Self-actuated leaching and integrated separation of spent lithium-ion batteries cathode and anode sheets

Ting He a,b,c, Jixing Zhao a,b,c, Dongxian Chen a,b,c, Shuai Gu a,b,c,* Jianguo Yu a,b,c* 

a. National Engineering Research Centre for Integrated Utilization of Salt Lake Resources, East China University of Science and Technology, Shanghai, 200237, China.
b. Engineering Research Center of Salt Lake Resources Process Engineering, Ministry of Education, East China University of Science and Technology, Shanghai, 200237, China
c. Joint International Laboratory for Potassium and Lithium Strategic Resources, East China University of Science and Technology, Shanghai, 200237, China

Corresponding authors: gushuai@ecust.edu.cn (S. Gu), jgyu@ecust.edu.cn (J. G. Yu).

Abstract: The heavy metals in spent lithium-ion batteries (LIBs) are potential safety hazards to the environment. Conventional hydrometallurgical recovery techniques suffer from both economic and environmental challenges. Here, a novel two-step leaching and solvent extraction process are proposed to improve the leaching efficiencies and achieve the integrated leaching of LIBs cathode and anode sheets. The current collector (Al) enables the self-actuated enhanced leaching of the spent cathode sheet, the leaching efficiencies of Al^{3+}, Li^{+}, and Co^{2+} are 100%, 71.29%, and 63.53%, respectively, under 0.4 M HCl and 40 min without external energy input. With di-2-Ethylhexyl phosphoric acid (D2EHPA), 98.99% Al^{3+} can be selectively extracted from the leachate. The following electrochemical leaching of both spent cathode residual and spent anode sheet is carried out at low cell voltage, 99.8% Li^{+} and 99.69% Co^{2+} can be obtained in 90 min. Meanwhile, Al(OH)_3, Co(OH)_2, Li_2CO_3, and Cu are obtained from spent cathode and anode sheets with high crystallinity and purity, respectively. This strategy provides novel approaches for the integrated recycling of spent LIBs, thus realizing an environmentally friendly process with more application potential.

Keywords: spent lithium-ion batteries; self-actuated leaching; extraction; electrochemical leaching; recycling

1. Introduction
Lithium-ion batteries (LIBs) have been extensively used in energy storage equipment and electric vehicles because of their unique advantages, e.g., low self-discharge rate, wide temperature range, and high energy density [1,2]. However, LIBs have a limited life span (3~5 years) and the impact of spent LIBs on the environment gradually increases with time [3]. According to projections, approximately 11 million tons of spent LIBs will be generated by 2030 [4]. The spent LIBs are combustible and explosive, and their toxic electrolyte would emit hazardous gases as well [5]. Furthermore, these spent LIBs contain a variety of valuable metals, such as Cu, Al, Co, and Li [6]. The recycling of spent LIBs has been an effective way to maintain the supply of battery resources [7,8].

Currently, the hydrometallurgical recovery processes are the most commonly used technology, but they require excessive acid consumption and the use of reducing agents for the efficient leaching of valuable metals [9–11]. Reducing the reagents consumption of the leaching process is essential for sustainable development and environmental protection [12,13]. Electrochemical techniques, as the green and environmentally friendly hydrometallurgy method, have been proposed and tested for the recycling of spent LIBs cathode, in recent years [14–16]. However, electro-reduction normally requires a complex pretreatment process, which not only increases the cost but also limits the solid-liquid (S/L) ratios (Table 1). The relatively low S/L ratio will in return hinder the industrial application. In addition, electrochemical leaching at high cell voltage ($E_{\text{cell}}$) generally involves side reactions, i.e., hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which lead to extremely low current efficiency ($\eta$) [17–19].

Meanwhile, the separation of valuable metals from the leachate also needs to be considered [20]. Solvent extraction has attracted the attention of researchers worldwide due to its simple operation, short extraction time, high selectivity, and low energy consumption [21–23]. Yang et al. achieved the extraction efficiency of Co$^{2+}$ up to 99.16 % under the conditions of 0.1M HNO$_3$, 1M NaNO$_2$, pH 4.2, 30 vol% methyl tri octyl ammonium chloride (N263), and A/O=2:1 [24], but additional chemical consumption is required. Xing et al. used 15 vol% di-decyl phosphinic acid (DDPA) for the separation of Co$^{2+}$/Ni$^{2+}$ at pH 5.6, Co$^{2+}$ extraction ratio reached 99.8% [25]. Dalini et al. recovered approximately 96% of Ni$^{2+}$ by a molar ratio of Ni$^{2+}$ to dimethylglyoxime of 1:2 and pH 5, subsequently, 93.38% Co$^{2+}$ extraction efficiency could be achieved using 30 v/v% di-2-ethylhexyl phosphoric acid (D2EHPA) and 5 v/v% tributyl phosphate (TBP) at pH 5 [26]. Currently, many solvent
extraction methods are focussed on the separation of Co$^{2+}$; however, the acidic nature of most leach solutions requires pH adjustment for the separation of Co$^{2+}$, which consumes a large amount of alkaline and potentially introduces new impurity ions into the effluent, which could also increase the environmental burden.

