



# Novel approach to recover cobalt and lithium from spent lithium-ion battery using oxalic acid



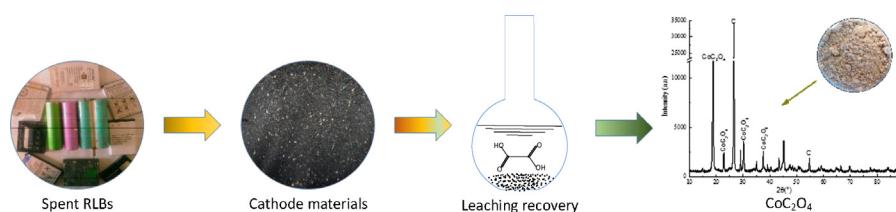
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## HIGHLIGHTS

- Short-cut recovery of cobalt and lithium was directly obtained using oxalic acid.
- Short-cut recovery process was optimized for a high recovery rate.
- Leaching process was controlled by chemical reaction.
- Leaching order of the sampling  $\text{LiCoO}_2$  using oxalic acid was first proposed.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 4 December 2014  
Received in revised form 14 February 2015  
Accepted 25 February 2015  
Available online 26 February 2015

### Keywords:

Spent lithium-ion battery  
Short-cut  
Recovery  
Oxalic acid  
Green chemistry

## ABSTRACT

With the booming of consumer electronics (CE) and electric vehicle (EV), a large number of spent lithium-ion battery (LIBs) have been generated worldwide. Resource depletion and environmental concern driven from the sustainable industry of CE and EV have motivated spent LIBs should be recovered urgently. However, the conventional process combined with leaching, precipitating, and filtering was quite complicated to recover cobalt and lithium from spent LIBs. In this work, we developed a novel recovery process, only combined with oxalic acid leaching and filtering. When the optimal parameters for leaching process is controlled at 150 min retention time, 95 °C heating spent LIBs, 15 g L<sup>-1</sup> solid-liquid ratio, and 400 rpm rotation rate, the recovery rate of lithium and cobalt from spent LIBs can reach about 98% and 97%, respectively. Additionally, we also tentatively discovered the leaching mechanism of lithium cobalt oxide ( $\text{LiCoO}_2$ ) using oxalic acid, and the leaching order of the sampling  $\text{LiCoO}_2$  of spent LIBs. All the obtained results can contribute to a short-cut and high-efficiency process of spent LIBs recycling toward a sound closed-loop cycle.

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## 1. Introduction

Lithium-ion battery (LIB) has been widely used in consumer electronics and even will be employed for the next generation of electric vehicles [1,2]. The increasing applications are resulting in boosting demand of resources such as energy metals. Plenty of

resources have been rapidly transferred from natural mineral to urban mine, which can cause the accelerated depletion of critical materials such as lithium and cobalt [3–6]. Meanwhile, a huge amount of spent LIBs has been generated worldwide. For instance in China, the quantity and weight of discarded LIBs in 2020 can surpass 25 billion units and 500 thousand tons, respectively [7].

From a functional view, a LIB cell is predominantly composed of cathode, anode, electrolyte, and separator. Despite the difference of cathode materials, the most sophisticated cathode material is  $\text{LiCoO}_2$  due to its good performance in terms of high specific energy density and durability [8]. A considerable metals (e.g., Co, Li, Cu, Al, Fe, and Ni) can be found in spent LIBs. The weight ratio of

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**Table 1**  
Main metals concentration of sampling and pure LiCoO<sub>2</sub> (wt.%).

Element	Co	Li	Cu	Al	Fe
–1.43 mm LiCoO <sub>2</sub>	24.53 ± 3.16	3.52 ± 0.25	2.45 ± 0.39	0.83 ± 0.18	0.25 ± 0.11
Standard LiCoO <sub>2</sub>	60.16	6.94	0.026	0.020	0.030

valuable metals ranged from 26% to 76%, and approximately 20% of total weight was Cu and Al [9]. On the other hand, LIBs can regularly release toxic organic compound and then cause an inescapable risk for environment and public health while disposed improperly [10,11]. The two facts and risk of resource depletion drive the spent LIBs should be recovered in an appropriate manner [12,13].

However, the most previous studies related to cobalt and lithium recovery were concentrated on (1) the relatively pure cathode materials from spent LIBs, and (2) single source of application like laptop computer [14–17]. Regarding small e-waste such as spent LIBs, mechanical crushing and screening are thought to be easier in industrial application than manual dismantling [18]. Accordingly, some valuable metals (e.g., Cu and Al) can enter into mixed cathode material in case of mechanical treatment, which can decline the recovery process of cobalt and lithium (see the text of Supplementary material (SM)).

