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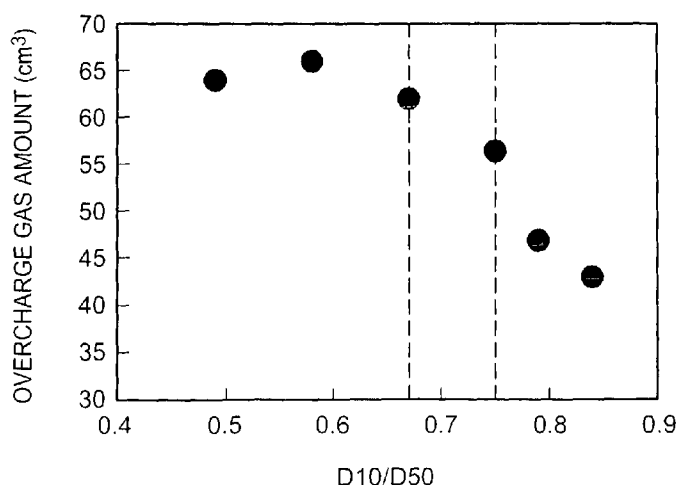
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(54) Title: POSITIVE ELECTRODE ACTIVE MATERIAL AND NONAQUEOUS ELECTROLYTE SECONDARY BATTERY PROVIDED WITH POSITIVE ELECTRODE ACTIVE MATERIAL

FIG. 8

(57) Abstract: A positive electrode active material includes composite oxide particles containing cobalt as a constituent metal, element. The composite oxide particles have a cobalt concentration which is higher in surface portions than in central portions of the composite oxide particles. In a particle size distribution of the composite oxide particles, a value of a ratio D10/D50 of a diameter D10 corresponding to 10% of a cumulative particle volume counted from a small particle diameter side in a particle size distribution of the composite oxide particles to a diameter D50 corresponding to 50% of the cumulative particle volume counted satisfies $D10/D50 \leq 0.75$.

POSITIVE ELECTRODE ACTIVE MATERIAL AND NONAQUEOUS ELECTROLYTE
SECONDARY BATTERY PROVIDED WITH POSITIVE ELECTRODE ACTIVE
MATERIAL

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BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The invention relates to a positive electrode active material and a
nonaqueous electrolyte secondary battery provided with a positive electrode active
10 material.

2. Description of Related Art

[0002] A lithium-ion secondary battery (see, e.g., Japanese Patent Application
Publication No. 2003-059489 (JP2003-059489A)) and other nonaqueous electrolyte
15 secondary batteries grow more important as vehicle-mounted power supplies or as power
supplies for personal computers, portable devices and so forth. In particular, a
lithium-ion secondary battery which is light in weight and capable of obtaining a high
energy density is desirably used as a vehicle-mounted high-output power supply. If the
nonaqueous electrolyte secondary battery comes into an overcharged state, charge carriers
20 are excessively emitted from a positive electrode and charge carriers are excessively
inserted into a negative electrode. Thus, the positive electrode and the negative electrode
become thermally instable. If the positive electrode and the negative electrode become
thermally instable, an organic solvent of an electrolyte is decomposed in the end and an
exothermic reaction occurs, whereby the stability of a battery is impaired.

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[0003] As a solution to this problem, there is disclosed, e.g., a nonaqueous
electrolyte secondary battery in which a current cutoff mechanism for cutting off a
charging current if an internal gas pressure of the battery becomes a predetermined
pressure or higher is provided in a battery case, and in which a gas generating agent for
generating a gas if the battery reaches a predetermined overcharged state is added to an

electrolyte. For example, cyclohexyl benzene (CHB), biphenyl (BP) or the like is used as the gas generating agent. When the battery is overcharged, a polymerization reaction of the CHB and the BP is activated, thereby generating a hydrogen gas. Thus, the internal pressure of the battery case is increased, and the current cutoff mechanism is operated to cut off an overcharging current.

SUMMARY OF THE INVENTION

[0004] As a positive electrode active material of a lithium-ion secondary battery, there has been extensively used an oxide (lithium-transition metal composite oxide) which contains lithium (Li) and a transition metal element (M) (e.g., nickel or cobalt) as its constituent metal elements. In an effort to improve output characteristics, the inventor conducted research on increasing a Li/M ratio in the lithium-transition metal composite oxide. However, when the Li/M ratio in the oxide increased, it was found that a battery resistance could be reduced but a post-cycle capacity decreased or a generation of the gas at the time of overcharging slowed down, thus causing the operation of a current cutoff mechanism to be delayed. JP2003-059489A discloses that cycle characteristics can be improved by making a cobalt concentration near surfaces of active material particles higher than a cobalt concentration within the active material particles. However, just increasing the cobalt concentration near the surfaces of active material particles leaves room for further improvement in terms of the post-cycle capacity and an overcharge gas amount. The invention intends to solve the problems noted above.

[0005] According to a first aspect of the invention, a positive electrode active material includes composite oxide particles which contain cobalt as a constituent metal element. The composite oxide particles have a cobalt concentration which is higher in surface portions of the particles than in central portions of the particles. A value of a ratio D10/D50 (hereinafter referred to as "particle diameter ratio") of a diameter D10 corresponding to 10% of a cumulative particle volume counted from a small particle diameter side in a particle size distribution of the composite oxide particles to a diameter D50 corresponding to 50% of the cumulative particle volume counted from the small

particle diameter side in the particle size distribution of the composite oxide particles satisfies $D_{10}/D_{50} \leq 0.75$.

[0006] In the positive electrode active material of the aforementioned configuration, the concentration of cobalt existing in the surface portions of the composite oxide particles is higher than the concentration of cobalt existing in the central portions thereof. Therefore, the durability is improved. Further, the value of the particle diameter ratio D_{10}/D_{50} of the diameter D_{10} corresponding to 10% of the cumulative particle volume from the small particle diameter side in the particle size distribution of the composite oxide particles to the diameter D_{50} corresponding to 50% of the cumulative particle volume from the small particle diameter side in the particle size distribution of the composite oxide particles is 0.75 or lower. Therefore, as compared with a positive electrode active material having the particle diameter ratio D_{10}/D_{50} of more than 0.75, the durability against expansion-contraction stresses is high. Moreover, it is easier for the composite oxide particles to make contact with a conductive material. In addition, the reaction of a gas generating agent is suitably generated on the surfaces of the composite oxide particles. This makes it possible to generate a sufficient amount of gas during overcharge. Thus, in the battery built using the positive electrode active material, the reliability during overcharge and the enhanced battery performance can be made compatible at a higher level.

[0007] In the first aspect of the invention, the value of the particle diameter ratio D_{10}/D_{50} may satisfy $D_{10}/D_{50} \leq 0.67$.

[0008] In the first aspect of the invention, the value of the particle diameter ratio D_{10}/D_{50} may satisfy $0.45 \leq D_{10}/D_{50}$.

[0009] In the first aspect of the invention, a value of a ratio X/Y of an average cobalt concentration X mol% in the surface portions of the composite oxide particles to an average cobalt concentration Y mol% of an entirety of the composite oxide particles may satisfy $1.1 \leq X/Y \leq 1.5$. According to this configuration, the content ratio of cobalt in the surface portions of the composite oxide particles is suitably high. Therefore, the aforementioned effects can be exhibited better. Moreover, if the ratio X/Y is set to satisfy

$X/Y \leq 1.5$, the durability required in the positive electrode active material particles is secured and the performance of the nonaqueous electrolyte secondary battery is stabilized.

[0010] In the first aspect of the invention, the composite oxide particles may be represented by general formula 1, $\text{Li}_x\text{Ni}_a\text{Co}_b\text{Mn}_c\text{Me}_d\text{O}_2$. In the general formula 1, Me may be one or more kinds of elements selected from a group consisting of a transition metal element, a typical metal element and boron. However, Me may be omitted from constituent elements of the formula 1. Further, in the general formula 1, x , a , b , c and d are numbers that satisfy $0.99 \leq x \leq 1.12$, $0.9 \leq a + b + c + d \leq 1.1$, $1.05 \leq x/(a + b + c + d) \leq 1.2$, $0 < a \leq 0.5$, $0 < b \leq 0.5$, $0 < c \leq 0.5$ and $0 \leq d \leq 0.2$. The composite oxide having a composition represented by the general formula 1 are superior in thermal stability and are capable of realizing a superior output characteristic and a superior cycle characteristic. Thus, the effects of application of the first aspect of the invention can be exhibited better.

[0011] A nonaqueous electrolyte secondary battery according to a second aspect of the invention includes an electrode body, a battery case, an external terminal, a nonaqueous electrolyte and a current cutoff mechanism. The electrode body includes a positive electrode, a negative electrode and a separator interposed between the positive electrode and the negative electrode. The positive electrode contains the positive electrode active material according to the first aspect of the invention and a conductive material. The negative electrode contains a negative electrode active material. The battery case accommodates the electrode body. The external terminal is installed in the battery case and is connected to the electrode body. The nonaqueous electrolyte is accommodated within the battery case. The nonaqueous electrolyte contains a gas generating agent which reacts at a voltage equal to or higher than a predetermined voltage to generate a gas. The current cutoff mechanism is configured to cutoff electric connection of the electrode body and the external terminal if an internal pressure of the battery case becomes equal to or higher than a predetermined voltage. In the nonaqueous electrolyte secondary battery, a gas is suitably generated when the battery comes into an overcharged state. This makes it possible to properly operate the current cutoff mechanism. Moreover, even after a charge-discharge cycle, the capacity can be kept high.

Accordingly, the enhanced battery performance (e.g., the enhanced durability) and the reliability during overcharge can be made compatible at a higher level.

[0012] In the second aspect of the invention, an average primary particle diameter of the conductive material may be 25 nm or less. If the positive electrode active material having the aforementioned particle diameter ratio D10/D50 is used, the rate of the particles having a small particle diameter in the positive electrode active material becomes higher. If the average primary particle diameter of the conductive material is controlled as described above, it is possible to suitably form and maintain conductive paths among the active material particles having a small particle diameter. Thus, the cycle characteristic is improved and the reaction of the gas generating agent on the surfaces of the active material particles is accelerated. This suppresses the reduction of an overcharge gas amount in the secondary battery configured as above. Accordingly, the enhanced battery performance (e.g., the enhanced durability) and the reliability during overcharge can be made compatible at a higher level.

[0013] In the nonaqueous electrolyte secondary battery according to the second aspect of the invention, the gas generation amount during overcharge is large as mentioned above and the capacity can be kept high even after the cycle. Therefore, the nonaqueous electrolyte secondary battery is suitable for use as, e.g., a battery mounted to a motor vehicle such as an automobile or the like (typically, a battery for a drive power supply). According to the second aspect of the invention, there is provided a motor vehicle provided with any one of the nonaqueous electrolyte secondary batteries (which may be a battery pack in which a plurality of batteries is connected to one another) disclosed herein. Particularly, there is provided a motor vehicle (e.g., a plug-in hybrid vehicle (PHV) or an electric vehicle (EV) capable of being charged by a household power supply) provided with the nonaqueous electrolyte secondary battery as the power source.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Features, advantages, and technical and industrial significance of exemplary embodiments of the invention will be described below with reference to the

accompanying drawings, in which like numerals denote like elements, and wherein:

FIG. 1 is a schematic diagram of a lithium-ion secondary battery according to one embodiment of the invention;

FIG. 2 is a view illustrating a wound electrode body according to one embodiment of the invention;

FIG. 3 is a graph plotting IV resistances of respective examples;

FIG. 4 is a graph plotting initial capacities and post-cycle capacities of respective examples;

FIG. 5 is a graph plotting overcharge gas amounts of respective examples;

FIG. 6 is a graph illustrating a relationship between a particle diameter ratio D10/D50 and an IV resistance;

FIG. 7 is a graph illustrating a relationship between the particle diameter ratio D10/D50 and a capacity retention rate;

FIG. 8 is a graph illustrating a relationship between the particle diameter ratio D10/D50 and the overcharge gas amount;

FIG. 9 is a graph illustrating a relationship between a primary particle diameter of a conductive material and the IV resistance; and

FIG. 10 is a graph illustrating a relationship between the primary particle diameter of a conductive material and the overcharge gas amount.

