

Amino Acid Leaching of Critical Metals from Spent Lithium-Ion Batteries Followed by Selective Recovery of Cobalt Using Aqueous Biphasic System

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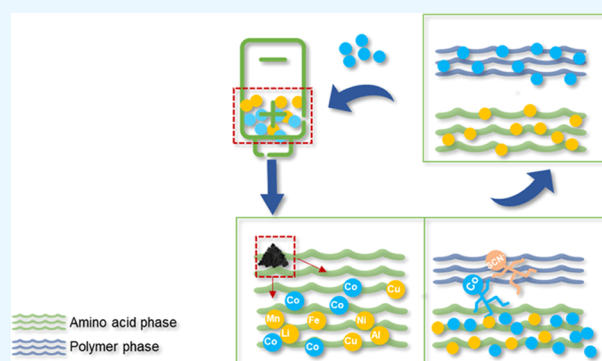


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Supporting Information

ABSTRACT: To reduce the exploitation of mine resources and decrease the harm to the environment caused by urban electronic wastes, the recovery of critical metals in secondary resources is crucial. In this study, we have successfully developed an eco-friendly process to integrate the leaching and separation of cobalt (Co) from a spent lithium-ion battery (LIB) cathode using an amino acid-based aqueous biphasic system (ABS). We, for the first time, demonstrated a simple method for leaching a LIB cathode using only amino acids. In addition, we have investigated the leaching mechanism using the typical cathode active material lithium cobalt oxide (LiCoO_2). Then, the Co was selectively extracted by a biphasic system (amino acid–PPG400– H_2O). This novel process has an excellent prospect in the field of spent-battery recycling because of its eco-friendly and process-simplified advantages.



1. INTRODUCTION

In the past two centuries, the predatory consumption of natural resources has been behind the prosperity of the world economy, resulting in the risk of energy depletion.¹ The emission of greenhouse gases in the process of the mineral-resource mining industry and the exponential growth of urban wastes have brought heavy disasters to the environment.²

Waste electronics in urban wastes, as a critical secondary resource, are called “urban mines” because they contain many valuable elements.^{3,4} To reduce the exploitation of mine resources and decrease the harm of urban electronic wastes to the environment, the recovery of critical metals in the secondary resources is important. Lithium-ion batteries (LIBs), because of their high energy density, are known to be the most important power source for these electronics including electric vehicles (EVs), energy storage devices, and various electrical appliances.⁵ In addition, the EV industry has presented a booming scene in the context of governments of all countries pursuing new energy sources to achieve “carbon neutrality” goals.⁶ However, LIBs in EVs have a life span of only 5–10 years,⁷ and many LIBs will be scrapped soon. It is estimated that 11 000 000 tons of spent LIBs will be processed globally by 2030.⁸ Therefore, the recycling of spent LIBs has received much attention.

The high metal content of the spent LIBs makes their recycling attractive. The metals in the spent LIBs include lithium (Li), cobalt (Co), manganese (Mn), nickel (Ni), copper (Cu), aluminum (Al), and iron (Fe).⁹ Among them,

Co has received more attention because of its high price. The price of a pound of Co was about \$25 in 2021, 2.8 times that of Ni and 21 times that of Mn.¹⁰ In addition, in the LIB of the usual electronic products, the weight ratio of Co is ~15 to 30%.¹¹ Therefore, the recovery of Co from spent LIBs becomes an economical target.

LIBs are named after the type of cathode active materials. In a typical LiCoO_2 LIB, the cathode accounts for about 25% by weight.¹¹ Most studies have focused on recycling the cathode materials.^{12–14} The recovery methods are generally divided into hydrometallurgy, pyrometallurgy, and electrochemical treatment.¹⁵ Hydrometallurgy has recently received extensive attention because of its advantages of low energy consumption, mature technology, high recovery rate, high purity of recovered metals, and the selective extraction of valuable metals.¹⁴ However, there are also disadvantages such as extensive use of toxic organic solvents, high concentration of inorganic acids, and complicated recovery steps. Conventional hydrometallurgy, which is a solvent extraction process, is divided into leaching, followed by metal separation and recovery.¹⁴

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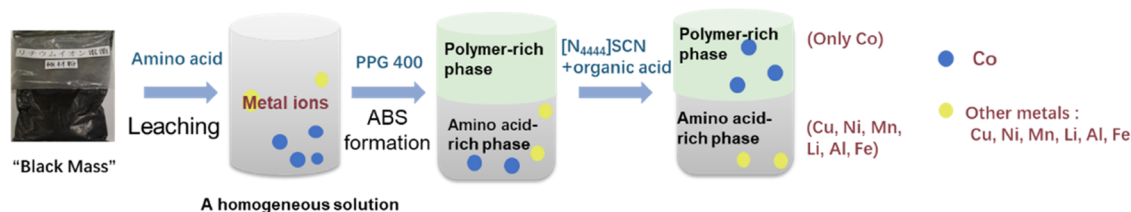


Figure 1. Schematic illustration of the proposed process for integrated leaching and selective recovery of Co from an actual lithium-ion battery cathode powder.

