

# Recovery of metal values from spent lithium-ion batteries with chemical deposition and solvent extraction

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## Abstract

This paper describes a new recycling process of metal values from spent lithium-ion batteries (LIBs). After the dismantling of the spent batteries steel crusts, the leaching of battery internal substances with alkaline solution and the dissolving of the residues with  $H_2SO_4$  solution were carried out. Then mass cobalt was chemically deposited as oxalate, and Acorga M5640 and Cyanex272 extracted the small quantities of copper and cobalt, respectively. Lithium was recovered as deposition of lithium carbonate. It is shown that about 90% cobalt was deposited as oxalate with less than 0.5% impurities, and Acorga M5640 and Cyanex272 were efficient and selective for the extraction of copper and cobalt in sulfate solution. Over 98% of the copper and 97% of the cobalt was recovered in the given process. In addition, the waste solution was treated innocuously, and  $LiCoO_2$  positive electrode material with good electrochemical performance was also synthesized by using the recovered compounds of cobalt and lithium as precursors. The process is feasible for the recycling of spent LIBs in scale-up.

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**Keywords:** Recycling process; Spent lithium-ion batteries; Chemical deposition; Solvent extraction; Metal values

## 1. Introduction

Nowadays, lithium-ion batteries (LIBs) are widely used as electrochemical power sources in mobile telephones, personal computers, video-cameras and other modern-life appliances. It must be noted that equal amounts of spent LIBs, which contain lots of chemical substances such as copper, cobalt, lithium and organic electrolyte, will be produced after the lifetime failure of these LIBs. Therefore, the recycling of major components from spent LIBs is considered to be a beneficial way to prevent environmental pollution and as alternative resources of cobalt and copper. By now, several processes for the recycling of spent LIBs have been proposed, and cobalt, lithium and copper are usually recovered [1–9].

As simple and economical treatment methods, the  $LiCoO_2$  electrodes were separated firstly from spent LIBs by Zhang et al. [2] and Lee and co-workers [3], and then the valuable cobalt was recovered. Therein, for Zhang  $LiCoO_2$

active material was peeled off from aluminum substrate and leached with hydrochloric acid, then using solvent extraction with PC-88A separated cobalt, lithium was precipitated as carbonate. For Lee,  $LiCoO_2$  was separated from spent electrodes in a single synthetic step using hydrothermal method in a concentrated  $LiOH$  solution at  $200^\circ C$  without any scraping procedure, and the renovated  $LiCoO_2$  cathode material was obtained simultaneously. Inevitably, a separation system should be developed to match the electrodes separation in the scale-up recycling process. Contestabile et al. [4] presented a laboratory-scale spent LIBs recycling process without the separation of anode and cathode electrodes. The battery rolls were treated with *N*-methylpyrrolidone (NMP) at  $100^\circ C$  for 1 h,  $LiCoO_2$  was effectively separated from their support substrate and recovered, and the recovery of both copper and aluminum in their metallic form was also achieved. Although this process was very convenient, the recovery effects of  $LiCoO_2$  were demonstrated to be influenced by the used adhesive agent and rolling method of electrodes.

In addition, because of the importance of treating the outer cases and shells in given recycling process of spent batteries,

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the pretreatment methods of spent LIBs were also studied. In the process given by Lee and Rhee [5,6], LIB samples were successively thermally treated at 100–150 °C, disassembled with a high-speed shredder and classified into the range 1–10 nm in size, then LiCoO<sub>2</sub> electrode material was finally separated from the current collectors by vibrating screening and burning off carbon and binder after a two-step thermal treatment. The obtained LiCoO<sub>2</sub> was leached with nitric acid solution and subsequently used to synthesize LiCoO<sub>2</sub> electrode material. In the process patented by Lin et al. [7], a prometallurgical process combined with hydrometallurgical process was reported. The spent batteries was firstly calcined and sieved to generate an ash containing metals and metal oxides, and then the ash was subjected to a dissolution etching treatment with hydrochloric acid. Secondly, metal copper and cobalt were separated out using a membrane electrolysis method after filtration, and carbonate ion was added to the solution to form lithium carbonate. In the method patented by Tanii et al. [8], the plastic cases of batteries were chilled to –50 °C or lower temperature and mechanically separated from sealed battery cells, then the sealed battery cells were heated to over 200 °C in a non-oxidizing atmosphere to separate mainly the organic materials, while the targeted valuable materials were separated in one or more separation processes. These recycling processes are suitable to the scale treatment of spent LIBs. It is also shown that some special equipment such as temperature controller, dismantling equipments and element separation must be designed to match these given methods.

