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(54) [Title of the invention] Positive electrode active material particle powder for nonaqueous electrolyte secondary battery and its manufacturing method, and nonaqueous electrolyte secondary battery

(57) [Abstract]

[Problems] A high capacity and high capacity maintenance rate provides positive electrode active material particle powder with excellent high temperature overcharging test, the manufacturing method thereof, and a secondary battery using the same.

[Means for solving] A positive electrode active material particle powder having a surface layer consisting of a layered structure of lithium cobalt oxide comprising element M (M is Mg and/or Al), and at least a layered structure of lithium cobalt oxide solidified by Ti, wherein the average layer thickness of the surface layer is 0.005 to 1.5  $\mu\text{m}$  and BET specific surface area is 0.02 to 0.25  $\text{m}^2/\text{g}$ .

[Representative drawing] None

[Scope of patent claims]

[Claim 1]

A positive electrode active material particle powder having a surface layer consisting of a layered structure of lithium cobalt oxide comprising element M (M is Mg and/or Al), and at least a layered structure of lithium cobalt oxide solidified by Ti, wherein the average layer thickness of the surface layer is 0.005 to 1.5  $\mu\text{m}$  and BET specific surface area is 0.02 to 0.25  $\text{m}^2/\text{g}$ .

[Claim 2]

Wherein the positive electrode active material particle powder in Claim 1 has a top surface consisting of a water-soluble lithium oxide comprising element A (where A is at least one element selected from W, Mo, and B), and the top surface has a content of 0.01 to 0.5%.

[Claim 3]

The positive electrode active material particle powder of Claim 1 or 2, wherein the median diameter of the volumetric basis is 10 to 35  $\mu\text{m}$ .

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[Claim 4]

The positive electrode active material particle powder according to any one of Claims 1 to 3, wherein the remaining alkaline component is 800 ppm or less and the unreacted cobalt oxide is 500 ppm or less.

[Claim 5]

The positive electrode active material particle powder in any one of Claims 1 to 4, in which the above layer Ti concentration is  $0.001 \leq \text{Ti/Co (mol ratio)} \leq 0.02$ .

[Claim 6]

The positive electrode active material particle powder in any one of Claims 1 to 5, wherein the coverage of the core particles of the surface layer is 80% or greater.

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[Claim 7]

A method of making a positive electrode active material particle powder according to any one of Claims 1 to 6, characterized where the first process of producing a layered lithium cobalt oxide particle powder is performed by firing at 800 to 1100°C after mixing a lithium raw material, cobalt raw material, and element M raw material (M is Mg and/or Al), and the second process of forming a surface layer after mixing a lithium cobalt oxide particle powder obtained in the first process and a titanium raw material and firing at 800 to 1100°C.

[Claim 8]

A method of making a positive electrode active material particle powder according to any one of Claims 2 to 6, characterized where the first process of producing a layered lithium cobalt oxide particle powder is performed by firing at 800 to 1100°C after mixing a lithium raw material, cobalt raw material, and element M raw material (M is Mg and/or Al), and the second process of forming a surface layer and a top surface layer after mixing a lithium cobalt oxide particle powder obtained in the first process, a titanium raw material and element A (A is at least one element selected from W, Mo and B) and firing at 800 to 1100°C.

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[Claim 9]

A nonaqueous electrolyte secondary battery made using the positive electrode active material particle powder according to any one of claims 1 to 6 for at least a part of the positive electrode active material.

[Claim 10]

For the positive electrode active material particle powder according to any one of Claims 1 to 6,  $\text{Li}(\text{Ni}_{1-a-b}\text{Co}_a\text{Mn}_b)\text{O}_2$  (a and b are  $0.15 \leq a \leq 0.4$ ,  $0.15 \leq b \leq 0.4$ ). A non-aqueous electrolyte secondary battery produced by using a mixture containing 3 to 25% by weight of the positive electrode active material particles represented by 5) as a positive electrode active material.

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[Detailed description of the invention]

[Technical field]

[0001]

The Present Invention provides, as a positive electrode active material for a secondary battery exhibiting high energy density, a positive electrode active material particle powder having excellent high temperature overcharging properties and charge/discharge repetition properties, a manufacturing method thereof, and a secondary battery therewith.

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[Background technology]

[0002]

In recent years, the miniaturization and weight reduction of electronic devices such as mobile phones and personal computers has spurred the demand for secondary batteries with high energy density as power sources for these drives. Under such circumstances, lithium-ion secondary batteries with the advantages of having a large charge and discharge capacity and high safety are attracting attention.

[0003]

Traditionally,  $\text{LiCoO}_2$ ,  $\text{Li}(\text{Ni}, \text{Co})\text{O}_2$ ,  $\text{Li}(\text{Ni}, \text{Co}, \text{Mn})\text{O}_2$ , and  $\text{LiMn}_2\text{O}_4$  of a spinel structure are commonly known as positive electrode active materials for high-energy lithium-ion secondary batteries with a voltage of 4V, of which high crystallinity is easy to obtain, and high-density-fillable lithium cobalt oxide  $\text{LiCoO}_2$  has been used as positive electrode active materials for mobile device drive power supplies for more than 20 years. However, further improvement of characteristics is required in conjunction with the improvement of the above-described equipment.

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[0004]

One way to improve characteristics is to increase the charging voltage of the secondary battery to achieve high energy density. However, with high charge voltage, i.e., if there is an overcharge, it has been pointed out that there are problems with battery pack swelling associated with deterioration of charge-discharge repeat characteristics and gas generation.

[0005]

In general, crystals of lithium  $\text{LiCoO}_2$  cobalt acid are composed of monovalent  $\text{Li}^+$ , trivalent  $\text{Co}^{3+}$ , and minus divalent  $\text{O}^{2-}$ , and upon charging,  $\text{Li}^+$  and electron  $e^-$  depart from the crystals and change to  $\text{Li}_{1-a}\text{CoO}_2$  ( $a>0$ ) in a delithiated state containing unstable  $\text{Co}^{4+}$  with Jahn-Teller properties. Therefore, in a delithiated state near the composition ratio of  $\text{Li}_{1.5}\text{CoO}_2$  with half of  $\text{Li}^+$ , cobalt ions elute from the crystals to the electrolyte solution, and phase transition and disintegration of the crystals occurs, exacerbating the battery charge and discharge repeating properties.

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[0006]

In addition, since the energy level of the d-orbit associated with  $\text{Co}^{3+/4+}$  and the energy level of the p-orbit associated with  $\text{O}^{2-}$  in  $\text{Li}_{1-a}\text{CoO}_2$  ( $a > 0$ ) in the delithiated state is relatively close, it is equivalent to electrochemically withdrawing electrons from the cobalt ions of  $\text{Li}_{1-a}\text{CoO}_2$  and withdrawing electrons from the oxygen ions, and releasing oxygen (ions) along with cobalt ion elution from crystals. When the battery is in a high charge state, the positive electrode is exposed to a high oxidation state in the vicinity of the positive electrode that deprives electrons, and the aforementioned released oxygen causes the oxidation state to be even higher, causing the electrolytes and binders around the positive electrode to oxidize, causing gas generation such as  $\text{CO}_2$ , etc., and causing the battery to inflate.

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[0007]

In particular, under high charging pressures at high temperatures, the reaction of oxygen (ions) with cobalt ion elution with the electrolytes becomes more active, and in order to ensure safety for the secondary battery, it is necessary that the structure of the lithium positive electrode active material in the delithiated state is more stable. That is, improvement of lithium cobalt oxide particle powder is necessary to raise the charging voltage and safely increase the amount of Li available for charge and discharge. Traditionally, techniques for replacement and coating with heterogeneous elements have been proposed for stabilizing the delithiated state of lithium cobalt oxide (Patent Documents 1-6).

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[0008]

In general,  $\text{Li}(\text{Ni}^{2+}, \text{Co}^{3+}, \text{Mn}^{4+})\text{O}_2$  has a close ion radius between  $\text{Li}^+$  and  $\text{Ni}^{2+}$ , so it is known that it is difficult for  $\text{Li}^+$  to enter the transition metal site or  $\text{Ni}^{2+}$  to enter the lithium site to create a complete crystal. In addition, in charge and discharge, the potential corresponding to  $\text{Ni}^{2+/4+}$  is taken, and it is low compared to battery voltage of lithium cobalt oxide positive electrodes. At the same time, no quadrivalent cobalt ion  $\text{Co}^{4+}$  is produced. Therefore, compared to  $\text{LiCoO}_2$  lithium cobalt oxide, the elution of cobalt ions in the high temperature overcharge state is extremely low, and it is used as a surface treatment for lithium cobalt oxide (Patent References 1-5).

[0009]

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It has also been reported that when  $\text{TiO}_2$  is mixed during the preparation of lithium cobalt oxide, in the resulting powder, it is present as  $\text{Li}_2\text{TiO}_3$  crystals on the surface layer of lithium cobalt oxide, suppressing gas generation due to the recharge and discharge repeated characteristics and rate characteristics of the secondary battery, as well as reaction with the nonaqueous electrolytes. (Patent literature 6).

(Prior art literature)

(Patent literature)

[0010]

[Patent literature 1] Published Japanese Translation of a PCT Application 2002-529361

[Patent literature 2] Japanese Unexamined Patent Application Publication 2006-331939

[Patent literature 3] Japanese Unexamined Patent Application Publication 2007-066745

[Patent literature 4] Japanese Unexamined Patent Application Publication 2007-258095

[Patent literature 5] Japanese Unexamined Patent Application Publication 2008-16243

[Patent literature 6] International Publication Number 2011/043296

[Outline of the invention]

[Problem to be solved by the invention]

[0011]

For positive electrode active material for secondary batteries exhibiting high energy density, the positive electrode active material particle powder with excellent high temperature overcharging and charge/discharge repeating characteristics, the manufacturing method thereof, and the secondary battery using the same, are currently the most in demand, but these have not yet been established.

[0012]

In other words, the technology described in Patent literature 1 does not precisely control the surface layer of active material particles, so it is difficult to say that the positive electrode active material with excellent high temperature overcharge characteristics and the manufacturing method are disclosed.

[0013]

Because the technology described in Patent literature 2 does not provide precise control of the phase containing nickel and manganese on the surface of lithium cobalt oxide, it is difficult to achieve high capacity, so it is difficult to say that a method of manufacturing positive electrode active substances for secondary batteries that exhibit high energy density and secondary batteries are disclosed.

[0014]

Regarding the technology described in Patent literature 3, it is difficult to achieve high capacity due to the presence of large amounts of nickel in lithium cobalt oxide, so it is difficult to say that a positive electrode active material for secondary batteries showing high energy density and secondary batteries are disclosed.

[0015]

Regarding the technology described in Patent Documents 4 and 5, it is hard to say that precise control of the coating layer of lithium cobalt oxide particles is established, and it is hard to say that positive electrode active materials and secondary batteries that have excellent stability when overcharged at high temperatures are disclosed.