**Table 1** Previously reported conditions for electrochemical recovery of spent LIBs cathodes

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Anode</th>
<th>Leaching conditions</th>
<th>Efficiencies</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2×4 cm cathode sheet</td>
<td>Pt</td>
<td>2 V, 0.5M H$_2$SO$_4$, 343 K, 90 min</td>
<td>Li$^+$, Co$^{2+}$, Ni$^{2+}$, Mn$^{2+}$&gt;97%</td>
<td>[27]</td>
</tr>
<tr>
<td>Pelletizing the mixture of cathode sheet and graphite</td>
<td>C</td>
<td>1.5 V, NaCl-Na$_2$CO$_3$ molten salt, 953K, 5 h</td>
<td>Li$^+$: 99.3%, Co: 98.1%</td>
<td>[28]</td>
</tr>
<tr>
<td>Cathode sheet glued to platinum</td>
<td>Pt</td>
<td>8 V, 2.5 M DL-malic acid, 343 K, 120 min</td>
<td>Li$^+$: 98.12 %, Co$^{2+}$: 97.36 %, Al$^{3+}$: 6.85%</td>
<td>[29]</td>
</tr>
<tr>
<td>3×1.5 cm cathode sheet</td>
<td>Pt</td>
<td>4 V, 1M acetic acid+0.1M VC, 200 ml, 298 K, 70 min</td>
<td>Ni$^{2+}$: 99.8%, Co$^{2+}$: 99.8%, Mn$^{2+}$: 99.8%, Li$^+$: 99.9%</td>
<td>[30]</td>
</tr>
<tr>
<td>1×1 cm cathode sheet glued to mixed metal oxide electrode</td>
<td>Ti-Pt</td>
<td>0.5 A ($E_{cell}$: 2~10 V), 0.5M H$_2$SO$_4$, 80 ml, 298 K, 4 h</td>
<td>Li$^+$&gt;90%, Ni$^{2+}$: 55%, Mn$^{2+}$: 35%, Co$^{2+}$: 40%, Al$^{3+}$:100%</td>
<td>[31]</td>
</tr>
</tbody>
</table>

In this research, a novel two-step leaching process and selectively solvent extraction of Al$^{3+}$ instead of Co$^{2+}$ are utilized to recover valuable metals from both spent LIBs cathode and anode sheets, which can effectively improve the S/L ratio, reduce the reagents consumption, and reduce energy consumption. This research paves a green and effective pathway for the recovery of valuable metals from spent LIBs and enables the selective extraction of all valuable metals (Li, Co, Al, and Cu) from spent cathode and anode sheets.

2. Experimental

2.1. Materials

All chemical reagents utilized in the experiments were analytical grade. Hydrochloric acid and sulfuric acid were purchased from Sinopharm Group Chemical Reagents Co., Ltd. D2EHPA and sulfonated kerosene were purchased from Shanghai Myrel Biochemical Technology Co., Ltd. L-ascorbic acid (VC) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Inductively coupled plasma optical emission spectrometry (ICP-OES, FHS12, Spectro Arcos) was utilized to measure the concentration of metal ions. Scanning electron microscopy (SEM, NanoSEM 450, FEI with Falion 60S, EDAX) and X-ray diffraction (XRD, SmartLab, Rigaku) were utilized to analyze the compositions, morphologies, and
structures of the cathode residuals and separated products. All electrochemical experiments were controlled and monitored current and voltage with an electrochemical workstation (Gamry, Reference 3000).

2.2. Methods

The closed-loop two-step leaching and separation process of spent LIBs cathode and anode sheet was divided into four steps as shown in Scheme 1:

**Step 1. Self-actuated leaching of the cathode sheet.** The spent cathode and anode sheets in the research were disassembled from spent mobile phone batteries purchased from the SEG electronic market, Shanghai. These batteries were first discharged in saturated Na$_2$SO$_4$ solution and then manually dismantled to recover the cathode sheet (Table S1), anode sheet, and separator in a glove box. The 4×10 cm cathode sheet was dissolved in 100 ml diluted HCl solution, different HCl concentrations (0.1, 0.25, and 0.4M), and leaching times (1, 3, 5, 8, 10, 20, 40, and 60 min) were adopted to optimize the self-actuated leaching conditions. This step is aimed at dissolving all Al, recovering part of Li$^+$ and Co$^{2+}$ in the cathode active material, and getting ready for the following Al$^{3+}$ removal step.

