LITHIUM EXTRACTION METHOD, AND METAL RECOVERY METHOD

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ABSTRACT

To provide a method for recovering lithium from a lithium ion battery using comparatively simple equipment and without using a cumbersome process. A lithium extraction method for extracting lithium from the positive electrode material of a lithium ion battery containing lithium and cobalt, the method being characterized in that the positive electrode material is immersed in an acidic solution at 50°C or less, lithium ions are selectively leached into the acid solution while inhibiting the leaching of cobalt ions, and the leaching of lithium ions is stopped while the amount of lithium contained in the positive electrode material is sufficient.

START

S101 DISMANTLED WASTE BATTERY

S102 SEPARATE MEMBERS

S103 ACID LEACHING OF ELECTRODE ACTIVE MATERIAL (SELECTIVELY LEACH LI)

S104 SEPARATE LI AND TRANSITION METALS

S105 SUPERNATANT

S106 SOLUTION A

S107 RECOVER TRANSITION METAL COMPONENTS

S108 SEPARATE AND RECOVER TRANSITION METALS (COMPONENTS a, b, c)

S109 RECOVER Li2CO3
<table>
<thead>
<tr>
<th>DISSOLUTION CONDITIONS</th>
<th>Co [ppm]</th>
<th>Li [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>COMPLETE DISSOLUTION (SULFURIC ACID:HYDROGEN PEROXIDE: HYDROCHLORIC ACID = 22:1)</td>
<td>835.9</td>
<td>4012.5</td>
</tr>
<tr>
<td>HYDROCHLORIC ACID:METHANOL = 1:1</td>
<td>152.0</td>
<td>612.8</td>
</tr>
<tr>
<td>SULFURIC ACID:METHANOL = 1:1</td>
<td>612.8</td>
<td>273.3</td>
</tr>
<tr>
<td>SULFURIC ACID:HYDROGEN PEROXIDE = 1:1</td>
<td>782.2</td>
<td>607.8</td>
</tr>
<tr>
<td>SULFURIC ACID ONLY</td>
<td>630.7</td>
<td>450.3</td>
</tr>
<tr>
<td>NITRIC ACID ONLY</td>
<td>575.1</td>
<td>523.9</td>
</tr>
<tr>
<td>HOT WATER (65°C)</td>
<td>579.7</td>
<td>18.6</td>
</tr>
</tbody>
</table>

FIG. 1
**FIG. 2**

START

S101 DISMANTLED WASTE BATTERY

S102 SEPARATE MEMBERS

S103 ACID LEACHING OF ELECTRODE ACTIVE MATERIAL (SELECTIVELY LEACH Li)

S104 SEPARATE Li AND TRANSITION METALS

S105

RESIDUE

SUPERNATANT

S106 RECOVER Li₂CO₃

S107 RECOVER TRANSITION METAL COMPONENTS

S108 SEPARATE AND RECOVER TRANSITION METALS (COMPONENTS a, b, c)
### FIG. 3

<table>
<thead>
<tr>
<th></th>
<th>Li(mol) / H₂SO₄ (mol)</th>
<th>TEMPERATURE (°C)</th>
<th>Li/Co RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PRESENT INVENTION</strong></td>
<td>(0.5/6.941)/(1x0.08)=0.9</td>
<td>25</td>
<td>EXCELLENT</td>
</tr>
<tr>
<td><strong>COMPARATIVE EXAMPLE 1</strong></td>
<td>(1.00/6.941)/(0.05x0.2)=14</td>
<td>65 ~ 70</td>
<td>FAIR</td>
</tr>
<tr>
<td><strong>COMPARATIVE EXAMPLE 2</strong></td>
<td>(100/6.941)/(0.7x0.224)=92</td>
<td>—</td>
<td>FAIR</td>
</tr>
</tbody>
</table>
FIG. 4

START

- S201 DISMANTLED WASTE BATTERY
- S202 SEPARATE MEMBERS
- S203 ACID LEACHING OF ELECTRODE ACTIVE MATERIAL (SELECTIVELY LEACH Li)
- S204 DISSOLVE RESIDUE (CATHODE ACTIVE MATERIAL)

SUPERNATANT

- S205 SEPARATE Li AND Co
- S206 RECOVER Co CONCENTRATED SOLUTION
- S207 RECOVER Li CONCENTRATED SOLUTION
- S208 RECOVER Li2CO3
- S209 RECOVER Co CONCENTRATED SOLUTION
LITHIUM EXTRACTION METHOD, AND METAL RECOVERY METHOD

TECHNICAL FIELD

[0001] The present invention relates to a metal recovery technique for simply recovering metals from batteries.