Leaching, an indispensable step in the hydrometallurgical process, mainly includes alkali leaching or acid leaching.¹³ For alkali leaching, Cu and Al are generally leached with sodium hydroxide or ammonia, and then Co is leached with reducing acids.¹⁶ For acid leaching, inorganic acids such as sulfuric acid, hydrochloric acid, and nitric acid, or organic acids such as citric acid, ascorbic acid (Ascor), and oxalic acid are used as leaching agents.¹⁷ According to previous studies, in the acid leaching process, it is often required to enhance the leaching rate by adding a reducing agent, which increases the cost.¹⁸ Moreover, the traditional leaching process involves a lot of energy consumption, and the corrosion loss of equipment cannot be ignored.¹⁹ Therefore, it is beneficial to develop a new leaching agent from an environmental and economic point of view. Amino acids have good prospects in industrial applications because of their high biocompatibility and relatively low price.²⁰ Recently, a few studies on the leaching of valuable metals using glycine (Gly) from spent LIBs have been reported.^{21–23} Chen and co-workers²¹ proposed the recovery of Co/Li from waste LIBs using Gly and hydrogen peroxide (H₂O₂) as the leaching agent. Nayaka and co-workers²² showed the excellent leaching of Co from spent LIBs using Gly and Ascor as leaching reagents. In addition, Zheng and co-workers²³ reported that Gly was applied for the hydrothermal leaching of LIB cathode materials. In this study, we report for the first time the leaching by an amino acid alone for the LIB cathode powder under a relatively mild temperature.

After leaching, a metal separation and recovery step follows. In this step, the relatively mature process in the industry is still liquid–liquid extraction (LLE). Aqueous biphasic system (ABS) technology is an environmentally friendly substitute for the traditional LLE technology, being a fully aqueous system.²⁴ Two solutes in the system with different entropies of hydration are concentrated in two different phases after salting out.²⁵ Recently, many studies on the separation of valuable metals from waste batteries using an ABS have been reported.^{26–28} Coutinho and co-workers²⁹ showed a remarkable separation ratio for Co(II) and Ni(II) using the ionic liquid (IL)-based ABS composed of tributyltetradecylphosphonium chloride ([P₄₄₄₁₄]Cl) and NiCl₂ for a spent-battery recovery. They also optimized the process route and integrated leaching and ion recovery. The first application of integrated leaching and separation of metals using the IL-based ABS consisting of [P₄₄₄₁₄]Cl and organic acid (CH₃COOH) was proposed by the Coutinho group in 2020.³⁰

Moreover, previous studies proposed a special biocompatible ABS, which is an amino acid-based ABS.^{31,32} It was found that amino acids have a salting-out effect on polymers in aqueous solutions and play an important role in the formation of two phases because of their zwitterionic identity. In the present study, we report for the first time the leaching operation by an amino acid alone for a LIB cathode powder

made from lithium manganese cobalt nickel oxide (LiMn_xCo_yNi_zO₂) followed by selective recovery of Co using an amino acid-based ABS. The effects of amino acid types, temperature, extraction time, and solid–liquid (S/L) ratio on leaching are discussed. In addition, we investigated the leaching mechanism using the typical cathode active material lithium cobalt oxide (LiCoO₂). Ultraviolet–visible (UV–vis) spectra and Fourier transform infrared (FT-IR) spectra were measured to verify the leaching mechanism. Then, polypropylene glycol 400 (PPG400) was added to the leaching solution to form a biphasic system. By adding different thiocyanate ions, the selective separation of Co was verified. We integrated the leaching and the selective recovery of Co using this amino acid-based ABS in this study. A schematic illustration of the process is presented in Figure 1.

2. EXPERIMENTAL SECTION

2.1. Materials. The powder of spent LIB cathode materials was supplied by Matsuda Sangyo Co., Ltd (Tokyo, Japan). LiCoO₂, tetrabutylammonium thiocyanate ([N₄₄₄₄]SCN), and methanesulfonic acid (MSA) were purchased from Sigma-Aldrich Co. Potassium thiocyanate (KSCN) and the polymer PPG400 were supplied by Kishida Chemical Co., Ltd. Acetic acid (AcOH), formic acid (HCOOH), and amino acids, namely, Gly, proline (Pro), serine (Ser), asparagine (Asn), histidine (His), cysteine (Cys), and glutamic acid (Glu), were purchased from Kishida Chemical Co., Ltd. Ascor, tartaric acid (TA), aceturic acid (Ac-Gly-OH), and glycine ethyl ester hydrochloride (H-Gly-OEt-HCl) were purchased from Fujifilm Wako Chemical Ltd. *p*-Toluenesulfonic acid (PTSA) was purchased from Tokyo Chemical Industry Co., Ltd. Deionized water (Milli-Q, Merck Millipore) was used in this work.

2.2. Methods. In the first step (leaching of LIB cathode powder), leaching experiments were conducted to evaluate the leaching efficiencies of Co, Ni, Li, Mn, Al, Cu, and Fe using various amino acid leaching agents. The powdered spent LIB cathode material was added to an amino acid solution in a glass vial equipped with a cap, and the samples were stirred at 400 rpm at 70 °C. The effects of the amino acid type (Gly, Pro, Ser, Asn, His, Cys, and Glu), extraction time (1, 3, 6, 12, 18, and 24 h), and S/L ratio (5, 7.5, 10, 12.5, 15, and 20 g/L) on the leaching operation are discussed.