In our opinions, the cost of treatment process must be given particular consideration to a large-scale recycling of spent batteries. So, with the exploitation of battery dismantling machine (CN Application No. 200410051922.1) and the investigation of solvent extraction on the separation of copper and cobalt [9], a recycling process based on hydrometallurgical method for spent LIBs has been developed in our laboratory. In this paper, the dismantling of spent LIBs, the recovery of cobalt, copper and lithium using chemical deposition and solvent extraction methods, and the reuse of recovered compounds to synthesize LiCoO<sub>2</sub> cathode material are presented.

## 2. Experimental

### 2.1. Materials

The square-shaped spent LIBs used in this work were kindly provided by Greatpower Battery Co. Ltd., in which LiCoO<sub>2</sub> pasted on aluminum foil, carbon powder pasted on copper foil, LiPF<sub>6</sub>/EC + DMC electrolyte and separator are contained. The single cell weighs an average of 25.1 g; its internal roll weighs about 15.4 g. In order to obtain the chemical composition of the desirable metal values in spent LIBs, a piece of internal roll was dissolved with 3 mol L<sup>-1</sup> HCl + HNO<sub>3</sub> at 80 °C and then the content of soluble elements were analyzed. It consisted of about 3.6 g cobalt, 4.5 g

copper, 0.36 g lithium and 1.2 g aluminum. The insoluble materials were separator, carbon powder and adhesive agents.

Sodium hydroxide and sulfuric acid were used to dissolve the spent batteries material, and then adding ammonium oxalate reclaimed most of the cobalt. The commercial extractions Acorga M5640 and Cyanex272 (di-(2,4,4 trimethyl pentyl) phosphinic acid) were used as the special extractants for the separation of a small quantity of copper and cobalt, respectively. Suffocated kerosene was used as diluents both for Acorga M5640 and Cyanex272. Sodium carbonate was used to precipitate lithium-ion. All reagents were utilized as received without further purification.

### 2.2. Experimental procedure

Based on the components and contents of internal rolls and the pre-experimental investigations, a series of tests for defining their recycling and treating process were carried out. Finally, an overall recycling process comprising of three parts was designed and studied:

- (i) The dismantling of spent LIBs, therein, the conditions of discharging the remainder capacities, opening the battery crusts and treating the battery rolls were investigated. After this treatment, the battery scraps without steel crusts were left for further separation.
- (ii) The dissolving of battery scraps and recovering of metal values, therein, the conditions of dissolving the battery scraps with sulfuric acid, the deposition of mass cobalt with oxalate and the extracting of remainder cobalt and copper with solvent extraction were optimized.
- (iii) The recovery of lithium and the reuse of recovered compounds, therein, lithium was recovered with carbonate deposition process. The recovered lithium carbonate and cobalt oxalate were used as precursors to produce LiCoO<sub>2</sub> positive material and waste solution produced were treated innocuously.

### 2.3. Analysis methods

The concentrations of various metallic ions in the initial solutions and sequent resultants were all determined by using the inductively coupled atomic absorption spectrophotometer (Model AA320, China). The pH values of the aqueous solutions were measured with a pH/mV meter (Model DF-801, China). The charge–discharge performance of LiCoO<sub>2</sub> synthesized was tested in a sealed and half-cell type of corn cell by using a computer controlled battery test system (Land, China).

## 3. Results and discussion

### 3.1. The dismantling of spent LIBs

The metal values including cobalt, copper and lithium contained in the inner part of batteries are mainly desirable sub-

stances in this recycling process. The steel crusts of spent LIBs should be dismantled and separated before the recovery of metal values.

As mentioned by Tanii et al. [8], it was shown that the positive and negative electrodes of batteries with remainder capacities easily came into contact with each other and caused a short-circuit current flow when spent LIBs were dismantled. These current generated Joule heat and ignited volatile (i.e. flammable) solvent in the electrolyte solution, causing the inflammation of battery rolls. So, a discharging pretreatment step was applied in the given process before the dismantling of battery steel crusts to avoid the potential danger of short-circuit or self-ignition for battery rolls when anode and cathode were put in contact with each other in the dismantling course. The spent LIBs were put into a stainless steel container, in which some amounts of water and electric iron powder were added beforehand. Under the help of mechanical stirring in the container, these batteries were short-circuited and discharged. The remainder capacities of spent LIBs were discharged completely for about 30 min.

