

# MECHANOCHEMICAL EFFICIENT RECOVERY OF COBALT FROM SPENT LITHIUM-ION BATTERIES (LiBs) BY CHLORIDE SOLUTIONS

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Herein, a mechanochemical approach was developed for recover the cobalt and from spent lithium-ion batteries using a high-concentration chloride solution. Effect of parameters on the leaching efficiency of cobalt was studied. 97, 6% of Co was recovered under optimum conditions: rotation speed 500 r/min, S/L ratio: 1:150 g/ml, ball/material ratio 25:1 g/g, milling time 30 min, respectively. The dissolved cobalt was recovered by selective precipitation method to ensure that the recycled Co can be reused for lithium-ion battery production. This research presents a highly efficient and environmentally friendly approach for recovering cobalt from spent LiBs.

*Keywords:* spent Lithium ion battery, recovery, mechanochemical, cobalt, X-Ray research

## INTRODUCTION

Spent Lithium-ion batteries (LiBs) contain numerous valuable resources, such as cobalt, which could be greatly recovered and reused [1]. The hydro- metallurgy advantages, such as high recovery efficiency and mild reaction conditions, which makes the hydro- metallurgy a preferable and promising approach for metal recovery from spent LiBs [2]. However, the methods could inevitably cause corrosion and liquor waste [3]. Hence, economical, highly effective and environmentally friendly processes for recovery of Co from spent LiBs are urgently desired. With a non-thermal process, mechanochemical method, a typical technique for mineral leaching, has been adopted to recover metals from spent LiBs[4,5].

In the present study, planetary ball milling, a novel mechanochemistry process with low energy consumption and high efficiency was developed for recovery cobalt from spent LiBs at room temperature. We examined the effects of various parameters on the recycling process to improve the metal leaching efficiency while reducing acid consumption and chlorine gas emission by using ternary chloride solutions system ( $\text{HCl} + \text{H}_2\text{O}_2 + \text{NH}_4\text{Cl}$ )[6].

## EXPERIMENTAL

$\text{NH}_4\text{Cl}$  (99,5 %, solid),  $\text{HCl}$  (36 - 38 %, liquid),  $\text{H}_2\text{O}_2$  (30 %, liquid) are analytical grade and purchased from Tianjin Damao Chemical Reagent Factory, China. The  $\text{LiCoO}_2$  of spent LiBs were supplied by Funeng Lithium Battery Co., Ltd, Jiangsu, China.

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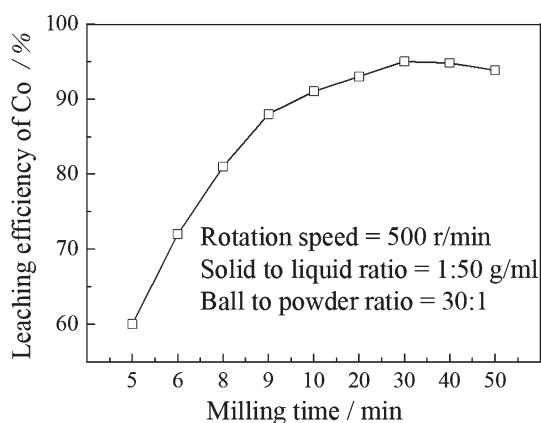
In the experiment, the  $\text{LiCoO}_2$  powder was firstly mixed with ternary chloride solutions system ( $\text{HCl} + \text{H}_2\text{O}_2 + \text{NH}_4\text{Cl}$ ), and then the acquired mixture were planetary ball milled at different rotation speed (100 – 600 rpm), ball to powder ratio (10:1 - 35:1), solid to liquid ratio (1:25 - 1:125) for different periods of time (5 – 150 min). Finally, cobalt in the leaching solution was converted into precipitation by adding  $\text{NaOH}$ . The  $\text{Co}_3\text{O}_4$  powder was obtained after heat treatment of the precipitation at 500 °C for 6 h.

Scanning electron microscopy (SEM, S-3400N, HITACHI) was used to analyze the particle morphology. Phases were characterized by X-ray diffractometry (XRD; Rigaku, Japan). Surface elements of the materials were detected by X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi, USA). The concentration of metal ions were analyzed using a PerkinElmer Optima 5300V ICP-OES system.