BACKGROUND ART

[0002] Recently, with the development of the portability of electronic devices, the number of rechargeable batteries used has been steeply increased. In addition to devices consuming relatively smaller electric power such as cellular phones and portable music players, the scope of the application of rechargeable batteries has been widened to also cover instruments requiring high output power such as electric tools, electric bicycles, and electric vehicles; thus, the lithium ion batteries capable of obtaining high energy density have been attracting attention. The increased application to high output power instruments has enhanced the necessity of recovering valuable substances from spent batteries, and there have been proposed various techniques to recover valuable metals from lithium ion batteries.

[0003] For example, Non Patent Literature 1 features the techniques for recycling lithium ion batteries, and systematically describes the methods for recovering valuable metals constituting lithium ion batteries. According to the typical recycling methods published in Non Patent Literature 1, for example, spent lithium ion batteries are subjected to mechanical separating such as unsealing, dismantling and shredding, then valuable metals are leached by acid leaching, and from the acid-leached metals, each of the components is separated and made to form precipitates by taking advantage of the differences between the solubility properties of the desired components, or alternatively, each of the desired components is separated and recovered by applying processing such as preferential solvent extraction of each of the desired components.

[0004] Patent Literature 1 also discloses a technique to recover copper and cobalt by using a leached solution of valuable metals obtained by acid leaching as a catholyte, and by applying diaphragm electrolysis method with a cation exchange membrane as the diaphragm.

CITATION LIST

Patent Literature


Non-Patent Literature


SUMMARY OF INVENTION

Technical Problem

[0009] Non Patent Literature 1 aims at, with the aid of various contrivances, the establishment of compatibility between the improvement of the yield of valuable substances and the achievement of high purities of the recovered substances; however, there is a large room for improvement in the fact that the steps involved are cumbersome and a huge equipment investment is required for the processing of a large amount of waste batteries.

[0010] In Patent Literature 1, specifically, an apparatus (a diaphragm electrolysis tank shown in FIG. 2 of Patent Literature 1) utilizing the ion selectivity possessed by a cation exchange membrane and a diffusion dialysis apparatus (not shown) utilizing the anion selective properties of an anion selective membrane are used. In a more specific description, the main valuable metals can be recovered by the following series of processings: the electrodeposition recovery of copper by diaphragm electrolysis → pH control → the electrodeposition recovery of cobalt by diaphragm electrolysis → pH control → the precipitation recovery of Fe(OH)₃ and Al(OH)₃ → the recovery of Li₂CO₃ by addition of a carbonate. According to this technique, copper (divalent ion) and cobalt (trivalent ion) are electrochemically reduced to recover copper and cobalt, and hence high purity metals can be obtained; however, there is a room for improvement in the fact that when a large amount of waste batteries are processed, it is necessary to apply a huge quantity of electricity.

[0011] For example, the recovery of about 100 kg of cobalt requires a continuous flow of an electric current of 1 ampere for 100 hours, and preceding the recovery of cobalt, a nearly the same quantity of electricity is applied in the electrodeposition of copper, hence the recovery of all the metals only by diaphragm electrolysis requires unexpected time and labor. Further, the multiple stages of pH control increase the liquid quantity at every stage, and hence when Li₂CO₃ is recovered at the final stage of the series of processings, the Li concentration is decreased and even the addition of a carbonate does not necessarily leads to the increase of the Li yield. This is because the saturated solubility of lithium carbonate is as high as 1.3 wt % at 20°C, and hence the amount of unrecovered component is increased with the increase of liquid quantity. In order to avoid such a situation, it is necessary to add a process such as a concentration step. Further, Fe(OH)₃ and Al(OH)₃ each have a tendency to be gelated in a weakly acidic to neutral aqueous solution, and hence the operation in the step of filtrating recovery of Fe(OH)₃ and Al(OH)₃ on the basis of the technique of Patent Literature 1 is not easy. On the other hand, the dilution of the solution for facilitation of the filtration operation results in a decrease of the Li yield. Since the surface of the gel-like precipitation of Fe(OH)₃ or Al(OH)₃ has a characteristic of absorbing Li ion, also from the viewpoint of this absorption, it is difficult to significantly improve the Li yield.

