



DECLARATION OF TRANSLATORS

We, Eric Vance and Seongweon Park, hereby declare as follows:

1. We personally prepared the attached translation from Japanese into English of the patent that is entitled “リチウム二次電池用正極活物質、リチウム二次電池用正極及びリチウム二次電池並びにリチウム二次電池用正極活物質の製造方法” in Japanese and “LITHIUM RECHARGEABLE BATTERY POSITIVE ELECTRODE ACTIVE MATERIAL, LITHIUM RECHARGEABLE BATTERY POSITIVE ELECTRODE, AND LITHIUM RECHARGEABLE BATTERY, AND METHOD FOR MANUFACTURING LITHIUM RECHARGEABLE BATTERY POSITIVE ELECTRODE ACTIVE MATERIAL” in English (also attached). This is the Japanese patent application number “P2003-59489A” from the Japanese patent gazette website.

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

3. We are competent to perform this translation, because we have 6 and 3 years of experience as a professional Japanese-to-English patent translator.

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

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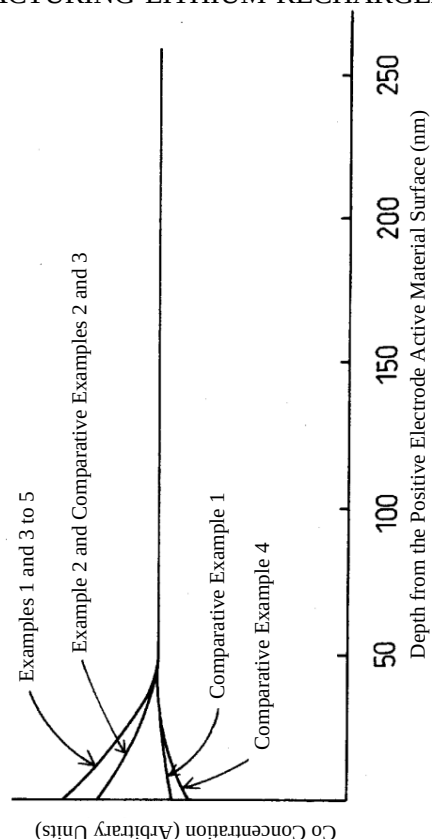
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(54) [Title of Invention] LITHIUM RECHARGEABLE BATTERY POSITIVE ELECTRODE ACTIVE MATERIAL, LITHIUM RECHARGEABLE BATTERY POSITIVE ELECTRODE, AND LITHIUM RECHARGEABLE BATTERY, AND METHOD FOR MANUFACTURING LITHIUM RECHARGEABLE BATTERY POSITIVE ELECTRODE ACTIVE MATERIAL

(57) [Abstract]

[Problem] To provide a lithium rechargeable battery positive electrode active material that is low in cost and has excellent cycle characteristics when applied to a lithium rechargeable battery.

[Resolution Means] A lithium rechargeable battery positive electrode active material, having a plurality of primary particles containing a layered rock salt structure lithium complex oxide containing at least lithium, nickel, and an element selected from among cobalt and zinc, wherein at least one of the lithium rechargeable battery positive electrode active material and the primary particles has a higher cobalt concentration in a portion near the surface than inside. In other words, by making the cobalt concentration in the portion near the surface of the particles of the lithium rechargeable battery positive electrode active material or the primary particles constituting the particles higher than the cobalt concentration inside, the crystal structure in the portion near the surface is stabilized, resulting in improved cycle characteristics. As a result, it is possible to effectively use expensive cobalt, leading to cost reduction.



[Scope of Patent Claims]

[Claim 1] A lithium rechargeable battery positive electrode active material, having a plurality of primary particles containing a layered rock salt structure lithium complex oxide containing at least lithium, nickel, and an element selected from among cobalt and zinc, wherein:

at least one of the lithium rechargeable battery positive electrode active material, and the primary particles have a higher cobalt concentration in a portion near the surface than inside.

[Claim 2] The lithium rechargeable battery positive electrode active material according to claim 1, wherein:

the primary particles have a particle diameter of 100 to 1000 nm, and

the particle diameter of the lithium rechargeable battery positive electrode active material is 1 to 50 μm .

[Claim 3] The lithium rechargeable battery positive electrode active material according to claim 1 or 2, wherein the layered rock salt structure lithium complex oxide contains nickel and cobalt at a content ratio of 99:1 to 50:50 in proportion of the number of atoms.

[Claim 4] The lithium rechargeable battery positive electrode active material according to any of claims 1 to 3, wherein the layered rock salt structure lithium complex oxide contains one or more elements selected from Fe, Cr, Al, and Mn.

