



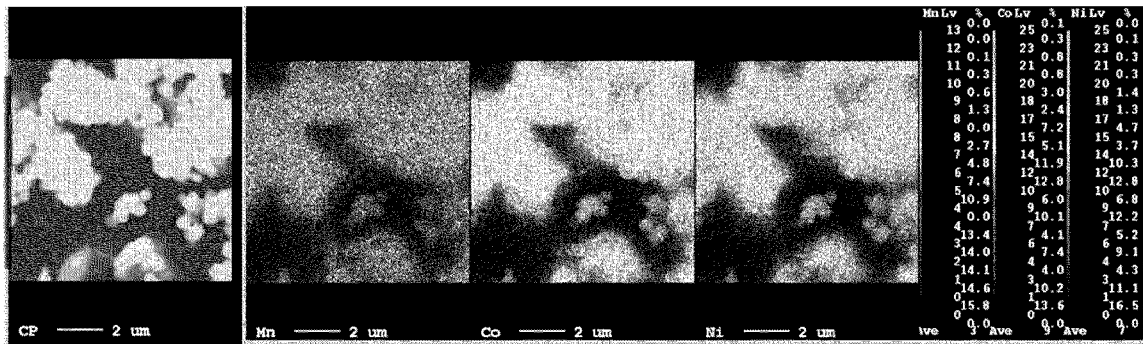
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(19) **United States**(12) **Patent Application Publication****NISHIZAKI et al.**(10) **Pub. No.: US 2023/0299285 A1**(43) **Pub. Date: Sep. 21, 2023**(54) **POSITIVE ELECTRODE ACTIVE MATERIAL
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City (JP)(21) Appl. No.: **18/323,608**(22) Filed: **May 25, 2023****Related U.S. Application Data**(63) Continuation of application No. PCT/JP2021/
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(57)

ABSTRACT

There is provided a positive electrode active material containing a lithium composite oxide having a layered rock salt structure containing Li, Ni, Co and Mn, and further containing at least one additive selected from Li_3BO_3 , Li_3PO_4 and Li_2SO_4 .



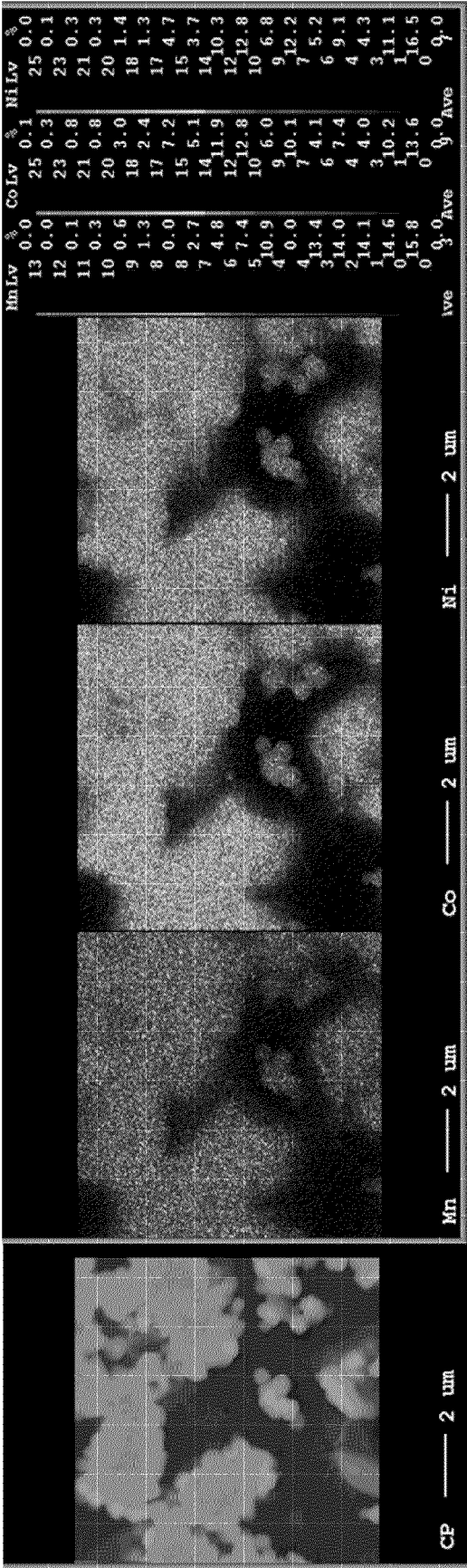


FIG. 1

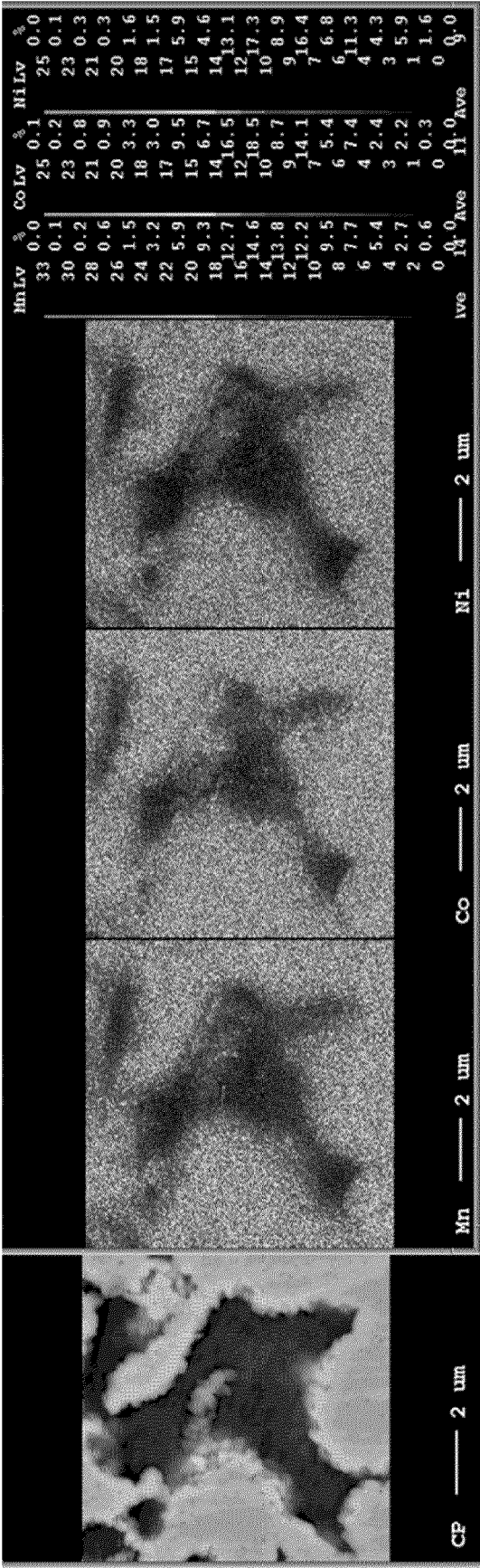


FIG. 2

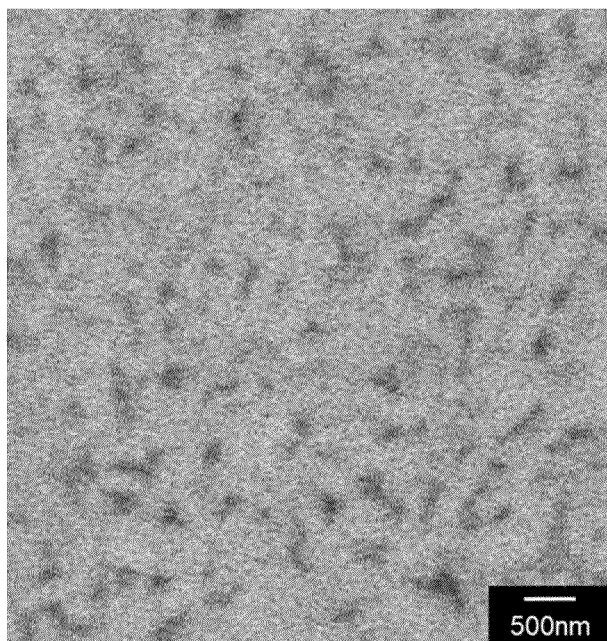


FIG. 3

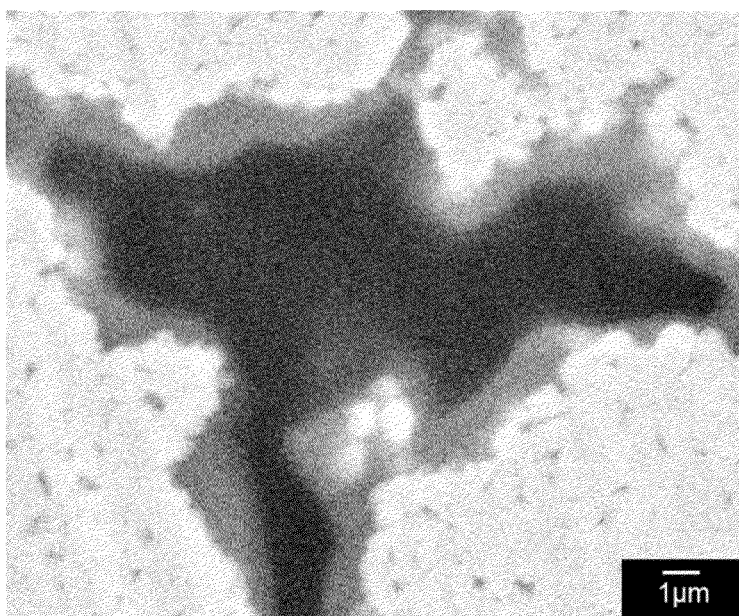


FIG. 4

POSITIVE ELECTRODE ACTIVE MATERIAL AND LITHIUM-ION SECONDARY BATTERY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation application of PCT/JP2021/045009 filed Dec. 7, 2021, which claims priority to PCT/JP2020/048035 filed Dec. 22, 2020 and PCT/JP2021/013156 filed Mar. 26, 2021, the entire contents all of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] The present invention relates to a positive electrode active material to be used for a lithium ion secondary battery, and a lithium ion secondary battery.

2. Description of the Related Art

[0003] As a positive electrode active material layer for lithium ion secondary batteries, there is broadly known a positive electrode of a dispersed power type obtained by kneading and shaping a powder of a lithium composite oxide (typically, a lithium transition metal oxide) and additives such as a binder and an electrically conductive agent. Since the positive electrode of a dispersed power type contains a relatively large amount (for example, about 10% by weight) of a binder not contributing to the capacity, the filling density of the lithium composite oxide as its positive electrode active material is low. The positive electrode of a dispersed power type thus has large room for improvement in the capacity and the charge/discharge efficiency. Then, an attempt is made to improve the capacity and the charge/discharge efficiency by constituting the positive electrode or the positive electrode active material layer of a lithium composite oxide sintered plate. In this case, since the positive electrode or the positive electrode active material layer contains no binder, the filling density of the lithium composite oxide becomes high, whereby a high capacity and a good charge/discharge efficiency are expected to be attained.

[0004] In addition, in lithium ion secondary batteries, a liquid electrolyte (electrolytic solution) using a flammable organic solvent as a diluting solvent is conventionally used as a medium for allowing ions to migrate. In batteries using such an electrolytic solution, problems might be posed such as leakage, inflammation and explosion of an electrolytic solution. In order to solve such problems and secure essential safety, all-solid-state batteries are under development in which a solid electrolyte is used in place of a liquid electrolyte and all of other elements are composed of solids. Since the electrolyte is a solid, the all-solid-state batteries have no possibility of inflammation, cause no leakage and are less likely to pose problems such as deterioration of battery performance due to corrosion.

[0005] There are proposed various all-solid-state batteries using a sintered electrode and a solid electrolyte. For example, Patent Literature 1 (WO2019/093222A1) discloses an all-solid-state lithium battery including an oriented positive electrode plate which is a lithium composite oxide sintered plate having a void ratio of 10 to 50%, a negative electrode plate which contains Ti and is capable of intercalating and

deintercalating lithium ions at 0.4 V (vs. Li/Li⁺) or higher, and a solid electrolyte which has a lower melting point than the melting point or the decomposition temperature of the oriented positive electrode plate or the negative electrode plate. In the literature, as solid electrolytes having such a low melting point, various materials are disclosed such as Li₃OCl, and $x\text{LiOH} \cdot y\text{Li}_2\text{SO}_4$ wherein $x+y = 1$, $0.6 \leq x \leq 0.95$ (for example, $3\text{LiOH} \cdot \text{Li}_2\text{SO}_4$). Such a solid electrolyte can be allowed to penetrate as a melt into voids of an electrode plate and can attain a firm interfacial contact. As a result, it is reportedly possible to attain a remarkable improvement in the battery resistance and the rate performance in charge/discharge, and a large improvement in the yield in the battery production. In addition, Patent Literature 2 (WO2015/151566A1) discloses an all-solid-state lithium battery having an oriented positive electrode plate which has a layered rock salt structure of a basic composition represented by $\text{Li}_p(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ wherein $0.9 \leq p \leq 1.3$, $0 < x < 0.8$, $0 < y < 1$, $0 \leq z \leq 0.7$, $x+y+z = 1$, a solid electrolyte layer composed of a Li-La-Zr-O-based ceramic material and/or a lithium phosphate oxynitride (LiPON)-based ceramic material, and a negative electrode layer.