DETAILED DESCRIPTION OF EMBODIMENTS

[0015] Preferred embodiments of the invention will now be described with reference to the accompanying drawings. The respective drawings are depicted schematically and do not necessarily reflect actual objects. It should be noted that matters necessary for carrying out the invention other than those specifically referred to in the subject specification may be suitably grasped based on the related art in this field. The invention may be carried out on the basis of the content disclosed herein and the common technical knowledge in this field. Hereinafter, the embodiments of the invention will be described in more detail by taking, as an example, a case where the invention is applied to

a lithium-ion secondary battery. The invention is not limited to the embodiments of the invention.

[0016] The term "particle size distribution" used herein refers to a volume-based particle size distribution measured by a particle size distribution measurement method based on an ordinary laser diffraction and light scattering method. Further, the term "overcharged state" used herein refers to a state in which a state of charge (SOC) exceeds 100%. In this regard, the term "SOC" refers to a charge state over a reversibly chargeable/dischargeable operation voltage range. A charge state (i.e., a full charge state) in which a voltage corresponding to an upper limit of the operation voltage range is obtained is assumed to be 100%. A charge state (i.e., a non-charge state) in which a voltage corresponding to a lower limit of the operation voltage range is obtained is assumed to be 0%.

[0017] The positive electrode active material used in the lithium-ion secondary battery disclosed herein is particulates (typically, secondary particles) composed of primary particles and includes composite oxide in a particle form which contain at least cobalt (Co) as constituent metal elements. The composite oxide particles (at least one, preferably both, of the secondary particles and the primary particles) have a Co concentration which is higher in surface portions of the particles than in central portions of the particles. For example, a value of a ratio X/Y of an average Co concentration X in the surface portions of the particles (hereinafter referred to as a surface Co concentration) to an average Co concentration Y of the entirety of the particles (hereinafter referred to as an entire Co concentration) satisfies $1.1 \leq X/Y \leq 1.5$, preferably $1.15 \leq X/Y \leq 1.4$, and more preferably $1.2 \leq X/Y \leq 1.3$. If the composite oxide particles containing a cobalt element are used as the positive electrode active material in this way, it is possible to improve electron conductivity of the positive electrode active material. Since the Co concentration in the surface portions is higher than the Co concentration in the central portions, the bonding between the primary particles is strong and therefore the durability is improved.

[0018] The term "surface Co concentration" used herein refers to an average percentage (mol%) of a Co element, which is measured by the well-known inductively

coupled plasma (ICP) emission spectroscopy, in the elements that constitute the outermost surface portions (extending about several nm from the surface, e.g., about 0.1 nm to 10 nm from the surface, which may vary depending on measurement conditions) of the composite oxide particles (the secondary particles and/or the primary particles). Alternatively, the surface Co concentration may be an average percentage (mol%) of a Co element, which is measured by the well-known X-ray photoelectron spectroscopy, in the entirety of the elements that constitute the outermost surface of a lithium-transition metal composite oxide. This measurement can be performed using an analytical instrument based on an X-ray photoelectron spectroscopy which is called, for example, an XPS (X-ray Photoelectron Spectroscopy), an ESCA (Electron Spectroscopy for Chemical Analysis) or the like. Further, the term "entire Co concentration" used herein refers to an average percentage (mol%) of a Co element, which is measured by the well-known inductively coupled plasma emission spectroscopy, in the elements that constitute the entirety of the composite oxide particles.

[0019] In the positive electrode active material disclosed herein, a value of a particle diameter ratio D10/D50 satisfies $D10/D50 \leq 0.75$, wherein the diameter D10 is a particle diameter corresponding to 10% of a cumulative particle volume counted from a small particle diameter side in a particle size distribution of the composite oxide particles and a diameter D50 is a particle diameter corresponding to 50% of the cumulative particle volume from the small particle diameter side in the particle size distribution of the composite oxide particles.

[0020] Herein, having a smaller particle diameter ratio D10/D50 means that the D10 has a value deviated farther from the D50 (in other words, the particles having a particle diameter smaller than an average particle diameter are widely distributed and the content of the particles having a particle diameter far smaller than the average particle diameter are large). Therefore, if the positive electrode active material having the aforementioned particle diameter ratio D10/D50 is used, the ratio of the particles having a small particle diameter in the positive electrode active material becomes higher. In this regard, the particles having a small particle diameter are higher in durability against

expansion and contraction than the large particles and are hardly ever cracked. Further, the particles having a small particle diameter are larger in specific surface area than the large particles, such that the particles having a small particle diameter easily make contact with the conductive material and the conductive path is hardly ever disconnected. For that reason, a battery provided with the aforementioned positive electrode active material is superior in cycle durability.

[0021] According to the findings of the inventor, reaction of the gas generating agent is more suitably generated on the surfaces of the particles having a high Co concentration than on the surfaces of the particles having a low Co concentration. For that reason, there is a tendency that, when overcharged, a gas is generated in a larger amount on the particle surfaces having a high Co concentration than on the particle surfaces having a low Co concentration. In the battery suggested therein, the Co concentration is higher in the surface portions of the positive electrode active material particles than in the central portions thereof. Further, when the positive electrode active material having the aforementioned particle diameter ratio D10/D50 is used, the rate of the particles having a small diameter in the positive electrode active material is high. Thus, the Co concentration on the surfaces of the small particles occupying the majority of a specific surface area becomes higher than that of the related art. Therefore, when overcharged, reaction of the gas generating agent is suitably generated on the surfaces of the small particles having a high surface Co concentration. This makes it possible to stably generate a desired amount of the gas. Since the internal pressure of a battery case is increased due to the generation of the gas, it is possible to operate the current cutoff mechanism within a shorter period of time. Accordingly, in the lithium-ion secondary battery built using the aforementioned positive electrode active material, the reliability during overcharge and the enhanced battery performance can be made compatible at a higher level.

[0022] According to the research conducted by the inventor, it was confirmed through the later-described experimental examples that an improvement in the battery performance and an increase in an overcharge gas amount obtained by defining the particle

diameter ratio D10/D50 to fall within a desirable range disclosed herein can be effectively manifested by using the composite oxide particles having a high surface Co concentration. In other words, if the definition of the particle diameter ratio D10/D50 and the composite oxide particles having a high surface Co concentration are applied in combination, it is possible to provide, as a synergistic effect of the combination, a lithium-ion secondary battery that exhibits significant improvement in the overcharge gas amount and the battery performance.

[0023] As the composite oxide particles disclosed herein, it is preferable to use a composite oxide particles in which the particle diameter ratio D10/D50 satisfies $D10/D50 \leq 0.75$. It is more preferable that the particle diameter ratio D10/D50 satisfies $D10/D50 \leq 0.67$. It is particularly preferable that the particle diameter ratio D10/D50 satisfies $D10/D50 \leq 0.6$. If the particle diameter ratio D10/D50 is too large, there may be a case where the gas amount during overcharge is insufficient and the cycle characteristic is reduced. On the other hand, the composite oxide particles in which the particle diameter ratio D10/D50 is too small, are hard to produce and are inferior in the aforementioned performance improvement effect. Therefore, these composite oxide particles do not have much merit. It is desirable that the particle diameter ratio D10/D50 is substantially in the range of $0.45 \leq D10/D50$, and preferably in the range of $0.5 \leq D10/D50$. For example, the composite oxide particles in which the particle diameter ratio D10/D50 is 0.45 or more and 0.75 or less (especially, 0.45 or more and 0.67 or less), are suitable from the viewpoint of making the improvement in the cycle characteristic and the ease of production compatible.

[0024] As the positive electrode active material, one or more kinds of materials which have been conventionally used in a lithium-ion secondary battery can be used with no particular limitation as long as the materials satisfy the aforementioned conditions. Examples of the positive electrode active material include a lithium-transition metal composite oxide having a layered structure (which may be a rock salt structure or a spinel structure), namely an oxide which contains, as its constituent metal elements, a lithium element and two or more kinds of transition metal elements including cobalt. If the

lithium-transition metal composite oxide having a layered structure is used as the positive electrode active material, it is possible to provide a battery having a high capacity and a high energy density. Therefore, the use of the lithium-transition metal composite oxide having a layered structure is preferred.

5 **[0025]** Examples of the lithium-transition metal composite oxide having a layered structure include a lithium-transition metal composite oxide represented by general formula 1, $\text{Li}_x\text{Ni}_a\text{Co}_b\text{Mn}_c\text{Me}_d\text{O}_2$, where Me may be omitted from the constituent elements of the formula 1 or may be one or more kinds of elements selected from a group consisting of the transition metal element, the typical metal element and boron (B) and where x, a, b, c and d are numbers that satisfy $0.99 \leq x \leq 1.12$, $0.9 \leq a+b+c+d \leq 1.1$, $1.05 \leq x/(a+b+c+d) \leq 1.2$, $0 < a \leq 0.5$, $0 < b \leq 0.5$, $0 < c \leq 0.5$ and $0 \leq d \leq 0.2$. In the general formula of the subject specification representing the lithium-transition metal composite oxide, for convenience, the composition ratio of O (oxygen) is indicated to be 2. However, the composition ratio of O is not strictly limited but may be slightly changed (typically, within a range of 1.95 or more and 2.05 or less).

15 **[0026]** As shown in the formula 1, the lithium-transition metal composite oxide used herein contains, as its essential constituent elements, lithium (Li), nickel (Ni), cobalt (Co) and manganese (Mn). The lithium-transition metal composite oxide may contain, in addition to Li, Ni, Co and Mn, at least one kind of metal element Me (namely, $d > 0$) or may not contain the metal element Me (namely, $d = 0$). Typically, the metal element Me may be one or more kinds of elements selected from the transition metal element, the typical metal element and so forth, other than Li, Ni, Co and Mn. More specifically, examples of the metal element Me may include tungsten (W), magnesium (Mg), calcium (Ca), strontium (Sr), titanium (Ti), zirconium (Zr), vanadium (V), niobium (Nb), chromium (Cr), molybdenum (Mo), iron (Fe), rhodium (Rh), palladium (Pd), platinum (Pt), copper (Cu), zinc (Zn), boron (B), aluminum (Al), gallium (Ga), indium (In), tin (Sn), lanthanum (La) and cerium (Ce). For example, W, Zr, Mg or Ca may preferably be used as the metal element Me. The amount of the metal element Me (namely, the value of d in the general formula 1) may be, but is not specifically limited to, $0 \leq d \leq 0.2$ (e.g., $0 \leq d \leq 0.02$).

[0027] In the formula 1, a, b and c are not particularly limited as long as they satisfy $0.9 \leq a + b + c + d \leq 1.1$, $1.05 \leq x/(a + b + c + d) \leq 1.2$, $0 < a \leq 0.5$, $0 < b \leq 0.5$ and $0 < c \leq 0.5$. One of a, b and c may have the largest value. In particular, a, b and c may be real numbers that satisfy $1.08 \leq x/(a + b + c + d) \leq 1.1$. In other words, among Ni, Co and Mn, a first element (an element contained in a largest amount in terms of the atomic number) may be any one of Ni, Co and Mn. For example, the value of a may be 0.1 or more (typically, 0.3 or more) and less than 0.5 (typically, 0.45 or less, e.g., 0.4 or less). The value of b may be 0.1 or more (typically, 0.3 or more) and 0.5 or less (typically, 0.45 or less, e.g., 0.4 or less). The value of c may be 0.1 or more (typically, 0.3 or more) and 0.5 or less (typically, 0.45 or less, e.g., 0.4 or less). In one preferred embodiment, a, b and c (namely, the amounts of Ni, Co and Mn) are substantially equal to one another.