Solution to Problem

[0012] The outline of a representative aspect of the invention disclosed in the present application can be briefly described as follows.

[0013] The present invention is characterized in that lithium is selectively leached from the cathode material containing lithium and transition metals, and the leaching is terminated while the ratio of the leached amount of lithium to the leached amount of cobalt is large.

Advantageous Effect of Invention

[0014] According to the present invention, a method for recovering lithium in a simple and easy manner and highly efficiently from lithium ion batteries can be provided.
BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a table showing compositions of the leaching liquids according to Examples of the present invention and the Li:Co ratios obtained with the leaching liquids.

FIG. 2 is a schematic flow chart of the steps of recovering valuable metals in Example 1 according to the present invention.

FIG. 3 is a table showing the concentrations of lithium ions in sulfuric acid in the acid leaching treatment.

FIG. 4 is a schematic flow chart of the steps of recovering valuable metals in Example 2 according to the present invention.

DESCRIPTION OF EMBODIMENTS

Hereinafter, the embodiments for implementing the present invention are described. When they are described with reference to the accompanying drawings, the description is made by denoting with a symbol each of the members constituting the drawings; however, when functions are the same, sometimes the symbols and description may be omitted. The dimensions of the members shown in the drawings are sometimes not necessarily proportional to the actual dimensions of the members.

EXAMPLE 1

The outline of the method for recovering valuable metals of present Example is described with reference to FIG. 2. FIG. 2 is a schematic flow chart of the steps of recovering valuable metals from waste lithium batteries (hereinafter, waste batteries) in present Example. First, the individual constituent members obtained by dismantling the waste batteries (S101) are sorted according to the types of the individual members (S102), and only the electrode active material containing valuable metals in high concentrations is extracted. The electrode active material thus extracted is treated with a Li-selective leachate (Li-selective leaching; S103) to yield a Li-leaching solution. The Li-leaching solution and the non-leached fraction are subjected to solid-liquid separation (S104). Mixing of a carbonate with the solution A containing Li (S105) enables the recovery of Li as Li2CO3 (S106). The B (S107) in which transition metals are relatively concentrated is still a solid. Then the B is subjected to acid dissolution and the pH of the resulting solution is adjusted. By such simple operations, transition metals are precipitated and sedimented as hydroxides, and these hydroxides are recovered by filtration (S108). Such a series of operations enable the valuable metals and the excessive acid to be respectively recovered.

Hereinafter, according to the steps shown in FIG. 2, the flow of the recovery of valuable metals is described in more detail.

The recovery of valuable metals from waste batteries first requires the dismantling of the batteries, however, before the dismantling, the batteries are discharged because charge may remain stored in the batteries. In present Example, the charge remaining stored in the batteries are discharged by soaking the batteries in an electrolyte-containing conductive liquid.

This discharge operation enables the Li ions scattered in each of the batteries to be concentrated within the cathode active material, and enables the Li yield to be maximized. By ensuring the condition in which Li is incorporated into a specific crystal structure, the Li selectivity is maximized. When the cathode active material is LiCo2O4, the completely charged condition is said to be Li4-xCoO2 and the completely discharged condition is said to be LiCo2O4, so that the omission of the discharge treatment results in a risk of the Li recovery loss of at most about 60%. Needless to say, the discharge provides an advantage capable of ensuring the safety.

