(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 September 2015 (11.09.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/132641 A1

(51) International Patent Classification:
H01M 4/04 (2006.01) *H01M 4/62* (2006.01)
H01M 4/131 (2010.01) *C01G 45/12* (2006.01)
H01M 4/1391 (2010.01) *C01G 53/00* (2006.01)
H01M 4/36 (2006.01) *H01M 10/04* (2006.01)
H01M 4/505 (2010.01) *H01M 4/525* (2010.01)

(21) International Application Number:
PCT/IB2015/000215

(22) International Filing Date:
24 February 2015 (24.02.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2014-040204 3 March 2014 (03.03.2014) JP

(71) Applicant: **TOYOTA JIDOSHA KABUSHIKI KAISHA** [JP/JP]; 1, Toyota-cho, Toyota-shi, Aichi-ken, 471-8571 (JP).

(72) Inventors: **KISHIMOTO, Naoya**; c/o TOYOTA JIDOSHA KABUSHIKI KAISHA, of 1, Toyota-cho, Toyota-shi, Aichi-ken, 471-8571 (JP). **KITAYOSHI, Masanori**; c/o TOYOTA JIDOSHA KABUSHIKI KAISHA, of 1, Toyota-cho, Toyota-shi, Aichi-ken, 471-8571 (JP).

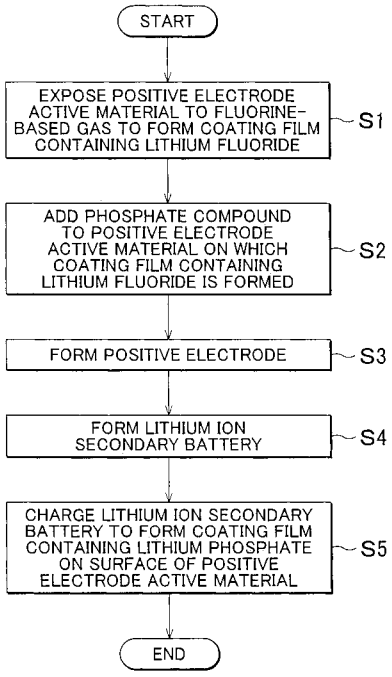
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH,

[Continued on next page]

(54) Title: POSITIVE ELECTRODE OF LITHIUM ION SECONDARY BATTERY, AND METHOD OF MANUFACTURING LITHIUM ION SECONDARY BATTERY

FIG. 1



(57) Abstract: In a method of manufacturing a lithium ion secondary battery, first, lithium nickel manganese oxide which is a positive electrode active material is exposed to fluorine-based gas to form a coating film containing amorphous lithium fluoride on a surface of the positive electrode active material. Next, a phosphate compound is added to the positive electrode active material on which the coating film containing the lithium fluoride is formed. After a lithium ion secondary battery which includes a positive electrode including the positive electrode active material is formed, the lithium ion secondary battery is charged to form a coating film containing amorphous lithium phosphate on the surface of the positive electrode active material.

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GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

POSITIVE ELECTRODE OF LITHIUM ION SECONDARY BATTERY, AND METHOD OF MANUFACTURING LITHIUM ION SECONDARY BATTERY

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a positive electrode of a lithium ion secondary battery, and a method of manufacturing a lithium ion secondary battery.

2. Description of Related Art

[0002] A lithium ion secondary battery is chargeable or dischargeable by lithium ions in an electrolyte moving between a positive electrode and a negative electrode which store and release lithium ions.

[0003] Published Japanese Translation of PCT application No. 2002-527873 (JP-A-2002-527873) discloses a technique regarding a lithium ion polymer battery. In the technique disclosed in JP-A-2002-527873, in order to improve battery characteristics, an insoluble lithium compound such as Li_3PO_4 or LiF is added to the lithium ion polymer battery. In addition, as a cathode material, a manganese oxide compound ($LiMn_2O_4$, $LiMnO_2$) is used.

[0004] One of the important characteristics of a lithium ion secondary battery is the cycle characteristics. The cycle characteristics are an index indicating to what extent a battery capacity of a lithium ion secondary battery after repetition of charging and discharging in predetermined cycles changes as compared to an initial battery capacity. In general, it is preferable that a decrease in the battery capacity after the repetition of charging and discharging be small as compared to the initial battery capacity.

[0005] In the technique disclosed in JP-A-2002-527873, in order to improve battery characteristics, an insoluble lithium compound such as Li_3PO_4 or LiF is added to the lithium ion polymer battery. However, as a result of investigation, the present inventors initially found that, in a lithium ion secondary battery in which lithium nickel manganese oxide is used as a positive electrode active material, cycle characteristics of the lithium ion secondary battery cannot be improved to a sufficient value with only the addition of Li_3PO_4 or LiF.

SUMMARY OF THE INVENTION

[0006] The invention has been made to provide a positive electrode of a lithium ion secondary battery capable of further improving cycle characteristics, and a method of

manufacturing a lithium ion secondary battery.

[0007] According to a first aspect of the invention, there is provided a positive electrode of a lithium ion secondary battery, the positive electrode including a positive electrode active material that contains lithium nickel manganese oxide, in which a coating film containing amorphous lithium fluoride and amorphous lithium phosphate is formed on a surface of the positive electrode active material.

[0008] According to a second aspect of the invention, there is provided a method of manufacturing a lithium ion secondary battery. This method includes: exposing lithium nickel manganese oxide, which is a positive electrode active material, to fluorine-based gas to form a coating film containing amorphous lithium fluoride on a surface of the positive electrode active material; adding a phosphate compound to the positive electrode active material, on which the coating film containing the lithium fluoride is formed, to prepare a positive electrode containing the positive electrode active material; forming a lithium ion secondary battery including the prepared positive electrode; and charging the formed lithium ion secondary battery to form a coating film containing amorphous lithium phosphate on the surface of the positive electrode active material.

[0009] According to a third aspect of the invention, there is provided a method of manufacturing a lithium ion secondary battery. This method includes: adding a fluorine compound and a phosphate compound to lithium nickel manganese oxide, which is a positive electrode active material, to prepare a positive electrode containing the positive electrode active material; forming a lithium ion secondary battery including the positive electrode; and charging the formed lithium ion secondary battery to form a coating film containing amorphous lithium fluoride and amorphous lithium phosphate on a surface of the positive electrode active material.

[0010] According to the invention, the coating film containing amorphous lithium fluoride and amorphous lithium phosphate is formed on the surface of the positive electrode active material. Here, the amorphous coating film has lower lithium ion diffusion resistance (in other words, higher lithium ion conductivity) than that of a crystalline coating film. Accordingly, by forming the amorphous coating film on the surface of the positive electrode active material, the lithium ion diffusion resistance of the surface of the positive electrode active material can be reduced. Therefore, cycle characteristics of the lithium ion secondary battery can be further improved.

[0011] According to the invention, a positive electrode of a lithium ion secondary battery capable of further improving cycle characteristics, and a method of manufacturing a lithium ion secondary battery can be provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Features, advantages, and technical and industrial significance of exemplary embodiments of the invention will be described below with reference to the accompanying drawings, in which like numerals denote like elements, and wherein:

FIG. 1 is a flowchart illustrating a first method of manufacturing a lithium ion secondary battery according to an embodiment of the invention;

FIG. 2 is a flowchart illustrating a second method of manufacturing a lithium ion secondary battery according to an embodiment of the invention;

FIG. 3 is a table illustrating a relationship between the amount of LiF, the amount of Li_3PO_4, and the capacity retention (after 200 cycles) of each sample;

FIG. 4 is a graph illustrating the capacity retention (after 200 cycles) of each sample;

FIG. 5 is a table illustrating the relationship between the amount of LiF, the amount of Li_3PO_4, and the capacity retention (after 200 cycles) of each sample; and

FIG. 6 is a graph illustrating the relationship between the amount of LiF, the amount of Li_3PO_4, and the capacity retention (after 200 cycles) of each sample.

DETAILED DESCRIPTION OF EMBODIMENTS

[0013] Hereinafter, a positive electrode of lithium ion secondary battery, and a method of manufacturing a lithium ion secondary battery according to an embodiment of the invention will be described. In regard to the method of manufacturing a lithium ion secondary battery according to the embodiment, FIG. 1 illustrates a first method, and FIG. 2 illustrates a second method. First, the first method will be described.