[0016]

The technology described in Patent literature 6 is a method of making  $\text{Li}_2\text{TiO}_3$  crystals on the surface layer of lithium cobalt oxide particles accidentally by firing once, so the primary particles of lithium cobalt oxide particles are very small and cannot suppress cobalt ion elution, so it is hard to say that positive electrode active materials and secondary batteries that have excellent stability when overcharged at high temperatures are disclosed.

[0017]

Therefore, the technical challenge of the Present Invention is the provision of a positive electrode active material particle powder with excellent high temperature overcharging characteristics and charge/discharge repeating characteristics and its manufacturing method and a secondary battery using it by precisely controlling a small amount of coating layer with lithium cobalt as core particles while maintaining high capacity.

[Means for solving the problem]

[0018]

The technical challenge can be achieved by the invention as follows.

[0019]

A positive electrode active material particle powder characterized by having a surface layer consisting of a layered structure of lithium cobalt oxide core particles comprising element M (M is Mg and/or Al), and at least a layered structure of lithium cobalt oxide solidified by Ti, wherein the average layer thickness of the surface layer is 0.005 to 1.5  $\mu\text{m}$  and BET specific surface area is 0.02 to 0.25  $\text{m}^2/\text{g}$  (the Present Invention 1).

[0020]

And the Present Invention is the above positive electrode active material particle powder in the Present Invention 1 which has a top surface consisting of a water-soluble lithium oxide comprising element A (where A is at least one element selected from W, Mo, and B), and the top surface has a content of 0.01 to 0.5% by weight (the Present Invention 2).

[0021]

The Present Invention is also a positive electrode active material particle powder according to the Present Invention 1 or 2 having a volumetric median diameter of 10 to 35  $\mu\text{m}$  (the Present Invention 3).

[0022]

Also, the Present Invention is the positive electrode active material particle powder according to any one of Claims 1 to 3, wherein the remaining alkaline component is 800 ppm or less and the unreacted cobalt oxide is 500 ppm or less (the Present Invention 4).

[0023]

Also, the Present Invention also provides the positive electrode active material particle powder according to any one of the Present Invention 1 to 4, wherein the surface layer has a Ti concentration of 0.02 (the Present Invention 5).

[0024]

In addition, the Present Invention is a positive electrode active material particle powder according to any of the Present Invention 1 to 5, wherein the coating rate for the core particles of the surface layer is 80% or more (the Present Invention 6).

[0025]

Also, the Present Invention is a method of making positive electrode active material particle powder according to any of the Present Invention 1 to 6, and is characterized by a first process of mixing a lithium raw material, a cobalt raw material, and an element M raw material (M is Mg and/or Al), followed by firing at 800 to 1100° C to produce a lithium cobalt oxide particle powder having a layered structure and a second process of mixing the lithium cobalt oxide particles obtained in the first process, a titanium raw material, and a lithium raw material, followed by firing at 800 to 1100° C to form a surface layer (the Present Invention 7).

[0026]

The Present Invention is also a method of making a positive electrode active material particle powder according to any of the Present Invention 2 to 6, and is characterized by a first process of mixing a lithium raw material, a cobalt raw material, and an element M raw material (M is Mg and/or Al), followed by firing at 800 to 1100° C to produce a lithium cobalt oxide particle powder having a layered structure and a second process of mixing the lithium cobalt oxide particles obtained in the first process, a titanium raw material, a lithium raw material, and element A raw material (where A is at least one element selected from W, Mo, and B) followed by firing at 800 to 1100° C to form a surface layer and the top surface layer (the Present Invention 8).

[0027]

Also, the Present Invention is a nonaqueous electrolyte secondary battery made using at least some of the positive electrode active material of the positive electrode active material particle powder according to any of the Present Invention 1 to 6 (the Present Invention 9).

[0028]

Also, for the positive electrode active material particle powder according to any one of the Present Invention 1 to 6, there is a non-aqueous electrolyte secondary battery produced by using, as a positive electrode active material, a mixture containing 3 to 25% by weight of a positive electrode active material particle powder represented by  $\text{Li}(\text{Ni}_{1-a-b}\text{Co}_a\text{Mn}_b)\text{O}_2$  (a and b are 0.5) having a volume-based median diameter of aggregated particles of 1 to 7  $\mu\text{m}$ .  $0.15 \leq a \leq 0.4$ ,  $0.15 \leq b \leq 0.5$ .

[Effect of the invention]

[0029]

The positive electrode active material particle powder according to the Present Invention uses lithium cobalt oxide, which exhibits high capacity in the core particles, and is a positive electrode active material particle powder in which a trace amount of Ti is solidified in its surface layer to suppress the elution of cobalt ions during high temperature overcharging, so the secondary battery using this is excellent in terms of high temperature overcharging characteristics and charge/discharge repetition characteristics. Therefore, the positive electrode active material particle powder according to the Present Invention is suitable as a positive electrode active material for nonaqueous electrolyte secondary batteries.

[0030]

In addition, the positive electrode active material particle powder according to the Present Invention can form a phase that inhibits the reaction of lithium cobalt oxide with the electrolyte on its top surface, and can produce secondary batteries with excellent high temperature overcharge characteristics and charge/discharge repetition characteristics.

[Brief description of the drawings]

[0031]

[Figure 1] SEM photograph of the particle powder obtained in each process of Example of Embodiment 1 of the Present Invention. (1) lithium cobalt oxide particle powder obtained in the first process; (2) lithium cobalt oxide particle powder coated with titanium dioxide; and (3) positive electrode active material particle powder obtained in the second process

[Figure 2] The results of analysis of STEM photographs and energy-dispersed X-rays (EDX) taken after resin embedding of the positive electrode active material particle powder obtained in Example of Embodiment 1 and thinning with a focused ion beam (FIB) +005, +001 and +008 are the most common surfaces of the particles, while others are inside the particles. Italics are Ti/Co (mol%).

[Figure 3] After resin embedding the positive electrode active material particle powder obtained in Example of Embodiment 1, there is thinning with a focused ion beam (FIB), and an  $[0, -1, 0]$  analysis pattern in (1) +003 about 600 nm from the surface, analyzed by nanobeam electron diffraction (NED), (2) +002 about 250 nm from the surface, (3) +001 on the outermost surface of the particle. These measurement points correspond to the points shown in Figure 2.

[Figure 4] This is the result of resin embedding the positive electrode active material particle powder obtained in Example of Embodiment 1, followed by a cross section polymer (CP) being used to create a particle cross section, and point analysis using field emission Auger electron microscope (FE-AES). Point analysis yielded elemental concentrations in the range of about 0.02  $\mu\text{m}$ . Point analysis was performed from the particle surface at each point in the particle cross-section as shown in the FE-AES image shown in the figure, and the Ti differential format Auger spectral intensities were plotted against the distance from the particle surface.

[Figure 5] This is the result of Rietveld analysis of the X-ray diffraction pattern of the positive electrode active material particle powder obtained in Example of Embodiment 1. Calculated values are shown as solid lines for the measurement point (+). The difference between the measured and calculated values at each  $2\theta$  is shown as a curve at the lower stage. The peak position of lithium cobalt oxide under the X-ray diffraction pattern was indicated by a short line ( $\text{||}$ ), and the peak position of lithium cobalt oxide solidified by Ti was indicated by a long line ( $\text{||}$ ). The inset in the upper right is an enlarged portion of the X-ray diffraction pattern in the range of  $2\theta$  from  $43.5$  to  $46.5^\circ$ . This is an enlarged part of the range up to  $5^\circ$ , with the vertical axis as a logarithm, and the peak of the two phases as a dashed line. The vertical axis is logarithmic, and the peaks of the two phases are indicated by dashed lines.

[Figure 6] This is the result of having made the positive electrode active material particle powder obtained in Example of Embodiment 1 into a positive electrode, and performing a charge/discharge test at  $25^\circ\text{C}$  and 4.4 V using a coin cell.

[Figure 7] This is the result of having made the positive electrode active material particle powder obtained in Example of Embodiment 1 into a positive electrode, and repeatedly performing a charge/discharge test at  $25^\circ\text{C}$  and 4.4 V using a coin cell. This indicates the number of discharges on the horizontal axis and the discharge capacity maintenance rate with the initial discharge capacity of 100% on the vertical axis.

[Figure 8] This is the result of having made the positive electrode active material particle powder into a positive electrode, and performing a high temperature overcharge test at  $25^\circ\text{C}$  and 4.5 V using a coin cell. The origin of time was set immediately after the start of the 0.1C constant current charging test, and after reaching 4.5 V, the test was switched to the constant voltage test, and the amount of leakage electricity was calculated from the integrated current value per positive electrode active material weight for 14 to 72 hours.

[Mode For carrying out the invention]

[0032]

The construction of the Present Invention will be described in more detail as follows.

[0033]

First, the positive electrode active material particle powder according to the Present Invention is described.

[0034]

The positive electrode active material particle powder according to the Present Invention has a surface layer consisting of a core particle consisting of a layered structure of lithium cobalt oxide comprising elements M (Mg and/or Al), and at least lithium cobalt oxide solidified with titanium.

[0035]

The chemical formula of lithium cobalt oxide in a layered structure, which is the core particle of the positive electrode active material particles according to the Present Invention, is  $\text{Li}_{1+x}(\text{Co}_{1-y}\text{M}_y)\text{O}_2$  ( $x$  and  $y$  are  $0 < x \leq 0.1$ ,  $0 < y \leq 0.03$ , M is Mg and/or Al). By making the core particles lithium cobalt oxide, a positive electrode active material particle powder with a high energy density can be obtained.

[0036]

Excessive amounts of lithium when making lithium cobalt oxide relative to the amount of cobalt and added element M increase the primary particle size after firing and improve the high temperature overcharging properties of the battery. If

the value of x is less than or equal to 0, the primary particles of lithium cobalt oxide will become smaller, exacerbating the high temperature overcharge characteristics of the battery. Also, if the value of x exceeds 0.1, capacity cannot be secured and high energy density batteries cannot be designed. In addition, the residual alkali component of the positive electrode active material increases, resulting in gas generation due to electrolyte decomposition during charging.

[0037]

Also, the addition element M is at least one of Mg and Al, which are solidly dissolved in lithium cobalt oxide. In particular, Mg also has the effect of increasing the discharge capacity so the addition element M is more preferable. The high temperature overcharging characteristics of the battery can become favorable by adding a small amount of the addition element M. If the value of y is 0, there is no effect on the high temperature overcharging characteristics of the battery. Also, if the value of x exceeds 0.3, capacity cannot be secured and high energy density batteries cannot be designed.

[0038]

The surface layer of the positive electrode active material particle powder according to the Present Invention is at least lithium cobalt oxide of a layered structure solidified with Ti.

[0039]

The surface layer of the positive electrode active material particle powder according to the Present Invention has an average layer thickness of 0.005 to 1.5  $\mu\text{m}$ . If the layer thickness of the surface layer is less than 0.005  $\mu\text{m}$ , cobalt ion elution cannot be prevented and the high temperature overcharging characteristics are poor. If the layer thickness of the surface layer exceeds 1.5  $\mu\text{m}$ , it is difficult to secure capacity, and it is difficult to design batteries with high energy density. The layer thickness of the surface layer is preferably 0.01 to 1.3  $\mu\text{m}$ , more preferably 0.05 to 1.2  $\mu\text{m}$ .

