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(54) Title: POSITIVE-ELECTRODE MATERIAL FOR LITHIUM-ION SECONDARY BATTERY AND METHOD OF PRODUCING SAME

(57) Abrégé/Abstract:

The present invention provides a positive-electrode material, for a lithium-ion secondary battery using olivine-type lithium iron phosphate, which has a low electric resistance, is capable of increasing the capacity of the battery when the battery is charged and discharged at a high current, and allows the battery to be charged and discharged for a long time and have a long life. A positive-electrode material contains a lithium-containing metal phosphate compound, carbon black, and a fibrous carbon material. The lithium-containing metal phosphate compound is coated with a carbon material and has at least one phase selected from among a graphene phase and an amorphous carbon phase formed on a surface thereof. The fibrous carbon material contains at least two kinds of the fibrous carbon materials. At least two kinds of the fibrous carbon materials have different fiber diameters or fiber lengths.

ABSTRACT

The present invention provides a positive-electrode material, for a lithium-ion secondary battery using olivine-type lithium iron phosphate, which has a low electric resistance, is capable of increasing the capacity of the battery when the battery is charged and discharged at a high current, and allows the battery to be charged and discharged for a long time and have a long life. A positive-electrode material contains a lithium-containing metal phosphate compound, carbon black, and a fibrous carbon material. The lithium-containing metal phosphate compound is coated with a carbon material and has at least one phase selected from among a graphene phase and an amorphous carbon phase formed on a surface thereof. The fibrous carbon material contains at least two kinds of the fibrous carbon materials. At least two kinds of the fibrous carbon materials have different fiber diameters or fiber lengths.

POSITIVE-ELECTRODE MATERIAL FOR LITHIUM-ION SECONDARY BATTERY AND METHOD OF PRODUCING SAME

FIELD OF THE INVENTION

The present invention relates to a positive-electrode material for a lithium-ion secondary battery and a method of producing the same.

BACKGROUND

A lithium-ion secondary battery in which a negative electrode is formed by using a material capable of absorbing and discharging lithium ions is capable of restraining deposit of dendrite to a higher extent than a lithium-ion secondary battery in which the negative electrode is formed by using metallic lithium. Therefore the former battery prevents the occurrence of a short circuit between electrodes and has enhanced safety. In addition the former battery has a high capacity and a high energy density.

In recent years, the former lithium-ion secondary battery is demanded to improve its capacity when the battery is charged and discharged at a high electric current and have a long life. The improvement of the capacity is obtained by decreasing the electric resistance of the battery. The battery is demanded to have a long life to such an extent that it is capable of maintaining its performance up to several tens of thousands of cycles.

The following devices have been made to comply with these demands: (a) a positive-electrode material made of a lithium metal oxide which is a reactive substance of the battery and a negative electrode material made of carbon is allowed to have a high capacity, (b) the specific surface areas of particles of a reactive substance of the battery are increased by decreasing the diameters of the particles or the area of the electrode is increased by optimizing the design of the battery, (c) liquid diffusion resistance is decreased by making a separator thin.

When the particles of the reactive material of the battery are set small in the diameters thereof, the specific surface areas of the particles increase. But this necessitates the amount of a binder to be increased. As a result, it is difficult to allow the battery to have a high capacity. In addition, the positive-electrode and negative-electrode materials may peel or drop from a metal foil which is an electricity collector. Which may result in the occurrence of an internal short circuit inside the battery. As a result, there occur a decrease in the voltage of the battery and thermal runaway. Thereby the safety of the lithium secondary battery is impaired.

To increase the adherence of the metal foil to the positive-electrode and negative-electrode materials, the method of altering the kind of the binder is known (patent document 1).

As a method of allowing the lithium-ion secondary battery to have a high capacity when it is charged and discharged at a high electric current, the method of using the carbon electrical conductive material to decrease the electric resistance of the electrode is known (patent documents 2, 3, and 4).