[0014] <First Method of Manufacturing Lithium Ion Secondary Battery>

FIG. 1 is a flowchart illustrating the first method of manufacturing a lithium ion secondary battery according to the embodiment.

[0015] In the first method of manufacturing a lithium ion secondary battery according to the embodiment, first, a positive electrode active material is exposed to fluorine-based gas to form a coating film containing amorphous lithium fluoride on a surface of the positive electrode active material (Step S1). In other words, fluorine atoms are made to be adsorbed on the surface of the positive electrode active material to treat the surface of the positive electrode active material. At this time, the coating film containing lithium fluoride is formed by making fluorine adsorbed on the surface of the positive electrode active material (that is, the coating film is formed without heating). Therefore, the coating film is amorphous without being crystalline.

[0016] As the positive electrode active material, a material capable of storing and releasing lithium can be used, and in the embodiment, lithium nickel manganese oxide ($LiNi_xMn_{2-x}O_4$: $0<x<2$) can be used. An example of the composition of lithium nickel manganese oxide is $LiNi_{0.5}Mn_{1.5}O_4$ ($x=0.5$).

[0017] As the fluorine-based gas, for example, fluorine gas (F_2), nitrogen trifluoride gas (NF_3), or carbon tetrafluoride gas (CF_4) can be used. In the embodiment, the fluorine-based gas is not limited to these gases, and any gas may be used as long as it can supply fluorine atoms to the surface of the positive electrode active material.

[0018] Next, a phosphate compound is added to the positive electrode active material on which the coating film containing the lithium fluoride is formed (Step S2). Here, as the phosphate compound, lithium phosphate (Li_3PO_4), lithium pyrophosphate ($Li_4P_2O_7$), or lithium metaphosphate ($LiPO_3$) can be used. In the embodiment, the phosphate compound is not limited to these examples, and any material may be used as long as it can supply phosphoric acid to the surface of the positive electrode active material.

[0019] Next, a positive electrode is formed using the positive electrode active material treated as described above (Step S3). During the formation of the positive electrode, a conductive material and a binder are mixed with the positive electrode active material treated as described above, and this mixture is put into NMP (N-methyl-2-pyrrolidone) or the like and is kneaded. A positive electrode current collector is coated with the kneaded positive electrode mixture, is dried, and is pressed. As a result, a positive electrode can be formed.

[0020] As the conductive material, for example, acetylene black (AB) or a graphite-based material can be used. As the binder, for example, polyvinylidene fluoride (PVdF), styrene-butadiene rubber (SBR), polytetrafluoroethylene (PTFE), or carboxymethyl cellulose (CMC) can be used. As the positive electrode current collector, aluminum or an alloy containing aluminum as a major component can be used.

[0021] Next, a lithium ion secondary battery is formed (Step S4). A negative electrode can be formed by kneading a negative electrode active material and a binder with a solvent (water), coating a negative electrode current collector with the kneaded negative electrode mixture, drying the negative electrode mixture, and pressing the dried negative electrode mixture. The negative electrode active material can store and release lithium ions, and for example, a powdered carbon material formed of natural graphite or the like can be used. As the binder, the above-described exemplary binders can be used. As the negative electrode current collector, for example, copper, nickel, or an alloy thereof can be

used.

[0022] The positive electrode and the negative electrode formed as above and a separator are laminated such that the separator is interposed between both of the electrodes, and then the laminate is made to have a structure of being wound flat (wound electrode body). The wound electrode body is accommodated in a container having a shape in which the wound electrode body can be accommodated. The container includes: a flat rectangular container body having an open upper end; and a lid that covers the opening. As a material constituting the container, a metal material such as aluminum or steel can be used. In addition, for example, a container obtained by molding a resin material such as polyphenylene sulfide resin (PPS) or polyimide resin may also be used. In a top surface (that is, the lid) of the container, a positive electrode terminal, which is electrically connected to the positive electrode of the wound electrode body, and a negative electrode terminal, which is electrically connected to the negative electrode of the wound electrode body, are provided. In addition, the inside of the container is filled with an electrolyte. The above-described configuration of the lithium ion secondary battery is merely exemplary, and the configuration of the lithium ion secondary battery (that is, the configurations of the electrode body and the container) according to the embodiment is not limited thereto.

[0023] As the separator, a porous polymer film such as a porous polyethylene film, a porous polyolefin film, or a porous polyvinyl chloride film; or a lithium ion or ion conductive polymer electrolyte film can be used alone or in a combination of two or more kinds thereof.

[0024] The electrolyte is a composition containing a supporting electrolyte in a non-aqueous solvent. As the non-aqueous solvent, one kind or two or more kinds of materials selected from the group consisting of propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and the like can be used. In addition, as the supporting electrolyte, one kind or two or more kinds of lithium compounds (lithium salts) selected from the group consisting of $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiAsF_6$, $LiCF_3SO_3$, $LiC_4F_9SO_3$, $LiN(CF_3SO_2)_2$, $LiC(CF_3SO_2)_3$, LiI, and the like can be used.

[0025] Next, the lithium ion secondary battery formed as described above is charged (initial charge) to form a coating film containing amorphous lithium phosphate on the surface of the positive electrode active material (Step S5). That is, by charging the lithium ion secondary battery, the phosphate compound added in Step S2 electrochemically reacts on the surface of the positive electrode active material to form the coating film

containing lithium phosphate.

[0026] In the embodiment, since the coating film is formed using the electrochemical reaction (that is, the reaction at a low temperature), the formed coating film containing lithium phosphate is amorphous without being crystalline. In addition, in the embodiment, since the phosphate compound is added to only the positive electrode, the coating film containing lithium phosphate is formed on only the surface of the positive electrode active material.

[0027] By using the above-described first method of manufacturing a lithium ion secondary battery, the positive electrode of the lithium ion secondary battery in which the coating film containing amorphous lithium fluoride and amorphous lithium phosphate is formed on the surface of the positive electrode active material, and the lithium ion secondary battery can be manufactured.

[0028] In the embodiment, in this way, the coating film containing amorphous lithium fluoride and amorphous lithium phosphate is formed on the surface of the positive electrode active material. Here, the amorphous coating film has lower lithium ion diffusion resistance (in other words, higher lithium ion conductivity) than that of a crystalline coating film. Accordingly, by forming the amorphous coating film on the surface of the positive electrode active material, the lithium ion diffusion resistance of the surface of the positive electrode active material can be reduced. Therefore, cycle characteristics of the lithium ion secondary battery can be improved. In addition, in the embodiment, since the coating film is formed on the surface of the positive electrode active material in this way, hydrogen fluoride present in the electrolyte can be inhibited from adversely affecting the positive electrode active material.

[0029] In the embodiment, the amount of lithium fluoride (that is, the amount of lithium fluoride formed as the coating film) with respect to lithium nickel manganese oxide which is the positive electrode active material is preferably 0.05 wt% to 1 wt%, more preferably 0.1 wt% to 0.5 wt%, and still more preferably 0.3 wt%. For example, when the amount of lithium fluoride with respect to lithium nickel manganese oxide is less than 0.05 wt%, the amount of the coating film containing lithium fluoride is excessively small, and thus hydrogen fluoride present in the electrolyte cannot be sufficiently inhibited from adversely affecting the positive electrode active material. In addition, when the amount of lithium fluoride with respect to lithium nickel manganese oxide is more than 1 wt%, the amount of lithium fluoride which is an insulating body is excessively large, and thus the resistance of the surface of the positive electrode active material increases.

[0030] For example, by adjusting the amount of the fluorine-based gas supplied to

the positive electrode active material during the formation of the coating film in Step S1, the amount of the coating film containing lithium fluoride formed on the surface of the positive electrode active material can be adjusted.