[Claim 5] The lithium rechargeable battery positive electrode active material according to any of claims 1 to 4, wherein the portion near the surface is a portion up to 50 nm from the surface of the lithium rechargeable battery positive electrode active material.

[Claim 6] The lithium rechargeable battery positive electrode, comprising a current collector, and a positive electrode active material layer containing the lithium rechargeable battery positive electrode active material according to any of claims 1 to 5, formed on the surface of the current collector.

[Claim 7] A lithium rechargeable battery, comprising the lithium rechargeable battery positive electrode according to claim 6.

[Claim 8] A method for producing a lithium rechargeable battery positive electrode active material, comprising:

a first firing step for forming a raw material containing at least lithium, nickel, and cobalt into a first fired product kept within a temperature range of 100 to 300°C in an oxygen-containing atmosphere, a second firing step for keeping the first fired product within a temperature range of 400 to 700°C in an oxygen-containing atmosphere to produce a second fired product,

a granulation step for disaggregating the second fired product and then granulating to form a granulated powder, and

a third firing step for firing the granulated powder at 600 to 900°C in an oxygen-containing atmosphere.

[Detailed Description of Invention]

[0001]

[Technical Field of Invention] The present invention relates to a lithium rechargeable battery positive electrode active material, a lithium rechargeable battery positive electrode using the positive electrode active material, a lithium rechargeable battery using the positive electrode, and a method for manufacturing the lithium rechargeable battery positive electrode active material.

[0002]

[Conventional Art] In the fields of information-related equipment and communication equipment, lithium rechargeable batteries have, in conjunction with the size reduction of personal computers, video cameras, mobile phones, and the like, been put to practical use and are widespread due to the fact that they have high energy density as a power source to be used for these pieces of equipment.

On the other hand, development of electric vehicles is being urged in the field of automobiles due to environmental problems and resource problems, and lithium rechargeable batteries are being considered as a power source for these electric vehicles as well.

[0003] Positive electrode active materials such as LiCoO_2 and LiNiO_2 having a layered rock salt structure, LiMn_2O_4 having a spinel structure, and lithium complex oxides in which a portion thereof is substituted with other elements are well known as lithium rechargeable batteries that provide an operating voltage on the order of 4 V. Among these, a LiCoO_2 lithium complex oxide is a practically applied lithium rechargeable battery positive electrode active material. However, because cobalt is rare and expensive in terms of resources, lithium composite oxides mainly composed of nickel such as LiNiO_2 and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$, which are more inexpensive and can achieve high energy density when applied to lithium rechargeable batteries, are being earnestly developed. In particular, $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ and a lithium complex oxide in which a portion of elements are substituted with another elements are expected to be used as preferable lithium rechargeable battery positive electrode active materials, such as LiCoO_2 , due to containing cobalt.

[0004] It has been difficult to use $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ and the like to produce lithium rechargeable battery positive electrode active materials having sufficient performance by general manufacturing methods. Therefore, conventionally, JP H11-219706 A discloses, as a method for manufacturing a lithium rechargeable battery positive electrode active material made of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ or the like, a method of firing a mixture of compounds containing lithium, nickel, cobalt, or the like at 500 to 800°C for 5 to 20 hours as a primary firing, disaggregating and dispersing the obtained fired product in water until the average particle diameter is 1 μm or less, granulating by a spray drying method, and then firing at a temperature 30°C or more higher than the primary firing temperature and 900°C or less as a secondary firing.

[0005] Furthermore, JP H9-251854 A discloses a method having a step for firing a mixture of compounds containing lithium, nickel, cobalt, and the like at 300 to 650°C for 2 to 20 hours as a primary firing, a step for grinding and mixing after cooling to 100°C or less, and a step for firing at a temperature of 700 to 900°C as a secondary firing.

[0006]

[Problem to Be Solved by Invention] However, lithium rechargeable battery positive electrode active materials produced by conventional production methods do not exhibit sufficient performance due to cracking at the bonding interface caused by repeated charge/discharge cycles in the lithium rechargeable battery.

[0007] Therefore, a problem of the present invention is to provide a lithium rechargeable battery positive electrode active material and a lithium rechargeable battery positive electrode that are low in cost and have excellent cycle characteristics when used in a lithium rechargeable battery, and a lithium rechargeable battery that is low in cost and has excellent cycle characteristics.

[0008] Another problem of the present invention is to provide a method for producing a lithium rechargeable battery positive electrode active material that is low in cost and has excellent cycle characteristics when applied to a lithium rechargeable battery.