## RESULTS AND DISCUSSION

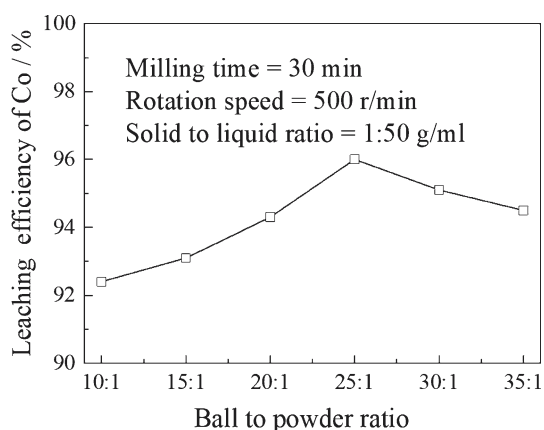
Planetary ball mills are known for good reproducibility, safe handling and short processing times. The high rotational speed of the pots and the disk, leads to large impact energies of milling balls inside the pots to achieve an effective grinding performance. The effects of milling time on the leaching efficiency of Co are shown in Figure 1. It can be seen that the leaching efficiency increased from 60,1 % to 95,0 % as milling time increased from 5 min to 30 min. The leaching efficiency of Co did not significantly change with the reaction time from 30 to 50 min.

The effect of the ball-to-powder ratio on the leaching efficiency was investigated (Figure 2). With increasing of



**Figure 1** Effect of milling time

mass ratio of ball to powder from 10:1 to 25:1, the leaching efficiency increased from 92,4 % to 96,0 %. Notably, further increase of the mass ratio of ball to powder is not corresponding to higher leaching efficiency. The high ratio would lead to smaller remaining space in the ball mill pot, which was not conducive to the abrasive.

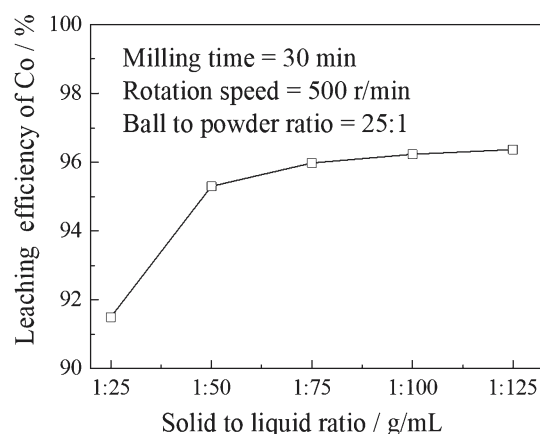


**Figure 2** Effect of ball to powder ratio

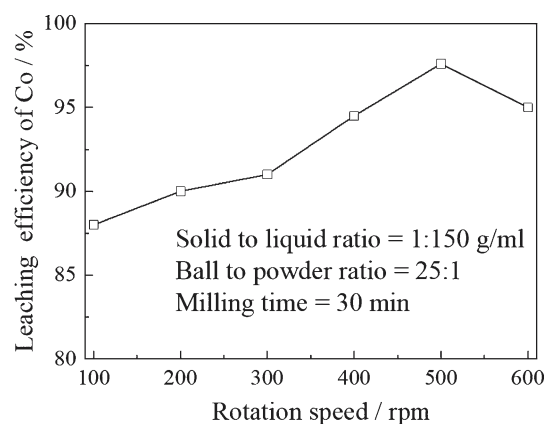
The solid to liquid ratio was another parameter for leaching efficiency of Co, which is shown in Figure 3. It is verified that the leaching efficiency of Co increases from 91,5 % to 97,6 % as the solid to liquid ratio decreased from 1:50 (g/mL) to 1:100 (g/mL). The lower solid to liquid ratio could enlarge the contact areas of activation powder and chloride solution, which accelerated the leaching reaction. Besides, a lower solid to liquid ratio was advantageous to the dispersion of  $\text{LiCoO}_2$  powder [7].

Figure 4 reflects the effect of rotation speed on the leaching efficiency of Co. It can be seen that the leaching efficiency increased from 88,0 % to 97,6 % with the speed increased from 100 to 500 rpm. The reason may be that high rotation speed would cause great damage to the particle size and crystal structure of the sample. It was also observed that the leaching efficiency decreased with the rotation speed of 600 rpm. This is due to the large centrifugal force, which can cause the material to stick to the wall and cannot fully react with the chlorinated solution [8].

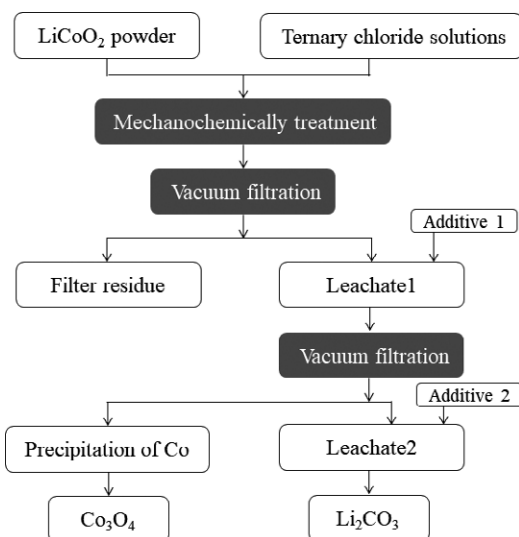
A full recycling scheme requires the recovery and repurposing of the metal ions. A flowchart of the whole technology was given in Figure 5.



