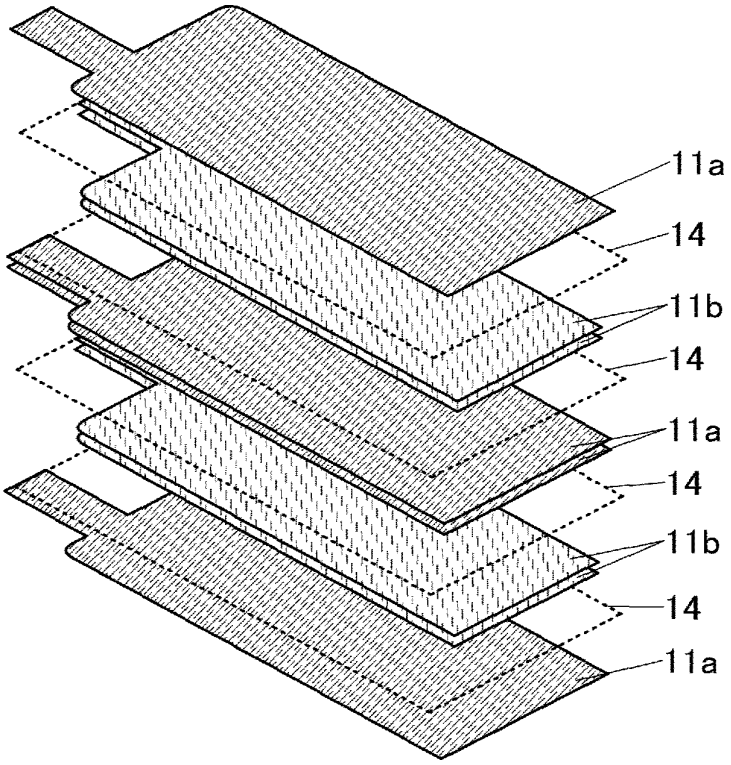

(A)
600
601
610
Li-ION BATTERY
Li-ION BATTERY
602
(B)
612
601
611
610
608
604
605
606
603
607
609
602

【図７】

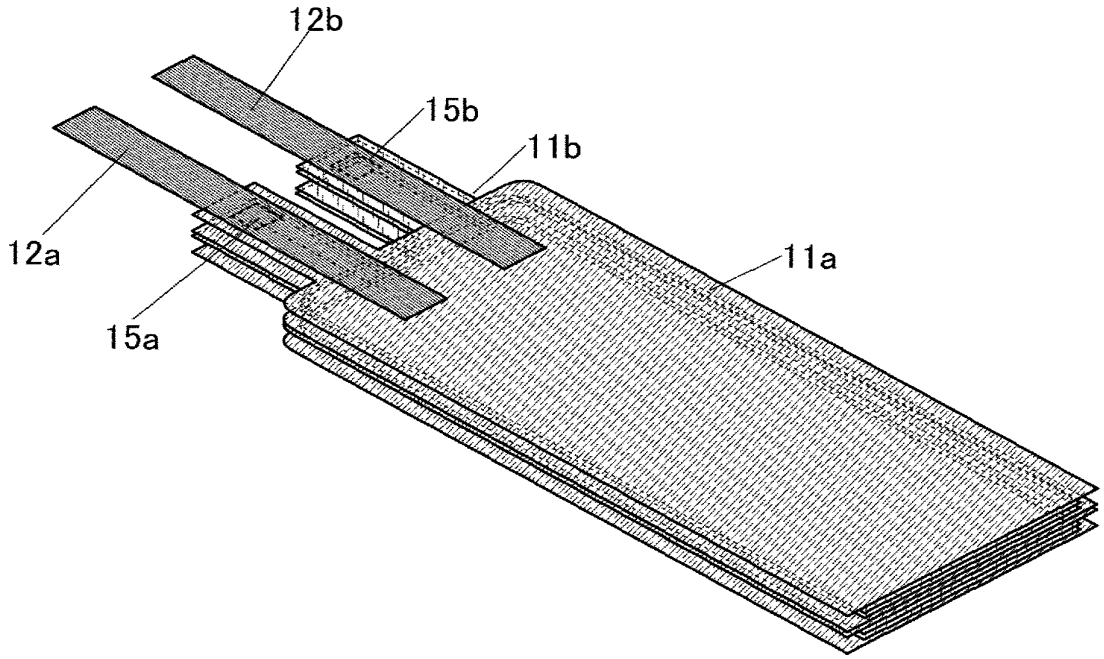

(A)
50
51
10
C1
C3
62
71
72
61
63
12a
A1
A2
B1
B2
12b
C2
