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N. Lehmann

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(22) Date of application	October 21, 1993	(72) Inventor	Shoichiro YASUNAMI c/o FUJIFILM Corporation 210 Nakanuma, Minamiashigara-shi, Kanagawa- ken

(54) (TITLE OF THE INVENTION) METHOD FOR CHARGING AND DISCHARGING A NON-AQUEOUS SECONDARY BATTERY

(57) (ABSTRACT)

(PROBLEM) Provide a non-aqueous secondary battery having a large discharge capacity, a high discharge operating voltage, and good charge/discharge cycle characteristics, and a method for charging and discharging the same.

(MEANS FOR SOLVING) Non-aqueous secondary battery that adopts a method whereby charging is performed after discharging to 0.5 to 1.5 V during the charge/discharge cycle of a non-aqueous secondary battery in which the negative electrode active material is a lithium-containing transition metal oxide represented by Li_xMO_j (where M represents at least one type of transition metal selected from among Ti, V, Mn, Co, Fe, Ni, Nb, and Mo, x is within the range of 0.17 to 11.25, and j is within the range of 1.6 to 4.1), the positive electrode active material is a lithium-containing transition metal oxide represented by Li_yNO_z (where N represents at least one type of transition metal, and at least one type of these transition metals represents at least one type of transition metal selected from among Co, Mn, Ni, V, and Fe, y is within the range of 0.2 to 1.2, and z is within the range of 1.4 to 3), and the end-of-charge voltage is set to 3.5 to 4.7 V.

(SCOPE OF PATENT CLAIMS)

(CLAIM 1) Method for charging and discharging a non-aqueous secondary battery comprising positive electrode active material, negative electrode active material, and non-aqueous electrolyte containing lithium chloride, wherein said negative electrode active material is a lithium-containing transition metal oxide represented by Li_xMO_j (where M represents at least one type of transition metal selected from among Ti, V, Mn, Co, Fe, Ni, Nb, and Mo, x is within the range of 0.17 to 11.25, and j is within the range of 1.6 to 4.1), and said positive electrode active material is a lithium-containing transition metal oxide represented by Li_yNO_z (where N represents at least one type of transition metal, and at least one type of these transition metals represents at least one type of transition metal selected from among Co, Mn, Ni, V, and Fe, y is within the range of 0.2 to 1.2, and z is within the range of 1.4 to 3), characterized in that the end-of-charge voltage is 3.5 to 4.7 V, and, during the charge/discharge cycle, charging is performed after discharging to 0.5 to 1.5 V.

(CLAIM 2) Method for charging and discharging a non-aqueous secondary battery set forth in claim 1, characterized in that the range for the end-of-discharge voltage that is used is 1.5 V or greater and 3.0 V or less.

(CLAIM 3) Method for charging and discharging a non-aqueous secondary battery set forth in claim 1, characterized in that the range for the end-of-discharge voltage that is used is 0.5 V or greater and less than 1.5 V.

(CLAIM 4) Method for charging and discharging a non-aqueous secondary battery set forth in claim 1, wherein said negative electrode active material is a transition metal oxide wherein the basic structure of the crystal is changed by insertion of lithium ions, and the basic structure of the crystal after this change is not subsequently changed by charging and discharging.

(CLAIM 5) Non-aqueous secondary battery set forth in claim 1, wherein said transition metal oxide prior to insertion of said lithium ions is a transition metal oxide represented by Li_pMO_j (where M represents at least one type of transition metal selected from among Ti, V, Mn, Co, Fe, Ni, Cr, Nb, and Mo, p is within the range of 0 to 3.1, and j is within the range of 1.6 to 4.1).

(CLAIM 6) Non-aqueous secondary battery set forth in claim 1 or 2, wherein said negative electrode material is an oxide of transition metal wherein lithium ions have been electrochemically inserted.

(CLAIM 7) Method for charging and discharging a non-aqueous secondary battery set forth in claim 1, wherein said negative electrode material is obtained by further inserting lithium ions into a lithium-containing transition metal oxide produced by firing.

(CLAIM 8) Method for charging and discharging a non-aqueous secondary battery set forth in claim 1, wherein said negative electrode material is a lithium-containing transition metal oxide represented by $\text{Li}_x\text{M}_q\text{V}_{1-q}\text{O}_j$ (where M represents a transition metal, p is within the range of 0 to 3.1, x is within the range of 0.17 to 11.25, q is within the range of 0 to 0.7, and j is within the range of 1.3 to 4.1).

(CLAIM 9) Method for charging and discharging a non-aqueous secondary battery set forth in claim 1, wherein said positive electrode active material is a lithium-containing transition metal oxide represented by Li_yCoO_2 , Li_yNiO_2 ,

$\text{Li}_y\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, $\text{Li}_y\text{Co}_b\text{V}_{1-b}\text{O}_2$, $\text{Li}_y\text{Co}_b\text{Fe}_{1-b}\text{O}_2$, $\text{Li}_y\text{Mn}_2\text{O}_4$, $\text{Li}_y\text{Mn}_c\text{Co}_{2-c}\text{O}_4$, $\text{Li}_y\text{Mn}_c\text{Ni}_{2-c}\text{O}_4$, $\text{Li}_y\text{Mn}_c\text{V}_{2-c}\text{O}_4$, and $\text{Li}_y\text{Mn}_c\text{Fe}_{2-c}\text{O}_4$ (where y is within the range of 0.5 to 1.2, a is within the range of 0.1 to 0.9, b is within the range of 0.8 to 0.98, c is within the range of 1.6 to 1.96, and z is within the range of 2.01 to 2.3).

(DETAILED DESCRIPTION OF THE INVENTION)

(0001)

(FIELD OF INDUSTRIAL APPLICATION) The present invention relates to a method for charging and discharging a non-aqueous secondary battery with improved charge/discharge cycle characteristics.

(0002)

(PRIOR ART) Lithium metal and lithium alloy are representative examples of materials that can be used as the negative electrode material of a non-aqueous secondary battery lithium. However, a problem with the same is that when these are used, the lithium metal grows dendritically during charging and discharging, which poses the risk of internal shorting as well as posing the risk of fire due to the fact that the dendritic metal itself is highly active. To combat this, fired carbonaceous materials have recently been developed that are able to absorb and release lithium. These carbonaceous materials proffer numerous advantages, including relatively low risk of igniting, high charge/discharge capacity, etc. However, a drawback is that, because the material itself is conductive, overcharging or rapid charging can cause lithium metal to precipitate onto the carbonaceous material, again leading to dendritic metal precipitation. A variety of methods have been adopted to avoid this, including modifying the charger or reducing the amount of positive electrode active material so as to prevent overcharging. However, a problem with the latter method is that limiting the amount of active material, which in turn limiting the discharge capacity. Furthermore, due to the fact that carbonaceous material has a relatively low density, the latter method also winds up having a low discharge capacity per unit volume. Consequently, discharge capacity ends up being limited in two ways: limited amount of active material and low capacity per unit volume.

(0003) In contrast, other than lithium metal, lithium alloy, and carbonaceous material, other types of negative electrode active materials that are known include: TiS_2 and LiTiS_2 , which are able to absorb and release lithium ions (U.S. Patent No. 3,983,476), WO_2 , which has a rutile structure (U.S. Patent No. 4,198,476), spinel compounds such as $\text{Li}_x\text{Fe}(\text{Fe}_2)\text{O}_4$, etc. (JUPAP [Japanese Unexamined Patent Application Publication] No. S58-220362), electrochemically synthesized lithium compounds of Fe_2O_3 (U.S. Patent No. 4,464,447), lithium compounds of Fe_2O_3 (JUPAP H3-112070), Nb_2O_5 (JUPAP No. S62-59412, JUPAP No. H2-82447), iron oxide, FeO , Fe_2O_3 , Fe_3O_4 , cobalt oxide, CoO , Co_2O_3 , and Co_3O_4 (JUPAP No. H3-291863).