In the second step (selective recovery of Co), the polymer PPG400 was added to the leachate at a volume ratio of 1:1, and the system formed two separate phases. Then, the effects of the addition of different types of SCN[−] salts ([N₄₄₄₄]SCN and KSCN) and various organic acids on the selective extraction of Co were investigated, in which only Co was transferred from the amino acid-rich phase to the polymer-rich phase.

2.3. Evaluation. In the first step, the leaching efficiency of various metals was calculated using eq 1.

Table 1. Composition of the Spent LIB Cathode Material^a

	Co	Ni	Mn	Li	Cu	Al	Fe
composition (g/kg)	162.56	27.02	40.16	38.30	11.56	17.86	0.55

^a10 g/L, 4 M HCl with 5% H₂O₂, 75 °C, 400 rpm for 3 h.

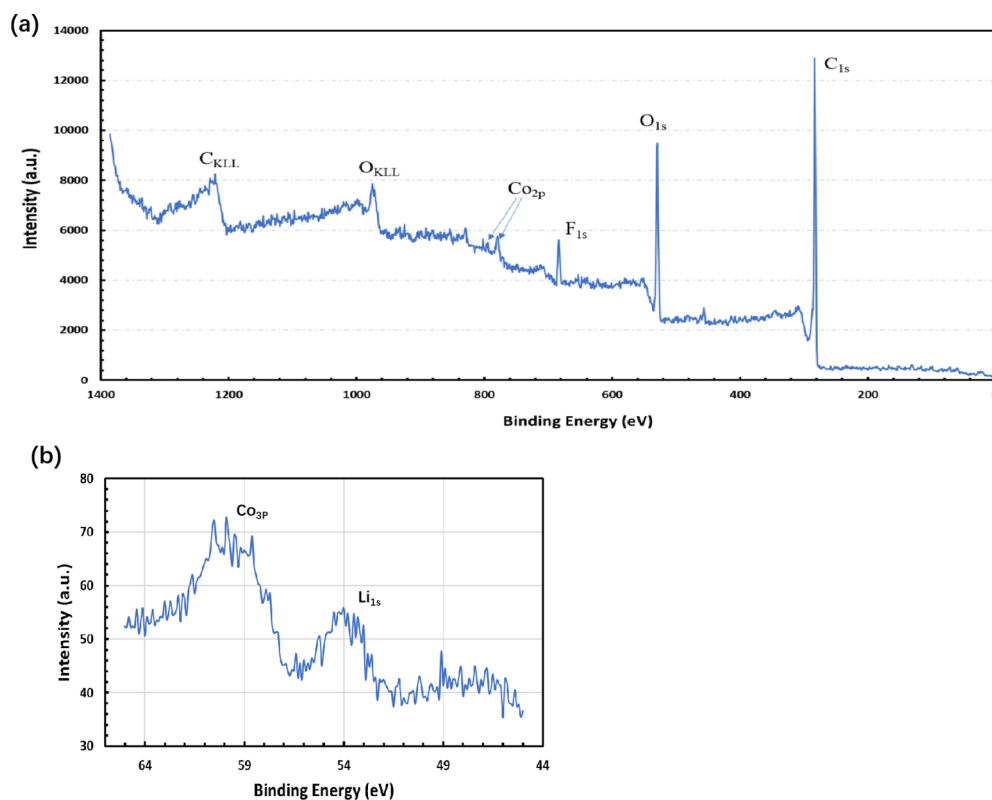


Figure 2. XPS spectra of spent LIB cathode powder. (a) Full spectrum of the material and (b) 1s orbital of Li and 3p orbital of Co.

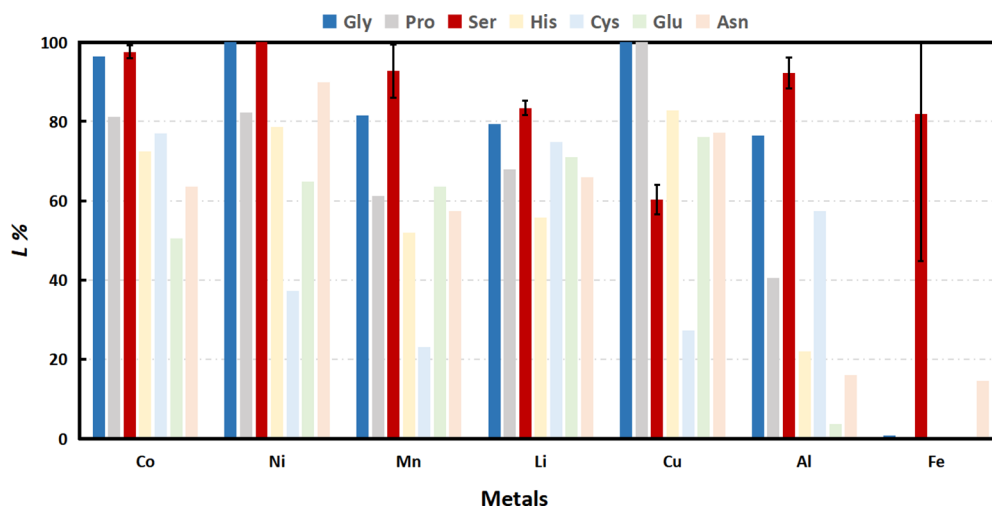


Figure 3. Effect of various amino acids on leaching efficiency (leaching of the spent LIBs cathode powder with different types of amino acids Gly, Pro, and Ser at 2 M; His, Cys, Glu, and Asn at saturation concentration); S/L ratio of 10/1 (g/L); 400 rpm at 70 °C, 3 h; the error bars are standard deviations.