CITATION LIST

Patent Literature

- [0006] Patent Literature 1: WO2019/093222A1
- [0007] Patent Literature 2: WO2015/151566A1

SUMMARY OF THE INVENTION

[0008] The present inventors have a finding that among the above-mentioned low-melting point solid electrolytes, particularly, a LiOH-Li₂SO₄-based solid electrolyte such as 3LiOH-Li₂SO₄ exhibits a high lithium ionic conductivity. However, as disclosed as Comparative Example in Patent Literature 1, when a cell is constituted by using a LiOH-Li₂SO₄-based solid electrolyte such as 3LiOH-Li₂SO₄ for a non-oriented sintered plate electrode and its battery is operated, there is a problem that the cycle characteristic becomes low. Since a non-oriented sintered plate has an advantage of being hardly susceptible to the restriction of raw material powders in control of the microstructure such as pore diameter, it is favorable if the cycle characteristic can be improved by using a non-oriented sintered plate. It can of course be said that the improvement in the cycle characteristic is similarly desired also in mixture electrodes, not limited to sintered plate electrodes.

[0009] The present inventors have currently found that the cycle characteristic can greatly be improved by incorporating at least one additive selected from Li₃BO₃, Li₃PO₄ and Li₂SO₄ in a lithium composite oxide to be used for a positive electrode of a lithium ion secondary battery.

[0010] Therefore, an object of the present invention is to provide a positive electrode active material capable of greatly improving the cycle characteristic when incorporated in a lithium ion secondary battery.

[0011] According to an aspect of the present invention, there is provided a positive electrode active material to be used for a lithium ion secondary battery,

[0012] wherein the positive electrode active material comprises a lithium composite oxide having a layered rock salt structure containing Li, Ni, Co and Mn, and

further comprises at least one additive selected from Li_3BO_3 , Li_3PO_4 and Li_2SO_4 .

[0013] According to another aspect of the present invention, there is provided a lithium ion secondary battery, comprising:

[0014] a positive electrode layer comprising the positive electrode active material;

[0015] a negative electrode layer comprising a negative electrode active material; and

[0016] a $\text{LiOH-Li}_2\text{SO}_4$ -based solid electrolyte interposed between the positive electrode layer and the negative electrode layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1 is an electron microscope photograph and EPMA mapping images of a positive electrode active material (NCM)/solid electrolyte cross-section of an all-solid-state battery prepared in Example 3. The image positioned on the leftmost side is an electron microscope photograph (white portions correspond to NCM, and black portions correspond to solid electrolyte), and rightward therefrom, EPMA mapping images of Mn, Co and Ni are shown in order.

[0018] FIG. 2 is an electron microscope photograph and EPMA mapping images of a positive electrode active material (NCM)/solid electrolyte cross-section of an all-solid-state battery prepared in Example 14. The image positioned on the leftmost side is an electron microscope photograph (white portions correspond to NCM, and black portions correspond to solid electrolyte), and rightward therefrom, EPMA mapping images of Mn, Co and Ni are shown in order.

[0019] FIG. 3 is an electron microscope photograph (reflection electron image) of a cross-section of a positive electrode plate prepared in Example 8.

[0020] FIG. 4 is an electron microscope photograph (reflection electron image) of a cross-section of a positive electrode plate prepared in Example 12 after being embedded in a resin.

DETAILED DESCRIPTION OF THE INVENTION

Positive Electrode Active Material

[0021] The positive electrode active material according to the present invention is one used for a lithium ion secondary battery. The positive electrode active material contains a lithium composite oxide having a layered rock salt structure containing Li, Ni, Co and Mn. Then, the positive electrode active material further contains at least one additive selected from Li_3BO_3 , Li_3PO_4 and Li_2SO_4 . In this way, by incorporating at least one additive selected from Li_3BO_3 , Li_3PO_4 and Li_2SO_4 in a lithium composite oxide to be used for a lithium ion secondary battery, the cycle characteristic (particularly, cycle retention rate) can greatly be improved.

[0022] As described above, although when a cell is constituted by using a $\text{LiOH-Li}_2\text{SO}_4$ -based solid electrolyte such as $3\text{LiOH-Li}_2\text{SO}_4$ for a non-oriented sintered electrode and its battery is operated, there is a problem that the cycle characteristic becomes low, according to the present invention, such a problem is favorably solved. For example, a lithium ion secondary battery having a positive electrode layer containing a positive electrode active material containing a lithium composite oxide having at least one selected

from Li_3BO_3 , Li_3PO_4 and Li_2SO_4 added thereto, a $\text{LiOH-Li}_2\text{SO}_4$ -based solid electrolyte, and a negative electrode layer has a higher cycle retention rate as compared with a battery using a lithium composite oxide with no additive. Its mechanism, though not being clear, is conceivably as follows. First, the causes of the deterioration of the cycle characteristic are presumably (1) that the solid electrolyte is deteriorated by occurrence of side reactions at interfaces between the positive electrode and the solid electrolyte in charge/discharge, and (2) that minute cracks are generated at grain boundaries of the lithium composite oxide by expansion and contraction of the lithium composite oxide along with charge/discharge. With regard to this point, it is presumed that in the present invention, with regard to the cause of the above (1), Li_3BO_3 , Li_3PO_4 and/or Li_2SO_4 deposited on at least a part of the surface of the lithium composite oxide suppresses the side reactions. Then, it is presumed that with regard to the cause of the above (2), Li_3BO_3 , Li_3PO_4 and/or Li_2SO_4 deposited on at least a part of a grain boundary relaxes stresses of the expansion and contraction. Therefore, it is preferable that the additive is present in the state of deposited on at least a part of a grain boundary and of a surface of the lithium composite oxide.

[0023] The positive electrode active material contains the lithium composite oxide having a layered rock salt structure containing Li, Ni, Co and Mn. The lithium composite oxide is one also called lithium cobaltate-nickelate-manganate, and abbreviated to NCM. The layered rock salt structure refers to a crystal structure in which a lithium layer and a transition metal layer other than lithium are alternately laminated with a layer of oxygen being sandwiched therebetween (typically, an $\alpha\text{-NaFeO}_2$ -type structure: a structure in which a transition metal and lithium are orderly arranged in the [111] axis of the cubic rock salt-type structure). A typical NCM has a composition represented by $\text{Li}_p(\text{Ni}_x, \text{Co}_y, \text{Mn}_z)\text{O}_2$ wherein $0.9 \leq p \leq 1.3$, $0 < x < 0.8$, $0 < y < 1$, $0 \leq z \leq 0.7$, $x + y + z = 1$; preferably, $0.95 \leq p \leq 1.10$, $0.1 \leq x < 0.7$, $0.1 \leq y < 0.9$, $0 \leq z \leq 0.6$, $x + y + z = 1$, and is, for example, $\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})\text{O}_2$ and $\text{Li}(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})\text{O}_2$. Therefore, the molar ratio of $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ in the positive electrode active material is preferably 0.95 to 1.10, more preferably 0.97 to 1.08 and still more preferably 0.98 to 1.05.

[0024] As described above, while the positive electrode active material according to the present invention is to be used for a lithium ion secondary battery, it is preferable that the positive electrode is in a form of a sintered plate made by sintering a positive electrode raw material powder. That is, the positive electrode active material is preferably in a form of a sintered plate. In other words, it is preferable that the positive electrode active material has a structure in which a plurality of primary particles having a layered rock salt structure containing Li, Ni, Co and Mn are bound. Since the sintered plate does not have to contain an electron conductive auxiliary of a binder, the energy density of the positive electrode can be increased. The sintered plate may be a compact body or a porous body, and a solid electrolyte may be contained in pores of the porous body. The positive electrode, however, may also be in a form generally called a mixture electrode, for example, a mixture of the positive electrode active material, an electron conductive auxiliary, a lithium ionic conductive material, a binder and the like, or a form (mixture form) made by forming a mixture of the positive electrode active material, a LiOH-

Li_2SO_4 -based solid electrolyte, an electron conductive auxiliary and the like. In this case, the positive electrode active material may be in a powdery form. Therefore, the positive electrode active material may be a mixed powder containing a powder of the lithium composite oxide, and at least one powder selected from Li_3BO_3 , Li_3PO_4 and Li_2SO_4 .

[0025] The content (that is, the content proportion of the additives to the total content of the lithium composite oxide and the additives) of the additives in the positive electrode active material is, without regard to the form (sintered plate or mixture) of the positive electrode, from the viewpoint of the improvement in the cycle characteristic, preferably 0.1 to 10% by weight, more preferably 0.5 to 7.0% by weight and still more preferably 1.0 to 6.0% by weight. Here, it is considered that with regard to the above content of the additives, the amount of the additives charged in preparation of the positive electrode active material is nearly equal to the content of the additives in the positive electrode active material finally obtained. This is presumable, for example, from that almost no weight change occurs in the case of thermogravimetry (TG) of simple substances of the additives.

[0026] In the case where the positive electrode active material is in a form of a sintered plate, the degree of orientation of the sintered plate, $I_{[003]}/I_{[104]}$, defined as a ratio of the diffraction intensity $I_{[003]}$ derived from the (003) plane to the diffraction intensity $I_{[104]}$ derived from the (104) plane, in an XRD profile measured by X-ray diffraction (XRD), is 1.2 to 3.6, preferably 1.2 to 3.5, more preferably 1.2 to 3.0 and still more preferably 1.2 to 2.6. Here, the lithium composite oxide having a layered rock salt-type crystal structure like NCM has crystal planes (planes other than the (003) plane, for example, the (101) plane and the (104) plane), where going-in and going-out of lithium ions well occur, and the (003) plane, where that does not occur. Herein, each diffraction intensity of the (003) plane and the (104) plane by XRD among these is used for convenience as an index for calculation of the degree of orientation. When the sintered plate has a degree of orientation, $I_{[003]}/I_{[104]}$, in the above-mentioned range, the degree of orientation becomes equal or nearly equal to the degrees of orientation, $I_{[003]}/I_{[104]}$, of NCM powders which become a measure of non-orientation (for example, 1.4 (a composition of Ni : Co : Mn = 5 : 2 : 3) and 2.3 (a composition of Ni : Co : Mn = 3 : 6 : 1), and therefore it can be said that the sintered plate is nearly in a non-oriented (random) state, that is, is substantially not oriented (or is not much oriented). As described above, since the non-oriented sintered body has an advantage of being hardly susceptible to the restriction of raw material powders in control of the microstructure such as pore diameter, it becomes easy to select raw material powders favorable in order to control the microstructure (for example, pore diameter) of the sintered body, and it becomes easier to attain an improvement in the cycle characteristic.

[0027] In the case where the positive electrode active material is in a form of the sintered plate, the porosity of the sintered plate is preferably 20 to 40%, more preferably 20 to 38%, still more preferably 20 to 36% and especially preferably 20 to 33%. When the porosity is in such a range, pores can sufficiently be filled with a solid electrolyte and the proportion of a positive electrode active material in a positive electrode is increased in preparation of a battery, leading to achievement of a high energy density as a battery.

[0028] The “porosity” herein is a volume ratio of pores in a sintered plate. The porosity can be measured by image analysis of a cross-sectional SEM image of the sintered plate. For example, the porosity (%) of a sintered plate may be determined by embedding a sintered plate in a resin; subjecting the resin-embedded sintered plate to cross-sectional polishing by ion milling; observing the polished cross-section by a SEM (scanning electron microscope) to acquire a cross-sectional SEM image (for example, a magnification of 500 to 1,000 times); and analyzing the acquired SEM image to calculate the proportion (%) of the area of parts filled with the resin in the total area consisting of parts of an electrode active material and the parts filled with the resin (parts which were pores originally). If the measurement can be carried out in a desired accuracy, the porosity may also be measured without embedding the sintered plate in the resin. For example, the measurement of the porosity of a sintered plate filled with a solid electrolyte in pores (a positive electrode plate taken out from an all-solid-state secondary battery) can be made in the state that the solid electrolyte remains filled.