[0040]

Previously, it was known that Ti has an effect that prevents the degradation of electrolytes. This time, it was found that Ti plays a role in preventing the elution of cobalt ions by solidifying it in the surface layer of lithium cobalt oxide crystals. In the surface layer of lithium cobalt oxide, the quadrivalent  $\text{Ti}^{4+}$  partially solidifies to the site of trivalent  $\text{Co}^{3+}$ , resulting in  $\text{Li}(\square_{a/3}\text{Co}_{1-4a/3}\text{Ti}_a)\text{O}_2$  with structural defects, which suppresses phase transition and crystal disintegration in the delithiated state. Here,  $\square$  means a hole.

[0041]

The Ti concentration of the surface layer is preferable 0.02. If the Ti concentration in the surface layer is  $\text{Ti}/\text{Co} < 0.001$ , the high temperature overcharge characteristics are not favorable. Also, for  $0.02 < \text{Ti}/\text{Co}$ , titanium that was not sufficiently soluble in the surface layer of lithium cobalt oxide forms  $\text{Li}_2\text{TiO}_3$ , reducing its capacity.

[0042]

Preferably, the coverage of the wick particles of the surface layer is 80% or greater. If the coverage rate was below 80%, the high temperature overcharge characteristics were poor.

[0043]

The positive electrode active material particle powder according to the Present Invention has a surface layer consisting of a core particle consisting of a layered structure of lithium cobalt oxide comprising the element M (Mg and/or Al), and a lithium cobalt oxide solid dissolved in titanium. It may also have a top surface composed of a water-soluble lithium oxide comprising element A (where A is at least one element selected from W, Mo, and B).

[0044]

The chemical formula of the lithium oxide present on the top surface of the positive electrode active material particle powder according to the Present Invention is  $\text{Li}_z\text{AO}_\delta$  (where A is at least one of Mo, W, and B; where A is Mo or W,  $z=2$ ,  $\delta=4$ ; where A is B,  $z=3$ ,  $\delta=3$ ). That is, if A is molybdenum (Mo), then  $\text{Li}_2\text{MoO}_4$ , if A is tungsten (W), then  $\text{Li}_2\text{WO}_4$ , and if A is boron (B), then  $\text{Li}_3\text{BO}_3$ . These compounds were quantified from the measurement results of soluble salts and residual alkaline components by the Walder method described below.

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[0045]

Since the lithium oxide present on the top surface exhibits solubility against carbon dioxide and water, it is believed that it traps carbon dioxide and water generated inside the battery under high temperature overcharge conditions, and inhibits gas swelling and electrolyte degradation of the battery. In addition, because the oxide exhibits resistance to hydrofluoric acid generated by the reaction of residual or generated water in the battery and the electrolyte, it is also thought to show a function to inhibit the collapse of lithium cobalt oxide crystals. Thus, it is possible to exhibit battery characteristics that are higher capacity and have better high temperature overcharging characteristics.

[0046]

The content of the lithium compound present on the top surface is preferably 0.01 to 0.5% by weight. If the content of the highest surface is less than 0.01% by weight, the effect is not seen in the battery characteristics, and if it exceeds 0.5% by weight, in some cases the capacity will decrease.

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[0047]

The positive electrode active material particle powder according to the Present Invention is a secondary particle in which the primary particles aggregate. As the primary particles grow, the edges specific to the layered structure can be observed, and it can be seen that they are close to the crystallite size. Therefore, the larger the primary particles, the better for the high temperature overcharge test. In addition, the larger the primary particles, the lower the BET specific surface area, which lowers the contact area with the electrolyte, which is favorable for the high temperature overcharge test.

[0048]

Preferably, the primary particles of the positive electrode active material particle powder according to the Present Invention have a particle size of 3  $\mu\text{m}$  or more. If it is less than that, the crystals will be weak, and it will be difficult to suppress crystal disintegration under high temperature overcharge conditions.

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[0049]

The median diameter of the volumetric basis of the secondary particles of the positive electrode active material particle powder according to the Present Invention is 10 to 35  $\mu\text{m}$ . If the median diameter is less than 10  $\mu\text{m}$ , the compressed mold density is lower, making it difficult to design a battery with a high energy density. It is difficult to obtain particle powders that meet other properties with a median diameter greater than 35  $\mu\text{m}$ . The median diameter is more preferably 11 to 30  $\mu\text{m}$ , and more preferably 12 to 25  $\mu\text{m}$ .

[0050]

The BET specific surface area of the positive electrode active material particles according to the Present Invention is 0.02 to 0.25  $\text{m}^2/\text{g}$ . It is currently difficult to produce particles with a BET specific surface area of less than 0.02  $\text{m}^2/\text{g}$ . When exceeding 25  $\text{m}^2/\text{g}$ , the contact area with the electrolyte becomes wider, and cobalt ion elution and gas generation from the positive electrode active material cannot be suppressed under high temperature overcharge conditions. The BET specific surface area is more preferably 0.07 - 0.23  $\text{m}^2/\text{g}$  and even more preferably 0.08 - 0.21  $\text{m}^2/\text{g}$ .

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[0051]

The remaining alkaline component in the positive electrode active material particle powder according to the Present Invention is preferably 800 ppm or less. If the value is exceeded, the alkalinity becomes high, which causes gelation when creating the electrode slurry, and adversely affects the battery characteristics.

[0052]

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The unreacted cobalt oxide  $\text{Co}_3\text{O}_4$  in the positive electrode active material particle powder according to the Present Invention is preferably 500 ppm or less. Exceeding this value will result in poor high temperature overcharging characteristics and difficulty in designing safe batteries.

[0053]

Desirably, the density of the compression-molded body at 2.5  $\text{ton}/\text{cm}^2$  of the positive electrode active material particle powder according to the Present Invention is 3.5 to 4.2  $\text{g}/\text{cc}$ . If under 3.5  $\text{g}/\text{cc}$ , it will be difficult to design batteries with high energy density. If over 4.2  $\text{g}/\text{cc}$ , it will be difficult to obtain particle powders that meet other properties.

[0054]

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In order to increase the compression mold density, it is acceptable to treat the positive electrode active material particle powder according to the Present Invention mixed with the positive electrode active material particle powder having a volumetric median diameter of 1 to 7  $\mu\text{m}$  at 3 to 25 weight by percent as the positive electrode active material. It is desirable that the positive electrode active material particle powder with a volumetric median diameter of 1 to 7  $\mu\text{m}$  be at least one of  $\text{LiCoO}_2$  and  $\text{Li}(\text{Ni}, \text{Co}, \text{Mn})\text{O}_2$ . If the volumetric median diameter is outside of the range of 1 to 7  $\mu\text{m}$ , it will be difficult to increase the compression mold density, so a high energy density battery cannot be obtained.

[0055]

For the positive electrode active material particle powder according to the Present Invention, it is desirable that the positive electrode active material to be mixed is  $\text{Li}(\text{Ni}_{1-a-b}\text{Co}_a\text{Mn}_b)\text{O}_2$  ( $a$  and  $b$  are  $0.15 \leq a \leq 0.4$ ,  $0.15 \leq b \leq 0.5$ ). When the value of  $a$  is less than 0.15 or the value of  $b$  exceeds 0.5, it becomes difficult to form the desired layered structure, and it therefore becomes difficult to function as high-performance positive electrode active material. Also, if the value of  $a$  exceeds 0.4 or if the value of  $b$  is less than 0.15, it will be a positive electrode active material that is inferior in the high temperature overcharge test, and there will be no mixing effect. The amount of each of  $\text{Li}$  and  $\text{O}$  of the positive electrode active material to be mixed may be slightly off the stoichiometric composition ratio of 1 and 2, and is not particularly limited.

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[0056]

For the positive electrode active material particle powder according to the Present Invention, the positive electrode active material to be mixed  $\text{Li}(\text{Ni}_{1-a-b}\text{Co}_a\text{Mn}_b)\text{O}_2$  ( $a$  and  $b$  are  $0.15 \leq a \leq 0.4$ ,  $0.15 \leq b \leq 0.5$ ) preferably has a median diameter of 1 to 7  $\mu\text{m}$  on a volume basis. No positive electrode active material with superior high temperature overcharge test is obtained at less than 1  $\mu\text{m}$ , and no positive electrode active material with improved compression mold density is obtained at more than 7  $\mu\text{m}$ .

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[0057]

For the positive electrode active material particle powder according to the Present Invention, the positive electrode active material to be mixed  $\text{Li}(\text{Ni}_{1-a-b}\text{Co}_a\text{Mn}_b)\text{O}_2$  ( $a$  and  $b$  are  $0.15 \leq a \leq 0.4$ ,  $0.15 \leq b \leq 0.5$ ) is preferably between 3 and 25% by weight. If it is less than 3% by weight, or greater than 25% by weight, no positive electrode active material with improved compression mold density is obtained.

[0058]

Next, the method of manufacturing the positive electrode active material particle powder according to the Present Invention is described.

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[0059]

The positive electrode active material particle powder according to the Present Invention is made based on a solid phase reaction method comprising two firings to form a multilayer structure of the particles. Solid phase reaction is a method of mixing raw materials containing the elements to be composed, promoting chemical reactions between solids by heat treatment at high temperatures, and obtaining the desired phase.

[0060]

The positive electrode active material particle powder according to the Present Invention can be manufactured by creating a layered structure of lithium cobalt oxide that becomes a core particle in the first firing, and forming a surface layer of lithium cobalt oxide solidified with  $\text{Ti}$  in the second firing in the particles. Also, the top surface of the lithium oxide comprising at least one of molybdenum, tungsten, and boron can be formed simultaneously with the top layer upon the second firing.

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[0061]

First, we will explain the first process. In the first process, the lithium and cobalt raw materials and element  $\text{M}$  materials ( $\text{M}$  is  $\text{Mg}$  and/or  $\text{Al}$ ) are mixed, then fired at 800 to 1100°C to produce a layered lithium cobalt oxide particle powder.

[0062]

Various compounds having constituent elements can be used as the raw materials for the lithium cobalt oxide particle powder of the core particles.

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[0063]

It is desirable to mix the raw materials of the core particles by a solvent-free dry method. High speed mixers, ball mills, Henschel mixers, raikai mixers, etc. can be used as mixing devices for raw material powders.

[0064]

$\text{LiOH}/\text{H}_2\text{O}$  and  $\text{Li}_2\text{CO}_3$  are preferred as lithium raw materials for core particles. It is desirable for the source powder of

lithium to use a fine particle size to facilitate the diffusion of lithium during the solid phase reaction.

[0065]

$\text{Co(OH)}_2$ ,  $\text{CoOOH}$  and  $\text{Co}_3\text{O}_4$  are preferred as cobalt raw materials for core particles. Since the cobalt raw materials powder particle size has a strong influence on the particle size of the positive electrode active material particle powder obtained in the Present Invention, it is preferred that the median diameter  $D_{50}$  be close to the desired positive electrode active material particle powder  $D_{50}$ .