In present Example, as the electrolyte-containing conductive liquid, a sulfuric acid-y-butyrolactone mixed solution was used. In the mixed solution, sulfuric acid acts as an electrolyte, and hence by regulating the sulfuric acid concentration, the electroconductivity (reciprocal of resistance value) can be regulated. In present Example, the electric resistance between the right end and the left end of the electrolysis tank was actually measured to be 100 kΩ. A too small resistance of the solution leads to a risk of a too rapidly proceeding discharge, and on the contrary, a too large resistance leads to degradation of practicability because of too long discharge time. In present Example, it is preferable that the solution resistance falls within a range from about 1 kΩ to 1000 kΩ, and the electrolyte concentration may be regulated so that the solution resistance falls within this resistance range.

The waste batteries of present Example include, for example, in addition to so-called spent batteries in which the predetermined limit of the charge-discharge cycle number is reached and the charging capacities are completely decreased, the pre-products occurring due to the failures in the battery production steps, and older-type clearance products in stock occurring due to product specification changes.

In S101, the waste batteries subjected to discharge treatment are dismantled. By using appropriate methods, the battery constituent members such as cases, packings and safety valves, circuit elements, spacers, current collectors, separators, cathode and anode electrode active materials are dismantled and separated according to the types of the individual members.

The interior of the waste batteries is often filled with gas to be in a pressurized condition, and hence, needless to say, consideration of safety in operation is necessary. In the present Example, the waste batteries were elutriated while the waste batteries were being soaked and cooled in the electrolyte-containing conductive liquid. The elutriation of this elutriation under cooling enabled the fragmentation to be safely performed without scattering the gas filled in the interior of the batteries in the air.

In order to promote the exfoliation of the cathode active material and the anode active material coated and formed on the surfaces of the current collector from each of the current collector surfaces, the regulation of the composition of the electrolyte-containing conductive liquid is permissible. In the conductive liquid used in the discharge step, the conductivity is the property to be noted, and in the conductive liquid used in the elutriation step, the viscosity and the dielectric constant are the properties to be noted. The elutriation step and the elutriation step are different in the required specifications, and hence the composition of the conductive liquid may be changed according to the steps. However, in such a case, two or more types of conductive liquids are required to be prepared. In the present Example, from the viewpoint of simplification and suppression of time and labor, and cost, the compositions of these conductive liquids were set to be the same.
Examples of the elution methods usable in the present Example include, without necessarily being limited to, a method using a ball mill. By omitting the roasting step before the shredding is performed, lithium cobalt oxide and polyvinylidene fluoride (PVDF) serving as a binder are not mixed with each other, and lithium and cobalt can be recovered with satisfactory purities. This is because the roasting step decomposes PVDF and generates a fluorine-containing compound to make the cathode material be water repellent. The cathode material made to be water repellent affects the below-described lithium extraction step. The waste batteries are fragmented under the conditions that the electrode active material of the cathode (hereinafter, the cathode active material) and the electrode active material of the anode (hereinafter, the anode active material) are preferentially fragmented among the constituent members such as cases, packings and safety valves, circuit elements, spacers, current collectors, separators and electrode active materials, then the resulting shredded matter is subjected to sieving. In this way, the cathode active material and the anode active material are separated and recovered under the sieve, and the rest of the shredded matter is separated and recovered on the sieve (S102).

Although sieving is applied in the present Example, elution is applied at the very start, so that the slurry obtained by the elution can also be filtrated for separation by using a comparatively coarse filter. By introducing a continuous processing involving the operations from the elution to the filtration, the yield may also be improved. The members such as cases, packings and safety valves, current collectors (aluminum foil, copper foil) are larger in deflected malleability than the cathode active material (typically, LiCoO₂) and the anode active material (typically graphite), and accordingly also larger in strength at fracture. Because of this property, the fragmented matter of the electrode active materials is smaller in size than the fragmented matters obtained from the members other than the electrode active materials, and consequently, the electrode active materials can be easily separated and recovered by sieving or filtrating.

The matter under the sieve obtained by the foregoing treatment is subjected to the leaching treatment (S103).

The leaching liquids used in present Example are shown as examples in FIG. 1. The cathode active material of the waste batteries used in the present Examples is a lithium compound mainly composed of LiCoO₂, and may include the cathode active materials having other compositions including, for example, iron phosphate, nickel and manganese.

