Green and Efficient Method for Recycling Valuable Metals from Scrapped Lithium Cobalt Oxide Cathode Materials

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Abstract. In this study, green and efficient method for recycling valuable metals from scrapped lithium cobalt oxide cathode materials to form lithium carbonate and cobalt powder was proposed. To this end, aluminum and iron impurities were efficiently removed from scrapped lithium cobalt oxide cathode materials through alkali dissolution and magnetic separation with removal rates of 99.9% and 98.3%, respectively. After removal of impurities, lithium cobalt oxides were reduced by hydrogen at high temperature of 650 ℃ for 3 h to yield Li2O, Co, and very small amounts of CoO and LiOH. Next, the mixture was subjected to water leaching and sodium carbonate precipitation to obtain lithium carbonate with purity of 99.5%. The water-leaching Co and small amounts of cobalt oxides were again reduced by hydrogen to form cobalt powder with purity of 99.4%. In sum, the proposed method looks promising in terms of efficiency, easy for implementation, environmentally-friendliness, and potential industrialization.

1. Introduction

Lithium cobalt oxides (LCOs) are one of the first active cathode materials used in commercial lithium-ion batteries (LIBs), and their applications have since diversified tremendously. Today, LCOs are widely used in new energy vehicles and storage devices [1-3]. Compared to traditional batteries, LCOs batteries possess high energy densities, superior operating voltages, better portability with no memory effect, and long cycle life [4-5]. As a result, various types of batteries are discarded year by year as LCOs batteries are being adopted. However, the heavy metals and electrolytes in positive electrodes of scrapped LCOs batteries do not only cause environmental pollution but also waste of rare metals, which should be entirely recycled.

Common methods used for the treatment and recycling of waste LCOs batteries include physical methods, pyrometallurgical, hydrometallurgical technologies, and biological dissolution technologies [6]. Note that physical methods are the most widely used for impurity removal and preliminary recovery [7]. Pyrometallurgy is characterized by different features, such as incineration dissolution, high-temperature oxidation melting, scum processing, and electric arc furnace sintering [8-9]. The pyrometallurgy treatment process is rather simple but toxic gases could easily be generated during the process along with too many impurities in the final product. On the other hand, bioleaching technology is advantageous in terms of low costs and low pollution [10-11]. However, it suffers from long bacterial
reproduction cycle and low efficiency. Hydrometallurgy is the most mature industrial recycling method [12-14]. It is based on mechanical crushing and sorting for pretreatment of impurity removal followed by acid/alkaline solution and reduction agent leaching. Note that the leaching solution is used for recovery of valuable metals through electrodeposition, liquid-liquid extraction, and/or fractional precipitation. In addition, almost no toxic and harmful gases are generated during recycling process, and residues after leaching are easy to process with significant environmental benefits. However, bioleaching technology still suffers from some challenges. For instance, it often requires the use of inorganic acids, such as H2SO4, HCl, and HNO3 as leaching agents. It can also easily produce sulfides and nitrides, causing secondary pollution to the environment. On the other hand, the method is also cumbersome and tedious, and often requires large amounts of acid/alkali and toxic organic extractants. To overcome these problems, Fang et al. [15] first obtained oxides of cobalt and lithium by calcining at 500 °C and then used acid leaching with sulfuric acid followed by precipitation with oxalate and carbonate to yield CoC2O4 and Li2CO3. Next, they added lithium source at 800 °C for 6 hours to regenerate LiCoO2. Although this method produces less pollution, the recovery of cobalt lithium metal alone was challenging. Lupi et al. [16] leached the positive electrode material in LIBs with properly prescribed H2SO4 and H2O2 to yield cobalt and nickel mixed solution. Next, the leached solution was extracted by three-stage extraction with Cyanex 272 solvent at O/A ratio of 3:1 to separate and recover Co. The second stage is easy to implement at the expense of high cost of acid leaching solution and extractant.

In this study, green and efficient method was proposed to recycle cobalt and lithium from scrapped LCOs. The process optimization and principle analysis were carried out to evaluate the applicability of the method. The scrapped LCOs cathode materials were extracted through pretreatment of scrapped LIBs, and both Fe and Al were removed by alkali leaching and magnetic separation to yield elementary substance of Co and Li oxides by H2 high-temperature reduction. For efficient recovery of valuable metals, lithium carbonate was recovered by water immersion and precipitation, and pure Co powder was obtained by H2 secondary high-temperature reduction.