(0004) Furthermore, examples of known combinations of positive electrode materials and negative electrode materials that are metal chalcogenides include: TiS_2 and LiTiS_2 (U.S. Patent No. 983,476), chemically synthesized $\text{Li}_{0.1}\text{V}_2\text{O}_5$ and $\text{LiMn}_{1-s}\text{Me}_s\text{O}_2$ ($0.1 < s < 1$, Me = transition metal; JUPAP S63-210028), chemically synthesized $\text{Li}_{0.1}\text{V}_2\text{O}_{0.1}$ and $\text{LiCo}_{1-s}\text{Fe}_s\text{O}_2$ ($s = 0.05$ to 0.3 ; JUPAP S63-211564), chemically synthesized $\text{Li}_{0.1}\text{V}_2\text{O}_5$ and $\text{LiCo}_{1-s}\text{Ni}_s\text{O}_2$ ($s = 0.5$ to 0.9 ; JUPAP H1-294364), V_2O_5 and Nb_2O_5 + lithium metal (JUPAP H2-82447), V_2O_5 or TiS_2 and electrochemically synthesized $\text{Li}_x\text{Fe}_2\text{O}_3$ (U.S. Patent No. 4,464,447; Journal of Power Sources, Vol. 8, p. 289, 1982), $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ for both the positive electrode active material and the negative electrode active material ($0 \leq x < 1$; JUPAP H1-120765; in the specification, the embodiment examples state that the positive electrode active material and the negative electrode active material are the same compound), LiCoO_2 or LiMn_2O_4 and iron oxide, FeO , Fe_2O_3 , Fe_3O_4 , cobalt oxide, CoO , Co_2O_3 , or Co_3O_4 (JUPAP H3-291862), etc.

(0005) Among these, the best candidate in terms of being the aforesaid negative electrode active material that exhibits high safety, high discharge capacity, and high battery voltage (3 V rating) is a non-aqueous secondary battery using lithium-containing transition metal oxide as the negative electrode active material. However, a major hurdle preventing development of this material is the fact that it exhibits poor cycle characteristics, which has led to strong demand for the improvement of its cycle characteristics.

(0006)

(PROBLEM TO BE SOLVED BY THE INVENTION) The objective of the present invention is to provide a non-aqueous secondary battery having a high battery voltage, a high discharge capacity (high energy density), and a long charge/discharge cycle lifespan, and a method for charging and discharging the same.

(0007)

(MEANS FOR SOLVING THE PROBLEM) The aforesaid objective is achieved by charging after discharging to 0.5 to 1.5 V during the charge/discharge cycle of a non-aqueous secondary battery in which the negative electrode active material is a lithium-containing transition metal oxide represented by Li_xMO_j (where M represents at least one type of transition metal selected from among Ti, V, Mn, Co, Fe, Ni, Nb, and Mo, x is within the range of 0.17 to 11.25, and j is within the range of 1.6 to 4.1), the positive electrode active material is a lithium-containing transition metal oxide represented by Li_yNO_z (where N represents at least one type of transition metal, and at least one type of these transition metals represents at least one type of transition metal selected from among Co, Mn, Ni, V, and Fe, y is within the range of 0.2 to 1.2, and z is within the range of 1.4 to 3), and the end-of-charge voltage is set to 3.5 to 4.7 V.

(0008) For the purposes of the present invention, transition metals include element number 21 (Sc) to element number 30 (Zn), element number 39 (Y) to element number 48 (Cd), and element number 57 (La) to element number 80 (Hg).

(0009) The non-aqueous secondary battery of the present invention has a basic structure comprising positive electrode active material, negative electrode active material, and non-aqueous electrolyte containing lithium salt. The aforesaid negative electrode active material can be either a transition metal oxide that may contain lithium or a material obtained by inserting lithium ions into this transition metal oxide, and is preferably obtained by inserting lithium ions into a transition metal oxide containing lithium (preferably by electrochemical insertion).

(0010) The transition metal oxide used in the present invention prior to insertion of lithium ions (referred to hereafter as the negative electrode active material precursor) is preferably synthesized by mixing two or more types of transition metal compounds in the desired ratio, or by mixing a lithium compound and one or more type of transition metal compound in such a way that the molar ratio of lithium compound to total transition metal compound attains no greater than 3.1. However, transition metal refers to a transition metal including at least one type among Ti, V, Mn, Co, Ni, Fe, Cr, Nb, and Mo. Furthermore, the aforesaid negative electrode active material precursor is preferably synthesized by mixing the lithium compound and the transition metal compound in such a way that the molar ratio of lithium compound to total transition metal compound attains 0.2 to 3.1. For the purposes here, transition metal refers to a transition metal including at least one type among Ti, V, Mn, Co, Ni, and Fe.

(0011) At least one type of transition metal oxide serving as a negative electrode active material precursor in the present invention is represented by Li_pMO_j (where M represents at least one type of transition metal, and at least one type of this transition metal is selected from among Ti, V, Mn, Co, Ni, Fe, Cr, Nb, and Mo, p is within the range of 0 to 3.1, and j is within the range of 1.6 to 4.1).

(0012) The aforesaid negative electrode active material precursor is furthermore preferably $\text{Li}_p\text{M}_1\text{q}_1\text{M}_2\text{q}_2 \dots \text{M}_n\text{q}_n\text{O}_j$ (where $\text{M}_1, \text{M}_2, \dots, \text{M}_n$ each represent said transition metal, at least one of which represents Ti, V, Mn, Co, Ni, or Fe, p is within the range of 0 to 3.1, $\text{q}_1 + \text{q}_2 + \dots + \text{q}_n = 1$, n is within the range of 1 to 10, and j is within the range of 1.6 to 4.1). Furthermore, in the aforesaid formula, it is even more preferred that p is within the range of 0.2 to 3.1, n is within the range of 1 to 4, and j is within the range of 1.8 to 4.1. It is particularly preferred, in the aforesaid formula, that p is within the range of 0.2 to 3.1, n is within the range of 1 to 3, and j is within the range of 1.8 to 4.1.

(0013) It is advantageous toward the aim of achieving high discharge capacity for the negative electrode active material precursor of the present invention to include at least one or more types of transition metals in which a valence of 5+ to 6+ is stably present, as described above (for example, V, Cr, Nb, or Mo).

(0014) The aforesaid negative electrode active material precursor containing V, etc. is preferably $\text{Li}p\text{M}q_1\text{M}q_2\text{O}_j$... $\text{Mn}q_n\text{X}q_v\text{O}_j$ (where M is a transition metal, X is V, Cr, Nb, or Mo, p is within the range of 0 to 3.1, $q_1 + q_2 + \dots + q_n + q_v = 1$, n is within the range of 1 to 9, and j is within the range of 1.3 to 4.1). Furthermore, toward the aim of achieving high discharge capacity, it is particularly preferred that these negative electrode active material precursors include at least V. It is even more preferred that the aforesaid negative electrode active material precursor including V is $\text{Li}p\text{M}q_1\text{M}q_2\text{V}_{1-(q_1+q_2)}\text{O}_j$ (where M is a transition metal, p is within the range of 0.2 to 3.1, $q_1 + q_2$ is within the range of 0 to 0.7, and j is within the range of 1.3 to 4.1). It is most preferred that the aforesaid negative electrode active material precursor including V is $\text{Li}p\text{Co}q\text{V}_{1-q}\text{O}_j$, $\text{Li}p\text{Ni}q\text{V}_{1-q}\text{O}_j$ (where p is within the range of 0.3 to 2.2, q is within the range of 0.02 to 0.7, and j is within the range of 1.5 to 2.5).

(0015) $\text{Li}p\text{CoVO}_4$ and $\text{Li}p\text{NiVO}_4$ (where p is within the range of 0.3 to 2.2) can be cited as particularly preferred examples of the negative electrode active material precursor of the present invention. Here, the aforesaid p value is the value prior to starting charging and discharging, which is increased or decreased by charging and discharging. Furthermore, the negative electrode active material consists of this precursor compositional formula with additional lithium content. Because the total transition metal M in the general formulae indicated in the present invention (for example, $\text{Li}p\text{MO}_j$) is set to 1, in the event that a plurality of transition metals should be included, or if using a crystallographic compositional formula, this number can be multiplied by the appropriate integer.