[0066]

The additive element M (M is Mg and/or Al) of the core particles may be contained in the cobalt raw materials or an element M compound may be added. Oxides, hydroxides and carbonates are preferred for compounds of element M. For the raw material powder of the additive element M, fine particles with high solid-phase reactivity are desirable.

[0067]

The temperature of the first firing to obtain core particles is 800 to 1100°C. The firing time at this temperature is about 5 to 15 hours, and the temperature rise and fall rate of firing is about 100 to 200°C/hour. The solid phase reaction is not sufficient when the firing temperature is less than 800°C, so the capacity of the battery with the obtained positive electrode active material is extremely low. On the other hand, if the firing temperature exceeds 1100°C, the evaporation of lithium cannot be suppressed, causing chemical composition shifts, and promoting the deterioration of the electric furnace. The firing temperature is more preferably between 930 and 1050°C.

[0068]

For firing furnaces, gas distribution box type muffle furnaces, gas distribution type rotary furnaces, and roller hearth kilns, etc. can be used.

[0069]

After firing, it is acceptable to pulverize and classify the fired material. Pulverizing equipment includes raikai machines, impact micropulverizers, and fluid pulverizers.

[0070]

Next, the second process will be described. In the second process, the lithium cobalt oxide particle powder obtained in the first process is mixed with the titanium raw material and the lithium raw material, and then fired at 800 to 1100°C to form a surface layer to create the positive electrode active material particle powder according to the Present Invention.

[0071]

In addition, in the second process, after mixing the lithium cobalt oxide particle powder obtained in the first process with the titanium raw material, the element A raw material (where A is at least one element selected from W, Mo, and B) and the lithium raw material, the surface and top surface may be formed by firing at 800 to 1100°C.

[0072]

Various compounds having constituent elements can be used for the surface and top surface raw materials.

[0073]

Mixing of the surface layer and the top surface raw materials may be by dry or wet method.

[0074]

When mixing surface and top surface layer raw materials by dry method, high speed mixers, ball mills, Henschel mixers, raikai mixers, etc. can be used as mixing devices for raw material powders.

[0075]

When mixing the surface layer and the top surface raw material by wet method, it is desirable to use a water solvent to co-precipitate the constituent element oxide, hydroxide, or carbonate, and to wash, filter, and dry to obtain the mixed raw material powder.

[0076]

Therefore, when dry mixing is used, it is desirable to use oxides, hydroxides, and carbonates as the raw materials, and when wet mixing is used, it is desirable to use sulfate, nitrate, and chloride as the raw materials.

[0077]

Preferably, the top and top surface lithium raw materials are  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Li}_2\text{CO}_3$ .

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[0078]

Preferably, the surface layer titanium raw materials are  $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ ,  $\text{Ti}(\text{SO}_4)_2$ , and  $\text{TiCl}_4$ .

[0079]

Preferably, the raw materials of the top surface additive element A are molybdenum (Mo), tungsten (W), oxides of boron (B), hydroxides, carbonates, sulfates, nitrates, and chlorides.

[0080]

The second firing temperature to obtain the surface layer and top surface layer is 800 to 1100°C. The firing time at this temperature is about 5 to 15 hours, and the temperature rise and fall rate of firing is about 100 to 200°C/hour. The solid phase reaction is not sufficient when the firing temperature is less than 800°C, so the capacity of the battery with the obtained positive electrode active material is extremely low. On the other hand, if the firing temperature exceeds 1100°C, the evaporation of lithium cannot be suppressed, causing chemical composition shifts, and promoting the deterioration of the electric furnace. The firing temperature is more preferably between 850 and 1040°C.

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[0081]

For firing furnaces, gas distribution box type muffle furnaces, gas distribution type rotary furnaces, and roller hearth kilns, etc. can be used.

[0082]

By mixing the lithium cobalt oxide obtained in the first process with the raw materials of the surface layer and firing a second time, a crystal phase in which Ti is dissolved in the surface layer of the core particles is formed. Also, by firing a mixture of said lithium cobalt oxide, and the surface layer and the top surface raw material, a top surface is formed consisting of a water-soluble lithium oxide comprising element A at the same time as the top layer. The surface layer is also formed by Ti diffusing to the core particle surface.

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[0083]

After firing, it is acceptable to pulverize and sieve the fired material. Pulverizing equipment includes raikai machines, impact micropulverizers, and fluid pulverizers.

[0084]

Next, the nonaqueous electrolyte secondary battery using the positive electrode active material particle powder according to the Present Invention as the positive electrode active material is described.

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[0085]

When a positive electrode sheet is manufactured using a positive electrode active material particle powder according to the Present Invention, a conductive agent and a bonding agent are added and mixed according to the usual method. Carbon black, graphite, etc. are preferred as conductive agents. Polytetrafluorethylene, polyvinylidene fluoride, and the like are preferred as bonding agents. Preferably, for example, N-methyl-pyrrolidone is used as the solvent. The slurry containing the positive electrode active material particle powder, conductive material and the additive is kneaded until it is honey-like. The resulting positive electrode mixture slurry is applied to the current collector with a doctor blade with a groove of 25  $\mu\text{m}$  to 500  $\mu\text{m}$  at an application rate of about 60 cm/sec, and dried at 80 to 180°C for solvent removal and bonding softening. Use about 20  $\mu\text{m}$  Al foil for the current collector. A current collector coated with the positive electrode mixture is subjected to calendar roll treatment at a linear pressure of 0.1 to 3 t/cm to obtain a positive electrode sheet.

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[0086]

Because the positive electrode active material particle powder according to the Present Invention has a high compression mold density and a low BET ratio surface area of the positive electrode active material, the amount of bonding agent added to the positive electrode mixture slurry can be reduced, resulting in a high density positive electrode sheet. In addition, a higher density positive electrode sheet can be obtained by mixing a positive electrode active material with a small particle diameter of 1 to 7  $\mu\text{m}$  median diameter.

[0087]

For an negative electrode active material, lithium metal, lithium/aluminum alloy, lithium/tin alloy, graphite, etc. can be used, and a negative electrode sheet is made by the same doctor blade method as the positive electrode and by metal rolling.

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[0088]

Also, for electrolyte solvents, in addition to the combination of ethylene carbonate and diethyl carbonate, organic solvents can be used that include at least one type of carbonates such as propylene carbonate and dimethyl carbonate, and ethers such as dimethoxyethane.

[0089]

In addition, for electrolytes, at least one type of lithium salt, such as lithium perchlorate and lithium borate tetrafluoride, can be dissolved in the above solvent and used.

[0090]

The counter electrode Li secondary battery manufactured using the positive electrode active material according to the Present Invention has an initial discharge capacity of 170 mAh / g and 190 mAh / g or more respectively after charging at 4.4 V and 4.5 V at 25°C. Also, at 25° C., the 51st discharge capacity retention rates in charging at 4.4 V and 4.5 V and discharging up to 3.0 V are 85% and 80% or more, respectively. Furthermore, in the high temperature overcharge test of the evaluation method described below, the leakage electrical quantity at 60°C is 25mAh/g or less, indicating excellent battery characteristics.

[0091]

&lt;Effect &gt;

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The positive electrode active material particle powder according to the Present Invention uses lithium cobalt oxide, which exhibits high capacity in the core particles. Because the surface of the lithium cobalt oxide particle forms a layer in which trace amounts of Ti are solidly dissolved, the elution of cobalt ions can be suppressed, and secondary batteries with high capacity, excellent high temperature overcharge testing and charge/discharge repeatability can be manufactured.

[0092]

In addition, when the positive electrode active material particle powder according to the Present Invention has a lithium compound consisting of molybdenum, tungsten, and boron with a small amount of oxidation resistance on the surface of the particles, it suppresses the degradation of the electrolyte, so it is possible to manufacture a secondary battery with high capacity, excellent high temperature overcharge testing and charge/discharge repetition characteristics.

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[Examples of Embodiment]

[0093]

Examples of specific implementations of the Present Invention are shown below.

[0094]

Lithium carbonate  $\text{Li}_2\text{CO}_3$  with a purity of 99.4% manufactured by Toyo Chemicals Co., Ltd. was used. Cobalt oxyhydroxide  $\text{CoOOH}$  was prepared based on the following reference document, and a powder of  $D_{50} = 17.2 \mu\text{m}$  was obtained. The obtained cobalt oxyhydroxide had a purity of 94.7% as measured by chelate titration with EDTA (ethylenediaminetetraacetic acid). Magnesium hydroxide  $\text{Mg}(\text{OH})_2$  was manufactured by Ube Material Industries, Ltd. and aluminum hydroxide  $\text{Al}(\text{OH})_3$  was manufactured by Nippon Light Metal Company, Ltd. The amount of raw material charged was determined from these chemical formulas and purity.

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[0095]

&lt;Reference Document&gt;

Patent No. 5296948, Toda Kogyo Corp.

[0096]

Powder evaluation of the positive electrode active material particle powder of the Present Invention was carried out as follows.

[0097]

The content of lithium, cobalt, magnesium, aluminum, titanium, molybdenum, tungsten, and boron, which are the main constituent elements of the sample obtained in the first and second processes, was measured by the calibration curve method using an ICP emission spectrometry device (ICP-OES) Optima 8300 (the Perkin Elmer Corp.) after completely dissolving the sample powder with 20% hydrochloric acid.

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[0098]

JSM-7100 (JEOL Ltd.) scanning electron microscope SEM with an energy-dispersed X-ray analyzer was used to observe the surface of the sample and analyze the chemical composition.

[0099]

The BET specific surface area was determined by drying the sample under nitrogen gas at 120 °C for 45 minutes, followed by use of Macsorb (Mountech Co., Ltd.) Also, the BET equivalent particle size was calculated from the following formula (1). At this time, the particles were spherical, and 5.1 g/cc was used as the true density of lithium cobalt oxide.

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BET-equivalent particle size ( $\mu\text{m}$ ) =  $6/\text{BET value (m}^2/\text{g) / true density (g/cc) ... (1)$

[0100]

In order to confirm the crystal structure and composition near the surface layer of the sample, resin embedding treatment was performed and it was fragmented with JEM-9320 (JEOL Ltd.) of FIB (focused ion beam) at 100 nm or less. Observation was performed using NED (nano-electron diffraction) attached to an transmission electron microscope TEM JEM-2100 (JEOL, Ltd.) and EDX (energy dispersive x-ray spectrometry).

[0101]

In order to calculate the solid solution area of Ti on the surface layer of the sample, i.e. the layer thickness of the surface layer in which Ti was dissolved, the particle powder was embedded in the resin, and the particles were cut with a cross section polisher (CP) SM-09010 (JEOL Ltd.), and then observed with a field-emission scanning electron microscope FE-AES JAMP-9500F (JEOL Ltd.). The acceleration voltage was 20 kV, and the irradiation current was 4 nA, so it was possible to analyze a depth direction of several nm in the range of 20 nm  $\phi$  at the cross-section point. For energy ranges, Ti was measured at 355-435 eV and Co was measured at 730-800 eV. Each was measured 10 times to obtain an averaged spectrum. The resulting spectrum is the product of  $E$  and  $N(E)$  for the energy  $E$  of the electrons. Here,  $N(E)$  is the distribution of energy.