C4
62
(B1)
Wb
62
51
10
11a
11b
t
C1
C2
La
Lb
(B2)
Wb
62
51
10
11a
11b
t
C3
C4
La
Lb
(C)
63
61
15a
51
71
72
10a
11a
11b
73
12a
A1
17
71
72
A2
(D)
11b
11a
10
71a
72a
51
71b
72b
61
17
B1
63
73
B2

【図８】

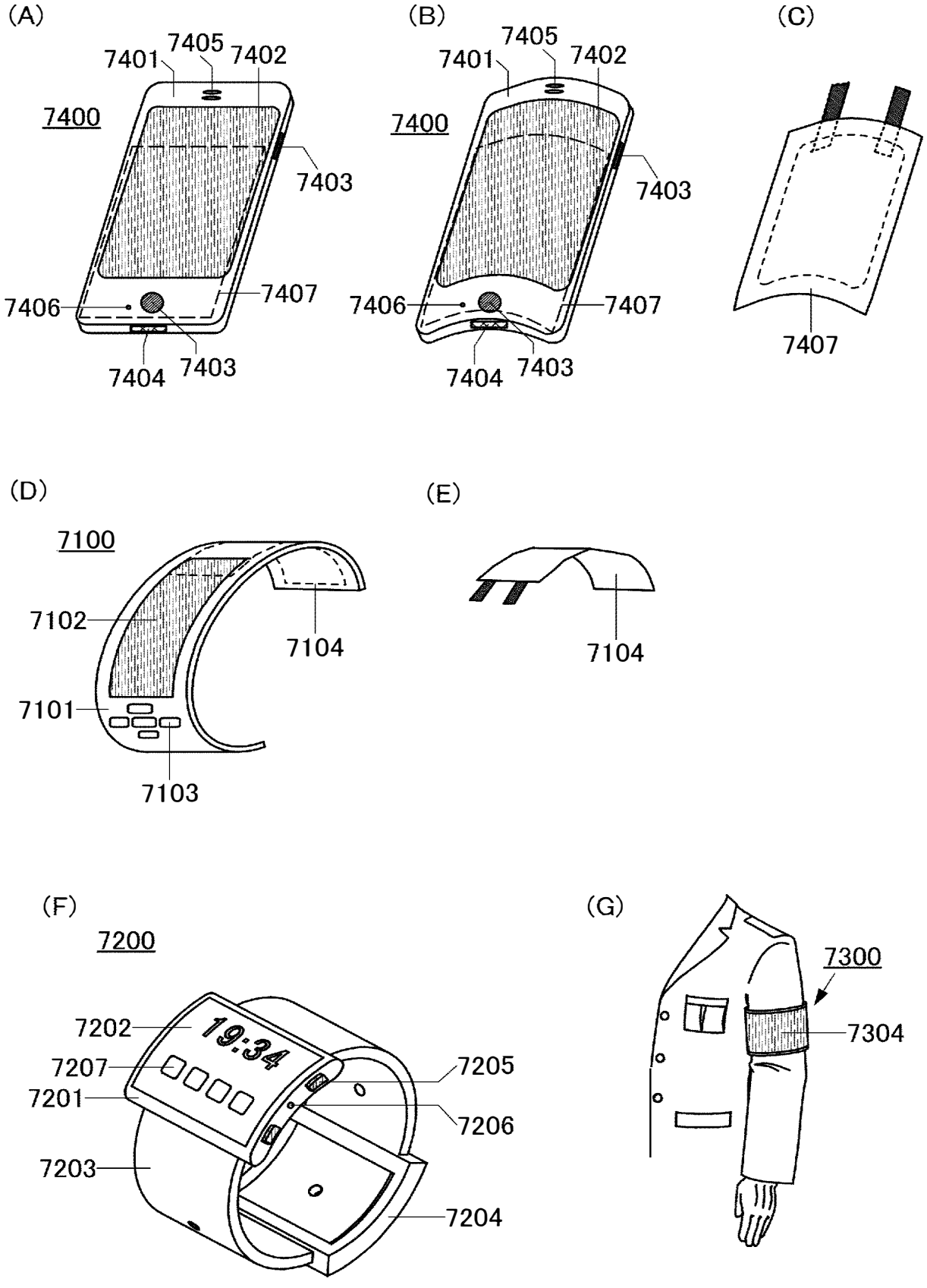
(A)