As the mineral acid usable in the present Example, an acidic solution prepared by adding hydrogen peroxide aqueous solution as an oxidation-reduction control agent to concentrated sulfuric acid (90% to 98%) is used. Those mineral acids that contain the alkali metals (sodium, potassium, rubidium and cesium) other than lithium, difficult to be separated from lithium, are not to be used. In consideration of, for example, the type and composition of the lithium compound, the treatment amount and the cost, the mineral acids to be used can be appropriately selected.

In the leaching treatment, it is understood that H₂SO₄, Li₂CO₃ and H₂O₂ are allowed to react with each other to produce Li₂SO₄, CO₂ and SO₂. This reaction is divided into two stages. In the first stage, while the crystal structure is being maintained, the lithium ion in the cathode material and the proton in the solution are exchanged. In the second stage, the crystal structure starts to collapse due to the increase of the amount of lithium eluted from the crystal structure of the cathode material. In this case, the ion elution behavior is changed and the elution of cobalt ion is also made easy. Accordingly, it is important that lithium is dissolved before the collapse of the crystal structure and the dissolution reaction is terminated before the crystal structure collapses and the amount of the elution of cobalt becomes large.

In the present Example, when sulfuric acid and hydrogen peroxide are allowed to react with the cathode material, first lithium ion leaches into the solution due to the easiness in reaction based on the reaction energy, and subsequently, cobalt ion leaches. When the leaching treatment is terminated after lithium ion leaches and before cobalt ion leaches, a selective acid dissolution can be performed in such a way that the lithium ion concentration is higher relative to the cobalt ion concentration. In the present Example, the selective acid leaching is performed by controlling the reaction conditions of the Li selective leaching step, and the leaching is terminated within a reaction percentage range of the lithium ion of at most 80% or less (the residual proportion is 20% or more). Practically, in consideration of errors, when the leaching treatment is terminated preferably at a reaction percentage of about 70 to 75% (the residual proportion is 25 to 30%), the elution of cobalt can be suppressed. Reaction percentages exceeding 80% enhance the risk of the degradation of the selection ratio in the Li selective leaching reaction, and reaction percentages lower than 70% decrease the yield to impair the economic efficiency.

The acid leaching treatment is performed at a temperature of 50°C or lower. The action of sulfuric acid allows lithium ion to leach as lithium sulfate (Li₂SO₄), and cobalt ion to leach as cobalt sulfate (CoSO₄). The activation energy for lithium ion to leach is remarkably smaller than the activation energy for cobalt ion to leach, and consequently, the lithium ion leaches in advance of the cobalt ion. This reaction selectivity appears more remarkably at lower temperatures. This is because at higher temperatures, the thermal energy is abundant and the effect of the magnitude of the activation energy on the reaction selectivity is smaller.

Since the solubility of lithium sulfate is increased with the decrease of the temperature and the solubility of cobalt sulfate is increased with the increase of the temperature, by performing the treatment at a low temperature of 50°C or lower, the selective dissolution of lithium can be enhanced. This is because when the dissolution amount of cobalt sulfate is small, the leaching amount of the cobalt ion forming cobalt sulfate is also small. In addition, since the dissolution rate of the ion is slow, the lithium ion which tends to be dissolved stably can be dissolved in advance of the cobalt ion.

The sulfuric acid to be used is preferably concentrated sulfuric acid (90% or more). Diluted sulfuric acid acts as a strong acid, and dissolves both lithium and cobalt at fast rates. On the other hand, when concentrated sulfuric acid is used, the content of isolated acid is small so that it does not act as a strong acid. Consequently, when concentrated sulfuric acid is used (also when the 90% sulfuric acid is diluted to some extent), the concentrated sulfuric acid does not act as a strong acid as the diluted sulfuric acid, and hence the dissolution rate of the metal ion becomes slow to facilitate the control of the dissolution rates of lithium and cobalt.

