Research Article

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Recovery of cobalt from spent lithium-ion battery cathode materials by using choline chloride-based deep eutectic solvent

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Abstract: Recycling of spent lithium (Li)-ion batteries has become a hot research topic due to its surge in the quantity and environmental problems. Herein we demonstrated a new chemical configuration of choline chloride-based deep eutectic solvent (DES) to recover the cobalt from lithium cobalt oxide (LiCoO₂), a representative cathode material for Li-ion battery. It was experimentally verified that the leaching efficiency of Co increased rapidly with the increase in the reaction temperature. Nearly 96% of Co can be leached from lithium cobalt oxide after a leaching treatment at 200°C for 20 h. The leaching mechanism of cobalt in DES was analyzed by using a variety of techniques, including cyclic voltammetric experiments, Fourier transform infrared radiation, and ultraviolet-visible spectra. The results showed that the LiCoO₂ dissolve into the DES via reduction of Co(III) to Co(II). In particular to this work, the leaching experiments were performed in a higher concentration than those in the previous studies, which significantly promoted the operating efficiency of the leaching process.

Keywords: cobalt recovery, deep eutectic solvent, reduction, spent lithium-ion batteries

1 Introduction

Rechargeable lithium (Li)-ion batteries with a high theoretical efficiency of converting chemical to electrical energy have been widely used in mobile devices, portable electronics, and electric vehicles. Because Li-ion batteries have a limited lifetime of 3–5 years, large numbers of spent Li-ion batteries (SLIB) have been generated, and it is expected that the number of SLIB will reach 900,000 by 2023 [1]. The development of recycling of SLIB is very important. Most of the recoverable value components in SLIB are in the cathode. For example, Cobalt (Co) is a strategic material that typically constitutes up to 15 wt% of LiCoO₂ (LCO, one of the main commercial cathode materials) [2–4]. The establishment of effective recycling strategies could balance the impact of end-of-life Li-ion batteries and the demands on raw materials in the battery supply chain.

Three routes, namely pyrometallurgy, bio-metallurgy, and wet-chemical methods have been considered as effective ways to recover Co from SLIB-related materials. As a typical method of pyrometallurgy-dominant way, direct reduction of metal oxides in electrodes has been widely studied to recover the Co from LCO-based materials [5–7]. Although pyrometallurgy treatment can obtain nearly 100% metal leaching rate, there are some inevitable disadvantages, such as high treatment temperature (>1,000°C), high energy consumption, and harmful gas emission.

Bio-metallurgy has been considered an alternative way to extract metals from LCO-based materials. Biswal et al. [8] used Aspergillus niger strains MM1 and SG1, and Acidithiobacillus thiooxidans 80191 to extract Co and Li from SLIB. After reaction for nearly a week at 30°C, high amount of Co precipitated in the form of cobalt sulfide (100%), cobalt hydroxide (100%), or cobalt oxalate (88%). Huang et al. [9] focused on constructing a bio-electro-hydrometallurgical platform to efficiently recover Co, Li, and Mn. Maximum recoveries of 91.45%, 93.64%, and 87.92% for Co, Li, and Mn, respectively, were achieved. To date, the main challenge of the bio-metallurgy method lies in the difficulty of strain culture and screening which lead to a long recovery period of metals (>1 week). Additionally, only a small number of LCO-based materials could be treated in the bio-metallurgy-dominated routine, which makes it difficult to scale up for the practical purpose.

Wet-chemical method, with its characteristic of high leaching efficiency (often higher than 90%) of Co, is the...
most popular strategy to recover Co components from LCO-based materials. Barik et al. [10] used hydrochloric acid (concentration of 1.75 M) to recover Co from the cobalt-manganese lithium battery, and 90% of Co was recovered. The cathode material of LiNi_{0.5}Co_{0.5}Mn_{0.5}O_2 battery was leached by using 1 M sulfuric acid and 1% hydrogen peroxide. The leaching efficiency of Co was higher than 99.7% [11]. Reduction agents, e.g., H_2O_2, NaHSO_3, and ascorbic acid, were used as additives to reduce the emission of toxic gases [12]. However, inorganic acid, such as sulfuric and hydrochloric acids, has to be added continuously in the recovery process, and environmental issue is often raised in the wet-chemical method.