**Step 2. Selective solvent extraction of Al$^{3+}$.** After self-actuated leaching, Al was dissolved completely and the leaching residual and leaching solution were separated after filtration. The selective extraction of Al$^{3+}$ from the leaching solution was adopted to reduce the losses of valuable metals induced by the direct precipitation of Al$^{3+}$ in the leachate. The effect of extractant concentrations (5–50vol%) and organic/aqueous (O/A) ratio (3:1, 2:1, 1:1, 1:2, and 1:3) on the extraction efficiency were investigated. After phase separation, Al$^{3+}$ in the organic phase was stripped with different concentrations of H$_2$SO$_4$ solution, i.e., 1, 2, 4, 6, and 8M, the stripping solution was collected and the pH was adjusted to 5.5 using NaOH to obtain the Al(OH)$_3$ product [32]. Eq. 1 was utilized to calculate the results of the extraction and stripping process [33].

\[
SX = \frac{(C_{org}^e \times V_{org})}{(C_{aq}^e \times V_{aq} + C_{org}^e \times V_{org})} \times 100%
\]

where $SX$ is the solvent extraction and stripping efficiency, $C_{org}$ and $C_{aq}$ are the equilibrium ion concentrations in the organic and aqueous phases, respectively, $V_{org}^e$ and $V_{aq}^e$ are the equilibrium volumes of the organic and aqueous phases, respectively.

**Step 3. Electrochemical leaching of the cathode residual and anode sheet.** In the electrochemical leaching process,
the cathode residues obtained from the self-actuated leaching acting as the working electrode (WE), which were fixed using carbon cloth (CC) and Ti mesh, the spent anode sheet working as the counter electrode (CE), the KCl-saturated Ag/AgCl electrode working as the reference electrode (RE), and the anion exchange membrane was used to separate the metal ions dissolved in the cathode and anode chamber. The aqueous effluent obtained from Al\(^{3+}\) extraction together with additional HCl was used as the cathode electrolyte (120 ml). The applied potentials (0.4, 0.2, 0, and -0.2V), acid concentrations (0.1, 0.5, 1, and 2M), and leaching time (1, 3, 5, 8, 10, 20, 40, 60, 90, and 120 min) were utilized in electrochemical leaching experiments. The residual from the electrochemical leaching was dissolved with a mixture of 0.5 M HCl and 0.5 M VC to obtain the total leaching efficiencies of metals (Eq. 2) [34].

\[
L_{R_{M(i,t)}} = \frac{L_{M(i,t)}}{L_{M} + R_{M}}
\]

where \(L_{R_{M(i,t)}}\) is the leaching efficiency of metal \(M\) at time \(t\) (min) for the \(i_{th}\) leaching process, \(L_{M(i,t)}\) is the mass of metal \(M\) in the leaching solution at time \(t\) (min) for the \(i_{th}\) leaching process, \(L_{M}\) is the mass of metal \(M\) in the leaching solution at the end of leaching experiments, \(R_{M}\) represents the mass of metal \(M\) in the leaching residual.

**Step 4. Precipitation and electro-deposition.** After the two-step leaching and solvent extraction, the cathode leachate and anode leachate were collected. Precipitation was utilized to separate Li\(^+\) and Co\(^{2+}\) from the cathode leachate, firstly pH was adjusted to 9 by using NaOH solution to obtain the Co(OH)\(_2\) precipitate [35], and equimolar concentration of Na\(_2\)CO\(_3\) was then added to the filtrated solution to precipitate Li\(_2\)CO\(_3\). The electrodeposition method was utilized to recover Cu\(^{2+}\) from the anode leachate with the titanium plate working as the WE, an excess of copper foil obtained from the anode residual working as the CE, and a current of 160 A/m\(^2\) was adopted for the two-electrode system. During this process, Cu\(^{2+}\) in the solution would be deposited on the titanium plate, and at the same time, the excess copper foil would be dissolved.
2.3. Electrochemical analysis