[0029] In the case where the positive electrode active material is in a form of the sintered plate, the mean pore diameter of the sintered plate is preferably $3.5\text{ }\mu\text{m}$ or larger, more preferably 3.5 to $15.0\text{ }\mu\text{m}$, still more preferably 3.5 to $10.0\text{ }\mu\text{m}$ and especially preferably 3.5 to $8.0\text{ }\mu\text{m}$. Such a range leads to an increase of a solid electrolyte part (solid electrolyte part at distances apart from the interface) hardly susceptible to deterioration due to side reactions between the solid electrolyte and the lithium composite oxide. Hence, it is considered that the elemental diffusion between the solid electrolyte and the lithium composite oxide is suppressed and the reduction of the Li ionic conduction due to the deterioration of the solid electrolyte is alleviated, whereby the discharge capacity and the cycle characteristic are more effectively improved.

[0030] The “mean pore diameter” herein is a mean value of the diameters of pores contained in a sintered plate of an electrode. The “diameter” is typically a length of a line segment bisecting the projected area of the pore (Martin diameter). In the present invention, the “mean value” calculated on the number base is suitable. The mean pore diameter can be measured by image analysis of a cross-sectional SEM image of the sintered plate. For example, the mean pore diameter of the sintered plate may be determined by analyzing the SEM image acquired in the above-mentioned porosity measurement to divide parts of an electrode active material from parts filled with a resin (parts which were pores originally) in a sintered plate; determining the maximum Martin diameter in each of regions of the parts filled with a resin; and calculating the mean value of the maximum Martin diameters as the mean pore diameter of the sintered plate. If the measurement can be carried out in a desired accuracy, the mean pore diameter may be measured without embedding the sintered plate in the resin. For example, the measurement of the mean pore diameter of a sintered plate filled with a solid electrolyte in pores (a positive electrode plate taken out from an all-solid-state secondary battery) can be made in the state that the solid electrolyte remains filled.

[0031] In the case where the positive electrode active material is in a form of the sintered plate, the interfacial length per $1\text{ }\mu\text{m}^2$ of unit cross-sectional area of the sintered plate is preferably $0.45\text{ }\mu\text{m}$ or shorter, more preferably 0.10

to 0.40 μm , still more preferably 0.10 to 0.35 μm and especially preferably 0.10 to 0.30 μm . Such a range leads to a reduction of the site where the lithium composite oxide and the solid electrolyte cause side reactions. Hence, it is considered that the elemental diffusion between the solid electrolyte and the lithium composite oxide is suppressed and the reduction of the Li ionic conduction due to the deterioration of the solid electrolyte is alleviated, whereby the discharge capacity and the cycle characteristic are more effectively improved.

[0032] The “interfacial length per 1 μm^2 of unit cross-sectional area” herein is a total length of all the interfaces between pores and the active material contained in the unit cross-sectional area of a sintered plate, per 1 μm^2 of unit cross-sectional area of the sintered plate. The interfacial length can be measured by image analysis of a cross-sectional SEM image of the sintered plate. For example, The interfacial length per 1 μm^2 of unit cross-sectional area may be determined by analyzing the SEM image acquired in the above-mentioned porosity measurement, dividing parts of an electrode active material from parts filled with a resin (parts which were pores originally) in a sintered plate; determining the perimeter of all regions (that is, the total length of interfaces between the parts of a positive electrode active material and the parts filled with a resin) and the area of all regions analyzed (that is, regions composed of both of the parts of a positive electrode active material and the parts filled with a resin) in regions of the parts filled with a resin; and then dividing the perimeter by the area of all the analyzed regions to obtain the quotient as the interfacial length per 1 μm^2 of unit cross-sectional area. If the measurement can be carried out in a desired accuracy, the interfacial length may also be measured without embedding the sintered plate in the resin. For example, the measurement of the interfacial length of a sintered plate filled with a solid electrolyte in pores (a positive electrode plate taken out from an all-solid-state secondary battery) can be made in the state that the solid electrolyte remains filled.

[0033] The thickness of the positive electrode is, without regard to the form (sintered plate or mixture) of the positive electrode, from the viewpoint of the improvement in the energy density of a battery, and the like, preferably 30 to 300 μm , more preferably 50 to 300 μm and still more preferably 80 to 300 μm .

Method for Producing the Lithium Composite Oxide Sintered Plate

[0034] The lithium composite oxide sintered plate according to a preferable aspect of the present invention may be one produced by any method, but is produced preferably through (a) preparation of an NCM raw material powder, (b) preparation of an NCM green sheet, and (c) firing of the NCM green sheet.

(A) Preparation of an NCM Raw Material Powder

[0035] First, an NCM raw material powder is prepared. A preferable NCM raw material powder is a $\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})\text{O}_2$ powder or a $\text{Li}(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})\text{O}_2$ powder. The $\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})\text{O}_2$ powder can be prepared by mixing a $(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})(\text{OH})_2$ powder and a Li_2CO_3 powder weighed to give a molar ratio of $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ being 1.00 to 1.30, and firing the mixture at 700 to 1,200° C. (preferably 750 to 1,000° C.) for 1 to 24 hours

(preferably 2 to 15 hours). Then, the $\text{Li}(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})\text{O}_2$ powder can be prepared by mixing a $(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})(\text{OH})_2$ powder and a Li_2CO_3 powder weighed to give a molar ratio of $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ being 1.00 to 1.30, and firing the mixture at 700 to 1,200° C. (preferably 750 to 1,000° C.) for 1 to 24 hours (preferably 2 to 15 hours).

[0036] In order to control the peculiar microstructure (particularly, pores) in the lithium composite oxide sintered plate of the present aspect, it is preferable to use a mixed powder made by preparing a rather large-particle NCM raw material powder having a volume base D50 particle size of 3 to 20 μm (preferably 5 to 15 μm) and a rather small-particle NCM raw material powder having a volume base D50 particle size of 0.05 to 1 μm (preferably 0.1 to 0.6 μm), and mixing these. The proportion of the rather large-particle NCM raw material powder in the mixed powder of these large and small two kinds is preferably 50 to 99% by weight and more preferably 70 to 95% by weight. The rather small-particle NCM raw material powder may be prepared by milling the rather large-particle NCM raw material powder by well-known means such as a ball mill.

[0037] The additives such as Li_3BO_3 , Li_3PO_4 and Li_2SO_4 may be added to the NCM raw material powder after being fired, prepared as described above, or may be added to an NCM precursor powder before being fired, such as a $(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})(\text{OH})_2$ powder or a $(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})(\text{OH})_2$ powder. Alternatively, when the mixed powder of the large and small two kinds as described above is obtained, the additives may be added to at least one of the rather large-particle NCM raw material powder and the rather small-particle NCM raw material powder.

(B) Preparation of an NCM Green Sheet

[0038] An NCM raw material powder (preferably, the above-mentioned NCM mixed powder), a solvent, a binder, a plasticizer and a dispersant are mixed to make a paste. The resulting paste is regulated in viscosity and then shaped into a sheet form to prepare an NCM green sheet.

(C) Preparation of an NCM Sintered Plate

[0039] The NCM green sheet thus prepared is cut out into a desired size and shape, and placed in a firing sagger and fired. It is desirable that the firing is carried out by raising the temperature to 800 to 1,000° C. (preferably 850 to 970° C.) at a temperature-rise rate of 50 to 600° C./h (preferably 100 to 300° C./h) and holding the temperature for 1 to 24 hours (preferably 2 to 12 hours). The lithium composite oxide sintered plate (NCM sintered plate) is thus obtained.

Lithium Ion Secondary Battery

[0040] The positive electrode active material according to the present invention is used for a lithium ion secondary battery (typically, an all-solid-state battery). Therefore, according to a preferable aspect of the present invention, there is provided a lithium ion secondary battery having a positive electrode layer containing the positive electrode active material of the present invention, a negative electrode layer, and a $\text{LiOH-Li}_2\text{SO}_4$ -based solid electrolyte. The negative electrode layer contains a negative electrode active material. The $\text{LiOH-Li}_2\text{SO}_4$ -based solid electrolyte is interposed between the positive electrode layer and the negative

electrode layer. As described above, the lithium ion secondary battery using, for the positive electrode, the lithium composite oxide having Li_3BO_3 , Li_3PO_4 and/or Li_2SO_4 added thereto can exhibit a higher cycle retention rate than conventional lithium ion secondary batteries using, for the positive electrode, a lithium composite oxide with no additive.

[0041] The positive electrode layer is preferably in a form of a sintered plate made by sintering a positive electrode raw material powder. That is, the positive electrode active material is preferably in a form of a sintered plate. Since the sintered plate does not have to contain an electron conductive auxiliary or a binder, the energy density of the positive electrode layer can be increased. The sintered plate may be a compact body or a porous body, and a solid electrolyte may be contained in pores of the porous body. It can be said that the positive electrode layer may be in a form generally called a mixture electrode, for example, a mixture of the positive electrode active material, an electron conductive auxiliary, a lithium ionic conductive material, a binder and the like, or a form (mixture form) made by shaping a mixture of the positive electrode active material, a $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte, an electron conductive auxiliary and the like. That is, the positive electrode layer may contain particles of the positive electrode active material, particles of the $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte and the electron conductive auxiliary in a mixture form. The compactness (filling rate) of the positive electrode active material in the positive electrode in a mixture form is, regarding the form of the positive electrode, preferably 50 to 80% by volume, more preferably 55 to 80% by volume, still more preferably 60 to 80% by volume and especially preferably 65 to 75% by volume. When the compactness is in such a range, voids in the positive electrode active material can fully be filled with the solid electrolyte, and the proportion of the positive electrode active material in the positive electrode increases, leading to achievement of a high energy density as a battery. Here, the value of the compactness (filling rate) in this mixture form is equivalent to a value obtained by subtracting the proportion of portions (including pores) excluding the positive electrode active material from 100.

[0042] The negative electrode layer (typically, negative electrode plate) contains a negative electrode active material. As the negative electrode active material, a negative electrode active material usually used for lithium ion secondary batteries can be used. Examples of such usual negative electrode active materials include carbon-based materials and metals or semimetals such as Li, In, Al, Sn, Sb, Bi and Si, or alloys containing any thereof. Besides, oxide-based negative electrode active materials may be used.

[0043] An especially preferable negative electrode active material contains a material capable of intercalating/deintercalating lithium ions at 0.4 V (vs. Li/Li^+) or higher, and preferably contains Ti. A negative electrode active material meeting such a condition is preferably an oxide containing at least Ti. Preferable examples of such a negative electrode active material include lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (hereinafter, referred to as LTO in some cases), a niobium titanium composite oxide Nb_2TiO_7 and titanium oxide TiO_2 ; more preferable are LTO and Nb_2TiO_7 ; and still more preferable is LTO. Here, LTO is known typically as having a spinel structure, but can assume another structure in charge/discharge. For example, with regard to LTO, the reactions in

charge/discharge progress in the coexistence of two phases of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (spinel structure) and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ (rock salt structure). Therefore, LTO is not limited to having a spinel structure.

[0044] The negative electrode may be in a form generally called a mixture electrode, for example, a mixture of the negative electrode active material, an electron conductive auxiliary, a lithium ion conductive material, a binder and the like, or a form made by shaping a mixture of the negative electrode active material, a $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte, an electron conductive auxiliary and the like. That is, the negative electrode may contain particles of the negative electrode active material, particles of a $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte, and an electron conductive auxiliary in a mixture form. The negative electrode, however, is preferably in a form of a sintered plate made by sintering a negative electrode raw material powder. That is, the negative electrode or the negative electrode active material is preferably in a form of a sintered plate. Since the sintered plate does not have to contain an electron conductive auxiliary or a binder, the energy density of the negative electrode can be increased. The sintered plate may be a compact body or a porous body, and a solid electrolyte may be contained in pores of the porous body. The particle size of particles of the negative electrode active material in a mixture form is preferably 0.05 to 50 μm , more preferably 0.1 to 30 μm and still more preferably 0.5 to 20 μm . The particle size of particles of the $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte is preferably 0.01 to 50 μm , more preferably 0.05 to 30 μm and still more preferably 0.1 to 20 μm . The electron conductive auxiliary is not especially limited as long as being one generally used for electrodes, but is preferably a carbon material. Preferable examples of the carbon material include carbon black, graphite, carbon nanotube, graphene, reduced graphene oxide, and any combinations thereof, but are not limited thereto, and various other carbon materials can be used.

[0045] The compactness (filling rate) of the negative electrode active material in the negative electrode is, without regard to the form (sintered plate or mixture) of the negative electrode, preferably 55 to 80% by volume, more preferably 60 to 80% by volume and still more preferably 65 to 75% by volume. When the compactness is in such a range, voids in the negative electrode active material can fully be filled with the solid electrolyte and the proportion of the negative electrode active material in the negative electrode increases, leading to achievement of a high energy density as a battery. Here, the value of the compactness (filling rate) in this mixture form is equivalent to a value obtained by subtracting the proportion of portions (including pores) excluding the negative electrode active material from 100.

