

METHOD FOR PRODUCING REGENERATED POSITIVE ELECTRODE MATERIAL PRECURSOR AND REGENERATED POSITIVE ELECTRODE MATERIAL, AND METHOD FOR USING REGENERATED POSITIVE ELECTRODE MATERIAL

Technical Field

[0001] The present disclosure relates to a method for producing a regenerated positive electrode material precursor and a regenerated positive electrode material from recovered material recovered from a lithium-ion secondary cell as an object to be processed, and also relates to a method for using the regenerated positive electrode material.

Background Art

[0002] Lithium-ion secondary cells have rapidly expanded in applications from the electronics field to the automotive field. In particular, in the automotive field, demand for large-sized cells is expected to rapidly increase due to increased capacity of units for hybrid vehicle applications and electric vehicle applications such as plug-in hybrid electric vehicles (PHEVs) and battery electric vehicles (BEVs). The rapid increase in demand for large-sized cells is also attributable to strong demands for reduction of CO₂ emissions in the transportation industry. With the expansion in demand for lithium-ion secondary cells, the amount of lithium-ion secondary cells that have reached the end of product life will also increase. Hereinafter, lithium-ion secondary cells may also be referred to as “LIBs”.

[0003] Since LIBs use expensive metal materials for positive electrode materials thereof, recycling metal materials from LIBs that have reached the end of product life is an industrially important issue.

[0004] For example, in Patent Document 1, impurities are removed from waste cells, waste positive electrode materials, or a mixture thereof containing a metal group consisting of at least two selected from Co, Ni, and Mn, and impurities, and the metal group is recovered as a mixture of the metal salts. Patent Document 1 proposes producing a positive electrode material using the recovered mixture of the metal salts.

[0005] Further, for example, Patent Document 2 filed by the present applicants discloses a regenerated positive electrode material containing at least one of a predetermined amount of iron, copper, and aluminum.

Citation List

Patent Document

[0006] Patent Document

[Patent Document 1] Japanese Patent No.5847742

[Patent Document 2] Japanese Patent No.7176707

Summary of Invention

Technical Problem

[0007] In order to recycle metal materials from waste LIBs that have reached the end of product life, it is needed to reduce environmental burdens associated with recycling and to reduce recycling costs. However, for example, the method described in Patent Document 1 uses a complicated separation process and a large amount of expensive extractants, and thus there is concern that environmental burdens associated with recycling may be large and costs may increase.

[0008] As an example, LIB cells for in-vehicle use such as PHEVs and BEVs need a robust package that can withstand strong mechanical impacts, intrusion of all kinds of liquids, fire, and high temperatures. The LIB laminate in an LIB cell is usually disassembled into internal components (a positive electrode, a negative electrode, and a separator) and an outer cover. The method described in Patent Document 1 needs disassembling the cell described above. Therefore, the method described in Patent Document 1 needs safety measures. Further, a robust package of the LIB laminate complicates the process of mechanically taking out the positive electrode active material from the cell described above. This becomes a more pronounced issue as the demand for large-sized cells rapidly increases and the processing amount of waste LIBs increases, as described above.

[0009] In contrast to the method described in Patent Document 1, which needs disassembling LIB cells needing safety measures, in the method described in Patent Document 2, heat treatment is performed on each waste LIB cell in order to automatically and safely take out a positive electrode active material from the waste LIB cell in a time-efficient manner. By this heat treatment, the LIB laminate in the cell is rendered harmless both electrically and chemically, and risks can be significantly reduced.

[0010] By employing this approach, a positive electrode active material can be extracted from the LIB laminate in a time-efficient and safe manner without complicated mechanical disassembly, using an electrically and chemically harmless method.

[0011] Further, it is suggested that the regenerated positive electrode material described in Patent Document 2, which contains at least one of a predetermined amount of aluminum, copper, or iron, maintains high energy density and high output density even after charge-discharge cycling. Thus, this regenerated positive electrode material has sufficient added value in terms of battery performance in regenerated LIBs. Meanwhile, as a result of studies conducted by the present inventors, it has been found that, depending on, e.g., the content of waste LIBs to be recycled and used, characteristics of a battery using the regenerated positive electrode material may be improved by using a regenerated positive electrode material having lower content of aluminum, copper, and iron.

[0012] The present disclosure has been made under the circumstances described above. A problem to be solved by the present disclosure relates to a method for producing a regenerated positive electrode material precursor having low content of aluminum, copper, and iron from LIBs as objects to be processed with low environmental burdens, low recycling costs, and high safety, a method for producing a regenerated positive electrode material from the regenerated positive

electrode material precursor, and a method for using the regenerated positive electrode material including assembling an LIB using the regenerated positive electrode material and performing an activation step of charging and discharging.

Solution to Problem

[0013] A first disclosure for solving the problems described above is a method for producing a regenerated positive electrode material precursor from a lithium-ion secondary cell as an object to be processed, the method including:

- heating the lithium-ion secondary cell as the object to be processed to obtain heat-treated material;

- crushing the heat-treated material to obtain crushed material;

- classifying and sorting the crushed material to obtain fine-grained products;

- subjecting the fine-grained products to acid leaching to obtain acid leachate;

- performing iron removal by adding an oxidation agent and alkali to the acid leachate to obtain an iron-removed liquid; performing ion exchange by bringing the iron-removed liquid into contact with a chelate resin to obtain an ion-exchanged liquid;

- adding alkali to the ion-exchanged liquid to generate a precipitate;

- and washing the precipitate with water to obtain a regenerated positive electrode material precursor.

A second disclosure is the method for producing a regenerated positive electrode material precursor according to the first disclosure, the method further including, after the classifying and sorting of the crushed material, subjecting the fine-grained products to magnetic separation to obtain a magnetically-attracted object.

A third disclosure is the method for producing a regenerated positive electrode material precursor according to the first disclosure, wherein sulfuric acid is used for the acid leaching.

A fourth disclosure is the method for producing a regenerated positive electrode material precursor according to the first disclosure, wherein, in the iron removal, a hydrogen peroxide aqueous solution is used as the oxidation agent, and oxidation reduction potential of the acid leachate is adjusted to 500-750 mV (Ag/AgCl).

A fifth disclosure is the method for producing a regenerated positive electrode material precursor according to the first disclosure, wherein, in the ion exchange, an aminomethyl phosphate-based chelate resin is used as the chelate resin to remove aluminum ions.

A sixth disclosure is the method for producing a regenerated positive electrode material precursor according to the first disclosure, the method further including: quantitatively analyzing a metal element contained in the ion-exchanged liquid; and adjusting makeup of the ion-exchanged liquid in a case in which a result of said quantitative analysis of the metal element contained in the ion-exchanged liquid differs from intended metal composition of the regenerated positive electrode material precursor.

A seventh disclosure is the method for producing a regenerated positive electrode material precursor according to the first disclosure, the method further including: quantitatively analyzing

a metal element contained in the ion-exchanged liquid; and adding a metal element lacking from intended metal composition of the regenerated positive electrode material precursor in a case in which a result of said quantitative analysis of the metal element contained in the ion-exchanged liquid differs from the intended metal composition of the regenerated positive electrode material precursor.

An eighth disclosure is the method for producing a regenerated positive electrode material precursor according to the sixth disclosure, wherein, in the ion-exchanged liquid the makeup of which has been adjusted, an aluminum content is 100 mg/L or less, a copper content is 1 mg/L or less, and an iron content is 1 mg/L or less.

A ninth disclosure is the method for producing a regenerated positive electrode material precursor according to the seventh disclosure, wherein, in the ion-exchanged liquid to which the metal element has been added, an aluminum content is 100 mg/L or less, a copper content is 1 mg/L or less, and an iron content is 1 mg/L or less.

A tenth disclosure is a method for producing a regenerated positive electrode material, wherein a regenerated positive electrode material is obtained by: adding a predetermined metal compound to the regenerated positive electrode material precursor produced by the method for producing a regenerated positive electrode material precursor according to any one of the first disclosure to the ninth disclosure; and then firing the regenerated positive electrode material precursor.

An eleventh disclosure is the method for producing a regenerated positive electrode material according to the tenth disclosure, wherein the metal compound is at least one selected from a lithium compound, a nickel compound, a cobalt compound, or a manganese compound.

A twelfth disclosure is a method for using a regenerated positive electrode material, including: assembling a lithium-ion secondary cell including the regenerated positive electrode material according to the tenth disclosure; and then activating the assembled lithium-ion secondary cell by charging and discharging the lithium-ion secondary cell.

Advantage of the Invention

[0014] According to the present disclosure, it is achievable to produce a regenerated positive electrode material precursor and a regenerated positive electrode material from LIBs as objects to be processed with low environmental burdens and low recycling costs, while maintaining high safety.

Brief Description of Drawings

[0015] [FIG. 1] FIG. 1 is a manufacturing flowchart of a regenerated positive electrode material precursor and a regenerated positive electrode material according to the present invention.

[FIG. 2] FIG. 2 is a schematic view of an example of a coin cell-type lithium-ion secondary cell used in Examples.

Description of Embodiments

[0016] Hereinafter, a method for producing a regenerated positive electrode material precursor and a regenerated positive electrode material, as an embodiment for carrying out the present disclosure, will be described with reference to FIG. 1, which is a manufacturing flowchart. An en dash “-” indicates a range of not less than a predetermined value to not more than a predetermined value. The present embodiment will be described in the following order:

- [1. Findings regarding the invention relating to the production method of the present disclosure]
- [2. Lithium-ion secondary cell as object to be processed]
- [3. Method for producing regenerated positive electrode material precursor]
 - (3-1. Heat Treatment Step)
 - (3-2. Crushing Step)
 - (3-3. Classification and Sorting Step)
 - (3-4. Magnetic Separation Step)
 - (3-5. Acid Leaching Step)
 - (3-6. Iron Removal Step)
 - (3-7. Ion Exchange Step)
 - (3-8. Alkali Treatment Step)
 - (3-9. Washing Step)
- [4. Method for producing regenerated positive electrode material]
 - (4-1. Step of Adding Lithium Source and the Like)
 - (4-2. Pulverization and Mixing Step)
 - (4-3. Firing Step)
 - (4-4. Pulverization Step)
- [5. Method for using regenerated positive electrode material]
 - (5-1. Regenerated Positive Electrode)
 - (5-2. Lithium-ion Secondary Cell Using Regenerated Positive Electrode Material According to the Present Disclosure)
- [6. Advantage of the Invention]

[0017] [1. Findings regarding the invention relating to the production method of the present disclosure]

The present inventors have conducted intensive studies in order to solve the problems of the present disclosure and, as a result, have arrived at the following approach.

[0018] As a measure for taking out a positive electrode active material from waste LIB cells in a time-efficient, automatic, and safe manner, heat treatment is performed on waste LIB cells as they are. By this heat treatment, the LIB laminate in the cell is rendered harmless both electrically and chemically, and risks can be significantly reduced.