[0009]

[Means for Solving Problem] As a result of diligent research with the object of solving the problems described above, the present inventor discovered that for conventional lithium rechargeable battery positive electrode active materials, the crystal structure cannot be stabilized because the cobalt concentration in a portion near the surface of the particles or the primary particles constituting the particles is lower than the cobalt concentration inside, and cracking occurs from this portion near the surface (bonding interface), reducing performance of the lithium rechargeable battery positive

electrode active material and impacting cycle characteristics, and arrived at the present invention.

[0010] That is, the lithium rechargeable battery positive electrode active material of the present invention is a lithium rechargeable battery positive electrode active material, having a plurality of primary particles containing a layered rock salt structure lithium complex oxide containing at least lithium, nickel, and an element selected from among cobalt and zinc, wherein at least one of the lithium rechargeable battery positive electrode active material and the primary particles has a higher cobalt concentration in a portion near the surface than inside.

[0011] In other words, by making the cobalt concentration in the portion near the surface of the particles of the lithium rechargeable battery positive electrode active material or the primary particles constituting the particles higher than the cobalt concentration inside, the crystal structure in the portion near the surface is stabilized, resulting in improved cycle characteristics. As a result, it is possible to effectively use expensive cobalt, leading to cost reduction.

[0012] The lithium rechargeable battery positive electrode and the lithium rechargeable battery of the present invention, which solves the above problem, are characterized in that they use the lithium rechargeable battery positive electrode active material.

[0013] Also, for the lithium rechargeable battery positive electrode active material, as a result of searching for a method for manufacturing a lithium rechargeable battery positive electrode active material that can have a higher cobalt concentration in a portion near the surface of the particles or the primary particles constituting the particles than the cobalt concentration inside, the present inventor has invented a method for producing a lithium rechargeable battery positive electrode active material, provided with a first firing step for forming a raw material containing at least lithium, nickel, and cobalt into a first fired product kept within a temperature range of 100 to 300°C in an oxygen-containing atmosphere, a second firing step for keeping the first fired product within a temperature range of 400 to 700°C in an oxygen-containing atmosphere to form a second fired product, a granulation step for disaggregating the second fired product and then granulating to form a granulated powder, and a third firing step for keeping the granulated powder at 600 to 900°C in an oxygen-containing atmosphere to form a third fired product.

[0014] In other words, the cobalt concentration in a portion near the surface of the particles of the second fired product to be generated can be made higher than the concentration inside by changing the raw material to at least two stages of temperatures via two firing steps: the first firing step and the second firing step. By firing the lithium rechargeable battery positive electrode active material in a third firing step on the basis of this second fired product, the cobalt concentration in the portion near the surface can be made higher than the concentration inside, even for the produced lithium rechargeable battery positive electrode active material.

[0015]

[Embodiments of Invention] (Lithium Rechargeable Battery Positive Electrode Active Material) The lithium rechargeable battery positive electrode active material of the present invention (hereinafter simply referred to as "positive electrode active material") is a secondary particle having a plurality of primary particles containing a layered rock salt structure lithium complex oxide containing at least lithium, nickel, and cobalt.

[0016] The size of the positive electrode active material is not particularly limited, but is preferably 1 μm or greater and more preferably 5 μm or greater from the perspective of improving cycle characteristics, and is preferably 50 μm or less and more preferably 30 μm or less from the perspective of improving capacity and output characteristics. The shape of the positive electrode active material is not particularly limited, but from the perspective of high capacity, a spherical shape is preferable.

[0017] The size of the primary particles is not particularly limited, but is preferably 1000 nm or less

and more preferably 700 nm or less from the perspective of improving cycle characteristics, and is preferably 100 nm or more and more preferably 300 nm or more from the perspective of improving cycle characteristics. The shape of the primary particles is not particularly limited, but from the perspective of improving cycle characteristics, a spherical shape is preferable.

[0018] The general formula for the average composition of layered rock salt structure lithium complex oxides is $\text{LiNi}_{1-X-Y}\text{Co}_X\text{M}_Y\text{O}_2$ ($0 < X < 1$; $Y \geq 0$; M is one or more elements selected from Fe, Mn, and Al). Note that X is preferably 0.01 or more and 0.5 or less, and more preferably 0.3 or less. This is because adding cobalt can stabilize the crystal structure during charging and discharging and improve cycle characteristics. Y is preferably 0.01 or more and 0.2 or less. By adding the element as M, it is possible to improve the thermal stability and the like of the positive electrode active material. Note that it goes without saying that the positive electrode active material of the present invention may contain any element as an impurity in addition to the element indicated by M. Furthermore, some of the primary particles constituting the positive electrode active material of the present invention may, as necessary, contain a positive electrode active material that can be used in a lithium rechargeable battery other than the layered rock salt structure lithium complex oxide indicated here (for example, another lithium-transition metal complex oxide, or the like).