The WE was the as-recovered spent cathode residual after the complete dissolution of Al foil, the CE was a Ti mesh electrode (6×3×0.2 mm), and the RE was a KCl-saturated Ag/AgCl electrode. Before retesting, the CE was polished with 1.0 µm, 0.3 µm and 0.05 µm Al₂O₃ sequentially, and then soaked in 3M HCl, methanol, and distilled water for 10 min with an ultrasonic cleaner, respectively, to remove impurities from the surface of the CE [36]. The electrolyte consisted of 0.01M HCl and 0.99M NaCl and was deoxygenated with Ar gas before each experiment. Eqs. 3-8 were utilized to calculate the transfer coefficient (α) and diffusion coefficient (D) for cyclic voltammetry (CV), chronoamperometry (CA), Tafel, and electrochemical impedance spectroscopy (EIS), respectively. All potentials reported are against the RE unless otherwise specified.

\[
\alpha_n = \frac{0.0477}{(|E_p - E_p/2|)} 
\]

\[
\alpha = 4.985 \times 10^{-4} n F D^{0.5} v^{0.5} (\alpha n F / RT)^{0.5} 
\]

\[
i = n F A D^{1/2} c / (n^{1/2} t^{1/2}) 
\]
\[
\eta = (-2.3RT/αnF) \times \log_{10}|i| + (2.3RT/αnF) \times \log_{10}|i_0|
\]

(6)

\[
\eta = (2.3RT/(1-α)nF) \times \log_{10}|i| - (2.3RT/(1-α)nF) \times \log_{10}|i_0|
\]

(7)

\[
D = \frac{R^2T^2}{(2A^2n^4F^4c^2σ^2)}
\]

(8)

where \(E_p\) is the peak potential (V) and \(E_{p/2}\) is the half-peak potential (V), \(i_p\) is the peak current (mA), \(α\) is the charge transfer coefficient, \(n_α\) is the number of electrons exchanged in the control step, \(F\) is the faraday constant (96485 C/mol), \(c\) is the bulk concentration of the electroactive species (mol/L), \(D\) is the diffusion coefficient (cm²/s), \(v\) is the scan rates (V/s), \(A\) is the area of WE (cm²), \(R\) is the molar gas constant (8.314 J/(mol*K)) and \(T\) is the temperature in K, \(t\) is time (s), \(η\) is the overpotential (V), \(n\) is the number of electrons transferred during the electrode reaction, \(σ\) is the slop of fundamental part (\(Z'\)) vs. \(w^{-1/2}\).

3. Results and discussion

3.1. Self-actuated leaching of the cathode sheet

The cathode sheet of lithium-ion batteries consists of Al foil, PVDF binder, carbon conductive agent, and cathode active material. The majority of hydrometallurgy recycling processes require complex pretreatment processes (dismantling, crushing, mechanical separation, solvent dissolution/binder thermal decomposition, drying) to separate the cathode active material from the Al foil, which undoubtedly increases the cost, energy consumption, and environmental threats [31,37–39]. Ye et al. proposed a novel galvanic cell by introducing Fe powder in contact with the cathode active powder, improving ammonia leaching efficiencies of spent LIBs [40]. As we all know, Al is a more active metal than Fe, so Al foil itself might also be utilized as a reducing agent to construct a galvanic cell with the cathode active material to enhance leaching. Al foil in the spent LIBs cathode sheet, working as the anode of the galvanic cell, got oxidized in the HCl leaching solution and lost electrons (Eq. 9), while LiCoO₂, in close contact with the Al foil, working as the cathode of the galvanic cell and gained electrons (Eq. 10), accompanied by HER under acidic conditions (Eq. 11). Apparently \(ΔG\) of the leaching reaction is negative, which verified that the overall reaction between Al dissolution and LiCoO₂ reduction is spontaneous. The formation of (-) Al(s) \(\mid\) Al³⁺ \(\parallel\) Co²⁺ \(\mid\) LiCoO₂ (s) (+) galvanic cell enabled the self-actuated leaching of the cathode sheet. Considering the impact of the HCl solution on the environment, further optimization of the acid concentration and improvement of the S/L
ratio are necessary to reduce the impact on the environment and human health. Therefore, in this paper, a two-step leaching was proposed to reduce both the energy and reagents consumption. The self-actuated leaching results of the cathode sheet are shown in Fig. 1. The leaching kinetics of Li$^+$ and Co$^{2+}$ reached equilibrium after 20 min, indicating fast leaching kinetics. 100% Al$^{3+}$ and more than 60% of Co$^{2+}$ and Li$^+$ were dissolved under 0.4 M HCl, 300 rpm, 338 K, and 40 min (Fig.1 a-c), and the S/L ratio was increased to about 5~6 times compared with our previously reported results [36], what’s more, no external electricity was inputted into the leaching system. The leaching efficiency of Al$^{3+}$ and the leachate pH after HCl leaching versus initial acid concentration are presented in Fig. 1d. With increasing acid concentration, the leaching efficiency of Al$^{3+}$ increased from 70.04% with 0.1 M HCl to 100% with 0.4 M HCl, and the end-point pH decreased from 4.00 to 2.23, which indicated that sufficient H$^+$ donor was required to dissolve all the Al foil. Moreover, considering the solvent extraction ratio and selectivity, the optimal pH range for Al$^{3+}$ extraction with D2HEPA was 2~2.5 as suggested in the following section, thus 0.4M HCl was considered to be the optimal acid concentration [41].