Although the method of altering the kind of the binder is capable of increasing the capacity of the battery, the method is insufficient for improving the property of the battery that it has a high capacity when it is charged and discharged at a high electric current by decreasing the electric resistance of the electrode.

When the battery is cyclically charged and discharged at a high electric current, the positive-electrode and negative-electrode materials expand and contract. Thus conductive paths of particles between the positive and negative electrodes are impaired. As a result, a high electric current cannot be flowed at an early stage after the use of the battery, and the battery has a short life.

In recent years, a lithium-containing metal phosphate compound such as an olivine-type lithium iron phosphate has attracted rising attention as the active substance of the positive electrode for the lithium-ion secondary battery (patent documents 5, 6). This active substance of the positive electrode is safe and contributes to a decrease in the cost of the battery. But the active substance has a high electric resistance and it is difficult to decrease its electric resistance.

PRIOR ART DOCUMENT

PATENT DOCUMENT

Patent document 1: Japanese Patent Application Laid-Open No. 5-226004

Patent document 2: Japanese Patent Application Laid-Open No. 2005-19399

Patent document 1: Japanese Patent Application Laid-Open No. 2001-126733

Patent document 1: Japanese Patent Application Laid-Open No. 2003-168429

Patent document 1: Japanese Patent Application Laid-Open No. 2000-509193

Patent document 1: Japanese Patent Application Laid-Open No. 9-134724

Patent document 1: US PCT Patent Application No. Wo2010/101276 A1

SUMMARY OF THE INVENTION

The present invention has been made to solve the above-described problems. It is an object of the present invention to provide a positive-electrode material, for a lithium-ion secondary battery, using a lithium-containing metal phosphate compound, and specifically olivine-type lithium iron phosphate, which has a low electric resistance and is capable of increasing the capacity of the battery when the battery is charged and discharged at a high current. It is another object of the present invention to provide a positive-electrode material, for the lithium-ion secondary battery, which allows the battery to be charged and discharged for a long time and have a long life. It is still another object of the present invention to provide a method of producing a positive-electrode material for the lithium-ion secondary battery.

The positive-electrode material of the present invention for a lithium-ion secondary battery contains a lithium-containing metal phosphate compound, carbon black, and a fibrous carbon material.

The lithium-containing metal phosphate compound is coated with a carbon material and has at least one phase selected from among a graphene phase and an amorphous carbon phase formed on a surface thereof. Preferably, the lithium-containing metal phosphate compound is olivine-type lithium iron phosphate.

The fibrous carbon material contains at least two kinds of the fibrous carbon materials. At least two kinds of the fibrous carbon materials have different fiber diameters or fiber lengths.

The following provides an outline of certain possibly preferable features of the invention which are to be considered non-restrictively and which will be more fully described hereinafter.

Electron conduction is made owing to compositeness of a surface of the lithium-containing metal phosphate compound coated with the carbon material, a surface of the carbon black, and a surface of the fibrous carbon material caused by bond between carbon atoms.

The above-described positive-electrode material for the lithium-ion secondary battery is produced by the production method of the present invention.

The production method has the steps of coating a surface of a lithium-containing metal phosphate compound with a carbon material and mixing carbon black and a fibrous carbon material with each other.

The mixing step is performed by a compression shear impact-type particle-compositing method.

A mixture is calcined under an inert atmosphere after the mixing step finishes.

The positive-electrode material of the present invention for the lithium-ion secondary battery contains the lithium-containing metal phosphate compound, and specifically the olivine-type lithium iron phosphate, the carbon black, and not less than two kinds of the fibrous carbon materials having different fiber diameters and fiber lengths. Therefore the components of the positive-electrode material and the fibrous carbon material are bonded to each other at the interface therebetween via a graphene layer present on the surfaces of the components of the positive-electrode material. That is, electron conduction is performed between the surfaces of the components owing to the compositeness caused by the bond between carbon atoms. Therefore compared with an electric resistance in contact conduction between electrodes composed of powders, the electric resistances between the powders of the positive-electrode material of the present invention for the lithium-ion secondary battery are low.