[0028] In the formula 1, x is a value which is set so as to satisfy a charge neutrality condition. For example, $0.99 \leq x \leq 1.12$ and $1.05 \leq x/(a + b + c + d) \leq 1.2$. In this regard, $x/(a + b + c + d)$ is a value that indicates a molar ratio (Li/M_{all}) of Li to the total sum of all other constituent metal elements M_{all} (Ni, Co, Mn and Me). Preferably, $1.05 \leq (\text{Li}/M_{\text{all}}) \leq 1.2$. More preferably, $1.08 \leq (\text{Li}/M_{\text{all}}) \leq 1.15$. Even more preferably, $1.08 \leq (\text{Li}/M_{\text{all}}) \leq 1.12$. The Li-rich lithium-transition metal composite oxide mentioned above exhibits low electron conductivity and can realize a superior output characteristic. In the meantime, the Li-rich lithium-transition metal composite oxide has a tendency that the amount of gas generated during overcharge gets reduced. However, according to the configuration of the invention, the definition of the particle diameter ratio D_{10}/D_{50} and the composite oxide particles having a high surface Co concentration are applied in combination. Therefore, even if the Li-rich lithium-transition metal composite oxide is used, it is possible to sufficiently secure an overcharge gas amount.

[0029] Typically, the lithium-transition metal composite oxide is particulate (secondary particles) composed of primary particles. The Co concentration of these particles is not particularly limited as long as a value of a ratio X/Y of the surface Co concentration X to the entire Co concentration Y satisfies $X/Y > 1$. For example, the entire Co concentration Y may be set at 5 mol% or more (preferably, 10 mol% or more) and 40

mol% or less (preferably, 30 mol% or less). Further, the surface Co concentration X may be set to be larger than the entire Co concentration Y. For example, the surface Co concentration X may be set to be 6 mol% or more (typically, 12 mol% or more) and 48 mol% or less (typically, 36 mol% or less). If the Co concentration (the surface Co concentration X, the entire Co concentration Y, or preferably both) falls within the aforementioned range, the enhanced battery performance and the reliability during overcharge can be made compatible at a higher level.

[0030] The properties of the particles are not particularly limited. For example, the average particle diameter (the diameter D50) may be set at 0.5 μm or more (typically, 1 μm or more, e.g., 2 μm or more, preferably 3 μm or more) and 20 μm or less (typically, 15 μm or less, e.g., 10 μm or less). Further, the diameter D10 may be set to satisfy $D10/D50 \leq 0.75$, but, for example, the diameter D10 may be set at 0.3 μm or more (typically, 0.7 μm or more, e.g., 1.5 μm or more, preferably 4.5 μm or more) and 15 μm or less (typically, 12 μm or less, e.g., 8 μm or less). If the properties of the positive electrode active material particles fall within the aforementioned range, a positive electrode active material layer formed using these particles can be made dense and highly conductive. Moreover, a suitable void space can be maintained within the positive electrode active material layer. Thus, the electrolyte easily migrates into the positive electrode active material layer. It is also possible to secure a wide reaction field for the reaction with the gas generating agent during overcharge. Accordingly, the enhanced battery performance (e.g., the enhanced durability) and the reliability during overcharge can be made compatible at a higher level.

[0031] A method for producing a particulate lithium-transition metal composite oxide is not particularly limited. For example, the particulate lithium-transition metal composite oxide can be produced by obtaining a hydroxide (precursor) of a metal element through a wet method (precursor forming step), mixing the obtained precursor with a suitable lithium source (mixing step) and calcining the mixture at a predetermined temperature (calcining step). Hereinafter, a method for producing a positive electrode active material will be described by taking, as an example, the positive electrode active

material having an average composition represented by the aforementioned general formula 1, $\text{Li}_x\text{Ni}_a\text{Co}_b\text{Mn}_c\text{Me}_d\text{O}_2$. However, this description is not intended to limit the invention to the specific form.

[0032] In the precursor forming step, typically, an aqueous solution (typically, an acidic solution) (hereinafter referred to as an "aqueous solution A") which contains a nickel (Ni) source, a cobalt (Co) source, a manganese (Mn) source and an Me element source as starting raw materials, and an aqueous solution (hereinafter referred to as an "aqueous solution B") which contains a cobalt (Co) source, are prepared as the respective solutions. The respective solutions are mixed under an alkaline condition (a condition of $\text{pH} > 7$), thereby precipitating (crystallizing) hydroxides of the aforementioned metal elements. In this regard, the amounts of the metal sources (a Ni source, a Mn source and a Me source) other than the Co source in the aqueous solution A may be properly determined so as to become equal to the molar ratios of a, c and d of the aforementioned general formula 1. Further, the amount of the Co source in the aqueous solution B may be properly determined such that a sum of the amount of the Co source in the aqueous solution B and the amount of the Co source in the aqueous solution A becomes equal to the molar ratio of b in the aforementioned general formula 1.

[0033] The aqueous solution A can be prepared by dissolving predetermined amounts of transition metal element sources (the Ni source, the Co source, the Mn source and the Me source) (typically, water-soluble ion compounds) in an aqueous solvent. The order of adding the transition metal element sources to the aqueous solvent is not particularly limited. Further, the aqueous solution A may be prepared by preparing respective aqueous solutions containing the respective transition metal element sources and mixing the aqueous solutions thus prepared. Anions of the metal element sources may be properly selected such that the metal element sources become water-soluble. The anions of the metal element sources may be, e.g., sulfate ions, nitrate ions, carbonate ions, hydroxide ions, chloride ions or the like. All or some of the anions of the metal element sources may be identical with one another or may differ from one another. Further, the metal element sources may be solvated ones such as hydrates or the like. Similarly, the

aqueous solution B can be prepared by dissolving a predetermined amount of Co source in an aqueous solvent. The method for producing the aqueous solution B may be the same as the method for producing the aqueous solution A. The same Co source as used in the aqueous solution A may be used.

5 **[0034]** The aqueous solvent used in producing the aqueous solutions (the aqueous solution A and the aqueous solution B) is typically water, but may be a mixed solvent mainly composed of water. As a solvent other than water, which constitutes the mixed solvent, it is possible to properly select and use one or more kinds of organic solvents (e.g., a lower alcohol, a lower ketone or the like) which can be uniformly mixed with water. In
10 the case where the compound of raw materials is low in water solubility, a compound (an acid, a base or the like) capable of increasing the water solubility may be properly added to the aqueous solvent.

[0035] As the compound capable of making the aqueous solutions alkaline, it is possible to desirably use a compound which contains a strong base (such as a hydroxide of
15 an alkali metal) and/or a weak base (such as ammonia) and which does not inhibit formation (precipitation) of the hydroxide. For example, it is possible to use one or more kinds of compounds selected from a group consisting of sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonium hydroxide (NH₄OH), lithium hydroxide (LiOH), sodium carbonate (NaCO₃), potassium carbonate (KCO₃), lithium carbonate (LiCO₃),
20 ammonium carbonate ((NH₄)₂CO₃), ammonium nitrate (NH₄NO₃), ammonia gas (NH₃) and the like. Among them, it is preferable to use the sodium hydroxide. Preferably, these compounds are added such that the pH of the aqueous solutions substantially satisfies $12 \leq \text{pH} \leq 13$ (e.g., $12 \leq \text{pH} < 13$) just after the production of the aqueous solutions (at the initial stage). If the pH is set to fall within the aforementioned range, a large number of
25 nuclei are precipitated slowly from a reaction solution. This makes it possible to suitably produce the hydroxide having a wide particle size distribution (e.g., containing a large amount of small particles whose particle diameter deviates by a large amount from an average particle diameter). In the subject specification, the value of pH denotes a value measured at a room temperature (a liquid temperature of 25°C) using a commercially

available pH meter.

[0036] In the precursor forming step, a compound (e.g., sodium hydroxide) capable of making the aqueous solution A alkaline is first added to the aqueous solution A. The compound and the aqueous solution A are mixed and stirred at a suitable speed, thereby precipitating (crystallizing) hydroxides of metal elements (Ni, Co, Mn and Me). In this step, a positive electrode active material having desired properties (a particle size distribution and a specific surface area) can be obtained by properly adjusting a precipitation condition (e.g., a reaction temperature, a reaction time, an alkali concentration of the aqueous solution and a pH). In order to obtain a positive electrode active material having a wider particle size distribution, the reaction time may be made longer. For example, the reaction time may be set at 10 hours or more and 30 hours or less, preferably 14 hours or more and 24 hours or less. Further, the temperature of the aqueous solutions may be set at a temperature equal to or lower than the boiling point of the aqueous solvent (typically, 20°C to 80°C, e.g., 40°C to 60°C).

[0037] Then, the hydroxide particles thus obtained are added to the aqueous solution B. A compound (e.g., sodium hydroxide) capable of making the aqueous solution B alkaline is also added to the aqueous solution B. The hydroxide particles, the compound and the aqueous solution B are mixed and stirred at a suitable speed, thereby precipitating hydroxides of cobalt (Co) on the surfaces of the hydroxide particles. Thus, it is possible to obtain a precursor in which the Co concentration (the surface Co concentration and the entire Co concentration) is adjusted to fall within a suitable range. The precursor may be a compound having an average composition represented by general formula 2, $\text{Ni}_a\text{Co}_b\text{Mn}_c\text{Me}_d(\text{OH})_2$, where a, b, c and d are the same as those of the general formula 1. If the hydroxides obtained by the aforementioned wet method are used as the precursor, it is possible to produce a positive electrode active material in which the Co concentration (the surface Co concentration and the entire Co concentration) is maintained in a suitable range.

[0038] In the mixing step, the precursor obtained as above is mixed with a lithium source. A mixing method is not particularly limited. It may be possible to employ a dry

mixing method or a wet mixing method well-known in the art. As the lithium source, it is possible to use, with no particular limitation, an ordinary lithium compound used in forming a lithium oxide. Examples of the lithium source include lithium salts such as lithium carbonate (LiCO_3), lithium hydroxide (LiOH), lithium nitrate (LiNO_3), lithium sulfate (Li_2SO_4), and lithium chloride (LiCl). These Li sources can be used either alone or in combination. A mixture ratio of the precursor and the Li source is properly determined based on a number of moles of the Li source to a total number of moles of all the metal elements contained in the precursor. The number of moles of the Li source is selected so that x in the aforementioned formula 1 may become a predetermined value.

[0039] In the calcining step, the positive electrode active material particles disclosed herein can be produced by calcining the mixture of the precursor and the Li source. A calcining temperature is not particularly limited. For example, the calcining temperature may be set at 650°C or higher (typically, 700°C or higher, e.g., 750°C or higher) and 1050°C or lower (typically, 1000°C or lower). In order to obtain higher output, it is preferred that a highest calcining temperature is set to fall within a range of 850°C to 980°C (more preferably, 850°C to 950°C). This calcining condition can be preferably employed in the production of a positive electrode active material which is used in a lithium secondary battery for an application such as a hybrid car in which high output performance is important.

[0040] The calcined product thus obtained is typically pulverized, and is, if necessary, sieved into a desired particle diameter. The resultant product can be used as the positive electrode active material. In this way, it is possible to produce the positive electrode active material in which the ratio X/Y of the Co concentrations and the particle size distribution (the ratio of D10/D50) fall within suitable ranges.