[0046] The thickness of the negative electrode is, without regard to the form (sintered plate or mixture) of the negative electrode, from the viewpoint of the improvement in the energy density of a battery, and the like, preferably 40 to 410 μm , more preferably 65 to 410 μm , still more preferably 100 to 410 μm and especially preferably 107 to 270 μm .

[0047] The solid electrolyte is a $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte. The $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte is a composite compound of LiOH and Li_2SO_4 ; the typical composition is represented by the general formula: $x\text{LiOH}\cdot y\text{Li}_2\text{SO}_4$ wherein $x + y = 1$, and $0.6 \leq x \leq 0.95$; and representative examples include $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ (a composition in which in the above general formula, $x = 0.75$ and $y =$

0.25). Preferably, the $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte contains a solid electrolyte identified as $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ by X-ray diffraction. This preferable solid electrolyte contains $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ as its main phase. Whether or not $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ is contained in the solid electrolyte can be confirmed by identification using 032-0598 in ICDD data base in an X-ray diffraction pattern. Here, “ $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ ” refers to one having a crystal structure which can be regarded as the same as that of $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$, and does not necessarily need to have the same crystal composition as $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$. That is, $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ whose composition deviates from $\text{LiOH}:\text{Li}_2\text{SO}_4=3:1$ is, as long as having the same crystal structure as $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$, determined to be also included in the “ $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ ”. Therefore, even a solid electrolyte (for example, $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ in which boron is dissolved as a solid solution and which exhibits an X-ray diffraction peak shifted to the larger angle side) containing a dopant such as boron is, as long as being regarded as having the same crystal structure as $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$, herein determined to be referred to as $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$. Similarly, the solid electrolyte to be used in the present invention is allowed to contain inevitable impurities.

[0048] Therefore, the $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte may contain, other than $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ as its main phase, heterophases. The heterophases may be ones containing a plurality of elements selected from Li, O, H, S and B, or may be ones consisting only of a plurality of elements selected from Li, O, H, S and B. Examples of the heterophases include LiOH , Li_2SO_4 and/or Li_3BO_3 , originated from raw materials. These heterophases are conceivably unreacted raw materials remaining when $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ is formed, but since the heterophases do not contribute to the lithium ionic conduction, it is desirable that the amount thereof other than Li_3BO_3 is small. Since it can be said that a heterophase containing boron like Li_3BO_3 can contribute to the improvement in the lithium ionic conductivity after high-temperature long-time holding, the heterophase is allowed to be contained in a desired amount. It can be said that the solid electrolyte may be composed of a single phase of $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ in which boron is dissolved as a solid solution.

[0049] It is preferable that the $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte (particularly, $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$) further contains boron. By making boron to be further contained in a solid electrolyte identified as $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$, the reduction of the lithium ionic conductivity can be significantly suppressed even after high-temperature long-time holding. It is presumed that boron is entrapped in any of sites of the crystal structure of $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$, and improves stability of the crystal structure to temperature. The molar ratio (B/S) of boron B to sulfur S contained in the solid electrolyte is preferably higher than 0.002 and lower than 1.0, more preferably 0.003 or higher and 0.9 or lower and still more preferably 0.005 or higher and 0.8 or lower. When the B/S is in the above range, the retention rate of the lithium ionic conductivity is enabled to be improved. Further when the B/S is in the above range, the content of unreacted heterophases containing boron decreases, and therefore the absolute value of the lithium ionic conductivity can be high.

[0050] The $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte may be a green compact made of a powder made by milling a melt-solidified body, but is preferably a melt-solidified body (that is, material heat melted and then solidified). A method of milling the melt-solidified body is not especially limited,

but there can be adopted a usual method using a mortar, a ball mill, a jet mill, a roller mill, a cutter mill, a ring mill or the like, and the method may be of a wet type or dry type.

[0051] It is preferable that the $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte is filled also in pores of the positive electrode layer and/or pores of the negative electrode layer, or is incorporated (as one component of the mixture) also in the positive electrode layer and/or the negative electrode layer. The thickness (excluding portions of the solid electrolyte having entered pores of the positive electrode layer and the negative electrode layer) of the solid electrolyte layer is, from the viewpoint of the charge/discharge rate characteristic and the insulation of the solid electrolyte, preferably 1 to 500 μm , more preferably 3 to 50 μm and still more preferably 5 to 40 μm .

Production of a Lithium Ion Secondary Battery

[0052] Production of a lithium ion secondary battery, in the case of using a sintered plate electrode, can be carried out by i) preparing a positive electrode (as required, having a current collector formed therein) and a negative electrode (as required, having a current collector formed therein), and ii) sandwiching a solid electrolyte between the positive electrode and the negative electrode and subjecting the resultant to pressing, heating or the like to unify the positive electrode, the solid electrolyte and the negative electrode. The positive electrode, the solid electrolyte and the negative electrode may be connected by another means. In this case, examples of means to form the solid electrolyte between the positive electrode and the negative electrode include means of placing a formed body or a powder of the solid electrolyte on one electrode, means of applying a paste of a solid electrolyte powder on the electrode by screen printing, means of collision solidifying a powder of the solid electrolyte on the electrode as a substrate by an aerosol deposition method or the like, and means of depositing a solid electrolyte powder on the electrode by electrophoresis to form a membrane. On the other hand, production of an all-solid-state secondary battery in the case of using a mixture electrode can be carried out, for example, by placing and pressing, in a press die, a positive electrode mixture powder (containing positive electrode active material particles, solid electrolyte particles and an electron conductive auxiliary), a solid electrolyte powder and a negative electrode mixture powder (containing negative electrode active material particles, solid electrolyte particles and an electron conductive auxiliary). The charging and pressing of the various powders in this case is allowed to be carried out in an arbitrary order so that a positive electrode layer, a solid electrolyte layer and a negative electrode layer are finally made in order. Here, as described above, the positive electrode active material particles may be in a form of a mixed powder containing a powder of the lithium composite oxide and at least one powder selected from Li_3BO_3 , Li_3PO_4 and Li_2SO_4 .

EXAMPLES

[0053] The present invention will be described more specifically by way of the following Examples. In the following description, lithium composite oxides having a layered rock salt structure containing Li, Ni, Co and Mn, such as $\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})\text{O}_2$ and $\text{Li}(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})\text{O}_2$, are abbreviated to “NCM”, while $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is abbreviated to “LTO”.

Examples 1 to 18

[0054] Examples described below were Examples in respect to all-solid-state secondary batteries whose positive electrodes and negative electrodes were in forms of sintered plates.

[0055] First, NCM raw material powders 1 to 22 were prepared in order to prepare positive electrode plates as described below. Then, the summary of features of these raw material powders is shown in Tables 1A to 1C.

Preparation of an NCM Raw Material Powder 1

[0056] A commercially available ($\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}$)(OH)₂ powder (mean particle size: 9 to 10 μm) and a commercially available Li_2CO_3 powder (mean particle size: 3 μm), which were weighed to give a molar ratio of Li/(Ni+Co+Mn) being 1.15, were mixed, and then held at 750° C. for 10 hours to obtain an NCM raw material powder 1. The volume base D50 particle size of the powder was 8 μm .

Preparation of an NCM Raw Material Powder 2

[0057] 2.45% by weight (with respect to the total amount of the NCM raw material powder 1 and Li_3BO_3) of Li_3BO_3 was added to the NCM raw material powder 1, and regulated in the volume base D50 particle size to about 0.4 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 2.

Preparation of an NCM Raw Material Powder 3

[0058] 9.2% by weight (with respect to the total amount of the NCM raw material powder 1 and Li_3BO_3) of Li_3BO_3 was added to the NCM raw material powder 1, and regulated in the volume base D50 particle size to about 0.4 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 3.

Preparation of an NCM Raw Material Powder 4

[0059] The NCM raw material powder 1 was regulated in the volume base D50 particle size to about 5.5 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 4.

Preparation of an NCM Raw Material Powder 5

[0060] 1.0% by weight (with respect to the total amount of the NCM raw material powder 1 and Li_3PO_4) of Li_3PO_4 was added to the NCM raw material powder 1, and regulated in the volume base D50 particle size to about 5.5 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 5.

Preparation of an NCM Raw Material Powder 6

[0061] 5.0% by weight (with respect to the total amount of the NCM raw material powder 1 and Li_3PO_4) of Li_3PO_4 was added to the NCM raw material powder 1, and regulated in the volume base D50 particle size to about 5.5 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 6.

Preparation of an NCM Raw Material Powder 7

[0062] A commercially available ($\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1}$)(OH)₂ powder (mean particle size: 7 to 8 μm) and a commercially available Li_2CO_3 powder (mean particle size: 3 μm), which were weighed to give a molar ratio of Li/(Ni+Co+Mn) being 1.15, were mixed, and then held at 850° C. for 10 hours to obtain an NCM raw material powder 7. The volume base D50 particle size of the powder was 6.5 μm .

Preparation of an NCM Raw Material Powder 8

[0063] 9.2% by weight (with respect to the total amount of the NCM raw material powder 7 and Li_3BO_3) of Li_3BO_3 was added to the NCM raw material powder 7, and regulated in the volume base D50 particle size to about 0.4 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 8.

Preparation of an NCM Raw Material Powder 9

[0064] 16.8% by weight (with respect to the total amount of the NCM raw material powder 7 and Li_3BO_3) of Li_3BO_3 was added to the NCM raw material powder 7, and regulated in the volume base D50 particle size to about 0.4 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 9.

Preparation of an NCM Raw Material Powder 10

[0065] 51% by weight (with respect to the total amount of the NCM raw material powder 7 and Li_3BO_3) of Li_3BO_3 was added to the NCM raw material powder 7, and regulated in the volume base D50 particle size to about 0.4 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 10.

Preparation of an NCM Raw Material Powder 11

[0066] 16.8% by weight (with respect to the total amount of the NCM raw material powder 7 and Li_2SO_4) of Li_2SO_4 was added to the NCM raw material powder 7, and regulated in the volume base D50 particle size to about 0.4 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 11.

Preparation of an NCM Raw Material Powder 12

[0067] 51% by weight (with respect to the total amount of the NCM raw material powder 7 and Li_2SO_4) of Li_2SO_4 was added to the NCM raw material powder 7, and regulated in the volume base D50 particle size to about 0.4 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 12.

Preparation of an NCM Raw Material Powder 13

[0068] The NCM raw material powder 7 was regulated in the volume base D50 particle size to about 0.4 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 13.

Preparation of an NCM Raw Material Powder 14

[0069] The NCM raw material powder 7 was regulated in the volume base D50 particle size to about 4.3 μm by wet

milling in a ball mill, and then dried to obtain an NCM raw material powder 14.

Preparation of an NCM Raw Material Powder 15

[0070] A commercially available ($\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1}$)(OH)₂ powder (mean particle size: 7 to 8 μm) and a commercially available Li_2CO_3 powder (mean particle size: 3 μm), which were weighed to give a molar ratio of Li/(Ni+Co+Mn) being 1.15, were mixed, and then held at 950° C. for 10 hours; and the resulting powder was regulated in the volume base D50 particle size to about 1.9 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 15.

Preparation of an NCM Raw Material Powder 16

[0071] 0.74% by weight (with respect to the total amount of the NCM hydroxide, Li_2CO_3 and Li_3PO_4) of a Li_3PO_4 powder (mean particle size: 0.5 μm) was added to a commercially available ($\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1}$)(OH)₂ powder (mean particle size: 9 to 10 μm) and a commercially available Li_2CO_3 powder (mean particle size: 3 μm), which were weighed to give a molar ratio of Li/(Ni+Co+Mn) being 1.15, and mixed, and then held at 870° C. for 10 hours to obtain an NCM raw material powder 16. The volume base D50 particle size of the powder was 7.4 μm .

Preparation of an NCM Raw Material Powder 17

[0072] 1.8% by weight (with respect to the total amount of the NCM hydroxide, Li_2CO_3 and Li_3PO_4) of a Li_3PO_4 powder (mean particle size: 0.5 μm) was added to a commercially available ($\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1}$)(OH)₂ powder (mean particle size: 9 to 10 μm) and a commercially available Li_2CO_3 powder (mean particle size: 3 μm), which were weighed to give a molar ratio of Li/(Ni+Co+Mn) being 1.15, and mixed, and then held at 870° C. for 10 hours to obtain an NCM raw material powder 17. The volume base D50 particle size of the powder was 7.5 μm .