[0019] By mechanically and magnetically recovering a positive electrode active material from the heat-treated LIB laminate, it is achievable to increase content of, for example, Ni, Co, and Mn in the pyrolysis residue. The pyrolysis residue in which Ni, Co, and Mn are concentrated can be

converted into a mixture of hydroxides of Ni, Co, and Mn (e.g., a precursor of a positive electrode active material).

[0020] By employing this approach, a positive electrode active material can be extracted from the LIB laminate in a time-efficient and safe manner without complicated mechanical disassembly, using an electrically and chemically harmless method. These advantages can provide a benefit of enabling automation of processing of waste LIBs. Hereinafter, the LIB laminate may also be simply referred to as an LIB.

[0021] [2. Lithium-ion secondary cell as object to be processed]

The LIB as the object to be processed is not particularly limited and may be appropriately selected depending on the intended purpose. Examples thereof include defective LIBs generated during the manufacturing process of LIBs, LIBs discarded due to failure of devices in which the LIBs are used, end of life of such devices, and the like, and used LIBs discarded due to the end of life.

[0022] An LIB refers to a secondary cell that is charged and discharged by movement of lithium ions between a positive electrode and a negative electrode, and examples thereof include an LIB including a positive electrode, a negative electrode, a separator, an electrolyte (an electrolytic solution containing an organic solvent or a solid electrolyte), and an exterior container serving as a cell case.

[0023] The shape, structure, size, material, and the like of the LIB as the object to be processed are not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the shape of the LIB include a laminate type, a cylindrical type, a button type, a coin type, a prismatic type, and a flat type.

[0024] The positive electrode is not particularly limited as long as the positive electrode includes a positive electrode material on a positive electrode current collector, and may be appropriately selected depending on the intended purpose. The shape of the positive electrode is not particularly limited and may be appropriately selected depending on the intended purpose, and examples thereof include a flat plate shape and a sheet shape.

[0025] The positive electrode current collector is not particularly limited in terms of its shape, structure, size, material, and the like, and may be appropriately selected depending on the intended purpose. Examples of the shape of the positive electrode current collector include a foil shape. Examples of the material of the positive electrode current collector include stainless steel, nickel, aluminum, copper, titanium, and tantalum. Among these, aluminum is frequently used.

[0026] Components of the positive electrode material may be appropriately selected depending on the intended purpose, and examples thereof include a positive electrode material including at least a positive electrode active material containing a rare valuable material and, if necessary, including a conductive agent and a binder resin. The rare valuable material is not particularly limited and may be appropriately selected depending on the intended purpose. Cobalt, nickel, and manganese (which are sometimes referred to as “NCM” in the present disclosure, and cobalt, nickel, and aluminum are sometimes referred to as “NCA”) are frequently used.

[0027] The positive electrode active material may be a lithium transition metal oxide (LTMO). Examples of the LTMO include lithium cobaltate (LiCoO_2), lithium nickelate (LiNiO_2), lithium manganate (LiMn_2O_4), lithium cobalt nickelate ($\text{LiCo}_{1/2}\text{Ni}_{1/2}\text{O}_2$), a ternary material ($\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ based on NCM) (where $x+y+z=1$, and each of x , y , and z is greater than 0 and less than 1) (hereinafter, even those containing Li may also be referred to as NCM), and a composite including any combination thereof.

[0028] Among these, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, which is the above-described NCM containing equal amount of Ni, Co, and Mn ($x=y=z=1/3$), exhibits favorable Li ion extraction/insertion characteristics when used as a positive electrode material of an LIB, and is suitable for automotive applications.

[0029] Meanwhile, Ni in a ternary LTMO is useful for providing a high specific capacity through slow Li ion extraction/insertion in a cell at a low charge-discharge current density. $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$, and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ are also regarded as promising as positive electrode active materials for automotive LIBs such as BEVs and PHEVs.

[0030] The conductive agent is not particularly limited and may be appropriately selected depending on the intended purpose, and examples thereof include carbon black, graphite, carbon fiber, and metal carbides.

[0031] The binder resin is not particularly limited and may be appropriately selected depending on the intended purpose, and examples thereof include homopolymers or copolymers of vinylidene fluoride, tetrafluoroethylene, acrylonitrile, ethylene oxide, and the like, and styrene-butadiene rubber.

[0032] The negative electrode is not particularly limited as long as the negative electrode includes a negative electrode material on a negative electrode current collector, and may be appropriately selected depending on the intended purpose. The shape of the negative electrode is not particularly limited and may be appropriately selected depending on the intended purpose, and examples thereof include a flat plate shape and a sheet shape.

[0033] The negative electrode current collector is not particularly limited in terms of its shape, structure, size, material, and the like, and may be appropriately selected depending on the intended purpose. Examples of the shape of the negative electrode current collector include a foil shape. Examples of the material of the negative electrode current collector include stainless steel, nickel, aluminum, copper, titanium, and tantalum. Among these, copper is frequently used.

[0034] The negative electrode material is not particularly limited and may be appropriately selected depending on the intended purpose, and examples thereof include carbon materials such as graphite and hard carbon, titanate, silicon, and composites thereof.

[0035] Note that the positive electrode current collector and the negative electrode current collector have a laminated structure, and the laminate is not particularly limited and may be appropriately selected depending on the intended purpose.

[0036] [3. Method for Producing Regenerated Positive Electrode Material Precursor]
(3-1. Heat Treatment Step)

As shown in FIG. 1, first, the LIB as the object to be processed is heat-treated. The heat treatment temperature is not particularly limited as long as it is not less than the melting point of the current collector having a lower melting point among the positive electrode current collector and the negative electrode current collector and is less than the melting point of the current collector having a higher melting point, and may be appropriately selected depending on the intended purpose. The heat treatment temperature is preferably 670 °C or higher, more preferably 670-1100 °C, further preferably 700 °C or higher, and particularly preferably 700-900 °C. When the heat treatment temperature is 670 °C or higher, embrittlement of the current collector having the lower melting point sufficiently occurs. When the heat treatment temperature is 1100 °C or lower, embrittlement of any of the current collector having the lower melting point, the current collector having the higher melting point, and the exterior container can be suppressed, and separation efficiency of the current collectors and the exterior container by crushing and classification can be maintained. Further, when the exterior container of the LIB melts during the heat treatment, the metal derived from the exterior container and the electrode portion can be easily separated by arranging a tray for collecting the molten metal under the LIB.

[0037] By heat-treating at a predetermined heat treatment temperature, for example, in a laminate in which the positive electrode current collector is aluminum and the negative electrode current collector is copper, the positive electrode current collector made of an aluminum foil becomes embrittled, and thus is easily reduced into fine particles in a crushing step described later. This embrittlement of the positive electrode current collector occurs due to melting or an oxidation reaction. Further, the molten aluminum that has flowed down is collected in the tray. Meanwhile, the negative electrode current collector made of copper is heat-treated at a temperature lower than the melting point of copper and thus does not melt, thereby enabling highly accurate separation in a dry magnetic separation step described later. Further, when either the laminate or the LIB is accommodated in an oxygen-shielding container and subjected to heat treatment, the positive electrode current collector made of an aluminum foil melts and becomes embrittled, and thus is easily reduced into fine particles in the crushing step described later, whereas the negative electrode current collector made of copper is heat-treated in a state where the oxygen partial pressure is low due to the oxygen-shielding effect of the oxygen-shielding container and a reducing effect of a negative electrode active material such as carbon contained in the laminate or the LIB, and thus embrittlement due to oxidation does not occur. Therefore, by crushing in the crushing step, the positive electrode current collector is crushed into fine pieces, and the negative electrode current collector remains as coarse particles even after crushing, thereby enabling more effective and highly accurate separation in a classification and separation step described later.

[0038] The heat treatment time is not particularly limited and may be appropriately selected depending on the intended purpose. The time may be 1 minute or longer, and may be 5 hours or shorter, 2 hours or shorter, or 1 hour or shorter. The heat treatment time may be any time as long as the current collector having the lower melting point reaches a desired temperature, and the holding time may be short. It is advantageous in terms of the cost for the heat treatment when the heat treatment time is within a particularly preferable range.

[0039] The heat treatment method is not particularly limited and may be appropriately selected depending on the intended purpose, and examples thereof include heat treatment using a heat treatment furnace. Examples of the heat treatment furnace include a rotary kiln, a fluidized bed furnace, a tunnel furnace, a batch-type furnace such as a muffle furnace, a cupola, and a stoker furnace.

[0040] The atmosphere used for the heat treatment is not particularly limited and may be appropriately selected depending on the intended purpose, and the heat treatment may be performed in air. Note that an atmosphere having a low oxygen concentration is preferable because a metal derived from the positive electrode current collector and a metal derived from the negative electrode current collector can be recovered with high quality and a high recovery rate.

[0041] As a method for realizing the above low-oxygen atmosphere, the LIB or the laminate may be accommodated in an oxygen-shielding container and heat-treated. The material of the oxygen-shielding container is not particularly limited as long as it does not melt at the above-described heat treatment temperature, and may be appropriately selected depending on the intended purpose, and examples thereof include iron and stainless steel. In order to release a gas pressure generated by combustion of the electrolytic solution in the LIB or the laminate, it is preferable to provide an opening in the oxygen-shielding container. The opening area of the opening is preferably set to be 12.5% or less of the surface area of the exterior container in which the opening is provided. The opening area of the opening is more preferably 6.3% or less of the surface area of the exterior container in which the opening is provided. When the opening area of the opening is larger than 12.5% of the surface area of the exterior container, most part of the current collectors tend to be oxidized by the heat treatment. The opening is not particularly limited in its shape, size, formation location, and the like, and may be appropriately selected depending on the intended purpose.

[0042] Ultimately, it is sufficient that the LIB or the laminate can be heat-treated at a high temperature (for example, 800 °C) and in an oxygen-free or low-oxygen state. Therefore, instead of using the above oxygen-shielding container, the LIB may be heat-treated in a heat treatment furnace while shutting off air supply or reducing the air supply amount to a small amount (for example, 11% or less in terms of oxygen concentration).

[0043] Here, if desired, it is also preferable to qualitatively and quantitatively analyze metal elements contained in the heat-treated product obtained in the heat treatment step using X-ray fluorescence analysis or the like. This is because the metal components contained in the heat-treated product may vary depending on the LIB as the object to be processed.

[0044] The results of the qualitative and quantitative analysis indicate that it is preferable, from the viewpoint of stabilizing the composition of metal components of the regenerated positive electrode material, to group heat-treated products having the same composition of metal components and send the heat-treated products separated for each group to a crushing step described later.

[0045] (3-2. Crushing Step)

Next, the heat-treated product obtained in the heat treatment step is crushed in a crushing step. In the crushing step, it is preferable to obtain crushed material by crushing the heat-treated product by impact.