(0016) Specific examples of the most preferred negative electrode active material precursors will be cited below, but the present invention is not limited to these. For example, $\text{LiVO}_{3.1}$, $\text{LiTiO}_{2.3}$, $\text{CoVO}_{3.7}$, LiCoVO_4 , $\text{LiCo}_{0.5}\text{V}_{0.5}\text{O}_{2.1}$, $\text{LiNiVO}_{4.0}$, $\text{Li}_{0.75}\text{Ni}_{0.5}\text{V}_{0.5}\text{O}_{2.1}$, $\text{Li}_{1.75}\text{Ni}_{0.5}\text{V}_{0.5}\text{O}_{2.4}$, $\text{LiTi}_{0.5}\text{V}_{0.5}\text{O}_{2.9}$, $\text{LiMn}_{0.5}\text{V}_{0.5}\text{O}_{2.5}$, $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{O}_{2.1}$, $\text{LiCo}_{0.25}\text{V}_{0.75}\text{O}_{2.8}$, $\text{LiNi}_{0.25}\text{V}_{0.75}\text{O}_{2.8}$, $\text{LiNi}_{0.05}\text{V}_{0.95}\text{O}_{3.1}$, $\text{LiFe}_{0.05}\text{V}_{0.95}\text{O}_{3.1}$, $\text{LiMn}_{0.05}\text{V}_{0.95}\text{O}_{3.0}$, $\text{LiCa}_{0.05}\text{V}_{0.95}\text{O}_{3.2}$, $\text{LiCo}_{0.75}\text{V}_{0.25}\text{O}_{1.9}$, $\text{LiMn}_{0.25}\text{Ti}_{0.5}\text{V}_{0.25}\text{O}_{2.6}$, $\text{LiCr}_{0.05}\text{V}_{0.95}\text{O}_{3.2}$, $\text{LiNb}_{0.05}\text{V}_{0.95}\text{O}_{3.1}$, $\text{LiMo}_{0.05}\text{V}_{0.95}\text{O}_{3.0}$, $\text{Li}_{0.8}\text{Na}_{0.2}\text{Co}_{0.5}\text{V}_{0.5}\text{O}_{2.1}$, $\text{Li}_{0.95}\text{Rb}_{0.05}\text{Ni}_{0.5}\text{V}_{0.5}\text{O}_{2.2}$, $\text{Li}_{0.9}\text{K}_{0.2}\text{Co}_{0.5}\text{V}_{0.5}\text{O}_{2.2}$, $\text{Li}_{0.85}\text{Ba}_{0.15}\text{Ni}_{0.5}\text{V}_{0.5}\text{O}_{2.2}$, $\text{Li}_{0.9}\text{Co}_{0.4}\text{Al}_{0.1}\text{V}_{0.5}\text{O}_{2.1}$, $\text{LiCo}_{0.45}\text{Ga}_{0.05}\text{V}_{0.5}\text{O}_{2.2}$, $\text{Li}_{0.9}\text{Ni}_{0.2}\text{In}_{0.3}\text{V}_{0.5}\text{O}_{2.3}$, $\text{Li}_{1.05}\text{Co}_{0.4}\text{Tl}_{0.1}\text{V}_{0.5}\text{O}_{2.3}$, $\text{Li}_{1.03}\text{Ge}_{0.5}\text{V}_{0.5}\text{O}_{2.3}$, $\text{Li}_{0.98}\text{Co}_{0.25}\text{Pb}_{0.25}\text{V}_{0.5}\text{O}_{2.1}$, $\text{LiCo}_{0.5}\text{Bi}_{0.5}\text{V}_{0.45}\text{O}_{2.1}$, $\text{Li}_{0.96}\text{Ni}_{0.25}\text{Zr}_{0.25}\text{V}_{0.5}\text{O}_{2.2}$, $\text{LiCo}_{0.2}\text{Ni}_{0.3}\text{Ag}_{0.05}\text{V}_{0.45}\text{O}_{2.1}$, $\text{LiCo}_{0.4}\text{Zr}_{0.1}\text{V}_{0.5}\text{O}_{2.0}$, $\text{Li}_{1.01}\text{Co}_{0.4}\text{La}_{0.1}\text{V}_{0.5}\text{O}_{2.1}$,

$\text{LiNi}_{0.2}\text{Cd}_{0.3}\text{V}_{0.5}\text{O}_{2.1}$, $\text{LiCo}_{0.25}\text{Ce}_{0.25}\text{V}_{0.5}\text{O}_{2.2}$, $\text{Li}_{1.03}\text{Co}_{0.2}\text{Sm}_{0.3}\text{V}_{0.5}\text{O}_{2.1}$, $\text{Li}_{0.85}\text{Na}_{0.15}\text{Co}_{0.4}\text{Ge}_{0.2}\text{V}_{0.4}\text{O}_{2.1}$. Note that the stoichiometric coefficient for oxygen is obtained from the weight of the compound prior to firing and the weight of the compound after firing. For this reason, it is necessary to factor in an error of -10 to 10% of the aforesaid value for the stoichiometric coefficient for oxygen in order to account for the precision of the measurement method.

(0017) The negative electrode active material of the present invention comprises the aforesaid negative electrode active material precursor into which lithium ions have been inserted. Accordingly, the transition metal oxide of the aforesaid negative electrode active material precursor that may contain lithium, or Lip, becomes Lix. In short, x is generally within the range of 0.17 to 11.25 (the amount of increase of lithium due to insertion of lithium ions, or x-p, is generally within the range of 0.17 to 8.15). For example, the negative electrode active material used in the present invention, which is obtained by inserting lithium ions into $\text{Li}p\text{MO}_j$, which serves as the aforesaid preferred negative electrode active material precursor, comprises at least one type of lithium-containing transition metal oxide represented by LixMO_j (where M represents at least one type of transition metal and at least one type of transition metal is selected from among Ti, V, Mn, Co, Fe, Ni, Nb, and Mo, p is within the range of 0 to 3.1, x is within the range of 0.17 to 11.25, and j is within the range of 1.6 to 4.1). x is preferably within the range of 0.26 to 10.2, and x is even more preferably within the range of 0.34 to 9.3. The preferred negative electrode active material comprises at least one type of transition metal oxide represented by $\text{LixM}q_1\text{V}_{1-q}\text{O}_j$ (where M represents a transition metal, p is within the range of 0 to 3.1, x is within the range of 0.17 to 8.15, q is within the range of 0 to 0.7, and j is within the range of 1.3 to 4.1). x is preferably within the aforesaid range.

(0018) The negative electrode active material of the present invention is preferably obtained by inserting lithium ions into the transition metal oxide and/or the lithium-containing transition metal oxide serving as the negative electrode active material precursor in the manner described below. For example, the preferred method is to react with lithium metal, lithium alloy, butyl lithium, or the like, or to insert lithium ions electrochemically. In the present invention, it is particularly preferred that lithium ions are inserted electrochemically into the transition metal oxide serving as the negative electrode active material precursor. Among these, the most preferred method is to use a lithium-containing transition metal oxide as the negative electrode active material precursor, and to electrochemically insert lithium ions therein. As a method of electrochemically inserting lithium ions, discharge can be conducted in a redox system (such as an open system (electrolysis) or a closed system (battery)) having the intended lithium-containing transition metal oxide as the positive electrode active material (i.e., the negative electrode active material precursor of the present invention) and a non-aqueous electrolyte containing lithium metal or lithium salt as the negative electrode active material. Preferably, lithium ions

can be inserted by conducting charging in a redox system (such as an open system (electrolysis) or a closed system (battery)) having lithium-containing transition metal oxide as the positive electrode active material and non-aqueous electrolyte containing lithium salt and negative electrode active material precursor with a composition different from that of the positive electrode active material as the negative electrode active material.'

(0019) There is no particular restriction on the amount of lithium ions inserted; however, 27 to 1340 mAh per 1 g of negative electrode active material precursor (equivalent to 1 to 50 mmol) is preferred. 40 to 1070 mAh (equivalent to 1.5 to 40 mmol) is particularly preferred. 54 to 938 mAh (equivalent to 2 to 35 mmol) is most preferred. There is no particular restriction on the ratio of the aforesaid positive electrode active material and negative electrode active material that is used; however, it is preferable to set the ratio such that each has a similar effective equivalent (an effective equivalent refers to an equivalent that is substantively able to maintain cyclability). At this time, it is also preferred to increase the amount of either the positive electrode active material or the negative electrode active material.

(0020) In the present invention, it is preferred that lithium-containing transition metal oxide in which the basic crystal structure of the precursor has been altered is used as the negative electrode active material, and this altered basic structure is not subsequently altered by charging and discharging. In short, it is preferred that the X-ray diffraction pattern of the negative electrode active material precursor of the present invention is altered by the insertion of lithium ions, but that subsequently it does not substantially change even after repeated charging and discharging.

(0021) For the positive electrode active material used in the present invention, any transition metal oxide capable of releasably storing and releasing lithium ions is acceptable, but lithium-containing transition metal oxide is preferred. Examples of preferred lithium-containing transition metal oxide positive electrode active materials include lithium-containing oxides that also contain Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, and/or W. It is preferred that the positive electrode active material and the negative electrode active material have different compositional formulae.