In general, pretreatment and secondary recycling process including mechanical crushing and separation has been well developed for spent LIBs [18–20]. Deep recovery for cobalt and lithium is substantially key and vital in the whole process. Almost all combined processes with leaching using strong acid (e.g., HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>) and chemical precipitation or solvent extraction are well sophisticated to recover cobalt and lithium [21–24]. For instance, hydrochloric acid (HCl) was adopted to dissolve the cathode material, and then the leaching solution would be precipitated using NaOH, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, or Na<sub>2</sub>CO<sub>3</sub> to achieve the recovered product such as Co(OH)<sub>2</sub>, CoC<sub>2</sub>O<sub>4</sub>, and CoCO<sub>3</sub> [22,25,26]. Additional process need to be initiated again to recover lithium. Obviously, the combined processes are of extreme prolixity and energy-consuming while cobalt is transferred from LiCoO<sub>2</sub> to dissolving Co<sup>2+</sup> in solution, and then precipitated Co<sup>2+</sup> [27].

The above two problems in terms of the complexities in composition and process should be overcome sharply toward industrial-scale recovery of spent LIBs. To release these bottlenecks, an innovative recovery process and its scientific fundament are focused in this work. This study will devote to discover a shortcut recovery of cobalt and lithium in the complicated LIBs only using oxalic acid so that cobalt and lithium can be directly separated only through acid leaching. Furthermore, the leaching mechanism

of cobalt and lithium using oxalic acid will be tentatively explored in the complex system.

## 2. Materials and methods

### 2.1. Materials and leaching reactor

Spent LIBs were collected from various consumer electronics including mobile phone, laptop computer, and digital camera. Then they were discharged, crushed by shear crusher, and sieved (the process can be seen at SM Fig. S2). The output materials with particle size below 1.43 mm (–1.43 mm) was chose for sampling for this study. The sampling and standard LiCoO<sub>2</sub> were determined by ICP-AES, XRF, and XRD (see SM Table S3), shown in Table 1, Fig. 1(A), and (B), respectively. Copper and aluminum were also found in the sampling, which could be attributed to the crushing process. Standard LiCoO<sub>2</sub> and oxalic acid were purchased from Alfa Aesar and Sinopharm Chemical Reagent Co., Ltd., respectively.

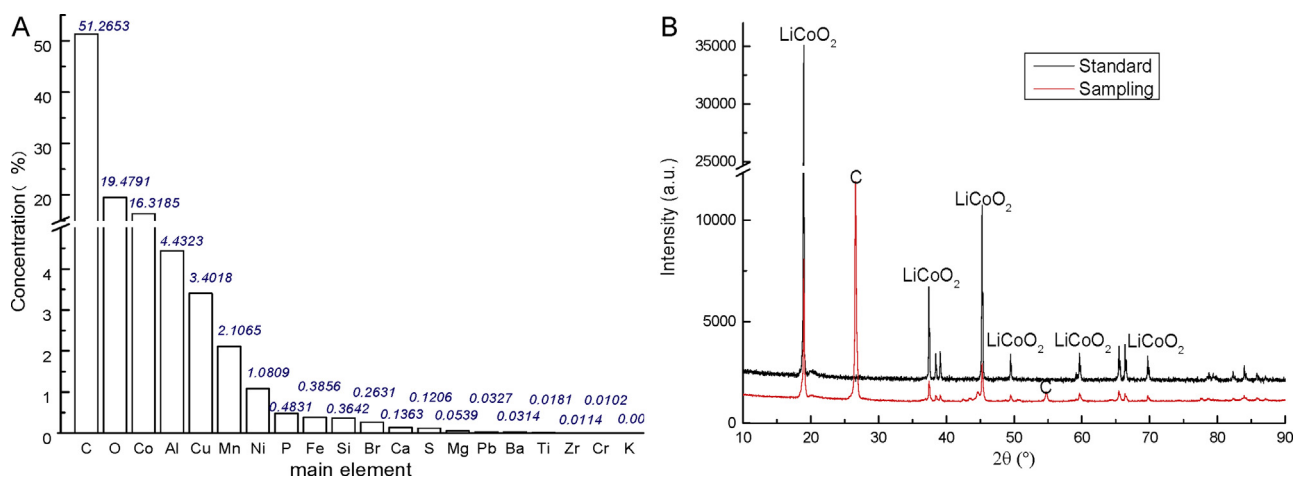
The leaching reactor was equipped with reflux flask, blender, water-heating device, and other supporting appliance (Fig. 2(A)). When oxalic acid solution was heated up to the presupposed temperature, the sampling or standard LiCoO<sub>2</sub> would enter into leaching reactor for recycling, assisted with the blender.

### 2.2. Proposed recovery process

The leaching and separation process for LiCoO<sub>2</sub> was proposed, demonstrated in Fig. 2(B). Firstly, the sampling or standard LiCoO<sub>2</sub> were leached using 1M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. After optimizing the leaching conditions, the obtained solution can contain the precipitated CoC<sub>2</sub>O<sub>4</sub>, and soluble Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, or LiHC<sub>2</sub>O<sub>4</sub>. Secondly, the solution would be filtered to separate CoC<sub>2</sub>O<sub>4</sub> from lithium-containing solution. Highly pure cobalt and lithium product could be achieved via cleaning and drying.

### 2.3. Experimental design

Orthogonal experiment design approach was adopted to optimize the leaching process for cobalt and lithium from spent LIBs.



**Fig. 1.** (A) XRF analysis of sampling; (B) XRD analysis of sampling and standard LiCoO<sub>2</sub>.

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