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[0102]

As shown in Figure 4(1), point analysis was performed linearly from the surface of the particles towards the interior of the particles in the sample cross section, and the intensity  $d[E \cdot N(E)]/dE$  of the differential form spectrum with a minimum around 385 eV due to Ti was read. That is, in Figure 4(1), the spectral intensity of the particle surface is 82. The further inside the particle, the spectral intensity dropped to 33, 20, 18, 16. As shown in Figure 4(2), the spectral intensities were plotted relative to the distance from the particle surface at 11 points, with the spectral intensities of 30 or less as the detection limit for Ti, and the distance from the surface was defined as the layer thickness of the surface layer in which Ti at each point was dissolved. The average of the layer thicknesses according to the arithmetic average is shown in Table 1. From the number of Ti detected relative to the number of measurement points, the percent coverage to the core particles is listed in Table 1.

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[0103]

Similarly, at any 10 to 14 points for each sample, the same point analysis and plot of Figure 4(2) as in Figure 4(1) were performed, and the average layer thickness and coverage rate of the surface layer of each sample were calculated and described in Table 1.

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[0104]

The Ti/Co ratio of the sample obtained in the ICP emission spectroscopy was determined to correspond to the Ti/Co ratio of the surface layer and the Co amount of the core particles of the BET-equivalent particle size assuming the above-mentioned true spherical particles. As the average layer thickness obtained by the above described method was formed, the volume of the core particles and the volume of the surface layer were calculated, and the Ti/Co (mol ratio) of the surface layer was calculated and described in Table 1.

[0105]

To confirm the crystal phase of the sample, it was measured using the powder X-ray diffraction device SmartLab (Rigaku Corporation). The X-ray diffraction pattern is measured through a monochromator under conditions of  $\text{Cu-K}\alpha$ , 45kV, and 200mA, and measurement was performed in the range of  $2\theta$  from 15 to 90° with a counting time of 1.0 second in process of 0.01° so that the count number of the highest peak intensity was 6000 to 12000. SRM660b from the National Institute of Standards and Technology (NIST) was used as the external standard sample, and RIETAN2000 was used in the Rietveld analysis program.

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[0106]

As a measurement method for water-soluble salt, 5 g of the sample was cooled to room temperature by boiling with 100 cc pure water for 20 minutes, filtered, and then analyzed using an ICP emission spectroscopy analyzer. Since the laminar structure of lithium cobalt oxide and lithium cobalt titanate is insoluble in water, the amount of elemental water-soluble compounds exposed to the top surface can be measured by measuring water-soluble salts. As a water-soluble salt, the amount of Li, W, Mo, and B detected and the amount of residual alkaline component according to the Walder method described below can be estimated to be the compound formed on the top surface. That is, the top surface is a compound represented by  $\text{Li}_z\text{AO}_\delta$  (A is at least one of W, Mo, B,  $z=2$ ,  $\delta=4$  if A is W and/or Mo,  $z=3$ ,  $\delta=3$  if A is B),  $\text{Li}_2\text{WO}_4$ ,  $\text{Li}_2\text{MoO}_4$ , and  $\text{Li}_3\text{BO}_3$ .

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[0107]

As the remaining alkaline component, the amount of lithium hydroxide and lithium carbonate obtained by the Walder method was converted to the amount of lithium carbonate. That is, 10.0 g of the sample was dispersed in 50 ml of water for 1 hour, then allowed to stand for 1 hour, and then the supernatant was titrated with hydrochloric acid. Lithium hydroxide and lithium carbonate were quantified using phenolphthalein and bromophenol blue as indicators at that time, and all of them were converted into amounts of lithium carbonate. However, the effects of the above-mentioned  $\text{Li}_2\text{WO}_4$ ,  $\text{Li}_2\text{MoO}_4$ , and  $\text{Li}_3\text{BO}_3$  have been calculated and excluded.

[0108]

The quantification of unreacted cobalt oxide  $\text{Co}_3\text{O}_4$  utilized differences in solubility of cobalt oxide and lithium cobalt oxide in iron sulfate solutions. That is, after the sample was dispersed in an iron sulfate solution and left for 1 hour, the undissolved component was considered unreacted cobalt oxide. The undissolved component was filtered by a filter, the residue on the filter was dissolved in hydrochloric acid, then the amount of cobalt was quantified using an ICP emission spectroscopy device, and converted to cobalt oxide  $\text{Co}_3\text{O}_4$ .

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[0109]

The median diameter  $D_{50}$  of the sample was measured using the Microtrac HRA (Nikkiso Co., Ltd) wet method laser diffraction and scattering particle size distribution meter.

[0110]

The density of the compression molded body was calculated from the weight and volume of the molded body by compacting a 5 g sample with a jig of 10 mm $\phi$  under a pressure of 2.5 t/cm<sup>2</sup>.

[0111]

The positive electrode was prepared using the resulting positive electrode active material particle powder with the following manufacturing method to evaluate the secondary battery properties in the CR2032 coin cell.

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[0112]

The positive electrode active material and the conductive agent acetylene black, graphite and the binder polyvinylidene fluoride were weighed to a weight ratio of 94:3:3, dispersed in N-methyl-2-pyrrolidone, and thoroughly mixed with a high-speed kneading device to prepare the positive electrode mixture slurry. The combination slurry is then applied to the aluminum foil of the current collector with a doctor blade, dried at 120°C, and pressurized to 0.5 t/cm to prepare a positive electrode sheet having a thickness of about 40  $\mu\text{m}$ . The positive electrode sheet was punched to 16 mm  $\phi$  to make the positive electrode.

[0113]

A metal lithium foil (Honjo Metal K.K.) punched to a diameter of 16 mm was used as the negative electrode.

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[0114]

Celgard #2400 (Celgard, LLC) 20 mm  $\phi$  was used as the separator. A mixed solvent of EC and DMC (ethylene carbonate: dimethyl carbonate = 1:2 volume ratio) dissolved in 1 mol/l  $\text{LiPF}_6$  was used as the electrolyte. These components were assembled to create a CR2032 coin cell (Hosen Corporation).

[0115]

The batteries were assembled in an argon-like glove box to prevent electrolytes and metallic lithium from decomposing due to the atmosphere.

[0116]

The initial discharge capacity at 25° C and the discharge capacity retention rate were measured under the two conditions of 3.0V as the lower limit of the discharge voltage and 4.4V and 4.5V as the upper limit of the charge voltage. After charging with a constant current and reaching each upper limit voltage, charging was finished when the charging current fell below 0.025 C with the upper limit voltage. The 1st, 11th, 21st, 31st, 41st, and 51st charge/discharge is performed at 0.2C, and the value obtained by dividing the first discharge capacity by the initial discharge capacity and the 51st discharge capacity by the first discharge capacity was evaluated as the discharge capacity retention rate.

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[0117]

In the high-temperature overcharge test, after charging at a constant current of 0.1 C to 4.5 V at 60° C., the current value was changed while maintaining 4.5 V. Current values from 14 hours to 72 hours after the start of charging were accumulated to determine the leakage electrical quantity per positive electrode active material weight. If the battery had a short circuit within 72 hours of starting charging, the test was terminated when the short circuit occurred.

[0118]

The amount of Co elution from the positive electrode active material at high temperature overcharge was quantified. That is, a battery was assembled using negative electrode graphite, then after charging to 4.4 V at 60° C. and 0.1 C constant current, the current value was varied while maintaining the same voltage, and after 72 hours, the battery was taken out and disassembled. The negative electrode and the amount of Co precipitated in the separator were then quantified by ICP emission spectroscopy.

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[0119]

[Embodiment 1]

(First process)

The raw material was weighed so that  $\text{Li}_2\text{CO}_3$ ,  $\text{CoOOH}$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$  is  $\text{Li}/(0.990\text{Co}+0.005\text{Mg}+0.005\text{Al})$  at a mol ratio, and the total weight of each raw material is 3.0 kg. The raw materials were mixed for 20 minutes to visually confirm that there was no unevenness in the mixed raw materials in the volume, and ICP emission spectroscopy confirmed that there was no compositional deviation. The mixed raw materials were placed in a sagger and fired in a firing furnace at 980° C. for 10 hours. The resulting fired matter was pulverized and classified to produce a lithium cobalt oxide particle powder dissolved by Mg and Al.

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[0120]

As shown in Figure 1(1), the SEM photograph shows little unevenness on the surface of the resulting lithium cobalt oxide particles. After dissolving the resulting lithium cobalt oxide particle powder in an acid solution, the content of each element was measured by ICP emission spectroscopy, and the composition of the resulting lithium cobalt oxide was  $\text{Li}_{1.05}(\text{Co}_{0.990}\text{Mg}_{0.005}\text{Al}_{0.005})\text{O}_2$ . These values were consistent with those expected from the raw materials.

[0121]

(Second process)

100 g of the obtained lithium cobalt oxide particle powder was weighed, and 0.2 mol % titanium dioxide ( $\text{Ti}/\text{Co}=0.002$  mol ratio, manufactured by Millennium Inorganic Chemicals, PC-500, 250m<sup>2</sup>/g) was mixed with cobalt in a ball mill for 1 hour.

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[0122]

SEM photos after mixing are shown in Figure 1(2). From Figure 1(2), it was confirmed that fine titanium dioxide completely covered the lithium cobalt oxide particles and had a high coverage.

[0123]

The coated product was placed in a crucible and refired in a box-type muffle furnace at 1000° C. for 5 hours. The material was ground with a mortar and sieved with a 45 μm mesh to obtain the positive electrode active material particle powder of the Present Invention (see Figure 1(3)). Element analysis was performed with an ICP emission spectroscopy device to obtain a Li/Co ratio and a Ti/Co ratio consistent with the charge amount.

[0124]

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Figures 2 and 3 show the results of analysis of STEM-EDX-NED for the particles of Example of Embodiment 1. As previously described, Ti diffused into lithium cobalt oxide particles, and the concentration of Ti was tilted from the surface of the active material particles toward the interior. That is, it was found that lithium cobalt oxide was formed in a layered structure with Ti dissolved in the surface layer.

[0125]

Figure 4 shows the FE-AES analysis results of the particle cross section of Example of Embodiment 1. Point analysis at point A as shown in Figure 4(1) showed that Ti was detectable near the particle surface from the spectral intensities in the differential form. As shown in Figure 4(2), the layer thickness of the surface layer in which Ti was dissolved was estimated to be a distance of 1.05 μm from the particle surface, that is to say, a place where the intensity of point A is 30 or less. Similarly, at any B-K point, point analysis was performed in the direction of the inside of the particles and extrapolated to estimate the layer thickness of the Ti dissolved layer. The average of the layer thickness at each point is 0.9 μm. The BET equivalent particle size is 9.8 μm, and the volume forming the average layer thickness is equivalent to 45.6% of the volume of particles consisting of a BET-equivalent particle size. Therefore, from the Ti/Co ratio by ICP emission spectroscopy, the average Ti/Co ratio of the layer was estimated to be 0.004 mol.