(0022) The lithium-containing transition metal oxide serving as the positive electrode active material of the present invention is preferably synthesized by mixing a lithium compound and one or more types of transition metal compounds in such a way that the molar ratio of lithium compound to total transition metal compound attains 0.3 to 2.2 (where the transition metal is at least one type selected from Ti, V, Cr, Mn, Fe, Co, Ni, Mo, and W). Furthermore, it is preferred that the transition metal is at least one type chosen from among V, Cr, Mn, Fe, Co, and Ni.

(0023) The aforesaid lithium-containing transition metal oxide serving as the positive electrode active material of the present invention can be represented as Li_yNO_z (where M is a transition metal including at least one type selected from among Co, Mn, Ni, V, and Fe, y is within the range of 0.3 to 1.2, and z is within the range of 1.4 to 3).

(0024) Preferred examples of lithium-containing metal oxide positive electrode active materials in the present invention include Li_yCoO_2 , Li_yNiO_2 , $\text{Li}_y\text{CoaNi}_{1-a}\text{O}_2$, $\text{Li}_y\text{CobV}_{1-b}\text{O}_z$, $\text{Li}_y\text{CobFe}_{1-b}\text{O}_2$, $\text{Li}_y\text{Mn}_2\text{O}_4$, $\text{Li}_y\text{MncCo}_2\text{-cO}_4$, $\text{Li}_y\text{MncNi}_2\text{-cO}_4$, $\text{Li}_y\text{MncV}_2\text{-cO}_4$, and $\text{Li}_y\text{MncFe}_2\text{-cO}_4$, as well as a mixture of $\text{Li}_y\text{Mn}_2\text{O}_4$ and MnO_2 , a mixture of $\text{Li}_2\text{yMn}_2\text{O}_3$ and MnO_2 , and a mixture of $\text{Li}_y\text{Mn}_2\text{O}_4$, $\text{Li}_2\text{yMn}_2\text{O}_3$, and MnO_2 (where y is within the range of 0.5 to 1.2, a is within the range of 0.1 to 0.9, b is within the range of 0.8 to 0.98, c is within the range of 1.6 to 1.96, and z is within the range of 2.01 to 5).

(0025) More preferred examples of lithium-containing metal oxide positive electrode active materials in the present invention include Li_yCoO_2 , Li_yNiO_2 , $\text{Li}_y\text{CoaNi}_{1-a}\text{O}_2$, $\text{Li}_y\text{CobV}_{1-b}\text{O}_z$, $\text{Li}_y\text{CobFe}_{1-b}\text{O}_2$, $\text{Li}_y\text{Mn}_2\text{O}_4$, $\text{Li}_y\text{MncCo}_2\text{-cO}_4$, $\text{Li}_y\text{MncNi}_2\text{-cO}_4$, $\text{Li}_y\text{MncV}_2\text{-cO}_4$, and $\text{Li}_y\text{MncFe}_2\text{-cO}_4$ (where y is within the range of 0.7 to 1.04, a is within the range of 0.1 to 0.9, b is within the range of 0.8 to 0.98, c is within the range of 1.6 to 1.96, and z is within the range of 2.01 to 2.3).

(0026) Most preferred examples of the aforesaid lithium-containing transition metal oxides in the present invention include Li_yCoO_2 , Li_yNiO_2 , $\text{Li}_y\text{CoaNi}_{1-a}\text{O}_2$, $\text{Li}_y\text{Mn}_2\text{O}_4$, and $\text{Li}_y\text{CobV}_{1-b}\text{O}_z$ (where y is within the range of 0.7 to 1.1, a is within the range of 0.1 to 0.9, b is within the range of 0.9 to 0.98, and z is within the range of 2.01 to 2.3). Furthermore, it is preferred that y is within the range of 0.7 to 1.04, a is within the range of 0.1 to 0.9, b is within the range of 0.9 to 0.98, and z is within the range of 2.02 to 2.3. Here, the aforesaid y value is the value prior to starting charging and discharging, which is increased or decreased by charging and discharging.

(0027) Particularly preferred examples of compounds used in the present invention will be cited below; however, the present invention is not exclusive thereto. These examples include LiCoO_2 , LiNiO_2 , $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, $\text{LiCo}_{0.95}\text{V}_{0.05}\text{O}_{2.05}$, LiMnO_2 , and LiMn_2O_4 . Although the positive electrode active material oxide used in the present invention may be either crystalline or non-crystalline, a crystalline compound is preferred.

(0028) In the present invention, the aforesaid phrase "the positive electrode active material and the negative electrode active material have different compositional formulae" signifies that:

1. The combination of metal elements differs; and
2. In the case of the example with positive electrode active material $\text{Li}_y\text{CobV}_{1-b}\text{O}_z$ and negative electrode active material $\text{Li}_x\text{CoqV}_{1-q}\text{O}_j$, that y and x, b and q, and z and j do not simultaneously have the same value. In particular, this signifies that b and q as well as z and j do not simultaneously have the same value.

For the positive electrode active material and the negative electrode active material used in the present invention, it is preferred to combine compounds that each have a different standard oxidation-reduction potential.

(0029) The positive electrode active material of the present

invention can be produced by chemically inserting lithium ions into a transition metal oxide, by electrochemically inserting lithium ions into a transition metal oxide, or by mixing a lithium compound with a transition metal compound and then firing.

(0030) When synthesizing the positive electrode active material of the present invention, an example of how to insert lithium ions into a transition metal oxide is to react either lithium metal, a lithium alloy, or butyl lithium with a transition metal oxide. The particularly preferred method of synthesizing the positive electrode active material used in the present invention is by mixing a lithium compound with a transition metal compound and then firing.

(0031) The firing temperature of the negative electrode active material and its precursor in the present invention need merely be high enough to be able to break apart and melt a portion of the mixed compounds used in this invention; for example, 250 to 2000 °C is preferred, and 300 to 1500 °C is particularly preferred. Synthesis may be performed in a stepped pattern of heating and cooling involving two or more steps. There is no particular restriction on the gas atmosphere used during firing in the present invention; however, in the case of the positive electrode active material, firing should preferably be performed either in the air or in a gas significantly comprised of oxygen (for example, roughly 30% or greater). The negative electrode active material and the precursor thereof may be favorably fired in either the air, a gas not significantly comprised of oxygen (for example, roughly 10% or greater), a gas significantly comprised of oxygen (for example, roughly 30% or greater), or an inert gas (nitrogen gas, argon gas). The negative electrode active material used in the present invention and the precursor thereof may be synthesized by firing after simultaneously mixing the starting materials, or may be synthesized by mixing and firing in a stepped pattern involving two or more steps. For example, synthesizing LiCoVO_4 as the negative electrode active material precursor can be done in one step by mixing together the Li compound, Co compound, and V compound serving as the starting compounds and then firing, or can be done by first synthesizing $\text{Co}_2\text{V}_{207}$ by firing the Co compound and the V compound, and then synthesizing the final product by mixing this with the Li compound and firing again.

(0032) The ratio of the positive electrode active material to the negative electrode active material used in the non-aqueous secondary battery of the present invention can be set arbitrarily according to the type of active materials to be combined.

(0033) The non-aqueous secondary battery of the present invention is discharged during the charge/discharge cycle to a battery voltage of 0.5 to 1.5 V. Two examples of methods for accomplishing this are cited below.

(1) With the usable range for discharge end voltage set to 1.5 V or greater and 3.0 V or less, first discharge to 0.5 to 1.5 V prior to charging, and then perform the next cycle of discharging. In this case, discharging may be performed to this voltage every time during the charge/discharge cycle, or discharging may be performed to 0.5 to 1.5 V after repeating several cycles. In the case of the latter, it is preferred to incorporate an operation for discharging to 0.5

to 1.5 V roughly once every 20 cycles in order to account for decrease in battery capacity due to cycling.

(2) Set the usable range for discharge end voltage to 0.5 V or greater and less than 1.5 V. During the aforesaid discharging to 0.5 to 1.5 V, discharging to 0.7 to 1.5 V is preferred, and discharging to 0.8 to 1.4 V is particularly preferred. There is a risk of melting the current collector, etc. if the discharge end voltage is lower than 0.5 V, and cyclability is impaired if the discharge end voltage is greater than 1.5 V, both of which are undesirable.

(0034) To ensure that the battery voltage performs up to its 3 V rating, the charge end voltage is preferably within a range of 3.5 to 4.7 V, even more preferably 3.7 to 4.5 V, and particularly preferably 3.8 to 4.4 V. Battery voltage decreases if this value is less than 3.5 V, and there is risk of breakdown of the positive electrode active material and electrolyte if this value is greater than 4.7 V, both of which are undesirable.