As a consequence, the organic acid is academically considered a suitable candidate for Co leaching. Zeng et al. [13] used oxalic acid to recover Co from LCO-based materials, 97% recovery of Co was achieved. Zhang et al. [14] recovered the LiNi_{0.5}Co_{0.5}Mn_{0.5}O_2 from the cathode of a ternary battery by using oxalic acid and the recycled materials were remade to a new cathode. Organic acids possess better characteristics than inorganic acids for Co leaching, e.g., no toxic gas emission and better reducibility [15,16]. Compared with inorganic acid reagents, the organic acid is higher in price, which makes the recovery process not cost-effective.

Recently, deep eutectic solvents (DES) find many applications in electrochemistry, metallurgy, and other fields due to their characteristics of low melting point (typically from room temperature to 180°C) and good solubility of metallic compounds [17,18]. Generally, the behavior of oxides in DES is similar to that in the molten state, and most metal compounds including metal salts have good solubility. Abbott et al. [19] used lactic acid-based DES to extract a large number of metals. Particularly, they mentioned the affinity between DES and Co. The abovementioned characteristic demonstrated that DES could be a good solvent for Co leaching from LCO-based materials.

According to the synthesis mechanism of DES and the principle of green chemistry, low-cost and environment-friendly green materials are preferred. Choline chloride (ChCl) is a commonly available feed additive and is also often used as a hydrogen bond receptor in the synthesis of DESs. There are a few reports on the recovery of waste lithium batteries with ChCl-based DES [20–29]. Tran et al. [23] are among the first in leaching Co from high concentration Co-DES solution (10 mg LCO with 50 mg DESs, ChCl + ethylene glycol [EG]), and the leaching efficiencies of Co and Li were both higher than 90%. However, the reaction temperature and time were still high to be 220°C and 24 h, respectively, which are not beneficial for commercial operation. Wang et al. [24] dissolved 10 mg of LCO powder in 10 g DES (ChCl + urea), and more than 95% of the Co was leached from LCO-based materials. Schiavi et al. [26] used DES (ChCl + EG) for the selective recovery of Co from mixed LIBs and the leaching yields attained 90% for Co and only 10% for Ni. By using DES (ChCl + formic acid), the leaching efficiency of Co was as high as 99.0% at 70°C [28].

The feasibility of recovering LCO using ChCl-based DES has been proved in the previous studies. However, there are still some problems to be addressed. The ability of ChCl-based DES to treat cathode materials is very limited. Meanwhile, the leaching process of Co still lacks systematic proof. At present, the selection of hydrogen bond donors for ChCl-based DES mainly focuses on urea and EG. The nature and ability of hydrogen bond donors may determine the leaching efficiency of Co [23]. In addition, with the increase in temperature, the leaching is accelerated, especially the short-term leaching effect that needs to be improved. Therefore, there is still room for the selection of hydrogen bond donors to meet larger, faster, and more industrialized processing systems.

In the present work, a new ChCl-based DES system was adopted to achieve better dissolution and higher yield of Co in DES than that in previous studies. Particularly, the leaching experiments were performed at higher concentration than those reported in previous studies, thereby greatly promoting the leaching efficiency of Co.

## 2 Materials and methods

### 2.1 Materials

Glycerol (C_3H_6O_3; Gly), absolute ethanol, and sodium carbonate (Na_2CO_3) are of analytical grade and were purchased from Tianjin Damao Chemical Reagent Factory, China. ChCl (C_5H_14ClNO) was from American McLean Company. The experimental lithium cobaltate(III) oxide (LiCoO_2) was obtained by manual disassembly from a local battery recycling company.

### 2.2 Preparation of DESs and leaching of Co components

ChCl and Gly were mixed with different molar ratios to prepare the DES. The mixture was melted at 80°C for 1 h with constant stirring until a clear, homogenous DES was obtained. The prepared DES was cooled to room temperature in a desiccator equipped with silica gel to avoid moisture absorption.
Typically, LCO powder (0.1 g) and DES (5 g) were mixed in a glass flask. The glass flask with a condenser tube was placed in an oil bath. The effect of time and temperature on metal leaching was investigated over the time range of 1–10 h and temperature range of 120–200°C. The effect of the molar ratio of ChCl:Gly was also assessed at 200°C for 20 h. The leachates were filtered using a filter membrane with a pore size of 0.45 μm at near to 100°C. The leachates were then precipitated by carbonate and subsequently calcined (500°C, 6 h) to obtain a black powder.

2.3 Characterization of samples

The metal cation concentration of the leachates was determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5,300 V). The Fourier-transform infrared (FT-IR) and ultraviolet-visible (UV-Vis) spectra of the DES and leachates were obtained using a Nicolet iS50 FT-IR spectrometer in the form of potassium bromide disks, and an EVOLUTION 201 UV-Vis spectrophotometer, with a 1 mm light path quartz cell, respectively.

