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

Meng-Meng Wang, Cong-Cong Zhang, Fu-Shen Zhang*

Research Center for Eco-environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China

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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.

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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

* Corresponding author.

E-mail address: fszhang@rcees.ac.cn (F.-S. Zhang).

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 $\text{In}_2\text{O}_3/\text{ITO}$ 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_2EDTA) 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_2EDTA 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_2EDTA 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 screw-driver. 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 $\text{Cu K}\alpha$ radiation ($\gamma = 1.5418 \text{ \AA}$) 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.

chlorides. As can be seen in Fig. 2, Co and Li could be leached out to a certain degree from LiCoO_2 after co-grinded with different additives, indicating that Co and Li inside LiCoO_2 powder were tentatively converted into their chloride forms during mechanochemical process. It has been reported that mechanical forces such as shear, impact and squeezing exerted by ball milling, will transmit energy to powder, diminished powder particles and destroy the crystal structures (James et al., 2012; Nasser and Mingelgrin, 2012). Moreover, the ball milling process can reduce specific surface energy of reaction products so as to promote the impossible solid-solid reaction and enhance the reaction efficiency (Friščić, 2010).

However, as showed in Fig. 2, only a small amount of Li was leached out when PVC was co-grinded with LiCoO_2 , indicating that PVC, the polar polymer with amorphous structure, is not suitable to co-grind with LiCoO_2 , which is a crystal structure compound. During the co-grinding of NaCl with LiCoO_2 powder, about 30% of Li and Cl were converted into water-soluble LiCl , but Co was not converted into chloride form since the ionic bond of NaCl (bond energy 412 kJ mol^{-1}) was broken by the mechanical force, thus Li in LiCoO_2 with reduced atom radius and improved polarization ability would first bind with Cl to form LiCl , while Co with lower reactivity could not form water-soluble compound (Zhang et al., 2007). Both Co and Li were leached out during ball milling between NH_4Cl and LiCoO_2 . This could be attributed to the fact that NH_4Cl was partially decomposed due to the external mechanical force, thus active Cl could react with Li and Co by solid-solid reaction. The chlorine donor FeCl_3 finitely improved the recovery rates of both Co and Li compared with NH_4Cl or NaCl. As a covalent compound and strong acid salt, FeCl_3 is more reactive than NaCl, the ionic compound. It is more likely to react with LiCoO_2 crystals whose surface activation energy was reduced during ball milling process. FeCl_3 has the ability to convert Li and bind with lower-activity Co to form water-soluble ions. However, the recovery rates were generally low when LiCoO_2 was co-grinded with the above chlorides since the ball milling system could not provide enough energy to break the chemical bonds of chlorides (Courtney and Dahn, 1997; Wang et al., 1999). Therefore, it is necessary to screen out more efficient co-grinding agents in view of the actual recovery effect and economic benefits.

Further experiments showed that, 71% of Co and 74% of Li were recovered when LiCoO_2 was co-grinded with Na_2EDTA powder, and 98% of Co and 99% of Li were recycled when EDTA-LiCoO_2 ball milling system was applied. Na_2EDTA and EDTA are all excellent metal chelating reagents, which could chelate with alkali metals, rare-earth elements or transition metals to form stable water-soluble coordination compounds, and they have been widely used

for the removal of heavy metals from industrial waste (Nowack, 2002; Sasai et al., 2008). Accordingly, it can be concluded that both Na_2EDTA and EDTA could react with LiCoO_2 to form water-soluble metal chelates, and thereby to recover Co and Li by solid-solid reaction. Meanwhile, owing to the presence of carboxyl, EDTA outperformed than Na_2EDTA in chelate with Co and Li. The relevant working mechanism of LiCoO_2 co-grinded with EDTA will be further discussed.

3.2. Effects of various parameters on recovery rates of Co and Li

The effects of LiCoO_2 to EDTA mass ratio on the recovery rates of Co and Li are shown in Fig. 3a. Both recovery rates of Co and Li increased rapidly along with the decrease of mass ratio, e.g., 26% for Co and 44% for Li were recovered at mass ratio 1:1, while 98% of Co and 99% of Li were recovered at mass ratio 1:4. Then recovery rates almost unchanged when the mass ratio were 1:5 and 1:6. The above results implied that 1:4 was the maximum mass ratio for the recovery process. This is consistent with a previous report, showing that EDTA generally coordinates with metal ions at the molar ratio of 1:1, with the LiCoO_2 to EDTA mass ratio of 1:3.6 (Wang et al., 2012).

Fig. 3b indicates that the recovery rates of Co and Li increased with the prolonging of ball milling time. The recovery rates increased significantly from 67% to 89% for Co and 66–90% for Li, respectively, as the ball milling time was prolonged from 1 h to 3 h. After ball milling treatment of 4 h, the recovery rates of Co and Li reached 98% and 99%, respectively, then the recovery rates remained almost the same at 4.5 h and 5 h ball milling time. It has been proved that prolonging reaction time would break down the crystal structure of ball milled powder thoroughly and provide more energy to the system (Balaz et al., 2013). Therefore, the recovery rates of both Co and Li increased with the grinding degree of sample powders. Considering the energy consumption and recovery rates, it is recommended that 4 h is the optimum milling time.

As reported, the mode of grinding medium on the material way and the magnitude of the force depend on the milling speed, which means that a higher speed provides larger force to totally destroy the material particles (Nasser and Mingelgrin, 2012). The effects of ball milling rotary speed on recovery rates of Co and Li are shown in Fig. 3c. The recovery rates increased sharply from 38% to 90% for Co and 42–97% for Li, respectively, as the rotary speed increased from 300 r/min to 500 r/min. Then, the recovery rates of Co and Li reached maximum values of 98% and 99% at the ball milling rotary speed of 600 r/min. Hence 600 r/min was the suitable rotary speed for Co and Li recovery.

