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(54) **POSITIVE ELECTRODE ACTIVE MATERIAL FOR LITHIUM-ION BATTERY, A POSITIVE ELECTRODE FOR LITHIUM-ION BATTERY, AND LITHIUM-ION BATTERY**

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(57) **ABSTRACT**

The present invention provides a positive electrode active material for lithium ion batteries having excellent battery property.

The positive electrode active material for lithium ion batteries is represented by composition formula: $Li_xNi_{1-y}M_yO_{2+\alpha}$, wherein

M is Co as an essential component and at least one species selected from a group consisting of Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Al, Bi, Sn, Mg, Ca, B and Zr, $0.9 \leqq x \leqq 1.2$, $0 < y \leqq 0.7$, $\alpha > 0.05$, and

an average particle size (D50) is 5 μm to 15 μm.

POSITIVE ELECTRODE ACTIVE MATERIAL FOR LITHIUM-ION BATTERY, A POSITIVE ELECTRODE FOR LITHIUM-ION BATTERY, AND LITHIUM-ION BATTERY

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to a positive electrode active material for lithium ion batteries, a positive electrode for lithium ion batteries, and a lithium ion battery.

BACKGROUND OF THE INVENTION

[0002] In general, lithium-containing transition metal oxides are used for a positive electrode active material for lithium ion batteries. In particular, they are lithium cobaltate ($LiCoO_2$), lithium nickelate ($LiNiO_2$), lithium manganite ($LiMn_2O_4$) and the like. A conjugation of the lithium-containing transition metal oxides is proceeding in order to improve properties such as high volume, cycle characteristic, storage characteristic, decreased internal resistance, rate performance, and safety. Lithium ion batteries, for large-size equipment use such as automobile use and load leveling use, require properties different from those of the past mobile phone use and personal computer use.

[0003] Traditionally, various methods have been conducted for improving the rate performance. For example, patent document 1 discloses a manufacturing method of a positive electrode material for a lithium secondary battery characterized in that a lithium-nickel composite oxide having a composition of $Li_xNi_{1-y}M_yO_{2-\delta}$($0.8 \leqq x \leqq 1.3$, $0 < y \leqq 0.5$, M is at least one element selected from a group consisting of Co, Mn, Fe, Cr, V, Ti, Cu, Al, Ga, Bi, Sn, Zn, Mg, Ge, Nb, Ta, Be, B, Ca, Sc and Zr. δ is oxygen loss or oxygen excess, $-0.1 < \delta < 0.1$) is passed through a classifier to separate particles having large particle diameters from particles having small particle diameters by equilibrium separation particle size D_h=1 to 10 μm, and the particles having large particle diameters are mixed with the particles having small particle diameters at weight ratios of 0:100 to 100:0, and the method can easily produce a positive electrode material for a lithium secondary battery having various balance of rate performance and capacity.

[0004] (Patent documents 1) Japanese Patent No. 4175026

SUMMARY OF THE INVENTION

[0005] The lithium-nickel composite oxide disclosed in Patent document 1 has excess oxygen in the composition formula, and there is still room for improvement as high-quality positive electrode active material for lithium ion batteries.

[0006] The present invention aims to provide a positive electrode active material for lithium ion batteries having excellent battery property.

[0007] The inventors have diligently studied and eventually have found out, there is a close correlation between amount of oxygen in the positive electrode active material and battery property. That is, they found out that excellent battery property can be provided especially when the amount of oxygen in the positive electrode active material is a certain value or more, and more excellent battery property can be provided by controlling average particle sizes of powder in the positive electrode active material having amount of oxygen, being a certain value or more.

[0008] The present invention, produced on the basis of the above findings, in one aspect, is a positive electrode active material for lithium ion batteries, represented by composition formula: $Li_xNi_{1-y}M_yO_{2+\alpha}$, wherein M is Co as an essential component and at least one species selected from a group consisting of Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Al, Bi, Sn, Mg, Ca, B and Zr, $0.9 \leqq x \leqq 1.2$, $0 < y \leqq 0.7$, $\alpha > 0.05$, and an average particle size (D50) is 5 μm to 15 μm. "D50" means a particle size corresponding to 50% in volume-based cumulative fractions.