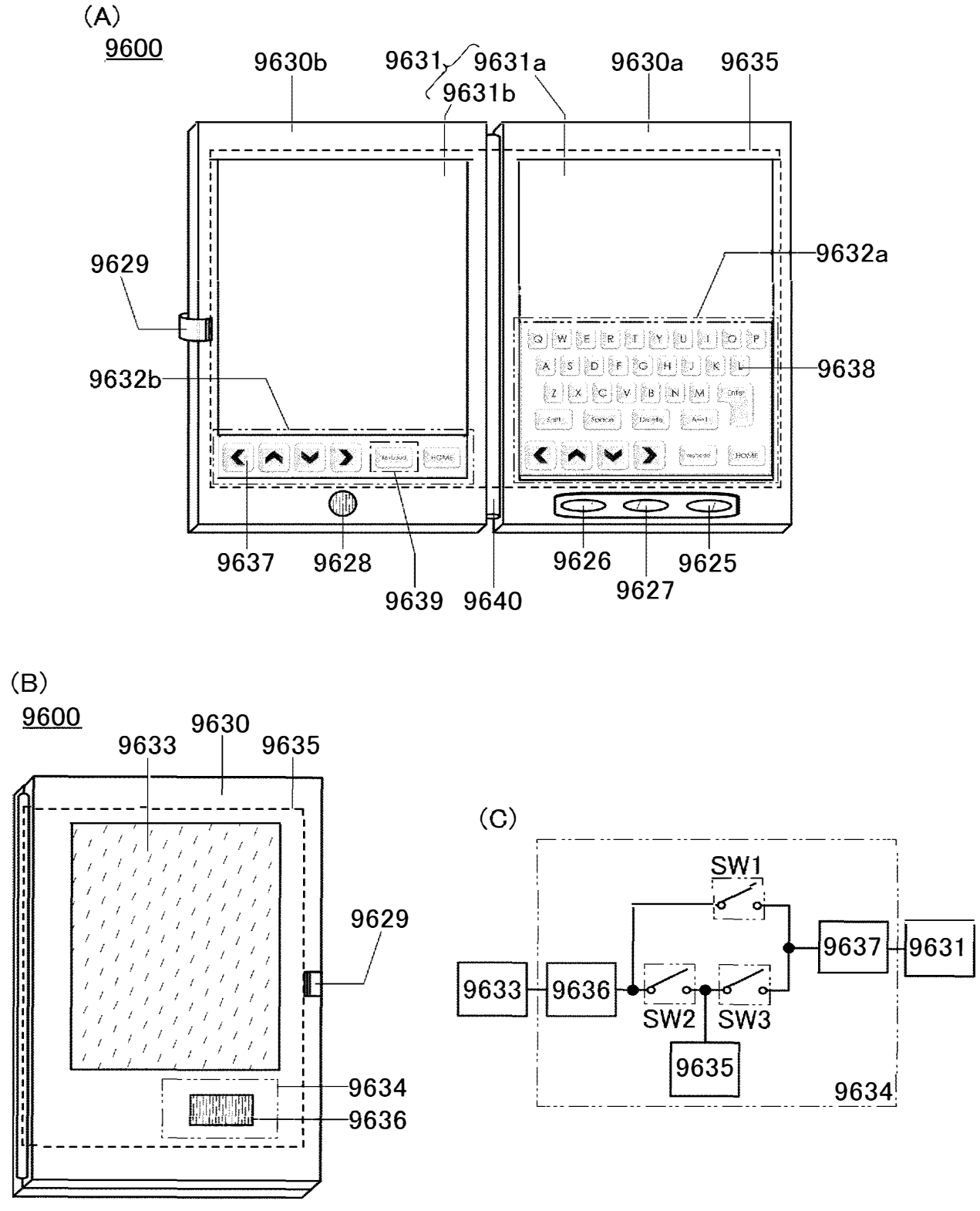
(B)