After the discharging treatment, the iron crusts of spent LIBs were dismantled by using a specially designed dismantling machine (CN Application No. 200410051922.1) that works with a pair of cutting molds. Using this machine, about 5000 pieces of spent LIBs were dismantled per hour; in particular, the steel crusts were easily separated from the dismantled substances by magnetism method. In addition, because the electrolyte absorbed in the internal rolls of spent LIBs are unstable when they interact with moist air [8], i.e. lithium phosphohexafluoride ( $\text{LiPF}_6$ ) dissolved in ethylene carbonate and dimethylcarbonate solvent may react with water and produce dangerous gases, such as pentafluoroarsenic, pentafluorophosphate and hydrogen fluoride. So, the dismantled substances were poured into alkaline solution immediately after the dismantling step.

As a result, it was also shown that most of the aluminum substrate could be dissolved and separated under a suitable alkaline solution condition [10,11] to avoid the introduction of  $\text{Al}^{3+}$  in the next separation steps. In our other experiments, it was demonstrated that lots of  $\text{Al}^{3+}$  would go against the separation of copper and cobalt if aluminum substrate were dissolved in acids in the next step, where cobalt and copper ions would deposit together with aluminum as well as changing the pH of the lixivium to eliminate  $\text{Al}^{3+}$ . Experimental results showed that about 98% of aluminum was dissolved by leaching the dismantled substance with alkaline solution under optimized condition, specifically by using 10 wt.% NaOH solution at room temperature and a solid-to-liquid ( $S:L$ ) ratio of 1:10 for 5 h. From Table 1, it can be seen that a little amount of cobalt and copper can be detected in the alkali lixivium, whose amounts are acceptable as compared with the total of  $\text{LiCoO}_2$  and copper foil.

The  $\text{AlO}_2^-$  lixivium was filtered and rinsed, then the battery scraps included cobaltite salts, copper foil, carbon powder and separator were left after the separating of the battery steel crusts with magnetism method.  $\text{AlO}_2^-$  solution would

Table 1

Contents of main elements in alkali lixivium of dismantling substances of spent LIBs

Element	Concentration ( $\text{g L}^{-1}$ )
Al	7.49
Co	$2.65 \times 10^{-4}$
Li	0.16
Cu	$6.73 \times 10^{-4}$

react with other acidic waste solution in solvent extraction. Or, it could also be deposited as  $\text{Al}(\text{OH})_3$  and recovered by changing the pH values of the lixivium from 4.8 to 5.2.

### 3.2. Dissolving of battery scraps with sulfuric acid

Theoretically, only  $\text{LiCoO}_2$  are soluble constituents in battery scraps for sulfuric acid solution with lower concentration range. So, in order to reduce the volatilization pollution caused by reactants, and decrease the solubility of copper foil in the acid dissolving process, sulfuric acid with suitable concentration was chosen as a more suitable leaching reagent as compared to hydrochloric acid and nitric acid. The reaction is as follows:



To obtain the optimum conditions for the dissolving of battery scraps, several sets of leaching experiments were conducted, i.e. various  $\text{H}_2\text{SO}_4$  concentrations, temperature, time and solid-to-liquid ( $S/L$ ) ratio were carried out. As a compendia method, equal amounts of battery scraps and  $\text{H}_2\text{SO}_4$  with different concentration were used in the leaching experiments. It was indicated that the leaching efficiency of Co was relatively low at lower reaction temperature and acid concentration. With the increasing of  $\text{H}_2\text{SO}_4$  concentration and temperature from 2 to 4 M and 50–90 °C, respectively, the leaching efficiency increased. More than 95% Co was leached within 4 h when the temperature approached 90 °C. Figs. 1 and 2 show the effect of  $\text{H}_2\text{SO}_4$  concentration and reaction time on the leaching percentages of cobalt at 50 and 90 °C, respectively.

At higher acid concentration and reaction temperature, the leaching efficiency of cobalt was favorable. In addition, the oxidation ability of sulfuric acid was increased, which means more copper foil would be dissolved. So, combined with the experiments on solid-to-liquid ratio, in order to lessen the dissolution of copper foil, the optimized leaching of battery scraps was carried out by using 3 M  $\text{H}_2\text{SO}_4$  at 70 °C and  $S/L=1:5$ . The curves of leaching efficiency including lithium, cobalt and copper in battery scraps are shown in Fig. 3. The contents of main components in acid lixivium of battery scraps for 6 h are given in Table 2.