[0009] The present invention is, in one embodiment, the positive electrode active material for lithium ion batteries where the average particle size (D50) is 7 μm to 13 μm.

[0010] The present invention is, in yet another embodiment, the positive electrode active material for lithium ion batteries, where M is at least one species selected from a group consisting of Mn and Co.

[0011] The present invention is, in yet another embodiment, the positive electrode active material for lithium ion batteries, where $\alpha > 0.15$.

[0012] The present invention is, in yet another embodiment, the positive electrode active material for lithium ion batteries, where $\alpha > 0.20$.

[0013] The present invention is, in yet another embodiment, the positive electrode active material for lithium ion batteries, where D90 is 20 μm or less in particle size distribution.

[0014] "D90" means a particle size corresponding to 90% in volume-based cumulative fractions.

[0015] The present invention, in another aspect, is a positive electrode for lithium ion batteries using the positive electrode active material for lithium ion batteries of the present invention.

[0016] The present invention, in yet another aspect, is a lithium ion battery using the positive electrode for lithium ion batteries of the present invention.

Advantageous Effect of the Invention

[0017] The present invention can provide a positive electrode active material for lithium ion batteries having excellent battery property.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0018] [Structure of Positive Electrode Active Material for Lithium Ion Batteries]

[0019] As raw materials for positive electrode active material for lithium ion batteries of the present invention, various compounds useful for positive electrode active material for general positive electrode for lithium ion batteries can be used. In particular, it is preferable to use lithium-containing transition metal oxides such as lithium cobaltate ($LiCoO_2$), lithium nickelate ($LiNiO_2$) and lithium manganite ($LiMn_2O4$). The positive electrode active material for lithium ion batteries of the present invention, produced by using such materials, is represented by composition formula: $Li_xNi_{1-y}M_yO_{2+\alpha}$, where M is Co as an essential component and at least one species selected from a group consisting of Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Al, Bi, Sn, Mg, Ca, B and Zr, $0.9 \leqq x \leqq 1.2$, $0 < y \leqq 0.7$, $\alpha > 0.05$. The lithium ratio to all metal amount in the positive electrode active material for lithium ion batteries is 0.9 to 1.2. This is because it is difficult to maintain stable crystal structure if the ratio is less than 0.9, and high volume of the battery cannot be secured if the ratio is more than 1.2.

[0020] Oxygen is contained excessively in the positive electrode active material for lithium ion batteries of the present invention such as a constituent of oxygen is indicated by $O_{2+\alpha}$($\alpha > 0.05$) in the chemical formula as described above. Accordingly, in a lithium ion battery using the material, battery property such as capacity, rate performance and capacity

retention rate can be excellent. Further, calcination in the manufacturing process can be adequately conducted because oxygen is contained excessively. Accordingly, particle configuration and size are uniformized. With regard to α, $\alpha>0.15$ is preferable and $\alpha>0.20$ is more preferable.

[0021] The positive electrode active material for lithium ion batteries consists of primary particles, secondary particles formed by aggregation of the primary particles or mixture of the primary particles and the secondary particles. An average particle size (D50) of primary particles, secondary particles formed by aggregation of the primary particles or mixture of the primary particles and the secondary particles is 5 μm to 15 μm. When the average particle size (D50) is 5 μm to 15 μm, powder in which a variability of size is inhibited can be produced. Accordingly, it is possible to apply the active material uniformly in the manufacturing process of an electrode of the lithium ion battery, and further, it is possible to inhibit a variability of composition of the electrode. Therefore, rate performance and cycle performance can be excellent when the electrode is used for the lithium ion battery. The average particle size (D50) is preferably 13 μm or less, more preferably 7 μm to 13 μm.

[0022] In the positive electrode active material for lithium ion batteries of the present invention, D90 is 20 μm or less in particle size distribution. When D90 is 20 μm or less, reaction variability among the particles decreases and then rate performance and cycle performance become more excellent. D90 is preferably 13 μm to 20 μm.

[0023] [Structure of Positive Electrode for Lithium Ion Batteries and Lithium Ion Battery Using the Same]

[0024] The positive electrode for lithium ion batteries of the present invention has a structure, for example, where positive electrode combination agent, prepared by mixing the positive electrode active material for lithium ion batteries having the above described structure, conductivity auxiliary agent and binder, is applied on one surface or both surfaces of a current collector made of aluminum foil and the like. The lithium ion battery of the embodiment of the present invention has the positive electrode for lithium ion batteries having the above described structure.