$$\%L = C_{M(\text{leaching solution})} / C_{M(\text{HCl and H}_2\text{O}_2)} \times 100 \quad (1)$$

where C_M is the concentration of metal M in the spent LIB cathode powder. C_M (HCl and H₂O₂) indicates the concentration of each metal in the powder material determined using hydrochloric acid (HCl) and H₂O₂ as the leaching agent.

C_M (leaching solution) expresses the concentration of each metal in this material determined using another leaching agent.

In the second step, the determination of metal concentrations in each phase after achieving reaction equilibrium was conducted using an inductively coupled plasma optical emission spectrometer (Optima 8300, PerkinElmer). The

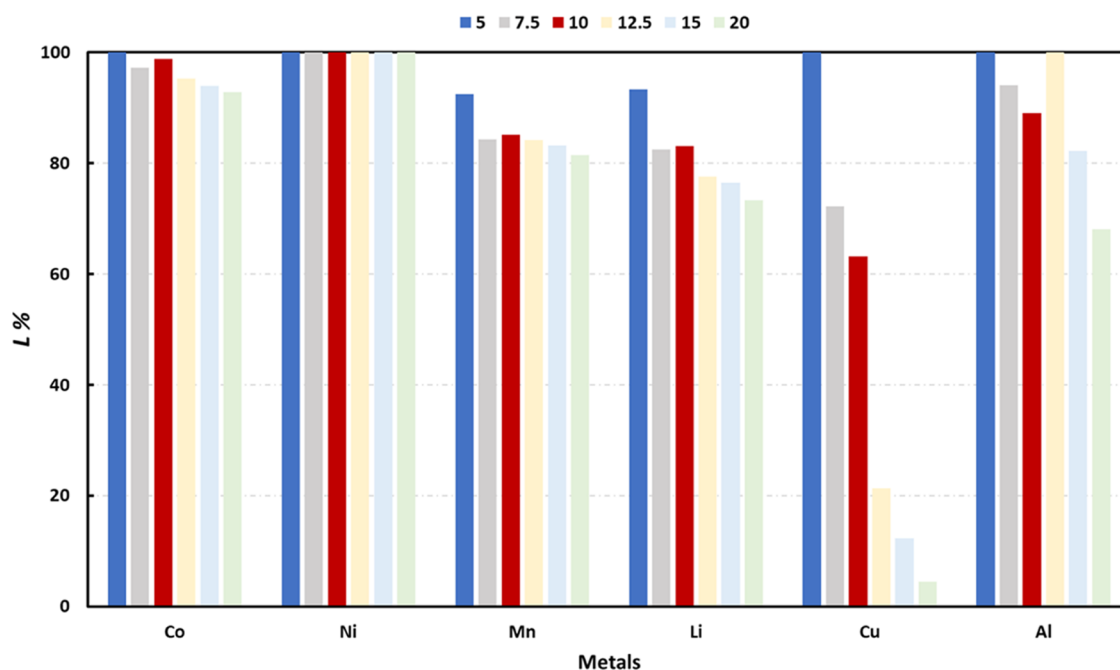


Figure 4. Effect of various solid–liquid (S/L) ratios (g/L) on leaching efficiency (leaching of the spent LIBs cathode powder with 2 M Ser; the S/L ratios were 5, 7.5, 10, 12.5, 15, and 20 g/L; 400 rpm at 70 °C, 3 h).

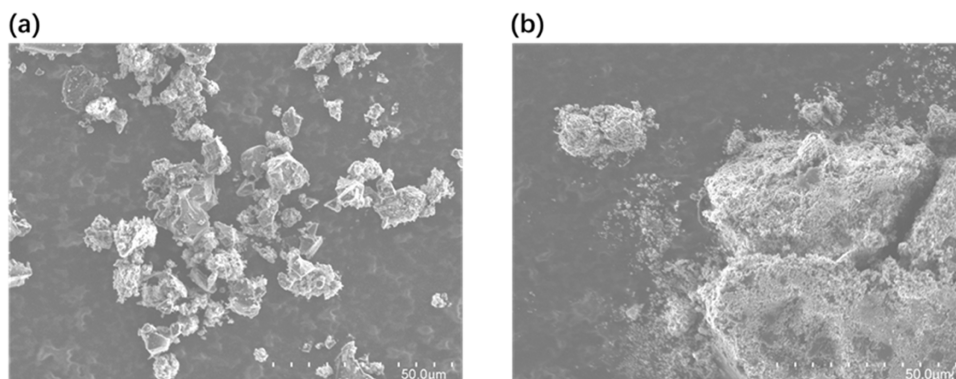


Figure 5. SEM images of the spent LIB cathode before (a) and after (b) leaching.

