Environmentally Friendly Suspension Electrolysis Technology for Regenerating Lithium Cobalt Oxide

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The extensive usage of portable electronic products and the acceleration of their replacement have led to the discarding of a growing amount of LiCoO₂ batteries. It is necessary to recycle the batteries from both viewpoints of environment and economic benefits. Current recycling approaches for LiCoO₂ are dominantly based on hydrometallurgy and pyrometallurgy, which usually require multiple complicated steps and involve the use of high temperature or harmful chemicals, like acids and alkalis. There remains an urgent need for a green and simple process. In this paper, suspension electrolysis technology is proposed to recycle spent batteries, in order to achieve the leaching, purification and regeneration of LiCoO₂ in one step. The most advantageous of the present technology are that reacting in one reactor at atmospheric condition and no use of highly corrosive and harmful reagents. The reaction of LiCoO₂ leaching in the anode region and simultaneously re-synthesizing in the cathode region in ammonia electrochemical system is established for the first time. Three chemical reaction systems of NH₄HCO₃, NH₄HCO₃–NH₃, and NH₄HCO₃–(NH₄)₂SO₃, are explored. The results of the laboratory scale experiments show that LiCoO₂ can be regenerated in NH₄HCO₃–(NH₄)₂SO₃ reaction system. Under the investigated conditions of this study, 66.3 % of Li and 75.4 % of Co were leached out in the anode region and 53.2 % of LiCoO₂ was regenerated in the cathode region under the conditions of 0.5 mol/L (NH₄)₂SO₃ concentration, 2.5 mol/L NH₄HCO₃ concentration, 1.5 A current, 2 g/L solid to liquid ratio, 50 °C, and 1.5 h. The reaction system for realizing LiCoO₂ leaching in the anode region and simultaneously re-synthesizing in the cathode region is established. This work provides a promising method for recovering LiCoO₂ efficiently and environmentally friendly, promoting the sustainable utilization of the resources.

1. Introduction

Lithium-ion battery (LIB) is acting a more and more important role in the development of electronic industry (Yang et al., 2017). LiCoO₂ is the most widely used cathode active material in portable electronic products (Santana et al., 2017), such as mobile phones, cameras, notebooks, since it was first commercialized by SONY in 1991 (Xiao et al., 2020) due to its competitive advantages of high specific energy, small self-discharge, excellent cycle life and high electronic conductivity (Chen et al., 2015). The increasing demand and the rapid replacement of the electronics have led to the continuous discard of LIBs in considerable quantities (Li et al., 2013). The dispose and recycling of LIBs is getting more and more attention from governments, companies, and researchers worldwide (Lv et al., 2018).

LIBs contain large amounts of valuable elements, especially Li and Co, indicating that LIBs are worth recycling from the viewpoints of economic benefits (Gu et al., 2017). LIBs also contain a lot of harmful substances, such as heavy metals and toxic electrolytes (Zeng et al., 2015). Once the LIBs cannot be handled properly, the above harmful substances will leak out into the environment, causing great harm to the environment and human health (Jha et al., 2013). Cobalt has been defined as strategic metal by many countries, such as China, European Union, and South Korea, etc (Zeng and Li, 2015). The demand for cobalt continues to grow (Li et al., 2017), although the natural deposits of cobalt are increasingly being exhausted (Zeng et al., 2020). The continuous supply of resources is a problem facing the world that must be resolved in order to guarantee the
sustainable development of electronic industry. Regarding spent LIBs as secondary resources for recycling is becoming a worldwide consensus to prevent pollution, conserve mineral resource, and sustainably utilize resource (Zeng and Li, 2016).

A great number of studies have been carried out focusing on the recovery of lithium and cobalt from spent LIBs (Wang et al., 2016). Several methods, which are mainly based on pyrometallurgy (Xiao et al., 2017) and hydrometallurgy (Li et al., 2009), have been developed. Pyrometallurgical processes have advantage like less additive usage and less loss of valuable elements (Li, 2016). Hazardous gas emission, particulate matter release, and high energy consumption are the main limitations of pyrometallurgical process applications (Santana et al., 2017). Hydrometallurgical process includes the following steps: (1) leaching by acid (Huang et al., 2016) or alkali (Ku et al., 2016) to total release of metal elements, such as Li, Co, Al, Cu, etc. (2) selective recycling different metal elements according to their unique physicochemical properties by fractional chemical precipitation (Nan et al. 2005) or multistage organic solvent extraction (Provazi et al., 2011) or electrochemistry (Freitas and Garcia, 2007). Although the hydrometallurgical method is more favoured and widely applied due to its advantages of high recovery efficiency, high purity of recovered product, and low energy consumption (Joulie et al., 2017), there are also several drawbacks, such as long process, large dosage of chemicals, and long period (Chen et al, 2017). A greener and shorter process is still urgently needed.