[0041] Hereinafter, the configuration of a lithium-ion secondary battery that makes use of the positive electrode active material described above will be described in sequence. A lithium-ion secondary battery in which a winding-type electrode body (hereinafter referred to as a "wound electrode body") and a nonaqueous electrolyte are accommodated within a case having a square shape (rectangular parallelepiped box shape)

will be taken as an example. The battery structure is not limited to the illustrated example, particularly the square battery.

[0042] FIG. 1 is a sectional view of a lithium-ion secondary battery 100 according to one embodiment of the invention. FIG. 2 is a view illustrating a wound electrode body 200 arranged within the lithium-ion secondary battery 100.

[0043] The lithium-ion secondary battery 100 according to one embodiment of the invention includes a flat square battery case (namely, an exterior container) 300 as shown in FIG. 1. In the lithium-ion secondary battery 100, a flat wound electrode body 200 shown in FIG. 2 and a liquid phase electrolyte (electrolyte solution) not shown are accommodated within the battery case 300.

<<Battery Case 300>>

[0044] The battery case 300 includes a box-shaped (namely, having a shape of bottom-closed rectangular parallelepiped) case body 320 which has an opening at one end (corresponding to an upper end in an ordinary use state of the battery 100) and a sealing plate (lid) 340 including a rectangular plate member which is attached to and closes the opening.

[0045] The material of the battery case 300 may be the same as used in a conventional sealed battery, but is not particularly limited. It is preferred that the battery case 300 is mainly composed of metallic material which is light in weight and superior in heat conductivity. Examples of the metallic material include aluminum.

[0046] As illustrated in FIG. 1, a positive electrode terminal 420 and a negative electrode terminal 440 for external connection are formed in the sealing plate 340. A thin safety valve 360 and a liquid injection port 350 are formed between the terminals 420 and 440 of the sealing plate 340. The thin safety valve 360 is configured to release an internal pressure of the battery case 300 when the internal pressure increases to a predetermined level or higher. In FIG. 1, the liquid injection port 350 is sealed by a sealing material 352 after liquid is injected therethrough.

<<Wound Electrode Body 200 (Electrode Body)>>

[0047] As shown in Fig. 2, the wound electrode body 200 includes an elongated sheet-like positive electrode (positive electrode sheet 220), an elongated sheet-like negative electrode (negative electrode sheet 240) similar to the positive electrode sheet 220, and two elongated sheet-like separators (separators 262 and 264).

<<Positive Electrode Sheet 220>>

[0048] The positive electrode sheet 220 includes a strip-shaped positive electrode current collector 221 and positive electrode active material layers 223. For example, a metal foil suitable for a positive electrode can be properly used for the positive electrode current collector 221. In the present embodiment, an aluminum foil is used as the positive electrode current collector 221. An uncoated portion 222 is defined along one edge portion of the positive electrode current collector 221 in a width direction thereof. In the illustrated example, the positive electrode active material layers 223 are held on the opposite surfaces of the positive electrode current collector 221 except the uncoated portion 222 defined in the positive electrode current collector 221. The aforementioned positive electrode active material particles, a conductive material and a binder are contained in the positive electrode active material layers 223.

<<Conductive Material>>

[0049] Examples of the conductive material include carbon material, such as a carbon powder and carbon fibers. As the conductive material, it is possible to use the examples of the conductive material either alone or in combination. Examples of the carbon powder may include various types of carbon black (e.g., acetylene black, oil-furnace black, graphitized carbon black, carbon black, graphite, and Ketjen black) and a graphite powder. In this regard, the average primary particle diameter of the conductive agent pursuant to an SEM observation and an image analysis is about 25 nm or less (e.g., 10 nm to 25 nm), preferably 20 nm or less, and particularly preferably 18 nm or less. If the positive electrode active material having the aforementioned particle size distribution

(the particle diameter ratio D10/D50 of 0.75 or less) is used, the ratio of the particles having a small particle diameter increases in the positive electrode active material. However, if the average primary particle diameter of the conductive material is controlled as described above, it is possible to suitably form and maintain conductive paths among the active material particles having a small particle diameter. Thus, the cycle characteristic is improved and the reaction of the gas generating agent on the surfaces of the active material particles is accelerated. This suppresses the reduction of the gas generation amount during overcharge of the secondary battery configured as described above. Accordingly, the enhanced battery performance (e.g., the enhanced durability) and the reliability during overcharge can be made compatible at a higher level.

<<Binder>>

[0050] The binder serves to bind the positive electrode active material particles and the conductive material particles contained in the positive electrode active material layer and to bind the particles and the positive electrode current collector 221. As the binder, it is possible to use polymers that can be dissolved or dispersed in the solvent used. For example, for the positive electrode mixture composition using an aqueous solvent, it is preferable to use water-soluble or water-dispersible polymers such as cellulose polymers (carboxy methyl cellulose (CMC), hydroxy propyl methyl cellulose (HPMC), and the like), and rubber materials (vinyl acetate copolymer, styrene-butadiene copolymer (SBR), acrylic acid-modified SBR resin (SBR latex), and the like). Further, for the positive electrode mixture composition using a nonaqueous solvent, it is preferable to use polymers (polyvinylidene fluoride (PVDF), polyvinylidene chloride (PVDC), polyacrylonitrile (PAN), and the like).

<<Thickening Agent and Solvent>>

[0051] The positive electrode active material layer 223 is formed by, for example, preparing a positive electrode mixture in which the positive electrode active material particles, the conductive material, and the binder are mixed with a solvent in a paste form

(slurry form), coating the positive electrode mixture onto the positive electrode current collector 221, drying the positive electrode mixture, and rolling the positive electrode mixture. In this case, an aqueous solvent or a nonaqueous solvent can be used as the solvent for the positive electrode mixture. A preferred example of the non-aqueous solvent is N-methyl-2-pyrrolidone (NMP). The polymer materials illustrated as the binder can also be used for the purpose of obtaining a function as a thickening agent for the positive electrode mixture or other additives, in addition to the function as the binder.

<<Negative Electrode Sheet 240>>

[0052] As shown in FIG. 2, the negative electrode sheet 240 includes a strip-shaped negative electrode current collector 241 and negative electrode active material layers 243. For example, a metal foil suitable for a negative electrode can be properly used as the negative electrode current collector 241. In the embodiment, a strip-shaped copper foil having a thickness of about 10 μm is used as the negative electrode current collector 241. An uncoated portion 242 is defined along one edge portion of the negative electrode current collector 241 in a width direction thereof. The negative electrode active material layers 243 are held on the opposite surfaces of the negative electrode current collector 241 except the uncoated portion 242 defined in the negative electrode current collector 241. Negative electrode active material particles are contained in the negative electrode active material layers 243. In this regard, the negative electrode active material layers 243 are formed by coating a negative electrode mixture containing negative electrode active material particles onto the negative electrode current collector 241, drying the negative electrode mixture, and pressing the negative electrode mixture into a predetermined thickness.

<<Negative Electrode Active Material Particles>>

[0053] As the negative electrode active material particles contained in the negative electrode active material layers 243, it is possible to use, with no particular limitation, one or more kinds of materials which have been conventionally used in a

lithium-ion secondary battery. Preferred examples of the negative electrode active material particles include a carbon material such as graphite carbon or amorphous carbon, a lithium-transition metal oxide, a lithium-transition metal nitride, and the like. Preferred examples of the aforementioned separators include separators made of a porous polyolefin resin.

<<Separators 262 and 264>>

[0054] As shown in FIG. 2, the separators 262 and 264 are members that keep the positive electrode sheet 220 and the negative electrode sheet 240 spaced apart from each other. In this example, the separators 262 and 264 are formed of a strip-shaped sheet material having a plurality of small holes and having a predetermined width. As the separators 262 and 264, it is possible to use single-layer separators or laminated separators made of, e.g., a porous polyolefin resin. In this example, as shown in FIG. 2, the width b1 of the negative electrode active material layers 243 is slightly wider than the width a1 of the positive electrode active material layers 223. Further, the width c1 or c2 of the separators 262 and 264 is slightly wider than the width b1 of the negative electrode active material layers 243 ($c1 \text{ or } c2 > b1 > a1$).

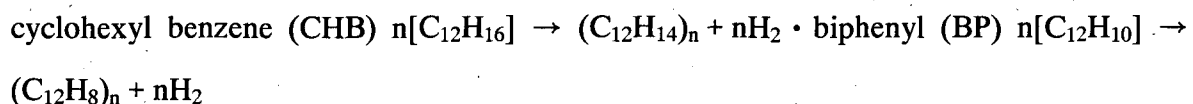
[0055] In the example shown in FIG. 2, the separators 262 and 264 are formed of sheet-like members. The separators 262 and 264 may be any member that insulates the positive electrode active material layers 223 and the negative electrode active material layers 243 while permitting movement of the electrolyte. Thus, the separators 262 and 264 are not limited to the sheet-like members. The separators 262 and 264 may be configured by, e.g., layers of insulating particles formed on the surfaces of the positive electrode active material layers 223 or the negative electrode active material layers 243, instead of the sheet-like members. In this regard, the insulating particles may be composed of insulating inorganic fillers (e.g., fillers of metal oxides, metal hydroxides or the like) or insulating resin particles (e.g., particles of polyethylene, polypropylene or the like).

<<Electrolyte (Nonaqueous Electrolyte)>>

[0056] As the electrolyte (nonaqueous electrolyte), it is possible to use, with no particular limitation, the same one as the nonaqueous electrolyte which has been conventionally used in the lithium-ion secondary battery. Typically, the nonaqueous electrolyte has a composition obtained by adding a supporting salt to a suitable nonaqueous solvent. As the nonaqueous solvent, it is possible to use, e.g., one or more kinds of solvents selected from a group consisting of ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, 1,2-dimethoxyethane, 1,2-diethoxy ethane, tetrahydrofuran and 1,3-dioxolane, and the like. As the supporting salt, it is possible to use, e.g., a lithium salt such as LiPF_6 , LiBF_4 , LiAsF_6 , LiCF_3SO_3 , $\text{LiC}_4\text{F}_9\text{SO}_3$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, or the like. As an example, it may be possible to use a nonaqueous electrolyte obtained by adding LiPF_6 to a mixed solvent of ethylene carbonate and diethyl carbonate at a concentration of about 1 mol/L.

<<Gas Generating Agent>>

[0057] In the embodiment, the nonaqueous electrolyte contains a gas generating agent that reacts and generates a gas, for example, when a battery voltage becomes equal to or higher than a predetermined voltage. As the gas generating agent, it is possible to use, e.g., cyclohexyl benzene (CHB), biphenyl (BP), or the like. When a battery is overcharged to, e.g., about 4.35 V to 4.6 V, cyclohexyl benzene (CHB) or biphenyl (BP) is oxidation-decomposed and polymerized to generate hydrogen ions by making contact with the surface of the positive electrode (typically, the surface of the positive electrode active material). Then, the hydrogen ions are diffused to the negative electrode to receive electrons on the negative electrode, thereby generating hydrogen which is a reducing gas. Typically, the following polymerization reaction is activated to generate a gas (a hydrogen gas in this example).



[0058] The additional amount of the gas generating agent added to the

nonaqueous electrolyte may be set at, e.g., about 0.05 wt% or more and 4.0 wt% or less, but is not limited thereto. The additional amount of the gas generating agent may be adjusted such that a specified amount of gas is generated under a predetermined condition. Further, the gas generating agent is not limited to cyclohexyl benzene (CHB) or biphenyl (BP). In this regard, $(C_{12}H_{14})_n$ or $(C_{12}H_8)_n$ may be formed into a polymerization film during the gas-generating polymerization reaction.

