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ET PILE SECONDAIRE A ELECTROLYTE NON AQUEUX

(54) Title: LITHIUM COBALT COMPOUND OXIDE AND MANUFACTURING METHODS THEREOF, AND NON-
AQUEOUS ELECTROLYTE SECONDARY CELL

(57) **Abrégé/Abstract:**

A non-aqueous electrolyte secondary cell having improved discharge properties is provided. The non-aqueous electrolyte secondary cell having improved discharge properties can be obtained when a lithium cobalt compound oxide, which has an average particle size in the range of 10 to 15 μ m, and a remaining lithium carbonate at a content of 0.1 percent by weight or less.



ABSTRACT OF THE DISCLOSURE

A non-aqueous electrolyte secondary cell having improved discharge properties is provided. The non-aqueous electrolyte secondary cell having improved discharge properties can be obtained when a lithium cobalt compound oxide, which has an average particle size in the range of 10 to 15 μm , and a remaining lithium carbonate at a content of 0.1 percent by weight or less.

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LITHIUM COBALT COMPOUND OXIDE AND MANUFACTURING METHODS
THEREOF, AND NON-AQUEOUS ELECTROLYTE SECONDARY CELL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to lithium cobalt compound oxides and manufacturing methods thereof, non-aqueous electrolyte secondary cells, and portable electronic apparatuses.

2. Description of the Related Art

It has been known that metal ions having an appropriate size can be introduced onto crystal lattice sites and/or between crystal lattice planes of a transition metal oxide having a hexagonal layer crystal structure. In particular, in lithium-containing interlayer compounds, under a specific potential-difference condition, lithium ions can be introduced onto crystal lattice sites and/or between lattice planes and can then be removed therefrom. In addition, since a lithium secondary cell using a lithium cobalt compound oxide, LiCoO_2 , as a positive active material has a high volume energy density, miniaturization and weight reduction of portable electronic apparatuses can be realized, and hence in recent years, the lithium secondary cells have been increasingly in demand as power sources of portable

personal computers and mobile phones.

In addition, research has also been carried out in which inexpensive transition metals, such as nickel or manganese, are used instead of expensive cobalt (for example, refer to Japanese Unexamined Patent Application Publication Nos. 11-71114 and 11-292550). In Japanese Unexamined Patent Application Publication No. 11-292550, a lithium compound oxide has been disclosed which is obtained from a starting material represented by a chemical formula $\text{LiCo}_x\text{Ni}_{(1-x)}\text{O}_2$ ($0.05 \leq x < 1$), and the crystal structure of this lithium compound oxide (LiCoO_2) can be stably maintained even after the Co component thereof is partly replaced with Ni. According to the related techniques as described above, it has been intended to replace expensive cobalt with nickel or the like.

SUMMARY OF THE INVENTION

However, through intensive research carried out by the inventors of the present invention, it was found that when the Co component of the lithium compound oxide (LiCoO_2) functioning as a positive active material is partly replaced with Ni, the discharge properties of a lithium secondary cell is adversely deteriorated. Accordingly, an object of the present invention is to provide a lithium secondary cell having improved discharge properties.

In more particular, the present invention provides the following.

(1) A lithium cobalt compound oxide obtained through a reaction of a lithium compound and cobalt oxyhydroxide, wherein the lithium cobalt compound oxide comprises particles having an average particle size in the range of 10 to 15 μm , and a remaining lithium carbonate at a content of 0.1 percent by weight or less.

(2) A method for manufacturing a lithium cobalt compound oxide, is provided which comprises: preparing a mixture of a lithium compound and cobalt oxyhydroxide having a repose angle of 50° or less and a tap density of 1.3 to 1.8 g/cm^3 ; and heating the mixture.

(3) In the method for manufacturing a lithium cobalt compound oxide, according to one of the above (1) to (2), primary particles of the cobalt oxyhydroxide having a particle diameter of 0.1 to 1 μm may aggregate to form secondary particles having an average particle diameter of 8 to 15 μm .