2. Experimental

2.1. Methods

Discarded battery LCOs were provided by Jingmen GEM New Material Co., Ltd. The materials were discharged and separated into positive electrode sheets followed by pre-treated with thermal decomposition, crushing, sieving and magnetic separation to yield LCOs positive electrode material. Next, 1 kg of positive electrode material was poured into 10L titanium reactor. Sodium hydroxide (n(NaOH)/n(Al)=1-2) solutions with different excess multiples were then added under continuous stirring at 100 rpm for 2 hours at room temperature. Afterward, solid-liquid separation was performed. Aluminum content in the liquid and solid was estimated and aluminum removal rate was calculated. Next, iron was removed by electromagnetic field at magnetic force of 350 Gauss. At normal temperature, 1kg of solid residue was then added to 10L of titanium reactor followed by water at different liquid-solid ratios (water (mL): dry slag (g), 1:1-9:1) under magnetic stirring. The iron and rust deposited on the magnetic stirrer were then washed every 0.5 hours, and the collected material was added into a reactor under continuous stirring. The iron removal was repeated 4 times for a total of 2 hours. The solids and residual solid slag after iron removal were weighed, and iron contents were measured to calculate the iron removal rate. The solid slag left after aluminum and iron removal was dried at 100 °C and then reduced in mixture of H2 and N2 at molar ratio of 3:1 for 3 hours. The effect of different reduction temperatures on reduction results of cobalt and lithium was investigated. Water leaching experiments of lithium were conducted by crushing and reducing followed by sieving of the samples by 400 mesh sieve using 200 g sample each time. Next, the samples were immersed in water for 30 min and the effect of different liquid-solid ratios (water (mL): dry slag (g), 2:1-5:1) on lithium leaching efficiency was analyzed. Finally, the 650 °C reduced sample water leaching supernatant was treated with certain amount of sodium carbonate to adjust the pH for better recovery of lithium carbonate. The
remaining solid residue was filtered off and dried by \( \text{H}_2 \) high-temperature reduction to obtain recycled Co powder.

Figure 1. Process Flow. Diagram
2.2. Characterization
The content and concentration of different metal ions were detected by plasma emission spectrometry (Shimadzu, Japan, ICPE-9810). A pH meter (METTLER TOLEDO, S210) was used to regulate the pH value during leaching and reaction processes. X-ray diffraction (XRD, Shimadzu XRD-6100, copper target) was used to analyze various intermediate products and phase structures of the products. The morphologies of reduced products were observed by scanning electron microscopy (SEM, QUANTA 250FEG, USA).

3. Results and discussion

3.1. Analysis of Cathode Materials From Scrapped LCOs Batteries
Scrapped LCOs based batteries were subjected to pretreatment to obtain LCOs cathode materials (Figure 1). The collected contents are listed in Table 1. The main detected elements were Co and Li at contents of 58.6% and 7.34%, respectively. Co and Li existed in the form of LiCoO₂, and Al impurities were present as aluminum foil. Fe was detected as elementary substance, and content of both Al and Fe were estimated to 1% to 2%, respectively. These features affected the purity of recovered cobalt, which required further removal.

| Element | Co  | Li   | Fe  | Al  | Na  | Ca  | Pb  | Mg  | Si  | Mn  | Ni  |
|---------|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Content (%) | 58.6 | 7.34 | 0.93 | 1.61 | 0.018 | 0.003 | 0.002 | 0.256 | 0.014 | 0.001 | 0.002 |

3.2. Impurity Removal by Alkali Leaching and Fluid Magnetic Separation

3.2.1. Effect of NaOH Concentration on Alkali Dissolution of Aluminum Removal. In treated lithium cobalt oxide positive electrode material, Al would exist as aluminum foil [17], which could react with alkali but lithium cobalt oxide would not. Hence, alkali solution was used for soaking of lithium cobalt oxide positive electrode and dissolving of Al impurities, as well as removal of small amounts of aluminum from the positive electrode material. The reaction is shown in Eq. (1), and the aluminum removal effect is presented in Figure 2.

\[
2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2
\]  

Figure 2. Effect of Excess Coefficient of Liquid Alkali on Aluminum Removal Efficiency.