Preparation of an NCM Raw Material Powder 18

[0073] 3.6% by weight (with respect to the total amount of the NCM hydroxide, Li_2CO_3 and Li_3PO_4) of a Li_3PO_4 powder (mean particle size: 0.5 μm) was added to a commercially available ($\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1}$)(OH)₂ powder (mean particle size: 9 to 10 μm) and a commercially available Li_2CO_3 powder (mean particle size: 3 μm), which were weighed to give a molar ratio of Li/(Ni+Co+Mn) being 1.15, and mixed, and then held at 870° C. for 10 hours to obtain an NCM raw material powder 18. The volume base D50 particle size of the powder was 7.7 μm .

Preparation of an NCM Raw Material Powder 19

[0074] A commercially available ($\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1}$)(OH)₂ powder (mean particle size: 9 to 10 μm) and a commercially available Li_2CO_3 powder (mean particle size: 3 μm), which were weighed to give a molar ratio of Li/(Ni+Co+Mn) being 1.15, were mixed, and then held at 750° C. for 10 hours to obtain an NCM raw material powder 19. The volume base D50 particle size of the powder was 7.0 μm .

Preparation of an NCM Raw Material Powder 20

[0075] 9.2% by weight (with respect to the total amount of the NCM raw material powder 19 and Li_3BO_3) of Li_3BO_3

and 1.0% by weight (with respect to the total amount of the NCM raw material powder 19 and Li_3PO_4) of Li_3PO_4 were added to the NCM raw material powder 19, and regulated in the volume base D50 particle size to about 0.5 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 20.

Preparation of an NCM Raw Material Powder 21

[0076] 9.2% by weight (with respect to the total amount of the NCM raw material powder 19 and Li_3BO_3) of Li_3BO_3 and 2.5% by weight (with respect to the total amount of the NCM raw material powder 19 and Li_3PO_4) of Li_3PO_4 were added to the NCM raw material powder 19, and regulated in the volume base D50 particle size to about 0.5 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 21.

Preparation of an NCM Raw Material Powder 22

[0077] 9.2% by weight (with respect to the total amount of the NCM raw material powder 19 and Li_3BO_3) of Li_3BO_3 and 5.0% by weight (with respect to the total amount of the NCM raw material powder 19 and Li_3PO_4) of Li_3PO_4 were added to the NCM raw material powder 19, and regulated in the volume base D50 particle size to about 0.5 μm by wet milling in a ball mill, and then dried to obtain an NCM raw material powder 22.

[0078] By using the above raw material powders 1 to 22, positive electrode plates and batteries were prepared as described below, and various evaluations were carried out.

Example 1

Preparation of a Positive Electrode Plate

(1A) Preparation of an NCM Green Sheet

[0079] First, the NCM raw material powders 1 and 2 were homogeneously mixed in a blend proportion of 80 : 20 (in weight ratio) as indicated in Tables 1A to 1C to prepare an NCM mixed powder A. The mixed powder A was mixed with a solvent for forming a tape, a binder, a plasticizer and a dispersant. The viscosity of the resulting paste was regulated, followed by shaping into a sheet form on a PET film (polyethylene terephthalate) to prepare an NCM green sheet. The thickness of the NCM green sheet was regulated such that the thickness after firing is 100 μm .

(1B) Preparation of an NCM Sintered Plate

[0080] The NCM green sheet peeled off from the PET film was punched out into a circle of 11 mm in diameter with a punch, and placed in a firing sagger. The temperature was raised at a temperature-rise rate of 200° C./h up to 940° C. and held for 10 hours to carry out firing. The thickness of the resulting sintered plate was about 100 μm by SEM observation. A Au film (thickness: 100 nm) was formed as a current collector layer on one surface of the NCM sintered plate by sputtering. A positive electrode plate was thus obtained.

Preparation of a Negative Electrode Plate

(2A) Preparation of an LTO Green Sheet

[0081] A commercially available TiO_2 powder (mean particle size: 1 μm or smaller) and a commercially available

Li_2CO_3 powder (mean particle size: 3 μm), which were weighed to give a molar ratio of Li/Ti being 0.84, were mixed, and then held at 1,000° C. for 2 hours to obtain a powder composed of LTO particles. The powder was regulated in the mean particle size to about 2 μm by wet milling in a ball mill, and mixed with a solvent for forming a tape, a binder, a plasticizer and a dispersant. The viscosity of the resulting paste was regulated followed by shaping into a sheet form on a PET film to prepare an LTO green sheet. The thickness of the LTO green sheet was regulated such that the thickness after firing is 130 μm .

(2B) Preparation of an LTO Sintered Plate

[0082] The LTO green sheet peeled off from the PET film was punched out into a circle of 11 mm in diameter with a punch, and placed in a firing sagger. The temperature was raised at a temperature-rise rate of 200° C./h up to 850° C. and held for 2 hours to carry out firing. The thickness of the resulting sintered plate was about 130 μm by SEM observation. A Au film (thickness: 100 nm) was formed as a current collector layer on one surface of the LTO sintered plate by sputtering. A negative electrode plate was thus obtained.

Preparation of a Solid Electrolyte

(3A) Preparation of a Raw Material Mixed Powder

[0083] A Li_2SO_4 powder (commercially available product, purity: 99% or higher), a LiOH powder (commercially available product, purity: 98% or higher) and Li_3BO_3 (commercially available product, purity: 99% or higher) were mixed so that $\text{Li}_2\text{SO}_4 : \text{LiOH} : \text{Li}_3\text{BO}_3 = 1 : 2.6 : 0.05$ (in molar ratio) to obtain a raw material mixed powder. These powders were handled in a glove box in an Ar atmosphere and enough caution was taken so as not to cause deterioration such as moisture absorption.

(3B) Melting Synthesis

[0084] The raw material mixed powder was placed in an Ar atmosphere in a high-purity alumina-made crucible. The crucible was set in an electric furnace, and heat treated at 430° C. for 2 hours in an Ar atmosphere to prepare a melt. Successively, the melt was cooled at 100° C./h in the electric furnace to form a solidified material.

(3C) Milling in a Mortar

[0085] The resulting solidified material was milled in a mortar in a glove box in an Ar atmosphere to obtain a solid electrolyte powder having a volume base D50 particle size of 5 to 50 μm .

Preparation of an All-Solid-State Battery

[0086] The solid electrolyte powder was placed on the positive electrode plate, and the negative electrode plate was placed thereon. A weight was further placed on the negative electrode plate, and heated at 400° C. for 45 min in an electric furnace. At this time, the solid electrolyte powder was melted and underwent subsequent solidification to form a solid electrolyte layer between the electrode plates. By using a cell composed of the resulting positive electrode plate/solid electrolyte/negative electrode plate, a battery was prepared.

Evaluations

(5A) Degree of Orientation

[0087] On the positive electrode plate prepared in the above (1), XRD (X-ray diffraction) measurement was carried out. The measurement was carried out by using an XRD device (manufactured by Bruker Corp., D8 ADVANCE) and measuring an XRD profile when the plate plane of the positive electrode plate was irradiated with X-ray. From the XRD profile, $I_{[003]}/I_{[104]}$ that is a ratio of the diffraction intensity (peak height) $I_{[003]}$ derived from the (003) plane of NCM to the diffraction intensity (peak height) $I_{[104]}$ derived from the (104) plane thereof was calculated, which was defined as the degree of orientation.

(5B) Measurements of the Thickness and the Porosity

[0088] Measurements of the thickness and the porosity (% by volume) of each of the positive electrode plate prepared in the above (1) (the NCM sintered plate in the state of not containing the solid electrolyte) and the negative electrode plate prepared in the above (2) (the LTO sintered plate in the state of not containing the solid electrolyte) were carried out as follows. First, the positive electrode plate (or the negative electrode plate) was embedded in a resin and then subjected to cross-sectional polishing by ion milling. The polished cross-section was observed by SEM to acquire a cross-sectional SEM image. The thickness was calculated from the SEM image. SEM images for porosity measurement were taken as images in magnifications of 1,000 times and 500 times. The acquired images were subjected to a binarization process using image analysis software (manufactured by Media Cybernetics, Inc., Image-Pro premier) to calculate the proportion (%) of the area of parts filled with the resin in the total area of parts of the positive electrode active material (or the negative electrode active material) and the parts filled with the resin in the positive electrode plate (or the negative electrode plate) (parts which had been pores originally) as the porosity (%) of the positive electrode plate (or the negative electrode plate). The threshold in the binarization was set by using the Otsu's binarization as a discriminant analysis method. The porosity of the positive electrode plate was as indicated in Table 2, and the porosity of the negative electrode plate was 38% (that is, the compactness was 62%).

(5C) Measurement of the Mean Pore Diameter

[0089] By using the SEM image used in the above porosity measurement, the mean pore diameter was measured as follows. By using image analysis software (manufactured by Media Cybernetics, Inc., Image-Pro premier), a binarization process was carried out to divide parts of the positive electrode active material (or the negative electrode active material) from parts filled with a resin (parts which had been pores originally) in the positive electrode plate (or the negative electrode plate). Thereafter, the maximum Martin diameter in each region in regions of the parts filled with a resin was determined and the mean value thereof was defined as the mean pore diameter (μm) of the positive electrode plate (or the negative electrode plate). The mean pore diameter of the positive electrode plate was as indicated in Table 2; and the mean pore diameter of the negative electrode plate was 2.1 μm .

(5D) Measurement of the Interfacial Length Per 1 Mm² of Unit Cross-Sectional Area

[0090] By using the SEM image used in the above porosity measurement, the interfacial length per 1 μm^2 of unit cross-sectional area was measured as follows. By using image analysis software (manufactured by Media Cybernetics, Inc., Image-Pro Premier), a binarization process was carried out to divide parts of the positive electrode active material from parts filled with a resin (parts which had been pores originally) in the positive electrode plate and then determine the perimeter of all regions (that is, the total length of the interfaces between the parts of the positive electrode active material and the parts filled with a resin) in regions of the parts filled with a resin, and the area of all analyzed regions (that is, regions composed of both of the parts of the positive electrode active material and the parts filled with a resin). The perimeter was divided by the area of the whole analyzed region to obtain a quotient as the interfacial length (μm) per 1 μm^2 of unit cross-sectional area. The result is shown in Table 2.

(5E) Measurement of the Molar Ratio of Metal Elements in the Positive Electrode Plate

[0091] The molar ratio $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ of the Li content in the positive electrode plate prepared in the above (1) to the total content of Ni, Co and Mn was calculated from the measurement result of metal element analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES method). The result is shown in Table 2.

(5F) Identification of the Solid Electrolyte by XRD

[0092] The $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte obtained in the above (3c) was analyzed by X-ray diffraction (XRD), and was identified as $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$.

(5G) Evaluation of the Charge/Discharge (Cycle Retention Rate)

[0093] For the battery prepared in the above (4), the discharge capacity of the battery at an operating temperature of 150° C. was measured in the voltage range of 2.5 V to 1.5 V. The measurement was carried out by carrying out constant current/constant voltage charging until the battery voltage reached the upper limit of the above voltage range and carrying out discharging until the battery voltage reached the lower limit thereof. This test was repeated (cycle test), and the retention rate of the discharge capacity in predetermined cycles ($= 100 \times (\text{a discharge capacity in the predetermined cycles}) / (\text{a first-cycle discharge capacity})$) was calculated. The result is shown in Table 2.

Example 2

[0094] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder B containing the NCM raw material powders 1 and 3 in a blend proportion (in weight ratio) of 90 : 10 indicated in Tables 1A to 1C in place of the mixed powder A in the preparation of the positive electrode plate of the above (1), and 2) altering the firing temperature therein to 950° C.

Example 3

[0095] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using the NCM raw material powder 5 alone indicated in Table 1A to 1C in place of the mixed powder A, and 2) altering the firing temperature therein to 920° C., in the preparation of the positive electrode plate of the above (1). Further, the battery prepared in the present Example was disassembled in a glove box, and observation by an electron microscope and element mapping by an electron probe microanalyzer (EPMA) were carried out on an interface between the positive electrode plate and the solid electrolyte. FIG. 1 shows an electron microscope photograph and EPMA mapping images of a positive electrode active material (NCM)/solid electrolyte cross-section of the all-solid-state battery prepared in present Example. In FIG. 1, the image positioned on the leftmost side is an electron microscope photograph (white portions correspond to NCM, and black portions correspond to solid electrolyte), and rightward therefrom, EPMA mapping images of Mn, Co and Ni are shown in order.

Example 4

[0096] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using the NCM raw material powder 6 alone indicated in Table 1A to 1C in place of the mixed powder A, and 2) altering the firing temperature therein to 920° C., in the preparation of the positive electrode plate of the above (1).