[0019] At least from among the particles themselves of the positive electrode active material of the present invention and the primary particles constituting the positive electrode active material has a higher cobalt concentration in a portion near the surface than inside. In particular, setting the cobalt concentration in the portion near the surface of the primary particles to be high enables suppression of occurrence of cracking at the bonding interface of the primary particles and thus is preferable.

[0020] Note that when the cobalt concentration in a region near the surface of the primary particle is set to be high, the cobalt concentration in the portion near the surface of the positive electrode active material formed from the primary particle is normally also high. Here, cobalt is preferably present in the lithium complex oxide, but there is no particular limitation. For example, the cobalt element may be present in a form such as CoO or Co_3O_4 .

[0021] Note that the present positive electrode active material is not limited to a positive electrode active material in which the cobalt concentration simply increases toward the surface. For example, even when the cobalt concentration drops locally on the outermost surface or the cobalt concentration repeatedly increases and decreases, insofar as the cobalt concentration is higher in a certain region near the surface (that is, the portion near the surface) than the inside, this is included in the positive electrode active material of the present invention.

[0022] Any method may be used for measuring the cobalt concentration. For example, as a form of the positive electrode active material during measurement, measurement can be performed as is or in a state aggregated by compression or the like. Furthermore, measurement can also be performed in a state wherein a lithium rechargeable battery positive electrode is manufactured using the positive electrode active material. When measuring the cobalt concentration, the relative ratio of the cobalt concentration between the portion near the surface and the inside in the positive electrode active material or the like is important.

[0023] A commonly used method such as Auger electron spectroscopy, X-ray photoelectron spectroscopy, or the like may be applied for measuring the cobalt concentration. A cobalt concentration profile can be produced by measuring the cobalt concentration while gradually etching the surface (for example, sputtering using a rare gas element such as Ar). In the positive electrode active material of the present invention, the cobalt concentration in the obtained profile is higher in the portion near the surface than inside. Here, the positive electrode active material of the present invention can be well-distinguished from the conventional positive electrode active material by

measuring the cobalt concentration after selecting a portion up to approximately 200 nm from the outermost surface as the portion near the surface.

[0024] For the positive electrode active material of the present invention described above, the present invention is also accomplished by suitably substituting a part or all of elemental cobalt with elemental zinc. Therefore, all of the instances of "cobalt" in (Lithium Rechargeable Battery Positive Electrode Active Material of the Present Invention) and (Manufacturing Method of Lithium Rechargeable Battery Positive Electrode Active Material of the Present Invention) of the "Embodiments of Invention" section in the present Specification can be replaced with "cobalt or zinc." Descriptions when all instances of "cobalt" are replaced with "cobalt or zinc" are largely the same except for the replaced portions, so further description will be omitted.

[0025] (Manufacturing Method of Lithium Rechargeable Battery Positive Electrode Active Material) The manufacturing method of the positive electrode active material lithium rechargeable battery (hereinafter simply referred to as "manufacturing method of positive electrode active material") of the present invention is a method for efficiently manufacturing the positive electrode active material described above. The manufacturing method of the positive electrode active material of the present invention has a first firing step, a second firing step, a granulation step, and a third firing step.

[0026] The raw materials to which the present manufacturing method is applied include at least lithium, nickel, and cobalt. For example, this is a mixture of oxides and hydroxides of each element. Additionally, a compound containing the necessary elements is added according to the composition of the target lithium metal complex oxide (for example, $\text{Fe}(\text{OH})_2$ and the like are added when the final lithium metal complex oxide contains Fe).

[0027] The first firing step is a step for keeping the product within a temperature range of 100 to 300°C in an environment containing oxygen, and the second firing step is a step for keeping the first product produced in the first firing step within a temperature range of 400 to 700°C in an environment containing oxygen and making the product into a second fired product. A more preferable temperature range in the first firing step is 150 to 300°C, and more preferably 150 to 250°C. A more preferable temperature range in the second firing step is 450 to 600°C, and more preferably 450 to 550°C. Through the first firing step and the second firing step, a fired product having a high cobalt concentration in the portion near the surface and fine primary particles can be obtained. Here, the time to keep within the temperature range of 100 to 300°C in the first firing step is not particularly limited, but a preferable range is 1 hour or more, and more preferably about 1 to 5 hours. Furthermore, the time to keep within a temperature range of 400 to 700°C in the second firing step is not particularly limited, but a preferable range is 3 hours or more, and more preferably about 3 to 10 hours.