The dissolution ratio of cobalt and lithium almost approached 98% under given conditions for 6 h, while that of copper was only 9%. The concentration of  $\text{Cu}^{2+}$ , which mainly came from the oxides on copper foil, only took up 5% of whole concentration of ions in solution. After filtra-

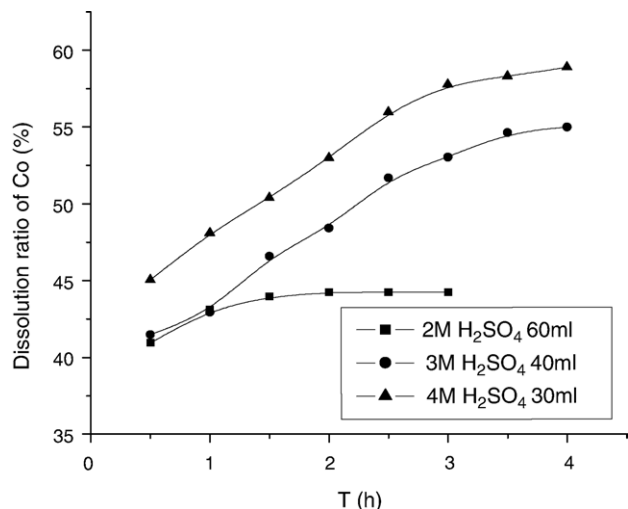


Fig. 1. Effect of H<sub>2</sub>SO<sub>4</sub> concentration and reaction time on the dissolution of LiCoO<sub>2</sub> at 50 °C.

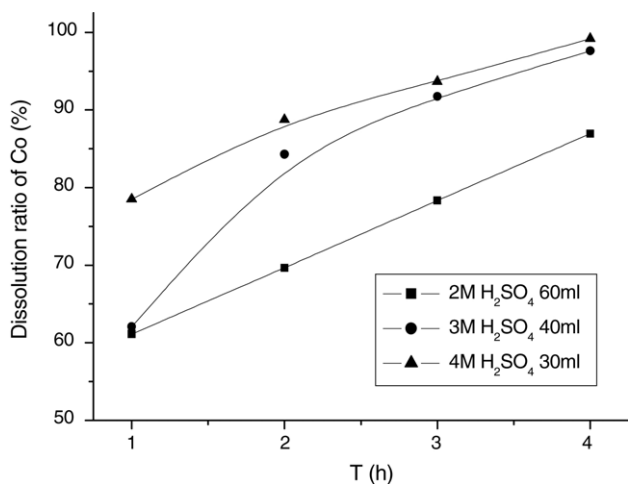


Fig. 2. Effect of H<sub>2</sub>SO<sub>4</sub> concentration and reaction time on the dissolution of LiCoO<sub>2</sub> at 90 °C.

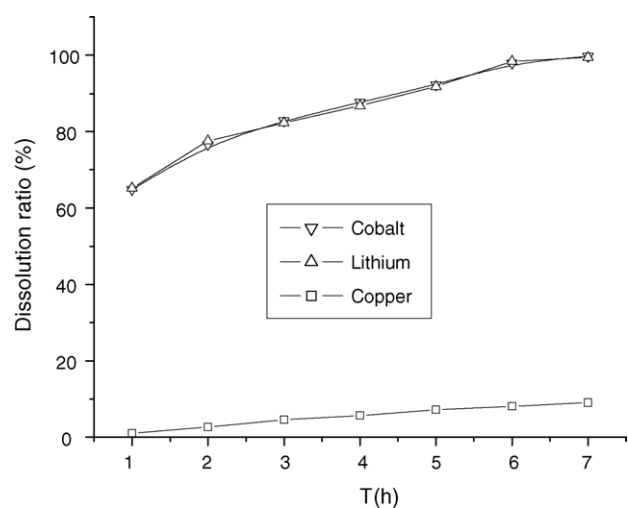


Fig. 3. Dissolution ratio of cobalt, lithium and copper of battery scraps with 3M H<sub>2</sub>SO<sub>4</sub> at 70 °C.