Figure 2 shows the effect of excess coefficient of liquid alkali on efficiency of aluminum removal. As excess coefficient of liquid alkali increased, the leaching rate of Al gradually rose. The addition of theoretical amount of liquid alkali (n(NaOH)/n(Al)=1) led to aluminum removal rate of only 72%. On the other hand, the removal rate of Al increased significantly when liquid alkali amount gradually enhanced. Using 1.75-fold excess sodium hydroxide, the removal rate of Al reached 97%. Afterward, the removal rate rose slowly, and increase in alkali solution amount showed no obvious effect on improving the aluminum removal rate. Therefore, the optimal liquid alkali excess coefficient was recorded as 1.75.
3.2.2. Influence of Magnetic Separation of Iron Removal on Iron Removal. Small amounts of Fe metal existed in the lithium cobalt oxide positive electrode [18]. Green magnetic separation was used to separate iron due to Fe metal with strong magnetic properties and LCOs positive electrode as non-magnetic metal without magnetic properties. Figure 3 shows the effect of different liquid-solid ratios on magnetic separation of iron. The removal rate of Fe was positively correlated to liquid-solid ratio. Larger liquid-solid ratios led to higher iron removal rates. At liquid-solid ratio of 8:1, the removal rate reached a peak of 98.3%. The reason for this had to do with increase in liquid-solid ratio, which led to more dispersed iron in lithium cobalt oxide. As a result, the concentration of iron dropped and magnetic field adsorption performance in fixed magnetic stirrer improved.

In sum, the iron content in waste LCOs cathode material after alkali dissolution removal of aluminum and magnetic separation of iron was estimated to 0.016%. The aluminum content was recorded as 0.002%, which was conducive to purity improvement of subsequent lithium and cobalt products.

![Figure 3. Effect of Different Liquid-Solid Ratios on Magnetic Separation of Iron.](image)

3.3. Influence of H$_2$ Reduction on Phase Structure and Lithium Water Leaching of Scrapped Lithium Cobalt Oxide Materials

3.3.1. Analysis of Reduction Temperature on Phase Structure of Scrapped Lithium Cobalt Oxide. Figure 4 shows SEM images of LCOs sample before and after reduction, and Figure 5 presents an XRD image of LiCoO$_2$ at different reduction temperatures. The surface of grains looked smooth and spheroid-like with uniform morphology (Figure 4). After hydrogen reduction at 650 °C, the morphology of original LCOs spherical particles was broken, forming aggregates with irregular small particles and some large particles. Such features should be conducive to leaching of lithium. The positions and intensities of the diffraction peaks of raw LCOs in Figure 5 were in accordance with PDF standard card (No. 50—0653) of lithium cobalt oxide. In addition, no obvious impurity peaks were observed, indicating formation of high-purity cobalt acid lithium phase after impurity removal. The reduction of raw LCOs by hydrogen at 350 °C for 3 hours led to generation of peaks related to LiCoO$_2$, CoO, and small amounts of Co, Li$_2$O and LiOH. Hence, small amounts of LCOs reacted at 350 °C to produce Co, CoO, Li$_2$O, and LiOH. Note that LiOH may be the reaction product of Li$_2$O and H$_2$O when most LCOs did not fully react. As reduction temperature further increased to 450 °C, cobalt with +3 charge in LCOs became completely reduced to lower charge products of cobalt, 0-Co, and + 2-CoO. In addition, lithium still existed as Li$_2$O and LiOH. As temperature further rose, CoO peak of cobalt gradually weakened and Li$_2$O peak of lithium further strengthened. At 650 °C, the reduced phase of lithium cobalt oxide contained Co, Li$_2$O, and small amounts of CoO and LiOH phases. These reactions could be described according to Eqs. (2)-(4) [19-20]:

\[
\begin{align*}
2\text{LiCoO}_2 + \text{H}_2 & \rightarrow 2\text{CoO} + 2\text{Li}_2\text{O} + 2\text{H}_2\text{O} \quad (2) \\
\text{CoO} + \text{H}_2 & \rightarrow \text{Co} + \text{H}_2\text{O} \quad (3) \\
\text{Li}_2\text{O} + \text{H}_2\text{O} & \rightarrow 2\text{LiOH} \quad (4)
\end{align*}
\]
3.3.2. Effect of Reduction Temperature on Lithium Leaching Efficiency. The effect of reduction temperature on leaching rate of lithium was studied and the results are shown in Figure 6. As temperature increased from 350 °C to 650 °C, Li recovery rate enhanced from 92.8% to 98.8%. XRD in Figure 4 and Eq. (2) revealed that LiCoO2 should be reduced by H2 at high temperatures to generate new phases of CoO and Li2O. As temperature increased, the decomposition of LiCoO2 became more complete, and proportions of CoO and Li2O components enhanced. As the reaction further progressed, the layered structure of waste LCOs sample gradually vanished to yield various complex phase particles. According to Eqs. (3) and (4), the particles should continue deoxidizing to form smaller particles as the reaction further progressed. In other words, particle with small size should induce better subsequent water immersion of solid mixture. Therefore, the recovery rate of Li increased with reduction temperature [21].