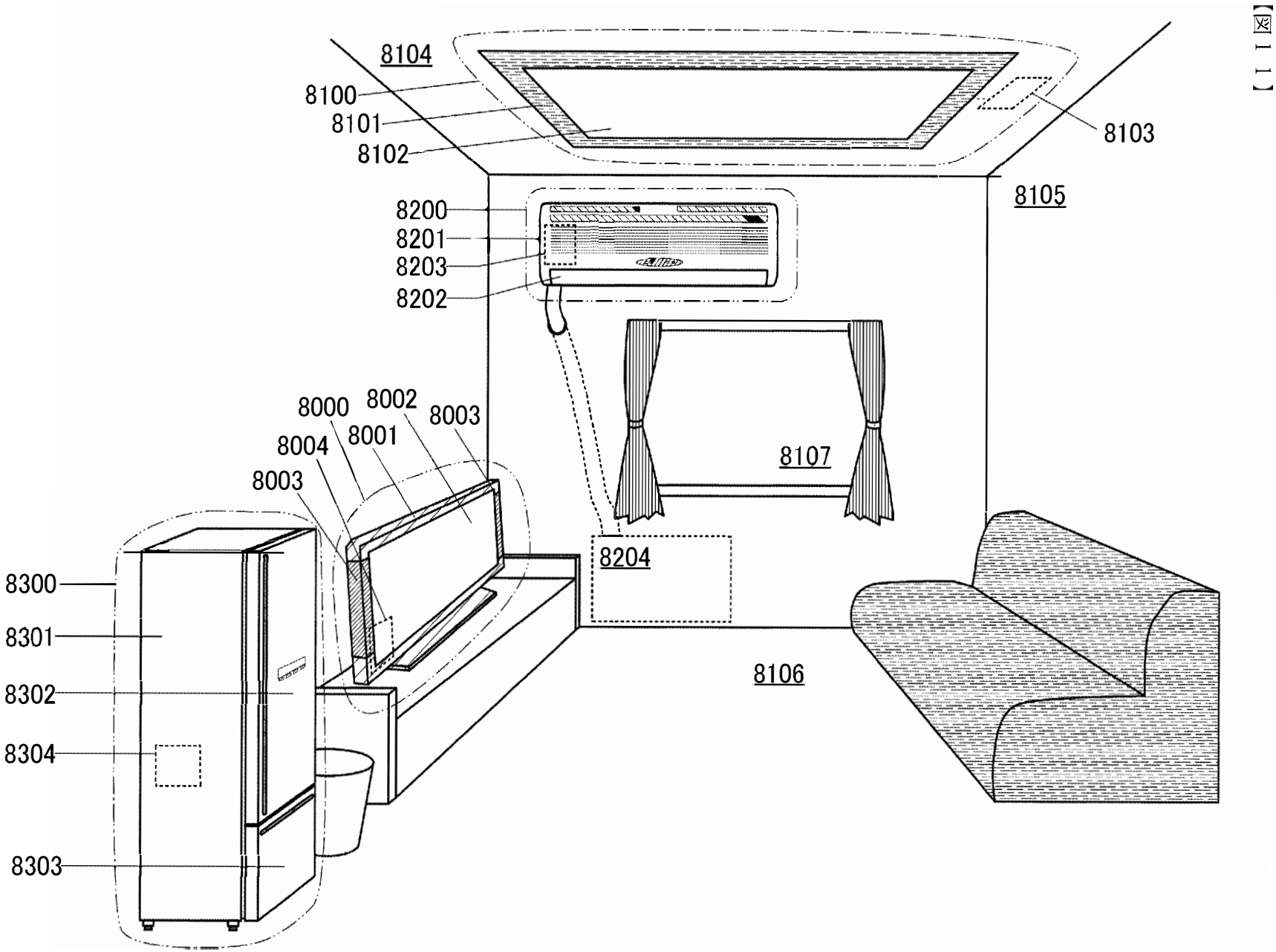
【図９】


(A)
7401
7405
7402
7400
7403
7406
7407
7404
7403
(B)
7405
7401
7402
7400
7403
7406
7407
7404
7403
(C)
7407
(D)
7100
7102
7104
7101
7103
(E)
7104
(F)
7200
7202
19:34
7207
7205
7201
7206
7203
7204
(G)
7300
7304