Table 2

Contents of main elements in acid lixivium of spent LIBs scraps

Element	Concentration (g L <sup>-1</sup> )
Al <sup>3+</sup>	0.222
Co <sup>2+</sup>	20.045
Li <sup>+</sup>	2.064
Cu <sup>2+</sup>	1.4172
Ni <sup>2+</sup>	0.0375
Fe <sup>2+</sup>	0.0067
Mn <sup>2+</sup>	0.0024

tion, most of the cuprum foil, carbon powder and separator were left. Residues were dissolved with 10 M H<sub>2</sub>SO<sub>4</sub> at 80 °C with a molar of 1.2 to copper, and then pure CuSO<sub>4</sub> was obtained after concentrating the filtrate. The last waste residue was dealt with according to innocuously residue.

Moreover, as for spent LIBs used in the actual market, the electrolytes decomposed and various solid compounds would be formed in the anode and cathode after several hundred cycles. So, as a comparison, an experiment was also carried out by using spent LIBs cycled for several hundred cycles. It showed that the inner reactions had negligible effect on the dissolution efficiency.

### 3.3. Recovery of the great mass of cobalt with oxalate deposition

Chemical deposition combined with solvent extraction was applied to separate cobalt, copper and lithium. There was no deposition of oxalate for aluminum and lithium. In the acid lixivium of spent LIBs scraps, the concentration of Cu<sup>2+</sup> is far lower than that of Co<sup>2+</sup>, though Cu<sup>2+</sup> can be deposited as oxalate with the solubility accumulating of 3 × 10<sup>-8</sup> while cobalt with that of 6 × 10<sup>-8</sup>. It is considered that most of the cobalt can be recovered by chemical deposition as oxalate [10], reducing the treatment cost effectively compared with solvent extraction or electrolysis methods.

It was indicated that more cobalt would be deposited with the addition of ammonium oxalate solution whose mole amounts exceeded that of cobalt oxalate at 70 °C. When ammonium oxalate came to triplication of the theoretical amount, about 97% of cobalt could be deposited. At the same time, the pH of the solution changed from the strong acid to about 2. Fig. 4 shows the effect of amount of ammonium oxalate on deposition ratio of cobalt.

Although a high deposition ratio of cobalt is desirable, the content of copper in the product approached 1% when the triplication of ammonium oxalate was added. In order to obtain a more pure cobalt oxalate, the deposition ratio of cobalt decreased to about 90% in the practical recovery process. Accordingly, only about 0.5% impurities that included copper, iron and lithium were detected in the deposit.

### 3.4. Recovery of the remainder cobalt and copper with solvent extraction

Lithium and a small quantity of cobalt and copper were left in the surplus filtrate after the deposition of mass cobalt. Be-

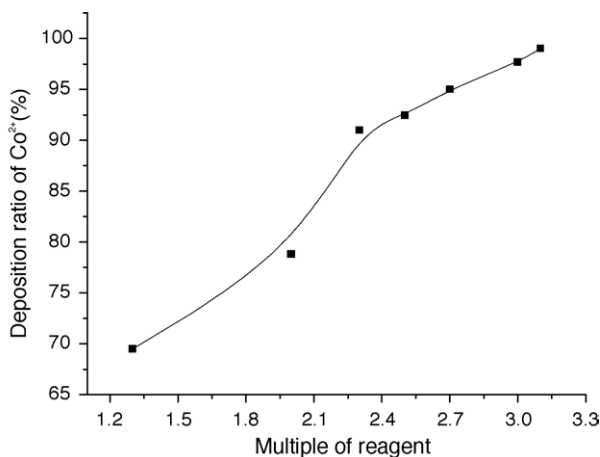
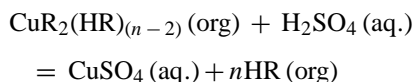
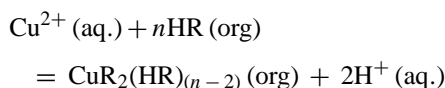


Fig. 4. Deposition of cobalt with different amount of ammonium oxalate solution.

fore the recovery of lithium, copper and cobalt were extracted with solvent extraction. Therein, Acorga M5640 has been used as a special extractant for copper in nitrate/nitric acid media [12]. The  $\log K_{\text{ext}}$  of the reaction between the organic parts of Acorga M5640 and copper is  $2.1 \pm 0.09$ . The oxime in Acorga M5640 is more selective for copper. The reactions in copper extraction and stripping process are as follows:



In the given process, Acorga M5640 was chosen as extractant for copper in sulfate solution based on previous experimental results [9]. Several extraction parameters including reaction temperature, phase ratio, extractant concentration, time, pH value and phase ratios of *O/A* were optimized. Because the extraction process of copper with Acorga M5640 is exothermic reaction ( $\Delta H^0 = 16.4 \text{ kJ mol}^{-1}$ ), the extraction experiments at room temperature were applied in the next experiments. Then, 10 wt.% Acorga M5640 was used to extract copper at different phase ratios of *O/A*, the contact time was 10 min according to literature[9,12]. The results are shown in Fig. 5. Therein, stripping with 2 M  $\text{H}_2\text{SO}_4$  at 1:1 (*O/A*) phase ratio, room temperature and 1 min of contact time for two times were applied.

From data presented in Fig. 5, it can be seen that over 92% copper was extracted when the phase ratio exceeded 1.0. Therefore, on the basis of economical thinking of extraction step, a rational phase ratio of 1:1 was used in the next experiments. The concentration of extractant and pH values were changed in turn, the results are shown in Figs. 6 and 7.

From Fig. 5, we can obtain a high extraction ratio when extractant concentration surpassed 5%, but 10% was thought to be more usable in practical production. In Fig. 7, the highest extraction ratio, which is similar to the results given here,

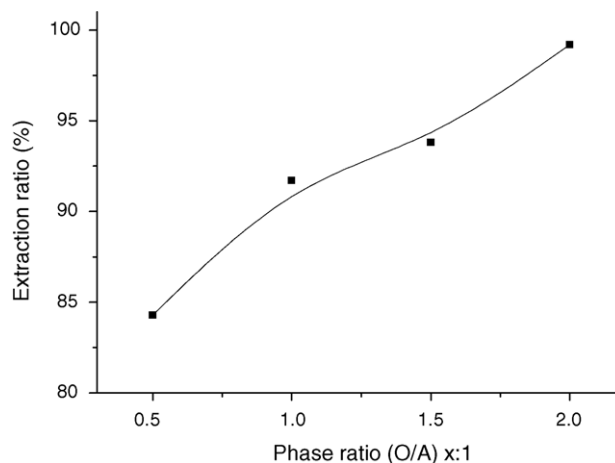


Fig. 5. Influence of phase ratio on extraction ratio of copper with 10 wt.% Acorga M5640.

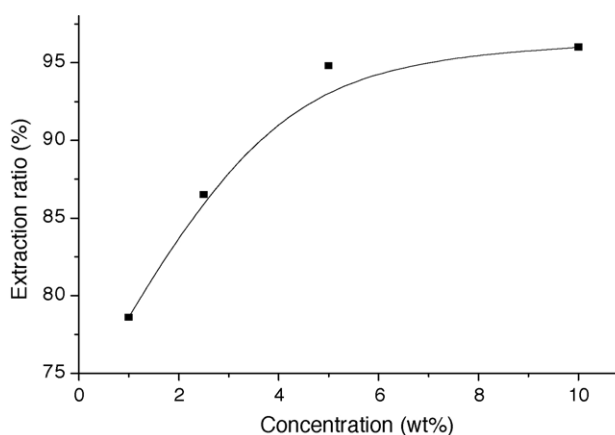


Fig. 6. Influence of extractant concentration on extraction ratio of copper.

can be obtained at pH 1.0. Under such experimental condition, about 96 and 2.4% of the remainder copper and cobalt were recovered, respectively. Finally, considering all of the influence factors, an optimized extraction condition was concluded and used in the given process. Namely extracting with

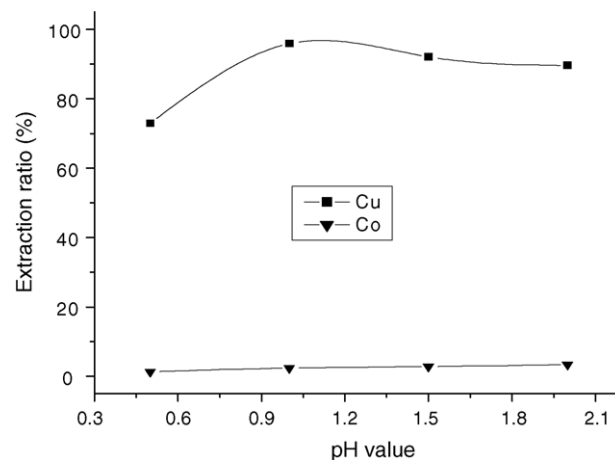


Fig. 7. Influence of pH values on extraction ratio of copper and cobalt.