$$\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad \Delta G_1 = -485.38 \text{ kJ/mol} \quad (9)$$

$$2\text{LiCoO}_2 + 8\text{H}^+ + 2e^- \rightarrow 2\text{Li}^+ + 2\text{Co}^{2+} + 4\text{H}_2\text{O} \quad \Delta G_2 = -205.18 \text{ kJ/mol} \quad (10)$$

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \uparrow \quad \Delta G_3 = 0 \text{ kJ/mol} \quad (11)$$

![Fig. 1](image-url) Fig. 1 Self-actuated leaching efficiencies of Li$^+$ (a), Co$^{2+}$ (b), and Al$^{3+}$ (c) from spent LIBs cathode sheet with varying initial HCl concentrations, the effect of initial HCl concentration on Al$^{3+}$ leaching efficiency and the end-point pH (d).
3.2. Selective solvent extraction of Al\(^{3+}\)

Al was dissolved completely at 0.4 M HCl, 300 rpm, 338 K, 40 min, and the end-point pH of the leaching solution was 2.23. Without further pH adjustment, Al\(^{3+}\) could be selectively extracted with D2EHPA from the leaching solution according to Eq. 12 (Fig. 2) [42], which provided a simple and low-cost process for impurity removal. The extraction efficiency of Al\(^{3+}\) significantly increased with the increase of D2EHPA concentration from 5 vol% to 10 vol%, then reached equilibrium afterward (Fig. 2a). As the concentration of D2EHPA continues to increase, the extraction ratio of Co\(^{2+}\) increased, which would result in the loss of Co\(^{2+}\) and lower the purity of the Al(OH)\(_3\) product. Furthermore, the extraction system may experience severe emulsification with excessive D2EHPA, resulting in phase separation difficulty. The extraction efficiency of Al\(^{3+}\) gradually decreased with the increase of O/A ratio and the extraction ratio of Al\(^{3+}\), Co\(^{2+}\), and Li\(^{+}\) was 98.99%, 1.157%, and 0.408%, respectively, when O/A=1:1 (Fig. 2b). However, with the further increase of O/A ratio, the extraction ratio of Li\(^{+}\) and Co\(^{2+}\) increase, which would also result in the loss of valuable metal ions. Thus, the optimum extraction conditions were determined to be 10 vol% D2EHPA, O/A=1:1, taking into account extraction efficiency, selectivity, and cost.

The stripping efficiency at different H\(_2\)SO\(_4\) concentrations and O/A ratios are shown in Fig. 2c and d, 82.17% Al\(^{3+}\) was stripped with single-stage stripping according to Eq. 13 under 4M H\(_2\)SO\(_4\) and the O/A ratio of 1:1. Continuing to increase the acid concentration and the O/A ratio was not effective in improving the stripping efficiency, thus multi-stage stripping could be selected to stripping all Al\(^{3+}\) into aqueous phase. The stripping solution was adjusted to pH 5.5 to precipitate all the Al\(^{3+}\) according to the thermodynamic calculations (Fig. 2e), and SEM-EDX images suggested that the major component was Al(OH)\(_3\) (Fig. 2f).

\[
\begin{align*}
\text{Extraction (12)} & \quad \text{Al}^{3+}(aq) + 3HA_2^{2-}(org) \rightarrow \text{Al}(HA_2)_3(\text{org}) + 3H^+(aq)
\end{align*}
\]

\[
\begin{align*}
\text{Stripping (13)} & \quad \text{Al}(HA_2)_3(\text{org}) + 3H^+(aq) \rightarrow \text{Al}^{3+}(aq) + 3HA_2^{2-}(org)
\end{align*}
\]

where A is the functional group of D2EHPA and HA\(_2^{2-}\) is the D2EHPA after breaking the hydrogen bond.
Fig. 2 Extraction efficiencies of Li\(^+\), Co\(^{2+}\), and Al\(^{3+}\) under different D2EHPA concentrations (a) and O/A ratios (b), stripping efficiencies of Al\(^{3+}\) under different H\(_2\)SO\(_4\) concentrations (c) and O/A ratios (d), calculated fraction of Al species in different pH at 303K (e), and SEM-EDX of the as-recovered Al(OH)\(_3\) precipitates.