(4) A non-aqueous electrolyte secondary cell is provided which comprises the lithium cobalt compound oxide according to the above (1) according to the above (3) as a positive active material used for a positive electrode.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a SEM photograph of cobalt oxyhydroxide used in Example 11 of the present invention;

Fig. 2 is a SEM photograph of cobalt oxyhydroxide used in Example 11 of the present invention; and

Fig. 3 is a SEM photograph of cobalt oxyhydroxide used in Example 11 of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, a positive active material and a non-aqueous electrolyte secondary cell, according to the present invention, will be described in detail.

<Lithium Cobalt Compound Oxide>

A lithium cobalt compound oxide obtained through a reaction of a lithium compound and cobalt oxyhydroxide, wherein the lithium cobalt compound oxide comprises particles having an average particle size in the range of 10 to 15 μm , and a remaining lithium carbonate at a content of 0.1 percent by weight or less.

The average particle diameter of the lithium cobalt compound oxide of the present invention is 10 to 15 μm and preferably 10 to 13 μm . For the measurement of the average particle diameter, the value of cumulative 50% (D50) of the particle distribution, which is obtained by a laser

scattering particle size distribution analyzer, is used.

In addition, as another characteristic feature of the lithium cobalt compound oxide of the present invention, the content of lithium carbonate remaining therein is 0.1 percent by weight or less and preferably 0.5 percent by weight or less.

A lithium cobalt compound oxide of the present invention is a lithium oxide represented by the chemical formula $\text{Li}_x\text{Co}_{1-y}\text{M}_y\text{O}_2\text{N}_z$.

In the formula described above, M is at least one element selected from the group consisting of transition metal elements except Co and Ni and elements of group II, XIII, XIV, and XV of the periodic table; N represents a halogen atom; and $0.10 \leq x \leq 1.25$, $0 \leq y \leq 0.05$, and $0 \leq z \leq 0.05$ are satisfied. It is more preferable when $0.4 \leq x \leq 1.0$, $0 \leq y \leq 0.01$, and $0 \leq z \leq 0.01$ are satisfied.

The lithium cobalt compound oxide described above can be preferably used as a positive active material for a lithium ion secondary cell using a non-aqueous electrolyte.

In addition to the elements mentioned above, for example, the lithium cobalt compound oxide of the present invention may also contain at least one element selected from the group consisting of B, Mg, Si, Cu, Ce, Y, Ti, V, Mn, Fe, Sn, Zr, Sb, Nb, Ru, Pb, Hf, Ta, La, Pr, and Nd.

In addition, the content of a sulfate group contained

in the lithium cobalt compound oxide of the present invention is preferably in the range of from 0.01 to 5 percent by weight and more preferably in the range of from 0.05 to 2 percent by weight.

The sulfate group mentioned above may be obtained by firing a sulfate in reaction performed for the lithium cobalt compound oxide, the sulfate being provided beforehand when starting materials are mixed together. As the sulfate, for example, calcium sulfate or cobalt sulfate may be mentioned.

For the quantitative determination of sulfate groups, various methods may be used, and for example, a method may be performed in which a sample is totally dissolved in nitric acid/hydrogen peroxide or the like, followed by quantitative determination of a sulfate group using ion chromatography. In addition, ICP spectrometric analysis or titrimetric analysis may also be used for quantitative determination. In the ICP spectrometric analysis, a sample is dissolved in nitric acid and perchloric acid, and the quantity of sulfur is then determined by ICP spectrometric analysis, followed by conversion into the quantity of the sulfate group.

In the titrimetric analysis, after barium chromate and a diluted hydrochloric acid solution are added to a sample, neutralization by ammonia is preformed, followed by

filtration, and CrO_4^{2-} obtained in a filtrate by replacement of the sulfate group is then titrated by iodometry, thereby indirectly determining the quantity of the sulfate group (in accordance with the description in "Jikken Kagaku Koza, vol. 15, Bunseki Kagaku (II)" (Courses in Experimental Chemistry, vol. 15, Analytical Chemistry (II)), edited by "The Chemical Society of Japan").

In addition, as the halogen atom contained in the lithium cobalt compound oxide, for example, fluorine or bromine may be mentioned, and fluorine is preferably used. The content of the halogen atom described above is 0.005 to 2.5 percent by weight and preferably 0.05 to 1.5 percent by weight.

<Cobalt Oxyhydroxide>

In a manufacturing method of the present invention, a cobalt oxyhydroxide having a repose angle of 50° or less, preferably 45° or less and a tap density of 1.3 to 1.8 g/cm³, preferably 1.5 to 1.8 g/cm³, is used.