[0046] The crushing is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the method of crushing by impact include a method of throwing the heat-treated product by a rotating impact plate and striking it against a collision plate to apply impact and a method of striking the heat-treated product by a rotating beater (a beater), in which, for example, a hammer crusher, a chain crusher can be used. Other examples include a method of striking the heat-treated product with balls or rods made of ceramic, iron, or the like, in which a ball mill, a rod mill, or the like can be used. Further, a biaxial crusher having a short blade width and a short blade length for crushing by compression can be used.

[0047] Obtaining crushed material by impact promotes crushing of the active material and the current collector having the lower melting point, while the current collector having the higher melting point whose form has not significantly changed remains in the form of a foil and the like. Therefore, in the crushing step, the current collector having the higher melting point is merely cut, and comminution of the current collector having the higher melting point is less likely to proceed as compared with the current collector having the lower melting point, so that crushed material can be obtained in a state in which the current collector having the lower melting point and the current collector having the higher melting point can be efficiently separated in a classification and separation step described later.

[0048] The crushing time is not particularly limited and may be appropriately selected depending on the intended purpose. The processing time per 1 kg of the LIB is preferably 1 second or longer and 30 minutes or shorter, more preferably 2 seconds or longer and 10 minutes or shorter, and particularly preferably 3 seconds or longer and 5 minutes or shorter. When the crushing time is shorter than 1 second, crushing may not occur, and when the crushing time exceeds 30 minutes, excessive crushing may occur. Further, it is preferable that the maximum particle diameter of the crushed material is 10 mm or less.

[0049] (3-3. Classification and Separation Step)

Next, in a classification and separation step as a physical separation step, the crushed material obtained in the crushing step can be classified into a coarse-grained product and a fine-grained product. The classification method is not particularly limited and may be appropriately selected depending on the intended purpose. For example, a vibrating sieve, a multistage vibrating sieve, a cyclone, a standard sieve of JIS Z8801, a wet vibrating table, an air table, or the like can be used in this step.

[0050] The classification point used in the classification and separation step may be appropriately selected depending on the intended purpose as long as it is 0.45 mm or more. For example, it is desirable to use a classification point of 0.6 to 2.4 mm. When the classification point exceeds 2.4 mm, contamination of the fine-grained product with metals derived from the exterior container and having the higher melting point increases, and separation performance from cobalt, nickel, and manganese derived from the active material may decrease. On the other hand, when the

classification point is less than 0.6 mm, contamination of the coarse-grained product with the metal derived from the current collector having the lower melting point and the active material increases, the grade of the metal derived from the current collector having the higher melting point in the coarse-grained product decreases, and the recovery rate of cobalt, nickel, and manganese derived from the active material into the fine-grained product may be less than 60%.

[0051] Further, when a sieve is used as the classification method, by sieving while placing a disintegration-promoting material, such as stainless steel balls or alumina balls, on the sieve, small crushed pieces adhering to large crushed pieces can be separated from the large crushed pieces, thereby enabling more efficient separation into large crushed pieces and small crushed pieces. This can further improve the grade of the recovered metal. Note that the crushing step and the classification and separation step may be simultaneous. For example, this may be a step (of crushing/classification) in which, while the heat-treated product obtained in the heat treatment step is crushed, the crushed material is classified into a coarse-grained product and a fine-grained product.

[0052] By the classification described above, metals derived from the exterior container and the current collector having the higher melting point can be recovered as the coarse-grained product, and cobalt, nickel, manganese, and lithium derived from the active material can be recovered as the fine-grained product (black mass (also referred to as black powder)). The fine-grained product may be classified again. By removing, for example, fine particles of 150 μm or less from the fine-grained material in this re-classification, the amount of negative electrode active material contained in the non-magnetically-attracted object of wet magnetic separation (hereinafter, magnetic separation is also simply referred to as magnetic separation) can be reduced.

[0053] (3-4. Magnetic Separation Step)

As a physical separation step, a dry magnetic separation step can be performed on the crushed material obtained in the crushing step or on the coarse-grained product obtained in the classification and separation step. Iron is recovered as a magnetically-attracted object, and a metal derived from the negative electrode current collector such as copper is recovered as a non-magnetically-attracted object.

[0054] As a physical separation step, preferably, a wet magnetic separation step (wet magnetic separation) can be performed on the crushed material obtained in the crushing step or on the fine-grained product (black mass) obtained in the classification and separation step. Cobalt and nickel are recovered as a magnetically-attracted object. When the fine-grained product (black mass) obtained in the classification and separation step is subjected to magnetic separation in a dry manner, aggregation of particles occurs due to moisture adhering between particles, and it is not possible to sufficiently separate metal particles derived from the negative electrode current collector and fine particles of the negative electrode active material contained in the fine-grained product at 10% or more from cobalt and nickel particles. In the present disclosure, in the wet magnetic separation step, a substance derived from the negative electrode active material and a metal derived from the negative electrode current collector are separated into a non-magnetically-attracted product slurry, and a magnetically-attracted object containing cobalt and nickel (black

mass magnetically-attracted object) can be recovered. Note that manganese is not ferromagnetic at room temperature; however, when manganese constitutes a composite oxide together with cobalt and nickel in the LIB, manganese accompanies cobalt and nickel when cobalt and nickel are magnetically separated. Therefore, a considerable amount of manganese is also recovered by magnetic separation. The magnetic force during magnetic separation is preferably 1500-8000 G. [0055] (3-5. Acid Leaching Step)

In this step, an acid such as H_2SO_4 , HCl , HNO_3 , or the like is added to the fine-grained product (black mass) obtained in the classification and separation step or to the magnetically-attracted object (black mass magnetically-attracted object) obtained in the magnetic separation step, metal elements such as cobalt, nickel, manganese, and lithium are dissolved into an acidic solution, while copper and carbon are removed as an insoluble residue.

[0056] The specific contents of the acid leaching step are not particularly limited as long as cobalt, nickel, and manganese can be leached. For example, the fine-grained product or the magnetically-attracted object after acid addition is heated for the time and at the temperature described in the Examples section below and, while maintaining the pH value described in the Examples section below, metal elements in the fine-grained product or the magnetically-attracted object are thermally decomposed and dissolved into the acid solution. When the change in pH value becomes equal to or less than the value described in the Examples section below, the acid solution is allowed to cool, the acid solution is filtered to remove an insoluble residue in the acid solution, and a filtrate (acid leachate) may be recovered. Although H_2SO_4 , HCl , HNO_3 , or the like can be used as the acid, use of H_2SO_4 is preferable from the viewpoint of removing copper in this step.

[0057] As the filtration method, various methods such as a membrane filter, filter paper, and centrifugation can be used. It is also preferable to use cross-flow filtration.

[0058] (3-6. Iron Removal Step)

In this step, an oxidizing agent is added to the recovered filtrate (acid leachate) to adjust the oxidation-reduction potential of the filtrate, and then an alkaline solution is added to generate a precipitate of iron hydroxide and remove iron.

[0059] The oxidizing agent to be added to the filtrate (acid leachate) may be any known oxidizing agent. Examples thereof include oxygen, ozone, metal oxides, oxyacids or salts thereof (e.g., potassium permanganate), halogens, and the like. However, from the viewpoint of usability and cost, an aqueous hydrogen peroxide solution is preferable. The oxidation-reduction potential of the filtrate preferably has an upper limit of 750 mV (Ag/AgCl: the description thereof will be omitted hereinafter since the same applies to the oxidation-reduction potential in this specification.), 700 mV, or 650 mV, and a lower limit of 500 mV, 550 mV, or 600 mV.

Next, a known alkaline solution may be employed as the alkaline solution to be added. For example, an aqueous alkali metal hydroxide solution (an aqueous sodium hydroxide solution and/or an aqueous potassium hydroxide solution) may be used. In this specification, an aqueous sodium hydroxide solution is exemplified. The concentration of the alkaline solution may be 0.5-10 mol/L. Then, after adjusting the pH value of the filtrate to 3-5.5 to generate a precipitate of

iron hydroxide, the iron hydroxide is aged by, for example, maintaining the liquid at a temperature described in the Examples section below for a predetermined period of time. Thereafter, the filtrate and the iron hydroxide precipitate are filtered, and a filtrate (iron-removed liquid) is recovered.

[0060] As the filtration method, various methods such as a membrane filter and filter paper can be used. It is also preferable to use cross-flow filtration.

[0061] (3-7. Ion Exchange Step)

In this step, the recovered filtrate (iron-removed liquid) is brought into contact with a predetermined chelate resin for ion exchange, and aluminum ions and copper ions are selectively adsorbed and removed to obtain a filtrate (ion-exchanged liquid).

[0062] There are a wide variety of chelate resins having an ion exchange capability. As a result of research, the present inventors have conceived that, for example, an aminomethylphosphonic acid-based chelate resin having an aminomethylphosphonic acid group, with a styrene-divinylbenzene copolymer as a base material, is suitable for selectively adsorb and remove aluminum ions and copper ions from the filtrate (iron-removed liquid). A preferred example of a commercially available product is “IRC747UPS manufactured by DuPont and Organo Corporation”.

The aminomethylphosphonic acid-based chelate resin includes an Na type and an H type. When the Na type is used, there is a concern that the pH value of the filtrate may increase after ion exchange and a metal hydroxide may unintentionally precipitate. Accordingly, when the Na type is used, it is preferable to set the pH value of the filtrate to 3 or less in advance.

[0063] An example of the content of each metal element in the ion-exchanged liquid (or the regenerated positive electrode material precursor described below) is as follows:

For aluminum, an upper limit may be 100 mg/L, 50 mg/L, or 10 mg/L.

For copper, an upper limit may be 1 mg/L, 0.1 mg/L, or 0.02 mg/L.

For iron, an upper limit may be 1 mg/L, 0.5 mg/L, or 0.2 mg/L.

[0064] (3-8. Alkali Treatment Step)

In this step, the obtained filtrate (ion-exchanged liquid) are mixed with an alkaline solution to adjust the pH value to 9-14, so that metal elements such as cobalt, nickel, manganese, and lithium in the filtrate as a hydroxide precipitate are generated. The acid leaching step described above and this step may collectively be referred to as a hydrometallurgical step.

[0065] For example, 0.5-10 mol/L of aqueous NaOH solution is added as an alkaline solution to the recovered filtrate, the pH value of the filtrate is adjusted to 11-12, and a hydroxide precipitate is generated. After the addition of the alkali is completed, the filtrate may be filtered to recover the hydroxide precipitate.

[0066] (3-9. Washing Step)

In this step, the recovered hydroxide precipitate are washed to obtain a regenerated positive electrode material precursor.