3.3. Electrochemical analysis of the self-actuated leaching residual

CV curves of the LiCoO\(_2\)/Co\(^{2+}\) presented a pair of redox peaks at different scan rates (Fig. 3a). The cathodic peak was observed at 1.047 V (E\(_{pc}\)) at 1 mV/s, and the current decreased as the potential exceeded E\(_{pc}\), indicating the existence of a diffusion-controlled region [43]. In addition, the OER occurred easily when the potential surpassed 1.2 V [44]. As can be seen, the cathodic peak potentials (E\(_{pc}\)) shifted negatively and the cathodic peak currents (i\(_{pc}\)) increased with increasing scan rates (Fig. 3a). What's more, a linear relationship between i\(_{pc}\) and v\(^{1/2}\) was also observed and the peak potential differences exceeding 0.059/n (V) at all scan rates. Thus the electrochemical redox reaction of LiCoO\(_2\)/Co\(^{2+}\) in the HCl system was electrochemically irreversible (Fig. 3a). According to Eqs. 3 and 4, the diffusion coefficient and \(\alpha n_a\) of Co\(^{2+}\) were calculated to be 4.74\times10\(^{-8}\) cm\(^2\)/s and 0.681, respectively. Meanwhile, the charge transfer coefficient of the reduction (\(\alpha_c\)) and oxidation (\(\alpha_a\)) were calculated to be 0.657 and 0.333, respectively, based on Eqs. 6 and 7. The \(\alpha_c\) was greater than \(\alpha_a\), indicating that the dissolution process of LiCoO\(_2\) was easier than the oxidation process. The calculated exchange current (i\(_0\)) and equilibrium potential (E\(_{eq}\)) were 3.69\times10\(^{-6}\) A and 0.7825 V, respectively. The current transient curves at different step potentials are
observed (Fig. 3c), and the diffusion coefficients at $E = 0.4, 0.2, 0,$ and $-0.2$ V were obtained by linearly fitting $i$ to $r^{1/2}$ in the diffusion-controlled region (Fig. 3d), and the specific parameter data were calculated (Table S2) according to Eq. 5.

![Fig. 3 CV curves of the self-actuated leaching residual at various scan rates and linear fitting of $i_p$ vs. $v^{1/2}$ (a), Tafel curve of the self-actuated leaching residual (b), CA curves of the self-actuated leaching residual (c), and linear fitting of $i$ vs. $r^{1/2}$ (d).]

A semicircle and a straight line were obtained in the high-frequency and low-frequency regions from EIS, respectively (Fig. 4a). With the equivalent circuit (Fig. 4a), the value of the charge transfer resistance $R_{ct}$ was calculated to be 15.54 Ω, which is much smaller than the resistance value (1449 Ω cm$^2$) reported before [17]. The diffusion coefficient calculated from Eq. 8 is $4.66 \times 10^{-9}$ cm$^2$/s, which is close to the $D$ value calculated by CA.

![Fig. 4 EIS curve of the self-actuated leaching residual and equivalent circuit diagram (a), and linear fitting of $Z'(a)$ vs. $W^{1/2}$]

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3.4. Electrochemical leaching of the cathode residual and anode sheet

Electrochemical analyses indicated that the reduction potential for LiCoO$_2$ to Co$^{2+}$ is around 0.8 V in HCl system (Fig. 3a). Considering the overpotential of the reduction reaction, the applied potential lower than 0.4 V (0.4, 0.2, 0, and -0.2 V) was selected for the electrochemical leaching (Fig. 5a). With the decrease of the applied potential on the cathode residual, the leaching ratio of Li$^+$ increased from 97.37% to 99.80%, the leaching ratio of Co$^{2+}$ increased from 90.17% to 99.69%, and the dissolved amount of Cu$^{2+}$ increased from 283.21 to 401.58 mg, which was attributed to the fact that the reduction of the electrode potential facilitated the breakage of the crystal structure of LiCoO$_2$, thus accelerating the dissolution of the cathode and anode sheets. In addition, the effects of different HCl concentrations ($c_{[\text{HCl}]}$) on the leaching efficiencies was explored at -0.2 V, 400 rpm, 338 K, and 90 min to further optimize the electrochemical leaching (Fig. 5b). With increasing $c_{[\text{HCl}]}$, both the leaching efficiencies of Li$^+$, Co$^{2+}$ and the dissolved amount of Cu$^{2+}$ increase, indicating that the H$^+$ donors are beneficial for the breakage the Co-O bond, thus increasing the leaching efficiency. Additionally, the leaching efficiencies of 1M and 2M HCl were almost equivalent, and considering the fact that an excessive amount of HCl would increase the equipment corrosion and the environmental burden, therefore, 1M HCl was selected as the optimal acid concentration.