In addition, primary particles of the cobalt oxyhydroxide having a particle diameter of 0.1 to 1 μm may aggregate to form secondary particles, and the average particle diameter of the secondary particles thus formed is preferably in the range of from 8 to 15 μm .

The formation of the secondary particles by aggregation of the primary particles can be confirmed from the

observation of SEM photographs. Figs. 1 to 3 are particular SEM photographs showing the particles of the cobalt oxyhydroxide.

It is believed that the cobalt oxyhydroxide is primarily composed of CoOOH ; however, Co_3O_4 , CoCO_3 , and the like may also be contained.

A method for manufacturing the cobalt oxyhydroxide used for the manufacturing method of the present invention is not particularly limited. For example, a material may be used which is formed by oxidizing a compound containing divalent cobalt, such as cobalt nitrate, cobalt chloride, or cobalt sulfate, with an oxidizing agent, followed by neutralization with an alkaline material.

The oxidizing agent mentioned above is not particularly limited, and for example, there may be mentioned air, oxygen, and ozone; permanganic acid (HMnO_4) and salts thereof represented by M^3MnO_4 and the like; chromic acid (CrO_3) and related compounds thereof represented by $\text{M}^3_2\text{Cr}_2\text{O}_7$, M^3_2CrO_4 , $\text{M}^3\text{CrO}_3\text{X}$, CrO_2X_2 , and the like; halogens such as F_2 , Cl_2 , Br_2 , and I_2 ; peroxides such as H_2O_2 , Na_2O_2 , and BaO_2 ; peroxy acids, compounds represented, for example, by $\text{M}^3_2\text{S}_2\text{O}_8$, M^3_2SO_5 , H_2CO_3 , and $\text{CH}_3\text{CO}_3\text{H}$ and salts thereof; and oxygen acids, compounds represented, for example, by M^3MClO , M^3BrO , M^3IO , M^3ClO_3 , M^3BrO_3 , M^3IO_3 , M^3ClO_4 , M^3IO_4 , $\text{Na}_3\text{H}_2\text{IO}_6$, and KIO_4 , and the salts thereof. In the formula, M^3 indicates an alkaline metal

element. The alkaline metal element mentioned above is not particularly limited, and for example, lithium, sodium, potassium, and rubidium may be mentioned. In addition, X indicates a halogen atom.

The alkaline materials used for neutralization are not particularly limited, and an aqueous solution containing an inorganic hydroxide such as lithium hydroxide, sodium hydroxide, potassium hydroxide, magnesium hydroxide, calcium hydroxide, barium hydroxide, or ammonium hydroxide may be preferably used.

The cobalt oxyhydroxide described above can be obtained by the steps of dissolving a compound containing divalent cobalt such as cobalt nitrate, cobalt chloride, or cobalt sulfate in water for forming an aqueous solution, and subsequently adding the oxidizing agent and the alkaline material described above for simultaneously performing the neutralization and oxidation. Alternatively, the cobalt oxyhydroxide can also be obtained by synthesizing divalent cobalt hydroxide by adding the alkaline material to an aqueous solution containing the above divalent cobalt compound, followed by oxidation with an oxidizing agent. Furthermore, the cobalt oxyhydroxide may also be obtained by neutralization by addition of the alkaline material after the oxidizing agent is added to an aqueous solution containing the above divalent cobalt compound.

<Lithium Compound>

The manufacturing method of the present invention uses a lithium compound. The lithium compound is not particularly limited; however, for example, an inorganic lithium salt, such as lithium hydroxide, lithium carbonate, or lithium nitrate may be preferably used. As the lithium compound, lithium carbonate is preferable since being easily available and inexpensive. A lithium compound having a higher purity is preferably used.

<Manufacturing Method>

According to the manufacturing method of the present invention, for example, a mixture is first obtained by mixing the cobalt oxyhydroxide with a lithium compound, preferably with lithium carbonate. A wet or a dry mixing method may be optionally performed; however, a dry mixing method is preferable since being easily performed. In the dry mixing method, a blender is preferably used for uniformly mixing starting materials. The mixing ratio of the lithium compound to the cobalt compound, which compounds are starting materials in the mixing step, on an atomic basis (Li/Co) is set to 0.99 to 1.06 and is preferably set to 0.99 to 1.02.