[0031] In addition, in the embodiment, when lithium phosphate is added as the phosphate compound, the addition amount of lithium phosphate with respect to lithium nickel manganese oxide which is the positive electrode active material is preferably 0.5 wt% to 3 wt%, more preferably 0.75 wt% to 1.5 wt%, and still more preferably 1 wt%. For example, when the addition amount of lithium phosphate with respect to lithium nickel manganese oxide is less than 0.5 wt%, the amount of the coating film containing the phosphate compound is excessively small, and thus hydrogen fluoride present in the electrolyte cannot be sufficiently inhibited from adversely affecting the positive electrode active material. In addition, when the addition amount of lithium phosphate with respect to lithium nickel manganese oxide is more than 3 wt%, the resistance of the surface of the positive electrode active material increases. In addition, since the amount of lithium phosphate with respect to the positive electrode active material increases, the battery capacity decreases.

[0032] For example, by adjusting the amount of the phosphate compound (lithium phosphate) added in Step S2, the amount of the coating film containing lithium phosphate formed on the surface of the positive electrode active material can be adjusted.

[0033] In addition, in the first method of manufacturing a lithium ion secondary battery according to the embodiment, after the phosphate compound is added to the positive electrode active material in Step S2, the positive electrode active material and the phosphate compound may be mixed while applying a shearing energy thereto. In this way, by mixing the positive electrode active material and the phosphate compound while applying a shearing energy thereto, the phosphate compound is temporarily dissolved in a positive electrode paste and then is redeposited in an amorphous state.

[0034] In this case, the coating film containing amorphous lithium phosphate is electrochemically formed on the surface of the positive electrode active material by charging (initial charge) the lithium ion secondary battery, and the shearing energy is applied during the mixing. As a result, lithium phosphate (phosphate compound) can be made to be in an amorphous state. Accordingly, the coating film containing amorphous lithium phosphate can be efficiently formed on the surface of the positive electrode active material.

[0035] In addition, in the first method of manufacturing a lithium ion secondary battery according to the embodiment, the positive electrode active material is exposed to

the fluorine-based gas to form the coating film containing amorphous lithium fluoride on the surface of the positive electrode active material (Step S1). Therefore, the coating film can be uniformly formed on the surface of the positive electrode active material. In addition, since the phosphate compound is added to only the positive electrode (Step S2), the coating film containing the phosphate compound can be formed on only the surface of the positive electrode active material (that is, an effect of the phosphate compound on the negative electrode can be inhibited).

[0036] <Second Method of Manufacturing Lithium Ion Secondary Battery>

Next, the second method of manufacturing a lithium ion secondary battery will be described. FIG. 2 is a flowchart illustrating the second method of manufacturing a lithium ion secondary battery according to the embodiment.

[0037] In the second method of manufacturing a lithium ion secondary battery according to the embodiment, first, a fluorine compound and a phosphate compound are added to a positive electrode active material (Step S11). As the positive electrode active material, a material capable of storing and releasing lithium can be used, and in the embodiment, lithium nickel manganese oxide ($LiNi_xMn_{2-x}O_4$: $0<x<2$) can be used. An example of the composition of lithium nickel manganese oxide is $LiNi_{0.5}Mn_{1.5}O_4$ ($x=0.5$).

[0038] As the fluorine compound, for example, lithium fluoride (LiF), aluminum fluoride (AlF_3), magnesium fluoride (MgF_2), or nickel fluoride (NiF_2) can be used. In the embodiment, the fluorine compound is not limited to these examples, and any material may be used as long as it can supply fluorine to the surface of the positive electrode active material.

[0039] As the phosphate compound, lithium phosphate (Li_3PO_4), lithium pyrophosphate ($Li_4P_2O_7$), or lithium metaphosphate ($LiPO_3$) can be used. In the embodiment, the phosphate compound is not limited to these examples, and any material may be used as long as it can supply phosphoric acid to the surface of the positive electrode active material.

[0040] Next, a positive electrode is formed using the positive electrode active material to which the fluorine compound and the phosphate compound are added (Step S12). During the formation of the positive electrode, a conductive material and a binder are mixed with the positive electrode active material to which the fluorine compound and the phosphate compound are added, and this mixture is put into NMP (N-methyl-2-pyrrolidone) or the like and is kneaded. A positive electrode current collector is coated with the kneaded positive electrode mixture, is dried, and is pressed. As a result, a positive electrode can be formed. Since the conductive material and the

binder used during the formation of the positive electrode are the same as described above in Step S3 of the first method, the description thereof will not be repeated.

[0041] Next, a lithium ion secondary battery is formed (Step S13). Since the method of forming a lithium ion secondary battery is the same as described above in S4 of the first method, the description thereof will not be repeated.

[0042] Next, the lithium ion secondary battery formed in Step S13 is charged (initial charge) to form a coating film containing amorphous lithium fluoride and amorphous lithium phosphate on the surface of the positive electrode active material (Step S14). That is, by charging the lithium ion secondary battery, the fluorine compound and the phosphate compound added in Step S11 electrochemically react on the surface of the positive electrode active material to form the coating film containing lithium fluoride and lithium phosphate.

[0043] In the embodiment, since the coating film is formed using the electrochemical reaction (that is, the reaction at a low temperature), the formed coating film containing lithium fluoride and lithium phosphate is amorphous without being crystalline. In addition, in the embodiment, since the fluorine compound and the phosphate compound are added to only the positive electrode, the coating film containing lithium fluoride and lithium phosphate is formed on only the surface of the positive electrode active material.

[0044] By using the above-described second method of manufacturing a lithium ion secondary battery, the positive electrode of the lithium ion secondary battery in which the coating film containing amorphous lithium fluoride and amorphous lithium phosphate is formed on the surface of the positive electrode active material, and the lithium ion secondary battery can be manufactured. Even in this case, due to the same reason as described in the first method, cycle characteristics of the lithium ion secondary battery can be improved.

[0045] In the embodiment, when lithium fluoride is added as the fluorine compound, due to the same reason as described in the first method, the addition amount of lithium fluoride with respect to lithium nickel manganese oxide which is the positive electrode active material is preferably 0.05 wt% to 1 wt%, more preferably 0.1 wt% to 0.5 wt%, and still more preferably 0.3 wt%. For example, by adjusting the addition amount of the fluorine compound (lithium fluoride) added in Step S11, the amount of the coating film containing lithium phosphate formed on the surface of the positive electrode active material can be adjusted.

[0046] In addition, in the embodiment, when lithium phosphate is added as the

phosphate compound, due to the same reason as described in the first method, the addition amount of lithium phosphate with respect to lithium nickel manganese oxide which is the positive electrode active material is preferably 0.5 wt% to 3 wt%, more preferably 0.75 wt% to 1.5 wt%, and still more preferably 1 wt%. For example, by adjusting the amount of the phosphate compound (lithium phosphate) added in Step S11, the amount of the coating film containing lithium phosphate formed on the surface of the positive electrode active material can be adjusted.

[0047] In addition, in the second method of manufacturing a lithium ion secondary battery according to the embodiment, after the fluorine compound and the phosphate compound is added to the positive electrode active material in Step S11, the positive electrode active material, the fluorine compound, and the phosphate compound may be mixed while applying a shearing energy thereto. In this way, by mixing these materials while applying a shearing energy thereto, the fluorine compound and the phosphate compound are temporarily dissolved in a positive electrode paste and then are redeposited in an amorphous state.

[0048] In this case, the coating film containing amorphous lithium fluoride and amorphous lithium phosphate is electrochemically formed on the surface of the positive electrode active material by charging (initial charge) the lithium ion secondary battery, and the shearing energy is applied during the mixing. As a result, lithium fluoride (fluorine compound) and lithium phosphate (phosphate compound) can be made to be in an amorphous state. Accordingly, the coating film containing amorphous lithium fluoride and amorphous lithium phosphate can be efficiently formed on the surface of the positive electrode active material.

[0049] In addition, in the above-described second method, since the fluorine compound and the phosphate compound are added to only the positive electrode (Step S11), the coating film containing lithium fluoride and lithium phosphate can be formed on only the surface of the positive electrode active material (that is, an effect of the fluorine compound and the phosphate compound on the negative electrode can be inhibited).

[0050] In addition, in the first method, the positive electrode active material is exposed to the fluorine-based gas to form the coating film containing amorphous lithium fluoride on the surface of the positive electrode active material (Step S1). Next, the phosphate compound is added to the positive electrode active material on which the coating film containing lithium fluoride is formed (Step S2). On the other hand, in the second method, the fluorine compound and the phosphate compound are added to lithium nickel manganese oxide in Step S11, and the coating film containing lithium fluoride and

lithium phosphate is electrochemically formed on the surface of the positive electrode active material in Step S14. Accordingly, the manufacturing steps of the second method can be made to be simpler than those of the first method.