The constituent material of the lithium-ion secondary battery which greatly contributes to the electric resistance when the lithium-ion secondary battery is charged and discharged is mainly the positive electrode. The lithium-ion secondary battery using the positive-electrode material of the present invention has an improved electron conduction network inside the electrode, a low electric resistance in the positive electrode, and can be charged and discharged at a high current. In addition, when particles of the positive electrode expand and contract when the battery is charged and discharged, the performance of contact between the particles of the positive electrode and an electrical conductive material is improved and maintained. Thus a rapid decrease of the capacity and output of the battery can be prevented.

In the production method of the present invention, because the components of the positive-electrode material are mixed with one another by using the compression shear impact-type particle-compositing method, even fine materials such as the carbon nanotube can be uniformly mixed with other components.

Therefore the electron conduction network inside the electrode is improved.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a pattern diagram of a positive-electrode material for a lithium-ion secondary battery.

Fig. 2 shows a photograph of the surface of the positive-electrode material taken by a transmission-type electron microscope.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A lithium-ion secondary battery is a secondary battery in which an electrolyte is penetrated into a group of electrodes wound or layered one upon another with a separator being interposed between a positive-electrode plate and a negative plate or the group of electrodes is immersed in the electrolyte to repeatingly absorb and release lithium ions. A positive-electrode material for the lithium-ion secondary battery is formed on the surface of the positive-electrode plate, whereas a negative-electrode material for the lithium-ion secondary battery is formed on the surface of the negative plate.

The positive-electrode plate for the lithium-ion secondary battery contains a lithium-containing metal phosphate compound, carbon black, and a fibrous carbon material.

Fig. 1 shows a pattern diagram of the positive-electrode material of the present invention for the lithium-ion secondary battery. Fig. 1 shows a state in which the lithium-containing metal phosphate compound coated with a carbon material having a graphene phase and the like on its surface, the carbon black, and the fibrous carbon material different in its fiber diameters or fiber lengths are composited with one another. Fig. 2 shows a photograph of the surface of the positive-electrode material taken by a transmission-type electron microscope.

As shown in Fig. 1, an active substance of a positive-electrode material 1 for the lithium-ion secondary battery is a lithium-containing metal phosphate compound 2 whose surface is coated with a carbon material 3. The thickness of the carbon material 3 is several nanometers. The surface of the carbon material 3 is composed of a graphene phase and the like. The lithium-containing metal phosphate compound 2 is composited with carbon black 4 and a fibrous carbon material 5. The fibrous carbon material 5 is a mixture of a fibrous carbon material 5a having a small fiber diameter and a short fiber length and a fibrous carbon material 5b having a large fiber diameter and a long fiber length. The fibrous carbon material 5a is mainly connected to the surface of the lithium-containing metal phosphate compound 2, whereas the fibrous carbon material 5b mainly connects the lithium-containing metal phosphate compounds 2 to each other.

As shown in Fig. 2, the fibrous carbon material 5a is mainly present on the surface of the lithium-containing metal phosphate compound 2. The fibrous carbon material 5b is present between the lithium-containing metal phosphate compounds 2.

As the lithium-containing metal phosphate compound to be used for the positive-electrode material of the present invention, $LiFePO_4$, $LiCoPO_4$, and $LiMnPO_4$ are listed. Of these lithium-containing metal phosphate compounds, olivine-type lithium iron phosphate expressed by $LiFePO_4$ is preferable because it is excellent in its electrochemical properties and safety, and inexpensive.

In another embodiment, the cathode material could be based on complex oxide corresponds to the general formula $A_aM_mZ_zO_oN_nF_f$ wherein A represents one or more alkaline metals, M represents one or more transition metals, and optionally at least one non-transition metal, or mixtures thereof, and Z represents one or more non-metallic elements, wherein $a \geq 0$, $m \geq 0$, $z \geq 0$, $o > 0$, $n \geq 0$ and $f \geq 0$, the coefficients a, m, o, n, f and z being selected to ensure electro neutrality.