(0035) The negative electrode active material or precursor thereof and the positive electrode active material of the present invention are preferably synthesized by firing a mixture of the following lithium compounds and transition metal compounds. Examples of lithium compounds include oxygen compounds, oxoacid salts, and halides. Examples of transition metal compounds include monovalent to hexavalent transition metal oxides, transition metal salts of the same, and transition metal complex salts of the same.

(0036) Preferred lithium compounds that can be used in the present invention include lithium oxide, lithium hydroxide, lithium carbonate, lithium nitrate, lithium sulfate [sulphate], dilithium sulphite, lithium phosphate, lithium tetraborate, lithium chlorate, lithium perchlorate, lithium thiocyanate, lithium formate, lithium acetate, lithium oxalate, lithium citrate, lithium lactate, lithium tartrate, lithium pyruvate, lithium trifluoromethanesulfonate, *lithium tetraborate* [sic], lithium hexafluorophosphate, lithium fluoride, lithium chloride, lithium bromide, and lithium iodide.

(0037) Preferred examples of transition metal compounds that can be used in the present invention include TiO_2 , lithium titanate, titanyl acetylacetonate, titanium tetrachloride, titanium tetraiodide, ammonium titanyl oxalate, VOd ($d = 2$ to 2.5 ; the compound with $d = 2.5$ is vanadium pentoxide), VOd lithium compounds, vanadium hydroxide, ammonium metavanadate, ammonium orthovanadate, ammonium pyrovanadate, vanadium oxosulfate, vanadium oxytrichloride, vanadium tetrachloride, lithium chromate, ammonium chromate, cobalt chromate, chromium acetylacetonate, MnO_2 , Mn_2O_3 , manganese hydroxide, manganese carbonate, manganese nitrate, manganese sulfate, manganese ammonium sulfate, manganese sulfite, manganese phosphate, manganese borate, manganese chlorate, manganese perchlorate, manganese thiocyanate, manganese formate, manganese acetate, manganese oxalate, manganese citrate, manganese lactate, manganese tartrate, manganese stearate, manganese fluoride, manganese chloride, manganese bromide, manganese iodide, manganese acetylacetonate, iron oxide (divalent, trivalent), ferrosiferic oxide iron oxide black, iron hydroxide (divalent, trivalent), iron chloride (divalent, trivalent), iron bromide (divalent, trivalent), iron iodide (divalent, trivalent), iron sulfate (divalent, trivalent), ammonium iron sulfate (divalent, trivalent), iron nitrate

(divalent, trivalent), iron phosphate (divalent, trivalent), iron perchlorate, iron chlorate, iron acetate (divalent, trivalent), iron citrate (divalent, trivalent), ammonium iron citrate (divalent, trivalent), iron oxalate (divalent, trivalent), and ammonium iron oxalate [ferric ammonium oxalate?] (divalent, trivalent),

(0038) CoO, Co₂O₃, Co₃O₄, LiCoO₂, cobalt carbonate, basic cobalt carbonate, cobalt hydroxide, cobalt sulfate, cobalt nitrate, cobalt sulfite, cobalt perchlorate, cobalt thiocyanate, cobalt oxalate, cobalt acetate, cobalt fluoride, cobalt chloride, cobalt bromide, cobalt iodide, hexaammine cobalt complex salts (salts of sulfuric acid, nitric acid, perchloric acid, thiocyanic acid, oxalic acid, acetic acid, fluorine, chlorine, bromine, iodine), nickel oxide, nickel hydroxide, nickel carbonate, basic nickel carbonate, nickel sulfate, nickel nitrate, nickel fluoride, nickel chloride, nickel bromide, nickel iodide, nickel formate, nickel acetate, nickel acetyl acetonate, copper oxide (monovalent, divalent), copper hydroxide, copper sulfate, copper nitrate, copper phosphate, copper fluoride, copper chloride, copper ammonium chloride, copper bromide, copper iodide, copper formate, copper acetate, copper oxalate, copper citrate, niobium oxychloride, niobium pentachloride, niobium pentafluoride, niobium monoxide, niobium dioxide, niobium trioxide, niobium pentoxide, niobium oxalate, niobium methoxide, niobium ethoxide, niobium propoxide, niobium butoxide, lithium niobate, MoO₃, MoO₂, LiMo₂O₄, molybdenum pentachloride, ammonium molybdate, lithium molybdate, ammonium molybdophosphate, molybdenum oxide acetylacetonate, WO₂, WO₃, tungstic acid, ammonium tungstate, and ammonium tungstophosphate.

(0039) Particularly preferred examples of transition metal compounds that can be used in the present invention include TiO₂, ammonium titanyl oxalate, VOd (d = 2 to 2.5), VOd lithium compounds, ammonium metavanadate, MnO₂, Mn₂O₃, manganese hydroxide, manganese carbonate, manganese nitrate, manganese ammonium sulfate, manganese acetate, manganese oxalate, manganese citrate, iron oxide (divalent, trivalent), triiron tetraoxide, iron hydroxide (divalent, trivalent), iron acetate (divalent, trivalent), iron citrate (divalent, trivalent), ammonium iron citrate (divalent, trivalent), iron oxalate (divalent, trivalent), ammonium iron oxalate (divalent, trivalent), CoO, Co₂O₃, Co₃O₄, LiCoO₂, cobalt carbonate, basic cobalt carbonate, cobalt hydroxide, cobalt oxalate, cobalt acetate, nickel oxide, nickel hydroxide, nickel carbonate, basic nickel carbonate, nickel sulfate, nickel nitrate, nickel acetate, copper oxide (monovalent, divalent), copper hydroxide, copper acetate, copper citrate, MoO₃, MoO₂, LiMo₂O₄, WO₂, and WO₃.

(0040) Particularly preferred combinations of lithium compounds and transition metal compounds that can be used in the present invention include lithium oxide, lithium hydroxide, lithium carbonate, lithium acetate and VOd (d = 2 to 2.5), VOd lithium compounds, ammonium metavanadate, MnO₂, Mn₂O₃, manganese hydroxide, manganese carbonate, manganese nitrate, iron oxide (divalent, trivalent), triiron tetraoxide, iron hydroxide (divalent, trivalent) iron acetate (divalent, trivalent), iron citrate (divalent, trivalent), ammonium iron citrate (divalent, trivalent), iron oxalate (divalent, trivalent), ammonium iron oxalate (divalent, trivalent), CoO, Co₂O₃, Co₃O₄, LiCoO₂, cobalt carbonate, basic cobalt carbonate, cobalt hydroxide, cobalt sulfate, cobalt nitrate, nickel oxide, nickel hydroxide, nickel carbonate, basic nickel carbonate, nickel sulfate, nickel nitrate, nickel acetate, MoO₃, MoO₂, LiMo₂O₄, and WO₃.

(0041) In addition to admixing lithium compounds and transition metal compounds, compounds that enhance ion conductivity such as Ca²⁺ (for example calcium carbonate, calcium chloride, calcium oxide, calcium hydroxide, calcium sulfate, calcium nitrate, calcium acetate, calcium oxalate, calcium citrate, calcium phosphate) or non-crystalline forming agents containing P, B, or Si (for example, P₂O₅, Li₃PO₄, H₃BO₃, SiO₂, etc.) may also be admixed before firing. Furthermore, alkali metal ions such as Na, K, Mg, or the like, and/or compounds containing Sn, Al, Ga, Ge, Ce, In, Bi, etc. (for example, oxides, hydroxides, carbonates, nitrates, etc. of the same) may also be admixed before firing. Among these, it is preferable to admix with calcium carbonate or P₂O₅ before firing. There is no particular restriction on the amount to admix, but 0.2 to 10 mol % is preferred.

(0042) There is no particular restriction on the average particle size of the positive electrode active material, the negative electrode active material, or the precursors thereof used in the present invention, but an average particle size (D50 particle size) of 0.03 to 50 μm is preferred. Any pulverizer or classifier commonly known in the art can be used to achieve a designated particle size. For example, a mortar, ball mill, vibrating ball mill, planetary ball mill, spiral air flow jet mill, or sieve can be used.

(0043) The chemical formula of the compound produced by the aforesaid firing can be calculated using inductively coupled plasma (ICP) emission spectrometry, but a simple method is to calculate the difference in weight between the powder before and after firing.