[0025] [Manufacturing Method for Positive Electrode Active Material for Lithium Ion Batteries]

[0026] Next, manufacturing method for positive electrode active material for lithium ion batteries of the embodiment of the present invention is explained in detail. First, metal salt solution is produced. The metal is Ni and at least one species selected from a group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Ga, Ge, Al, Bi, Sn, Mg, Ca, B and Zr. The metal salt is sulfate, chloride, nitrate, acetate and the like. In particular, nitrate is preferable because nitrate can be directly calcined and therefore cleaning process can be omitted when nitrate is mixed in raw material for calcination as impurities, and nitrate acts as an oxidant to promote oxidation of metals in the raw material for calcination. Each metal contained in the metal salt is prepared such that it has a desired molar ratio. In this way, molar ratio of each metal in the positive electrode active material is determined.

[0027] Next, lithium carbonate is suspended in pure water, and then metal salt solution of the above metal is poured to produce metal carbonate solution slurry. At this time, microparticles of lithium-containing carbonate precipitate in the slurry. When the lithium compounds do not react at heat treatment as with sulfate, chloride and the like as metal salt, they are cleaned by saturated lithium carbonate solution and then filtered. When the lithium compounds react at heat treatment as with nitrate and acetate, as the lithium raw material, they are not cleaned but directly filtered. Then they are dried and then they can be used as precursor of calcination.

[0028] Next, the filtered lithium-containing carbonate is dried and then powder of lithium salt complex (precursor for positive electrode active material for lithium ion batteries) is provided.

[0029] Next, the powder of the precursor for positive electrode active material for lithium ion batteries, provided by drying, is classified to provide only powder having the particle size of 1 μm to 30 μm, by using a sifter or a commercially available classification apparatus and the like.

[0030] Next, a calcination holder, having a predetermined content, is prepared. Precursor for positive electrode active material for lithium ion batteries, having the particle size of 1 μm to 30 μm, is filled in the calcination holder. Next, the calcination holder, filled with powder of precursor for positive electrode active material for lithium ion batteries, is moved to a calcination furnace and then calcined. The calcination is conducted by heat preservation for predetermined time under oxygen atmosphere. Further, it is preferable to conduct the calcination under increased pressure of 101 KPa to 202 KPa because amount of oxygen in the composition increases.

[0031] After that, the powder is taken from the calcination holder and then powder of positive electrode active material is provided by pulverization with commercially available pulverization apparatus and the like. The pulverization is conducted by controlling pulverization power and pulverization time accordingly, to provide desired median diameter and repose angle.

EXAMPLES

[0032] Examples of the present invention will be described as follows, but the following examples are provided for better understanding of the present invention and its advantages, and intended to be non-limiting.

Working Examples 1 to 15

[0033] At first, lithium carbonate, the amount of which is described in Table 1, was suspended in 3.2 L of pure water and then 4.8 L of metal salt solution was poured. The metal salt solution was prepared such that the composition ratio of each metal became the value described in Table 1 with regard to each hydrate of nitrate and all molar number of the metals became 14 mol.

[0034] Suspension amount of lithium carbonate was such that a product (positive electrode material for lithium ion batteries, that is, positive electrode active material) was $Li_x(Ni_{1-y}M_y)O_{2+\alpha}$, where x is described in Table 1, and each of the amount was respectively calculated by the following formula.

$$W(g)=73.9\times14\times(1+0.5X)\times A$$

In the above formula, "A" is a value to be multiplied in order to subtract the amount of lithium in lithium compound other than lithium carbonate remaining in raw materials after filtration, in addition to needed volume for precipitation reaction, from the suspension amount beforehand. "A" is 0.9 when lithium salt reacts as raw material of calcination as with nitrate and acetate. "A" is 1.0 when lithium salt does not react as raw material of calcination as with sulfate and chloride.

[0035] Microparticles of lithium-containing carbonate precipitated in the solution by the treatment. Then the precipitate was filtered by using a filter press. Next, the precipitate was dried and then the lithium-containing carbonate (precursor for positive electrode active material for lithium ion batteries) was produced.