For example, the recovered hydroxide precipitate is heated at 20-200 °C for 0.1-48 hours and dried by ignition to obtain a dried product. The dried product is pulverized to obtain a

pulverized product. Water in an amount of the same amount to ten times the amount (by weight) of the pulverized product is added to the pulverized product to obtain a slurry. The obtained slurry is filtered to recover the hydroxide precipitate.

As the filtration method, various methods such as a membrane filter and filter paper can be used. It is also preferable to use cross-flow filtration.

[0067] The recovered hydroxide precipitate can be heated at 20-200 °C for 0.1-48 hours and dried to obtain the regenerated positive electrode material precursor according to the present disclosure.

The obtained regenerated positive electrode material precursor is a solid (solid matter). In subsequent steps, the regenerated positive electrode material precursor may be handled as a solid, or may be formed into a slurry. Even when formed into a slurry, the regenerated positive electrode material precursor contained in the slurry remains as a solid.

Note that salts remaining in the hydroxide precipitate may be removed by washing after “(4-3) Firing Step” in “4. Method for Producing Regenerated Positive Electrode Material” described below.

[0068] It is also preferable to qualitatively and quantitatively analyze metal elements contained in the obtained regenerated positive electrode material precursor according to the present disclosure. This is because the metal components contained in the regenerated positive electrode material precursor may differ depending on the LIB as the object to be processed, and the metal components contained in the regenerated positive electrode material precursor may differ depending on the process conditions up to this point.

[0069] For example, the metal elements contained in the ion-exchanged liquid described above can be subjected to ICP analysis or X-ray fluorescence analysis. When the composition of the metal elements contained in the ion-exchanged liquid described above differs from the intended metal composition of the regenerated positive electrode material, a makeup-adjusting step or an addition step can be performed on the ion-exchanged liquid described above.

[0070] Specifically, when there is a difference between the quantitative analysis result of the ion-exchanged liquid described above and the intended metal composition of the regenerated positive electrode material precursor, a makeup-adjusting step of adjusting the composition of metal elements contained in the ion-exchanged liquid (e.g., a step of appropriately adjusting makeup of ion-exchanged liquids having different metal compositions derived from different LIBs to obtain an ion-exchanged liquid having an intended metal composition, etc.) or an addition step of adding a deficient metal element to the ion-exchanged liquid can be performed. These steps can also be used in combination.

[0071] [4. Method for Producing Regenerated Positive Electrode Material]

(4-1) Step of Adding Lithium Source and the like

In the step of adding a lithium source and the like, a predetermined amount of a lithium source, a nickel source, a cobalt source, a manganese source and the like is added to the regenerated positive electrode material precursor when there is a difference between the intended composition of metal elements that function as a positive electrode material for the regenerated positive electrode material and the composition of metal elements of the obtained regenerated positive

electrode material according to the present disclosure. Note that, in the regenerated positive electrode material precursor, manganese is rarely insufficient.

[0072] Examples of the lithium source include lithium compounds such as lithium carbonate, lithium hydroxide, lithium nitrate, and lithium chloride.

Examples of the nickel source include nickel compounds such as nickel carbonate, nickel hydroxide, nickel nitrate, nickel chloride, and nickel sulfate.

Examples of the cobalt source include cobalt compounds such as cobalt carbonate, cobalt hydroxide, cobalt nitrate, cobalt chloride, and cobalt sulfate.

Examples of the manganese source include manganese compounds such as manganese carbonate, manganese hydroxide, manganese nitrate, manganese chloride, and manganese sulfate.

[0073] The amount of the lithium source, etc. to be added may be an amount necessary to obtain a composition of the regenerated positive electrode material that provides desired battery characteristics when the obtained regenerated positive electrode material is used as a battery. The amount of lithium to be added is preferably an amount (mol) of 0.2-2.0 times the total amount (mol) of metal elements functioning as a positive electrode material contained in the regenerated positive electrode material precursor.

[0074] (4-2) Pulverization and Mixing Step

The mixture to which a predetermined amount of the lithium source and the like has been added is preferably pulverized for homogenization.

The mixture to which a predetermined amount of the lithium source and the like has been added is pulverized to obtain a pulverized mixture. For example, a disk mill, a mixer mill, a bead mill, a vibration mill, a ball mill, a planetary ball mill, an attritor, or the like can be used for pulverization.

[0075] (4-3) Firing Step

The regenerated positive electrode material according to the present disclosure can be obtained by firing the obtained mixture. The firing temperature is preferably 650-900 °C. The firing time is preferably 0.1-20 hours, and more preferably 0.5-8 hours. For example, firing can be performed using an alumina crucible under holding conditions of 600 °C for 1 hour and then 900 °C for 4 hours. In the regenerated positive electrode material obtained after firing the regenerated positive electrode material precursor, iron, copper, and aluminum are oxidized. Specifically, iron, copper, and aluminum, which were mostly hydroxides in the regenerated positive electrode material precursor, are oxides in the regenerated positive electrode material.

[0076] (4-4) Pulverization Step

The obtained regenerated positive electrode material is preferably pulverized using a disk mill or the like to make the regenerated positive electrode material fine-grained.

In addition, a washing treatment can be performed on the regenerated positive electrode material after being made fine-grained, and in this case, the firing step can be performed again after the washing treatment.

[0077] The obtained regenerated positive electrode material according to the present disclosure contains lithium, nickel, cobalt, manganese, aluminum in an amount of 0.01-1.5 mass%, and at least one of copper and iron in an amount of less than 1 mass%, and can exhibit a specific capacity at the same level as an LIB using a conventional positive electrode material, and can achieve cycle characteristics substantially comparable to those of an LIB using a conventional positive electrode material.

[0078] [5. Method for Using Regenerated Positive Electrode Material]

(5-1) Regenerated Positive Electrode

The regenerated positive electrode according to the present disclosure contains the regenerated positive electrode material according to the present disclosure as a positive electrode active material, and further contains, as other components as necessary, a conductive agent, a binder resin, and the like.

[0079] (5-2) Lithium-Ion Secondary Battery Using Regenerated Positive Electrode Material According to the Present Disclosure

The LIB according to the present disclosure includes a positive electrode, a negative electrode, and a separator, wherein the positive electrode contains the regenerated positive electrode material according to the present disclosure.

Using the regenerated positive electrode material according to the present disclosure, the LIB according to the present disclosure can be manufactured by a known LIB manufacturing method.

Advantage of the Invention

[0080] [6. Advantage of the Invention]

As described above, according to the present disclosure, a fine-grained product (black mass) is recovered by performing, on an LIB as an object to be processed, treatments that are easy to reduce environmental load and low in cost, namely, heat treatment, crushing treatment, and classification treatment. Then, the fine-grained product (black mass) is subjected to treatments that are also easy to reduce environmental load and low in cost, namely, magnetic separation treatment, acid leaching treatment, iron removal treatment, ion exchange treatment, alkali treatment, and washing treatment, thereby enabling production of a high-quality regenerated positive electrode material precursor having low content of iron, copper, and aluminum.

The above effects mean that various LIBs can be processed together. That is, by collectively subjecting various LIBs to the heat treatment step and then to each of the above steps, a regenerated positive electrode material precursor and a regenerated positive electrode material can be produced. Moreover, this production can achieve low environmental load and low recycling cost and ensure high safety.

In view of the current situation in which recycling has become an issue due to the rapid spread of LIBs in recent years, the advantages of the present disclosure are considered to be significant.

Examples

[0081] Hereinafter, the present disclosure will be described in more detail with reference to the examples. Note that the present disclosure is not limited to these examples.

In Examples 1 and 2, as regenerated positive electrode materials produced by the production method according to the present disclosure, two types of regenerated positive electrode materials were produced: “regenerated positive electrode material (without composition adjustment),” which was fired without adjusting the component of the regenerated positive electrode material precursor, and “regenerated positive electrode material (with composition adjustment),” which was fired after adjusting the component of the regenerated positive electrode material precursor.

In Comparative Examples 1-3, three types of comparative example materials were prepared: “regenerated positive electrode material (conventional type)” produced by a conventional production method; “commercially available positive electrode material” prepared from a commercially available positive electrode material (Note that refiring was at 900 °C for 4 hours in air); and “trace product of commercially available positive electrode material” produced by the production method according to the present disclosure from a solution obtained by dissolving a commercially available positive electrode material in an acid (sulfuric acid).

[0082] (Example 1) Regenerated Positive Electrode Material (Without Composition Adjustment)
<Heat Treatment Step>

A battery pack (about 75 kg) of an LIB as an object to be processed was heat-treated at a heat treatment temperature of 800 °C (temperature was raised over 1 hour and then held for 2 hours) to obtain a heat-treated product. As the heat treatment apparatus, a batch-type burner furnace manufactured by Ecosystem Akita Co., Ltd. was used. Although the inside of the furnace was set to the atmosphere at the start of the heat treatment, the heat treatment was performed with the supply of air blocked.

[0083] <Crushing Step>

Next, using a hammer crusher (Makino-type swing hammer crusher HC-20-3.7, manufactured by MAKINO MFG. Co., Ltd.) as a crushing apparatus, under conditions of 50 Hz (hammer peripheral speed: 38 m/sec) and a screen at the outlet portion being a grate-type opening of 30 mm × 200 mm, the heat-treated product (the heat-treated LIB) obtained in the heat treatment step was crushed to obtain a crushed product of the LIB.

[0084] <Classification and Separation Step>

Subsequently, using a sieve having an opening size of 1.2 mm (diameter: 200 mm, manufactured by Tokyo Screen Co., Ltd.), the crushed product of the LIB was sieved and subjected to separation treatment into an oversize fraction (coarse-grained product) and an undersize fraction (fine-grained product). Then, the fine-grained product (black mass) according to Example 1 was obtained as the undersize fraction, i.e., the fine-grained product (black mass). A composition table of the fine-grained product (black mass) is shown in Table 1. Hereinafter, each composition table is obtained by ICP analysis. ICP analysis was performed using iCAP 6300 Duo manufactured by Thermo Fisher Scientific Inc. (the same applies hereinafter for ICP analysis).

[0085] <Magnetic Separation Step>

The fine-grained product (black mass) according to Example 1 was subjected to wet magnetic separation using a drum-type magnetic separator under the conditions of: magnetic force: 1500 G; drum rotational speed: 45 rpm; solid-liquid ratio: 10%; and slurry feed rate: 100 mL/min, thereby recovering a magnetically-attracted object (black mass magnetically-attracted object) according to Example 1. A composition table of the magnetically-attracted object (black mass magnetically-attracted object) is shown in Table 1. In Table 1, when comparing the compositions of the fine-grained product (black mass) and the magnetically-attracted object (black mass magnetically-attracted object), the content (mass%) of nickel, cobalt, and manganese in the magnetically-attracted object were increased as compared with those in the fine-grained product.