[0051] Although the first method and the second method are different from each other, the positive electrodes of the lithium ion secondary batteries which are formed using these methods are substantially the same.

[0052] In addition, whether or not the formed coating film is amorphous can be determined using, for example, a transmission electron microscope (TEM). That is, during the observation of the coating film on the surface of the positive electrode active material using a transmission electron microscope, when a lattice fringe is observed, it can be determined that the coating film is crystalline, and when a lattice fringe is not observed, it can be determined that the coating film is amorphous.

[0053] In addition, whether or not the formed coating film is amorphous may be determined, for example, using electron beam diffraction. That is, when a diffraction pattern of the coating film on the surface of the positive electrode active material is made of diffraction spots, it can be determined that the coating film is crystalline, and when a clear diffraction pattern is not obtained (halo pattern), it can be determined that the coating film is amorphous.

[0054] In addition, the effects of the embodiment of the invention are particularly high in the lithium ion secondary battery in which lithium nickel manganese oxide is used as the positive electrode active material. That is, in the lithium ion secondary battery in which lithium nickel manganese oxide is used as the positive electrode active material, the operation voltage is high (4.5 V or higher), and thus a reaction between the positive electrode active material and the electrolyte is promoted. Therefore, decomposition of the electrolyte is promoted, and the amount of hydrogen fluoride present in the electrolyte increases. The amount of hydrogen fluoride is more than that of, for example, a lithium ion secondary battery (operation voltage: about 4.1 V) in which lithium nickel manganese cobalt oxide ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$) is used as the positive electrode active material.

[0055] Therefore, in order to inhibit hydrogen fluoride present in the electrolyte from adversely affecting the positive electrode active material, it is necessary to form the coating film on the surface of the positive electrode active material. However, when the coating film (crystalline coating film) is formed on the surface of the positive electrode active material, the lithium ion diffusion resistance of the surface of the positive electrode active material increases, and cycle characteristics of the lithium ion secondary battery deteriorate.

[0056] Therefore, in the embodiment of the invention, the coating film containing amorphous lithium fluoride and amorphous lithium phosphate is formed on the surface of the positive electrode active material. Here, the amorphous coating film has lower lithium ion diffusion resistance (in other words, higher lithium ion conductivity) than that of a crystalline coating film. Accordingly, by forming the amorphous coating film on the surface of the positive electrode active material, the lithium ion diffusion resistance of the surface of the positive electrode active material can be reduced. Therefore, cycle characteristics of the lithium ion secondary battery can be improved. That is, according to the embodiment of the invention, cycle characteristics of a lithium ion secondary battery can be improved while reducing the effect of hydrogen fluoride present in an electrolyte.

[0057] Next, Examples of the invention will be described. In order to investigate an effect during formation of a coating film on a surface of a positive electrode active material, the following samples were prepared.

[0058] <Example 1>

A lithium ion secondary battery was prepared using the above-described first method. As the positive electrode active material, $LiNi_{0.5}Mn_{1.5}O_4$ was used. In addition, the positive electrode active material was exposed to fluorine gas so as to fluorinate the surface of the positive electrode active material. At this time, fluorination conditions were adjusted such that 0.3 wt% of a LiF coating film with respect to the positive electrode active material was formed. The amount of LiF formed on the surface of the positive electrode active material was measured using X-ray photoelectron spectroscopy (XPS). Hereinafter, $LiNi_{0.5}Mn_{1.5}O_4$ on which 0.3 wt% of LiF was formed will be referred to as "0.3F-$LiNi_{0.5}Mn_{1.5}O_4$".

[0059] Next, a phosphate compound, a conductive material, and a binder were mixed with 0.3F-$LiNi_{0.5}Mn_{1.5}O_4$. Li_3PO_4 was used as the phosphate compound, acetylene black (AB) was used as the conductive material, and polyvinylidene fluoride (PVdF) was used as the binder. At this time, these components were mixed with each other such that the addition amount of the phosphate compound (Li_3PO_4) was 1 wt%. Specifically, the components were mixed such that a weight ratio (Positive Electrode Active Material (0.3F-$LiNi_{0.5}Mn_{1.5}O_4$):Phosphate Compound (Li_3PO_4):Conductive Material (AB):Binder (PVdF)) thereof was 92.07:0.93:4:3.

[0060] Next, this mixture was dissolved in a solvent (N-methyl-2-pyrrolidone) and was kneaded. A positive electrode current collector (aluminum foil) was coated with the kneaded positive electrode mixture, was dried, and was pressed. As a result, a positive electrode was formed. In the positive electrode, the weight per unit area of a

single surface was 16.2 mg/cm^2, and the density was 2.8 g/cm^3.

[0061] In addition, during formation of a negative electrode, natural graphite (negative electrode active material), carboxymethyl cellulose (CMC), and styrene-butadiene rubber (SBR) were mixed at a weight ratio of 98.6:0.7:0.7. Next, this mixture was dissolved in a solvent (water) and was kneaded. A negative electrode current collector (copper foil) was coated with the kneaded negative electrode mixture, was dried, and was pressed. As a result, a negative electrode was formed. In the negative electrode, the weight per unit area of a single surface was 7.4 mg/cm^2, and the density was 1.3 g/cm^3.

[0062] A separator was interposed between the positive electrode and the negative electrode prepared as above to form an electrode body. As the separator, a porous polyethylene film was used. This electrode body was accommodated in a bag-shaped container formed of a laminated film, and an electrolyte was poured thereinto. As a result, a lithium ion secondary battery was prepared. As the electrolyte, a mixture was used in which 1 mol/L (dm_3) of $LiPF_6$ as a lithium salt was mixed with a mixed solvent (EC/EMC=5/5) of ethylene carbonate (EC) and ethyl methyl carbonate (EMC). Next, the prepared lithium ion secondary battery was charged (initial charge) to form a coating film on the surface of the positive electrode active material.

[0063] <Example 2>

As in the case of Example 1, $LiNi_{0.5}Mn_{1.5}O_4$ was used as the positive electrode active material. In addition, the positive electrode active material was exposed to fluorine gas so as to fluorinate the surface of the positive electrode active material. In Example 2, fluorination conditions were adjusted such that 0.1 wt% of a LiF coating film with respect to the positive electrode active material was formed.

[0064] Next, a phosphate compound, a conductive material, and a binder were mixed with 0.1F-$LiNi_{0.5}Mn_{1.5}O_4$. Li_3PO_4 was used as the phosphate compound, acetylene black (AB) was used as the conductive material, and polyvinylidene fluoride (PVdF) was used as the binder. At this time, these components were mixed with each other such that the addition amount of the phosphate compound (Li_3PO_4) was 1 wt%. Specifically, the components were mixed such that a weight ratio (Positive Electrode Active Material (0.1F-$LiNi_{0.5}Mn_{1.5}O_4$):Phosphate Compound (Li_3PO_4):Conductive Material (AB):Binder (PVdF)) thereof was 92.07:0.93:4:3. Next, using the same method as that of Example 1, a lithium ion secondary battery according to Example 2 was prepared.

[0065] <Example 3>

A lithium ion secondary battery was prepared using the above-described second method. First, a positive electrode active material, a fluorine compound, and a phosphate

compound were mixed, and a conductive material and a binder were further mixed the mixture. $LiNi_{0.5}Mn_{1.5}O_4$ was used as the positive electrode active material, LiF was used as the fluorine compound, Li_3PO_4 was used as the phosphate compound, acetylene black (AB) was used as the conductive material, and polyvinylidene fluoride (PVdF) was used as the binder. At this time, the components were mixed such that the addition amount of the fluorine compound (LiF) was 0.3 wt%, and the addition amount of the phosphate compound (Li_3PO_4) was 1 wt%. Specifically, the components were mixed such that a weight ratio (Positive Electrode Active Material ($LiNi_{0.5}Mn_{1.5}O_4$):Fluorine Compound (LiF):Phosphate Compound (Li_3PO_4):Conductive Material (AB):Binder (PVdF)) thereof was 91.791:0.279:0.93:4:3. Next, using the same method as that of Example 1, a lithium ion secondary battery according to Example 3 was prepared.