Example 5

[0097] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder C containing the NCM raw material powders 7 and 8 indicated in Table 1A to 1C in a blend proportion (in weight ratio) of 90 : 10 in place of the mixed powder A, and 2) altering the firing temperature therein to 920° C., in the preparation of the positive electrode plate of the above (1).

Example 6

[0098] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder D containing the NCM raw material powders 7 and 8 in a blend proportion (in weight ratio) of 95 : 5 indicated in Tables 1A to 1C in place of the mixed powder A in the preparation of the positive electrode plate of the above (1), and 2) altering the firing temperature therein to 950° C.

Example 7

[0099] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder E containing the NCM raw material powders 7 and 9 in a blend proportion (in weight ratio) of 95 : 5 indicated in Tables 1A to 1C in place of the mixed powder A in the preparation of the positive electrode plate of the above (1), and 2) altering the firing temperature therein to 920° C.

Example 8

[0100] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder F containing the NCM raw material powders 7 and 10 in a blend proportion (in weight ratio) of 95 : 5 indicated in Tables 1A to 1C in place of the mixed powder A in the preparation of the positive electrode plate of the above (1), and 2) altering the firing temperature therein to 920° C. In addition, FIG. 3 shows an electron microscope photograph (reflection electron image) of a cross-section of the positive electrode plate prepared in the present Example.

Example 9

[0101] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder G containing the NCM raw material powders 7 and 11 indicated in Table 1A to 1C in a blend proportion (in weight ratio) of 95 : 5 in place of the mixed powder A, and 2) altering the firing temperature therein to 920° C., in the preparation of the positive electrode plate of the above (1).

Example 10

[0102] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder H containing the NCM raw material powders 7 and 12 indicated in Table 1A to 1C in a blend proportion (in weight ratio) of 95 : 5 in place of the mixed powder A, and 2) altering the firing temperature therein to 920° C., in the preparation of the positive electrode plate of the above (1).

Example 11

[0103] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder I containing the NCM raw material powders 16 and 20 in a blend proportion (in weight ratio) of 90 : 10 indicated in Tables 1A to 1C in place of the mixed powder A in the preparation of the positive electrode plate of the above (1), and 2) altering the firing temperature therein to 920° C.

Example 12

[0104] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder J containing the NCM raw material powders 17 and 21 indicated in Table 1A to 1C in a blend proportion (in weight ratio) of 90 : 10 in place of the mixed powder A, and 2) altering the firing temperature therein to 920° C., in the preparation of the positive electrode plate of the above (1). In addition, FIG. 4 shows an electron microscope photograph (reflection electron image) of a cross-section of the positive electrode plate prepared in the present Example after being embedded in a resin.

Example 13

[0105] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder K contain-

ing the NCM raw material powders 18 and 22 indicated in Table 1A to 1C in a blend proportion (in weight ratio) of 90 : 10 in place of the mixed powder A, and 2) altering the firing temperature therein to 920° C., in the preparation of the positive electrode plate of the above (1).

Example 14 (Comparative)

[0106] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using the NCM raw material powder 4 in Tables 1A to 1C alone in place of the mixed powder A in the preparation of the positive electrode plate of the above (1), and 2) altering the firing temperature therein to 920° C. Further, the battery prepared in the present Example was disassembled in a glove box, and observation by an electron microscope and element mapping by an electron probe microanalyzer (EPMA) was carried out on an interface between the positive electrode plate and the solid electrolyte. FIG. 2 shows an electron microscope photograph and EPMA mapping images of a positive electrode active material (NCM)/solid electrolyte cross-section of the all-solid-state battery prepared in present Example. In FIG. 2, the image positioned on the leftmost side is an electron microscope photograph (white portions correspond to NCM, and black portions correspond to solid electrolyte), and rightward therefrom, EPMA mapping images of Mn, Co and Ni are shown in order.

Example 15 (Comparative)

[0107] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using the NCM raw material powder 14 alone indicated in Table 1A to 1C in place of the mixed powder A, and 2) altering the firing temperature therein to 920° C., in the preparation of the positive electrode plate of the above (1).

Example 16 (Comparative)

[0108] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using the NCM raw material powder 15 alone indicated in Table 1A to 1C in place of the mixed powder A, and 2) altering the firing temperature therein to 890° C., in the preparation of the positive electrode plate of the above (1).

Example 17 (Comparative)

[0109] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder L containing the NCM raw material powders 7 and 13 indicated in Table 1A to 1C in a blend proportion (in weight ratio) of 90 : 10 in place of the mixed powder A, and 2) altering the firing temperature therein to 950° C., in the preparation of the positive electrode plate of the above (1).

Example 18 (Comparative)

[0110] A positive electrode plate and a battery were prepared and various evaluations were carried out, as in Example 1, except for 1) using an NCM mixed powder M containing the NCM raw material powders 7 and 13 indicated in Table 1A to 1C in a blend proportion (in weight ratio) of

95 : 5 in place of the mixed powder A, and 2) altering the firing temperature therein to 950° C., in the preparation of the positive electrode plate of the above (1).

Results

[0111] Table 2 shows the specification of the positive electrode plate prepared in each Example and evaluation results of the cell therein. Then, the charge/discharge characteristic was compared under the same rate and same number of cycles, and the retention rate of the discharge capacity in predetermined cycles ($= 100 \times (\text{a discharge capacity in the predetermined cycles}) / (\text{a first-cycle discharge capacity})$) was calculated. Here, in each Example, the LiOH-Li₂SO₄-based solid electrolyte was analyzed by X-ray diffraction (XRD), and identified to be 3LiOH·Li₂SO₄.

TABLE 1A

Raw material powder	Blend proportion of raw material powders in each mixed powder (% by weight)												
	A	B	C	D	E	F	G	H	I	J	K	L	M
1 NCM523 powder of 8 μm in volume base D50 particle size, obtained by mixing a (Ni _{0.5} Co _{0.2} Mn _{0.3})(OH) ₂ powder and an Li ₂ CO ₃ powder weighed to give a molar ratio of Li/(Ni+Co+Mn) being 1.15, and then firing the mixture at 750° C.	80	90	-	-	-	-	-	-	-	-	-	-	-
2 NCM523-containing powder obtained by adding 2.45% by weight (blend-inclusive) of Li ₃ BO ₃ to the raw material powder 1 and regulating the volume base D50 particle size to 0.4 μm	20	-	-	-	-	-	-	-	-	-	-	-	-
3 NCM523-containing powder obtained by adding 9.2% by weight (blend-inclusive) of Li ₃ BO ₃ to the raw material powder 1 and regulating the volume base D50 particle size to 0.4 μm	-	10	-	-	-	-	-	-	-	-	-	-	-
4 NCM523 powder obtained by regulating the volume base D50 particle size of the raw material powder 1 to 5.5 μm	-	-	-	-	-	-	-	-	-	-	-	-	-
5 NCM523-containing powder obtained by adding 1.0% by weight (blend-inclusive) of Li ₃ PO ₄ to the raw material powder 1 and regulating the volume base D50 particle size to 5.5 μm	-	-	-	-	-	-	-	-	-	-	-	-	-
6 NCM523-containing powder obtained by adding 5.0% by weight (blend-inclusive) of Li ₃ PO ₄ to the raw material powder 1 and regulating the volume base D50 particle size to 5.5 μm	-	-	-	-	-	-	-	-	-	-	-	-	-
7 NCM361 powder of 6.5 μm in volume base D50 particle size, obtained by mixing a (Ni _{0.3} Co _{0.6} Mn _{0.1})(OH) ₂ powder and the Li ₂ CO ₃ powder weighed to give a molar ratio of Li/(Ni+Co+Mn) being 1.15, and then firing the mixture at 850° C.	-	-	90	95	95	95	95	95	-	-	-	90	95
8 NCM361-containing powder obtained by adding 9.2% by weight (blend-inclusive) of Li ₃ BO ₃ to the raw material powder 7 and regulating the volume base D50 particle size to 0.4 μm	-	-	10	5	-	-	-	-	-	-	-	-	-

The “NCM523” means Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O₂, and the “NCM361” means Li(Ni_{0.3}Co_{0.6}Mn_{0.1})O₂.

The “% by weight (blend-inclusive)” means a weight percentage of a powder added when the total amount of a mixture after the addition is taken to be 100% by weight.

TABLE 1B

Raw material powder	Blend proportion of raw material powders in each mixed powder (% by weight)												
	A	B	C	D	E	F	G	H	I	J	K	L	M
9 NCM361-containing powder obtained by adding 16.8% by weight (blend-inclusive) of Li ₃ BO ₃ to the raw material powder 7 and regulating the volume base D50 particle size to 0.4 μm	-	-	-	-	5	-	-	-	-	-	-	-	-
10 NCM361-containing powder obtained by adding 51% by weight (blend-inclusive) of Li ₃ BO ₃ to the raw material powder 7 and regulating the volume base D50 particle size to 0.4 μm	-	-	-	-	-	5	-	-	-	-	-	-	-
11 NCM361-containing powder obtained by adding 16.8% by weight (blend-inclusive) of Li ₂ SO ₄ to the raw material powder 7 and regulating	-	-	-	-	-	-	5	-	-	-	-	-	-

TABLE 1B-continued

Raw material powder	Blend proportion of raw material powders in each mixed powder (% by weight)												
	A	B	C	D	E	F	G	H	I	J	K	L	M
the volume base D50 particle size to 0.4 μm													
12 NCM361-containing powder obtained by adding 51% by weight (blend-inclusive) of Li_2SO_4 to the raw material powder 7 and regulating the volume base D50 particle size to 0.4 μm	-	-	-	-	-	-	-	5	-	-	-	-	-
13 NCM361 powder obtained by regulating the volume base D50 particle size of the raw material powder 7 to 0.4 μm	-	-	-	-	-	-	-	-	-	-	-	10	5
14 NCM361 powder obtained by regulating the volume base D50 particle size of the raw material powder 7 to 4.3 μm	-	-	-	-	-	-	-	-	-	-	-	-	-
15 NCM361 powder obtained by mixing the $(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})(\text{OH})_2$ powder and an Li_2CO_3 powder weighed to give a molar ratio of $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ being 1.15, and then firing the mixture at 950° C., and regulating the volume base D50 particle size to 1.9 μm	-	-	-	-	-	-	-	-	-	-	-	-	-
16 NCM361-containing powder of 7.4 μm in volume base D50 particle size, obtained by adding 0.74% by weight (blend-inclusive) of the Li_3PO_4 powder to the $(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})(\text{OH})_2$ powder and the Li_2CO_3 powder weighed to give a molar ratio of $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ being 1.15, and mixing, and then firing the mixture at 870° C.	-	-	-	-	-	-	-	-	90	-	-	-	-

The “NCM523” means $\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})\text{O}_2$, and the “NCM361” means $\text{Li}(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})\text{O}_2$.

The “% by weight (blend-inclusive)” means a weight percentage of a powder added when the total amount of a mixture after the addition is taken to be 100% by weight.

TABLE 1C

Raw material powder	Blend proportion of raw material powders in each mixed powder (% by weight)												
	A	B	C	D	E	F	G	H	I	J	K	L	M
17 NCM361-containing powder of 7.5 μm in volume base D50 particle size, obtained by adding 1.8% by weight (blend-inclusive) of the Li_3PO_4 powder to the $(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})(\text{OH})_2$ powder and the Li_2CO_3 powder weighed to give a molar ratio of $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ being 1.15, and mixing, and then firing the mixture at 870° C.	-	-	-	-	-	-	-	-	-	90	-	-	-
18 NCM361-containing powder of 7.7 μm in volume base D50 particle size, obtained by adding 3.6% by weight (blend-inclusive) of the Li_3PO_4 powder to the $(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})(\text{OH})_2$ powder and the Li_2CO_3 powder weighed to give a molar ratio of $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ being 1.15, and mixing, and then firing the mixture at 870° C.	-	-	-	-	-	-	-	-	-	-	90	-	-
19 NCM361 powder of 7.0 μm in volume base D50 particle size, obtained by mixing the $(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})(\text{OH})_2$ powder and the Li_2CO_3 powder weighed to give a molar ratio of $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ being 1.15, and then firing the mixture at 750° C.	-	-	-	-	-	-	-	-	-	-	-	-	-
20 NCM361-containing powder obtained by adding 9.2 % by weight (blend-inclusive) of Li_3BO_3 and 1.0% by weight (blend-inclusive) of Li_3PO_4 to the raw material powder 19, and regulating the volume base D50 particle size to 0.5 μm	-	-	-	-	-	-	-	-	10	-	-	-	-
21 NCM361-containing powder obtained by adding 9.2 % by weight (blend-inclusive) of Li_3BO_3 and 2.5% by weight (blend-inclusive) of Li_3PO_4 to the raw material powder 19, and regulating the volume base D50 particle size to 0.5 μm	-	-	-	-	-	-	-	-	-	10	-	-	-
22 NCM361-containing powder obtained by adding 9.2 % by weight (blend-inclusive) of Li_3BO_3 and 5.0% by weight (blend-inclusive) of Li_3PO_4 to the raw material powder 19, and regulating the volume base D50 particle size to 0.5 μm	-	-	-	-	-	-	-	-	-	-	10	-	-

The “NCM523” means $\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})\text{O}_2$, and the “NCM361” means $\text{Li}(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})\text{O}_2$.