**Figure 3** Effect of solid to liquid ratio

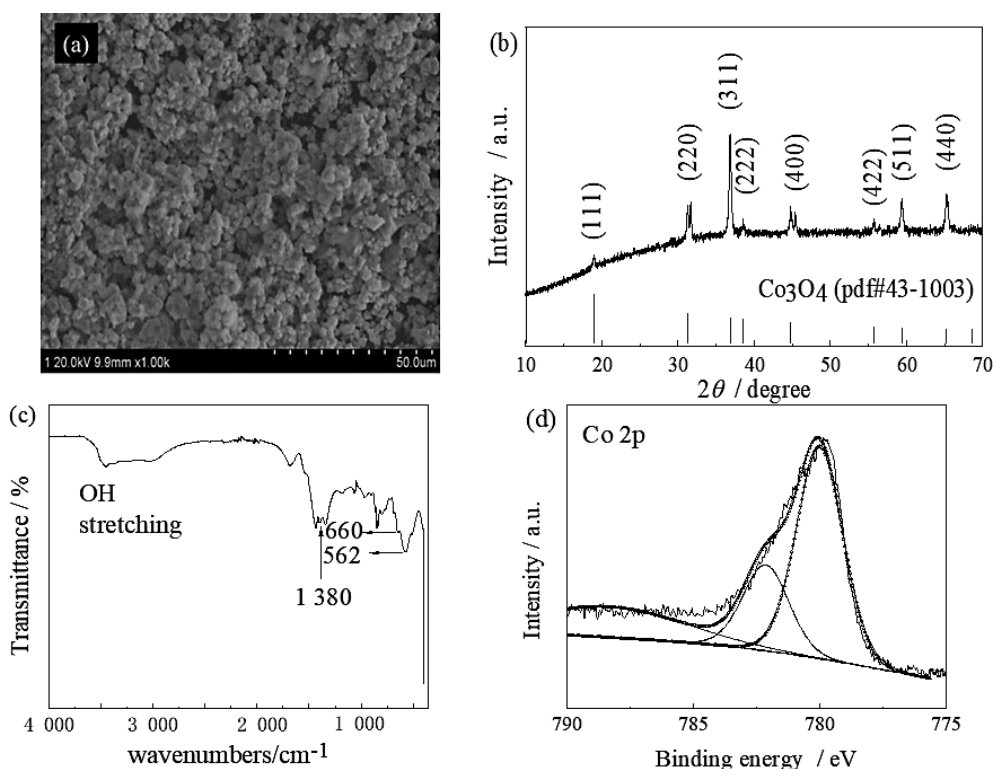


**Figure 4** Effect of rotation speed.



**Figure 5** Schematic diagram for Co and Li recovery from spent LiBs.

To create a more useful compound for synthetic purposes, the precipitate of recovered powder was calcined at 500 °C for 6 h [9], which can convert the components into uniformly spherical particles (Fig 6a). The X-ray diffraction (XRD) pattern of the calcined powder (Fig 6b) aligns well with that of  $\text{Co}_3\text{O}_4$  (JCPDS 43 - 1003). The Fourier transform infrared (FTIR) spectrum of the recovered powder (Fig 6(c)) showed intense bands at 562, 660, and 1 380  $\text{cm}^{-1}$ , which were respectively indicative of stretching modes from octahedrally and tet-



**Figure 6** (a) SEM image, (b) XRD patterns, (c) FTIR spectra and (d) XPS spectra of precipitate was calcined at 500 °C for 6 h

rahedrally coordinated  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  metal oxide ions corresponding with spinel  $\text{Co}_3\text{O}_4$  [5].

Fig 6 (d) shows the XPS curve fitting of the  $\text{Co}2p_{3/2}$  band with peaks at 780,2 and 782,5, which also correspond to the binding energies of  $\text{Co}_3\text{O}_4$  [10].

## CONCLUSIONS

A high efficiency and environmentally friendly mechanochemical process with ternary chloride solutions was established for Co recovery from spent LIBs. The optimal mechanochemical conditions were: rotation speed 500 r/min, S/L ratio 1:150 g/ml, ball/material ratio 25:1, milling time 30 min, respectively, under which 97,6 % of Co could be recovered. It is believed that the developed process is efficient for materials recycling from spent LIBs, and furthermore, this process is feasible to scale up the reduction of environmental loads resulting from spent LiBs recycling.

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**Note:** The responsible translator for English language is Z. Y. Tan, School of Material Science and Engineering, Shenyang Ligong University, Shenyang, China