[0066] <Example 4>

A lithium ion secondary battery was prepared using the above-described second method. First, a positive electrode active material, a fluorine compound, and a phosphate compound were mixed, and a conductive material and a binder were further mixed the mixture. $LiNi_{0.5}Mn_{1.5}O_4$ was used as the positive electrode active material, LiF was used as the fluorine compound, Li_3PO_4 was used as the phosphate compound, acetylene black (AB) was used as the conductive material, and polyvinylidene fluoride (PVdF) was used as the binder. At this time, the components were mixed such that the addition amount of the fluorine compound (LiF) was 0.1 wt%, and the addition amount of the phosphate compound (Li_3PO4) was 1 wt%. Specifically, the components were mixed such that a weight ratio (Positive Electrode Active Material ($LiNi_{0.5}Mn_{1.5}O_4$):Fluorine Compound (LiF):Phosphate Compound (Li_3PO_4):Conductive Material (AB):Binder (PVdF)) thereof was 91.977:0.093:0.93:4:3. Next, using the same method as that of Example 1, a lithium ion secondary battery according to Example 4 was prepared.

[0067] <Comparative Example 1>

In Comparative Example 1, a lithium ion secondary battery in which additives (LiF, Li_3PO_4) were not added to a positive electrode active material was prepared. First, the positive electrode active material, a conductive material, and a binder were mixed. $LiNi_{0.5}Mn_{1.5}O_4$ was used as the positive electrode active material, acetylene black (AB) was used as the conductive material, and polyvinylidene fluoride (PVdF) was used as the binder. At this time, the components were mixed such that a weight ratio (Positive Electrode Active Material ($LiNi_{0.5}Mn_{1.5}O_4$):Conductive Material (AB):Binder (PVdF)) thereof was 93:4:3. Next, using the same method as that of Example 1, a lithium ion secondary battery according to Comparative Example 1 was prepared.

[0068] <Comparative Example 2>

In Comparative Example 2, a lithium ion secondary battery in which additives (LiF, Li_3PO_4) were added to an electrolyte was prepared. First, the positive electrode active material, a conductive material, and a binder were mixed. $LiNi_{0.5}Mn_{1.5}O_4$ was used as the positive electrode active material, acetylene black (AB) was used as the conductive material, and polyvinylidene fluoride (PVdF) was used as the binder. At this time, the components were mixed such that a weight ratio (Positive Electrode Active Material ($LiNi_{0.5}Mn_{1.5}O_4$):Conductive Material (AB):Binder (PVdF)) thereof was 93:4:3. Next, using the same method as that of Example 1, a lithium ion secondary battery according to Comparative Example 2 was prepared. In the lithium ion secondary battery according to Comparative Example 2, 0.3 wt% of LiF and 1 wt% of Li_3PO_4 were added to the electrolyte.

[0069] <Comparative Example 3>

In Comparative Example 3, a lithium ion secondary battery in which a coating film containing a crystalline fluorine compound (LiF) and a crystalline phosphate compound (Li_3PO_4) was formed on the surface of the positive electrode active material was prepared. First, for $LiNi_{0.5}Mn_{1.5}O_4$ which was a positive electrode active material, a mixed solution in which lithium nitrate ($LiNO_3$), ammonium fluoride (NH_4F), and diammonium hydrogenphosphate [$(NH_4)_2HPO_4$] were dissolved was prepared. The positive electrode active material was coated with the mixed solution using a spray drying method (tumbling fluidized bed granulating-coating method), followed by firing at 400°C for 4 hours. At this time, coating conditions were adjusted such that the coating amount of the fluorine compound (LiF) was 0.3 wt%, and the coating amount of the phosphate compound (Li_3PO_4) was 1 wt% with respect to the positive electrode active material.

[0070] Next, the coated positive electrode active material, a conductive material, and a binder were mixed. Acetylene black (AB) was used as the conductive material, and polyvinylidene fluoride (PVdF) was used as the binder. At this time, the components were mixed such that a weight ratio (Positive Electrode Active Material ($LiNi_{0.5}Mn_{1.5}O_4$):Conductive Material (AB):Binder (PVdF)) thereof was 93:4:3. Next, using the same method as that of Example 1, a lithium ion secondary battery according to Comparative Example 3 was prepared.

[0071] <Comparative Example 4>

In Comparative Example 4, a lithium ion secondary battery in which a phosphate compound was added (a fluorine compound was not added) to a positive electrode active material was prepared. First, the positive electrode active material, the phosphate

compound, a conductive material, and a binder were mixed. $LiNi_{0.5}Mn_{1.5}O_4$ was used as the positive electrode active material, Li_3PO_4 was used as the phosphate compound, acetylene black (AB) was used as the conductive material, and polyvinylidene fluoride (PVdF) was used as the binder. At this time, these components were mixed with each other such that the addition amount of Li_3PO_4 was 1 wt%. Specifically, the components were mixed such that a weight ratio (Positive Electrode Active Material ($LiNi_{0.5}Mn_{1.5}O_4$):Phosphate Compound (Li_3PO_4):Conductive Material (AB):Binder (PVdF)) thereof was 92.07:0.93:4:3. Next, using the same method as that of Example 1, a lithium ion secondary battery according to Comparative Example 4 was prepared.

[0072] <Comparative Example 5>

In Comparative Example 5, a lithium ion secondary battery in which a fluorine compound was added (a phosphate compound was not added) to a positive electrode active material was prepared. First, the positive electrode active material, the fluorine compound, a conductive material, and a binder were mixed. $LiNi_{0.5}Mn_{1.5}O_4$ was used as the positive electrode active material, LiF was used as the fluorine compound, acetylene black (AB) was used as the conductive material, and polyvinylidene fluoride (PVdF) was used as the binder. At this time, these components were mixed with each other such that the addition amount of LiF was 1 wt%. Specifically, the components were mixed such that a weight ratio (Positive Electrode Active Material ($LiNi_{0.5}Mn_{1.5}O_4$):Fluorine Compound (LiF):Conductive Material (AB):Binder (PVdF)) thereof was 92.72:0.28:4:3. Next, using the same method as that of Example 1, a lithium ion secondary battery according to Comparative Example 5 was prepared.

[0073] <Measurement of Capacity Retention>

In order to investigate durability characteristics of the prepared lithium ion secondary batteries, the capacity retention of each of the lithium ion secondary batteries was measured. During the measurement of the capacity retention, each of the lithium ion secondary batteries was charged and discharged in 200 cycles at 60°C in a voltage range of 3.5 V to 4.9 V at a charge and discharge rate of 2C. The discharge capacity in the first cycle was 100%, and the capacity retention in each cycle was evaluated.

[0074] FIG. 3 is a table illustrating a relationship between the amount of LiF, the amount of Li_3PO_4, and the capacity retention (capacity retention of the 200-th cycle) of each sample. FIG. 4 is a graph illustrating the capacity retention of each sample. As illustrated in FIGS. 3 and 4, the capacity retentions (93.0%, 89.9%) of the lithium ion secondary batteries according to Examples 1 and 2 which were formed using the first method and the capacity retentions (92.1%, 89.0%) of the lithium ion secondary batteries

according to Examples 3 and 4 which were formed using the second method were higher than the capacity retention (79.2%) of the lithium ion secondary battery according to Comparative Example 1 to which the additives (LiF, Li_3PO_4) were not added. Accordingly, the capacity retention of the lithium ion secondary battery was improved by forming the coating film containing amorphous lithium fluoride and amorphous lithium phosphate on the surface of the positive electrode active material.

[0075] In addition, in Comparative Example 2, the capacity retention was 76.7%, and the capacity retention of the lithium ion secondary battery was not improved only with the addition of the additives (LiF, Li_3PO_4) to the electrolyte.

[0076] In Comparative Example 3, the capacity retention was 86.3%. That is, when the coating film containing crystalline LiF and crystalline Li_3PO_4 was formed on the surface of the positive electrode active material, the capacity retention was lower than those of Examples 1 to 4 in which the amorphous coating film was formed. The reason can be presumed to be that the lithium ion diffusion resistance of the crystalline LiF and Li_3PO_4 was higher than that of the amorphous LiF and Li_3PO_4.