A represents preferably lithium.

M represents a transition metal element preferably selected from Fe, Mn, V, Ti, Mo, Nb, W, Zn and mixtures thereof, and optionally a non transition metal, preferably selected from Mg and Al.

Z represents a non metal preferably selected from P, S, Se, As, Si, Ge, B and mixtures thereof.

Non limiting examples of complex oxides include phosphate, oxyphosphate, silicate, oxysilicate, and fluorophosphate. $LiFePO_4$, $LiMnPO_4$, $LiFeSiO_4$, SiO, and SiO_2 or SiOx ($0 \leqq x < 2$) are preferred complex oxides.

The surface of the olivine-type lithium iron phosphate is coated with the carbon material. At least one phase selected from among the graphene phase and an amorphous carbon phase is formed on the surface of the olivine-type lithium iron phosphate. These phases are formed by (a) a method of dispersing conductive carbon black such as acetylene black, Ketjen Black or graphite crystal in a solvent to form a slurry coating solution, dispersing particles of the olivine-type lithium iron phosphate in the coating solution, and thereafter drying the solvent; (b) a method of applying an organic substance or an organic polymer solution to the surface of the particles of the olivine-type lithium iron phosphate and thermally decomposing the organic substance or the organic polymer in a reducing atmosphere; (c) an ion deposit method; and (d) a method of forming a thin film on the surface of the particles of the olivine-type lithium iron phosphate by using a chemical evaporation method (CVD) and/or a physical evaporation method (PVD).

In the present invention, the graphene phase means one layer of a plain six-membered ring structure of sp^2-connected carbon atoms. The amorphous carbon layer means a three-dimensional six-membered ring structure. "That electron conduction is performed owing to compositeness caused by bond between carbon atoms" means that electron conduction is made owing to the bond between the carbon atoms caused by turbulence of the graphene phase and/or the amorphous carbon phase.

The carbon material coating the surface of the active substance of the positive-electrode material closely contacts the surface of the active substance. The graphene phase and the like are formed on the surface of the carbon material. The thickness of the coating layer of the carbon material is 1 to 10nm and preferably 2 to 5nm. When the thickness of the coating layer of the carbon material is less than 1nm, it is difficult to accomplish electron conduction to be performed by the bond of the carbon atoms. When the thickness of the coating layer of the carbon material is more than 10nm, the carbon material layer is thick and the extent of the diffusion of lithium ions to the surface of the active substance which is the reaction portion of the battery becomes low. Therefore the output property of the battery deteriorates.

The carbon black which can be used in the present invention is the conductive carbon black. As the conductive carbon black, acetylene black and Ketjen black are listed.

The fibrous carbon material which can be used in the present invention is at least one selected from among a carbon nanotube and a carbon nanofiber. The carbon nanotube means a tube consisting of a single-walled ring. The carbon nanofiber means a tube consisting of a multi-walled ring.

In the present invention, at least two kinds of fibrous carbon materials different in the fiber diameters and the fiber lengths thereof are used. That is, it is possible to use (a) the fibrous carbon materials different in both the fiber diameters and the fiber lengths thereof, (b) the fibrous carbon materials equal in the fiber diameters thereof and different in the fiber lengths thereof, and (c) the fibrous carbon materials different in the fiber diameters thereof and equal in the fiber lengths thereof.

The fibrous carbon materials different in both the fiber diameters and the fiber lengths thereof are preferable.

The diameter of one of the fibrous carbon materials is 5 to 15nm, whereas the diameter of the other fibrous carbon material is 70 to 150nm. It is preferable that the diameter of one of the fibrous carbon materials is 10nm, whereas the diameter of the other fibrous carbon material is 100nm.

The fiber length of the fibrous carbon material having the diameter of 5 to 15nm is 1 to 3μm and preferably 3μm. The fiber length of the fibrous carbon material having the diameter of 70 to 150nm is 5 to 10μm and preferably 5μm. That is, in the present invention, it is preferable to use the fibrous carbon material having a small fiber diameter and a short fiber length and the fibrous carbon material having a large fiber diameter and a long fiber length.