【図１０】

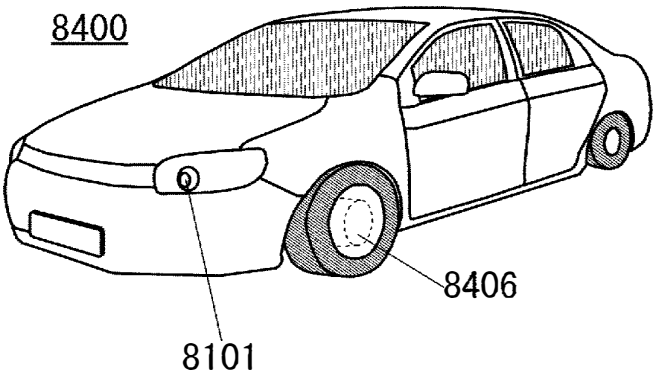

(A)
9600
9630b
9631
9631a
9631b
9630a
9635
9629
9632a
9632b
9638
9637
9628
9639
9640
9626
9627
9625
(B)
9600
9633
9630
9635
9629
9634
9636
(C)
SW1
9637
9631
9633
9636
SW2
SW3
9635
9634

【図１１】

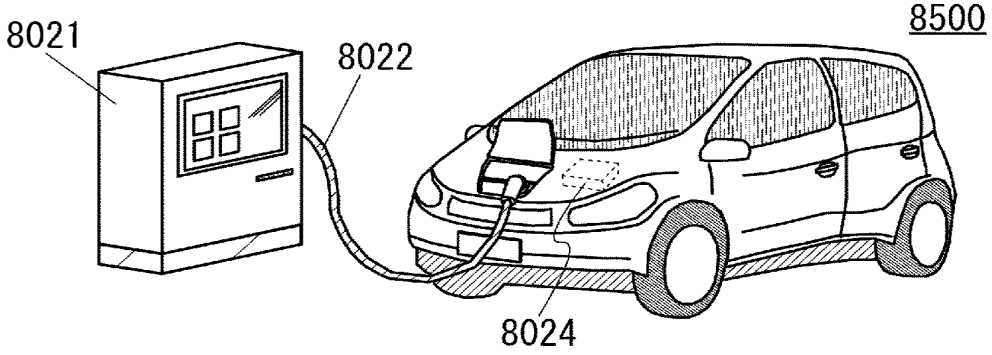

8104
8100
8101
8102
8103
8105
8200
8201
8203
8202
8000
8002
8003
8004
8001
8003
8107
8204
8300
8301
8302
8304
8303
8106

【図１２】

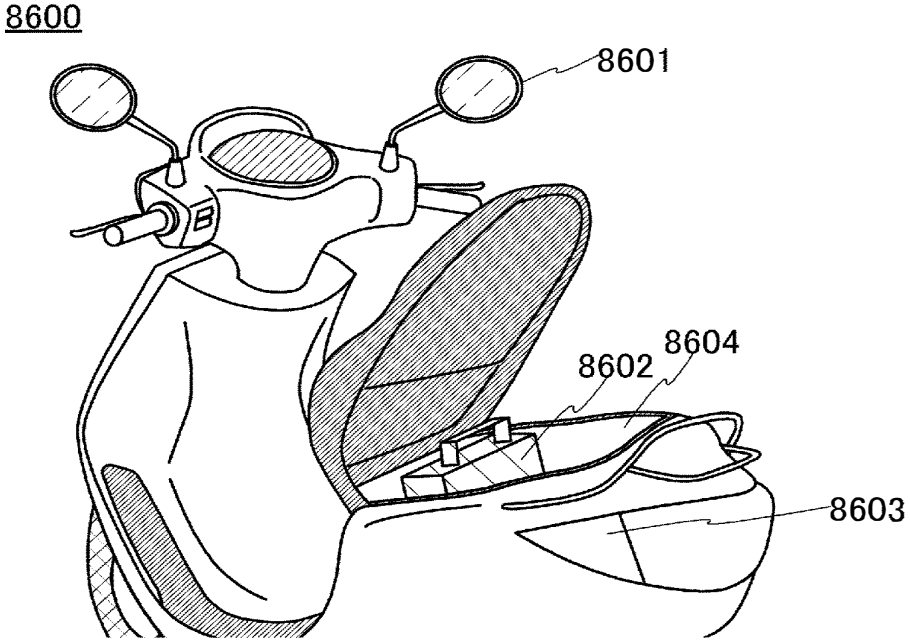
(A)