[0086] [Table 1]

	Ni	Co	Mn	Li	Al	Cu	Fe	Insoluble residue
	(mass%)	(mass%)	(mass%)	(mass%)	(mass%)	(mass%)	(mass%)	(mass%)
Fine-grained product (black mass)	10.9	10.2	14.1	3.2	6.0	1.6	0.7	36.3
Physically processed material (black mass magnetized object)	21.9	19.4	21.6	1.1	2.1	2.7	1.5	15.3

[0087] <Acid Leaching Step>

250 g of the recovered magnetically-attracted object (black mass magnetically-attracted object) according to Example 1 was placed in a 5000 mL straight beaker, 750 mL of ion-exchanged water was added thereto, and the mixture was stirred while adjusting the liquid temperature to 45 °C using a magnetic stirrer with a heater. Then, a 50 wt% sulfuric acid solution was added thereto so as to maintain the pH at 1, and acid leaching was performed. The end point was defined as the time point when the change in pH per hour became less than 0.02. After allowing the acid leachate to cool, an insoluble residue in the acid leachate was removed using No.5C filter paper, and a filtrate (acid leachate) was recovered. A composition table of the filtrate (acid leachate) is shown in Table 2.

[0088] <Iron Removal Step>

An oxidizing agent (hydrogen peroxide aqueous solution) was added to the filtrate (acid leachate), and the oxidation-reduction potential was adjusted to 634 mV (Ag/AgCl). Thereafter, an alkaline solution was added to the filtrate whose oxidation-reduction potential had been adjusted, and the pH was adjusted to 4.42 to generate a precipitate of iron hydroxide. Then, the filtrate was maintained at a liquid temperature of 40 °C for 12 hours to age the iron hydroxide, and thereafter the filtrate (acid leachate) and the iron hydroxide precipitate were separated by filtration, thereby recovering a filtrate (iron-removal liquid). A composition table of the filtrate (iron-removal liquid) is shown in Table 2.

[0089] <Ion Exchange Step>

A PVC column having an inner diameter of 40 mm was filled with 150 mL of AmberSep IRC747 UPS (manufactured by DuPont and Organo Corporation) as a chelate resin to prepare an ion exchange column. Then, the filtrate (iron-removal liquid) adjusted to pH 2.90 by adding a 50 wt% sulfuric acid solution was passed through the column at a flow rate of 25.0 mL/min (SV = 10) to remove aluminum ions, thereby obtaining a filtrate (ion-exchanged liquid). A composition table of the filtrate (ion-exchanged liquid) is shown in Table 2.

[0090] [Table 2]

	Ni	Co	Mn	Li	Al	Cu	Fe
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Acid leachate	4450	4100	6530	813	1590	< 0.02	1160
Iron-removed liquid	6850	6270	9890	623	759	< 0.02	0.519
Ion-exchanged liquid	7500	6850	9100	626	30.1	< 0.02	0.139

[0091] <Alkali Treatment Step>

The obtained filtrate (ion-exchanged liquid) was mixed with an aqueous solution of %NaOH with a concentration of about 7.5 mass to adjust the pH to 11.3, thereby precipitating hydroxides. Then, the hydroxides were recovered using No.5C filter paper.

[0092] <Washing Step>

A sufficient amount of ion-exchanged water was added to the hydroxides recovered on the filter paper to remove water-soluble salts by washing with water. Thereafter, the hydroxides were dried in a vacuum constant-temperature chamber at 85 °C to obtain a regenerated positive electrode material precursor sample.

[0093] <Pulverization Step>

The obtained regenerated positive electrode material precursor sample was pulverized using a disk mill to obtain a pulverized product.

[0094] <Lithium Addition Step>

Lithium, in an amount corresponding to 1.0 times the total amount (moles) of metal elements functioning as a positive electrode material contained in the pulverized precursor, was added as lithium carbonate, and the mixture was mixed using a mortar.

<Firing Step>

The above mixture was placed in an alumina crucible and fired in an air atmosphere under conditions of 600 °C for 1 hour, and then 900 °C for 4 hours, thereby obtaining a regenerated positive electrode material sample.

[0095] <Pulverization Step>

The obtained regenerated positive electrode material sample was pulverized using a mortar.

The obtained regenerated positive electrode material sample was subjected to acid decomposition using a mixed acid of HCl and HNO₃, and thereafter composition analysis was performed using ICP-AES (SPECTRO GREEN, manufactured by Hitachi High-Tech Science Corporation).

A composition table of the constituent elements of the regenerated positive electrode material sample expressed in mass% is shown in Table 3.

A composition table expressed in moles per 100 g is shown in Table 4.

Table 5 shows molar ratios of predetermined elements calculated from the moles per 100 g. MCN represents the total moles of Mn, Co, and Ni, and MCNCuFeAl represents the sum of the total moles of Mn, Co, and Ni and the respective moles of Cu, Fe, and Al.

The regenerated positive electrode material (with composition adjustment), the regenerated positive electrode material (conventional type), the commercially available positive electrode material, and the trace product of the commercially available positive electrode material described below are also shown in the above tables.

[0096] (Example 2) Regenerated Positive Electrode Material (with Composition Adjustment)

<Addition Step>

In Example 1 described above, composition analysis was performed on the filtrate (ion-exchanged liquid) obtained in the ion exchange step. As a result, compared with the manganese, cobalt, and nickel contained in the commercially available positive electrode material used in Comparative Example 2, cobalt and nickel were insufficient, and therefore sulfuric acid solutions of cobalt hydroxide and nickel hydroxide are added to adjust the insufficient cobalt and nickel to adjust the composition.

<Alkali Treatment Step>

The obtained composition-adjusted liquid was mixed with an aqueous solution of %NaOH with a concentration of about 7.5 mass to adjust the pH to 11.3, thereby precipitating hydroxides. Then, the hydroxides were recovered using No.5C filter paper.

[0097] <Washing Step>

A sufficient amount of ion-exchanged water was added to the hydroxides recovered on the filter paper to remove water-soluble salts by washing with water. Thereafter, the hydroxides were dried in a vacuum constant-temperature chamber at 85 °C to obtain a regenerated positive electrode material precursor sample.

[0098] <Pulverization Step>

The obtained regenerated positive electrode material precursor sample was pulverized using a disk mill to obtain a pulverized product.

<Lithium Addition Step>

Lithium, in an amount corresponding to 1.1 times the total amount (moles) of metal elements functioning as a positive electrode material contained in the pulverized precursor, was added as lithium carbonate, and the mixture was mixed using a mortar.

Except for the above, the same steps as in Example 1 were performed to obtain the regenerated positive electrode material of this example. The obtained sample was subjected to composition analysis in the same manner as in Example 1.

[0099] (Comparative Example 1) Regenerated Positive Electrode Material (Conventional Type)

To obtain a regenerated positive electrode material (conventional type) of this example, the same steps as for the regenerated positive electrode material of Example 1 described above were performed, except that the <Iron Removal Step> and the <Ion Exchange Step> were not performed. The obtained sample was subjected to composition analysis in the same manner as in Example 1.

[0100] (Comparative Example 2) Commercially Available Positive Electrode Material

A commercially available typical cobalt-nickel-manganese-based positive electrode material ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, PLB-H1, manufactured by Gelon LIB Group Ltd.) was prepared. The cobalt-nickel-manganese-based positive electrode material was fired again at 900 °C for 4 hours in air to obtain a commercially available positive electrode material. The obtained sample was subjected to composition analysis in the same manner as in Example 1.

[0101] (Comparative Example 3) Trace Product of Commercially Available Positive Electrode Material

A commercially available typical cobalt-nickel-manganese-based positive electrode material was dissolved in an acid, and the obtained solution was subjected to the <Alkali Treatment Step>, the <Washing Step>, the <Pulverization Step>, the <Firing Step>, and the <Pulverization Step> in the same manner as in the Examples, thereby obtaining a trace product of the commercially available positive electrode material. The obtained sample was subjected to composition analysis in the same manner as in Example 1.

	Samples	Mn (mass%)	Co (mass%)	Ni (mass%)	Li (mass%)	Cu (mass%)	Fe (mass%)	Al (mass%)	Na (mass%)	Ca (mass%)	Mg (mass%)	O (diff.) (mass%)	Total CuFeAl (mass%)
Example 1	Regenerated PEM (w/o composition adjustment)	24.54	17.60	19.21	6.91	0.00032	0.00053	0.07	0.36990	0.05102	0.04898	31.19	0.07
Example 2	Regenerated PEM (with composition adjustment)	18.42	21.46	18.83	7.19	0.00002	0.00106	0.23	0.00154	0.06881	0.03253	33.76	0.23
Com.Ex. 1	Regenerated PEM (conventional type)	18.54	16.21	17.77	7.44	0.00274	0.01835	1.74	0.02874	0.02272	0.03330	38.20	1.76
Com.Ex. 2	Commercially available PEM	18.71	20.08	20.15	7.67	0.00002	0.00063	0.00	0.00161	0.01257	0.01016	33.35	0.00
Com.Ex. 3	Trace product of commercially available PEM	18.62	20.09	20.30	7.28	0.00007	0.00119	0.00	0.03283	0.01417	0.01173	33.65	0.00

* Com.Ex. = Comparative Example * PEM = Positive electrode material

	Samples	O (diff.) (mol/100g)	Mn (mol/100g)	Co (mol/100g)	Ni (mol/100g)	Li (mol/100g)	Cu (mol/100g)	Fe (mol/100g)	Al (mol/100g)	Na (mol/100g)	Ca (mol/100g)	Mg (mol/100g)
Example 1	Regenerated PEM (w/o composition adjustment)	1.9497	0.4467	0.2987	0.3273	0.9960	0.0000	0.0000	0.0026	0.0161	0.0013	0.0020
Example 2	Regenerated PEM (with composition adjustment)	2.1102	0.3354	0.3641	0.3208	1.0365	0.0000	0.0000	0.0085	0.0001	0.0017	0.0013
Com.Ex. 1	Regenerated PEM (conventional type)	2.3873	0.3375	0.2751	0.3027	1.0714	0.0000	0.0003	0.0644	0.0013	0.0006	0.0014
Com.Ex. 2	Commercially available PEM	2.0846	0.3406	0.3408	0.3433	1.1057	0.0000	0.0000	0.0000	0.0001	0.0003	0.0004
Com.Ex. 3	Trace product of commercially available PEM	2.1036	0.3389	0.3408	0.3459	1.0486	0.0000	0.0000	0.0000	0.0014	0.0004	0.0005

* Com.Ex. = Comparative Example * PEM = Positive electrode material

[0104] [Table 5]

	Samples	Li/O	Li/MCN	Li/MCNCuFeAl	Co/Mn	Ni/Mn
Example 1	Regenerated PEM (w/o composition adjustment)	0.5109	0.9285	0.9262	0.6686	0.7327
Example 2	Regenerated PEM (with composition adjustment)	0.4912	1.0159	1.0075	1.0857	0.9567
Com.Ex. 1	Regenerated PEM (conventional type)	0.4488	1.1705	1.0931	0.8151	0.8968
Com.Ex. 2	Commercially available PEM	0.5304	1.0790	1.0790	1.0005	1.0079
Com.Ex. 3	Trace product of commercially available PEM	0.4985	1.0224	1.0224	1.0057	1.0207

* Com.Ex. = Comparative Example * PEM = Positive electrode material

[0105] 2. Production of Lithium-Ion Secondary Battery

<Production of Positive Electrode>

As positive electrode active materials, the respective positive electrode materials obtained in Examples 1 and 2 and Comparative Examples 1-3 described above were prepared, and acetylene black (Denka Black, manufactured by Denka Company Limited) was prepared as a conductive additive, polyvinylidene fluoride (KF Polymer F #9130, manufactured by Kureha Corporation) was prepared as a binder, and N-methylpyrrolidone was prepared as a solvent.