<<Attachment of Wound Electrode Body 200>>

[0059] In the present embodiment, as shown in FIG. 2, the wound electrode body 200 is pressed to be flat and bent in one direction orthogonal to a winding axis WL. In the example shown in FIG. 2, the uncoated portion 222 of the positive electrode current collector 221 and the uncoated portion 242 of the negative electrode current collector 241 are respectively exposed in a spiral shape at the opposite sides of the separators 262 and 264. In the embodiment, as illustrated in FIG. 1, an intermediate portion of the uncoated portion 222 (242) is gathered and welded to current collecting taps 420a and 440a of the electrode terminals 420 and 440 (the internal terminal) disposed within the battery case 300. In the wound electrode body 200, the electrolyte migrates into the wound electrode body 200 in the direction of the winding axis WL.

<<Current Cutoff Mechanism 460>>

[0060] In the lithium-ion secondary battery 100, as described above, the gas generating agent is added to the electrolyte. When the battery is overcharged to, e.g., about 4.35 V to 4.6 V, a gas is generated and the internal pressure of the battery case grows higher. A current cutoff mechanism 460 is configured to cut off a current path if the internal pressure of the battery case becomes considerably high. In the embodiment, as shown in FIG. 1, the current cutoff mechanism 460 is built inside the positive electrode terminal 420 so as to cut off a battery current conduction path of the positive electrode. A concrete structure of the current cutoff mechanism 460 is disclosed in, e.g., JP2003-059489A. The current cutoff mechanism disclosed in JP2003-059489A can be

suitably employed as the current cutoff mechanism 460 of the lithium-ion secondary battery 100. Thus, the concrete structure of the current cutoff mechanism 460 will not be specifically described herein. The concrete structure of the current cutoff mechanism 460 is not limited to the structure disclosed in JP2003-059489A. Various kinds of mechanisms may be employed as the current cutoff mechanism 460.

<<Experimental Example 1>>

[0061] Some examples according to the invention will now be described. However, the following description is not intended to limit the invention to these examples.

<<Example 1>>

[0062] An NiCoMn aqueous solution (aqueous solution A) was prepared by dissolving nickel sulfate (NiSO_4) as a nickel source, cobalt sulfate (CoSO_4) as a cobalt source and manganese sulfate (MnSO_4) as a manganese source in an aqueous solvent such that a molar ratio of Ni, Co and Mn becomes 0.4:0.2:0.4. Further, a Co aqueous solution (aqueous solution B) was prepared by dissolving cobalt sulfate (CoSO_4) as a cobalt source in an aqueous solvent.

[0063] A suitable amount of NaOH was added to the aqueous solution A, and stirred to obtain a reaction solution. A hydroxide having a basic composition represented by $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ was precipitated (crystallized) from the reaction solution. The precipitated product was added to the aqueous solution B, and then NaOH was added to the aqueous solution B. The precipitated product, the aqueous solution B and the NaOH were mixed and stirred at a suitable speed, thereby precipitating a hydroxide of cobalt (Co) on the surfaces of particles of the aforementioned hydroxide. The precipitated product was taken out from a reaction vessel, washed with water, and dried to obtain a precursor which contains a hydroxide having a total composition represented by $\text{Ni}_{0.334}\text{Co}_{0.333}\text{Mn}_{0.333}(\text{OH})_2$. Lithium carbonate (Li_2CO_3) as a lithium source was mixed with the precursor such that a molar ratio of (Ni + Co + Mn) and Li becomes 1:1.09. The mixture was calcined at 800°C to 950°C for 5 to 15 hours under an air atmosphere, thereby obtaining particulate

positive electrode active material having a total composition represented by $\text{Li}_{1.09}(\text{Ni}_{0.334}\text{Co}_{0.333}\text{Mn}_{0.333})\text{O}_2$.

[0064] The Co concentration of the positive electrode active material particles thus obtained was measured by an ICP emission spectroscopy (using "ICPE-9000" made by Shimadzu Corporation). More specifically, a sample solution was prepared by melting the surface portions (the regions extending about 1000 nm from the particle surfaces) of the positive electrode active material particles in an acid. The surface Co concentration X (mol%) of the positive electrode active material particles was obtained by measuring the Co concentration in the sample solution. In addition, a sample solution was prepared by melting the entire positive electrode active material particles in an acid. The entire Co concentration Y (mol%) of the positive electrode active material particles was obtained by measuring the Co concentration in the sample solution. As a result, the surface Co concentration (X) was about 40 mol%. The entire Co concentration (Y) was 33.3 mol%. The value X/Y obtained by dividing the surface Co concentration (X) by the entire Co concentration (Y) was about 1.2.

[0065] The properties of the positive electrode active material particles were measured. As a result, the average particle diameter (the diameter D50) was 6.50 μm . The diameter D10 was 4.36 μm . The value D10/D50 obtained by dividing the diameter D10 by the diameter D50 was 0.67. The specific surface area was 1.18 m^2/g .

[0066] The obtained positive electrode active material particles, acetylene black (AB) as the conductive material, and polyvinylidene fluoride (PVDF) as a binder were kneaded with N-methylpyrrolidone (NMP) such that the mass ratio of the positive electrode active material particles, the acetylene black and the polyvinylidene fluoride becomes 93:4:3, thereby preparing a paste form composition (positive electrode paste) for the formation of positive electrode active material layers. The positive electrode paste was coated on the opposite surfaces of an elongated aluminum foil (positive electrode current collector) having a thickness of about 15 μm such that the total coating weight (the solid-content-converted coating amount, namely dry mass of positive electrode active material layers) on the opposite surfaces becomes 30 mg/cm^2 . The positive electrode

paste thus coated was dried with a hot air of 120°C, thereby forming positive electrode active material layers. Subsequently, a positive electrode sheet was produced by pressing the positive electrode active material layers such that density of the positive electrode active material layers becomes 2.8 g/cm³. In this example, Denka Black HS-100 having
5 an average primary particle diameter of 35 nm was used as the AB.

[0067] Graphite (powder) as a negative electrode active material, styrene butadiene rubber (SBR) and carboxy methyl cellulose (CMC) were mixed with ion-exchanged water such that the mass ratio of the graphite, the styrene butadiene rubber, and the carboxy methyl cellulose becomes 98:1:1, thereby preparing a paste form
10 composition (negative electrode paste) for the formation of negative electrode active material layers. The negative electrode paste was coated on the opposite surfaces of an elongated copper foil (a negative electrode current collector) having a thickness of about 10 µm such that a facing capacity ratio with respect to the positive electrode becomes 1.4. Negative electrode active material layers were formed by drying the negative electrode
15 paste thus coated. Subsequently, a negative electrode sheet was produced by pressing the negative electrode active material layers such that the density of the negative electrode active material layers becomes 1.3 g/cm³.

[0068] The positive electrode sheet and the negative electrode sheet thus produced were overlapped with each other through two separators and were wound to
20 produce an electrode body. The electrode body and a nonaqueous electrolyte were accommodated within a battery case. The solution obtained by dissolving LiPF₆ at a concentration of about 1 mol/L in a mixed solvent which contains ethylene carbonate (EC) and diethyl carbonate (DEC) at a volume ratio of 3:7 was used as the nonaqueous electrolyte. Further, cyclohexyl benzene (CHB) as a gas generating agent was added to
25 the nonaqueous electrolyte. The additional amount of the gas generating agent was set at 1 mass% in terms of a mass ratio with respect to the nonaqueous electrolyte. Subsequently, an evaluation-purpose lithium-ion secondary battery was built by performing a conditioning treatment.

<<Example 2>>

[0069] A lithium-ion secondary battery was built in the same manner as in Example 1 except that the average primary particle diameter of the AB (conductive material) contained in the positive electrode active material layers was changed to 16 nm.

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<<Comparative Example 1>>

[0070] An NiCoMn aqueous solution was prepared by dissolving nickel sulfate (NiSO_4) as a nickel source, cobalt sulfate (CoSO_4) as a cobalt source, and manganese sulfate (MnSO_4) as a manganese source in an aqueous solvent such that a molar ratio of Ni, Co, and Mn becomes 1:1:1. A suitable amount of NaOH was added to the NiCoMn aqueous solution, and stirred to obtain a reaction solution. A hydroxide was precipitated (crystallized) from the reaction solution. The precipitated product was taken out from a reaction vessel, washed with water and dried to obtain a precursor which contains a hydroxide having a basic composition represented by $\text{Ni}_{0.334}\text{Co}_{0.333}\text{Mn}_{0.333}(\text{OH})_2$. Lithium carbonate (Li_2CO_3) as a lithium source was mixed with the precursor such that a molar ratio of (Ni + Co + Mn) and Li becomes 1:1.09. The mixture was calcined at 800°C to 950°C for 5 to 15 hours under an air atmosphere, thereby obtaining a particulate positive electrode active material represented by $\text{Li}_{1.09}(\text{Ni}_{0.334}\text{Co}_{0.333}\text{Mn}_{0.333})\text{O}_2$. The value D10/D50 obtained by dividing the diameter D10 of the obtained positive electrode active material particles by the diameter D50 thereof was 0.84. Using the positive electrode active material thus obtained, a lithium-ion secondary battery was built in the same manner as in Example 1.

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<<Comparative Example 2>>

[0071] A particulate positive electrode active material represented by $\text{Li}_{1.09}(\text{Ni}_{0.313}\text{Co}_{0.375}\text{Mn}_{0.312})\text{O}_2$ was produced by changing the molar ratio of Ni, Co, and Mn to 1:1.2:1 in the production process of the positive electrode active material of Comparative Example 1 described above. Using the positive electrode active material thus produced, a lithium-ion secondary battery was built in the same manner as in Example

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1.

<<Comparative Example 3>>

[0072] A particulate positive electrode active material represented by $\text{Li}_{1.09}(\text{Ni}_{0.294}\text{Co}_{0.412}\text{Mn}_{0.294})\text{O}_2$ was produced by changing the molar ratio of Ni, Co and, Mn to 1:1.4:1 in the production process of the positive electrode active material of Comparative Example 1 described above. Using the positive electrode active material thus produced, a lithium-ion secondary battery was built in the same manner as in Example 1.

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<<Comparative Example 4>>

[0073] A positive electrode active material was produced by changing the production conditions of the precursor (e.g., the precipitation conditions of the hydroxide (e.g., a reaction temperature, a reaction time and a pH of the aqueous solution)) in the production process of the positive electrode active material of Example 1 described above. The value D10/D50 obtained by dividing the diameter D10 of the obtained positive electrode active material particles by the diameter D50 thereof was 0.84. Using the positive electrode active material thus produced, a lithium-ion secondary battery was built in the same manner as in Example 1.

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<<Comparative Example 5>>

[0074] A particulate positive electrode active material having total composition represented by $\text{Li}_{1.09}(\text{Ni}_{0.334}\text{Co}_{0.333}\text{Mn}_{0.333})\text{O}_2$ was produced by changing the molar ratio of Ni, Co, and Mn of the aqueous solution A to 0.45:0.1:0.45 in the production process of the positive electrode active material of Example 1 described above. The surface Co concentration (X) of the obtained positive electrode active material particles was about 46.6 mol%. The entire Co concentration (Y) was 33.3 mol%. The value X/Y obtained by dividing the surface Co concentration (X) by the entire Co concentration (Y) was about 1.4. The value D10/D50 obtained by dividing the diameter D10 of the positive electrode

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active material particles by the diameter D50 thereof was 0.84. Using the positive electrode active material thus produced, a lithium-ion secondary battery was built in the same manner as in Example 1.