[0077] In addition, among the additives (LiF and Li_3PO_4), when only Li_3PO_4 was added (Comparative Example 4), the capacity retention was 84.3%, and when only LiF was added (Comparative Example 5), the capacity retention was 79.6%. Accordingly, with the addition of only one additive among the additives (LiF and Li_3PO_4), the capacity retention of the lithium ion secondary battery was not significantly improved. In other words, by forming the coating film containing both LiF and Li_3PO_4 on the surface of the positive electrode active material, the capacity retention of the lithium ion secondary battery was significantly improved.

[0078] <Capacity Retention When Addition Amounts Of Additives were Varied>

Next, when the addition amounts of the additives (LiF and Li_3PO_4) were varied, the capacity retention of the lithium ion secondary battery was investigated. In other words, when the amount of the coating film containing LiF and Li_3PO_4 formed on the surface of the positive electrode active material was varied, the capacity retention of the lithium ion secondary battery was investigated. At this time, the addition amount of LiF was varied in a range of 0 wt% to 1.5 wt%. In addition, the addition amount of Li_3PO_4 was varied in a range of 0 wt% to 5 wt%. In addition, each of the lithium ion secondary batteries was prepared using the above-described second method. The method of preparing the lithium ion secondary batteries was the same as that of Example 3. The addition amount of LiF in the second method corresponds to the amount of the LiF coating film which was formed in the fluorination of the first method.

[0079] FIG. 5 is a table illustrating a relationship between the amount of LiF, the amount of Li_3PO_4, and the capacity retention. FIG. 6 is a graph illustrating the relationship between the amount of LiF, the amount of Li_3PO_4, and the capacity retention. As illustrated in FIGS. 5 and 6, when the addition amount of LiF with respect to the positive electrode active material ($LiNi_{0.5}Mn_{1.5}O_4$) was 0.05 wt% to 1 wt%, the capacity retention of the lithium ion secondary battery was improved. In particular, when the addition amount of LiF with respect to the positive electrode active material ($LiNi_{0.5}Mn_{1.5}O_4$) was preferably 0.1 wt% to 0.5 wt% and more preferably 0.3 wt%, the capacity retention of the lithium ion secondary battery was improved.

[0080] In addition, when the addition amount of Li_3PO_4 with respect to the positive electrode active material ($LiNi_{0.5}Mn_{1.5}O_4$) was 0.5 wt% to 3 wt%, the capacity retention of the lithium ion secondary battery was improved. In particular, when the addition amount of Li_3PO_4 with respect to the positive electrode active material ($LiNi_{0.5}Mn_{1.5}O_4$) was preferably 0.75 wt% to 1.5 wt% and more preferably 1 wt%, the capacity retention of the lithium ion secondary battery was improved.

[0081] As described above, the capacity retention of the lithium ion secondary battery was able to be improved by forming the coating film containing amorphous lithium fluoride and amorphous lithium phosphate on the surface of the positive electrode active material. Accordingly, with the configurations according to the invention, cycle characteristics of the lithium ion secondary battery were able to be improved.

[0082] Hereinabove, the invention has been described using the embodiment and Examples. However, the invention is not limited to the embodiment and Examples and includes various modifications, alternations, and combinations thereof.

CLAIMS:

1. A positive electrode of a lithium ion secondary battery, the positive electrode comprising:

a positive electrode active material that contains lithium nickel manganese oxide,

wherein a coating film containing amorphous lithium fluoride and amorphous lithium phosphate is formed on a surface of the positive electrode active material.

2. The positive electrode according to claim 1, wherein

an amount of the lithium fluoride with respect to the lithium nickel manganese oxide is 0.05 wt% to 1 wt%.

3. The positive electrode according to claim 1 or 2, wherein

an amount of the lithium phosphate with respect to the lithium nickel manganese oxide is 0.5 wt% to 3 wt%.

4. A method of manufacturing a lithium ion secondary battery, comprising:

exposing lithium nickel manganese oxide, which is a positive electrode active material, to fluorine-based gas to form a coating film containing amorphous lithium fluoride on a surface of the positive electrode active material;

adding a phosphate compound to the positive electrode active material, on which the coating film containing the lithium fluoride is formed, to prepare a positive electrode containing the positive electrode active material;

forming a lithium ion secondary battery including the prepared positive electrode; and

charging the formed lithium ion secondary battery to form a coating film containing amorphous lithium phosphate on the surface of the positive electrode active material.

5. The method according to claim 4, wherein

the positive electrode active material is exposed to the fluorine-based gas such that an amount of the lithium fluoride with respect to the lithium nickel manganese oxide is 0.05 wt% to 1 wt%.

6. The method according to claim 4 or 5, wherein

when lithium phosphate is added as the phosphate compound, an addition amount of

the lithium phosphate with respect to the lithium nickel manganese oxide is 0.5 wt% to 3 wt%.

7. The method according to any one of claims 4 to 6, wherein

after the phosphate compound is added to the positive electrode active material on which the coating film containing the lithium fluoride is formed, the positive electrode active material and the phosphate compound are mixed while applying a shearing energy to the positive electrode active material and the phosphate compound.

8. A method of manufacturing a lithium ion secondary battery, comprising:

adding a fluorine compound and a phosphate compound to lithium nickel manganese oxide, which is a positive electrode active material, to prepare a positive electrode containing the positive electrode active material;

forming the lithium ion secondary battery including the positive electrode; and

charging the formed lithium ion secondary battery to form a coating film containing amorphous lithium fluoride and amorphous lithium phosphate on a surface of the positive electrode active material.

9. The method according to claim 8, wherein

when lithium fluoride is added as the fluorine compound, an addition amount of the lithium fluoride with respect to the lithium nickel manganese oxide is 0.05 wt% to 1 wt%.

10. The method according to claim 8 or 9, wherein

when lithium phosphate is added as the phosphate compound, an addition amount of the lithium phosphate with respect to the lithium nickel manganese oxide is 0.5 wt% to 3 wt%.

11. The method according to any one of claims 8 to 10, wherein

after the fluorine compound and the phosphate compound are added to the positive electrode active material, the positive electrode active material, the fluorine compound, and the phosphate compound are mixed while applying a shearing energy to the positive electrode active material, the fluorine compound, and the phosphate compound.