Electrochemical tests were performed on CHI760E electrochemical workstation. A standard three-electrode system was used with glassy carbon as the working electrode, Ag/AgCl as the reference electrode, and graphite as the counter electrode. The calcined powders were characterized by X-ray diffractometry (XRD, Rigaku Ultima IV, Japan) using Cu Kα radiation, SEM images of the samples were carried out using Hitachi S-3400N.

2.4 Calculation of leaching efficiency

The leaching efficiency (η) was defined as:

\[
\eta = \left( \frac{CV}{m_0} \right) \times 100\%
\]

where \(C\) is the final concentration of Co in the solution (mg·L\(^{-1}\)), \(V\) is the volume of the initial resulting solution (in L), and \(m_0\) is the mass of the initial amount of Co in the original material (in mg).

3 Results and discussion

3.1 Effect of process parameters on leaching efficiency of Co

The effect of the molar ratio of ChCl:Gly on the leaching efficiency of Co is shown in Figure 1a. When the molar ratio of ChCl:Gly was 1:1, 1:1.5, 1:2, and 1:4, the leaching efficiency of Co was 91.7%, 95.41%, 91.18%, and 78.82%, respectively.

The LCO contains a number of polymetallic lithium oxide with a high valence of Co. However, Co(III) oxides are usually insoluble. Reducing the valence of Co plays a key role in the recycling of valuable elements from spent LCO. In the recycling of valuable elements from spent LCO, the reducibility of DES is one of the factors to be considered. In the recycling of LIB using ChCl:EG DES, EG could be chemically acting as such an acceptor. This implies the proton acceptor has some reductive ability. The reducibility of DES could be evaluated by its characteristic reduction potential [16]. The results of voltammetric experiments with the different molar ratios of ChCl:Gly DES are shown in Figure 1b. When the molar ratio of ChCl:Gly reaches 1:1.5, DES has the largest reduction potential, −0.96 V (vs Pt wire). In Figure 1a, the
highest leaching efficiency of Co attained 95.41% in DES with most negative decomposed onset potential.

There is a good correspondence between the leaching efficiency of Co and the reduction potential of DES. Operating parameters play a key role in the extraction of Co. The effect of the reaction time and temperature on the leaching efficiency of Co is shown in Figure 2. When the temperature was below 160°C, the rate of solid dissolution was very slow, and the leaching efficiency of Co was below 20%, even if the reaction time exceeds 10 h. The leaching efficiency of Co increased with the increase in temperature. When the reaction temperature was 180°C, the reaction speed of the system was accelerated, and the leaching efficiency of Co is rapidly increased to 76.5% in 10 h. When the temperature was further increased to 200°C, the leaching efficiency of Co was increased from 14.0% in 2 h to 90.5% in 6 h. The color of the leaching solution also changed with the change in treatment temperature as shown in the optical image in Figure 2. DES slowly changed from turbid to transparent emerald green and then gradually change to dark green during the dissolution of LCO. The leaching efficiency of Co can be directly reflected in the color of DES. We choose 200°C as the optimal temperature to obtain the highest leaching efficiency. Reaction time is another important experimental factor. Figure 2 also shows that in the first 2 h, the leaching of Co almost did not occur, as the reaction goes on, the leaching efficiency increased rapidly, and reached a plateau at 6 h, indicating the leaching was almost complete. When the reaction temperature is 200°C and the reaction time is 10 h, the leaching efficiency reaches 92.7%.

Leaching efficiency data of the previous studies and this work are shown in Table 1. A higher leaching efficiency is seen than the previously reported routes by using other chemical configurations of DES.

3.2 Leaching mechanism of Co in DES

The FT-IR spectra were applied to analyze the functional groups in the eutectic solvents and leachates (Figure 3). The methylene (2,940 cm$^{-1}$) and hydroxyl absorption peaks (3,400 and 1,150 cm$^{-1}$) of DES were weakened with the increase in the reaction time, respectively. A new band corresponding to C=O, likely aldehyde or carboxyl group, emerged at 1,740 cm$^{-1}$, indicating a redox reaction in the leaching process as shown in Figure 3 (purple color line). It is suggested that the polyol structure of Gly is more likely to be oxidized to aldehyde or carboxyl in the presence of two strong oxidants, Co$^{3+}$ and O$_2$. Like the traditional wet acid leaching reaction, the emergence of H$^+$ accelerates the destruction of metal oxygen bond in LCO through proton and accelerates the consumption of O$_2$ [23].