[0036] Next, the lithium-containing carbonate, provided by drying, was classified to provide powder having the particle size of 1 μm to 30 μm by using a sifter. Next, a calcination holder was prepared and then filled with the lithium-containing carbonate. Then the calcination holder was set in an oxygen atmosphere furnace at atmospheric pressure, heat preservation was conducted for 10 hours at the calcination temperature described in Table 1, and then oxides were provided by cooling.

[0037] Next, the provided oxides were pulverized to 5 μm to 15 μm of the average particle size with a compact pulverization apparatus (HOSOKAWA MICRON ACM-2EC), and then powder of positive electrode active materials for lithium ion batteries were provided.

Working Example 16

[0038] With regard to working example 16, composition of each metal of raw materials is shown in Table 1, metal salt was chloride. After precipitating lithium-containing carbonate, washing treatment was conducted by saturated lithium carbonate solution and then filtration treatment was conducted. Other than that, treatments similar to working examples 1 to 15 were conducted.

Working Example 17

[0039] With regard to working example 17, composition of each metal of raw materials is shown in Table 1, metal salt was sulfate. After precipitating lithium-containing carbonate, washing treatment was conducted by saturated lithium carbonate solution and then filtration treatment was conducted. Other than that, treatments similar to working examples 1 to 15 were conducted.

Working Example 18

[0040] With regard to working example 18, composition of each metal of raw materials is shown in Table 1. Calcination treatment was conducted under increased pressure of 120 KPa instead of conducting under atmosphere pressure. Other than that, treatments similar to working examples 1 to 15 were conducted.

Comparative Examples 1 to 3

[0041] With regard to comparative examples 1 to 3, composition of each metal of raw materials is shown in Table 1, classification after drying the precursor was not conducted, and the last pulverization of oxides was conducted such that the average particle size became 5 μm or less, or 20 μm or more. Other than that, treatments similar to working examples 1 to 15 were conducted.

Comparative examples 4 to 7

[0042] With regard to comparative examples 4 to 7, composition of each metal of raw materials is shown in Table 1. Calcination treatment was conducted in an air atmosphere furnace instead of conducting in an oxygen atmosphere furnace. Other than that, treatments similar to comparative example 1 were conducted.

[0043] [Evaluation]

—Evaluation of Composition of Positive Electrode Material—

[0044] Contained amounts of metal in the positive electrode material were measured by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and then composition ratio (molar ratio) of each metal was calculated, and it was confirmed that they resulted in the values described in Table 1. Further, oxygen content was measured by LECO method and a was calculated.

—Evaluations of Average Particle Size (D50) and D90—

[0045] Powders of each positive electrode material were taken and D50 and D90 were measured by Laser Diffraction Particle Size Analyzer (SHIMADZU: SALD-3000).

—Evaluation of Battery Property—

[0046] The positive electrode active material, an electrical conducting material and a binder were weighed in a proportion of 85:8:7. Next, the positive electrode active material and the electrical conducting material were mixed in an organic solvent (N-methylpyrrolidone) where the binder dissolved, and then slurry was produced. Next, the slurry was applied to aluminum foil, and then a positive electrode was produced by pressing after drying the slurry.

[0047] Next, 2032-type coin cell for evaluation, where the other electrode was Li, was produced and discharged capacity when current density was 0.2C, was measured by using an electrolyte where 1M-$LiPF_6$ was dissolved in EC-DMC(1:1). Further, a ratio of the discharged capacity when current density was 2C, to a battery capacity when current density was 0.2C, was calculated and then a rate performance was provided. Further, capacity retention rate was measured by comparing an initial discharged capacity provided with 1C of discharge current at room temperature with a discharged capacity after 100 cycles. The results are shown in Table 1.