The “% by weight (blend-inclusive)” means a weight percentage of a powder added when the total amount of a mixture after the addition is taken to be 100% by weight.

TABLE 2

	Amount of additive added to NCM (% by weight (blend-inclusive))				Degree of orientation (I_{003}/I_{104})	Porosity (%)	Mean pore diameter (μm)	Interfacial length per 1 μm^2 of unit cross-sectional area (μm)	Molar ratio $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$	Plate thickness (μm)	Cycle retention rate (%)
	Li_3BO_3	Li_3PO_4	Li_2SO_4	Total							
Example 1	0.5	-	-	0.5	1.59	30	4.5	0.26	1.03	100	91
Example 2	1.0	-	-	1.0	1.53	32	5.1	0.21	0.99	100	84
Example 3	-	1.0	-	1.0	1.43	28	2.4	0.39	1.00	100	86

TABLE 2-continued

	Amount of additive added to NCM (% by weight (blend-inclusive))				Degree of orientation (I_{1003}/I_{1104})	Porosity (%)	Mean pore diameter (μm)	Interfacial length per 1 μm^2 of unit cross- sectional area (μm)	Molar ratio Li/(Ni+Co +Mn)	Plate thickness (μm)	Cycle retention rate (%)
	Li_3BO_3	Li_3PO_4	Li_2SO_4	Total							
Example 4	-	5.0	-	5.0	1.49	25	2.3	0.35	1.01	100	80
Example 5	1.0	-	-	1.0	1.90	36	3.5	0.37	1.02	80	93
Example 6	0.5	-	-	0.5	1.63	33	5.5	0.27	1.00	80	80
Example 7	1.0	-	-	1.0	1.86	28	4.6	0.26	1.03	80	76
Example 8	5.0	-	-	5.0	1.81	25	4.6	0.23	1.01	80	79
Example 9	-	-	1.0	1.0	1.98	31	4.3	0.31	1.04	80	77
Example 10	-	-	5.0	5.0	1.95	27	4.4	0.29	1.01	80	80
Example 11	1.0	1.0	-	2.0	1.71	33	5.1	0.30	1.02	80	99
Example 12	1.0	2.5	-	3.5	1.72	33	2.9	0.34	1.01	80	89
Example 13	1.0	5.0	-	6.0	1.66	35	5.2	0.30	1.02	80	97
Example 14*	-	-	-	-	1.25	33	2.5	0.42	1.04	100	68
Example 15*	-	-	-	-	2.04	27	1.9	0.66	1.00	80	59
Example 16*	-	-	-	-	178.19	33	1.7	1.14	1.02	80	50
Example 17*	-	-	-	-	2.18	27	3.9	0.33	1.06	80	69
Example 18*	-	-	-	-	1.89	37	3.5	0.42	1.00	80	67

* represents Comparative Example

The “% by weight (blend-inclusive)” means a weight percentage of an additive when the total amount of NCM and the additive is taken to be 100% by weight.

The “amount of an additive added to NCM” refers to an amount of the additive charged in preparation of a sintered plate, but conceivably nearly coincides with the content of the additive in the sintered plate finally obtained.

[0112] From the SEM observation and the element mapping (FIGS. 1 and 2) by EPMA, it could be confirmed that in the NCM (Example 3: see FIG. 1) having the additive (Li_3PO_4) added therein, as compared with the pure NCM (Example 4 (Comparative): see FIG. 2) having no additive such as Li_3PO_4 , the diffusion of the transition metals into solid electrolyte portions in voids of the positive electrode plate was suppressed. From this fact, it is considered that in the positive electrode plates using NCM having Li_3PO_4 added therein (Examples 3, 4 and 11 to 13), the reduction in the Li ionic condition due to the deterioration of the solid electrolyte was alleviated, consequently leading to the improvement in the cycle retention rate. Further, since also in the NCM having Li_3BO_3 or Li_2SO_4 added therein (Examples 1, 2 and 5 to 10), as compared with the pure NCM, the cycle retention rate was improved, it is considered that the addition of Li_3BO_3 or Li_2SO_4 had the same effect as the addition of Li_3PO_4 .

[0113] From FIG. 3 showing a SEM image (reflection electron image) of a cross-section of the positive electrode plate obtained in Example 8, it could be confirmed that another element other than Ni, Co and Mn was present in the NCM bulk. That is, since the element exhibits a darker color than the NCM part in FIG. 3, the element was conceivably an element lighter than Ni, Co and Mn, B (boron). Then, it is considered that the B was present at grain boundaries.

[0114] From FIG. 4 showing a SEM image (reflection electron image) of a cross-section of the positive electrode plate embedded in a resin obtained in Example 12, it could be confirmed that other elements were present so as to cover pore portions of the sintered plate. In the SEM image, regions of three colors could be confirmed and it is considered that portions in the brightest color were NCM; portions in the darkest color were the resin (C: carbon); and portions in neutral colors of these were portions containing other elements present on the surface of NCM. Since the portions in neutral colors exhibited a color darker than NCM and brighter than the resin, it is considered that the portions con-

tained B (boron) and P (phosphorus) contained in the additives. Then, it is considered that the B and the P were deposited on the NCM surface.

[0115] The batteries of Examples 1 to 13 using the positive electrode active materials meeting the requirement of the present invention exhibited significantly higher cycle retention rates than the batteries of Examples 14 to 18 (Comparative) not meeting the requirement of the present invention. It is considered that this was due to that Li_3BO_3 , Li_3PO_4 and/or Li_2SO_4 deposited on a part of the surface of the lithium composite oxide suppressed side reactions between the lithium composite oxide and the solid electrolyte, and Li_3BO_3 , Li_3PO_4 and/or Li_2SO_4 deposited on a part of a grain boundary relaxed stresses of expansion and contraction of the positive electrode active material. It is considered that this alleviated the phenomena such as the reduction of the Li ionic conduction due to the deterioration of the solid electrolyte, the formation of a high resistance layer to become a hindrance to the Li ionic conduction at interfaces between the positive electrode layer and the solid electrolyte, and the increase in the diffusion resistance between the positive electrode active materials, leading to the improvement in the cycle retention rate.

Examples 19 to 33

[0116] Examples to be described below are Examples in respect to all-solid-state secondary batteries whose positive electrode and negative electrode were in a form of a mixture.

Example 19

Preparation of a Positive Electrode Active Material Powder

[0117] A commercially available $(\text{Ni}_{0.3}\text{Co}_{0.6}\text{Mn}_{0.1})(\text{OH})_2$ powder (mean particle size: 9 to 10 μm) and a commercially available Li_2CO_3 powder (mean particle size: 3 μm), which were weighed to give a molar ratio of Li/(Ni+Co+Mn) being 1.07, were mixed, and then held at 950° C. for 10 hours to

obtain an NCM raw material powder 23. 1.0% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_3BO_3) of Li_3BO_3 and 1.0% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_3PO_4) of Li_3PO_4 were added to the NCM raw material powder 23 obtained and mixed, and then held at 950° C. for 10 hours to obtain an NCM powder.

Preparation of a Negative Electrode Active Material Powder

[0118] A commercially available carbon powder (mean particle size: 10 to 14 μm) was prepared.

Preparation of a Solid Electrolyte

(3A) Preparation of a Raw Material Powder

[0119] A Li_2SO_4 powder (commercially available product, purity: 99% or higher), a LiOH powder (commercially available product, purity: 98% or higher) and Li_3BO_3 (commercially available product, purity: 99% or higher) were mixed so that $\text{Li}_2\text{SO}_4 : \text{LiOH} : \text{Li}_3\text{BO}_3 = 1 : 2.2 : 0.05$ (in molar ratio) to obtain a raw material mixed powder. These powders were handled in a glove box in an Ar atmosphere and enough caution was taken so as not to cause deterioration such as moisture absorption.

(3B) Melting Synthesis

[0120] The raw material mixed powder was placed in an Ar atmosphere in a high-purity alumina-made crucible. The crucible was set in an electric furnace, and heat treated at 430° C. for 2 hours in an Ar atmosphere to prepare a melt. Successively, the melt was cooled at 100° C./h in the electric furnace to form a solidified material.

(3C) Milling

[0121] The resulting solidified material was milled in a mortar in a glove box in an Ar atmosphere and further milled using grinding balls to obtain a solid electrolyte powder having a volume base D50 particle size of 1 to 20 μm .

Preparation of an All-Solid-State Battery

(4A) Preparation of a Positive Electrode Mixture Powder and a Negative Electrode Mixture Powder

[0122] The positive electrode active material powder obtained in the above (1), the solid electrolyte powder obtained in the above (3) and an electron conductive auxiliary (acetylene black (commercially available product)) were weighed so as to give a volume ratio of 60 : 40 : 2 in volume ratio, and mixed in a mortar to prepare a positive electrode mixture powder. Similarly, the negative electrode active material powder obtained in the above (2), the solid electrolyte powder obtained in the above (3) and an electron conductive auxiliary (acetylene black (commercially available product)) were weighed so as to give a volume ratio of 60 : 40 : 2, and mixed in a mortar to prepare a negative electrode mixture powder.

(4B) Press Forming

[0123] The corresponding powders were placed and pressed at 100 MPa in a press die of 10 mm in hole diameter so as to form a positive electrode layer, a solid electrolyte

layer and a negative electrode layer in order so the thicknesses as to become 100 μm , 500 μm and 110 μm , respectively. After the three layers were thus laminated, the laminate was pressed at 150 MPa to obtain a press formed body.

(4C) Installation of Pressing Jigs

[0124] The press formed body was sandwiched by a pair of stainless steel plates so as to make a layer structure of stainless steel plate/positive electrode layer/solid electrolyte layer/negative electrode layer/stainless steel plate, and was put in a state that the press formed body together with the stainless steel plates was held at 150 MPa, to obtain an all-solid-state battery as a cell for evaluation.

Evaluations

(5A) Measurement of the Molar Ratio of Metal Elements in the Positive Electrode Layer

[0125] The molar ratio $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ of the Li content in the positive electrode layer prepared in the above (1) to the total content of Ni, Co and Mn therein was calculated from the measurement result of metal element analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES method). The result is shown in Table 3.

(5B) Identification of the Solid Electrolyte by XRD

[0126] The $\text{LiOH-Li}_2\text{SO}_4$ -based solid electrolyte obtained in the above (3c) was analyzed by X-ray diffraction (XRD), and was identified as $3\text{LiOH-Li}_2\text{SO}_4$.

(5C) Evaluation of the Charge/Discharge (Cycle Retention Rate)

[0127] For the battery prepared in the above (4), the discharge capacity of the battery at an operating temperature of 150° C. was measured in the voltage range of 4.15 V to 2.0 V. The measurement was carried out by carrying out constant current/constant voltage charging until the battery voltage reached the upper limit of the above voltage range and carrying out discharging until the battery voltage reached the lower limit thereof. This test was repeated (cycle test), and the retention rate of the discharge capacity in predetermined cycles ($= 100 \times (\text{a discharge capacity in the predetermined cycles}) / (\text{a first-cycle discharge capacity})$) was calculated. The result is shown in Table 3.

(5D) Measurement of the Filling Rate

[0128] The filling rate (% by volume) of the active material of each of the positive electrode and the negative electrode of the all-solid-state battery prepared in the above (4) was measured as follows. First, the all-solid-state battery was cross-sectionally polished by ion milling, and then, the polished cross-section of the positive electrode (or the negative electrode) was observed by a SEM to acquire a cross-sectional SEM image. The SEM image was taken as an image of a magnification of 1,000 times. The acquired image was subjected to a binarization process using image analysis software (manufactured by Media Cybernetics, Inc., Image-Pro Premier). The threshold in the binarization was set by using the Otsu's binarization as a discriminant analysis method. Based on the acquired binarized image, the filling rate F (%) of the positive electrode active material (or the negative electrode active material) of the positive

electrode (or the negative electrode) was calculated by the following expression:

$$\text{Filling rate } F(\%) = [S_A / (S_A + S_B)] \times 100$$

wherein S_A is an area of portions the positive electrode active material (or the negative electrode active material) occupies in the binarized image; and S_B is an area of portions excluding the positive electrode active material (or the negative electrode active material) in the binarized image, and contains the area occupied by the solid electrolyte, the electron conductive auxiliary and voids. The result is shown in Table 3.