(B)



(C)



出願人履歴

０００１５３８７８

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新規登録

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This is to certify that the annexed is a true copy of the following application as filed with this Office.

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出願番号 Application Number:	特願２０１７－００２８３１
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２０１７年　８月１５日

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　【物件名】　図面　1

【書類名】明細書
【発明の名称】正極活物質、二次電池および正極活物質の作製方法
【技術分野】
【０００１】
本発明の一様態は、物、方法、又は、製造方法に関する。または、本発明は、プロセス、マシン、マニュファクチャ、又は、組成物（コンポジション・オブ・マター）に関する。本発明の一態様は、半導体装置、表示装置、発光装置、蓄電装置、照明装置または電子機器の製造方法に関する。特に、電子機器およびそのオペレーティングシステムに関する。
【０００２】
なお、本明細書中において、蓄電装置とは、蓄電機能を有する素子及び装置全般を指すものである。例えば、リチウムイオン二次電池などの蓄電池（二次電池ともいう）、リチウムイオンキャパシタ、及び電気二重層キャパシタなどを含む。
【０００３】
また、本明細書中において電子機器とは、蓄電装置を有する装置全般を指し、蓄電装置を有する電気光学装置、蓄電装置を有する情報端末装置などは全て電子機器である。
【背景技術】
【０００４】
近年、リチウムイオン二次電池、リチウムイオンキャパシタ、空気電池等、種々の蓄電装置の開発が盛んに行われている。特に高出力、高エネルギー密度であるリチウムイオン二次電池は、携帯電話、スマートフォン、タブレット、もしくはノート型コンピュータ等の携帯情報端末、携帯音楽プレーヤ、デジタルカメラ、医療機器、又は、ハイブリッド車（ＨＥＶ）、電気自動車（ＥＶ）、もしくはプラグインハイブリッド車（ＰＨＥＶ）等の次世代クリーンエネルギー自動車など、半導体産業の発展と併せて急速にその需要が拡大し、充電可能なエネルギーの供給源として現代の情報化社会に不可欠なものとなっている。
【０００５】
リチウムイオン二次電池に要求されている特性としては、さらなる高エネルギー密度化、サイクル特性の向上及び様々な動作環境での安全性、長期信頼性の向上などがある。これらの特性の向上のために、正極活物質の改良、負極活物質の改良、電解液の劣化抑制など、様々な面からのアプローチが行われている。中でも正極活物質の改良としては、特許文献１のように、正極活物質に被覆層を設けることが行われている。
【先行技術文献】
【特許文献】
【０００６】
【特許文献１】特開２０１２―０１８９１４
【発明の概要】
【発明が解決しようとする課題】
【０００７】
リチウムイオン二次電池およびそれに用いられる正極活物質には、充放電特性、サイクル特性、信頼性、安全性、又はコストといった様々な面で改善の余地が残されている。
【０００８】
本発明の一態様は、リチウムイオン二次電池に用いることで、充放電サイクルにおける容量の低下が抑制される正極活物質を提供することを課題の一とする。本発明の一態様は、充放電特性の優れた二次電池を提供することを課題の一とする。または、本発明の一態様は、充放電サイクルにおける容量の低下が抑制された二次電池を提供することを課題の一とする。または、本発明の一態様は、安全性又は信頼性の高い二次電池を提供することを課題の一とする。
【０００９】
または、本発明の一態様は、新規な物質、活物質粒子、二次電池、又はそれらの作製方法を提供することを課題の一とする。
【００１０】