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[0126]

As shown in Figure 5, the presence of two phases of lithium cobalt oxide with layered structure from the lattice

constant obtained by the Rietveld analysis and lithium cobalt oxide with solid titanium dissolved was confirmed. The lattice constants of the lithium cobalt oxide obtained in the first process are  $a=2.8164 \text{ \AA}$  and  $c=14.057 \text{ \AA}$ , and the lattice constants of the lithium cobalt oxide obtained in the second process are  $a=2.8161 \text{ \AA}$  and  $c=14.056 \text{ \AA}$ , almost the same as the value obtained in the first process. Therefore, the composition of the lithium cobalt oxide obtained in the first process was regarded as the composition of the core particles. In addition, the lattice constants of the surface layer are  $a=2.819 \text{ \AA}$  and  $c=14.07 \text{ \AA}$ , and the lattice constants  $a$  and  $c$  of the surface layer are longer than those of the core particles, so it was presumed that the surface layer was lithium cobalt oxide in which titanium was dissolved.

[0127]

As shown in Table 2, residual alkali and unreacted cobalt oxide, which are the powder properties of the obtained positive electrode active material particle powder, were low, the median diameter was large, and high compression mold density was obtained.

[0128]

The obtained particle powder was positively polarized and evaluated using a coin cell. As shown in Table 3, the results were that the initial discharge capacity was high, the charge/discharge repetition characteristics were good, and the high temperature overcharge test results were good. The amount of cobalt ions eluted from the graphite negative electrode at  $60^\circ \text{C}$  was  $0.20 \text{ wt\%}$  with respect to the positive electrode active material, and the eluted amount was suppressed as compared with Comparative Example 1 described later.

[0129]

For the following Examples of Embodiment and Comparative Examples as well, powder properties are shown in Tables 1 and 2, and battery properties are shown in Table 3.

[0130]

[Embodiments 2-4]

When preparing the core particle lithium cobalt oxide, raw materials were weighed so that the  $\text{Li}/(0.0025\text{Mg}+0.0075\text{Al})=1.02$  mol ratio was obtained. and the total weight of each raw material is  $3.0 \text{ kg}$ . Other conditions were treated in the same manner as Example of Embodiment 1, with the firing temperature in the second process being  $1050^\circ \text{C}$  for Example of Embodiment 2,  $1000^\circ \text{C}$  for Example of Embodiment 3, and  $950^\circ \text{C}$  for Example of Embodiment 4. As a result, good powder properties and battery properties were obtained. However, Example of Embodiment 2 had too much dissolution of Ti, or there were some particle surfaces on which Ti could not be detected, so the coating rate was slightly reduced. As a result, the leakage electrical quantity at  $60^\circ \text{C}$  from the high temperature overcharge test was slightly higher.

[0131]

[Embodiments 5-7]

When preparing the core particle lithium cobalt oxide, raw materials were weighed so that the  $\text{Li}/(0.0025\text{Mg}+0.0075\text{Al})=1.02$  mol ratio was obtained. Raw materials were weighed so that  $995 \text{ Co} + 0.005 \text{ Mg} = 1.03$  mol ratio. Other conditions in the first process were treated in the same way as Example 1. In the second process,  $100 \text{ g}$  of the resulting lithium cobalt oxide was weighed, and  $0.1 \text{ mol \%}$  titanium dioxide was ball-mill mixed with cobalt. In Examples of Embodiment 5, 6, and 7, submicron  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{H}_3\text{BO}_3$  and a predetermined amount of  $\text{Li}_2\text{CO}_3$  were mixed in a ball mill so that each of Mo, W, and B, which could be the top surface phase, was  $0.1 \text{ mol \%}$  with respect to cobalt. Here, the predetermined amount is the amount of mol of Li that  $\text{Li}_2\text{MoO}_4$ ,  $\text{Li}_2\text{WO}_4$ ,  $\text{Li}_3\text{BO}_3$  can form. The firing temperature in the second process was set to  $950^\circ \text{C}$ . SEM-EDX analysis of the resulting positive electrode active material particle powder revealed that Mo, W, B are on the particle surface. Also, by ICP emission analysis, water-soluble Mo, W, and B were 88, 91, and 83% of the Mo, W, and B amounts in the sample. Good powder and battery characteristics were obtained as shown in Tables 1-3.

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[0132]

[Embodiment 8]

When preparing the core particle lithium cobalt oxide, raw materials were weighed so that the  $\text{Li}/(0.0025\text{Mg}+0.0075\text{Al})=1.02$  mol ratio was obtained. Raw materials were weighed so that there would be an 0.25mol ratio. Other conditions in the first process were treated in the same way as Example 1. In the second process, 100 g of the resulting lithium cobalt oxide was weighed, 2 mol % titanium dioxide was mixed in a ball mill and fired at 950°C. As a result, good powder and battery characteristics were obtained as shown in Tables 1-3.

[0133]

[Embodiment 9]

The particle powder of lithium cobalt oxide obtained in Example of Embodiment 8 was 85% by weight, and  $\text{Li}_{1.03}\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  having a volume-based median diameter of 3.4  $\mu\text{m}$  was mixed to 15% by weight, and the mixture was used as a positive electrode active material. A high value of 3.97 g/cc was obtained for the compression molding density. Battery characteristics were evaluated and showed high initial discharge capacity and low leakage electrical capacity as shown in Table 4.

[0134]

[Embodiment 10]

The particle powder of lithium cobalt oxide obtained in Example of Embodiment 8 was 85% by weight, and A high value of  $\text{Li}_{1.06}\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.91}\text{g/cc}$  was obtained. A high value of 3.97 g/cc was obtained for the compression molding density. Battery characteristics were evaluated and showed high discharge capacity and low leakage electricity as shown in Table 4.

[0135]

[Comparative Example 1]

Lithium cobalt oxide obtained in the first process of Example of Embodiment 1 was used as a positive electrode active material. That is, there is no layered compound comprising titanium in the surface layer of the particles of the Present Invention, and no heterogenous phase consisting of molybdenum, tungsten, or boron on the top surface. As a result, The initial discharge capacity and discharge capacity maintenance rate of 4.5V were poor, and the leakage electrical quantity at 60°C was high. The amount of cobalt ions eluted from the graphite negative electrode at 60° C was 0.37 wt% with respect to the positive electrode active material, which was a high value compared with Comparative Example 1.

[0136]

[Comparative Example 2]

$\text{Li}_2\text{CO}_3$ ,  $\text{CoOOH}$ , and  $\text{Mg}(\text{OH})_2$  were weighed to have an  $\text{Li}/(0.996\text{Co}+0.004\text{Mg})=0.996$  mol ratio. Here, submicron  $\text{ZrO}_2$  ( $\text{Zr}/\text{Co}=0.1$  mol %) was added to suppress particle growth. The raw materials were mixed, fired at 980°C, pulverized, and separated, and the lithium cobalt oxide obtained only in the first process was used as the positive electrode active material particle powder. No solid dissolution of Zr in lithium cobalt oxide was observed in the resulting positive electrode active material particle powder. In addition, the primary particle size was small at 2  $\mu\text{m}$  by SEM observation, so the BET specific surface area was high, but the  $D_{50}$  was slightly larger. As a result, although the initial discharge capacity and discharge capacity maintenance rate were high, the amount of electrical leakage was high.

[0137]

[Comparative Example 3]

$\text{Li}_2\text{CO}_3$ ,  $\text{CoOOH}$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{TiO}_2$  were weighed to have an  $\text{Li}/(0.985\text{Co}+0.01\text{Ti})=1.02$  mol ratio. 01Ti) = 1. The raw materials were mixed, fired at 1000°C, pulverized, and classified, and the lithium cobalt oxide obtained only in the first process was used as the positive electrode active material particle powder. When the obtained positive electrode active material particle powder was confirmed by XRD, a layered structure single phase was obtained, and a lattice constant with an a-axis of 2.8176 Å and a c-axis of 14.067 Å due to Ti dissolution was obtained. In addition, the primary particle size by SEM observation was small at 2  $\mu\text{m}$ , so the BET specific surface area was high, but the  $D_{50}$  was slightly larger. As a result, the initial discharge capacity and discharge capacity maintenance rate were also low, and the leakage electrical quantity was high.

[0138]

[Comparative Example 4]

Measure 100 g of the lithium cobalt oxide particle powder obtained in Comparative Example 2, and mix 0.2 mol % titanium dioxide with cobalt and re-fire at 1000°C. As a result, although particles with titanium dissolved in the surface layer of lithium cobalt oxide particles were obtained, the primary particle size was approximately the same as in Comparative Example 2, and did not improve. In addition, due to the small primary particle size, the surface treatment with titanium dioxide was insufficient, so the coating rate of the core particles of the surface layer dissolved with Ti was reduced. As a result, the initial discharge capacity and discharge capacity maintenance rate were good as battery characteristics, but the leakage electrical quantity was high.

[0139]

[Comparative Example 5]

100 g of the lithium cobalt oxide obtained in the first process of Example of Embodiment 2 was mixed with 0.2 mol % of  $\text{MoO}_3$  relative to cobalt and a predetermined amount of  $\text{Li}_2\text{CO}_3$  in a ball mill, and then fired at 1050°C. The surface coating state was inferior in terms of oxidation resistance, or the initial discharge capacity was high, but the discharge capacity maintenance rate was low and the leakage electrical quantity was high.

[0140]

[Comparative Example 6]

$\text{Li}_2\text{CO}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ , and Li/ (0. and the total weight of each raw material is 3.0 kg. wherein the fine particles  $\text{Co}_3\text{O}_4$  ( $D_{50}=2.4 \mu\text{m}$ ) was used. The raw materials were mixed, baked at 920°C, pulverized, and classified, and the lithium cobalt oxide obtained only in the first process was used as the positive electrode active material particle powder. The resulting positive electrode active material particle powder had a high BET specific surface area, high residual alkali components, high unreacted cobalt oxide, low  $D_{50}$ , and low compression mold density. This can be assumed to be due to the low firing temperature. As a result, although the initial discharge capacity and discharge capacity maintenance rate were high, the amount of electrical leakage was high.

[0141]

[Comparative Example 7]

$\text{Li}_{1.03}\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  having a volume-based median diameter of  $3.4 \mu\text{m}$  was mixed to 15% by weight, and the mixture was used as a positive electrode active material. Mixing was performed so that the positive electrode active material particle powder obtained in Comparative Example 1 was 85% by weight and  $3.333\text{Co}_{0.333}\text{Mn}_{0.333}\text{O}_2$  having a volume-based median diameter of [text missing] is 15% by weight, and this compound was used as a positive electrode active material. A high value of 3.97 g/cc was obtained for the compression molding density. Battery characteristics were evaluated, and as shown in Table 4, high discharge capacity was shown, but the capacity maintenance rate was low so high leakage electrical capacity was shown.

[0142]

[Comparative Example 8]

A high value of  $\text{Li}_{1.06}\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.91}\text{g/cc}$  was obtained. A high value of  $_{05}\text{Ni}_{0.}$  A high value of 3.97 g/cc was obtained for the compression molding density. 90g/cc was obtained. Battery characteristics were evaluated, and as shown in Table 4, high discharge capacity was shown, but the capacity maintenance rate was low so high leakage electrical capacity was shown.