[0028] The granulation step is a step in which a second fired product produced in the second firing step is made into a powder or granular material for which properties such as particle diameter and bulk density are preferable. Specifically, the fired product produced in the first firing step is disaggregated to about the level of the primary particles constituting the fired product and then granulated to obtain a preferable powder. Known methods such as a ball mill can be applied as the method for disaggregation. Furthermore, by adding water, it becomes easier to move to the granulation operation that follows. Known methods can be applied to granulation. Examples include a spray granulation method, an extrusion granulation method, a tumbling granulation method, a stirring granulation method, and the like. By making the granulation conditions appropriate, the powder and granular material having the intended properties can be obtained.

[0029] The third firing step is a step in which the powder and granular material obtained in the granulation step is fired at 600 to 900°C in an atmosphere containing oxygen. The primary particles constituting the powder and granular material are fired through this step. A preferable temperature

range is 600 to 800°C. The time for performing this step is not limited, but a preferable range is 2 hours or more, and more preferably about 2 to 5 hours.

[0030] (Lithium Rechargeable Battery Positive Electrode) The lithium rechargeable battery positive electrode of the present invention (hereinafter simply referred to as "positive electrode") is formed by mixing a conductive material and a binding agent into a positive electrode active material that can occlude and desorb lithium ions, adding an appropriate solvent as needed, making a paste-like positive electrode mixture, applying the mixture to the surface of a current collector made of metal foil such as aluminum and the like, drying the mixture, and then increasing the active material density by pressing and the like.

[0031] The positive electrode active material of the present invention described above is used as the positive electrode active material. A description is given in section above and will be omitted here. As the positive electrode active material, a known positive electrode active material such as a lithium transition metal complex oxide or the like can be further added and used as necessary. Lithium transition metal complex oxides have low electrical resistance, excellent lithium ion diffusion performance, and high charge/discharge efficiency and favorable charge/discharge cycle characteristics and thus are preferable materials for the present positive electrode active material. For example, this a lithium cobalt oxide, a lithium nickel oxide, a lithium manganese oxide, a material formed by adding or substituting transition metals such as Li, Al, and Cr in each of these, or the like. Note that a plurality of types of these lithium complex oxides may be used mixed together.

[0032] The conductive material is for ensuring electrical conductivity of the positive electrode and may one type or a mixture of two or more types of carbon material powders such as carbon black, acetylene black, graphite, and the like. A fluorine-containing resin such as polytetrafluoroethylene, polyvinylidene fluoride, fluororubber, and the like, and a thermoplastic resin such as polypropylene, polyethylene, and the like, may be used as a binding agent that functions to bind together the active material particles and the conductive material particles. An organic solvent such as N-methyl-2-pyrrolidone or the like can be used as the solvent in which the active material, conductive material, and binding agent are dispersed.

[0033] (Lithium Rechargeable Battery) The lithium rechargeable battery of the present invention may have a known battery structure such as a coin-shaped battery, a button-shaped battery, a cylindrical battery, a square-shaped battery, or the like. Regardless of which shape is adopted, the positive electrode and the negative electrode are superimposed or wound having a separator interposed therebetween to form an electrode body, and after connecting the positive electrode current collector and the negative electrode current collector to the positive electrode terminal and the negative electrode terminal that communicate with the outside using a collector lead or the like, this electrode body is inserted into a battery case together with a nonaqueous electrolyte solution, and this is sealed to complete the lithium battery.

[0034] The positive electrode of the present invention described above is used as the positive electrode. The details are explained in the previous section, and therefore description thereof is omitted here.

[0035] For the negative electrode, when a negative electrode active material that occludes lithium ions during charging and releases such during discharging can be used, the material configuration thereof is not particularly limited, and a material having a known material configuration can be used. For example, this is a carbon material or the like, such as lithium metal, graphite, or amorphous carbon. Among these, it is particularly preferable to use a carbon material. The specific surface area can be relatively large, and lithium occlusion and release rates are fast, and thus the charging/discharging characteristics and the output and regeneration density at a high current are

favorable. In particular, in consideration of the balance between output and regeneration density, it is preferable to use a carbon material having a comparatively large voltage change in conjunction with charging and discharging. Among these, it is preferable to use materials composed of highly crystalline natural graphite or artificial graphite. By using such a highly crystalline carbon material, the delivery efficiency of lithium ions in the negative electrode can be improved.

[0036] When using a carbon material as the negative electrode active material in this manner, it is preferable to use a material where a negative electrode mixture obtained by mixing a conductive material and a binding material such as that described in the positive electrode is applied to the current collector as necessary.

[0037] The nonaqueous electrolyte solution is obtained by dissolving an electrolyte in an organic solvent.