[0106]

Each of the positive electrode materials, acetylene black, and polyvinylidene fluoride were mixed at a ratio of 80:10:10 (mass%) to obtain a mixture. N-methylpyrrolidone was added

to the mixture to obtain a slurry. The amount of N-methylpyrrolidone added to the mixture was set such that the mass ratio of the mixture:N-methylpyrrolidone was 1:1.25.

After stirring the obtained slurry for 10 minutes with a stirrer, the slurry was applied onto an aluminum foil (t 20 μm) as a current collector for the positive electrode material using a Baker-type applicator. Then, the slurry was dried together with the aluminum foil in a dryer at 100 °C. The dried aluminum foil and the positive electrode material applied thereon were pressed at 4 t, and thereafter punched out to a diameter of $\phi 15$ mm to obtain a positive electrode.

[0107] <Production of Negative Electrode>

Graphite (CGB-10, manufactured by Nippon Graphite Industries, Co., Ltd.) was prepared as a negative electrode active material, acetylene black (Denka Black, manufactured by Denka Company Limited) was prepared as a conductive additive, carboxymethyl cellulose (Cellogen 7A, manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) and styrene-butadiene rubber (TRD2001, manufactured by JSR Corporation) were prepared as binders, and pure water was prepared as a solvent.

Then, graphite:acetylene black:carboxymethyl cellulose:styrene-butadiene rubber were mixed at a ratio of 90:5:2.5:2.5 (mass%). Distilled water was added to the mixture to obtain a slurry. The amount of distilled water added to the mixture was set such that the mass ratio of the mixture:distilled water was 1:1.6.

After stirring the obtained slurry for 10 minutes with a stirrer, the slurry was applied onto a copper foil (t 20 μm) as a current collector for graphite as the negative electrode material using a Baker-type applicator. Then, the slurry was dried together with the copper foil in a dryer at 100 °C. The dried copper foil and the negative electrode material applied thereon were pressed at 4 t, and thereafter punched out to a diameter of $\phi 15$ mm to obtain a negative electrode.

[0108] <Assembly of Lithium-Ion Secondary Battery>

In a glove box filled with pure argon gas, using a CR2032-type coin cell, a positive electrode current collector (stainless steel) 1, a positive electrode (an aluminum foil current collector coated with a positive electrode material) 2, a separator 3, a gasket 4, a negative electrode (a copper foil current collector coated with a negative electrode material) 5, a spacer 6, a washer 7, and a negative electrode current collector (stainless steel) 8 were stacked in this order, as shown in FIG. 2.

Then, full cells of lithium-ion secondary batteries each using the respective positive electrode materials obtained in Examples 1 and 2 and Comparative Examples 1-3 were assembled by crimping the stainless-steel positive electrode current collector and the stainless-steel negative electrode current collector.

[0109]

Porous polypropylene having a diameter of $\phi 19$ mm (#2500, manufactured by Celgard LLC) was used as the separator, and the electrolyte used LiPF_6 at a concentration of 1 mol/L as a solute and ethylene carbonate + diethyl carbonate (volume ratio 1:1) as a solvent.

For the full cells, the assumed specific capacity of the ordinary positive electrode material and the regenerated positive electrode material was set to 140 mAh/g or 150 mAh/g depending on

the range of change in the cell voltage during charge and discharge. The assumed specific capacity of graphite as the negative electrode material was set to 340 mAh/g. The ratio of the negative electrode capacity to the positive electrode capacity (NP ratio) was set to 1.2. The assumed specific capacity of the positive electrode material used in the full cell is specified each time.

[0110]

Next, half cells of lithium-ion secondary batteries each using the respective positive electrode materials obtained in Examples 1 and 2 and Comparative Examples 1-3 were assembled in the same manner as for the full cells of the lithium-ion secondary batteries described above. The configuration of the half cell was the same as that of the full cell, except that the graphite negative electrode was replaced with a lithium foil having $\phi 15$ mm and $t 0.2$ mm. Also for the half cells, the assumed specific capacity of the ordinary positive electrode material and the regenerated positive electrode material was set to 140 mAh/g or 150 mAh/g depending on the range of change in the potential of the positive electrode. The assumed specific capacity of the positive electrode material used in the half cell is also specified each time.

[0111] 3. Charge-Discharge Test of Lithium-Ion Secondary Battery

For the manufactured half cells and full cells of lithium-ion secondary batteries, a charge-discharge test by a cycle test was performed as described below, and the charge-discharge specific capacity and coulombic efficiency (charge-discharge efficiency, hereinafter simply referred to as “efficiency”) of each positive electrode material obtained in Examples 1 and 2 and Comparative Examples 1-3 were measured. In the half cells and the full cells, the capacity measured during charging and discharging of the cell was divided by the mass of the regenerated positive electrode material in the cell to evaluate the cell performance in terms of the positive-electrode-based specific capacity.

[0112] <Charge-Discharge Test in Positive-Electrode Half Cell>

(Rate Test of Positive-Electrode Half Cell)

Under the following conditions, charging and discharging of the positive electrode, i.e., desorption and insertion of lithium ions, were performed, and the specific capacity and coulombic efficiency at that time were measured.

(1) regenerated positive electrode material (without composition adjustment), (2) regenerated positive electrode material (with composition adjustment), (3) regenerated positive electrode material (conventional type), (4) commercially available positive electrode material, and (5) trace product of commercially available positive electrode material: Assumed specific capacity of the positive electrode material: 140 mAh/g (based on positive electrode material mass)

Test temperature: 25 °C.

Positive electrode potential range: 3.0-4.2 V vs Li/Li⁺.

Current density: 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, 5 C, 10 C, 0.1 C (where 1 C = 140 mA/g (based on positive electrode material mass)).

Number of cycles: 5 at each current density.

[0113] The measurement items are described below.

(I) Specific capacity during charging (lithium-ion desorption) at 0.1 C in the first cycle.

This value indicates the amount of lithium ions desorbed in the process in which lithium ions are initially drawn out from the positive electrode material.

(II) Specific capacity during discharging (lithium-ion insertion) at 0.1 C in the first cycle.

This value indicates the amount of lithium ions inserted in the process in which lithium ions are initially drawn out from the positive electrode material and the lithium ions return to the positive electrode material again.

(III) Coulombic efficiency during charging and discharging at 0.1 C in the first cycle.

This value indicates, in the initial desorption and insertion of lithium ions in the positive electrode material, to what extent the desorbed lithium ions return to the positive electrode material.

(IV) Specific capacity during discharging (lithium-ion insertion) at 0.1 C in the third cycle.

This value indicates the reversible amount of lithium ions in the positive electrode material when the current density is the lowest and the repetition of desorption and insertion of lithium ions in the positive electrode material proceeds slowly and is stabilized to a certain extent.

(V) Specific capacity during discharging (lithium-ion insertion) at 10 C in the third cycle.

This value indicates the reversible amount of lithium ions in the positive electrode material at the highest current density and indicates the degree of compatibility with rapid charge and discharge.

(VI) Specific capacity during discharging (lithium-ion insertion) at 0.1 C in the third cycle of the second stage after the test at 10 C.

This value indicates the reversible amount of lithium ions in the positive electrode material when the repetition of desorption and insertion of lithium ions in the positive electrode material proceeds sufficiently slowly and is stabilized after 35 cycles of charging and discharging while changing the current density from 0.1 C to 10 C.

The results of the rate test of the positive-electrode half cell are shown in Table 6.

[0114]

From the results in Table 6, it was found that the conventional regenerated positive electrode material (Comparative Example 1) having a high aluminum content exhibited low specific capacity and low coulombic efficiency. In contrast, it was found that the regenerated positive electrode materials (Examples 1 and 2) in which the aluminum content was reduced achieved specific capacity and coulombic efficiency values close to those of the trace product of the commercially available positive electrode material (Comparative Example 3). Furthermore, it was also found that the regenerated positive electrode material (Example 2) subjected to composition adjustment of lithium, nickel, and cobalt exhibited specific capacity and coulombic efficiency values almost comparable to those of the commercially available positive electrode material (Comparative Example 2) and the trace product of the commercially available positive electrode material (Comparative Example 3), and depending on the item, even higher values could also be obtained.

	Samples	Rate test (3.0 – 4.2 V vs. Li/Li ⁺)					
		0.1 C, 1st cycle, Li-ion extraction	0.1 C, 1st cycle, Li-ion insertion	0.1 C, 1st cycle, Coulombic efficiency	0.1 C, 3rd cycle, Li-ion insertion	10 C, 3rd cycle, Li-ion insertion	2nd-stage 0.1 C, 3rd cycle, Li-ion insertion
		(mAh/g)	(mAh/g)	(%)	(mAh/g)	(mAh/g)	(mAh/g)
Example 1	Regenerated PEM (w/o composition adjustment)	137.0	119.5	87.2	121.0	28.6	121.7
Example 2	Regenerated PEM (with composition adjustment)	155.0	139.4	90.0	141.8	56.7	139.7
Com.Ex. 1	Regenerated PEM (conventional type)	137.1	98.9	72.1	99.1	14.1	98.9
Com.Ex. 2	Commercially available PEM	160.1	135.3	84.5	141.9	67.7	143.5
Com.Ex. 3	Trace product of commercially available PEM	160.0	143.9	89.9	133.5	56.5	144.4

* Com.Ex. = Comparative Example * PEM = Positive electrode material

[0116] <Charge-Discharge Test of Full Cell>

(A) (Rate Test of Full Cell)

The full cell was charged and discharged at constant current density under the following conditions.

(1) regenerated positive electrode material (without composition adjustment), (2) regenerated positive electrode material (with composition adjustment), (3) regenerated positive electrode material (conventional type), (4) commercially available positive electrode material, and (5) trace product of commercially available positive electrode material: Assumed specific capacity of the positive electrode material regarding: 140 mAh/g (based on positive electrode material mass).

Test temperature: 25 °C.

Cell voltage range: 2.5-4.2 V (initial charge: 0 V-4.2 V).