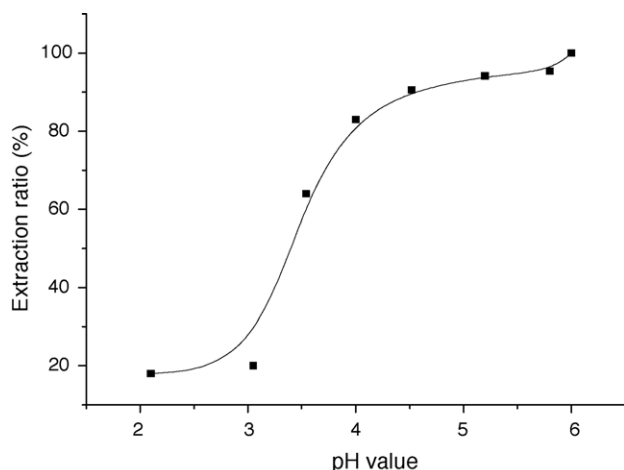
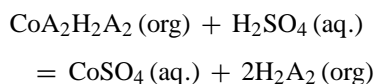
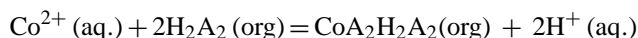


Fig. 8. Influence of pH values on extraction ratio of cobalt.

10% Acorga M5640 at 1:1 (*O/A*) phase ratio, pH of 1.0, room temperature and 10 min of contact time, and stripping with 2 M H<sub>2</sub>SO<sub>4</sub> at 1:1 (*O/A*) phase ratio, room temperature and 1 min of contact time for two times. Combined with the recovery of copper in the upper section, it was indicated that 97% copper in batteries could be recovered as CuSO<sub>4</sub>.

After the extraction of copper, 1 M Cyanex272 was chosen as extractant for the extraction of cobalt [13]. The reactions in the extraction and stripping process are as follows:



Similar to the extraction of copper, the extraction condition for cobalt was also optimized. The extraction ratio of cobalt at different pH value is shown in Fig. 8. Therein, extracting with 1 M Cyanex272 (10% saponification ratio) at 1:1 (*O/A*) phase ratio, room temperature and 1 min of contact time, and stripping with a 2 M H<sub>2</sub>SO<sub>4</sub> solution at 1:1 (*O/A*) phase ratio, room temperature and 1 min of contact time for two times were used. It was shown that the recovery ratio of cobalt was over 96% at pH 5.5, i.e. about 99% of cobalt in batteries were recovered.

In the practical operation, after the extraction of copper, some H<sub>2</sub>O<sub>2</sub> was firstly added to the solution to oxidize Fe<sup>2+</sup> to Fe<sup>3+</sup>, and then pH value was adjusted to 5.5 with 10 wt.% NaOH to eliminate the impurities of Fe<sup>3+</sup> and Al<sup>3+</sup> in the solution through the formation of their hydroxide deposition. After the filtration of Fe(OH)<sub>3</sub> and Al(OH)<sub>3</sub>, the extraction of cobalt with 1 M Cyanex272 was carried out.

### 3.5. Recovery of lithium and synthesis of LiCoO<sub>2</sub>

Referring to the recovery process given by Zhang et al., [2] the raffinate was concentrated and treated with a saturated sodium carbonate solution to precipitate lithium carbonate at 100 °C. The lithium carbonate was recovered after filtration

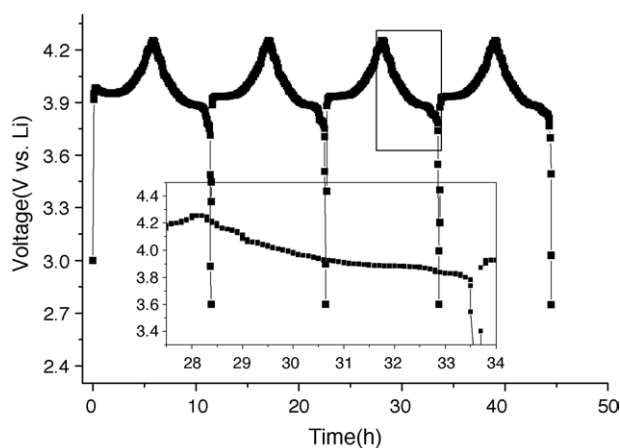


Fig. 9. Charge-discharge curves of LiCoO<sub>2</sub> electrode at 0.2 °C.

and washing with hot water to remove the residual mother liquor. The results showed that about 80% lithium was recovered as a precipitate, which is similar to Zhang's recovery ratio. In addition, the analytical results showed that the contents of cobalt and copper in the precipitate were less than 0.96 and 0.001%, respectively.