In the positive-electrode material of the present invention for the lithium-ion secondary battery, the total of the content of the carbon black and that of the fibrous carbon material is not less than 2 mass % and preferably 2 to 10 mass % for the total of the amount of the lithium-containing metal phosphate compound coated with the carbon material, that of the carbon black, and that of the fibrous carbon material.

It is preferable that the mixing ratio between the carbon black and the fibrous carbon material is [carbon black/fibrous carbon material = (2 to 8)/(1 to 3)] in a mass ratio.

In the positive-electrode material of the present invention for the lithium-ion secondary battery, the lithium-containing metal phosphate compound coated with the carbon material, the carbon black, and the fibrous carbon material are mixed with one another by using a compression shear impact-type particle-compositing method.

In the compression shear impact-type particle-compositing method, powders applied to an inner wall of a rotary container by a centrifugal force are mixed between the rotary container and a press head, having a radius of curvature different from that of the rotary container, which is fixed to the inside of the rotary container, while a strong compression shearing force is being applied to the powders. A mixing apparatus to be operated by using these methods, a Nobilta and Mechanofusion mixing machines (produced by Hosokawa Micron Corporation) is known. Manipulating these machines requires some knowledge on the mixing powder conditions in order to prevent any undesirable changes of the materials; like shopping fibers.

In the positive-electrode material of the present invention for the lithium-ion secondary battery, it is preferable to mix the lithium-containing metal phosphate compound, the carbon black, and the fibrous carbon material with one another by using the compression shear impact-type particle-compositing method and thereafter calcine the mixture. By calcining the mixture, the surfaces of the mixed materials are composited with one another owing to the bond between the carbon atoms. As a result, the electron conduction between the surfaces of the materials is improved to a higher extent.

It is preferable to calcine the mixture in the condition of 700 to 850°C under an inert atmosphere for 0.5 to two hours.

It is preferable that binders which can be used for the positive-electrode material for the lithium-ion secondary battery are physically and chemically stable in the atmosphere inside the battery. As such materials, fluorine-containing resin such as polytetrafluoroethylene, vinylidene polyfluoride, and fluororubber; thermoplastic resin such as polypropylene and polyethylene; and dispersion-type resin such as styrene butadiene rubber and polymers of acrylic acid are listed.

The separator which can be used together with the positive-electrode material for the lithium-ion secondary battery holds the electrolyte with the separator electrically insulating the positive electrode and the negative electrode from each other. As the separator, a film made of a synthetic resin, fibers, and inorganic fibers are listed. As examples of materials for the separator, a polyethylene film or a polypropylene film; woven cloth and unwoven cloth made of these resins; and glass fibers and cellulose fibers are listed.

As electrolytes of the lithium secondary battery in which the group of electrodes is immersed, it is preferable to use non-aqueous electrolytes containing lithium salts or ion-conducting polymers.

As non-aqueous solvents in the non-aqueous electrolytes containing the lithium salts, ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and methyl ethyl carbonate (MEC) are listed.

As the lithium salts which can be dissolved in the non-aqueous solvents, lithium hexafluorophosphate ($LiPF_6$), lithium borotetrafluoride ($LiBF_4$), lithium trifluoromethanesulfonate ($LiSO_3CF_4$) are listed.

The positive-electrode material for the lithium-ion secondary battery is formed by layering the components on the surface of the positive-electrode plate serving as an electricity collector. Metal thin films can be exemplified as the positive-electrode plate. An aluminum foil can be exemplified as the electricity collector of the positive electrode. The carbon material can be exemplified as the negative-electrode plate. A copper foil can be exemplified as the electricity collector of the negative electrode.

EXAMPLES

The positive electrode of the present invention for the lithium secondary battery is described in detail below by way of examples and comparative examples. But the present invention is not limited to the examples described below unless the examples depart from the gist of the present invention.