(0044) The positive electrode active material and negative electrode active material used in the present invention obtained in the manner described above are compounds in which the valence of the transition metal is likely to change as lithium ions are absorbed and released during charging and discharging. Accordingly, the negative electrode active material of the present invention is fundamentally different in concept from metallic negative electrode active materials

made of lithium metal and lithium alloy and the like, in which charging and discharging causes lithium to precipitate and dissolve. Furthermore, even in comparison with carbonaceous compounds, carbon in a compound clearly does not change valence, and its high conductivity facilitates the precipitation of lithium metal during charging. Consequently, the negative electrode active material of the present invention is a negative electrode active material that differs fundamentally in concept from lithium metals and carbonaceous materials.

(0045) Examples of other materials that can be used together with the negative electrode active material of the present invention include lithium metal, lithium alloy (Al, Al-Mn (U.S. Patent No. 4,820,599), Al-Mg (JUPAP S57-98977), and Al-In, Al-Cd (JUPAP H1-144573), as well as fired carbonaceous compounds able to store and release lithium ions or lithium metal (for example, JUPAP S58-209864, JUPAP S61-214417, JUPAP S62-88269, JUPAP S62-216170, JUPAP S63-13282, JUPAP S63-24555, JUPAP S63-121247, JUPAP S63-121257, JUPAP S63-155568, JUPAP S63-276873, JUPAP S63-314821, JUPAP H1-204361, JUPAP H1-221859, JUPAP H1-274360, etc.). The purpose of adding these lithium metals and lithium alloys is to insert lithium ions into the battery, and not to use the dissolution/precipitation reaction of lithium metal, etc. as a battery reaction.

(0046) A conductive agent, a binder, or a filler can be added into the electrode mixture. Any conductive agent may be used as long as it is made of an electron-conducting material that does not cause a chemical reaction in the assembled battery. Typically, it is possible to add either one or a mixture of several conductive materials such as natural graphite (vein graphite, flake graphite, amorphous graphite, etc.), artificial graphite, carbon black, acetylene black, Ketjen black, carbon fiber or metal (copper, nickel, aluminum, silver (JUPAP S63-148554), etc.) powder, metal fiber, or polyphenylene derivatives (JUPAP S59-20971), etc. A mixture of graphite and acetylene black is preferred. There is no particular restriction on the amount added, but 1 to 50 % by weight is preferred, and 2 to 30 % by weight is particularly preferred. In the case of carbon and graphite, 2 to 15 % by weight is particularly preferred.

(0047) In the case of binders, it is possible to use one or a mixture of several binders such as polysaccharides, thermoplastic resins, and rubber elastic polymers. Preferred examples include starch, polyvinyl alcohol, carboxymethyl cellulose, hydroxypropyl cellulose, regenerated cellulose, diacetyl cellulose, polyvinyl chloride, polyvinylpyrrolidone, polytetrafluoroethylene, polyvinylidene fluoride,

polyethylene, polypropylene, ethylene-propylene-diene terpolymer (EPDM), sulfonated EPDM, styrene butadiene rubber, polybutadiene, fluoro rubber, and polyethylene oxide. If using compounds such as polysaccharides containing a functional group that reacts with lithium, the functional group should preferably be inactivated by adding a compound such as an isocyanate group. There is no particular restriction on the amount of binder to add, but 1 to 50 % by weight is preferred, and 2 to 30 % by weight is particularly preferred. Any filler may be added as long as it is made of a fibrous material that does not cause a chemical reaction in the assembled battery. Typically, olefin polymers such as polypropylene or polyethylene, or glass or carbon fibers are used. There is no particular restriction on the amount of filler to add, but 0 to 30 % by weight is preferred.

(0048) The electrolyte typically comprises a solvent and a lithium salt (anion and lithium cation) dissolved in this solvent. Examples of solvents include aprotic organic solvents such as propylene carbonate, ethylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, γ -butyrolactone, methyl formate, methyl acetate, 1,2-dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, dimethyl sulfoxide, 1,3-dioxolane, formamide, dimethylformamide, dioxolane, acetonitrile, nitromethane, ethyl monoglyme, phosphate triester (JUPAP S60-23973), trimethoxymethane (JUPAP S61-4170), dioxolane derivatives (JUPAP S62-15771, JUPAP S62-22372, JUPAP S62-108474), sulfolane (JUPAP S62-31959), 3-methyl-2-oxazolidinone (JUPAP S62-44961), propylene carbonate derivatives (JUPAP S62-290069, JUPAP S62-290071), tetrahydrofuran derivatives (JUPAP S63-32872), ethyl ether (JUPAP S63-62166), 1,3-propane sultone (JUPAP S63-102173), etc., which can be used alone or in combinations of two or more. Examples of lithium salt cations that can be dissolved in these solvents include ClO_4 , BF_4 , PF_6 , CF_3SO_3 , CF_3CO_2 , AsF_6 , SbF_6 , $(\text{CF}_3\text{SO}_2)_2\text{N}$, $\text{B}_{10}\text{C}_{11}\text{O}_{12}^{2-}$ (JUPAP S57-74974), $(1,2\text{-dimethoxyethane})_2\text{ClO}_4^-$ (JUPAP S57-74977), lower fatty-acid carboxylate ions (JUPAP S60-41773), AlCl_4^- , Cl^- , Br^- , I^- (JUPAP S60-247265), anions of chloroborane compounds (JUPAP S61-165957), and tetraphenylborate ions (JUPAP S61-214376). These may be used alone or in combinations of two or more. Among these, the preferred electrolyte is electrolyte containing LiCF_3SO_3 , LiClO_4 ,

LiBF₄ and/or LiPF₆ in a mixture of propylene carbonate or ethylene carbonate and 1,2-dimethoxyethane and/or diethylcarbonate, or electrolyte containing LiCF₃SO₃, LiClO₄, LiBF₄ and/or LiPF₆ in a mixture of ethylene carbonate, diethyl carbonate, and butylene carbonate.

(0049) There is no particular restriction on the amount of these electrolytes added into the battery; the appropriate amount may be chosen based on the amount of the positive electrode active material and negative electrode active material and the size of the battery. There is no particular restriction on the volume ratio of the solvent; however, in the case of a mixture of propylene carbonate or ethylene carbonate to 1,2-dimethoxyethane and/or diethyl carbonate, a ratio of 0.4:0.6 to 0.5:0.4 (mixture ratio when using both 1,2-dimethoxyethane and diethyl carbonate is 0.4:0.6 to 0.6:0.4) is preferred. There is no particular restriction on the concentration of the supporting electrolyte; however, 0.2 to 3 mol per 1 liter of electrolyte is preferred.

(0050) Apart from an electrolyte solution, it is also possible to use solid electrolytes such as the following. Solid electrolytes are classified as either inorganic solid electrolytes or organic solid electrolytes. Some examples of well-known inorganic solid electrolytes include Li nitrides, halides, oxoacid salts, etc. Among these, Li₃N, LiI, Li₅Ni₂, Li₃N-LiI-LiOH, LiSiO₄, LiSiO₄-LiI-LiOH (JUPAP S49-81899), xLi₃PO₄-(1-x)Li₄SiO₄ (JUPAP S59-60866), Li₂SiS₃ (JUPAP S60-501731), phosphorus sulfide (JUPAP S62-82665), etc. are effective.

(0051) Among organic solid electrolytes, polyethylene oxide derivatives or polymers containing said derivatives (JUPAP S63-135447), polypropylene oxide derivatives or polymers containing said derivatives and polymers containing ion-dissociable groups (JUPAP S62-254302, JUPAP S62-254303, JUPAP S63-193954), a mixture of polymers containing ion-dissociable groups and the aforesaid aprotic electrolyte solution (U.S. Patent No. 4,792,504, U.S. Patent No. 4,830,939, JUPAP S62-22375, JUPAP S62-22376, JUPAP S63-22375, JUPAP S63-22776, JUPAP H1-95117), phosphate ester polymers (JUPAP S61-256573), and polymer matrix materials containing aprotic polar solvent (U.S. Patent No. 4,822,70, U.S. Patent No. 4,830,939, JUPAP S63-239779, Japanese Patent Application Publication H2-30318, JPAP H2-78531) are effective. Another method is to add polyacrylonitrile to the electrolyte solution (JUPAP S62-278774). Another known method is to combine inorganic and organic solid electrolytes (JUPAP S60-1768).