SEM-EDX was utilized to obtain the micromorphology and elemental composition of the cathode residual (Fig. 5c). As can be seen, the leaching residue was mainly composed of porous and loose flakes, and the elemental mapping analysis reveals the presence of C, F, and a small amount of O and Co elements (Table S3).
Moreover, the leaching process can be divided into three stages based on the curves of the leaching efficiencies and $E_{\text{cell}}$ vs. time of Li$^+$ and Co$^{2+}$ under optimal conditions (Fig. 6). **Stage I:** During the first 5 min, Li$^+$ and Co$^{2+}$ presented rapid leaching kinetics and higher $E_{\text{cell}}$ at -0.2 V applied potential, which could be attributed to the current step driven by the applied electric field, and the whole leaching reaction required to reach a relatively high current at the beginning. **Stage II:** During the 5 to 90 minutes, the leaching kinetics of Li$^+$ and Co$^{2+}$ slowed down gradually, indicating a stable redox reaction occurs in this stage, meanwhile, as the leaching reaction proceeded, the LiCoO$_2$ content gradually decreased which may cause the slowing down of the leaching reaction. **Stage III:** During 90 to 120 min, Li$^+$ and Co$^{2+}$ reached leaching equilibrium, while $E_{\text{cell}}$ also reached equilibrium, indicating that the leaching reaction was complete.

![Fig. 5](https://ssrn.com/abstract=4752009)  
Fig. 5 Electrochemical leaching efficiencies of Li$^+$, Co$^{2+}$, and Cu$^{2+}$ of the spent cathode residual and anode sheet under different applied potentials (a) and HCl concentrations (b), SEM-EDX of the spent cathode leaching residual (c).  

![Fig. 6](https://ssrn.com/abstract=4752009)  
Fig. 6 Electrochemical leaching efficiencies of Li$^+$, Co$^{2+}$ of spent cathode residual and anode sheet with times (a), and $E_{\text{cell}}$ curves with time of electrochemical leaching process (b).
3.5. Precipitation and electro-deposition

After the two-step leaching and solvent extraction, the cathode leachate mainly contained two strategic metals, i.e., Li$^+$ and Co$^{2+}$, which could be easily separated by precipitation. The optimal pH range for the separation was determined to be 8.5 to 11 according to thermodynamic calculations, and the solution pH was adjusted to 9 to precipitate Co(OH)$_2$ comprehensively (Fig. 7a). The XRD pattern of the as-recovered precipitate indicated that the main phase was α-Co(OH)$_2$, which was in excellent agreement with PDF#30-0443 (Fig. 7b). SEM image of the as-recovered precipitate revealed that the α-Co(OH)$_2$ was mainly composed of three-dimensional lamellar structure by stacking of nanosheet with hexagonal morphology (Fig. 7c and Fig. S1). To obtain a higher Li$^+$ recovery ratio, the effluent from the Co(OH)$_2$ precipitation process was concentrated approximately 20 times. The XRD pattern indicates that the as-recovered Li$_2$CO$_3$ had higher crystallinity and purity, thus the recovered Li$_2$CO$_3$ can be applied to the preparation of cathode materials for LIBs. The overall recovery efficiencies of Al$^{3+}$, Co$^{2+}$, and Li$^+$ were 81.34%, 98.54%, and 97.4%, respectively (Table 2).

![Fig. 7](https://ssrn.com/abstract=4752009) Calculated fractions of Li$^+$ and Co$^{2+}$ species in the pH range of 0 to 14 at 303K (a), XRD pattern (b) and SEM image (c) of the as-recovered Co(OH)$_2$, and SEM image of the precipitated Li$_2$CO$_3$ (d).
Table 2 The overall recovery efficiencies of Al³⁺, Co²⁺, and Li⁺.