[0038] The organic solvent is not particularly limited so long as the solvent is an organic solvent normally used for nonaqueous electrolyte of lithium rechargeable batteries, and for example, carbonates, halogenated hydrocarbons, ethers, ketones, nitriles, lactones, oxolane compounds and the like can be used. In particular, propylene carbonate, ethylene carbonate, 1,2-dimethoxyethane, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, tetrahydrofuran, and the like, and a mixed solvent thereof are suitable. For example, a mixed organic solvent of a main solvent having a high dielectric constant such as ethylene carbonate and propylene carbonate and an auxiliary solvent having a low viscosity such as dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate is preferable. Dimethoxyethane, tetrahydrofuran, butyrolactone, and the like may be used as an auxiliary solvent.

[0039] For electrolytes, the type thereof is not particularly limited, but at least one of inorganic salts selected from LiPF_6 , LiBF_4 , LiClO_4 , and LiAsF_6 , derivatives of the inorganic salts, organic salts selected from LiSO_3CF_3 , $\text{LiC}(\text{SO}_3\text{CF}_3)_2$, $\text{LiN}(\text{SO}_3\text{CF}_3)_2$, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, and $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$, and derivative of organic salts thereof is preferable.

[0040] By the use of these electrolytes, the battery performance can be made even more excellent and the battery performance can be maintained even at a temperature range other than room temperature. The concentration of the electrolyte is also not particularly limited, and appropriate selection in consideration of the types of the electrolyte and the organic solvent according to the purpose is preferred.

[0041] The separator electrically insulates the positive electrode and the negative electrode, and plays a role of holding the electrolyte. For example, a porous synthetic resin film, particularly a porous film of a polyolefin polymer (polyethylene or polypropylene) may be used. Note that the separator is preferably set larger than the size of the positive electrode and the negative electrode in order to ensure insulation between the positive electrode and the negative electrode.

[0042] The case is not particularly limited and can be produced using known materials or forms.

[0043] The gasket ensures electrical insulation between the case and both of the positive terminal and the negative terminal portions, and airtightness inside the case. For example, the electrolytic solution can be configured from a polymer or the like such as polypropylene that is chemically and electrically stable.

[0044]

[Examples] (Manufacture of Each Positive Electrode Active Material of Examples 1 to 5 and Comparative Examples 1 to 3) After nickel hydroxide, lithium hydroxide, and cobalt hydroxide were mixed until a molar ratio reached 1:1:0.05 and then fired in an oxygen stream at the temperature and time shown in column A of Table 1 (first firing step), the fired products were obtained by continuously firing in an oxygen stream at the temperature and time shown in column B of Table 1 thereafter

(second firing step).

[0045] After mixing the obtained fired product with ion-exchange water at a mass ratio of 30:70, the mixture is disaggregated and dispersed in a wet bead mill for 1 hour to obtain a slurry, granulated by a spray granulation method, and a granulated product as a powder and granular material is obtained (granulation step).

[0046] The obtained granulated products were fired in an oxygen stream at the temperature and for the time shown in column C of Table 1 (third firing step) to obtain each of the positive electrode active materials for Examples 1 to 5 and Comparative Examples 1 to 3.

[0047]

[Table 1]

	A		B		C	
	Temperature (°C)	Time	Temperature (°C)	Time	Temperature (°C)	Time
Example 1	200	3	500	5	800	5
Example 2	300	3	500	5	800	5
Example 3	200	3	700	5	800	5
Example 4	200	3	500	5	600	5
Example 5	200	3	500	5	700	5
Comparative Example 1	400	3	500	5	800	5
Comparative Example 2	200	3	800	5	800	5
Comparative Example 3	200	3	500	5	500	5

[0048] (Manufacture of the Positive Electrode Active Material of Comparative Example 4) After nickel hydroxide, lithium hydroxide, and cobalt hydroxide were mixed at a molar ratio of 1:1:0.05, a fired product was obtained by firing at 700°C for 8 hours in an oxygen stream.

[0049] The obtained fired product was disaggregated using the same method as in Example 1 and the like, granulated using a spray granulation method thereafter, and a granulated product was obtained.

[0050] The obtained granulated product was fired at 800°C in an oxygen stream for 3 hours, and the positive electrode active material of Comparative Example 4 was obtained.

[0051] (Measurement of Cobalt Concentration) For the positive electrode active material of each Example and Comparative Example, the powder was set to be the measurement sample as is. The elemental composition of this sample was measured by Auger electron spectroscopy while cutting the surface using irradiating argon ions, and a profile of the cobalt concentration was produced. The profile of cobalt concentrations was produced up to about 250 nm in the depth direction.