TABLE 1

	suspension amount of lithium carbonate	composition ratio of each metal in all metals except Li										holding temperature			average particle size (D50)	D90	discharged capacity	rate performance	capacity retention rate
	(g)	Ni	Co	Mn	Ti	Cr	Fe	Cu	Al	Sn	Mg	(° C.)	x	α	(μm)	(μm)	(mAh/g)	(%)	(%)
Working example 1	1393	33.3	33.3	33.3								1000	1.00	0.13	5.5	10.2	153	92	90
Working example 2	1393	33.3	33.3	33.3								1000	1.00	0.12	8.1	15.1	154	92	91
Working example 3	1393	33.3	33.3	33.3								1000	1.00	0.12	11.3	17.6	155	92	92
Working example 4	1393	33.3	33.3	33.3								1000	1.00	0.12	14.3	19.8	154	91	91
Working example 5	1393	33.3	33.3	33.3								970	1.00	0.16	10.8	17.5	155	95	92

TABLE 1-continued

	suspension amount of lithium carbonate	composition ratio of each metal in all metals except Li										holding temperature			average particle size (D50)	D90	discharged capacity	rate performance	capacity retention rate
	(g)	Ni	Co	Mn	Ti	Cr	Fe	Cu	Al	Sn	Mg	(° C.)	x	α	(μm)	(μm)	(mAh/g)	(%)	(%)
Working example 6	1393	33.3	33.3	33.3								950	1.00	0.18	10.0	16.9	155	95	92
Working example 7	1350	33.3	33.3	33.3								1000	0.90	0.11	10.6	17.3	160	91	88
Working example 8	1490	33.3	33.3	33.3								1000	1.20	0.14	11.4	18.5	150	95	92
Working example 9	1393	33	33	33						1		1000	1.00	0.13	13.0	19.6	153	93	90
Working example 10	1393	80	10	10								750	1.00	0.15	10.0	17.2	195	90	85
Working example 11	1393	80	15		2.5						2.5	750	1.00	0.16	7.6	15.1	190	87	85
Working example 12	1393	80	15			5						750	1.00	0.18	7.8	15.4	187	87	84
Working example 13	1393	80	15				5					750	1.00	0.17	8.2	15.5	180	85	82
Working example 14	1393	80	15					5				750	1.00	0.17	7.9	15.3	190	89	82
Working example 15	1393	80	15						5			750	1.00	0.15	7.8	15.3	178	85	82
Working example 16	1393	33.3	33.3	33.3								1000	1.00	0.10	12.0	19.3	153	91	90
Working example 17	1393	33.3	33.3	33.3								1000	1.00	0.11	12.4	19.2	152	91	90
Working example 18	1393	33.3	33.3	33.3								950	1.00	0.21	9.8	17.1	155	95	93
Comparative example 1	1393	33.3	33.3	33.3								1000	1.00	0.18	4.2	9.2	153	92	88
Comparative example 2	1393	33.3	33.3	33.3								1000	1.00	0.13	23.5	30.7	154	89	88
Comparative example 3	1393	80	10	10								750	1.00	0.15	27.5	34.2	180	75	77
Comparative example 4	1393	33.3	33.3	33.3								1100	1.00	−0.02	14.8	19.9	148	89	83
Comparative example 5	1393	80	10	10								750	1.00	0.00	10.5	17.6	170	77	77
Comparative example 6	1393	80	15						5			750	1.00	−0.01	8.2	15.0	165	75	73
Comparative example 7	1393	80	15		2.5						2.5	750	1.00	0.00	8.5	15.3	170	79	72

1. A positive electrode active material for lithium ion batteries, represented by composition formula: $Li_xNi_{1-y}M_yO_{2+\alpha}$, wherein

M is Co as an essential component and at least one species selected from a group consisting of Sc, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, Al, Bi, Sn, Mg, Ca, B and Zr, $0.9 \leqq x \leqq 1.2$, $0 < y \leqq 0.7$, $\alpha > 0.05$, and

an average particle size (D50) is 5 μm to 15 μm.

2. The positive electrode active material for lithium ion batteries of claim **1**, wherein the average particle size (D50) is 7 μm to 13 μm.

3. The positive electrode active material for lithium ion batteries of claim **1**, wherein M is at least one species selected from a group consisting of Mn and Co.

4. The positive electrode active material for lithium ion batteries of claim **1**,

wherein $\alpha > 0.15$.

5. The positive electrode active material for lithium ion batteries of claim **4**, wherein $\alpha > 0.20$.

6. The positive electrode active material for lithium ion batteries of claim **1**,

wherein D90 is 20 μm or less in particle size distribution.

7. A positive electrode for lithium ion batteries comprising the positive electrode active material for lithium ion batteries of claim **1**.

8. A lithium ion battery comprising the positive electrode for lithium ion batteries of claim **7**.

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