Sulfuric acid (Zou et al., 2013), hydrochloric acid (Li et al., 2009), and nitric acid (Li et al., 2011) are the most commonly used reagents for leaching Li and Co due to their natures of high efficiency, strong adaptability to the complex system, and mature operations (Qi et al., 2020). These inorganic acid solutions produce leachates of low pH, posing a threat to the environment and making them unfavourable for subsequent waste water treatment (Zheng et al., 2017). Ammoniacal agents were investigated for leaching Co from cathode active materials. The results showed that at least 94 % of Co can be selectively leached out into the solution, achieving separation from metals such as Mn and Al (Wang et al., 2017). Electrochemical technologies have also been investigated for metals recovery from spent LIBs. Prabaharan (2017) developed an electrochemical process to recycle Co from cathode active materials. The leaching and deposition of Co were processed in two different electrolytic cells, and sulphuric acid was used as electrolyte in the former process. Above 96 % of Co was recovered. Li (2011) developed a process to electrodeposit lithium cobalt oxides directly from the nitric acid leaching solution of lithium cobalt oxides. The result pointed out that the alkaline environment is a necessary condition to achieve the above reaction. An idea is proposed in the present work that can the leaching, purification and regeneration of lithium cobalt oxide be achieved in one reactor in an electrochemical system? A suspension electrolysis technology is put forward to testify the above hypothesis. The composition of the electrolyte that can realize the above reaction was investigated and selected. The factors that would affect the leaching and re-synthesis of lithium cobalt oxide during the electrolysis process were examined in detail. The as-synthesized products were analyzed. The objective of this article is to provide a perspective approach for recovering Li and Co from spent lithium cobalt oxide in an environmentally friendly, easy operation, and cost-effective way.

2. Experimental

2.1 Materials and chemicals

The core of the proposed technology for recycling spent LIBs is the regeneration of lithium cobalt oxide. Whether lithium cobalt oxide can be regenerated determines the effectiveness of this technology for the recovery of spent lithium ion batteries. Pure lithium cobalt oxide (6.74 % of Li concentration and 57.2 % of Co concentration, Aladdin) was used as representative of spent cathode active material to avoid the influence of impurities to verify the feasibility of this technology. Chemical reagents used in the experiments were all analytical reagents unless otherwise mentioned.

2.2 Apparatus

Electrochemical experiments were conducted in a custom-made rectangular cell (length × width × height = 15 × 7 × 6 cm) made of Teflon. The cell was divided into the anode zone and the cathode zone by an installed acrylic fabric. The anode was graphite plate (7 × 6 × 0.3 cm) and the cathode was platinum-plated titanium base electrode plate (7 × 6 × 0.3 cm). The electrodes were connected to a DC constant current source (R-3005, Kingrang, China) through a copper wire. For each run, 250 mL electrolyte was added into the cell, and then heated to a desired temperature. A proper mass of pure lithium cobalt oxide was added into the anode zone of the cell. A proper current was introduced for a certain time. The deposited product in the cathode region of the cell was separately collected by filtering through a 0.45-μm membrane filter, washed with distilled water for several times to remove impurities, and dried at 105 °C for 12 h.
2.3 Analytical techniques

X-ray diffraction (XRD, X’Pert Pro, PANalytical, Netherlands) was used to identify the phase of the regenerated product. Scanning electron microscopy (SEM, SUPRA 55, Zeiss) was used to examine the morphology of the regenerated product. Field-emission transmission electron microscope (TEM, Tecnai G2F20 S-Twin, FEI, U.S.) was used to detect the selected area electron diffraction (SAED) of the regenerated product. The metallic elemental concentrations of the regenerated product were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 1067700, Thermo, U.S.) after being digested by HNO3 method.

3. Results and discussion

3.1 Regeneration performance of lithium cobalt oxide in NH4HCO3 reaction system

Generally, LiCoO2 must be dissolved by the ammoniacal method in the presence of a reducing agent (Zheng et al., 2017). This study attempts to verify whether the electric field can strengthen the complex of Co and NH3, reducing the use of reducing agents. With the principle of using as few and environmentally friendly reagents as possible, NH4HCO3 was selected in this work as electrolyte due to two reasons: (1) NH3, which could complex with Co3+ to form Co(NH3)n3+ (Zheng et al., 2017), promoting the dissolve of LiCoO2, can be provided via hydrolysis reaction of NH4+ (Qi et al., 2020); (2) NH4HCO3 can act a pH buffer (Zheng et al., 2017) so that the pH of leaching solution changes little during leaching.