[0052] The results are shown in FIG. 1. As evident from FIG. 1, for all of the positive electrode active materials of each of the Example and Comparative Examples 2 and 3, the cobalt concentrations increased as the surface was approached within a range from the surface to near 50 nm (portion near the surface). Compared thereto, on the contrary, for the positive electrode active materials of Comparative Examples 1 and 4, the cobalt concentration decreased as the surface was approached. It is conceivable that this is due to the heating temperature in the first firing step of the manufacturing step being outside an appropriate range.

[0053] (Microscopic Observation) The positive electrode active material of each Example and Comparative Example was observed using a Scanning Electron Microscope (SEM). In the particle diameter measurement method, the average diameter of the particles in the field of view was calculated for the particle diameter of the positive electrode active material itself. For the particle diameter of the primary particles constituting each particle, cross sections of the positive electrode

active material of each Example and Comparative Example were observed using SEM, and an average diameter of the size of primary particles in the field of view of SEM was calculated. The cross section of the positive electrode particles for observation was prepared using the FIB method (etching by irradiation of Ga ions).

[0054] As a result, it was found that each of the positive electrode active materials of Examples 1 to 5 and Comparative Examples 1 and 4 had substantially the same particle diameters (about 5 μm) and particle diameter of the primary particles constituting the particles thereof (about 500 nm).

[0055] In contrast, the positive electrode active material of Comparative Example 2 had substantially the same particle diameter, but the primary particles constituting the particles had a large particle diameter (about 1200 nm). It is conceivable that the growth of the primary particles was significant due to the heating temperature in the process that corresponds to the second firing process being high.

[0056] The positive electrode active material of Comparative Example 3 had a particle diameter of about 500 nm, which is the same as that of the positive electrode active material of Examples, but the size of the particles themselves was small at about 800 nm. It is conceivable that the growth of the secondary particles (positive electrode active material) was insufficient as the heating temperature in the step corresponding to the third firing step of the manufacturing step was low.

[0057] (Manufacture of Lithium Rechargeable batteries) A paste-like positive electrode mixture was obtained by mixing 90 parts by mass of each positive electrode active material of Examples 1 to 5 and Comparative Examples 1 to 4 with 5 parts by mass of graphite as a conductive material and 5 parts by mass of polyvinylidene fluoride as a binding agent, adding an appropriate amount of N-methyl-2-pyrrolidone, and kneading; this positive electrode mixture was applied to both surfaces of a positive electrode current collector made of an Al foil having a thickness of 30 μm , dried, and then pressed to prepare a sheet-like positive electrode.

[0058] 95 parts by mass of graphite as a negative electrode active material and 5 parts by mass of polyvinylidene fluoride as a binding agent were mixed, and an appropriate amount of N-methyl-2-pyrrolidone was added and kneaded to obtain a paste-like negative electrode mixture, and this negative electrode mixture was applied to both surfaces of a negative electrode current collector made of Cu foil having a thickness of 35 μm , dried, and then pressed to prepare a sheet-like negative electrode.

[0059] The positive electrode and the negative electrode were cut into predetermined sizes, respectively, and the cut positive electrode and the cut negative electrode were sandwiched by a separator made of polyethylene having a thickness of 20 μm therebetween and wound to form a roll-shaped electrode body. A collector lead is attached to this electrode body, and inserted into the 18650 battery case, and then the nonaqueous electrolyte was injected into the battery case. As the nonaqueous electrolyte solution, LiPF_6 was dissolved at a concentration of 1 mol/L in a mixed solvent wherein ethylene carbonate (EC) and diethyl carbonate (DEC) were mixed at a volume ratio of 30:70. Finally, the battery case was sealed, and the lithium rechargeable batteries of the test examples of Examples 1 to 5 and Comparative Examples 1 to 4 were completed.

[0060] (Cycle Durability Test) After performing 2 C charging to 4.1 V, the charging is paused for 10 minutes. Subsequently, 2 C discharging is performed to 3.0 V, and the discharging is paused for 10 minutes. By setting this as one cycle, 1000 cycles of charging and discharging were performed on the batteries of each Example and Comparative Example. The battery capacity before and after 1000 cycles of charging and discharging was measured, and the capacity after 1000 cycles of charging and discharging was found in percentage with respect to the capacity before 1000 cycles of charging and discharging. Note that the battery capacities of the Examples and the Comparative Examples before the cycle charging and discharging were all substantially the same and were within the error range.

The results are shown in Table 2.