5 <<Evaluation of Lithium-Ion Secondary Battery for Evaluation Test>>

[0075] An initial capacity, a post-cycle capacity retention rate, an IV resistance and an overcharge gas amount were evaluated with respect to the evaluation-purpose lithium-ion secondary batteries of the respective examples described above.

10 <<Measurement of Initial Capacity>>

[0076] With respect to the evaluation-purpose lithium-ion secondary batteries of the respective examples described above, the initial capacity was measured according to the following procedures 1 to 3. Procedure 1: The battery is discharged at a constant current of 1 C until the voltage reaches 3.0 V, and is then discharged at a constant voltage for 2 hours. Thereafter, the discharging is paused for 10 seconds. Procedure 2: The battery is charged at a constant current of 1 C until the voltage reaches 4.1 V, and is then charged at a constant voltage for 2.5 hours. Thereafter, the charging is paused for 10 seconds. Procedure 3: The battery is discharged at a constant current of 0.5 C until the voltage reaches 3.0 V, and is then discharged at a constant voltage for 2 hours. Thereafter, the discharging is stopped for 10 seconds. In this regard, the discharge capacity (CCCV discharge capacity) in the discharging process from the constant current discharging to the constant voltage discharging of procedure 3 was defined as an "initial capacity".

<<Post-Cycle Capacity>>

25 [0077] After the initial charging, a cycle test was performed with respect to each of the test-purpose batteries in such a charge-discharge pattern that CC charging and CC discharging are repeated at a constant current of 10 C. More specifically, a charge-discharge cycle in which, at 25°C, the test-purpose battery is charged to 4.1 V at a constant current of 10 C, and then discharged to 3.0 V at a constant current of 10 C was

continuously performed 500 times. Then, a post-cycle discharge capacity was measured under the same conditions as the measurement conditions of the initial capacity.

<<IV Resistance>>

5 **[0078]** The measurement of a IV resistance was performed pursuant to the following procedures. Procedure 1: Under a temperature condition of 25°C, the battery was discharged to 3.0 V at a constant current of 1 C, and was then charged at a constant current of 1 C and at a constant voltage, whereby the battery is brought into a charge state in which the SOC is 20%. Procedure 2: After the procedure 1, the battery is discharged at
10 10 A (corresponding to 10 C) for 10 seconds. The current value measured in the procedure 2 is divided by a voltage drop value obtained by subtracting a voltage value available at a time point of 10 seconds from an initial voltage value of the procedure 2. The value thus obtained was defined as a IV resistance value.

15 <<Overcharge Gas Amount>>

[0079] An overcharge gas amount was calculated as follows. The same electrode plate group as the electrode plate group (the laminated body of a positive electrode sheet, a negative electrode sheet, and separators) used in the aforementioned lithium-ion secondary battery is put into a laminate bag together with an electrolyte to
20 which a gas generating agent is added. A laminate cell is produced by hermetically sealing the laminate bag. The laminate cell is subjected to a conditioning process. Prior to performing an overcharge test, an underwater weight of the laminate cell was measured in advance. Thereafter, the laminate cell is charged at a constant current of 0.5 C within a test chamber of 25°C and is brought into an overcharge state in which the SOC is 145%.
25 Thereafter, the laminate cell is discharged to 3 V and is taken out from the test chamber. The underwater weight of the laminate cell is measured again. The volume change of the laminate cell is measured according to Archimedes' method, and is divided by a 1 C capacity. The value thus obtained was defined as an overcharge gas amount.

[0080] That is to say, the volume change ΔV of the laminate cell is found by the

following equation: $\Delta V = \rho_w \times (W - W_1)$, where ρ_w is the density of water, W is the underwater weight of the laminate cell before overcharging, and W_1 is the underwater weight of the laminate cell after overcharging.

[0081] The results of the tests performed with respect to the respective examples are shown in Table 1 and FIGS. 3 to 5. Table 1 is a table that summarizes the configurations of the respective examples. FIG. 3 is a graph plotting the IV resistances of the respective examples. FIG. 4 is a graph plotting the initial capacities and the post-cycle capacities of the respective examples. In FIG. 4, the initial capacities and the post-cycle capacities of the respective examples are indicated as the relative values available when the initial capacity of Comparative Example 1 is assumed to be 100. FIG. 5 is a graph plotting the overcharge gas amounts of the respective examples.

[Table 1]

	Total Composition Ratio Ni/Co/Mn	Co Concentration Ratio (Surface X/Entire Y)	Particle Diameter Ratio D10/D50	Conductive Material Primary Particle Diameter (nm)
Com. Example 1	1/1/1	1	0.84	35
Com. Example 2	1/1.2/1	1	-	35
Com. Example 3	1/1.4/1	1	-	35
Com. Example 4	1/1/1	1.2	0.84	35
Com. Example 5	1/1/1	1.4	0.84	35
Example 1	1/1/1	1.2	0.67	35
Example 2	1/1/1	1.2	0.67	16

[0082] As shown in Table 1 and FIGS. 3 to 5, in the case of the batteries of Examples 1 and 2, the IV resistance is kept relatively low, and the high output characteristic can be provided at a higher level. In contrast, in the case of the battery of Comparative Example 1, the IV resistance is relatively high, and the output characteristic is low. Further, in case of the batteries of Examples 1 and 2, the initial capacity is high, and the capacity is kept high even after the cycle. In contrast, in the case of the batteries of Comparative Examples 2 and 3, the initial capacity is low, and the post-cycle capacity retention rate is also low. In the case of the batteries of Comparative Examples 4 and 5, the initial capacity is relatively high. However, the post-cycle capacity retention rate

tends to become lower than that of Examples 1 and 2. Further, in the case of the batteries of Examples 1 and 2, the overcharge gas amount is large, and is at such a level that the current cutoff mechanism can operate properly (relatively early). In contrast, in the case of the batteries of Comparative Examples 1 to 5, the gas generation amount is lowered, and the operation of the current cutoff mechanism tends to be delayed as compared with Examples 1 and 2. As can be noted from the tests described above, the use of the positive electrode active material in which the Co concentration is higher in the surface portion than in the central portion and in which the particle diameter ratio D10/D50 is 0.75 or less makes it possible to increase the overcharge gas amount while keeping the output characteristic, the initial capacity and the post-cycle capacity at a high level, and to properly operate the current cutoff mechanism.

<<Experimental Example 2>>

[0083] In this example, a positive electrode active material was produced by changing the production conditions of the precursor (e.g., the deposition conditions of the hydroxide (e.g., a reaction temperature, a reaction time, and an alkali concentration of the aqueous solution, and a PH)) and consequently changing the particle diameter ratio D10/D50 to different values in the production process of the positive electrode active material of Example 1 described above. Using the positive electrode active material thus produced, a lithium-ion secondary battery was built in the same manner as in Example 1, and the IV resistance, the capacity retention rate, and the overcharge gas amount of the battery were evaluated. In this regard, the capacity retention rate was calculated by dividing the initial capacity by the post-cycle capacity. The results are shown in FIGS. 6 to 8. FIG. 6 is a graph illustrating the relationship between the particle diameter ratio D10/D50 and the IV resistance. FIG. 7 is a graph illustrating the relationship between the particle diameter ratio D10/D50 and the capacity retention rate. FIG. 8 is a graph illustrating the relationship between the particle diameter ratio D10/D50 and the overcharge gas amount.

[0084] As is apparent in FIG. 6, the IV resistance tends to decrease as the particle

diameter ratio D10/D50 becomes smaller. In the case of the battery offered for the experiment, an extremely low IV resistance of 39.2 mΩ or less could be realized by setting the particle diameter ratio D10/D50 at 0.75 or less. From the viewpoint of the output characteristic improvement, the particle diameter ratio D10/D50 is set preferably at 0.75 or less, and more preferably at 0.67 or less. As is apparent in FIG. 7, the capacity retention rate tends to increase as the particle diameter ratio D10/D50 becomes smaller. In the case of the battery offered for the experiment, an extremely high capacity retention rate of 0.91 or more could be realized by setting the particle diameter ratio D10/D50 at 0.75 or less. From the viewpoint of improving durability, the particle diameter ratio D10/D50 is set preferably at 0.75 or less, and more preferably at 0.6 or less. As is apparent in FIG. 8, the overcharge gas amount tends to increase as the particle diameter ratio D10/D50 becomes smaller. In case of the battery offered for the experiment, an extremely high overcharge gas amount of 55 cm³ or more could be realized by setting the particle diameter ratio D10/D50 at 0.75 or less. From the viewpoint of the reliability during overcharge, the particle diameter ratio D10/D50 is set preferably at 0.75 or less, more preferably at 0.67 or less, and particularly preferably 0.5 or more and 0.6 or less.

<<Experimental Example 3>>

[0085] In this example, a lithium-ion secondary battery was built by changing the primary particle diameter of the conductive material (AB) to different values in the production process of the lithium-ion secondary battery of Example 1 described above, and the IV resistance and the overcharge gas amount of the battery were evaluated. The results are shown in FIGS. 9 and 10. FIG. 9 is a graph illustrating the relationship between the primary particle diameter of the conductive material and the IV resistance. FIG. 10 is a graph illustrating the relationship between the primary particle diameter of the conductive material and the overcharge gas amount.

[0086] As is apparent in FIG. 9, the IV resistance tends to decrease as the primary particle diameter of the conductive material becomes smaller. In the case of the battery offered for the experiment, an extremely low IV resistance of 37.3 mΩ or less could be

realized by setting the primary particle diameter of the conductive material at 25 nm or less. From the viewpoint of the output characteristic improvement, the primary particle diameter of the conductive material is set preferably at 25 nm or less, and more preferably at 20 nm or less. As is apparent in FIG. 10, the overcharge gas amount tends to increase as the primary particle diameter of the conductive material becomes smaller. In the case of the battery offered for the experiment, an extremely high overcharge gas amount of 74 cm³ or more could be realized by setting the primary particle diameter of the conductive material at 25 nm or less. From the viewpoint of the reliability during overcharge, the primary particle diameter of the conductive material is set preferably at 25 nm or less, and more preferably at 20 nm or less.

[0087] While the invention has been described in detail, the embodiments and the examples described above are nothing more than exemplifications. Different changes and modifications of the aforementioned concrete examples are also included in the invention disclosed therein.

[0088] The lithium-ion secondary battery suggested herein exhibits superior performance as mentioned above and, therefore, can be used as a lithium-ion secondary battery for different purposes. For example, the lithium-ion secondary battery may be properly used as a power supply for a motor (electric motor) mounted to a motor vehicle such as an automobile. The lithium-ion secondary battery may be used in the form of a battery pack that includes a plurality of batteries connected in series and/or in parallel. According to the technology disclosed herein, it is possible to provide a motor vehicle (typically, an automobile) (particularly, an automobile provided with an electric motor such as a hybrid car, an electric car, or a fuel cell car) which is provided with the lithium-ion secondary battery (possibly, the battery pack) as a power supply.

[0089] While the lithium-ion secondary battery has been described herein by way of example, the invention may be employed in the structure of a secondary battery other than the lithium-ion secondary battery unless specifically limited otherwise.