Figure 1a shows the effect of current on the regeneration performance of LiCoO2 under the conditions of 2.5 mol/L NH4HCO3 concentration, 6 g/L solid to liquid ratio, 50 °C, and 3 h. Figure 1b shows the effect of NH4HCO3 concentration on the regeneration performance of LiCoO2 under the conditions of 1.5 A current, 6 g/L solid to liquid ratio, 50 °C, and 3 h. Figure 1c shows the effect of temperature on the regeneration performance of LiCoO2 under the conditions of 1.5 A current, 2.5 mol/L NH4HCO3 concentration, 6 g/L solid to liquid ratio, and 3 h. Figure 1d shows the effect of solid to liquid ratio on the regeneration performance of LiCoO2 under the conditions of 1.5 A current, 2.5 mol/L NH4HCO3 concentration, 50 °C, and 3 h. Figure 1e shows the effect of holding time on the regeneration performance of LiCoO2 under the conditions of 1.5 A current, 2.5 mol/L NH4HCO3 concentration, 6 g/L solid to liquid ratio, and 50 °C.

Figure 1: Effects of (a) current, (b) NH4HCO3 concentration, (c) temperature, (d) solid to liquid ratio, and (e) time on leaching rates of Li and Co and regeneration rate of LiCoO2.

From Figure 1, three conclusions could be concluded: (1) the dissolving of LiCoO2 in the electrolytic system was occurred, indicating that the electric field can strengthen the complex of Co and NH3; (2) the leaching rate of Li are overall higher than the leaching rate of Co, indicating that the dissolving of LiCoO2 in the electrolytic system was a step-by-step process; (3) the leaching rates of Li (<9 %) and Co (<2%) were both low; (4) the regeneration rate of LiCoO2 is 0, indicating that LiCoO2 is cannot be synthesised in the above reaction system. The improvement of the composition of the electrolyte for the suspension electrolysis technology to regenerate LiCoO2 is needed.
3.2 Regeneration performance of lithium cobalt oxide in NH₄HCO₃-NH₃ reaction system

The above experiments demonstrated that in NH₄HCO₃ electrochemical system, the dissolution of LiCoO₂ was thermodynamically feasible but the reaction kinetic was extremely low, which is consistent with the results of LiCoO₂ leaching with ammoniacal agents under non-electrochemical system (Zheng et al., 2017), and LiCoO₂ was failed to be re-synthesised. The efficient dissolution of Li and Co is the necessary prerequisite for the re-synthesis of LiCoO₂. NH₃ acts an important role for dissolving LiCoO₂ because Co is mainly dissolved in the form of complex with NH₃ in this process (Zheng et al., 2017). Previous study (Ku et al., 2016) pointed out that the increase of NH₃ concentration can significantly promote the dissolve of LiCoO₂. More NH₃ in the solution can no longer be obtained by increasing the concentration of NH₄HCO₃ because 2.5 mol/L is close to the saturated solubility of NH₄HCO₃. Ammonia water was added to investigate the influence of NH₃ concentration on the regeneration performance of LiCoO₂ in the present electrolysis system.

Table 1 shows the effect of ammonia water concentration on the regeneration performance of LiCoO₂ under the conditions of 2.5 mol/L NH₄HCO₃ concentration, 1.5 A current, 2 g/L solid to liquid ratio, 50 °C, and 3 h. The leaching rates of Li and Co were unaffected by changes in the ammonia concentration from 0.5 to 3 mol/L. LiCoO₂ was still failed to be re-synthesised in the cathode region by the addition of ammonia water during the electrolysis process. The leaching rate of Li and Co was even lower when ammonia water was added than when ammonia water was not added, indicating that excessive NH₃ would negatively affect the leaching of LiCoO₂. The above tests demonstrated that the concentration of NH₃ is not the key for LiCoO₂ dissolving in the electrochemical process. The composition of the electrolyte for the suspension electrolysis technology to regenerate LiCoO₂ is still needed to be improved.

Table 1: Influence of ammonia water concentration on the regeneration performance of LiCoO₂

<table>
<thead>
<tr>
<th>Ammonia water concentration (mol/L)</th>
<th>Li leaching rate (%)</th>
<th>Co leaching rate (%)</th>
<th>LiCoO₂ regeneration rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>4.0</td>
<td>0.7</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>3.6</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>3.3</td>
<td>0.6</td>
<td>0</td>
</tr>
</tbody>
</table>

3.3 Regeneration performance of lithium cobalt oxide in NH₄HCO₃-(NH₄)₂SO₃ reaction system

According to a study by Zheng et al. (2017), Co(NH₃)₆³⁺, Co(NH₃)₅²⁺, Co(NH₃)₄²⁺ are the major soluble species in the solution over the pH range of 9–11 in the Co-NH₃-H₂O system. Co is easier to be dissolved from LiCoO₂ by complex with NH₃ in lower valence. Co³⁺ was usually reduced to Co²⁺ by adding reducing agent to promote the dissolution of LiCoO₂ in chemical leaching processes. In this study, (NH₄)₂SO₃ was selected as the reducing agent to avoid the introduction of metal impurities to investigate whether it would contribute to the leaching and re-synthesis of LiCoO₂ during the present suspension electrolysis process.