Examples 1, 2 and Comparative Examples 1 through 5

The olivine-type lithium iron phosphate ($LiFePO_4$) having a secondary particle diameter of 0.5 to 2μm was used as the active substance of the positive electrode. The olivine-type lithium iron phosphate was coated with the carbon material having a thickness of about 3nm by using an evaporation method in which carbonized gas was used.

Carbon nanotube and acetylene black having configurations and amounts shown in table 1 were added to the active substance of the positive electrode and mixed with one another with the Nobilta mixing machine (produced by Hosokawa Micron Corporation) by using the compression shear impact-type particle-compositing method. The mixing ratio between the carbon nanotube and the acetylene black was [acetylene black/carbon nanotube = 8/2] in a mass ratio. The mixing method carried out by using the Nobilta mixing machine is shown as "mixing" in the column of "electrical conductive material addition method" in table 1.

Six parts by mass of vinylidene polyfluoride was added to 97 parts by mass of the mixture as a binder. N-methylpyrrolidone was added as a dispersion solvent to the mixture. The components were kneaded to prepare a positive-electrode slurry as the active substance of the positive electrode for the lithium-ion secondary battery.

An aluminum foil having a thickness of 20μm and a width of 150mm was prepared. The positive-electrode slurry was applied to both surfaces of the aluminum foil and dried. Thereafter the aluminum foil to which the positive-electrode slurry was applied was pressed and cut to obtain a positive-electrode plate for the lithium secondary battery. The total thickness of the positive-electrode plate after the positive-electrode slurry was applied to both surfaces of the aluminum foil and the aluminum foil was dried and pressed was 160μm.

A laminate battery of 20mAh was produced by using the positive-electrode plate. A negative pole made of a graphite material was used as the electrode opposite to the positive-electrode plate. Unwoven cloth made of olefin fiber was used as a separator for electrically insulating the positive-electrode plate and the negative-electrode plate from each other. An electrolyte used was composed of lithium hexafluorophosphate ($LiPF_6$) dissolved at 1 mol/l in a solution in which ethylene carbonate (EC) and methyl carbonate (MEC) were mixed with each other at a volume ratio of 30:70.

To examine the discharge performance of the batteries, a discharge test and a cycle life test were conducted.

Discharge Test

After the battery was charged, charge/discharge efficiency became nearly 100% was confirmed, a discharged capacity was measured when each battery was discharged up to 2.0V at a constant electric current of 4mA. Thereafter a discharged capacity was measured at electric current of 200mA. The discharged capacity at the electric current of 200mA was expressed as the ratio with respect to the discharged capacity at the electric current of 4mA. The discharge performance is shown in table 1 as evaluation of discharge test (%).

Cycle Life Test

Each battery was charged (finished at electric current of 1mA) at a constant electric current and a constant voltage of 4.0V (limited electric current of 60mA). Each battery was discharged up to 2.0V at a constant electric current of 60mA. Each charging and discharging operation was suspended for 10 minutes. A series of charge, suspension, and discharge was set as one cycle. The ratio of a discharged capacity at the 200th cycle to that at the first cycle was calculated as the discharge capacity maintenance ratio. The discharge capacity maintenance ratio is shown in table 1 as a cycle life test (%).

Examples 3 through 5

The olivine-type lithium iron phosphate ($LiFePO_4$) having a secondary particle diameter of 0.5 to 2μm was used as the active substance of the positive electrode. The olivine-type lithium iron phosphate was coated with the carbon material having a thickness of about 3nm by using an evaporation method in which carbonized gas was used.

Carbon nanotube and acetylene black having configurations and amounts shown in table 1 were added to the active substance of the positive electrode and mixed with one another with the Nobilta mixing machine (produced by Hosokawa Micron Corporation) by using the compression shear impact-type particle-compositing method.

The mixture was calcined at 700 to 800°C for one hour in a reducing atmosphere. The case in which the mixture was calcined after the above-described components were mixed with each other by using the Nobilta mixing machine is shown as "compositing" in the column of "electrical conductive material addition method" in table 1.