Current density: 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, 5 C, 10 C, 0.1 C (where 1 C = 140 mA/g (based on positive electrode material mass)).

Number of cycles: 5 at each current density.

[0117] The measurement items are described below.

(I) Specific capacity during charging at 0.1 C in the first cycle. This value indicates the amount of lithium ions desorbed from the positive electrode material in the process in which the full cell is initially charged.

(II) Specific capacity during discharging at 0.1 C in the first cycle. This value indicates the amount of lithium ions inserted into the positive electrode material in the process in which the full cell is initially charged and then discharged.

(III) Coulombic efficiency during charging and discharging at 0.1 C in the first cycle. This value indicates, in the initial charge-discharge process of the full cell, to what extent the lithium ions desorbed during charging return to the positive electrode material during discharging.

(IV) Specific capacity during discharging at 0.1 C in the third cycle. This value indicates the reversible amount of lithium ions in the positive electrode material when the current density is the lowest and the repetition of charging and discharging of the full cell proceeds slowly and is stabilized to a certain extent.

(V) Specific capacity during discharging at 10 C in the third cycle. This value indicates the reversible amount of lithium ions in the positive electrode material during charging and discharging at the highest current density and indicates the degree of compatibility with rapid charging and discharging.

(VI) Specific capacity during discharging at 0.1 C in the second stage after the charge-discharge test at 10 C. This value indicates the reversible amount of lithium ions in the positive electrode material when the repetition of charging and discharging of the full cell proceeds slowly and is stabilized after 35 cycles of charging and discharging while changing the current density from 0.1 C to 10 C.

The results of the full-cell rate test are shown in Table 7.

[0118]

From the results in Table 7, it was found that the conventional regenerated positive electrode material (Comparative Example 1) having a high aluminum content exhibited low specific capacity and low coulombic efficiency. In contrast, it was found that the regenerated positive electrode materials (Examples 1 and 2) in which the aluminum content was reduced showed specific capacity and coulombic efficiency values close to those of the commercially available positive electrode material (Comparative Example 2) and the trace product of the commercially available positive electrode material (Comparative Example 3). In particular, it was found that the regenerated positive electrode material (Example 2) subjected to composition adjustment of nickel and cobalt had performance comparable to that of the positive electrode materials using the virgin materials of Comparative Examples 2 and 3 in both specific capacity and coulombic efficiency.

	Samples	Rate test (2.5 – 4.2 V)					
		0.1 C, 1st cycle, Li-ion extraction	0.1 C, 1st cycle, Li-ion insertion	0.1 C, 1st cycle, Coulombic efficiency	0.1 C, 3rd cycle, Li-ion insertion	10 C, 3rd cycle, Li-ion insertion	2nd-stage 0.1 C, 3rd cycle, Li-ion insertion
		(mAh/g)	(mAh/g)	(%)	(mAh/g)	(mAh/g)	(mAh/g)
Example 1	Regenerated PEM (w/o composition adjustment)	147.6	122.4	82.9	121.7	28.7	115.1
Example 2	Regenerated PEM (with composition adjustment)	152.9	123.4	80.7	133.0	60.1	130.5
Com.Ex. 1	Regenerated PEM (conventional type)	139.7	105.5	75.5	105.8	32.9	109.2
Com.Ex. 2	Commercially available PEM	160.9	129.4	80.5	137.9	67.1	137.6
Com.Ex. 3	Trace product of commercially available PEM	166.8	145.6	87.3	147.1	64.7	144.2

* Com.Ex. = Comparative Example * PEM = Positive electrode material

[0120]

(B) (Cycle Test of Full Cell)

After the rate test of the full cell, the full cell was charged and discharged for a predetermined number of cycles at a constant current density under the following conditions.

Test temperature: 25 °C.

Cell voltage range: 2.5-4.2 V.

Current density: 2 C (280 mA/g (based on positive electrode material mass)).

Number of cycles: 500.

[0121] The measurement items are described below.

(I) Specific capacity during discharging in the first cycle. This value indicates the amount of lithium ions desorbed from the positive electrode material when the full cell is first discharged in a practically required cycle process of repeated charging and discharging at a current density of 2 C, which allows charging or discharging of the full cell to be completed in 30 minutes.

(II) Specific capacity during discharging in the 200th cycle. This value indicates the amount of lithium ions desorbed from the positive electrode material after the full cell has repeated charging and discharging 200 times at a current density of 2 C. In a lithium-ion secondary battery, this corresponds to performance assumed in the early to middle life stage as a product.

(III) Retention rate of discharge specific capacity in the 200th cycle based on the first cycle. This value indicates the cycle durability of the full cell after 200 repetitions of charging and discharging, i.e., up to the early to middle life stage.

(IV) Specific capacity during discharging in the 500th cycle. This value indicates the amount of lithium ions desorbed from the positive electrode material after the full cell has repeated charging and discharging 500 times at a current density of 2 C. This corresponds to performance assumed in the late life stage as a product.

(V) Retention rate of discharge specific capacity in the 500th cycle based on the first cycle. This value indicates the cycle durability of the full cell after 500 repetitions of charging and discharging, i.e., up to the late life stage.

The results of the full-cell cycle test are shown in Table 8.

[0122]

From the results in Table 8, it was found that the conventional regenerated positive electrode material (Comparative Example 1) having a high aluminum content had a specific capacity retention rate comparable to those of the other positive electrode materials, but the specific capacity itself was small. In contrast, it was found that the regenerated positive electrode materials (Examples 1 and 2) in which the aluminum content was reduced had increased specific capacity and higher specific capacity retention rate than the conventional regenerated positive electrode material. In particular, it was found that the regenerated positive electrode material (Example 2) subjected to composition adjustment of nickel and cobalt exhibited a specific capacity and retention rate thereof equivalent to those of the commercially available positive electrode material (Comparative Example 2) and the trace product of the commercially available positive

electrode material (Comparative Example 3), and had cycle durability comparable to that of the positive electrode material using virgin materials.

[0123] [Table 8]

	Samples	Cycle test (2.5 – 4.2 V)				
		2 C, 1st cycle, Li-ion insertion	2 C, 200th cycle, Li-ion insertion	2 C, 200th cycle, Retention	2 C, 500th cycle, Li-ion insertion	2 C, 500th cycle, Retention
		(mAh/g)	(mAh/g)	(%)	(mAh/g)	(%)
Example 1	Regenerated PEM (w/o composition adjustment)	78.9	76.5	96.9	77.0	97.6
Example 2	Regenerated PEM (with composition adjustment)	114.8	106.9	93.2	101.4	88.3
Com.Ex. 1	Regenerated PEM (conventional type)	62.8	60.7	96.7	57.7	91.9
Com.Ex. 2	Commercially available PEM	116.9	110.8	94.8	94.5	80.8
Com.Ex. 3	Trace product of commercially available PEM	120.4	114.0	94.7	107.7	89.5

* Com.Ex. = Comparative Example * PEM = Positive electrode material

[0124] <Charge-Discharge Test of Positive Electrode Half Cell at High Potential>
(Rate Test of Positive Electrode Half Cell at High Potential)

When lithium ions are desorbed and inserted with respect to a positive electrode material at high potential, the specific capacity of the positive electrode material increases, and the storage capacity (energy density) of the full cell increases. On the other hand, when the positive electrode material is exposed to a high potential, i.e., a highly oxidizing atmosphere, stable operation of the positive electrode material becomes difficult. In this test, the specific capacity of the positive electrode material during charging and discharging at high potential and the operational stability thereof are evaluated.

Under the following conditions, charging and discharging of the positive electrode, i.e., desorption and insertion of lithium ions, were performed, and the specific capacity and coulombic efficiency were measured.

(1) regenerated positive electrode material (without composition adjustment), (2) regenerated positive electrode material (with composition adjustment), (3) regenerated positive electrode material (conventional type), (4) commercially available positive electrode material, and (5) trace product of commercially available positive electrode material: Assumed specific capacity of the positive electrode material regarding: 150 mAh/g (based on positive electrode material mass).

Test temperature: 25 °C.

Positive electrode potential range: 3.0 V to 4.5 V vs Li/Li⁺.

Current density: 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, 5 C, 10 C, 0.1 C (where 1 C = 150 mA/g (based on positive electrode material mass)).

Number of cycles: 5 at each current density.

[0125] The measurement items are described below.

(I) 0.1 C, 1st cycle, specific capacity during charging (lithium-ion desorption).

(II) 0.1 C, 1st cycle, specific capacity during discharging (lithium-ion insertion).

(III) 0.1 C, 1st cycle, coulombic efficiency during charging and discharging.

(IV) 0.1 C, 3rd cycle, specific capacity during discharging (lithium-ion insertion).

(V) 10 C, 3rd cycle, specific capacity during discharging (lithium-ion insertion).

(VI) After the test at 10 C, specific capacity during discharging (lithium-ion insertion) in the 3rd cycle at 0.1 C in the second stage.

The results of the rate test of the positive electrode half cell at high potential are shown in Table 9.

[0126] From the results in Table 9, it was found that the conventional regenerated positive electrode material (Comparative Example 1) having a high aluminum content exhibited low specific capacity and low coulombic efficiency even when lithium ions were desorbed up to a high potential of 4.5 V vs Li/Li⁺. The specific capacity and coulombic efficiency of the regenerated positive electrode materials (Examples 1 and 2) in which the aluminum content was reduced were close to those of the commercially available positive electrode material (Comparative Example 2) and the trace product of the commercially available positive electrode material (Comparative Example 3). In particular, the regenerated positive electrode material (Example 2) subjected to composition adjustment of nickel and cobalt exhibited performance comparable to that of the positive electrode materials using virgin materials in Comparative Examples 2 and 3. That is, it

was found that by reducing the aluminum content, the regenerated positive electrode material can achieve high specific capacity and stable desorption and insertion of lithium ions even at a high potential.

	Samples	Rate test (3.0 – 4.5 V vs. Li/Li ⁺)					
		0.1 C, 1st cycle, Li-ion extraction	0.1 C, 1st cycle, Li-ion insertion	0.1 C, 1st cycle, Coulombic efficiency	0.1 C, 3rd cycle, Li-ion insertion	10 C, 3rd cycle, Li-ion insertion	2nd-stage 0.1 C, 3rd cycle, Li-ion insertion
		(mAh/g)	(mAh/g)	(%)	(mAh/g)	(mAh/g)	(mAh/g)
Example 1	Regenerated PEM (w/o composition adjustment)	182.3	159.3	87.3	158.3	56.1	155.1
Example 2	Regenerated PEM (with composition adjustment)	197.7	177.8	89.9	177.1	59.0	171.1
Com.Ex. 1	Regenerated PEM (conventional type)	172.8	131.4	76.0	130.7	15.2	130.2
Com.Ex. 2	Commercially available PEM	206.7	178.5	86.3	178.9	85.7	176.8
Com.Ex. 3	Trace product of commercially available PEM	199.2	177.0	88.9	176.4	0.0	177.5

* Com.Ex. = Comparative Example * PEM = Positive electrode material

[0128] <Charge-Discharge Test of Full Cell at High Cell Voltage>

(A) (Rate Test of Full Cell at High Cell Voltage)

When a full cell is charged and discharged at a high voltage, the storage capacity (energy density) of the full cell increases. On the other hand, in the positive electrode material, since a larger amount of lithium ions are desorbed, the positive electrode material is exposed to a high potential, i.e., a highly oxidizing atmosphere, and thus stable operation as a full cell becomes difficult. Therefore, in this test, the specific capacity of the full cell during charging and discharging at a high voltage and the operational stability thereof are evaluated.