Even when diluted sulfuric acid is used, the dissolution amount of cobalt sulfate, which has a sulfate ion, becomes small in a solution having a small pH to enhance the lithium ion selectivity. In particular, it is preferable to regulate
the concentration and amount of sulfuric acid and the addition amount of lithium in such a way that the concentration ratio of lithium ion to sulfuric acid is 7 or less during the acid leaching treatment. This is because such a concentration ratio range allows the selective solubility to be high. FIG. 3 shows the examples of the concentration ratio of lithium ion to sulfuric acid during the acid leaching treatment. As in Comparative Example 1 (Patent Literature 2) and Comparative Example 2 (Patent Literature 3), in the case where the concentration ratio of lithium ion to sulfuric acid during the acid leaching treatment is an incomparably larger value as compared to the present Example, the Li/Co ratio takes a low value.

[0040] Hydrogen peroxide is used as an oxidation-reduction control agent for regulating the electric potential in the acid solution, increased by the dissolution. This is because the electric potential falling out of the predetermined range affects the selective solubility.

[0041] When the leaching step is performed without performing the roasting step in the battery dismantling, it is possible to avoid the situation in which the surface of the cathode material is made to repel water as described above by the substance due to PVD serving as the binder and the selective dissolution does not occur.

[0042] In the present Example, FIG. 1 shows Li/Co concentration ratios of the acid leachates obtained by dismantling spent lithium ion batteries for use in digital cameras. The spent lithium ion battery was processed as follows.

[0043] First, the waste lithium ion battery was subjected to the shredding process and the sieving process to beforehand remove the members such as a case, packing and safety valve, circuit elements, separators and current collectors, and then the valuable metals constituting the lithium ion battery were subjected to acid leaching (dissolving) by using mineral acids. The Li-selective leaching liquids used in the present Example are shown in FIG. 1. The resulting leachate was stirred at room temperature for 1 hour, subjected to centrifugal separation with a centrifuge separator at 15000 rpm, at 20° C. for 15 minutes, thus a supernatant and a residue were separated to terminate the leaching reaction, and the supernatant was recovered.

[0044] In the present Example, the centrifugal separation was adopted as the solid-liquid separation to simply terminate the Li leaching reaction from the cathode active material such as lithium cobalt oxide.

[0045] As the acid used in the leaching liquid, nitric acid, sulfuric acid and hydrochloric acid were used. To these acids, the oxidation-reduction control agent such as methanol or hydrogen peroxide was added. The addition of the oxidation-reduction control agent provides an effect to stabilize the acid leaching and the effect to increase the recovery amount. The leaching time is preferably at the longest 2 hours or less and more preferably about 1 hour. The leaching for a short time significantly less than 1 hour, for example, 15 minutes tends to give a small yield. The crystal structure of the cathode active material from which lithium ion has been removed by leaching is not stable against a strong acid, and accordingly when a leaching treatment for a long time exceeding 2 hours is performed, the crystal of the cathode active material collapses to start the leaching of cobalt. Consequently, the Li selectivity in the acid leaching reaction is degraded. In addition, sufficient attention is paid so that the leaching liquid temperature may not reach the leaching liquid temperature of 80° C. to 90° C. adopted in the nonselective leaching (complete leaching) described in Non Patent Literature 1. In the present Example, the leaching liquid temperature is most preferably room temperature (15° C. to 30° C.), and the highest acceptable temperature is 50° C. or lower. When the leaching liquid temperature significantly exceeded 50° C., the Li selectivity tended to be degraded in the leaching reaction.

[0046] FIG. 1 shows results obtained by performing the leaching reaction under respective dissolution conditions at 20° C. (exclusive of the case of hot water) for 1 hour. As shown in FIG. 1, in the case where the cathode material (LiCoO₂) was completely leached (complete dissolution), the Li/Co concentration ratio of the acid leachate was about 0.2. When the acid leaching liquid was composed only of sulfuric acid, the Li/Co concentration ratio was about 1.2, and when the acid leaching liquid was composed only of nitric acid, the Li/Co concentration ratio was about 0.8. When the acid leaching was performed with the acid leaching liquid having a composition of sulfuric acid:hydrogen peroxide=1:1, the Li/Co concentration ratio was about 1.7. In the recovery solution (A) obtained by the selective leaching, in addition to Li, the acid added excessively at the time of the acid leaching is simultaneously recovered.