extraction efficiency (E , %), distribution ratio (D), and purity (P , %) of the metal ions were calculated using eqs 2–4, respectively.

$$\%E = n_M^{\text{TP}} / n_M^{\text{T}} \times 100 \quad (2)$$

$$D_M = [M]_{\text{TP}} / [M]_{\text{BP}} \quad (3)$$

$$\%P_M = [M]_{\text{TP}} / ([M]_{\text{TP}} + [N]_{\text{TP}}) \times 100 \quad (4)$$

where n_M^{TP} is the amount of metal M in the top or the polymer-rich phase, n_M^{BP} is the amount of metal M in the bottom or the amino acid-rich phase, n_M^{T} is the total amount of metal M , $[M]_{\text{TP}}$ (mg/L) is the equilibrium concentration of metal M in the top phase, $[M]_{\text{BP}}$ (mg/L) is the equilibrium concentration of metal M in the bottom phase, and D_M is the distribution ratio of metal M .

The valence state of Co in this spent LIB cathode powder material was investigated by measuring X-ray photoelectron spectra (XPS) using an AXIS-165. The appearance changes of this material before and after the leaching operation were measured using a scanning electron microscope (SEM-SU3500). The valence state change of Co during leaching

was investigated by measuring UV–vis spectra of the leaching solution at various times using a UV–vis spectrometer (JASCO V-670) at 25 °C with 1 nm spectral resolution. FT-IR spectra of the amino acid before and after leaching were also obtained using an FT-IR spectrometer (Spectrum Two, PerkinElmer).

3. RESULTS AND DISCUSSION

3.1. Characterization of Spent LIB Cathode Powder Material. With 4 M HCl and 5% H₂O₂ as the leaching agent, the composition of the spent LIB cathode powder is shown in Table 1. The table shows that in this material, the content of Co is the highest, accounting for about 55% of the total metal content, whereas Mn, Li, Ni, Al, and Cu contents are relatively low, and Fe, in particular, is negligibly small.

In addition, the composition of the spent LIB cathode powder is very complex because of the frequent charging and discharging of the battery and a series of pretreatments. To determine the valence state of the Co, we measured the XPS spectrum (Figure 2). In the spectrum of the material, the characteristic photoelectron spectra of Co, O, C, and F can be

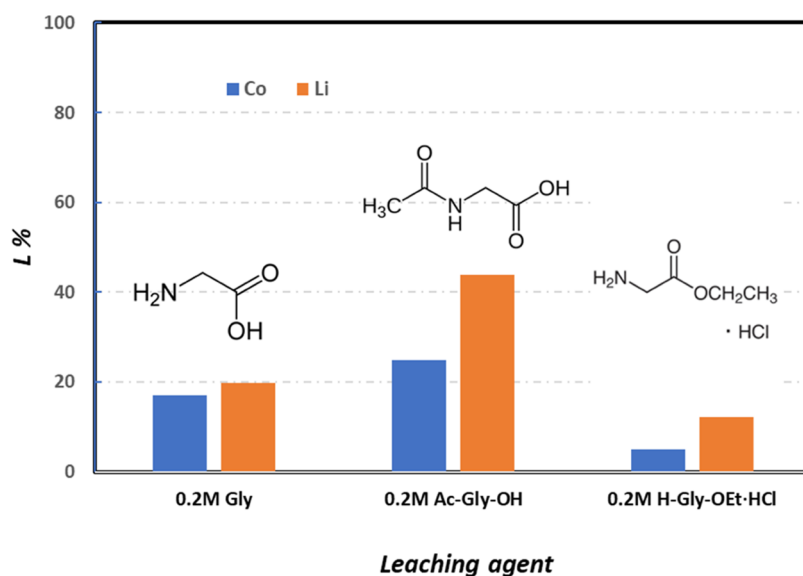


Figure 6. Variation of leaching efficiency of LiCo₂ over various leaching agents based on Gly-backbone (the S/L ratio was 10 g/L; 400 rpm at 80 °C, 24 h).

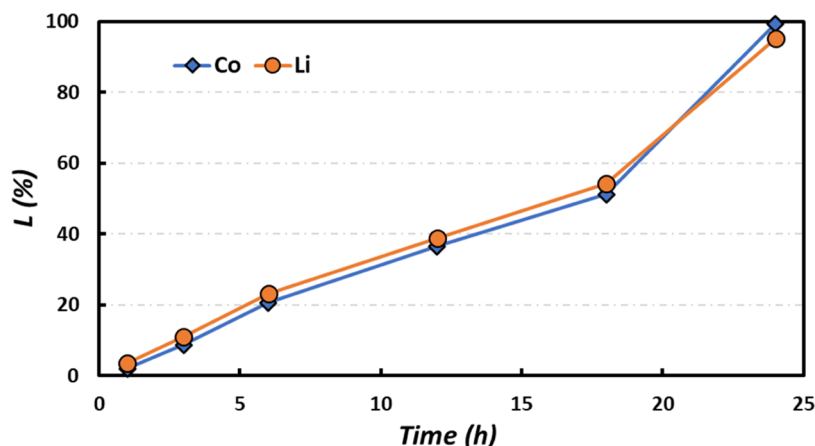


Figure 7. Leaching efficiency of LiCo₂ using Ser over a prolonged time (leaching of the LiCo₂ with 3 M Ser; the S/L ratio was 10 g/L; 400 rpm at 80 °C, 1, 3, 6, 12, 18, and 24 h).