Next, the mixture thus prepared is fired. The firing

temperature is preferably 700 to 1,110°C and more preferably 850 to 1,050°C. The firing time is 1 to 24 hours and preferably 2 to 10 hours. When the firing temperature is decreased below 700°C, the lithium cobalt compound oxide cannot be sufficiently synthesized, and as a result, the cobalt oxyhydroxide and the lithium compound used as the starting materials unfavorably remain. On the other hand, when the firing temperature is increased above 1,100°C, the decomposition of the desired lithium cobalt compound oxide will start, and when this lithium cobalt compound oxide is used as a positive active material, the degradation in cell properties may occur, that is, in particular, the decrease in capacity at a voltage at the stage of the end of discharge and the degradation in cyclic properties unfavorably occur.

The firing may be performed either in the air or in an oxygen atmosphere and is not particularly limited. After the firing, cooling is optionally performed, followed by pulverization whenever necessary, thereby forming the lithium cobalt compound oxide. The pulverization performed whenever necessary is optionally performed, for example, when particles of the lithium cobalt compound oxide obtained by firing are loosely bonded to each other in the form of a block.

<Measurement Method of Particle Distribution>

The measurement was performed using a Microtrack particle distribution measurement apparatus 9320-X100 (manufactured Leed & Nortrup Instruments) under the following conditions. Ultra pure water in an amount of 300 ml was added to a sample embedded in the particle distribution measurement apparatus, followed by addition of 2 ml of a solution containing 10% of sodium hexamethaphosphate. Next, a sample was added until the concentration thereof became suitable for this particle distribution measurement apparatus. The step described above was performed using a reflux amount of 40 ml/sec. Next, after dispersion treatment was performed by applying ultrasonic waves at an output of 40 W for 60 seconds, the average particle diameter was measured.

<Measurement of Tap Density>

A sample in an amount of 50 g in a 50-ml graduated cylinder was placed in a Dual Autotap apparatus manufactured by Yuasa Ionic Co. Ltd. and was tapped 500 times, and subsequently the volume was measured to obtain the tap density.

<Measurement of Repose Angle>

A powder tester PT-N type apparatus (manufactured by Hosokawa Micron Corporation) was used. Particles passing through a sieve having a mesh size of 250 μm were allowed to fall on a repose angle measurement table through a funnel. After the shape of the particles, that is, a mountain shape, became stable, the repose angle was measured.

<Formation Method of Cell>

As the positive active material for a lithium secondary cell, the lithium cobalt compound oxide described above is used. The positive active material is one of stating materials for a positive electrode compound of a lithium secondary cell, the positive electrode compound, which will be described later, being a mixture formed of the positive active material, a conductive agent, a binder, filler whenever necessary, and the like. Since the positive active material of the lithium secondary cell, according to the present invention, is formed of the lithium cobalt compound oxide described above, kneading with the other starting materials can be easily performed when the positive electrode compound is prepared, and in addition, coating of a positive electrode collector with the positive electrode compound thus obtained can also be easily performed.

The lithium secondary cell of the present invention uses the lithium cobalt compound oxide as a positive active

material and comprises a positive electrode, a negative electrode, separators, and a non-aqueous electrolyte containing a lithium salt. The positive electrode is formed, for example, by applying a positive electrode compound onto a positive electrode collector, followed by drying, and the positive electrode compound is composed of a positive active material, a conductive agent, a binder, and filler whenever necessary, and the like.

A material for the positive electrode collector is not particularly limited as long as being inactive in an assembled cell in view of chemical reaction, and for example, there may be mentioned stainless steel, nickel, aluminum, titanium, baked carbon, and aluminum or stainless steel surface-treated with carbon, nickel, titanium, or silver.

As the conductive agent, for example, there may be mentioned conductive materials, such as graphite including natural graphite and manmade graphite, carbon black, acetylene black, carbon fiber, carbon nanotube, and metal such as powdered nickel. As the natural graphite, for example, scaly graphite, flake graphite, and earthy graphite may be mentioned. Those mentioned above may be used alone or in combination. The content of the conductive agent in the positive electrode compound is 1 to 50 percent by weight and preferably 2 to 30 percent by weight.