Figure 7 compares the XRD images before and after water immersion at 650 °C. After water leaching, the diffraction peaks of Li2O and LiOH completely vanished but those of CoO and Co remained basically unchanged. Most lithium in LCOs cathode material reduced at 650 °C was converted into soluble Li2O and LiOH. During water leaching, the leaching rate of lithium reached 98.8%. Figure 8 illustrates the morphologies before and after water leaching reduction roasting at 650 °C. The sample changed from dense structure to loose and porous structure visible on the surface. Also, fine particles attached to the surface had vanished. After water leaching, large amounts of Li2O and LiOH became dissolved on the surface and bulk of each sample, resulting in porous structure.
3.3.3. Influence of Different Liquid-Solid Ratios of Water Leaching on Lithium Leaching Efficiency.

Figure 9 presents the effect of water leaching with different liquid-solid ratios on leaching rate of lithium. Note that Li removal efficiency at different water-liquid-solid ratios remained above 98%. As solid-liquid ratio increased, the removal efficiency showed slight upward trend. At liquid-solid ratio of 4:1, maximum Li-removal efficiency reached 99.1%, suggesting that solid-liquid ratio had no significant effect on Li removal efficiency. Thus, the optimal solid-liquid ratio was determined as 4:1.
3.4. Lithium Recovery Process and Mechanism Analysis

Li$_2$O would change to LiOH solution in water, then sodium carbonate was added to the supernatant after extraction filtration, lithium carbonate precipitation would be formed. The reaction equations could be expressed by Eqs. (4)–(5) [22]:

$$2\text{LiOH} + \text{Na}_2\text{CO}_3 = \text{Li}_2\text{CO}_3 + 2\text{NaOH}$$  \hspace{1cm} (5)

The LiCoO$_2$ sample obtained by reduction at 650 °C was then immersed in water at room temperature and solid-liquid ratio of 1:4 for 30 minutes. The supernatant was adjusted with sodium carbonate to pH=14. XRD profile of the obtained lithium carbonate is shown in Figure 10. The peak shape looked sharp and basically smooth without presence of hetero-peaks. This indicated well-crystallized product, consistent with crystal form of pure lithium carbonates. The purity after testing was estimated to 99.5%.

3.5. $H_2$ Secondary Reduction into Cobalt Powder

Figure 11 compares the XRD profiles of regenerated cobalt powder with primary cobalt powder obtained by reduction of the solid at 650 °C after removal of lithium. Both regenerated cobalt and primary cobalt contained mixed α-Co with β-Co. Also, no obvious diffraction peaks related to other impurities in cobalt were present. The purity of regenerated cobalt powder measured by the subtraction method was recorded as 99.4%. The electron microscopy images of regenerated cobalt and primary cobalt are shown in Figure 12. Both morphologies displayed spherical Co powder. The surface of regenerated Co powder obtained after the second reduction looked smooth with uniform morphology and some agglomeration. Basically
no difference could be distinguished, except that the first particles looked a bit larger than those of primary cobalt.

![XRD Profiles](image1)

Figure 11. XRD Profiles of Regenerated Co Powder and Primary Co Powder after H2 Reduction at 650 °C.

![SEM Profiles](image2)

Figure 12. Comparison of SEM Profiles of Regenerated Cobalt Powder Reduced by H2 at 650 °C with Primary Cobalt Powder.

4. Conclusions
Scrapped cathode material was removed from aluminum and iron by alkali leaching and magnetic separation combined with water leaching, alkali precipitation and high-temperature hydrogen reduction. Lithium and cobalt recovery process and treatment approach were proposed and optimized. This approach was found efficient, easy to implement, environmentally-friendly, and potential for industrialization.

Impurity removal data identified the optimal process conditions as room temperature, 1.75-fold excess NaOH, liquid-to-solid ratio of 8:1, and 2 hours reaction time for alkaline and magnetic separation. Under these conditions, the removal rates of Al and Fe reached 99.9% and 98.3%, respectively. The removal efficiency was significant without loss of Co and Li during the reaction.

The recovery data of lithium and cobalt showed that reduction of scrapped cobalt carbonate cathode material by hydrogen at 650 °C for 3 hours led to reaction of lithium cobalt oxide to produce Co, LiO2, and small amounts of CoO and LiOH. After water leaching and alkali precipitation at normal temperature, the optimal water-to-solid-liquid ratio was identified as 1:4 for reaction time of 30 min. Under these conditions, lithium leaching rate reached 99.1% and final obtained sodium carbonate precipitation Li2CO3 showed purity of 99.5%. After second high-temperature hydrogen reduction of water leaching slag, Co powder with purity of 99.4% was obtained and found comparable to primary cobalt powder.

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