FIG. 1

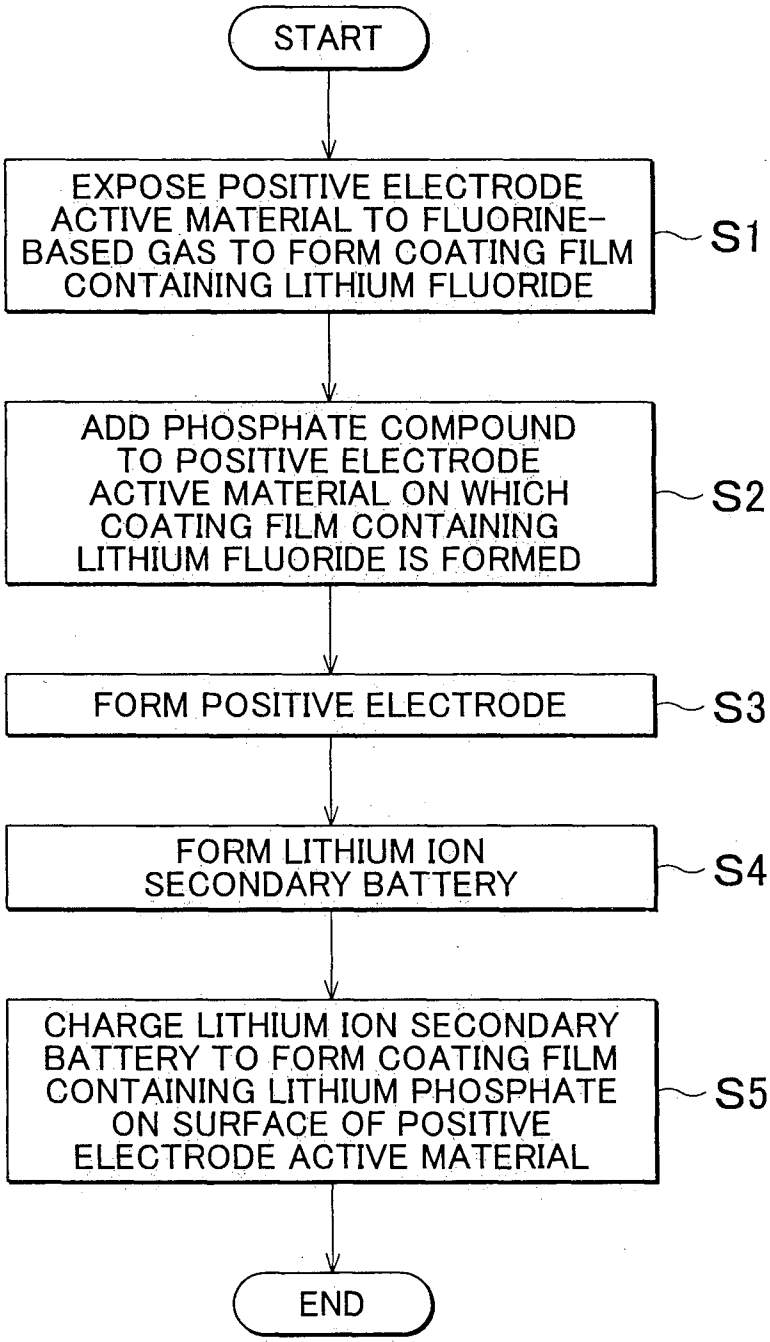

START
EXPOSE POSITIVE ELECTRODE ACTIVE MATERIAL TO FLUORINE-BASED GAS TO FORM COATING FILM CONTAINING LITHIUM FLUORIDE
S1
ADD PHOSPHATE COMPOUND TO POSITIVE ELECTRODE ACTIVE MATERIAL ON WHICH COATING FILM CONTAINING LITHIUM FLUORIDE IS FORMED
S2
FORM POSITIVE ELECTRODE
S3
FORM LITHIUM ION SECONDARY BATTERY
S4
CHARGE LITHIUM ION SECONDARY BATTERY TO FORM COATING FILM CONTAINING LITHIUM PHOSPHATE ON SURFACE OF POSITIVE ELECTRODE ACTIVE MATERIAL
S5
END

FIG. 2

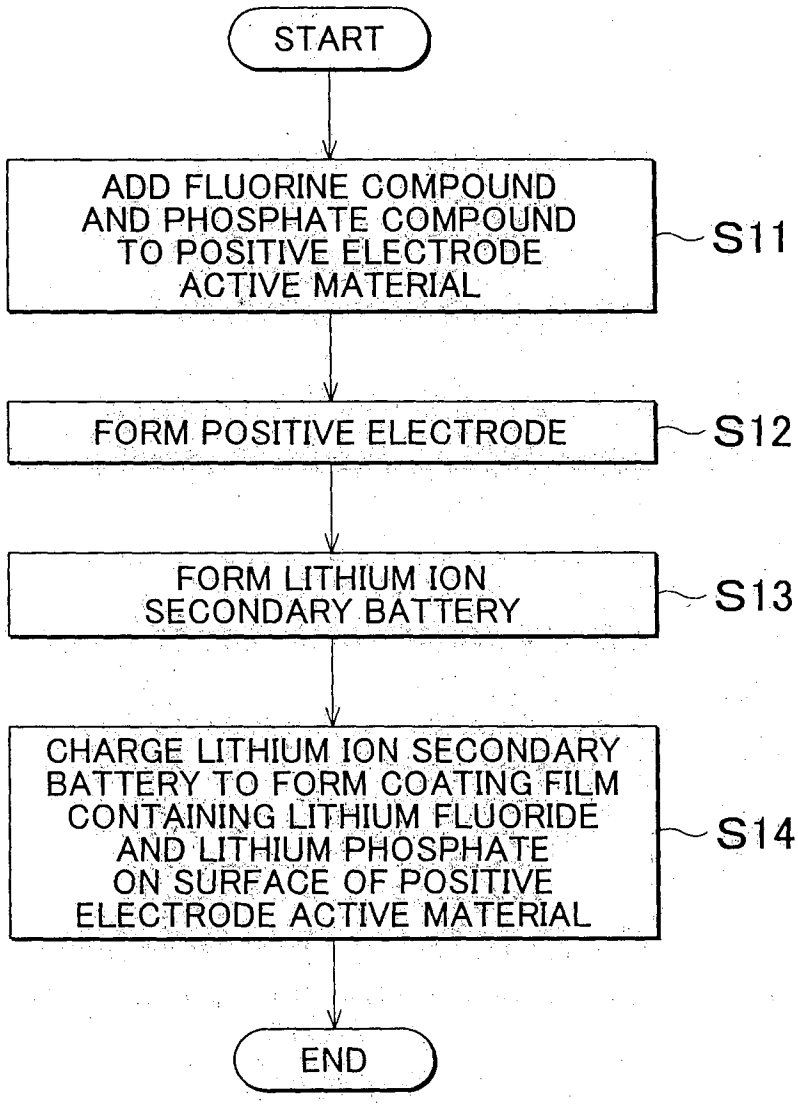

START
ADD FLUORINE COMPOUND AND PHOSPHATE COMPOUND TO POSITIVE ELECTRODE ACTIVE MATERIAL
S11
FORM POSITIVE ELECTRODE
S12
FORM LITHIUM ION SECONDARY BATTERY
S13
CHARGE LITHIUM ION SECONDARY BATTERY TO FORM COATING FILM CONTAINING LITHIUM FLUORIDE AND LITHIUM PHOSPHATE ON SURFACE OF POSITIVE ELECTRODE ACTIVE MATERIAL
S14
END

FIG. 3

SAMPLE	AMOUNT OF LiF (wt%)	AMOUNT OF Li_3PO_4 (wt%)	CAPACITY RETENTION (%) (AFTER 200 CYCLES)	DESCRIPTION OF SAMPLE
EXAMPLE 1	0.3	1.0	93.0	FIRST METHOD
EXAMPLE 2	0.1	1.0	89.9	FIRST METHOD
EXAMPLE 3	0.3	1.0	92.1	SECOND METHOD
EXAMPLE 4	0.1	1.0	89.0	SECOND METHOD
COMPARATIVE EXAMPLE 1	–	–	79.2	ADDITIVES NOT ADDED
COMPARATIVE EXAMPLE 2	0.3	1.0	76.7	ADDITIVES ADDED TO ELECTROLYTE
COMPARATIVE EXAMPLE 3	0.3	1.0	86.3	CRYSTALLINE COATING FILM FORMED
COMPARATIVE EXAMPLE 4	–	1.0	84.3	LiF NOT ADDED
COMPARATIVE EXAMPLE 5	0.3	–	79.6	Li_3PO_4 NOT ADDED