As the binder, for example, there may be mentioned

polysaccharides, thermoplastic resins, and polymers having elasticity, such as poly(vinylidene fluoride), poly(vinyl chloride), carboxymethylcellulose, hydroxylpropylcellulose, recycled cellulose, diacetylcellulose, poly(vinyl pyrrolidone), ethylene-propylene-diene-terpolymer (EPDM), sulfonated EPDM, styrene-butadiene rubber, fluorinated rubber, and polyethylene oxide. Those mentioned above may be used alone or in combination. The content of the binder in the positive electrode compound is 2 to 30 percent by weight and preferably 5 to 15 percent by weight.

The filler of the positive electrode compound has a function of suppressing the volume expansion or the like of the positive electrode and is used whenever necessary. As the filler, any fiber materials may be used as long as being in active in an assembled cell in view of chemical reaction, and for example, fibers made of olefinic polymers such as polypropylene and polyethylene, glass fibers, and carbon fibers may be used. The content of the filler is not particularly limited and is preferably 0 to 30 percent by weight of the positive electrode compound.

The negative electrode is formed by applying a negative electrode material onto a negative electrode collector, followed by drying. As the negative electrode collector, any material may be used as long as being in active in an assembled cell in view of chemical reaction, and for example,

there may be mentioned stainless steel, nickel, copper, titanium, aluminum, baked carbon, copper or stainless steel surface-treated with carbon, nickel, titanium, or silver, and aluminum-cadmium alloy.

The negative electrode material is not particularly limited, and for example, there may be mentioned carbonaceous materials, metal composite oxides, metal lithium, and lithium alloys. As the carbonaceous material, for example, hard-graphitized carbon materials and graphite-base carbon materials may be mentioned. As the metal composite oxide, for example, there may be mentioned a compound represented by $\gamma \text{Sn}_p\text{M}^1_{1-p}\text{M}^2_q\text{O}_r$ (where, M^1 is at least one element selected from the group consisting of Mn, Fe, Pb, and Ge; M^2 is at least one element selected from the group consisting of Al, B, P, Si, elements of group I, II, and III of the periodic table, and halogen atoms; and $0 < p \leq 1$, $1 \leq q \leq 3$, and $1 \leq r \leq 8$ are satisfied).

As the separator, an insulating thin film having a high ion transmittance and a predetermined mechanical strength is used. Sheets and nonwoven cloths may be used which are made of glass fibers or an olefinic polymer, such as polyethylene or polypropylene, having organic-solvent resistance and hydrophobic properties. The pore diameter of the separator is not particularly limited as long as effectively used for a general cell application and is, for example, 0.01 to 10

μm. The thickness of the separator may be in the range used for a general cell application and is, for example, 5 to 300 μm. In addition, in the case in which a solid electrolyte such as a polymer is used as described later, the solid electrolyte may also be used as the separator. In addition, in order to improve the discharge properties and the charge and discharge properties, a compound such as pyridine, triethyl phosphite, or triethanolamine may be added to the electrolyte.

The non-aqueous electrolyte containing a lithium salt is a mixture of a non-aqueous electrolyte and a lithium salt. As the non-aqueous electrolyte, a non-aqueous electrolyte or an organic solid electrolyte is used. As the non-aqueous electrolyte, for example, there may be mentioned aprotic organic solvents such as N-methyl-2-pyrrolidinone, propylene carbonate, ethylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, γ-butyrolactone, 1,2-dimethoxyethane, tetrahydrofuran, 2-methyl tetrahydrofuran, dimethyl sulfoxide, 1,3-dioxolane, formamide, dimethyl formamide, dioxolane, acetonitrile, nitromethane, methyl formate, methyl acetate, a phosphoric acid triester, trimethoxymethane, a dioxolane derivative, sulfolane, 3-methyl-2-oxazolidinone, a propylene carbonate derivative, a tetrahydrofuran derivative, diethyl ether, and 1,3-propanesultone. Those mentioned above may be used alone or

in combination.