[0143]

[Table 1]

|                         | Core particles<br>$\text{Li}_{1+x}(\text{Co}_{1-y}\text{M}_y)\text{O}_2$ |         |       | Ti-dissolved surface layer      |                  |                 | BET<br>specific<br>surface<br>area | Top surface<br>$\text{Li}_2\text{AO}_\delta$ |                  |
|-------------------------|--------------------------------------------------------------------------|---------|-------|---------------------------------|------------------|-----------------|------------------------------------|----------------------------------------------|------------------|
|                         | x                                                                        | M       | y     | Average<br>surface<br>thickness | Average<br>Ti/Co | Coating<br>rate |                                    | A                                            | Content          |
|                         |                                                                          |         |       | [ $\mu\text{m}$ ]               | [mol ratio]      | [%]             |                                    |                                              | [Weight<br>by %] |
| Example of Embodiment 1 | 0.05                                                                     | 1Mg+1Al | 0.010 | 0.9                             | 0.004            | 100             | 0.12                               | -                                            | -                |
| Example of Embodiment 2 | 0.02                                                                     | 1Mg+3Al | 0.010 | 0.3                             | 0.009            | 86              | 0.16                               | -                                            | -                |
| Example of Embodiment 3 | 0.02                                                                     | 1Mg+3Al | 0.010 | 0.6                             | 0.005            | 100             | 0.16                               | -                                            | -                |
| Example of Embodiment 4 | 0.02                                                                     | 1Mg+3Al | 0.010 | 0.4                             | 0.006            | 100             | 0.17                               | -                                            | -                |
| Example of Embodiment 5 | 0.03                                                                     | Mg      | 0.005 | 0.1                             | 0.001            | 90              | 0.14                               | Mo                                           | 0.16             |
| Example of Embodiment 6 | 0.03                                                                     | Mg      | 0.005 | 0.1                             | 0.001            | 90              | 0.14                               | W                                            | 0.24             |
| Example of Embodiment 7 | 0.03                                                                     | Mg      | 0.005 | 0.1                             | 0.001            | 90              | 0.13                               | B                                            | 0.07             |
| Example of Embodiment 8 | 0.025                                                                    | Mg      | 0.005 | 0.7                             | 0.003            | 100             | 0.13                               | -                                            | -                |
| Comparative Example 1   | 0.05                                                                     | 1Mg+1Al | 0.010 | -                               | -                | 0               | 0.16                               | -                                            | -                |
| Comparative Example 2   | -0.004                                                                   | Mg      | 0.004 | -                               | -                | 0               | 0.31                               | -                                            | -                |
| Comparative Example 3   | 0.02                                                                     | 1Mg+2Ti | 0.015 | -                               | -                | 0               | 0.33                               | -                                            | -                |
| Comparative Example 4   | -0.004                                                                   | Mg      | 0.004 | 0.3                             | 0.002            | 86              | 0.31                               | -                                            | -                |
| Comparative Example 5   | 0.02                                                                     | 1Mg+3Al | 0.010 | -                               | -                | 0               | 0.18                               | Mo                                           | 0.27             |
| Comparative Example 6   | 0.02                                                                     | 1Mg+1Al | 0.010 | -                               | -                | 0               | 0.90                               | -                                            | -                |

[0144]

[Table 2]

|                         | Residual alkaline<br>components | Unreacted cobalt oxide | Median diameter $D_{50}$ | Compression mold<br>density |
|-------------------------|---------------------------------|------------------------|--------------------------|-----------------------------|
|                         | [ppm]                           | [ppm]                  | [ $\mu\text{m}$ ]        | [g/cc]                      |
| Example of Embodiment 1 | 421                             | 150                    | 18.4                     | 3.85                        |
| Example of Embodiment 2 | 356                             | 362                    | 14.3                     | 3.74                        |
| Example of Embodiment 3 | 492                             | 309                    | 14.2                     | 3.74                        |
| Example of Embodiment 4 | 652                             | 179                    | 13.9                     | 3.74                        |
| Example of Embodiment 5 | 371                             | 100                    | 15.6                     | 3.75                        |
| Example of Embodiment 6 | 330                             | 187                    | 15.5                     | 3.76                        |
| Example of Embodiment 7 | 607                             | 162                    | 14.5                     | 3.75                        |
| Example of Embodiment 8 | 551                             | 242                    | 15.7                     | 3.78                        |
| Comparative Example 1   | 650                             | 59                     | 18.2                     | 3.76                        |
| Comparative Example 2   | 348                             | 85                     | 15.2                     | 3.77                        |
| Comparative Example 3   | 2976                            | 158                    | 15.3                     | 3.79                        |
| Comparative Example 4   | 550                             | 180                    | 14.5                     | 3.74                        |
| Comparative Example 5   | 476                             | 74                     | 13.8                     | 3.77                        |
| Comparative Example 6   | 973                             | 644                    | 3.8                      | 3.43                        |

[0145]

[Table 3]

|                         | 25°C initial discharge capacity |         | 25°C discharge capacity maintenance rate |      | 60°C leakage electrical quantity |
|-------------------------|---------------------------------|---------|------------------------------------------|------|----------------------------------|
|                         | 4.4V                            | 4.5V    | 4.4V                                     | 4.5V | 4.5V                             |
|                         | [mAh/g]                         | [mAh/g] | [%]                                      | [%]  | [mAh/g]                          |
| Example of Embodiment 1 | 171                             | 190     | 89                                       | 81   | 16                               |
| Example of Embodiment 2 | 172                             | 191     | 87                                       | 85   | 24                               |
| Example of Embodiment 3 | 172                             | 191     | 89                                       | 85   | 17                               |
| Example of Embodiment 4 | 172                             | 190     | 90                                       | 82   | 19                               |
| Example of Embodiment 5 | 173                             | 191     | 85                                       | 80   | 18                               |
| Example of Embodiment 6 | 173                             | 192     | 87                                       | 78   | 17                               |
| Example of Embodiment 7 | 174                             | 193     | 89                                       | 85   | 20                               |
| Example of Embodiment 8 | 175                             | 193     | 87                                       | 79   | 17                               |
| Comparative Example 1   | 170                             | 186     | 87                                       | 78   | 31                               |
| Comparative Example 2   | 177                             | 196     | 91                                       | 83   | Short circuit during test        |
| Comparative Example 3   | 172                             | 182     | 77                                       | 64   | 59                               |
| Comparative Example 4   | 176                             | 195     | 94                                       | 85   | 286                              |
| Comparative Example 5   | 172                             | 190     | 80                                       | 68   | 33                               |
| Comparative Example 6   | 174                             | 192     | 87                                       | 81   | Short circuit during test        |

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[0146]

[Table 4]

|                          | Lithium cobalt oxide    | Li(Ni <sub>1-a-b</sub> Co <sub>a</sub> Mn <sub>b</sub> )O <sub>2</sub> |       |       |                       | Compr<br>ession<br>mold<br>density<br>[g/cc] | 25°C initial discharge capacity |                 | 25°C capacity maintenance rate |             | 60°C leakage electrical quantity |
|--------------------------|-------------------------|------------------------------------------------------------------------|-------|-------|-----------------------|----------------------------------------------|---------------------------------|-----------------|--------------------------------|-------------|----------------------------------|
|                          |                         | D <sub>50</sub><br>[μm]                                                | a     | b     | Content<br>[Weight %] |                                              | 4.4V<br>[mAh/g]                 | 4.5V<br>[mAh/g] | 4.4V<br>[%]                    | 4.5V<br>[%] |                                  |
| Example of Embodiment 9  | Example of Embodiment 8 | 3.4                                                                    | 0.2   | 0.3   | 15                    | 3.97                                         | 177                             | 194             | 83.4                           | 78.3        | 16                               |
| Example of Embodiment 10 | Example of Embodiment 8 | 3.5                                                                    | 0.3   | 0.3   | 15                    | 3.91                                         | 176                             | 191             | 84.9                           | 79.5        | 17                               |
| Comparative Example 7    | Comparative Example 1   | 3.4                                                                    | 0.333 | 0.333 | 15                    | 3.91                                         | 170                             | 183             | 73.2                           | 67.3        | 28                               |
| Comparative Example 8    | Comparative Example 1   | 3.5                                                                    | 0.3   | 0.3   | 15                    | 3.90                                         | 171                             | 183             | 71.5                           | 70.0        | 26                               |

[0147]

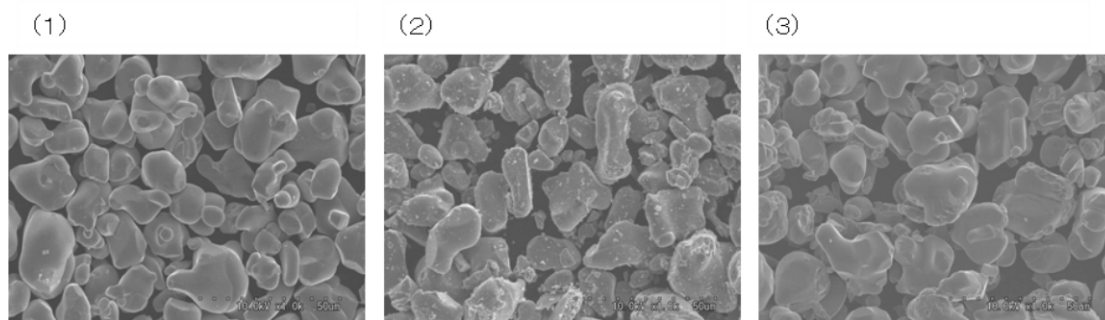
Based on the above results, it was confirmed that the positive electrode material active material according to the Present Invention uses lithium cobalt oxide, which exhibits high capacity in the core particles, and forms a layer with a small amount of Ti dissolved on the surface of the lithium cobalt oxide particles, so that cobalt ion elution can be suppressed, and that it is also high capacity and excellent in high temperature overcharge testing and charge/discharge repetition characteristics.

[Industrial applicability]

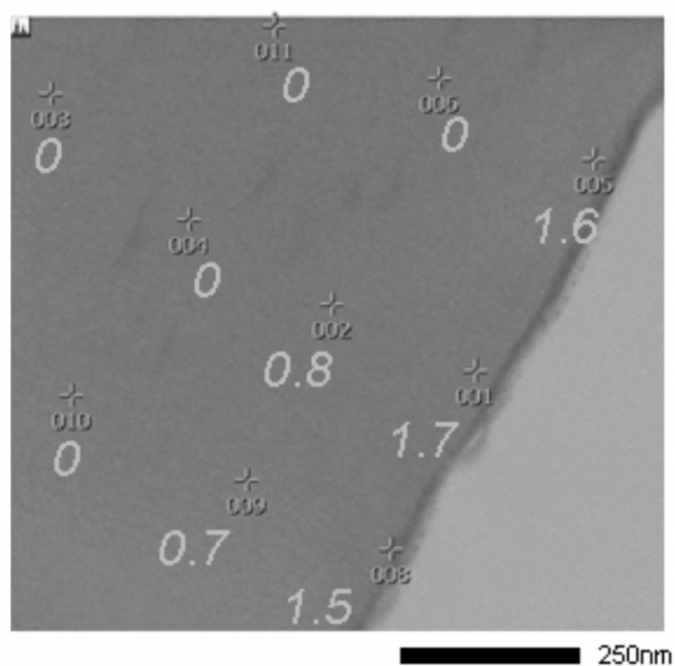
[0148]

By using the positive electrode active material particle powder made by a low environmental impact manufacturing method at a low cost, the Present Invention can obtain a nonaqueous solvent-based secondary battery with high energy density per volume, excellent charge/discharge repeatability, and high temperature resistance overcharge.