[0047] In the present Example, the residue left after the completion of the leaching treatment is composed of the transition metal component of the anode active material and the cathode active material. The acidic solution, the anode active material and the cathode active material can be easily separated from each other by taking advantage of the different specific gravities thereof ((S104) in FIG. 2). Specifically, these can be separated from each other by performing centrifugal separation of the leachate. In the present Example, although the separation and recovery were performed by adopting centrifugal separation and treating at 15000 rpm for 15 minutes, a more larger frequencies of rotation facilitates the mutual separation of the supernatant acidic solution (recovery solution, Li), the anode active material (C: carbon) and the cathode active material (Co). As a method for separating and recovering other than by taking advantage of the specific gravity difference, by filtrating the leachate, the leachate can be separated into the supernatant and the residue (the anode active material and the cathode active material) to be recovered. In this case, a step of further separating the residue into the anode active material and the cathode active material is to be performed.

[0048] The Li-containing supernatant may be subjected to further separation of lithium and cobalt by performing the treatments such as a diffusion dialysis treatment or a pressure dialysis treatment using an anion exchange resin, and an ion exchange resin treatment, each alone or in combinations, or in multi-stages,. Alternatively, lithium and cobalt can be further separated, for example, by using a dialysis treatment using an anion permselective membrane, a solvent extraction method or an acid retardation method. Although various methods can be used for the purpose of separating and recovering each of the elements from these residual solutions, a diaphragm electrolysis method, a recovery of hydroxide precipitation by neutralization (pH=6 to 9) and a combination of these methods can be used. By performing these methods, the Li/Co concentration ratio can be further enhanced.

[0049] High-purity lithium can be recovered (S105) by neutralizing the recovery solution (A) having a large content proportion of lithium obtained as described above with a carbonate containing no sodium.

[0050] Specifically, lithium can be recovered by precipitation as lithium carbonate by adding calcium carbonate or a
carbonate containing no sodium. Additionally, for example, there is a method in which CO₂ gas is made to blow in while the electrodialysis is being performed. In the present Example, the transition metal component (B) can be separated and recovered from the Li-containing solution (A) by the centrifugal separation step taking advantage of the specific gravity difference (S106).

[0051] On the other hand, in the recovery of Co from the acid leachate in which Co was selectively separated, first, from the fraction separated in S104, the cathode active material is recovered (S107). Then, the cathode material is soaked in an acidic solution and cobalt ion is leached (or eluted). To the solution in which cobalt ion is leached, a precipitation recovery method in which cobalt is precipitated and recovered as hydroxide by pH control can be used (S108). For the purpose of separating and recovering each of the metals in the transition metal component (B), the transition metal component (B) is dissolved in an acid, then by a treatment utilizing the solubility property difference between the hydroxides of the individual metal elements, basically by repeating a cycle of pH control and recovery by precipitation, each of the transition metal elements can be separated and recovered. When the cathode active material contains lithium compounds other than LiCO₃, specifically, when the cathode active material is LiNiO₂, LiMnO₂, Li(NiₓCoₓ)O₂, or one of olivine-based cathode materials such as LiCoPO₄, LiFePO₄, LiCoPO₄ and LiFePO₄, Co, Ni, Mn and Fe can be separated as hydroxides and recovered by precipitation by the pH control of the solution.

EXAMPLE 2

[0052] FIG. 4 shows a flow chart of the metal recovery method in Example 2.

[0053] S201 and S202 are the same as S101 and S102 in Example 1, respectively. In S203, the cathode material is subjected to acid leaching in the same manner as in Example 1, and then the resulting leachate is separated into a supernatant and a residue. The supernatant is an acidic solution in which lithium ion and cobalt ion are leached and the Li/Co ratio is high, and the residue is the cathode active material left after the leaching of the anode active material and ions. By using a method such as centrifugal separation or filtration, these are separated into the supernatant and the residue.