After the recovery of metal contents, an amount of waste solution was left from the dissolution, extraction and deposition steps. Because they were acidic or alkaline, these waste solutions could be treated innocuously by mixing them altogether and then adjusting their pH values to neutral solution.

Moreover, lithium carbonate and cobalt oxalate recovered from spent LIBs were used as precursors to produce LiCoO<sub>2</sub> electrode material of lithium-ion batteries. The cobalt oxalate was baked, and a molar ratio of cobalt:lithium 1:1 was grinded until they were mixed equally. The mixed samples were heated firstly at 600 °C for 6 h, and then they were grinded again and pressed into tablets. LiCoO<sub>2</sub> active material was synthesized after the tablets were heated at 800 °C for 10 h in the tube type stove. Then, LiCoO<sub>2</sub> material, graphite, ethyne and PVDF were mixed in a proportion of 86:6:2:6. The mixture with *N*-methylpyrrolidone as solvent was pasted on aluminum foil to prepare the test electrode; pure lithium piece was used as auxiliary electrode. From the data given in Fig. 9, it can be seen that LiCoO<sub>2</sub> synthesized from the recovered compounds of spent LIBs have a specific capacity of 136 mAh g<sup>-1</sup> at 0.2 C charge-discharge current.

## 4. Conclusions

To sum up, an overall flow chart for the recycling of metal values from spent LIBs based on a hydrometallurgical process is presented in Fig. 10.

According to the given process, our scale experimental results have demonstrated that metal values of cobalt, copper and lithium could be effectively recovered and reused, and the recovered products had a high purity. It was particularly indicated that the treatment cost could be reduced effectively because the spent LIBs were dismantled with the

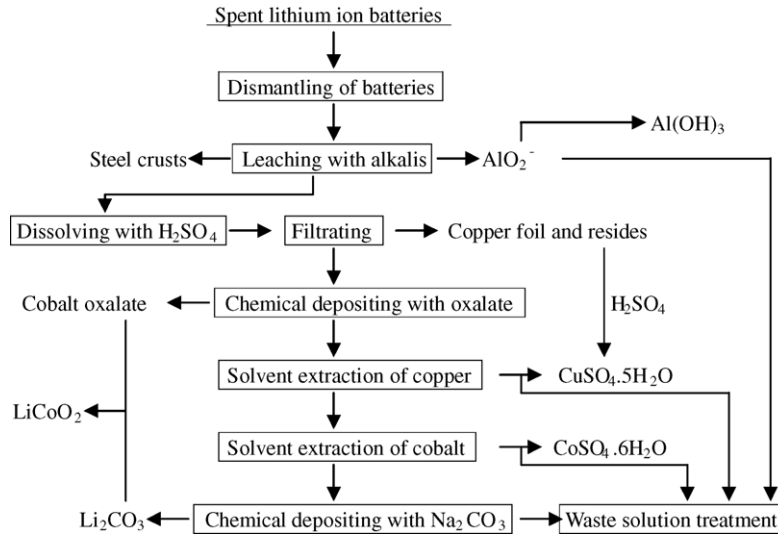


Fig. 10. The flow chart of the recovery of metal values from spent lithium-ion batteries.

pecially designed machine and most of the cobalt was recovered by chemical deposition as oxalate. In addition, Acorga M5640 and Cyanex272 extractants could be recycled after stripping with sulfuric acid. Waste solutions produced in the different steps could also be treated innocuously. Moreover, it is noted that the cathodes of commercial LIBs are not always pure  $\text{LiCoO}_2$  with the development of the commercial LIBs, some other cathode material such as  $\text{LiCo}_{1-x}\text{Sn}_x\text{O}_2$ ,  $\text{LiCo}_{1-x}\text{Mg}_x\text{O}_2$  and  $\text{Li(MnNiCo)O}_2$  will be used. Although these additive elements are impurities when resultants are used as chemical reagents, while these impurities can be acted as additive elements when the resultants are used as precursors to synthesize  $\text{LiCoO}_2$  electrode materials. Therefore, it is thought that this process is feasible for the large-scale recycling of spent LIBs.

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