

# 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  $\text{H}_2\text{SO}_4$  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  $\text{LiCoO}_2$  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  $\text{LiCoO}_2$  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  $\text{LiCoO}_2$

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,  $\text{LiCoO}_2$  was separated from spent electrodes in a single synthetic step using hydrothermal method in a concentrated  $\text{LiOH}$  solution at  $200^\circ\text{C}$  without any scraping procedure, and the renovated  $\text{LiCoO}_2$  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  $100^\circ\text{C}$  for 1 h,  $\text{LiCoO}_2$  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  $\text{LiCoO}_2$  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-

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