CLAIMS:

1. A positive electrode active material, comprising:
 composite oxide particles which contain cobalt,
 wherein the composite oxide particles have a cobalt concentration which is higher in surface portions than in central portions of the composite oxide particles,
 a value of a ratio $D10/D50$ of a diameter $D10$ to a diameter $D50$ satisfies $D10/D50 \leq 0.75$, the diameter $D10$ corresponding to 10% of a cumulative particle volume counted from a small particle diameter side in a particle size distribution of the composite oxide particles, and the diameter $D50$ corresponding to 50% of the cumulative particle volume counted from the small particle diameter side in the particle size distribution of the composite oxide particles.
2. The material according to claim 1, wherein the value of the ratio $D10/D50$ satisfies $D10/D50 \leq 0.67$.
3. The material according to claim 1 or 2, wherein the value of the ratio $D10/D50$ satisfies $0.45 \leq D10/D50$.
4. The material according to any one of claims 1 to 3, wherein a value of a ratio X/Y of an average cobalt concentration X mol% in the surface portions of the composite oxide particles to an average cobalt concentration Y mol% of an entirety of the composite oxide particles satisfies $1.1 \leq X/Y \leq 1.5$.
5. The material according to any one of claims 1 to 4, wherein the composite oxide particles are represented by general formula, $Li_xNi_aCo_bMn_cMe_dO_2$, where x , a , b , c and d are numbers that satisfy $0.99 \leq x \leq 1.12$, $0.9 \leq a + b + c + d \leq 1.1$, $1.05 \leq x/(a + b + c + d) \leq 1.2$, $0 < a \leq 0.5$, $0 < b \leq 0.5$, $0 < c \leq 0.5$ and $0 \leq d \leq 0.2$ and where Me is one or more kinds of elements selected from a group consisting of a transition metal element, a typical metal element, and

boron, or is omitted from constituent elements of the general formula.

6. A nonaqueous electrolyte secondary battery, comprising:

an electrode body including a positive electrode which contains the positive electrode active material according to any one of claims 1 to 5 and a conductive material, a negative electrode which contains a negative electrode active material, and a separator interposed between the positive electrode and the negative electrode;

a battery case which accommodates the electrode body;

an external terminal provided in the battery case and connected to the electrode body;

a nonaqueous electrolyte accommodated within the battery case, the nonaqueous electrolyte containing a gas generating agent which reacts and generates a gas at a voltage equal to or higher than a predetermined voltage; and

a current cutoff mechanism configured to cutoff electric connection of the electrode body and the external terminal if an internal pressure of the battery case becomes equal to or higher than a predetermined pressure.

7. The battery according to claim 6, wherein an average primary particle diameter of the conductive material is 25 nm or less.

