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# An environmental benign process for cobalt and lithium recovery from spent lithium-ion batteries by mechanochemical approach

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ABSTRACT

In the current study, an environmental benign process namely mechanochemical approach was developed for cobalt and lithium recovery from spent lithium-ion batteries (LIBs). The main merit of the process was that neither corrosive acid nor strong oxidant was applied. In the proposed process, lithium cobalt oxide (obtained from spent LIBs) was firstly co-grinded with various additives in a hermetic ball milling system, then Co and Li could be easily recovered by a water leaching procedure. It was found that EDTA was the most suitable co-grinding reagent, and 98% of Co and 99% of Li were respectively recovered under optimum conditions: $LiCoO_2$ to EDTA mass ratio 1:4, milling time 4 h, rotary speed 600 r/min and ball-to-powder mass ratio 80:1, respectively. Mechanisms study implied that lone pair electrons provided by two nitrogen atoms and four hydroxyl oxygen atoms of EDTA could enter the empty orbit of Co and Li by solid-solid reaction, thus forming stable and water-soluble metal chelates Li-EDTA and Co-EDTA. Moreover, the separation of Co and Li could be achieved through a chemical precipitation approach. This study provides a high efficiency and environmentally friendly process for Co and Li recovery from spent LIBs.



## 1. Introduction

Environmental pollution and energy crisis have driven the progressing of new energy vehicles and the development of power batteries (Kang et al., 2013). Compared with lead-acid batteries and nickel metal hydride, lithium-ion batteries (LIBs) are expected to dominate the market in terms of their high working-voltage, large capacity, long circle-life and non-memory effect, especially with the rise of plug-in hybrid and purely electrically driven battery electric vehicles (Majeau-Bettez et al., 2011; Notter et al., 2010; Scrosati and Garche, 2010). Recently, with the rapid upgrade and replacement of new energy vehicle, as well as electronic devices, huge amounts of spent LIBs are generated worldwide without any proper disposal. Take China for example, the total quantity and weight of discarded LIBs were estimated to reach 25 billion units up to 500 thousand tons by 2020 (Zeng et al., 2012). Generally, spent LIBs are composed of cathode, anode, electrolyte and separator, and the most widely used cathode material is lithium cobalt oxide ($LiCoO_2$), which is characterized by high specific energy density and durability (Scrosati and Garche, 2010). In view of the growing interest in environmental protection and resources sustainable use, recovery of spent LIBs especially $LiCoO_2$ is becoming increasingly important, as it will largely help to alleviate the potential environmental pressures and solve the crisis of cobalt shortage.

Authorities have enforced regulations on spent batteries' disposal. In 2006, the European Parliament and the EU Council of Ministers revised the 1991 Battery Directive 91/157/EEC (Directive, 1991) covering batteries and accumulators. Since 2008 the new Battery Directive 2006/66/EC (Directive, 2006, 2008) prescribes the currently valid collecting targets and recycling efficiencies. The member states are obliged to reach a minimum collection rate for spent batteries and accumulators of 25% by 2012 and of 45% by 2016. Furthermore, Li-ion battery recycling processes will be obliged to reach a minimum recycling efficiency of 50% by average weight. A huge number of researches going on with respect to recycling processes, as comprehensively reviewed by Xu et al. (2008) and Zeng et al. (2014). The major drawback is that, the amount of spent batteries available for recycling is small and does not match the large number of secondary cells produced for every year. For example, 97 tons of spent NiMH batteries were recycled in Germany in 2003 which represents only 3% of NiMH batteries produced in that year (Al-Thyabat et al., 2013).

Thus far, most researches on spent LIBs generally have been focused on valuable metals recovery. The main methods for metal recovery comprise physical dismantling (Bertuol et al., 2015; Zhang et al., 2013), metal leaching (Chen et al., 2011; Paulino

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et al., 2008; Sun and Qiu, 2011) and the separation of Co and Li (Joulié et al., 2014; Provazi et al., 2011; Wang et al., 2009). Among these studies, leaching of Co and Li from $LiCoO_2$ powder using hydrometallurgical techniques had attracted wide attention, besides inorganic acids (Chen et al., 2015; Jha et al., 2013), organic oxalate (Sun and Qiu, 2012), organic citric acid (Li et al., 2010a), succinic acid (Li et al., 2015), oxalic acid (Zeng et al., 2015), tartaric acid and ascorbic acid (Nayaka et al., 2016) were used as leaching agents with satisfactory achievements. However, these acids could inevitably cause corrosion and liquor waste. Hence, economical, highly effective and environmentally friendly processes for recovery of Co and Li from spent LIBs are urgently desired.