clearly observed. The strong peak of F 1s indicates the presence of the electrolyte or the binder residue in the used cathode material. The mass contents of O and C are 21.53 and 66.56%, respectively. The mass content of Co is only 3.26%, and the content of other metals is even lower. The presence of LiCo₂ could be determined by the two peaks located at binding energies of 54 and 60 eV (Figure 2b), corresponding to Li 1s and Co 3p, respectively.³³

3.2. Effect of Amino Acid Types on Leaching. Seven amino acids (see Figure S1) were chosen based on the nature of their side chains, i.e., Pro is hydrophobic, Ser has hydroxyl groups (–OH), Asn is an amide type, Glu is acidic, Gly belongs to the small-molecular-weight representative, His is basic, and Cys has sulfur groups (–HS). The experimental results are shown in Figure 3. For the target ion, Co, the three amino acids Gly, Pro, and Ser, all exhibit high leaching efficiencies, exceeding 80%. Especially for Gly and Ser, the leaching efficiency of Co is more than 95%. Even if the concentration of His, Cys, Glu, and Asn was saturated, the leaching efficiency of Co is still not very ideal, indicating that they are not the most optimal. Overall, Ser exhibits excellent

leaching ability for all metals except Cu. However, because Cu and the target ion Co are transition elements, they often interfere with each other in the field of ion separation.³⁴ In addition, the content of Cu in the material is around 1/14 that of Co. Therefore, the low leaching efficiency of Cu is beneficial to the subsequent selective extraction of Co. Based on the result, we choose Ser as the most suitable leaching agent. The effects of the concentration of the Ser, leaching temperature, and time on the leaching efficiency were investigated. It can be seen from Figures S2–S4 that the optimal leaching conditions are the concentration of the Ser is 2 M; the leaching time is 3 h; and the leaching temperature is 70 °C.

3.3. Effect of Solid–Liquid Ratio on Leaching. The S/L ratio has a significant impact on the leaching efficiency. As shown in Figure 4, when the S/L ratio is increased from 5 to 20 g/L, the leaching efficiency of Ni remained unchanged, and the leaching efficiency of metals such as Co, Mn, Li, and Al had a slight downward trend. However, as the value of S/L increases, the leaching efficiency for Cu decreases significantly. The cathode powder material contains Al and Cu, during the leaching process, part of them will react with Ser and enter the

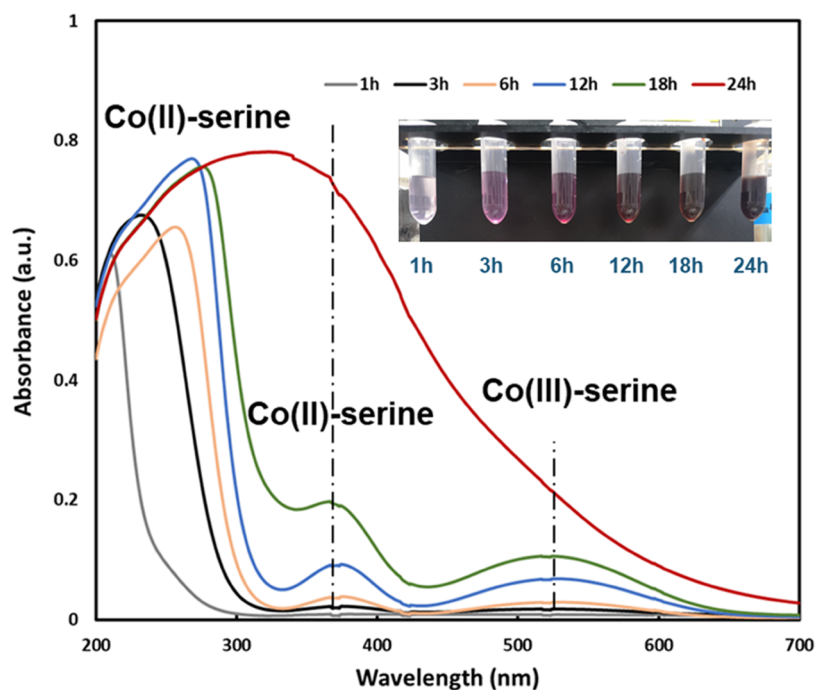


Figure 8. UV-vis spectra of the leaching solution at different times.