Example 20

[0129] A battery was prepared and evaluated as in Example 19, except for preparing a negative electrode active material powder as follows, and measuring the discharge capacity of the battery at an operating temperature of 150° C. in the voltage range of 2.7 V to 1.5 V in the charge/discharge evaluation of the above (5c).

Preparation of a Negative Electrode Active Material Powder

[0130] A commercially available TiO_2 powder (mean particle size: 1 μm or smaller) and a commercially available Li_2CO_3 powder (mean particle size: 3 μm) were mixed so that the molar ratio of Li/Ti became 0.84, and then held at 1,000° C. for 2 hours to obtain a powder composed of LTO particles and having a mean particle size of 3.5 μm .

Example 21

[0131] A battery was prepared and evaluated as in Example 19, except for adding 1.0% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_3BO_3) of Li_3BO_3 and 2.5% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_3PO_4) of Li_3PO_4 to the NCM raw material powder 23 and mixing, and then holding the mixture at 950° C. for 10 hours, in the preparation of the positive electrode active material powder of the above (1), to obtain an NCM powder.

Example 22

[0132] A battery was prepared and evaluated as in Example 19, except for adding 1.0% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_3BO_3) of Li_3BO_3 and 5.0% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_3PO_4) of Li_3PO_4 to the NCM raw material powder 23 and mixing, and then holding the mixture at 950° C. for 10 hours, in the preparation of the positive electrode active material powder of the above (1), to obtain an NCM powder.

Example 23

[0133] A battery was prepared and evaluated as in Example 19, except for adding 1.0% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_3PO_4) of Li_3PO_4 to the NCM raw material powder 23 and mixing, and then holding the mixture at 950° C. for 10 hours, in the preparation of the positive electrode active material powder of the above (1), to obtain an NCM powder.

Example 24

[0134] A battery was prepared and evaluated as in Example 19, except for adding 5.0% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_3PO_4) of Li_3PO_4 to the NCM raw material powder 23 and mixing, and then holding the mixture at 950° C. for 10 hours, in the preparation of the positive electrode active material powder of the above (1), to obtain an NCM powder.

Example 25

[0135] A battery was prepared and evaluated as in Example 19, except for adding 1.0% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_2SO_4) of Li_2SO_4 to the NCM raw material powder 23 and mixing, and then holding the mixture at 950° C. for 10 hours, in the preparation of the positive electrode active material powder of the above (1), to obtain an NCM powder.

Example 26

[0136] A battery was prepared and evaluated as in Example 19, except for adding 5.0% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_2SO_4) of Li_2SO_4 to the NCM raw material powder 23 and mixing, and then holding the mixture at 950° C. for 10 hours, in the preparation of the positive electrode active material powder of the above (1), to obtain an NCM powder.

Example 27

[0137] A battery was prepared and evaluated as in Example 19, except for adding 1.0% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_3BO_3) of Li_3BO_3 to the NCM raw material powder 23 and mixing, and then holding the mixture at 950° C. for 10 hours, in the preparation of the positive electrode active material powder of the above (1), to obtain an NCM powder.

Example 28

[0138] A battery was prepared and evaluated as in Example 19, except for adding 5.0% by weight (with respect to the total amount of the NCM raw material powder 23 and Li_3BO_3) of Li_3BO_3 to the NCM raw material powder 23 and mixing, and then holding the mixture at 950° C. for 10 hours, in the preparation of the positive electrode active material powder of the above (1), to obtain an NCM powder.

Example 29

[0139] A battery was prepared and evaluated as in Example 19, except for preparing a positive electrode active material powder as follows.

(1') Preparation of a Positive Electrode Active Material Powder

[0140] A commercially available $(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})(\text{OH})_2$ powder (mean particle size: 9 μm) and a commercially available Li_2CO_3 powder (mean particle size: 3 μm), which were weighed to give a molar ratio of Li/(Ni+Co+Mn) being 1.05, were mixed, and then held at 920° C. for 10 hours to obtain an NCM raw material powder 24. 1.0% by weight (with respect to the total amount of the NCM raw material powder 24 and Li_3BO_3) of Li_3BO_3 and

1.0% by weight (with respect to the total amount of the NCM raw material powder 24 and Li_3PO_4) of Li_3PO_4 were added to the resulting NCM raw material powder 24 and mixing, and then holding the mixture at 920° C. for 10 hours to obtain an NCM powder.

Example 30

[0141] A battery was prepared and evaluated as in Example 29, except for adding 1.0% by weight (with respect to the total amount of the NCM raw material powder 24 and Li_3PO_4) of Li_3PO_4 to the NCM raw material powder 24 and mixing, and then holding the mixture at 920° C. for 10 hours, in the preparation of the positive electrode active material powder of the above (1'), to obtain an NCM

electrode active material powder), in the preparation of the positive electrode active material powder of the above (1').

Results

[0145] Table 3 shows the specification of the mixture cell prepared in each Example and evaluation results of the cell therein. Then, the charge/discharge characteristic was compared under the same rate and same number of cycles, and the retention rate of the discharge capacity in predetermined cycles ($= 100 \times (\text{a discharge capacity in the predetermined cycles}) / (\text{a first-cycle discharge capacity})$) was calculated and is shown in Table 3. Here, in each Example, the $\text{LiOH} \cdot \text{Li}_2\text{SO}_4$ -based solid electrolyte was analyzed by X-ray diffraction (XRD), and identified to be $3\text{LiOH} \cdot \text{Li}_2\text{SO}_4$.

TABLE 3

	Positive electrode					Negative electrode				
	Amount of additive added to NCM				Molar ratio Li/(Ni+Co +Mn)	Filling rate of active material (% by volume)				Cycle retention rate (%)
	(% by weight (blend-inclusive))									
	Li ₃ BO ₃	Li ₃ PO ₄	Li ₂ SO ₄	Total			Material	Filling rate of active material (% by volume)	Solid electrolyte	
Example 19	1	1	-	2	1.02	61	carbon	60	2.2LHS-0.05LBO	93
Example 20	1	1	-	2	1.02	61	LTO	59	2.2LHS-0.05LBO	90
Example 21	1	2.5	-	3.5	1.01	60	carbon	61	2.2LHS-0.05LBO	85
Example 22	1	5	-	6	1.00	60	carbon	58	2.2LHS-0.05LBO	87
Example 23	-	1	-	1	1.04	59	carbon	60	2.2LHS-0.05LBO	83
Example 24	-	5	-	5	1.02	60	carbon	61	2.2LHS-0.05LBO	80
Example 25	-	-	1	1	1.03	61	carbon	59	2.2LHS-0.05LBO	75
Example 26	-	-	5	5	1.02	60	carbon	61	2.2LHS-0.05LBO	78
Example 27	1	-	-	1	1.03	59	carbon	59	2.2LHS-0.05LBO	74
Example 28	5	-	-	5	1.00	60	carbon	60	2.2LHS-0.05LBO	80
Example 29	1	1	-	2	1.03	60	carbon	60	2.2LHS-0.05LBO	91
Example 30	-	1	-	1	1.04	58	carbon	59	2.2LHS-0.05LBO	81
Example 31*	-	-	-	-	1.04	61	carbon	62	2.2LHS-0.05LBO	71
Example 32*	-	-	-	-	1.04	60	LTO	60	2.2LHS-0.05LBO	64
Example 33*	-	-	-	-	1.02	61	carbon	59	2.2LHS-0.05LBO	69

* represents Comparative Example

The “% by weight (blend-inclusive)” means a weight percentage of an additive when the total amount of NCM and the additive is taken to be 100% by weight. 2.2LHS-0.05LBO: an $\text{LiOH} \cdot \text{Li}_2\text{SO}_4$ -based solid electrolyte (identified to be $3\text{LiOH} \cdot \text{Li}_2\text{SO}_4$ by XRD) synthesized in a blend composition $\text{LiOH} \cdot \text{Li}_2\text{SO}_4 \cdot \text{Li}_3\text{BO}_3 = 2.2:1:0.05$

powder.

Example 31 (Comparative)

[0142] A battery was prepared and evaluated as in Example 19, except for not carrying out the addition of Li_3BO_3 and Li_3PO_4 and the heat treatment thereafter (that is, using the NCM raw material powder 23 as it was as a positive electrode active material powder), in the preparation of the positive electrode active material powder of the above (1).

Example 32 (Comparative)

[0143] A battery was prepared and evaluated as in Example 20, except for not carrying out the addition of Li_3BO_3 and Li_3PO_4 and the heat treatment thereafter (that is, using the NCM raw material powder 23 as it was as a positive electrode active material powder), in the preparation of the positive electrode active material powder of the above (1).

Example 33 (Comparative)

[0144] A battery was prepared and evaluated as in Example 29, except for not carrying out the addition of Li_3BO_3 and Li_3PO_4 and the heat treatment thereafter (that is, using the NCM raw material powder 24 as it was as a positive

[0146] Also in the all-solid-state secondary batteries whose positive electrode and negative electrode were in forms of mixtures, the batteries of Examples 19 to 30 using the positive electrode active materials meeting the requirement of the present invention exhibited significantly higher cycle retention rates than the batteries of Examples 31 to 33 (Comparative) not meeting the requirement of the present invention. It is considered that the improvement in the cycle retention rate may have been achieved thanks to the suppression of side reactions between the lithium composite oxide and the solid electrolyte by Li_3BO_3 , Li_3PO_4 and/or Li_2SO_4 deposited on a part of the surface of the lithium composite oxide, the relaxation of stresses of expansion and contraction of the positive electrode active material by Li_3BO_3 , Li_3PO_4 and/or Li_2SO_4 deposited on a part of a grain boundary, and the like, which were confirmed in the all-solid-state secondary batteries in which the positive electrode and the negative electrode were in forms of the sintered plates, also in the batteries in the mixture forms.

What is claimed is:

1. A positive electrode active material to be used for a lithium ion secondary battery, wherein the positive electrode active material comprises a lithium composite oxide having a layered rock salt

- structure containing Li, Ni, Co and Mn, and further comprises at least one additive selected from Li_3BO_3 , Li_3PO_4 and Li_2SO_4 and wherein a content of the additive is 0.1 to 10% by weight with respect to a total content of the lithium composite oxide and the additive.
2. The positive electrode active material according to claim 1, wherein the additive is present in a state of being deposited on at least a part of a grain boundary and of a surface of the lithium composite oxide.
 3. The positive electrode active material according to claim 1, wherein the positive electrode active material is in a form of a sintered plate.
 4. The positive electrode active material according to claim 3, wherein the sintered plate has a degree of orientation $I_{[003]}/I_{[104]}$ that is defined as a ratio of a diffraction intensity $I_{[003]}$ derived from the (003) plane to a diffraction intensity $I_{[104]}$ derived from the (104) plane in an XRD profile measured by X-ray diffraction (XRD), of 1.2 to 3.6.
 5. The positive electrode active material according to claim 3, wherein the sintered plate has an interfacial length per $1\text{ }\mu\text{m}^2$ of unit cross-sectional area of $0.45\text{ }\mu\text{m}$ or shorter.
 6. The positive electrode active material according to claim 3, wherein the sintered plate has a porosity of 20 to 40%.
 7. The positive electrode active material according to claim 3, wherein the sintered plate has a mean pore diameter of $3.5\text{ }\mu\text{m}$ or larger.
 8. The positive electrode active material according to claim 3, wherein the sintered plate has a thickness of 30 to $300\text{ }\mu\text{m}$.

9. The positive electrode active material according to claim 1, wherein the positive electrode active material is in a form of a powder.
10. The positive electrode active material according to claim 1, wherein a molar ratio of $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ in the positive electrode active material is 0.95 to 1.10.
11. A lithium ion secondary battery, comprising:
 - a positive electrode layer comprising the positive electrode active material according to claim 1;
 - a negative electrode layer comprising a negative electrode active material; and
 - a $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte interposed between the positive electrode layer and the negative electrode layer.
12. The lithium ion secondary battery according to claim 11, wherein the positive electrode active material is in a form of a sintered plate.
13. The lithium ion secondary battery according to claim 11, wherein the positive electrode layer comprises a particle of the positive electrode active material, a particle of the $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte and an electron conductive auxiliary in a form of a mixture.
14. The lithium ion secondary battery according to claim 11, wherein the negative electrode active material is $\text{Li}_4\text{Ti}_5\text{O}_{12}$.
15. The lithium ion secondary battery according to claim 11, wherein the $\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ -based solid electrolyte comprises a solid electrolyte identified to be $3\text{LiOH}\cdot\text{Li}_2\text{SO}_4$ by X-ray diffraction.

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