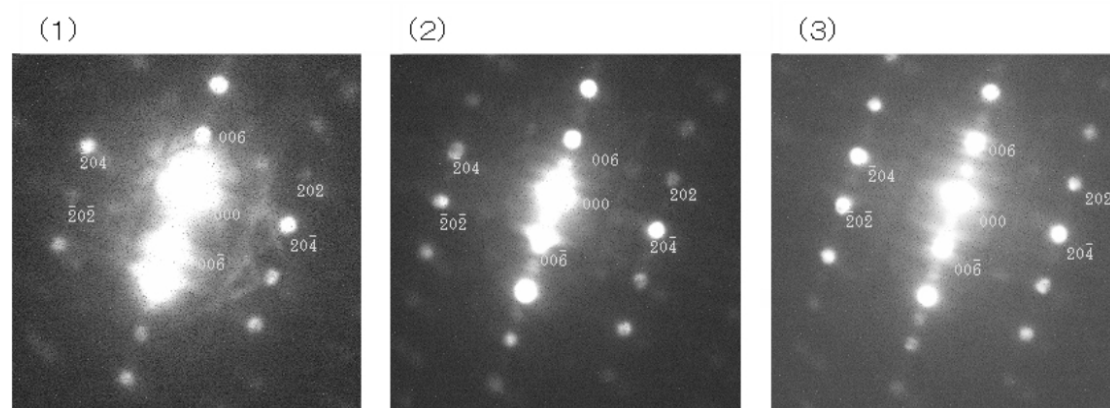
[Figure 1]



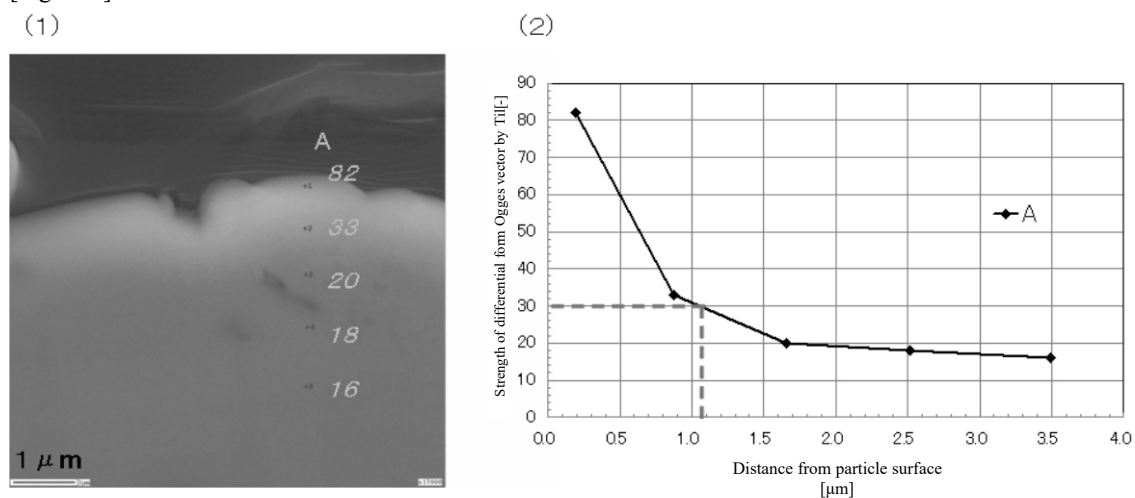
[Figure 2]



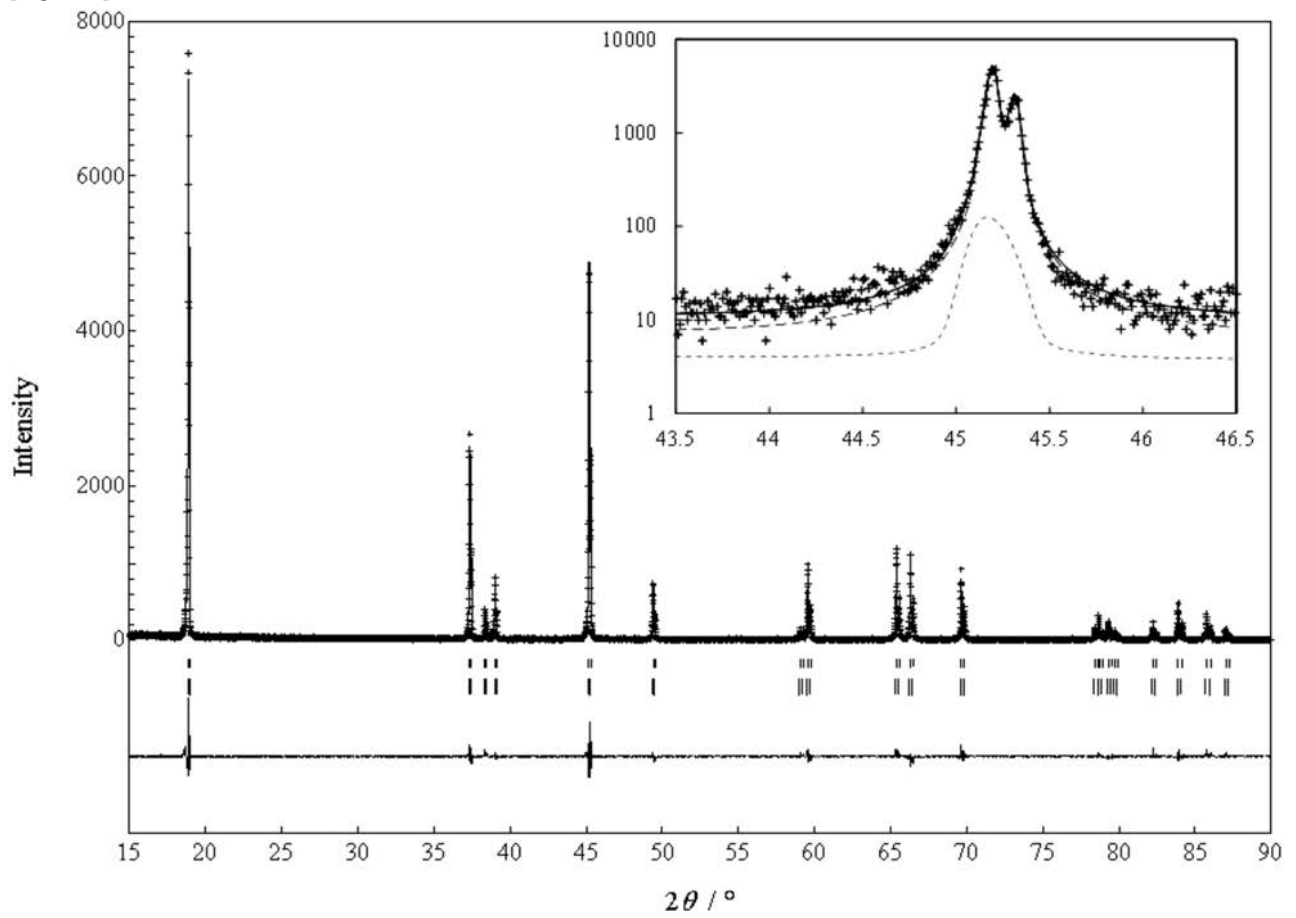
[Figure 3]



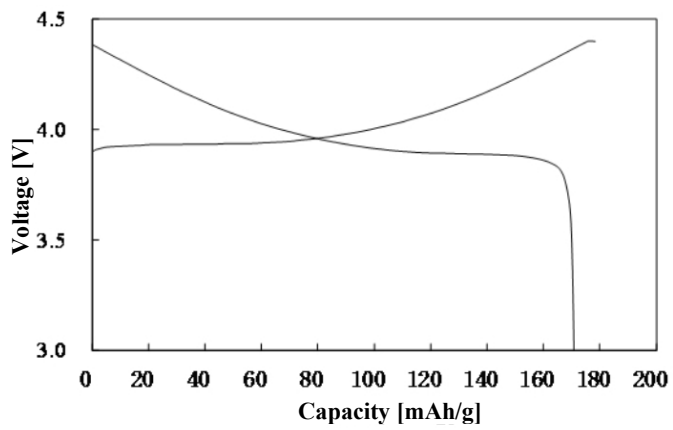
[Figure 4]



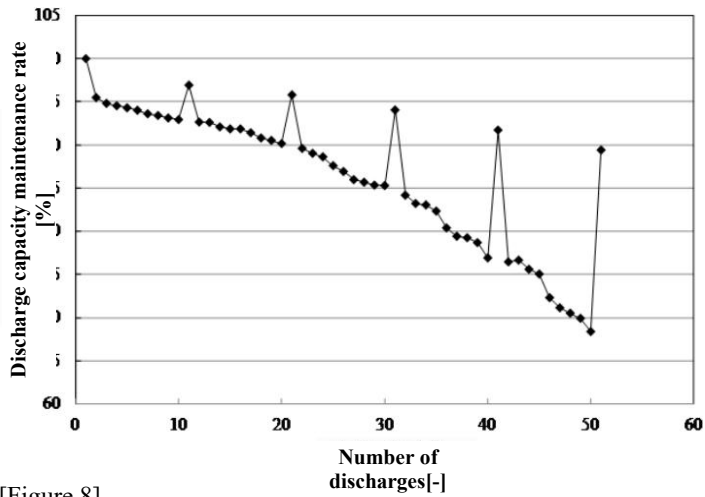
[Figure 5]



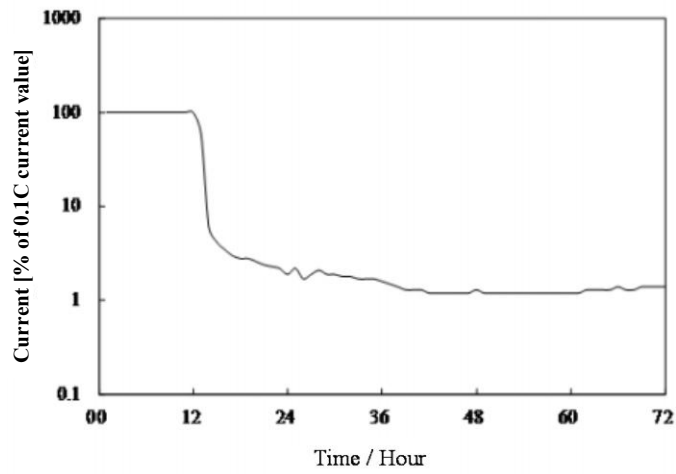
[Figure 6]



[Figure 7]



[Figure 8]



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HA07 HA14

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