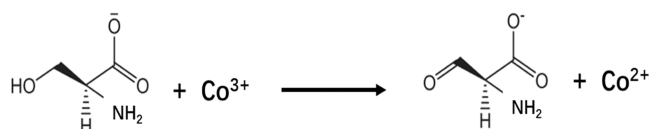


Figure 9. Mechanism of serine's reduction of Co(III) to Co(II).

solution in the form of ions.³⁵ However, the electrode potential of Al ($E(\text{Al}^{3+}/\text{Al}^0)$) is -1.662 V, which is lower than that of Cu ($E(\text{Cu}^{2+}/\text{Cu}^0) = +0.337$ V). Therefore, Al will be continuously oxidized, whereas Cu will be reduced. With the increase in the S/L ratio, the amount of Ser is not enough to react with Cu, so Cu^{2+} will be continuously reduced to copper element by Al and remain in the residue. Considering the scale requirements and economic benefits in industrial production, an S/L ratio of 10/1 is found to be optimal. Figure 5 shows the change in surface

morphology of the LIB cathode before and after leaching. After leaching, the particles become smaller, indicating that the metals were leached into the solution, leaving only carbon and other residues.

3.4. Plausible Leaching Mechanism. In this part, a standard LiCoO_2 was used for the leaching experiment to discuss the leaching mechanism because the composition of the spent LIB cathode powder is too complex. Another important factor is that the valence state of Co in LiCoO_2 is 3+, which is insoluble in an aqueous solution. In fact, to make it clear, the leaching mechanism is important for establishing battery cathode recycling using amino acids. Regarding amino acids, we selected two kinds of amino acids, one is the amino acid with the simplest structure—Gly, and the other is the amino acid with the best leaching ability—Ser.

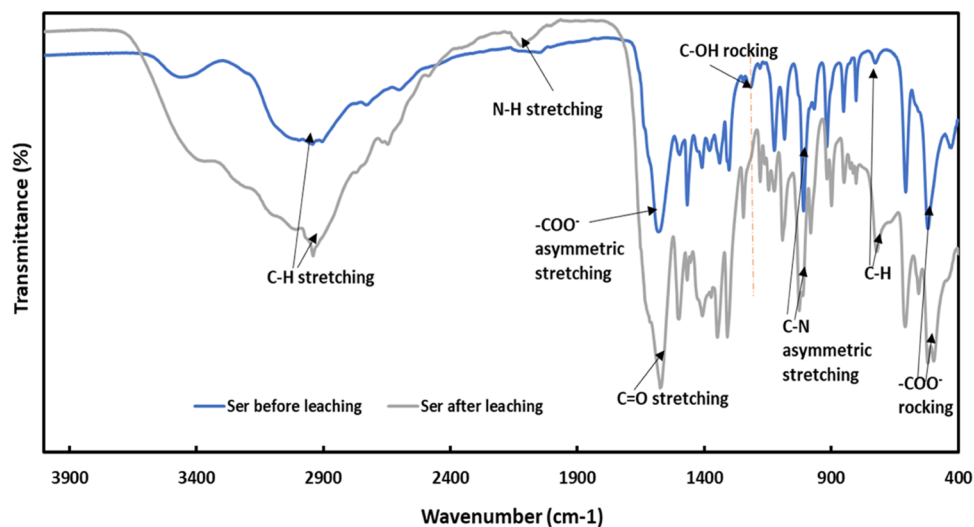


Figure 10. FT-IR spectrum of Ser before and after leaching.

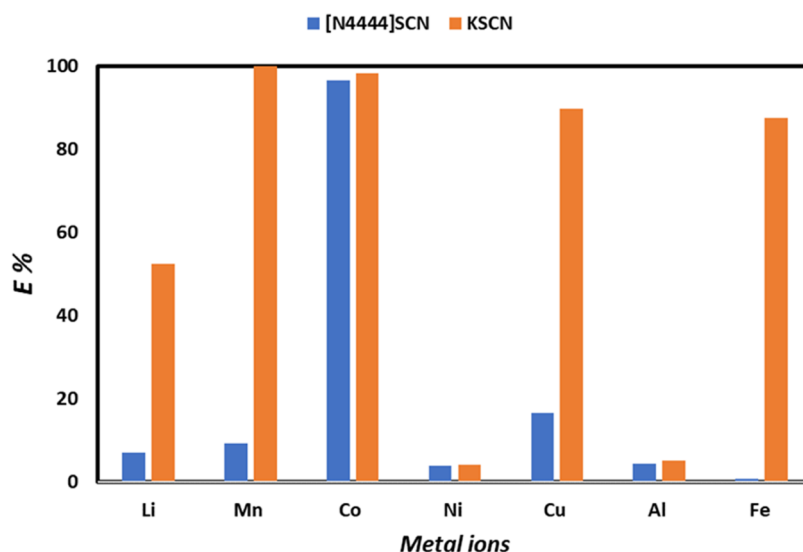


Figure 11. Effect of the two thiocyanate ions on extraction efficiency of metals.