By using the calcined mixture, a positive-electrode slurry was produced by a method similar to that of example 1. By using the positive-electrode slurry, a laminate battery of 20mAh was produced in a method similar to that of the example 1. Table 1 shows results of evaluation made in a method similar to that of the example 1.

[Table 1]

Kind of battery	Electrical conductive material addition method	Carbon nanotube		Total amount of electrical conductive material (mass %)	Evaluation of discharge test (%)	Cycle life test (%)
		Diameter (nm)	Length (μm)			
Example 1	Mixing	10 100	10 10	3	86	83
Example 2	Mixing	10 100	2 10	3	91	89
Example 3	Compositing	10 100	10 10	3	92	91
Example 4	Compositing	10 100	2 10	3	95	96
Example 5	Compositing	10 100	2 10	8	99	98
Comparative example 1	Mixing	200	15	1	22	19
Comparative example 2	Mixing	200	7	1	31	33
Comparative example 3	Mixing	3	15	1	53	48
Comparative example 4	Mixing	3	7	1	60	55
Comparative example 5	Mixing	3	7	3	82	72

The results of the evaluation of the discharge test shown in table 1 indicate that the lithium-ion secondary batteries using the positive-electrode materials of the examples 1 through 5 were superior to the batteries using the positive-electrode materials of the comparative examples 1 through 5.

For example, in the example 1, the carbon nanotubes small and large in the fiber diameters thereof were mixedly used. In the comparative example 1, the carbon nanotube large in its fiber diameter and long in its fiber length was singly used. In the comparative example 2, the carbon nanotube large in its fiber diameter and short in its fiber length was singly used. In the comparative example 3, the carbon nanotube small in its fiber diameter and long in its fiber length was singly used. In each of the comparative examples 4 and 5, the carbon nanotube small in the fiber diameter thereof and short in the fiber length thereof were singly used.

The results of the evaluation of the comparative examples 1 through 5 indicate that the battery has excellent performance when it contains a large amount of the carbon nanotube small in its fiber diameter and the carbon nanotube large in its fiber diameter. It is considered that this is attributed to the conductivity of the olivine-type lithium iron phosphate which is active substance particles and excellence in a conductive network of particles. As in the case of the battery of the comparative example 5, the battery containing a large absolute amount of electrical conductive materials is excellent in its property.

But as shown in the examples 1 through 5, when the carbon nanotubes small and large in the fiber diameters thereof are mixedly used, excellent results were obtained in the discharge test and the cycle life test. It is considered that this is attributed to an improved electron conductivity owing to the disposition of the mixed carbon nanotubes on the surface of the active substance particles and between the active substance particles.

It is more favorable to vary the fiber length of the carbon nanotubes and form a network between the carbon nanotubes and particles disposed on the periphery thereof.

The carbon nanotubes of the examples 3 through 5 bond with the surfaces of the particles of the positive-electrode active substance by compositeness not by contact resistance between carbon particles but by bond between carbon atoms (C-C). This is the reason why the batteries of the examples 3 through 5 have an improved electron conductivity.

The acetylene black is present tangly with the surfaces of the particles of the active substance of the positive electrode and carbon nanotubes. Therefore the acetylene black bonds not only with the carbon coating the surfaces of the particles of the active substance of the positive electrode, but also with the carbon nanotubes. It is considered that all particles are coated with two layers of the electrical conductive material.

The results of the evaluation made in the cycle life test in which each battery was charge and discharged at a high current had a tendency similar to that of the results of the evaluation made in the discharge test. The discharge test and the cycle life test prove that the lithium-ion secondary battery using the positive-electrode material of the present invention is excellent.

INDUSTRIAL APPLICABILITY

The positive-electrode material of the present invention for the lithium secondary battery allows the battery to have a high capacity when the battery is charged and discharged at a high electric current and allows the battery to be charged and discharged for a long time and stably repeated at the high electric current. Therefore the positive-electrode material can be preferably utilized for uses such as electric vehicles, hybrid cars, and the like which require durability and batteries to be charged and discharged at a high electric current, travel a long distance, and consume a large amount of fuel.