[0061]

[Table 2]

	Battery Capacity (%) After 1000 Cycles of Charging and Discharging
Example 1	73
Example 2	71
Example 3	70
Example 4	70
Example 5	74
Comparative Example 1	52
Comparative Example 2	52
Comparative Example 3	53
Comparative Example 4	51

[0062] As is evident from Table 2, the battery capacities for all of the batteries in the Examples were 70% or more. In contrast, for the battery in the Comparative Examples, the battery capacity was about 50%, which was about 17 to 20% lower. As the reason, it is conceivable that, this is caused by the particle diameter of the primary particles configuring the positive electrode active material being large in Comparative Example 2. It is conceivable that, in Comparative Example 3, this is caused by insufficient growth of the particles of the positive electrode active material. In Comparative Examples 1 and 4, the cause is conceivable to be that the particle diameter of the positive electrode active material and the primary particle was preferable, but that the cobalt concentration in the portion near the surface was lower than that of inside.

[0063] From the result above, it has become evident that, from the perspective of cycle characteristics, it was preferable that a positive electrode active material composed of a lithium complex oxide containing nickel and cobalt has a higher cobalt concentration in the portion near the surface than inside. Additionally, it has become evident that appropriate values also exist for the particle diameter of the positive electrode active material and for the particle diameter of the primary particles constituting the particles.

[0064] Furthermore, as such a method for manufacturing a positive electrode active material having a higher cobalt concentration in a portion near a surface than inside, an appropriate particle diameter of the positive electrode active material, and a particle diameter of primary particles constituting the particles, it was also found from the performance of the manufactured positive electrode active material (lithium rechargeable battery) that the method wherein manufacture is performed via the first firing step, the second firing step, the granulation step, and the third firing step was excellent, as described in the manufacturing method of positive electrode active materials above.

[0065]

[Effect of Invention] As described above, for the lithium rechargeable battery positive electrode active material and the lithium rechargeable battery positive electrode of the present invention, the cobalt concentration of a portion near the surface of the lithium rechargeable battery positive electrode active material and the primary particles constituting the lithium rechargeable battery positive electrode active material I is made higher than that of inside, and thus, when applied to lithium rechargeable

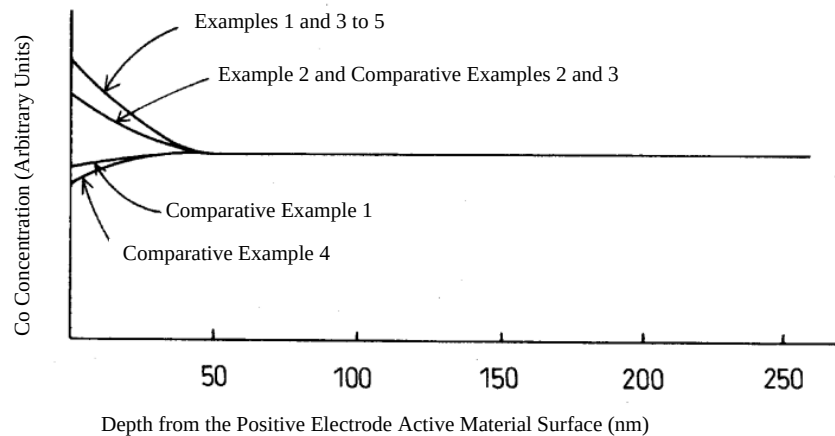
batteries, performance having excellent cycle characteristics at low cost is exhibited. The lithium rechargeable battery positive electrode of the present invention uses the lithium rechargeable battery positive electrode of the present invention, and thus the lithium rechargeable battery can exhibit excellent cycle characteristics at low cost.

[0066] Additionally, the method for manufacturing the lithium rechargeable battery positive electrode active material of the present invention can provide a method for manufacturing the lithium rechargeable battery positive electrode active material that has excellent cycle characteristics at low cost when applied to lithium rechargeable batteries.

[Brief Description of Drawings]

[FIG. 1] This is a diagram illustrating a surface profile of a cobalt concentration of the positive electrode active material of each Example and Comparative Example.

[FIG. 1]



Continued from front page

F Term (Reference) 4G048 AA04 AB01 AB05 AC06 AD03
AD06 AE05
5H029 AJ05 AJ14 AK03 AL06 AL07
AL08 AL12 AN02 AN03 AN04
AN05 AN07 CJ01 CJ02 CJ28
DJ12 DJ17 EJ04 EJ12 HJ02
HJ04 HJ05 HJ14
5H050 AA07 AA19 BA16 BA17 CA08
CB07 CB08 CB09 CB12 EA09
EA24 FA12 FA19 GA02 GA05
GA06 HA02 HA04 HA05 HA14

1. In [0038], the first sentence reports the phrase “の用いられる”, which appears to be a typographical error of “に用いられる”. As using “の用いられる” does not make up a reasonable meaning, the translation corrects this possible typographical error.
2. In paragraph [0038], the last sentence in the source reports “ブチルラクトン”, which appears to be a typographical error of “ブチロラクトン”. The translation corrects this possible typographical error and “ブチルラクトン” is translated as “butyrolactone.”