Table 2 presents the effect of (NH₄)₂SO₃ concentration on the regeneration performance of LiCoO₂ under the conditions of 2.5 mol/L NH₄HCO₃ concentration, 1.5 A current, 2 g/L solid to liquid ratio, 50 °C, and 1.5 h. The addition of (NH₄)₂SO₃ significantly promoted the leaching of LiCoO₂. LiCoO₂ was successfully re-synthesised in the cathode region, as shown in Figure 2c. The results also showed that higher (NH₄)₂SO₃ concentration could promote the leaching of LiCoO₂ in the anode region and the re-synthesis of LiCoO₂ in the cathode region, while excessive (NH₄)₂SO₃ hindered the regeneration of LiCoO₂. The above results proved that LiCoO₂ can be regenerated in one reactor by suspension electrolysis technology, and the reaction system was established for the first time. The detailed investigation of the factors which might affect LiCoO₂ regeneration performance will be conducted in the next study.

Table 2: Influence of (NH₄)₂SO₃ concentration on the regeneration performance of LiCoO₂

<table>
<thead>
<tr>
<th>(NH₄)₂SO₃ concentration (mol/L)</th>
<th>Li leaching rate (%)</th>
<th>Co leaching rate (%)</th>
<th>LiCoO₂ regeneration rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>55.4</td>
<td>64.1</td>
<td>42.2</td>
</tr>
<tr>
<td>0.5</td>
<td>66.3</td>
<td>75.4</td>
<td>53.2</td>
</tr>
<tr>
<td>1</td>
<td>61.5</td>
<td>68.9</td>
<td>51.3</td>
</tr>
</tbody>
</table>

Figure 2a shows that Co was leached out in the form of Co(NH₃)₆³⁺ (yellow) in the NH₄HCO₃-(NH₄)₂SO₃ electrolysis process. Figure 2e and 2f show that the regenerated LiCoO₂ is different from the raw material LiCoO₂ in molecular structure. Figure 2g shows the pH value changes of the electrolyte in the anode region and cathode region under different (NH₄)₂SO₃ concentration with the increase of time. The electrochemical characteristics of the regenerated LiCoO₂ will be studied in the future work.

This work only focused on the core cause of recycling Li and Co from spent LIBs, which is potential to instead the current hydrometallurgy and pyrometallurgy, to make the recycling process more efficient and
environmentally friendly. The expected flow-sheet of the present technology applied to the recycling of spent LiBs is shown in Figure 3.

Figure 2: Products analysis of LiCoO$_2$ regeneration test in NH$_4$HCO$_3$-(NH$_4$)$_2$SO$_3$ system at 0.5 mol/L (NH$_4$)$_2$SO$_3$: (a) electrolyte after electrolysis, (b) cathodic deposition product, (c) XRD, (d) SEM of cathodic product, (e) SAED of LiCoO$_2$, (f) SAED of cathodic deposition product, and (g) pH values of electrolyte at different (NH$_4$)$_2$SO$_3$ concentrations in anode region and cathode region.

![Electrolyte after electrolysis](image1.png)
![Cathodic deposition product](image2.png)
![XRD](image3.png)
![SEM of cathodic product](image4.png)
![SAED of LiCoO$_2$](image5.png)
![SAED of cathodic deposition product](image6.png)
![pH values of electrolyte](image7.png)

Figure 3: Expected flow-sheet of the present technology applied for the recovery of Li and Co from spent LIBs.

4. Conclusions

This paper proposes a novel technology of suspension electrolysis for regenerating LiCoO$_2$ in one step, and the reaction system was established for the first time. The main findings can be concluded as follows: (1) high concentration of NH$_3$ in the electrolyte is not the key to its complexion with Co$^{3+}$; (2) LiCoO$_2$ can be regenerated by electrolysis in NH$_4$HCO$_3$-(NH$_4$)$_2$SO$_3$ electrolyte system; (3) Co was leached out from LiCoO$_2$ in the form of Co(NH$_3$)$_6^{3+}$ in NH$_4$HCO$_3$-(NH$_4$)$_2$SO$_3$ electrolyte system. This work is an exploratory study at the laboratory scale. The reaction mechanisms of anode and cathode are not yet clear. Further study will be conducted in future work to better understand and develop this technology.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21808190) and Doctoral Fund of Southwest University of Science and Technology (18zx7116, 18zx7153). The authors are grateful to the reviewers who helped them improve the paper by many pertinent comments and suggestions.

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