(0052) As a separator, any insulating thin film having a

high ionic permeability and designated mechanical strength can be used. Sheets or nonwoven fabric made of olefin-based polymers such as polyolefin or the like, or glass fiber, or polyethylene or the like, can be used due to their organic solvent resistance and hydrophobicity. The pore size of the separator can be set according to the pore sizes that are commonly used for batteries. For example, a pore size of 0.01 to 10 μm can be used. The thickness of the separator can be set according to the thicknesses that are commonly used for batteries. For example, a thickness of 5 to 300 μm can be used.

(0053) Other compounds may be added into the electrolyte for the purpose of improving the discharging or charging characteristics. For example, it is possible to add pyridine (JUPAP S49-108525), triethyl phosphite (JUPAP S47-4376), triethanolamine (JUPAP S52-72425), cyclic ether (JUPAP S57-152684), ethylene diamine (JUPAP S58-87777), n-glyme (JUPAP S58-87778), hexaphosphate triamide (JUPAP S58-87779), nitrobenzene derivatives (JUPAP S58-214281), sulfur (JUPAP S59-8280), quinoneimine dye (JUPAP S59-68184), N-substituted oxazolidinone and N,N'-substituted imidalidinone (JUPAP S59-154778), ethylene glycol dialkyl ether (JUPAP S59-205167), quaternary ammonium salt (JUPAP S60-30065), polyethylene glycol (JUPAP S60-41773), pyrrole (JUPAP S60-79677), 2-methoxyethanol (JUPAP S60-89075), AlCl₃ (JUPAP S61-88466), monomer of conductive polymer electrode active material (JUPAP S61-161673), triethylene phosphoramidate (JUPAP S61-208758), trialkyl phosphine (JUPAP S62-80976), morpholine (JUPAP S62-80977), aryl compounds with a carbonyl group (JUPAP S62-86673), crown ethers such as 12-crown-4 (Physical Review B, vol. 42, p. 6424 (1990)), hexamethylphosphoric triamide and 4-alkyl morpholine (JUPAP S62-217575), bicyclic tertiary amine (JUPAP S62-217578), oils (JUPAP S62-287580), quaternary phosphonium salt (JUPAP S63-121268), tertiary sulfonium salt (JUPAP S63-121269), etc.

(0054) Halosolvents such as carbon tetrachloride or chlorotrifluoroethylene may be added into the electrolyte solution in order to make the electrolyte solution non-flammable (JUPAP S48-36,632). Carbon gas may be added into the electrolyte solution in order to impart suitability for

hot holding (JUPAP S59-134567).

(0055) Electrolyte solution or solid electrolyte may also be added into the mixture for the positive electrode or the negative electrode. For example, this can be done by adding the aforesaid ion-conductive polymer or nitromethane (JUPAP S48-36633) or electrolyte solution (JUPAP S57-124870).

(0056) The surface of the positive electrode active material may be improved. For example, this can be done by processing the surface of a metal oxide with esterifying agent (JUPAP S55-163779), or by processing with chelating agent (JUPAP S55-163780), or by processing with conductive polymer (JUPAP S58-163188, JUPAP S59-14274), polyethylene oxide (JUPAP S60-97561), etc. Similarly, the surface of the negative electrode active material can also be improved. For example, this can be done by providing an ion-conductive polymer or polyacetylene layer (JUPAP S58-111276) or by processing with LiCl (JUPAP S58-142771), etc.

(0057) The current collector used for the electrode active material can be any electron conductor that does not undergo chemical changes in the assembled battery. For example, as the material for the positive electrode, it is possible to use stainless steel, nickel, aluminum, titanium, baked carbon, etc., as well as aluminum or stainless steel whose surface has been coated with carbon, nickel, titanium, or silver, and as the material for the negative electrode, it is possible to use stainless steel, nickel, copper, titanium, aluminum, baked carbon, etc., as well as steel or stainless steel whose surface has been coated with carbon, nickel, titanium, or silver, as well as Al-Cd alloy, etc. These materials may also be used after oxidizing their surface. Any of various shapes may be used, including foil, film, sheet, net, punched, lathed, porous, foamed, fibrous compact, etc. There is no particular restriction on the thickness, but a thickness of 1 to 500 μm can be used.

(0058) The battery may be given any of various shapes including coin, button, sheet, cylinder, cube, etc. If the battery has a coin or button shape, the mixtures for the positive electrode active material and the negative electrode active material will primarily be used compressed into pellet form. The thickness and diameter of this pellet will be determined by the size of the battery. If the battery has a sheet, cylinder, or cube shape, the mixture for the positive electrode active material and the negative electrode active material will be primarily be used by being coated onto the current collector, dried, and compressed. Any commonly used coating method may be used. Examples of such methods include reverse rolling, direct rolling, blade coating, knife coating, extrusion coating, curtain coating, gravure coating, bar coating, dip coating, and squeeze coating. Blade, knife, and extrusion coating are preferred. Coating is preferably performed at a speed of 0.1 to 100 m/min. Good quality can be achieved in the surface of the coat by selecting one of the aforesaid coating methods according to the solution properties and dryness of the mixture. The thickness, length, and width of the coating

layer will be determined by the size of the battery, but it is particularly preferable for the thickness of the coating layer to be 1 to 2000 μm after drying and compression.

(0059) Any commonly used method of drying or dehydrating a pellet or sheet may be used. Notably, it is preferred to use hot air, vacuum, infrared, far infrared, electron beam, or low-temperature air, either singly or in combination. The temperature is preferably in the range of 80 to 350 $^{\circ}\text{C}$, particularly preferably within the range of 100 to 250 $^{\circ}\text{C}$. Overall battery moisture content is preferably no greater than 2000 ppm, and it is preferred from the perspective of cyclability that the positive electrode mixture, the negative electrode mixture, and the electrolyte each have a moisture content of no greater than 500 ppm. Any pressing method that is commonly used can be used to press the pellet or sheet, with die pressing and calendar pressing being particularly preferred. There is no particular restriction on the pressing pressure, but 0.2 to 3 t/cm^2 is preferred. In the case of calendar pressing, a pressing speed of 0.1 to 50 m/min is preferred. A pressing temperature of room temperature to 200 $^{\circ}\text{C}$ is preferred.

(0060) A battery canister is formed by inserting said mixture sheet into a canister by rolling or folding, establishing an electrical connection between the canister and the sheet, injecting electrolyte solution, and closing with a sealing plate. At this time, a safety valve can be used as the sealing plate. Apart from a safety valve, any of various previously known safety elements may be provided. For example, a fuse, bimetal, PTC element, or the like may be used as an overcurrent protector element. Methods other than a safety valve can also be adopted to address increased pressure in the battery canister, such as cutting a notch in the battery canister, allowing the gasket to crack, or allowing the sealing plate to crack. The charger can furthermore be furnished with a circuit equipped with over-charging or over-discharging countermeasures. Electrically conductive metal or alloy can be used for the canister and lead plate. For example, metals such as iron, nickel, titanium, chrome, molybdenum, copper, aluminum, etc., or alloys of the same, can be used. Any known method of welding the cap, canister, sheet, and lead plate can be used (for example, DC or AC electrical welding, laser welding, ultrasonic welding). Any previously known compound or mixture, such as asphalt or the like, can be used as sealant for the seal.

(0061)

(EMBODIMENT EXAMPLES) The present invention will be described in greater detail below with reference to concrete examples. However, as long as the spirit of the invention is not exceeded, the present invention is not restricted to these embodiment examples.

(0062) Embodiment example 1

The lithium-containing transition metal oxide negative electrode active materials (a) through (c) were synthesized according to the following materials and firing conditions.

(a) Li_2CO_3 , CoO , and V_2O_5 were mixed together and then fired in the air for 18 hours at 750 $^{\circ}\text{C}$.

(b) CoO and V_2O_5 were mixed together and then fired in the air for 12 hours at 800 $^{\circ}\text{C}$, after which Li_2CO_3 and V_2O_5 were then further added to and mixed into this fired product before being fired in the air for 10 hours at 650 $^{\circ}\text{C}$.

(c) Li_2CO_3 , NH_4VO_3 , and $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ were mixed together and fired in the air for 6 hours at 800 °C.

(0063) 86 parts by weight of the aforesaid negative electrode active material, 3 parts by weight of acetylene black as conductive agent, and 6 parts by weight of graphite were mixed in those proportions, after which 4 parts by weight of styrene-butadiene copolymer (weight ratio = 1:1) and 1 part by weight of carboxymethyl cellulose were added thereto, and kneaded with water as the medium, yielding a slurry. Said slurry was applied to both sides of a copper foil measuring 18 μm in thickness using a doctor blade coater, and then, after drying, compression molded in a calendar press machine to create band-shaped negative electrode sheets (3). The thickness of the negative electrode sheet after compression molding was 124 μm .