As the organic solid electrolyte, for example, a polyethylene derivative, a polymer including the same, a propylene oxide derivative, a polymer including the same, and a phosphate polymer may be mentioned. As the lithium salt, a material dissolved in the non-aqueous electrolyte described above is used, and for example, LiClO_4 , LiBF_4 , LiPF_6 , LiCF_3SO_3 , LiCF_3CO_2 , LiAsF_6 , LiSbF_6 , $\text{LiB}_{10}\text{Cl}_{10}$, LiAlCl_4 , chloroboran lithium, a lithium lower aliphatic carboxylate, and lithium tetraphenylborate may be used alone or in combination.

The shape of the lithium secondary cell of the present invention may be a button, sheet, cylinder, rectangle, or the like. The application of the secondary cell of the present invention is not particularly limited and may be applied to electronic apparatuses, such as notebook personal computers, laptop personal computers, pocket type word processors, mobile phones, cordless phone handsets, portable CD players, and radios, and consumer electronic apparatuses for automobiles, electric vehicles, and game machines. In addition, the lithium secondary cell is categorized in a non-aqueous electrolyte secondary cell.

<Portable Electronic Apparatuses>

The present invention provides a portable electronic

apparatuses incorporating the non-aqueous electrolyte secondary cell described above. As the portable electronic apparatuses, for example, notebook personal computers, pocket type word processors, mobile phones, cordless phone handsets, portable CD players, radios, and game machines may be mentioned.

EXAMPLES

Hereinafter, the lithium cobalt compound oxide and the non-aqueous electrolyte secondary cell, according to the present invention, will be further described in detail.

(Lithium Cobalt Compound Oxide)

Example 1

Lithium carbonate and cobalt oxyhydroxide were prepared so that the ratio Li/Co on an atomic basis was 1.00, the cobalt oxyhydroxide having an average particle diameter of 10 μm , a repose angle of 45°, and a tap density of 1.5 g/cm³, and were then sufficiently mixed in a mortar, thereby forming a uniform mixture. Subsequently, the mixture thus formed was placed in an alumina crucible and was then fired at 800 to 1,100°C for 10 hours in an air atmosphere, thereby forming a lithium cobalt compound oxide. After the firing, pulverization and classification were performed. SEM photographs, having different magnifications, of the cobalt

oxyhydroxide used as the starting material are shown in Figs. 1 to 3.

The lithium cobalt compound oxide thus obtained had an average particle diameter of 12.3 μm , a content of remaining lithium carbonate of 0.05 percent by weight, and a pressed density of 3.77 g/cm^3 .

Example 2

A process was performed in the same manner as that in Example 1 except that cobalt oxyhydroxide was used having an average particle diameter of 12 μm , a repose angle of 45°, and a tap density of 1.6 g/cm^3 . The lithium cobalt compound oxide thus obtained had an average particle diameter of 12.5 μm , a content of remaining lithium carbonate of 0.04 percent by weight, and a pressed density of 3.78 g/cm^3 .

Example 3

A process was performed in the same manner as that in Example 1 except that cobalt oxyhydroxide was used having an average particle diameter of 14 μm , a repose angle of 40°, and a tap density of 1.7 g/cm^3 . The lithium cobalt compound oxide thus obtained had an average particle diameter of 12.8 μm , a content of remaining lithium carbonate of 0.05 percent by weight, and a pressed density of 3.75 g/cm^3 .

Comparative Example 1

A process was performed in the same manner as that in Example 1 except that cobalt oxyhydroxide was used having an average particle diameter of 2 μm , a repose angle of 63° , and a tap density of 1.1 g/cm^3 . The lithium cobalt compound oxide thus obtained had an average particle diameter of 12.8 μm , a content of remaining lithium carbonate of 0.15 percent by weight, and a pressed density of 3.51 g/cm^3 .

Comparative Example 2

A process was performed in the same manner as that in Example 1 except that cobalt oxyhydroxide was used having an average particle diameter of 3 μm , a repose angle of 60° , and a tap density of 1.2 g/cm^3 . The lithium cobalt compound oxide thus obtained had an average particle diameter of 12.7 μm , a content of remaining lithium carbonate of 0.18 percent by weight, and a pressed density of 3.52 g/cm^3 .