<table>
<thead>
<tr>
<th>Steps</th>
<th>Al³⁺</th>
<th>Co²⁺</th>
<th>Li⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-actuated leaching efficiency (%)</td>
<td>100</td>
<td>63.53</td>
<td>71.29</td>
</tr>
<tr>
<td>Extraction efficiency organic phase (%)</td>
<td>98.99</td>
<td>1.157</td>
<td>0.408</td>
</tr>
<tr>
<td>Stripping efficiency aqueous phase (%)</td>
<td>82.17</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>Electrochemical leaching efficiency (%)</td>
<td>\</td>
<td>99.69</td>
<td>99.8</td>
</tr>
<tr>
<td>Overall recovery efficiency (%)</td>
<td>81.34</td>
<td>98.54</td>
<td>97.40</td>
</tr>
</tbody>
</table>

To ensure the total leaching of the cathode residual under low $E_{cell}$, an excessive amount of the anode sheet was utilized in the electrochemical leaching process, thus the anode chamber contains both unreacted Cu foil and leached Cu²⁺. Considering that the anode material also requires to be recovered, an electrodeposited Cu system was constructed with a titanium plate working as the WE, unreacted Cu foil working as the CE, and anode leachate as the electrolyte (Fig. 8a). According to the thermodynamic calculations, the electrode reactions of Cu/Cu⁺ and Cu/Cu²⁺ are relatively easier to take place (Fig. 8b). The detailed thermodynamic parameters at different temperatures were shown in Table S4. SEM maps suggested that the deposited Cu showed a fine particle size and well-cubed morphology (Fig. 8c). Amazingly, the deposited Cu exhibited a cubic crystalline accumulation of “pine needle type” morphology (Fig. S2). What's more, sharp reflection peaks were observed in the XRD pattern and the deposit was identified as a mixture of Cu (PDF#04-0836) and CuO/Cu₂O (PDF#05-0667) (Fig. 8d). As is well-known, Cu is a very reactive metal and once removed from the titanium plate in powder form and exposed to air, CuO and Cu₂O could easily form [45]. Therefore, the purity of the as-recovered Cu is quite high [46].
3.6. Mechanism analysis

During the self-actuated leaching process, the spontaneous reaction between Al and LiCoO$_2$ was made possible with the assistance of HCl, since HCl as a reductive acid is effective in restraining the formation of compact oxide layer of Al$_2$O$_3$ (Fig. 9). And the tightly connected Al and LiCoO$_2$ facilitated the electron transfer from Al foil to LiCoO$_2$, forming the (-) Al(s) | Al$^{3+}$ || Co$^{2+}$ | LiCoO$_2$ (s) (+) galvanic cell. The strong coordination between Al$^{3+}$ to D2EHPA in the leachate was proven to be effective for the selective extraction of Al$^{3+}$ from the self-actuated leaching leachate. This step is vitally important for the efficient recovery of valuable metals since the traditional precipitation method for Al$^{3+}$ removal would induce a 3~5% loss of valuable Li$^+$ and Co$^{2+}$. During the extraction process, H$^+$ in the D2EHPA dimer broke and formed new coordination bonds with Al$^{3+}$ in the aqueous phase, achieving selective separation of Al$^{3+}$ (Eq. 12). Subsequently, the Al-removed leachate was used in a second step electrochemical leaching to recover spent cathode residual and spent anode sheet by the "sandwich-type" electrode structure [36]. The cathode residual obtains electrons and gets reduced, releasing the remaining Co$^{2+}$ and Li$^+$ from the cathode residual to the leachate, and the spent anode collector (Cu foil) in the anode gets oxidized, achieving the comprehensive leaching of both spent cathode and anode sheet (Eqs. 10 to 14).

$$Cu\rightarrow Cu^{2+} + 2e^-$$

(14)
4. Conclusions

In this research, a novel method for the integrated leaching and separation of spent LIBs cathode and anode sheet was proposed and tested. By constructing a galvanic cell and the following solvent extraction with D2EHPA, Al$^{3+}$ impurity can be selectively removed from the leached without adjusting the pH of the solution. During the self-actuated leaching process, no external electricity was inputted into the system and more than 60% of Li$^{+}$ and Co$^{2+}$ can be leached, which significantly reduced the energy input in the following electrochemical leaching step and reagents consumption. The introduction of an anode sheet into the electrochemical leaching process not only significantly reduced the $E_{\text{cell}}$ ($< 2$ V) but also achieved the integrated leaching of both spent cathode and anode sheet. Also, the S/L ratio was increased by 5–6 times compared to the traditional electrochemical method with the assistance of the "sandwich-type" electrode structure, which can also effectively reduce the cost and environmental impact. Eventually, aluminum, cobalt, lithium, and copper were recovered in the form of Al(OH)$_3$, Co(OH)$_2$, Li$_2$CO$_3$, and Cu, respectively. Thus, the integrated leaching and separation process was an environmentally friendly and green technique.
**CRediT authorship contribution statement**

**Ting He:** investigation, data curation, writing–original draft and visualization; **Jixing Zhao:** conceptualization and investigation; **Dongxian Chen:** validation and formal analysis; **Shuai Gu:** writing–review & editing and supervision; **Jianguo Yu:** resources, project administration, funding acquisition.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online.
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