(0064) 87 parts by weight of LiCoO_2 as positive electrode active material and 9 parts by weight of graphite as conductive agent were mixed together in those proportions, after which 3 parts by weight of polytetrafluoroethylene as binder and 1 part by weight of sodium polyacrylate were added, and then kneaded with water as a medium, yielding a slurry that was then applied to both sides of a 20 μm thick aluminum foil (support) current collector. After drying said coating, it was compression-molded in a calendar press to create band-shaped positive electrode sheets (5) (220 μm). After spot-welding a lead plate to the ends of each of the aforesaid negative electrode sheets (3) and positive electrode sheets (5), heat treatment was performed for 2 hours at 200 °C in dry air at a temperature of no greater than dew point – 40 °C. Next, the heat-treated positive electrode sheets (5), separators made of microporous polypropylene film (Celgard 2400) (4), heat-treated

negative electrode sheets (3), and separators (4) were laminated in that sequence, and the result was rolled into a roll shape.

(0065) These rolls were then housed in closed-end cylindrical canisters made of nickel-plated steel (2), which simultaneously served as the negative electrode terminal. Next, 1 mol/liter LiPF_6 (isovolume mixture of ethylene carbonate, butylene carbonate, and diethyl carbonate) was injected into the battery canisters as electrolyte solution. Battery covers with a positive terminal electrode (8) were then crimped with a gasket (1), yielding cylindrical batteries. Note that the positive electrode terminals (8) and the positive electrode sheets (5), and the battery canisters (2) and the negative electrode sheets (3) were connected in advance by way of a lead terminal. A cross-section of the cylindrical battery is shown in FIG. 1. Note that 7 is a safety valve.

(0066) The resultant batteries were then subjected to a charge/discharge cycle test at a charging end voltage of 3.9 to 4.3 V and a discharging end voltage of 1.8 V with a current density of 2 mA/cm^2 . The number of cycles required to attain 60% of the initial discharge capacity was deemed the charge/discharge cycle lifespan. For embodiment example 1 of the present invention, prior to charging, discharging was first performed to 0.5 to 1.5 V, after which charging was performed. In the comparative examples, discharging was either not performed prior to charging, or discharging was performed to a discharging end voltage either less than 0.5 V or greater than 1.5 V. The results are shown in TABLE 1.

(0067)

(TABLE 1)

TABLE 1

No.		Negative electrode active material	Charging end voltage	Discharging end voltage prior to charging	Energy density after discharge to 1.8 V	Cyclability (cycles)
1	Present invention	a	4.3 V	1.0 V	2450 mWH	220
2	"	a	4.2	1.0	2310	255
3	"	a	4.1	0.8	2250	200
4	"	a	4.0	0.6	2120	280
5	"	a	"	1.0	"	290
5	"	a	"	1.3	"	285
6	"	a	"	1.5	"	195
7	"	a	3.9	0.9	1990	305
8	"	b	4.2	1.0	2290	260
9	"	b	4.0	1.0	2030	275
10	"	c	4.2	1.0	2210	190
11	"	c	4.0	1.0	1950	245
a	Comparative ex.	a	4.0 V	1.8 V	2120 mWH	120
b	"	b	"	1.8	2030	95
c	"	c	"	1.8	1950	115
d	"	a	"	1.6	2120	140
e	"	a	4.1	0.4	2250	120

(0068) Embodiment example 2

Cylindrical batteries were prepared in exactly the same manner as embodiment example 1. The resultant batteries were then subjected to a charge/discharge cycle test at

a charging end voltage of 3.9 to 4.3 V and a discharging end voltage of 0.5 to 1.5 V with a current density of 2 mA/cm². The results are shown in TABLE 2.

(0069)

(TABLE 2)

TABLE 2

No.		Negative electrode active material	Charging end voltage (V)	Discharging end voltage (V)	Energy density after discharge to 1.8 V	Cyclability (cycles)
1	Present invention	a	4.3	1.2	2300 mWH	225
2	"	a	4.2	1.0	2320	250
3	"	a	4.1	1.0	2200	235
4	"	a	4.1	0.6	2200	220
5	"	a	4.0	0.6	2140	265
6	"	a	"	1.0	"	310
7	"	a	"	1.5	"	205
8	"	a	3.9	1.0	1975	325
9	"	b	4.2	0.9	2265	240
10	"	b	4.0	1.1	2030	295
11	"	c	4.2	1.0	2210	195
12	"	c	4.0	1.1	2120	230
a	Comparative ex.	a	4.0	1.8	2140 mWH	105
b	"	b	"	1.7	"	120
c	"	c	"	1.6	"	130
d	"	a	"	0.4	"	115
e	"	a	4.3	1.9	2300	90

(0070) Embodiment example 3

As shown in TABLE 3, cylindrical batteries were produced in exactly the same way as embodiment example 1, with the sole exception that, instead of using LiCoO_2 for the positive electrode active material, (d) LiNiO_2 , (e) $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, (f)

$\text{LiCo}_{0.95}\text{V}_{0.05}\text{O}_{2.05}$, and (g) LiMn_2O_4 were used, respectively. The resultant batteries were then subjected to the same charge/discharge cycle test as embodiment example 1. The results are shown in TABLE 3.

(0071)

(TABLE 3)

TABLE 3

No.		Negative electrode active material	Positive electrode active material	Charging end voltage	Discharging end voltage prior to charging	Energy density after discharge to 1.8 V	Cyclability (cycles)
1	Present invention	a	d	4.2 V	1.0 V	2400 mWH	225
2	"	a	d	4.0	1.3	2150	280
3	"	a	e	4.1	0.9	2020	270
4	"	a	e	3.9	0.6	1850	205
5	"	a	f	4.3	1.5	2320	230
6	"	a	f	4.0	1.1	2050	260
7	"	a	g	4.2	1.0	2100	250
8	"	a	g	4.0	1.4	1900	210
9	"	b	d	4.2	0.8	2350	245
10	"	b	e	4.0	1.1	2100	285
11	"	c	f	4.0	1.2	2000	290
12	"	c	g	3.9	1.0	1950	305
a	Comparative ex.	a	d	4.0 V	1.8 V	2150 mWH	115
b	"	a	e	4.1	1.8	2020	100
c	"	a	f	4.0	1.7	2050	125
d	"	a	g	4.2	0.4	2100	120
e	"	b	d	4.2	1.8	2350	95
f	"	b	e	4.0	1.7	2100	135
g	"	c	f	4.0	1.8	2000	120
h	"	c	g	3.9	0.4	1950	140

(0072) Comparing the present invention with the comparative examples in embodiment example 1 through embodiment example 3 clearly indicates that the battery of the present invention, in which charging is only performed after first having discharged to 0.5 to 1.5 V during the charge/discharge cycle, has a longer charge/discharge cycle lifespan than the comparative examples.

(0073)

(EFFECT OF THE PRESENT INVENTION) Because charging is performed after discharging to 0.5 to 1.5 V during the charge/discharge cycle of a non-aqueous secondary battery in which the negative electrode active material is a lithium-containing transition metal oxide represented by Li_xMO_j (where M represents at least one type of transition metal selected from among Ti, V, Mn, Co, Fe, Ni, Nb, and Mo, x is within the range of 0.17 to 11.25, and j is within the range of 1.6 to 4.1), the positive electrode active material is a lithium-containing transition metal oxide represented by Li_yNO_z (where N represents at least one type of transition metal, and at least one type of these transition metals represents at least one type of transition metal selected from among Co, Mn, Ni, V, and Fe, y is within the range of 0.2 to 1.2, and z is within the range of 1.4 to 3), and the

end-of-charge voltage is set to 3.5 to 4.7 V, it is possible to obtain a non-aqueous secondary battery with greater charging capacity and longer charge/discharge cycle lifespan.

(BRIEF DESCRIPTION OF THE DRAWINGS)

(FIG. 1) Cross-section of the cylindrical battery used in the embodiment examples.

(DESCRIPTION OF THE SYMBOLS)

- 1 Polypropylene insulated sealant
- 2 Negative electrode canister also serving as negative electrode terminal (battery canister)
- 3 Negative electrode sheet
- 4 Separator
- 5 Positive electrode sheet
- 6 Liquid non-aqueous electrolyte solution
- 7 Valve made of pliable thin plate
- 8 Positive electrode cap also serving as positive electrode terminal
- 9 PTC element
- 10 Sealing plate
- 11 Ring

(FIG. 1)