EXPLANATION OF REFERENCE SYMBOLS AND NUMERALS

1: positive-electrode material for lithium-ion secondary battery

2: lithium-containing metal phosphate compound

3: carbon material

4: carbon black

5: fibrous carbon material

While embodiments of the invention have been illustrated in the accompanying drawings and described above, it will be evident to those skilled in the art that modifications may be made therein without departing from the invention.

CLAIMS

1. A positive-electrode material for a lithium-ion secondary battery containing a lithium-containing metal phosphate compound, carbon black, and a fibrous carbon material,

wherein said lithium-containing metal phosphate compound is coated with a carbon material and has at least one phase selected from among a graphene phase and an amorphous carbon phase formed on a surface thereof; and

said fibrous carbon material contains at least two kinds of said fibrous carbon materials, and at least two kinds of said fibrous carbon materials have different fiber diameters or fiber lengths.

2. The composite material of claim 1, wherein the complex oxide corresponds to the general formula $A_aM_mZ_zO_oN_nF_f$ wherein A represents one or more alkaline metals, M represents one or more transition metals, and optionally at least one non-transition metal, or mixtures thereof, and Z represents one or more non-metallic elements, wherein $a \geq 0$, $m \geq 0$, $z \geq 0$, $o > 0$, $n \geq 0$ and $f \geq 0$, the coefficients a, m, o, n, f and z being selected to ensure electro neutrality.

3. The composite material of claim 2, wherein A represents lithium.

4. The composite material of claim 2, wherein M represents a transition metal element preferably selected from Fe, Mn, V, Ti, Mo, Nb, W, Zn and mixtures thereof, and optionally a non transition metal.

5. The composite material of claim 2, wherein Z represents a non metal selected from P, S, Se, As, Si, Ge, B and mixtures thereof.

6. The composite material of claim 2, wherein the complex oxide is selected from phosphate, oxyphosphate, silicate, oxysilicate, and fluorophosphate.

7. A positive-electrode material for a lithium-ion secondary battery according to claim 1, wherein electron conduction is made owing to compositeness of a surface of said carbon material on said lithium-containing metal phosphate compound, a surface of said carbon black, and a surface of said fibrous carbon material caused by bond between carbon atoms.

8. A positive-electrode material for a lithium-ion secondary battery according to claim 1, wherein said lithium-containing metal phosphate compound is olivine-type lithium iron phosphate.

9. A positive-electrode material for a lithium-ion secondary battery according to claim 1, wherein said fibrous carbon material is a mixture of a fibrous carbon material having fiber diameters of 5 to 15nm and fiber lengths of 1 to 3μm and a fibrous carbon material having fiber diameters of 70 to 150nm and fiber lengths of 5 to 10μm.

10. A positive-electrode material for a lithium-ion secondary battery according to claim 9, wherein said fibrous carbon material is at least one fibrous carbon material selected from among a carbon nanotube and a carbon nanofiber.

11. A positive-electrode material for a lithium-ion secondary battery according to claim 1, wherein said carbon black is conductive carbon black.

12. A positive-electrode material for a lithium-ion secondary battery according to claim 1, wherein a total of a content of said carbon black and that of said fibrous carbon material is not less than 2 mass % for a total of an amount of said lithium-containing metal phosphate compound coated with said carbon material, an amount of said carbon black, and an amount of said fibrous carbon material.

13. A method of producing a positive-electrode material for a lithium-ion secondary battery according to claim 1, comprising the steps of:

coating a surface of a lithium-containing metal phosphate compound with a carbon material; and

mixing carbon black and a fibrous carbon material with each other,

wherein said mixing step is performed by a compression shear impact-type particle-compositing method.

14. A method, according to claim 13, of producing a positive-electrode material for a lithium-ion secondary battery,

wherein a mixture is calcined under an inert atmosphere after said mixing step finishes.

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Figures: 1, 2

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