<Cell Performance Test>

(I) Formation of Lithium Secondary Cell

A positive electrode material was formed by mixing 91 percent by weight of each of the lithium cobalt compound oxides formed in accordance with Examples 1 to 3 and Comparative Examples 1 and 2, 6 percent by weight of powdered graphite, and 3 percent by weight of poly(vinyliden

fluoride), and the positive electrode material thus obtained was dispersed in N-methyl-2-pyrrolidinone, thereby forming a paste compound. After this paste compound was applied onto an aluminum foil and then dried, a disc 15 mm in diameter was punched out therefrom, and hence a positive electrode plate was obtained.

(II) Evaluation of Load Characteristic

A coin type non-aqueous electrolyte secondary cell was formed and was then operated at room temperature, and the load characteristic of the cell was evaluated. First, the cell described above was charged in a CCCV mode by applying 0.5C for five hours so as to obtain a voltage of 4.3 V with respect to the positive electrode, and subsequently, the cell was discharged to a voltage of 2.7 V at a discharge rate of 0.2C. After the charge and discharge operation described above were repeated, the arithmetic mean of the discharge capacity was obtained from the first to the third cycles, and the value thus obtained was regarded as a discharge capacity at 0.2C. The same operation as described above was performed at 2C, and a discharge capacity at 2C was also obtained in the same manner as described above. From the values at 0.2C and 2C, a discharge capacity ratio $2C/0.2C$ was obtained. A larger ratio indicates superior load characteristic.

(III) Formation of Aluminum Laminate Type Non-Aqueous Electrolyte Secondary Cell

A positive electrode material was formed by mixing 91 percent by weight of each of the lithium cobalt compound oxides formed in Examples 1 to 3 and Comparative Examples 1 and 2, 6 percent by weight of powdered graphite, and 3 percent by weight of poly(vinyliden fluoride), and the positive electrode material thus obtained was dispersed in N-methyl-2-pyrrolidinone, thereby forming a paste compound. After this paste compound was applied onto an aluminum foil and then dried, a positive electrode sheet 50 cm long and 5 cm wide was obtained by cutting. In addition, 85 percent by weight of mesocarbon microbeads (MCMB) and 15 percent by weight of poly(vinylidene fluoride) was mixed together to form a negative electrode material. This material was dispersed in N-methyl-2-pyrrolidinone to form a paste compound. After applied onto a copper foil, followed by drying, this paste compound was cut into a sheet 50 cm long and 5 cm wide, thereby forming a negative electrode sheet. A separator is provided between the negative electrode sheet and the positive electrode sheet, and a laminate thus formed is folded with a spacer having a size of 2.5 cm as a base member. The folded body thus obtained was placed in an aluminum laminate case and was then impregnated with an

electrolyte under a vacuum condition, followed by heat sealing of the case, thereby forming an aluminum laminate cell.

(IV) Evaluation of Bulge

After being held in a charged state at 4.3 V for 20 days at 60°C, the aluminum laminate type non-aqueous electrolyte secondary cell thus formed was observed whether the bulge was generated. The results are also shown in Table 1.

Table 1

	Load Characteristic (%)	Bulge
Example 1	80	O
Example 2	82	O
Example 3	89	O
Comparative Example 1	40	x
Comparative Example 2	45	x

WHAT IS CLAIMED IS:

1. A lithium cobalt compound oxide obtained through a reaction of a lithium compound and cobalt oxyhydroxide, wherein the lithium cobalt compound oxide comprises particles having an average particle size in the range of 10 to 15 μm , and a remaining lithium carbonate at a content of 0.1 percent by weight or less.

2. A method for manufacturing a lithium cobalt compound oxide, is provided which comprises: preparing a mixture of a lithium compound and cobalt oxyhydroxide having a repose angle of 50° or less and a tap density of 1.3 to 1.8 g/cm^3 ; and heating the mixture.

3. In the method for manufacturing a lithium cobalt compound oxide, according to Claims 1 or 2, primary particles of the cobalt oxyhydroxide having a particle diameter of 0.1 to 1 μm may aggregate to form secondary particles having an average particle diameter of 8 to 15 μm .

4. A non-aqueous electrolyte secondary cell is provided which comprises the lithium cobalt compound oxide according to Claim 1 as a positive active material used for a positive electrode.

Application number / numéro de demande: 2,462,684

Figures: 1-2-3

Pages: _____

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