FIG. 4

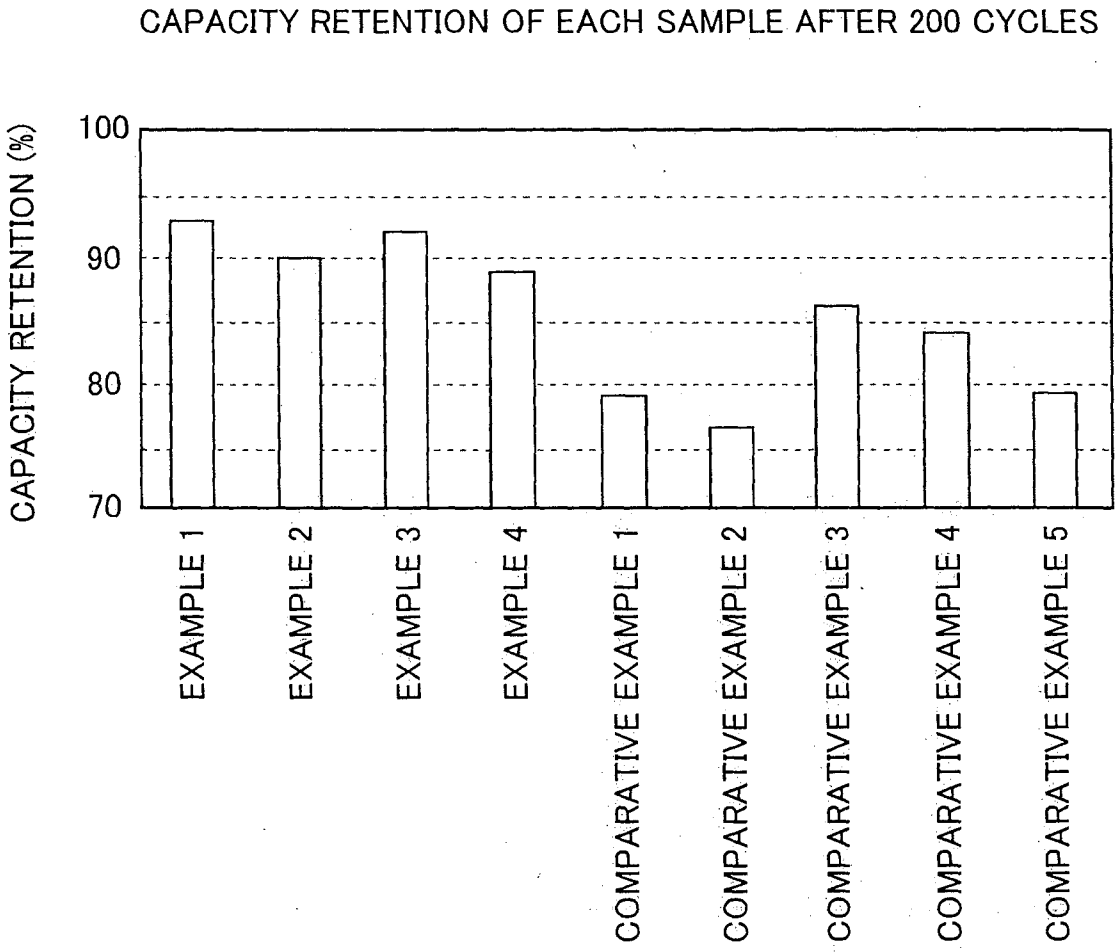
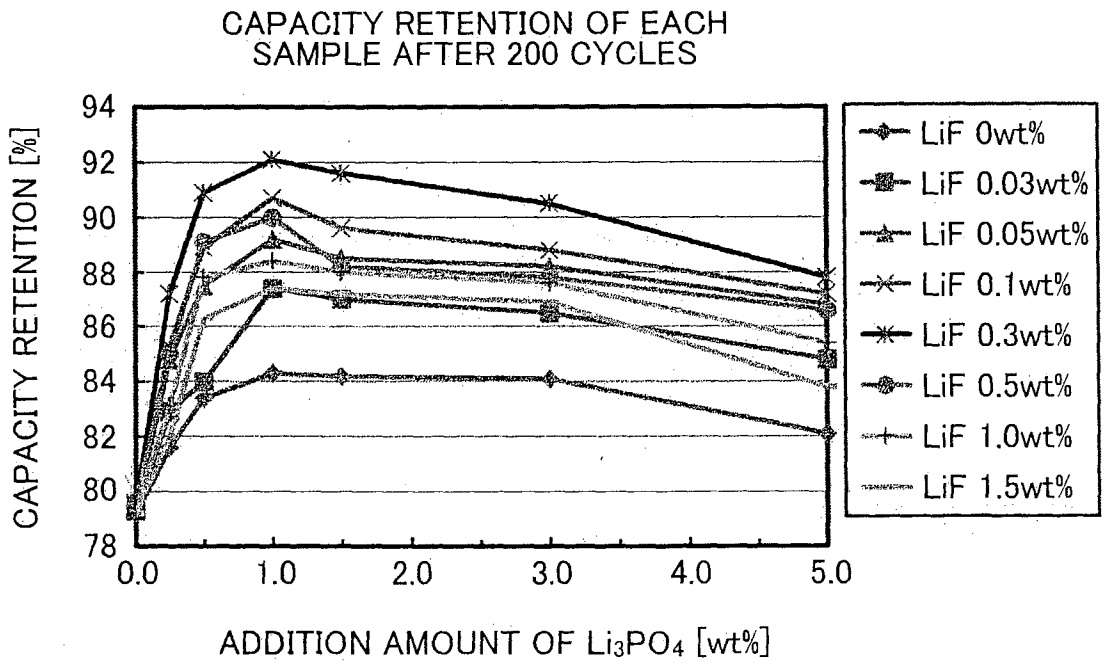

CAPACITY RETENTION OF EACH SAMPLE AFTER 200 CYCLES
CAPACITY RETENTION (%)
100
90
80
70
EXAMPLE 1
EXAMPLE 2
EXAMPLE 3
EXAMPLE 4
COMPARATIVE EXAMPLE 1
COMPARATIVE EXAMPLE 2
COMPARATIVE EXAMPLE 3
COMPARATIVE EXAMPLE 4
COMPARATIVE EXAMPLE 5

FIG. 5

AMOUNT OF Li_3PO_4 [wt%]	AMOUNT OF LiF [wt%]							
	0	0.03	0.05	0.1	0.3	0.5	1	1.5
0	79.2	79.3	79.4	79.5	79.6	79.6	79.4	79.2
0.25	81.6	82.9	84.8	85.3	87.2	85.0	83.1	82.0
0.5	83.4	84.0	87.5	88.9	90.9	89.1	87.8	86.3
1	84.3	87.4	89.2	90.7	92.1	90.0	88.4	87.4
1.5	84.2	87.0	88.5	89.6	91.6	88.2	88.0	87.2
3	84.1	86.5	88.2	88.8	90.5	87.8	87.6	86.9
5	82.1	84.8	86.8	87.2	87.8	86.6	85.4	83.8

CAPACITY RETENTION OF EACH SAMPLE AFTER 200 CYCLES

FIG. 6



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/000215

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/04 H01M4/131 H01M4/1391 H01M4/36 H01M4/505
H01M4/62 C01G45/12 C01G53/00 H01M10/04
ADD. H01M4/525
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/054743 A1 (ASAHI GLASS CO LTD [JP]) 18 April 2013 (2013-04-18)	1
A	paragraphs [0012] - [0031]	2,3
A	US 2013/260210 A1 (TAKAMI NORIO [JP] ET AL) 3 October 2013 (2013-10-03) paragraphs [0023], [0026]; claim 6; examples 2,4	1-3
A	WO 2006/027925 A2 (NISSAN MOTOR [JP]; ITO TAKANORI [JP]) 16 March 2006 (2006-03-16) page 4, line 13 - page 14, line 15; figures 1,2	1-3
X	EP 2 237 348 A1 (HITACHI LTD [JP]) 6 October 2010 (2010-10-06)	1,3,4, 6-8,10, 11
A	paragraphs [0018], [0035], [0041], [0053], [0066] - [0089]	2,5,9

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 August 2015	17/08/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schwake, Andree

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2015/000215

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-3

A positive electrode of a lithium ion secondary battery, the positive electrode comprising: a positive electrode active material that contains lithium nickel manganese oxide,wherein a coating film containing amorphous lithium fluoride and amorphous lithium phosphate is formed on a surface of the positive electrode active material.

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2. claims: 4-11

A method of manufacturing a lithium ion secondary battery, comprising: exposing lithium nickel manganese oxide, which is a positive electrode active material, to fluorine-based gas to form a coating film containing amorphous lithium fluoride on a surface of the positive electrode active material; adding a phosphate compound to the positive electrode active material, on which the coating film containing the lithium fluoride is formed, to prepare a positive electrode containing the positive electrode active material;forming a lithium ion secondary battery including the prepared positive electrode; and charging the formed lithium ion secondary battery to form a coating film containing amorphous lithium phosphate on the surface of the positive electrode active material.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2015/000215

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013054743 A1	18-04-2013	JP WO2013054743 A1	30-03-2015
		WO 2013054743 A1	18-04-2013
US 2013260210 A1	03-10-2013	CN 103367792 A	23-10-2013
		JP 5710535 B2	30-04-2015
		JP 2013206735 A	07-10-2013
		KR 20130110004 A	08-10-2013
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