In recent decades, considerable researches have been focused on metal recovery by mechanochemical method (Tan and Li, 2015; Yuan et al., 2012). With a non-thermal process, Kano et al. (2009) recovered indium (In) through mechanochemical reduction of $In_2O_3$/ITO by milling with $Li_3N$ under a non-oxidative state of $NH_3$ and/or $N_2$ gas environment. Lee et al. (2013) recovered In from spent liquid crystal display (LCD) panels assisted with high energy ball milling and acid leaching. Shibata et al. (2011, 2012) used a mechanochemical method to recover tungsten and cobalt from tungsten carbide tool wastes. Saeki et al. (2004) and Zhang et al. (2007) developed a process for metal recovery from alloy-wastes and $LiCoO_2$ powder via co-grinding with polyvinyl chloride (PVC). Compared with hydrometallurgical processes, these studies revealed that mechanochemical processes could not only obviously simplify metal leaching, but also avoid the generation of liquor waste in point of solid-solid reaction. Meanwhile, more than 99% lead was extracted from spent lead-glass by a mechanochemical method when ethylenediaminetetraacetic acid disodium salt ($Na_2$EDTA) was used as metal chelate reagent (Sasai et al., 2008). Furthermore, EDTA had been applied as metal-ion chelation in a process for separating metals in a mixed solution of Co and Li (Iizuka et al., 2013) and separating nickel from cobalt solutions (Chaudhary et al., 2000). The study implied that $Na_2$EDTA and EDTA are important chelating reagents which could form stable metal complexes with various metals.

In the present study, a novel mechanochemistry process with low energy consumption and high efficiency was developed for the recovery of Co and Li from spent LIBs. EDTA and $Na_2$EDTA were tentatively used as co-grinding reagents to chelate Co and Li from $LiCoO_2$ powder. Various operating parameters were optimized and the mechanochemical residues were characterized. Furthermore, the reaction mechanisms of $LiCoO_2$ co-grinding with different additives were discussed in detail and efficient approaches for Co and Li separation were established as well.

## 2. Experimental

### 2.1. Materials and methods

Spent LIBs were supplied by Beijing HuaXing Environmental Protection Co. Ltd, China. The LIBs were firstly discharged completely to avoid short-circuit or self-ignition during dismantling. The metallic shell, cathode material, anode material and organic separators were separated manually using a plier and a screwdriver. Then the cathode materials were crushed with a small high-speed universal pulverizer to separate aluminum film and $LiCoO_2$ powder. Contents of Co and Li in $LiCoO_2$ powder were measured by inductively coupled plasma optical emission spectrometer (ICP-OES, Prodigy, Leeman, USA) after digestion with aqua regia. Results indicated that Co and Li accounted for 51.8% and 6.5% of the total cathode materials (wt%). All chemical reagents were of analytical grade and purchased from Chemical Reagent Company of Beijing.

### 2.2. Analytical methods

The concentrations of Co and Li in leaching liquor were measured by ICP-OES (ICP-OES, Prodigy, Leeman, USA). The crystal structure and surface morphology of the original and ball milled samples were characterized by X-ray diffraction (XRD, Philips PW 1700) using Cu Kα radiation ($\gamma$ = 1.5418 Å) with 30 kV voltage and 30 mA current. The analysis of XRD data were carried out by MDI Jade 6.0 software.

### 2.3. Recovery procedure

The schematic diagram of Co and Li recovery from spent LIBs is shown in Fig. 1. All mechanochemical experiments were carried out in a planetary ball mill (QM-3SP2J) comprised of four 50 mL zirconia pots with zirconia balls as grinding medium. First, an appropriate proportion of $LiCoO_2$ powder and co-grinding reagents, together with zirconia balls were sealed in the zirconia pots. Then the powder mixtures were ball milled at different rotary speed for different periods of time. The milled products and zirconia balls adherent with powder were then rinsed with 100 mL of deionized water and agitated for 30 min. The leaching solution and residues were separated by vacuum filtration. In the subsequent chemical precipitation process, Co and Li in the leaching liquor were separated and recycled by addition of NaOH and $Na_2CO_3$, respectively. Cobalt oxides were first obtained after calcination of the precipitate at 500 °C for 2 h, and then lithium carbonate was recovered after recrystallization and drying. The recovery rates of Co and Li, determined by ICP-OES, were expressed in percentage by the following formula:

$$W = \frac{C \cdot V}{C_0 \cdot V_0} \times 100\%$$

where W is the recovery rate; $C_0$ and C are metal concentrations in solution before and after mechanochemical treatment; $V_0$ and V are volumes of leaching liquor before and after mechanochemical treatment.

## 3. Results and discussion

### 3.1. Screening of co-grinding reagents

Five types of chlorides, including PVC, NaCl, $NH_4Cl$, $ZnCl_2$ and $FeCl_3$, were tested as co-grinding reagents to supply exogenous

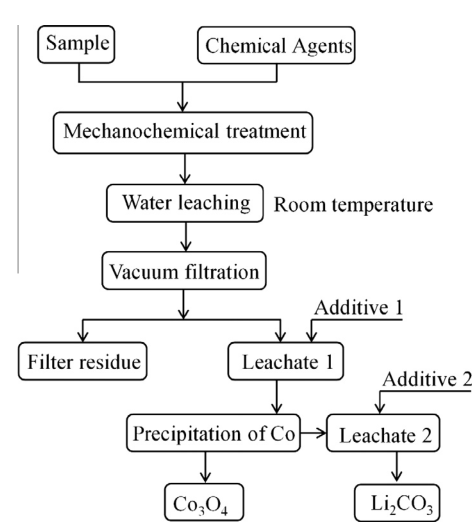


**Fig. 1.** Schematic diagram for Co and Li recovery from spent LIBs.