FIG. 1

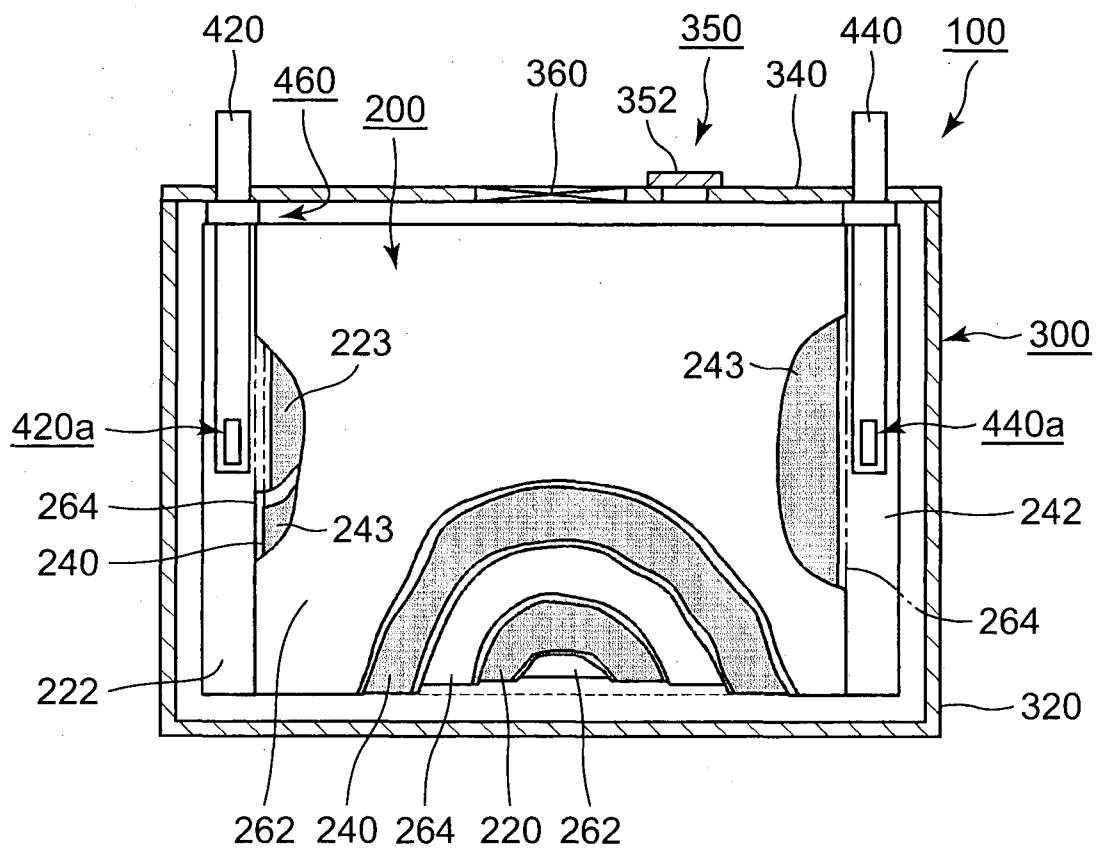


FIG. 2

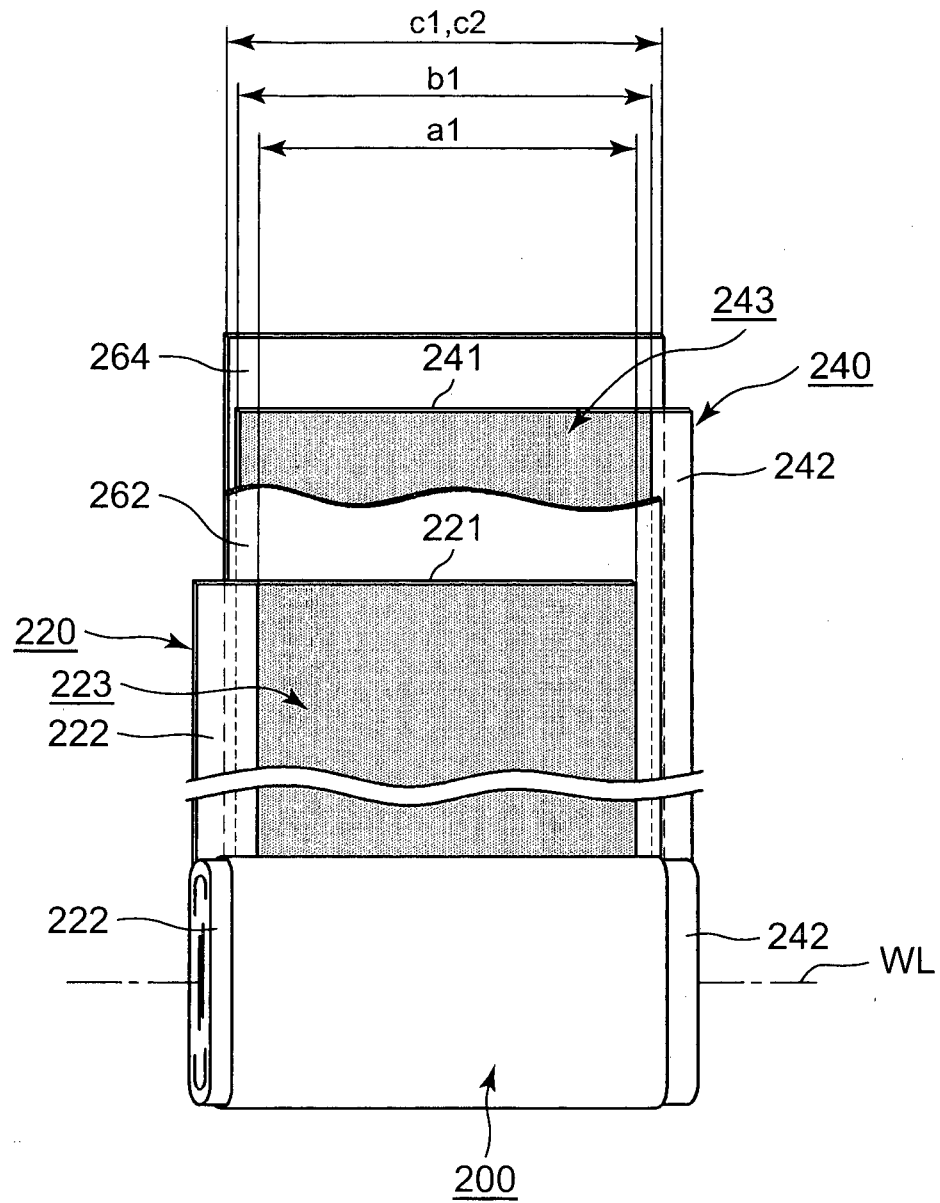


FIG. 3

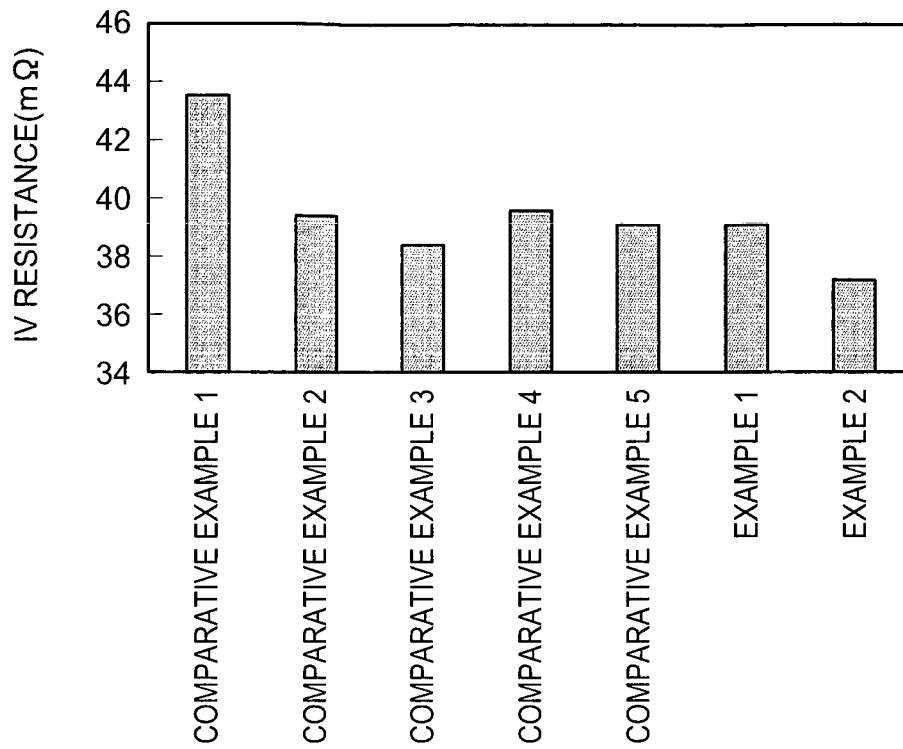


FIG. 4

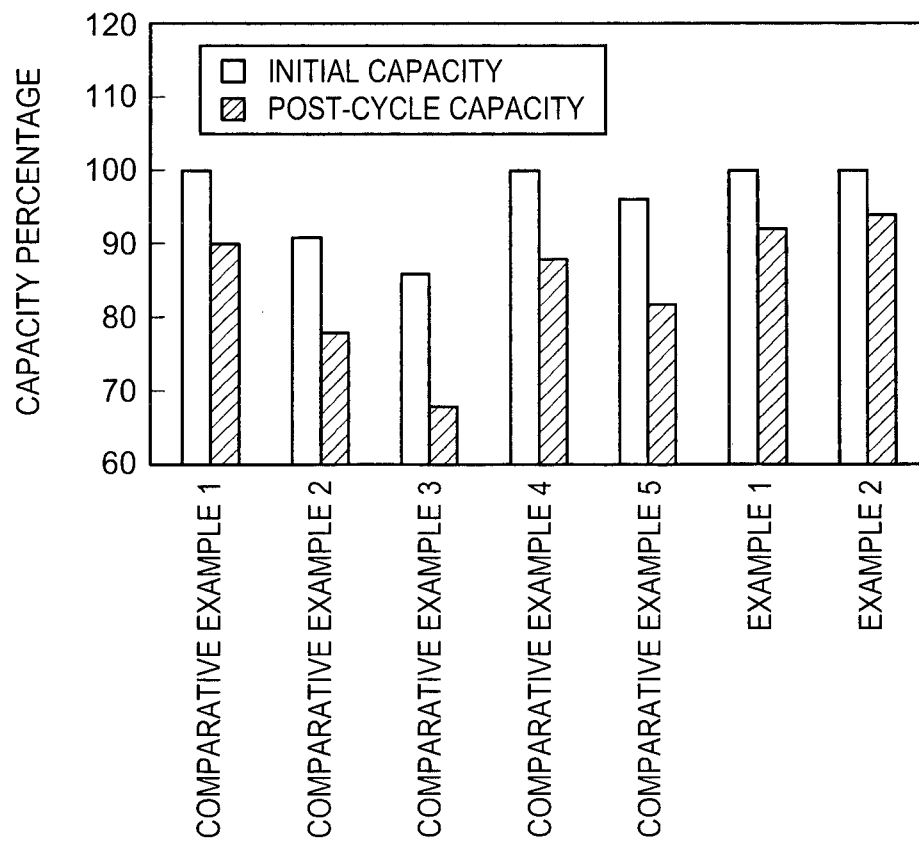


FIG. 5

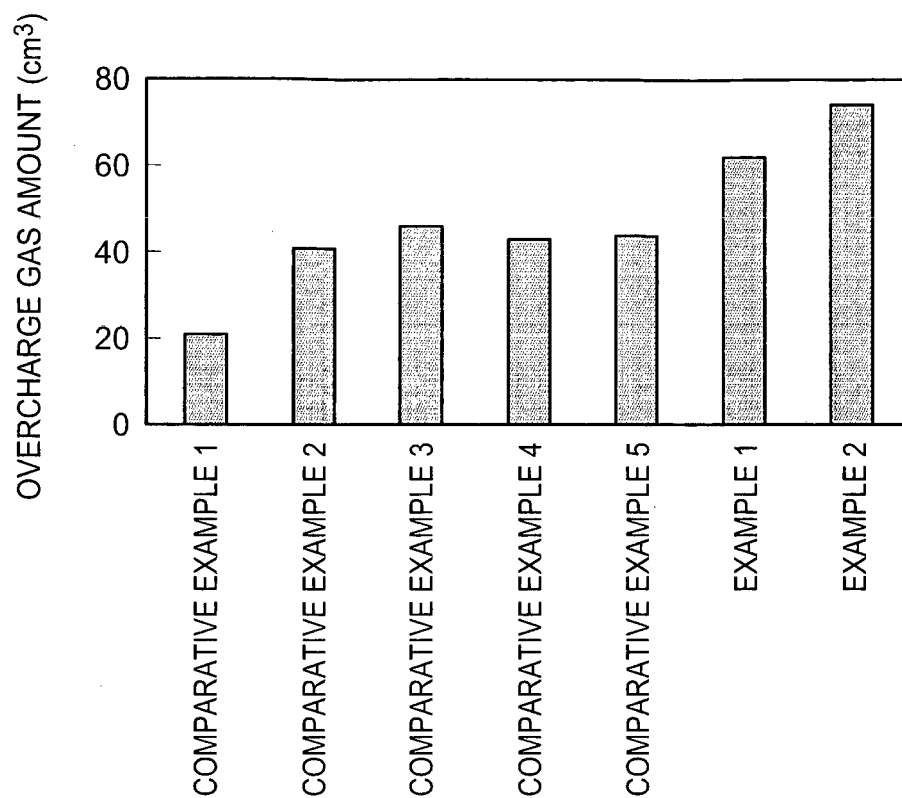


FIG. 6

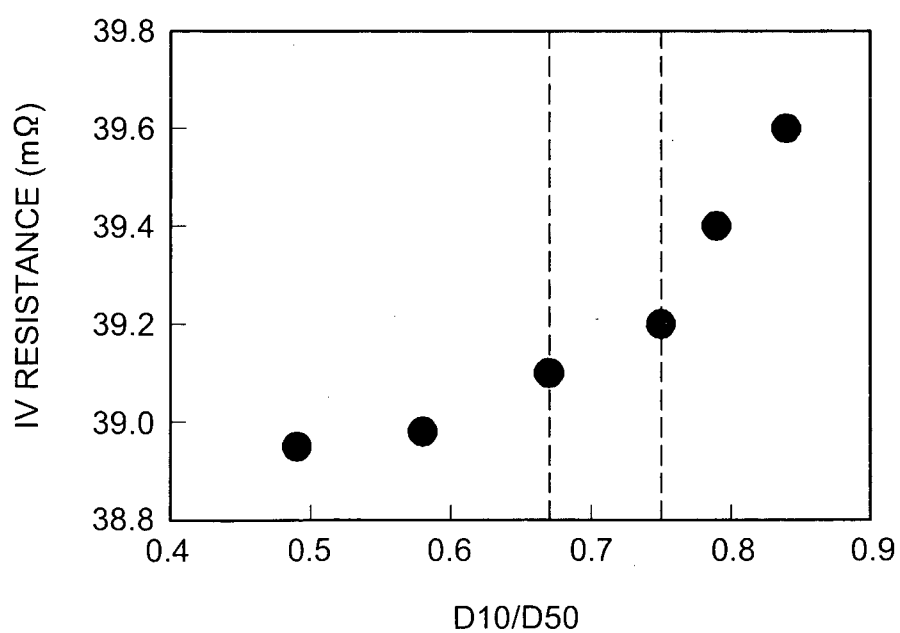


FIG. 7

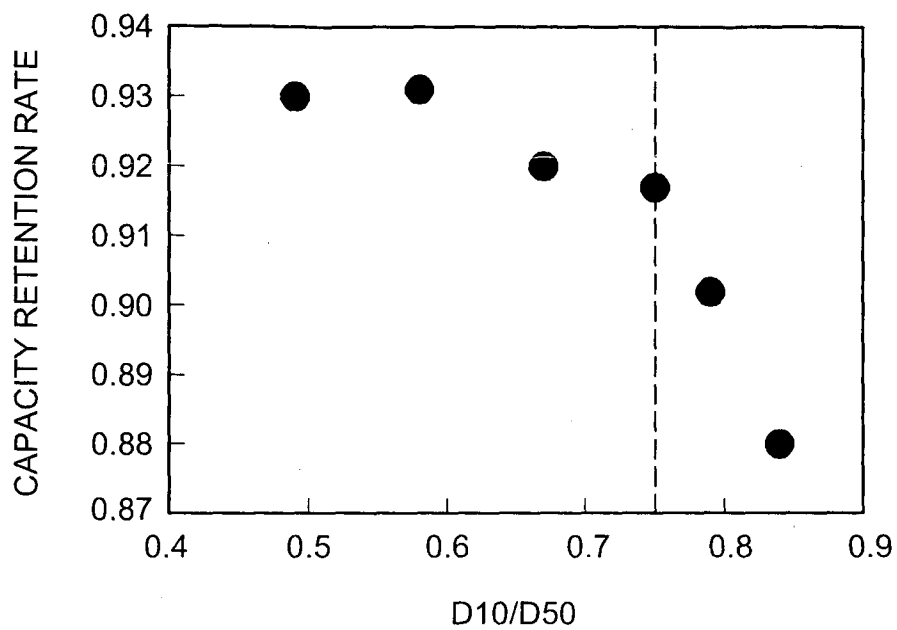


FIG. 8

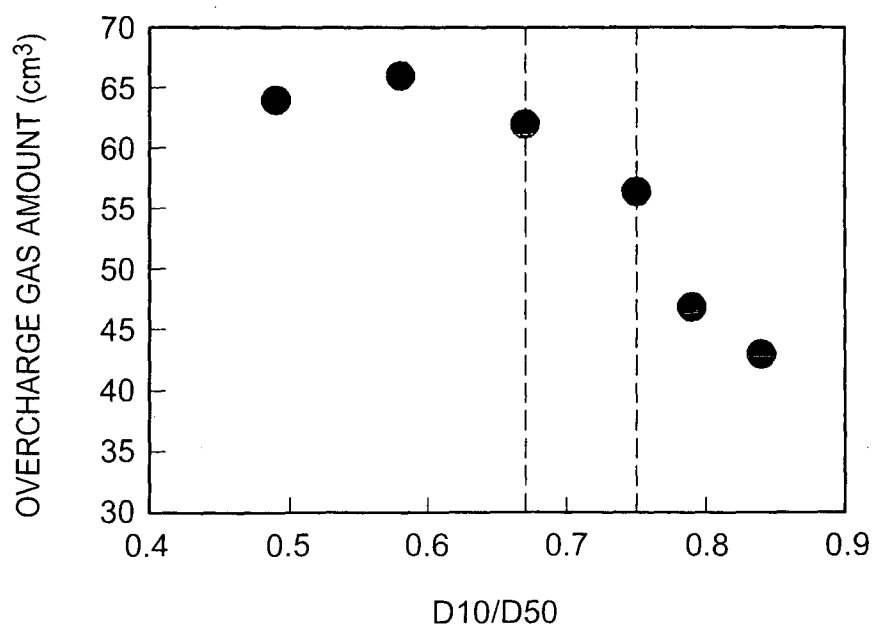


FIG. 9

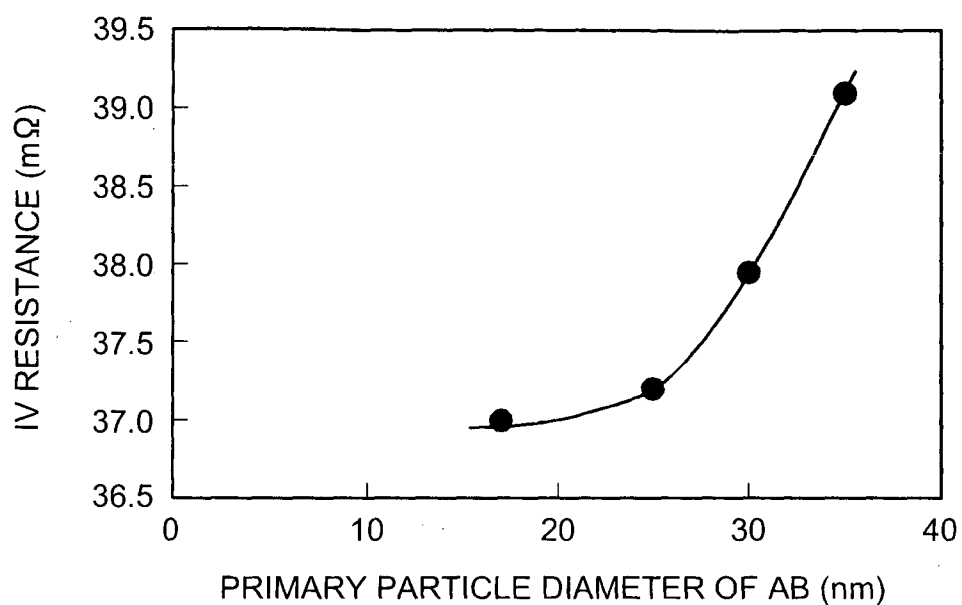


FIG. 10