Ball-to-powder mass ratio is a specific value of grinding medium quality and material quality during ball milling treatment. It also plays an important role in the ball milling process as inappropriate ball-to-powder mass ratio will increase the unnecessary energy loss and weaken the ball milling ability (Guo et al., 2010). Fig. 3d shows the effects of ball-to-powder mass ratio on the recovery of Co and Li. The results indicated that the recovery rates of Co and Li both enhanced with the increase of ball-to-powder mass ratio. The recovery rate of Co and Li reached maximum values of 97% and 99% for Co and Li respectively at a ball-to-powder mass ratio of 80:1. To summarize, the optimum conditions of Co and Li recovery from spent LIBs were: 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. Further separation of Co and Li could be achieved by addition of sodium hydroxide and sodium carbonate solutions.

Fig. 2. Co and Li recovery rates influenced by different co-grinding reagents. (LiCoO_2 to chlorides mass ratio 1:5, milling time 24 h, rotary speed 600 rpm, ball-to-powder mass ratio 125:1.)

Fig. 3. Effects of various parameters on Co and Li recovery. (a) Mass ratio of LiCoO₂ (rotary speed 600 r/min, milling time 5 h, ball-to-powder mass ratio 125:1), (b) milling time (mass ratio of LiCoO₂ to EDTA 1:5, rotary speed 600 r/min, ball-to-powder mass ratio 125:1), (c) rotary speed (mass ratio of LiCoO₂ to EDTA 1:5, milling time 5 h, ball-to-powder mass ratio 125:1) and (d) ball-to-powder mass ratio (mass ratio of LiCoO₂ to EDTA 1:5, milling time 5 h and rotary speed 600 r/min).

3.3. Reaction mechanism of LiCoO₂ with EDTA during ball milling

LiCoO₂-EDTA ball milling process under the influence of mechanochemical treatment can be divided into two stages, i.e. enhancement of reactant activity and diffusion of reactant into water. In general, the reactant activity of raw material could be promoted by mechanical force. The crystal lattice structure of reactant could be destroyed, inducing the reorganization and distortion of the lattice when reactant is subjected to external forces in the confined system (Li et al., 2010b; Yuan et al., 2012; Yuan et al., 2013a,b).

During ball milling progress, the dispersal mixture of LiCoO₂ and EDTA was grinded evenly. The crystal grain was being tiniest along with collision with high speed grinding balls and the steel tank wall, which caused the rapid increase of specific surface area and energy. Accordingly, the crystal lattice of LiCoO₂ and EDTA generated lattice distortion and local damage, and formed surface defects and high density dislocation, which resulting the increase

of internal energy and the enhancement of reactant activity. Fig. 4a clearly identified the reflections of EDTA and LiCoO₂ phase, while in Fig. 4b, no reflections of EDTA was observed and the reflections of LiCoO₂ became weaker after ball milling treatment. The inner energy of crystal lattice was enhanced after mechanical activation treatment, which was feasible for atomic transition (Kaupp, 2009). In fact, the following water leaching process was a disordering diffusion process for the activated material in water. The diffusion was intensified along with the decrease of diffusion activation energy through ball milling, which realized the rapid leaching for reactants at low temperature.

The distance between reactants was shortened by the friction and wear performance between powders, furthermore, atomic spontaneous diffusion rate was directly increased by mechanical force as well, then chemical reaction was induced between EDTA and LiCoO₂ (Wu et al., 2013; Yang et al., 2015). The chelate reaction mechanism of EDTA-LiCoO₂ milling is shown below:

Fig. 4. XRD patterns of different samples: (a) LiCoO₂ and EDTA mixture before ball milling, (b) LiCoO₂ and EDTA mixture after ball milling, (c) water leaching residues after ball milling. Conditions: LiCoO₂ to EDTA mass ratio 1:5, milling rotary speed 600 r/min, milling time 5 h, ball-to-powder mass ratio 125:1 and (d) XRD pattern of recovered Co₃O₄ particle.

It has been reported that metal chelates are cyclic structure of metal atoms and organic ligand formed by donation of electrons from the ligand donor atoms, usually oxygen, nitrogen, or sulfur is the electron acceptor metal ion. The chemical bond formed in this manner may vary in characteristics from the covalent to the almost completely ionic type (Rubin and Princiotto, 1963). EDTA, which is an aminopolycarboxylic acid containing six ligands, two amines and four carboxyl groups, can coordinate with metal ions at the molar ratio of 1:1. During the ball milling process, lone pair electrons provided by nitrogen oxygen atoms of EDTA could enter the empty orbit of Co and Li by solid-solid reaction, forming stable and water-soluble metal complexes Li-EDTA (stability constant lg K = 2.79) and Co-EDTA (stability constant lg K = 36.0), respectively. The XRD pattern of recovered particle was shown in Fig. 4d, where the reflections of Co₃O₄ phase were clearly identified. Furthermore, ICP-OES result showed about 94% cobalt was recovered in the form of Co₃O₄.

4. Conclusions

A high efficiency and environmentally friendly mechanochemical process with EDTA as metal chelate reagent was established for Co and Li recovery from spent LIBs. The process includes 3 procedures: (1) co-grinding LiCoO₂ powder with EDTA, (2) leaching the ball milled mixture with water, and (3) recovery of Co and Li in the form of Co₃O₄ and Li₂CO₃ by chemical precipitation. The optimal mechanochemical conditions were: LiCoO₂ to EDTA mass ratio 1:4, milling time 4 h, rotary speed 600 r/min and ball-to-powder mass ratio 80:1, respectively, under which 98% of Co and 99% of Li could be recovered. It is believed that the developed process is efficient and practical 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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