Charging and discharging were performed at a constant current density under the following conditions.

(1) regenerated positive electrode material (without composition adjustment), (2) regenerated positive electrode material (with composition adjustment), (3) regenerated positive electrode material (conventional type), (4) commercially available positive electrode material, and (5) trace product of commercially available positive electrode material: Assumed specific capacity of the positive electrode material: 150 mAh/g (based on positive electrode material mass).

Test temperature: 25 °C.

Cell voltage range: 2.5-4.4 V (initial charge: 0-4.4 V).

Current density: 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, 5 C, 10 C, 0.1 C (where 1 C = 150 mA/g (based on positive electrode material mass)).

Number of cycles: 5 at each current density.

[0129] The measurement items are described below.

(I) 0.1 C, 1st cycle, specific capacity during charging.

(II) 0.1 C, 1st cycle, specific capacity during discharging.

(III) 0.1 C, 1st cycle, coulombic efficiency during charging and discharging.

(IV) 0.1 C, 3rd cycle, specific capacity during discharging.

(V) 10 C, 3rd cycle, specific capacity during discharging.

(VI) After the charge-discharge test at 10 C, specific capacity during discharging at 0.1 C in the second stage.

The results of the rate test of the full cell at high cell voltage are shown in Table 10.

[0130] From the results in Table 10, it was found that the conventional regenerated positive electrode material (Comparative Example 1) having a high aluminum content exhibited low specific capacity and low coulombic efficiency even at a high cell voltage. It was confirmed that the regenerated positive electrode materials (Examples 1 and 2) in which the aluminum content was reduced exhibited specific capacity and initial coulombic efficiency close to those of the commercially available positive electrode material and the trace product thereof even when charged and discharged at a high cell voltage.

	Samples	Rate test (2.5 – 4.4 V)					
		0.1 C, 1st cycle, Li-ion extraction	0.1 C, 1st cycle, Li-ion insertion	0.1 C, 1st cycle, Coulombic efficiency	0.1 C, 3rd cycle, Li-ion insertion	10 C, 3rd cycle, Li-ion insertion	2nd-stage 0.1 C, 3rd cycle, Li-ion insertion
		(mAh/g)	(mAh/g)	(%)	(mAh/g)	(mAh/g)	(mAh/g)
Example 1	Regenerated PEM (w/o composition adjustment)	166.1	140.3	84.5	144.8	53.5	144.9
Example 2	Regenerated PEM (with composition adjustment)	182.0	145.9	80.2	144.4	24.7	140.6
Com.Ex. 1	Regenerated PEM (conventional type)	169.7	129.7	76.4	129.8	22.8	127.3
Com.Ex. 2	Commercially available PEM	185.3	148.6	80.2	155.8	72.0	154.7
Com.Ex. 3	Trace product of commercially available PEM	191.9	165.9	86.4	167.6	76.2	158.3

* Com.Ex. = Comparative Example * PEM = Positive electrode material

[0132] (B) (Cycle Test of Full Cell at High Cell Voltage)

After the rate test of the full cell at a high voltage (2.5-4.4 V), charging and discharging at a high cell voltage were performed at a constant current density for a predetermined number of cycles under the following conditions.

Test temperature: 25 °C.

Cell voltage range: 2.5-4.4 V.

Current density: 2 C (300 mA/g (based on positive electrode material mass)).

Number of cycles: 500.

[0133] The measurement items are described below.

(I) 1st cycle, specific capacity during discharging.

(II) 200th cycle, specific capacity during discharging.

(III) 200th cycle, retention rate of discharge specific capacity with the 1st cycle taken as a reference.

(IV) 500th cycle, specific capacity during discharging.

(V) 500th cycle, retention rate of discharge specific capacity with the 1st cycle taken as a reference.

The results of the cycle test of the full cell at a high voltage after 500 repetitions of charging and discharging i.e., up to the late life stage are shown in Table 11.

[0134] From the results in Table 11, it was found that the conventional regenerated positive electrode material (Comparative Example 1) having a high aluminum content exhibited both a lower specific capacity and a lower retention rate thereof than the other positive electrode materials. The regenerated positive electrode materials (Examples 1 and 2) in which the aluminum content was reduced exhibited increased specific capacity and a higher specific capacity retention rate compared with the conventional regenerated positive electrode material. In particular, the regenerated positive electrode material (Example 2) subjected to composition adjustment of nickel and cobalt had a low initial specific capacity; however, the specific capacity gradually increased with repeated charging and discharging, and extremely high cycle stability was observed. Also in the commercially available positive electrode material (Comparative Example 2), the specific capacity tended to increase up to 200 cycles, and in the cycle test at a high voltage of 2.5 V to 4.4 V, a different behavior from that in the test at a normal voltage of 2.5 V to 4.2 V was observed. The specific capacity of the regenerated positive electrode material in which the aluminum content was reduced after 500 cycles was lower than the value of the commercially available positive electrode material but higher than the value of the trace product of the commercially available positive electrode material (Comparative Example 3), and the specific capacity retention rate after 500 cycles was not low. That is, it was found that even when charged and discharged at a high voltage, the regenerated positive electrode material in which the aluminum content was reduced exhibits cycle durability comparable to that of a positive electrode material using virgin materials.

	Samples	Cycle test (2.5 – 4.4 V)				
		2 C, 1st cycle, Li-ion insertion	2 C, 200th cycle, Li-ion insertion	2 C, 200th cycle, Retention	2 C, 500th cycle, Li-ion insertion	2 C, 500th cycle, Retention
		(mAh/g)	(mAh/g)	(%)	(mAh/g)	(%)
Example 1	Regenerated PEM (w/o composition adjustment)	111.4	102.6	92.1	94.2	84.6
Example 2	Regenerated PEM (with composition adjustment)	89.0	97.6	109.7	105.9	119.0
Com.Ex. 1	Regenerated PEM (conventional type)	62.2	48.6	78.0	44.7	71.8
Com.Ex. 2	Commercially available PEM	128.6	135.2	105.1	126.9	98.6
Com.Ex. 3	Trace product of commercially available PEM	134.9	115.3	85.5	90.3	67.0

* Com.Ex. = Comparative Example * PEM = Positive electrode material

Reference Signs List

[0136]

1: positive electrode current collector

2: positive electrode

- 3: separator
- 4: gasket
- 5: negative electrode
- 6: spacer
- 7: washer
- 8: negative electrode current collector
- 10: lithium-ion secondary battery

CLAIMS

[Claim 1] A method for producing a regenerated positive electrode material precursor from a lithium-ion secondary cell as an object to be processed, the method comprising:

- heating the lithium-ion secondary cell as the object to be processed to obtain heat-treated material;

- crushing the heat-treated material to obtain crushed material;

- classifying and sorting the crushed material to obtain fine-grained products;

- subjecting the fine-grained products to acid leaching to obtain acid leachate;

- performing iron removal by adding an oxidation agent and alkali to the acid leachate to obtain an iron-removed liquid;

- performing ion exchange by bringing the iron-removed liquid into contact with a chelate resin to obtain an ion-exchanged liquid;

- adding alkali to the ion-exchanged liquid to generate a precipitate; and

- washing the precipitate with water to obtain a regenerated positive electrode material precursor.

[Claim 2] The method for producing a regenerated positive electrode material precursor according to claim 1, the method further comprising, after the classifying and sorting of the crushed material, subjecting the fine-grained products to magnetic separation to obtain a magnetically-attracted object.

[Claim 3] The method for producing a regenerated positive electrode material precursor according to claim 1, wherein sulfuric acid is used for the acid leaching.

[Claim 4] The method for producing a regenerated positive electrode material precursor according to claim 1, wherein, in the iron removal, a hydrogen peroxide aqueous solution is used as the oxidation agent, and oxidation reduction potential of the acid leachate is adjusted to 500-750 mV (Ag/AgCl).

[Claim 5] The method for producing a regenerated positive electrode material precursor according to claim 1, wherein, in the ion exchange, an aminomethyl phosphate-based chelate resin is used as the chelate resin to remove aluminum ions.

[Claim 6] The method for producing a regenerated positive electrode material precursor according to claim 1, the method further comprising: quantitatively analyzing a metal element contained in the ion-exchanged liquid; and adjusting makeup of the ion-exchanged liquid in a case in which a result of said quantitative analysis of the metal element contained in the ion-exchanged liquid differs from intended metal composition of the regenerated positive electrode material precursor.

[Claim 7] The method for producing a regenerated positive electrode material precursor according to claim 1, the method further comprising: quantitatively analyzing a metal element contained in the ion-exchanged liquid; and adding a metal element lacking from intended metal composition of the regenerated positive electrode material precursor in a case in which a result of said quantitative analysis of the metal element contained in the ion-exchanged liquid differs from the intended metal composition of the regenerated positive electrode material precursor.

[Claim 8] The method for producing a regenerated positive electrode material precursor according to claim 6, wherein, in the ion-exchanged liquid the makeup of which has been adjusted, an aluminum content is 100 mg/L or less, a copper content is 1 mg/L or less, and an iron content is 1 mg/L or less.

[Claim 9] The method for producing a regenerated positive electrode material precursor according to claim 7, wherein, in the ion-exchanged liquid to which the metal element has been added, an aluminum content is 100 mg/L or less, a copper content is 1 mg/L or less, and an iron content is 1 mg/L or less.

[Claim 10] A method for producing a regenerated positive electrode material, wherein a regenerated positive electrode material is obtained by: adding a predetermined metal compound to the regenerated positive electrode material precursor produced by the method for producing a regenerated positive electrode material precursor according to any one of claims 1 to 9; and then firing the regenerated positive electrode material precursor.

[Claim 11] The method for producing a regenerated positive electrode material according to claim 10, wherein the metal compound is at least one selected from a lithium compound, a nickel compound, a cobalt compound, or a manganese compound.

[Claim 12] A method for using a regenerated positive electrode material, comprising:
assembling a lithium-ion secondary cell comprising the regenerated positive electrode material according to claim 10; and then
activating the assembled lithium-ion secondary cell by charging and discharging the lithium-ion secondary cell.