The existing forms of cobalt ions in the liquid phase were further analyzed by UV-Vis spectrophotometry (Figure 4). When the temperature was below 180°C, there was no characteristic peak of Co$^{2+}$ (628, 665, and 690 nm) when the temperature reached 180°C. Three absorption peaks at 628, 665, and 690 nm, were observed in the range of 600–700 nm when the temperature reached 180°C.

### Table 1: Comparison between reported EDS-based approaches for recycling of Co from LIBs

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction system</th>
<th>Reaction conditions</th>
<th>Leaching efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$SO$_4$ (1 M)</td>
<td>40°C, 1 h</td>
<td>40</td>
<td>[11]</td>
</tr>
<tr>
<td>2</td>
<td>DES (ChCl + EG)</td>
<td>195°C, 24 h</td>
<td>69.14</td>
<td>[23]</td>
</tr>
<tr>
<td>3</td>
<td>DES (ChCl + urea)</td>
<td>160°C, 2 h</td>
<td>60</td>
<td>[24]</td>
</tr>
<tr>
<td>4</td>
<td>DES (ChCl + CA)</td>
<td>60°C, 4 h</td>
<td>99</td>
<td>[30]</td>
</tr>
<tr>
<td>5</td>
<td>DES (ChCl + Gly)</td>
<td>200°C, 10 h</td>
<td>92.7</td>
<td>This work</td>
</tr>
</tbody>
</table>
A d–d broadband peak at 628 nm was present due to the formation of Co(II) complexes. The Co$^{2+}$ cation can coordinate with Cl$^-$ or O$_2^-$ to be six-coordinated with octahedral geometry. In the chloride-containing system, the absorption peak near 665 nm may be attributed to the presence of [CoCl$_4$]$^{2-}$ anion. The as-observed peaks correspond to the characteristic absorption peaks of [CoCl$_4$]$^{2-}$ anion emerged, which verifies the existence of Co(II) complexes in the Co-containing leachates.

The dissolution of LCO in DES resulted in the contact of cobalt(III) to the part of the system with strong reducibility. The reducibility of the DES promoted the consumption of positive cobalt(III) in Eq. 3. At the same time, it was oxidized to Aldehyde or carboxyl group, which increased the formation of H, which was rapidly consumed with O$_2^-$ in Eq. 2, thus increasing the efficiency of the reaction. The coordination of Cl$^-$ further stabilized the cobalt(II) in the solution, thus allowing Eq. 3 to continue.

The leaching process of LCO in ChCl/Gly DES can be expressed as follows:

\[
\text{LiCoO}_2(s) \rightleftharpoons \text{Li}^+(\text{DES}) + \text{Co}^{3+}(\text{DES}) + 2\text{O}^{2-}(\text{DES}) \quad (2)
\]

\[
8\text{Co}^{3+} + 5\text{O}^{2-} + 2\text{CH}_2\text{OH} \rightarrow 8\text{Co}^{2+} + 2\text{COO}^- + 3\text{H}_2\text{O} \quad (3)
\]

\[
\text{Co}^{2+} + 4\text{Cl}^- = [\text{CoCl}_4]^{2-} \quad (4)
\]

### 3.3 Co-containing leachates precipitation and recovery

The cobalt recovery experiment was carried out by precipitation using 20% sodium carbonate solution.
The obtained pink precipitate is roasted to obtain a black powder. Figure 5a shows the XRD patterns of the calcined samples, the peak of the crystalline powders can be well matched to cubic cobalt oxide spinel (JCPDS no. 43-1003). SEM image of the acquired Co₃O₄ powders with particle size ranging from 2 to 10 μm is shown in Figure 5b. The result showed that the most Co in the ChCl:Gly DES was recycled in the process of precipitation–calcination to be cubic cobalt oxide spinel (Co₃O₄).

4 Conclusion

In the present work, we demonstrated a new chemical configuration by using the mixture ChCl and Gly to recover the Co from LCO-based materials. The high leaching efficiency of Co 95.7% was achieved at 200°C for 20 h. It was found that the Co component dissolved into the DES by reduction of Co(II) into Co(I), the reducibility of DES was evaluated by CV tests, the most negative decomposed onset potential was found to be −0.96 V. The structure of the Co complexes in the choline chloride-based DES was verified from UV spectra. A new band, C=O, emerged at 1,740 cm⁻¹ in DES after leaching, indicating a redox reaction in the leaching process was verified by FTIR as evidenced in CV. Recovery of Co was performed by the carbonate precipitation method, and 94.7% of the Co was achieved in form of Co₃O₄.

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