[0054] In S204, by further dissolving the residue in an acidic solution, the cobalt and lithium contained in the cathode active material in the residue are ionized and dissolved in an acidic solution. Here, since the targets are the cobalt and lithium, anode active materials composed of carbon may be removed before the dissolution, and only the cathode active material may be dissolved. Thus, an acidic solution having a low Li/Co ratio is produced.

[0055] In S205, the lithium ion and the cobalt ion in the supernatant obtained in S203 are separated. Examples of the separation method include the following.

[0056] By using an anion permeselective membrane (dialysis membrane), lithium ion and cobalt ion can be separated. The anion permeselective membrane is a membrane allowing anions to permeate, however, although lithium ion is a cation, a phenomenon occurs in which lithium ion permeates the anion permeselective membrane. Consequently, when the acidic solution in which ions were leached in S203 is made to flow on one side of the anion permselective membrane, and a recovery liquid (for example, pure water) for recovering lithium ion is made to flow on the other side, lithium ion permeates the dialysis membrane and transfers from the acidic solution into the recovery liquid. In this case, cobalt ion does not permeate the dialysis membrane and stays in the acidic solution. In this way, the lithium ion can be separated into the recovery liquid, and the cobalt ion can be separated in the acidic solution.

[0057] Additionally, by using an ion exchange resin, the lithium ion and the cobalt ion can be separated. The acid retardation is known in which when an acidic solution is made to pass through the ion-exchange resin, first a salt of the acid is eluted, and subsequently the acid is eluted. In this case, when the lithium ion and the cobalt ion are contained as the salts of the acid, first the cobalt ion is eluted and subsequently the lithium ion is eluted, and finally the acid is eluted. When the eluted liquid is divided as a function of time, the solution eluted first is large in the cobalt ion concentration, the solution eluted subsequently is large in the lithium ion concentration, and thus, the lithium ion and the cobalt ion can be separated.

[0058] In this way, the supernatant can be separated into the Li concentrated solution having a high Li/Co concentration ratio and the Co concentrated solution having a low Li/Co concentration ratio.

[0059] In S206, the lithium ion and cobalt ion in the acidic solution obtained in S204 are separated, and the Li concentrated solution and the Co concentrated solution are obtained. As the separation method, the same method as in S205 can be applied.

[0060] In S207, the Li concentrated solutions obtained in S204 and S205 are recovered. In S208, by the same method as in S106, lithium is recovered from the Li concentrated solution.

[0061] In S209, the Co concentrated solutions obtained in S204 and S205 are recovered. In S208, by the same method as in S108, lithium is recovered from the Li concentrated solution.

[0062] In Example 2, in this way, lithium and Co are recovered. As compared to Example 1, in addition to the step of separating lithium and Co, the obtained Li concentrated solution and the Co concentrated solution are respectively collected and recovered, and thus the yields of lithium and Co are improved.

1. A lithium extraction method extracting from a cathode material of a lithium ion battery, containing lithium and cobalt, the lithium extraction method comprising:

a step of leaching lithium ion into an acidic solution by soaking the cathode material in the acidic solution at 50°C or lower, and

a step of terminating the leaching of lithium ion when a lithium content of the cathode material is 30% or more of a lithium content of the cathode material before the step of leaching.

2. The lithium extraction method according to claim 1, wherein the acidic solution comprises sulfuric acid.

3. The lithium extraction method according to claim 2, wherein the acidic solution is concentrated sulfuric acid.

4. The lithium extraction method according to claim 1, wherein the acidic solution comprises an oxidation-reduction control agent.

5. The lithium extraction method according to claim 4, wherein the oxidation-reduction control agent is hydrogen peroxide.
6. A metal recovery method comprising:
   a step of recovering lithium from the leached lithium ion-
   containing solution obtained by the lithium extraction
   method according to claim 1; and
   a step of recovering Co from the cathode material used in
   the lithium extraction method according to claim 1.
7. The metal recovery method according to claim 6,
   wherein the metal recovery method comprises a step of
   further separating the leached lithium ion-containing
   solution into a solution having a larger proportion of
   lithium ion and a solution having a larger proportion of
   Co ion; and
   lithium is recovered from the solution having a larger pro-
   portion of lithium ion.