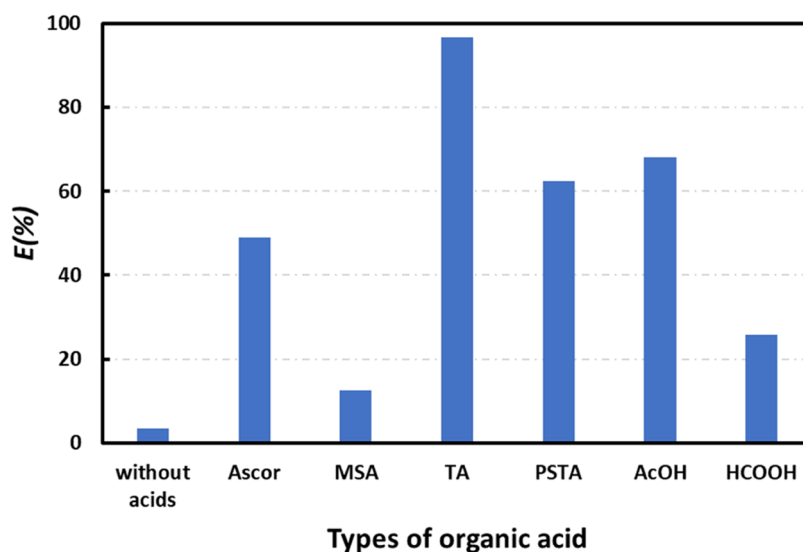


Figure 12. Variation of the extraction efficiency of Co over different types of organic acids.

To verify whether the amino group ($-\text{NH}-$) or the carboxyl group ($-\text{COOH}$) in the amino acid plays a role in the leaching experiment of LiCoO_2 , 0.2 M Gly, Ac-Gly-OH, and H-Gly-OEt-HCl were selected as leaching agents. The experimental results are shown in Figure 6. H-Gly-OEt-HCl basically has no leaching capacity for Co, and Gly and Ac-Gly-OH have comparable leaching capacity for Co. Compared with Gly, H-Gly-OEt-HCl lacks a carboxyl group and Ac-Gly-OH lacks a coordinative amino group. It was concluded that the carboxyl group played a major role in the leaching operation.

To further explore the reducing ability of amino acids to trivalent Co ions, 3 M Ser (see Figure S5) was selected as the leaching agent at $80\text{ }^\circ\text{C}$ (see Figure S6) to discuss the corresponding leaching mechanism of LiCoO_2 .

As shown in Figure 7, the leaching efficiencies of Co and Li increased with operation time. After 24 h, the leaching efficiencies of Co and Li increased to 99.44 and 95.37%, respectively. During the leaching process, the color of the leaching solution was also constantly changing, from bright purple to dark red (Figure 8). To verify the change of Co

valence, the UV-vis spectrum was investigated, as shown in Figure 8. The UV spectrum of the leachate taken out at 24 h changed significantly. Figure 8 clearly shows the reduction of Co(III)-serine to Co(II)-serine. The observed absorption maxima around 375 and 520 nm are attributed to Co(II)-serine and Co(III)-serine, respectively.²² We found that with the leaching time increasing from 1 to 18 h, the intensity of the leaching solution was also increased, which is attributed to the continuous entry of Co into the solution. In addition, another obvious behavior is a clear absorption peak broadening between 210 and 300 nm. At the initial time of 1 h, the absorption peak around 210 nm belongs to the Ser. With the continuous complexation of the Ser and the reduced Co(II), the absorption peak continues to widen, and the absorption peak near 375 nm also tends to fuse with it. At 24 h, the absorption peak of Co(III)-serine near 520 nm disappeared, indicating that Co(III)-serine in the solution was completely reduced to Co(II)-serine.

In this study, Ser exhibits its potent reducibility, which is an attractive finding. As a zwitterionic species,³⁶ Ser exhibits a

negative charge when the pH in the solution is higher than its isoelectric point (IP), that is, the carboxylic acid group is converted from $-\text{COOH}$ to $-\text{COO}^-$, and its electron-donating ability will increase significantly.³⁷ The IP of Ser is 5.68, and after the leaching operation, the pH in the leachate is around 7.8. The $-\text{OH}$ group of Ser is also oxidized to the aldehyde group when it reduces Co(III) to Co(II) .³⁸ The reaction mechanism is shown in Figure 9. Figure 10 shows the FT-IR spectrum of Ser before and after leaching. For the FT-IR spectrum of pure Ser, the band at 1217 cm^{-1} was assigned to $\text{C}-\text{OH}$ rocking. However, after leaching, this band disappeared. The intensity of the band at 1571 cm^{-1} increased, indicating that the $-\text{OH}$ group was oxidized to $\text{C}=\text{O}$ during the leaching operation.³⁸ The increase in the band intensities of the other functional groups clearly indicated the presence of the reaction of Co and Ser.

3.5. Selective Extraction of Co in Ser-Based ABS. The polymer PPG400 was added to the leachate in a volume ratio of 1:1, and the system formed two phases. However, almost all ions were present in the bottom Ser-rich phase. Because thiocyanate ion can form complexes with such metals as Cu, Co, and Mn,³⁹ two different thiocyanates (KSCN and $[\text{N}_{4444}]\text{SCN}$) were tested in this experiment (Figure 11). Because Ser was complexed with Co, to improve the extraction efficiency, we added a little organic acid (0.01 M) to the system to disrupt the complexation of Co with Ser. As shown in Figure 12, the type of organic acids has a significant effect on the extraction efficiency of Co with the addition of $[\text{N}_{4444}]\text{SCN}$. This is related to the ability of different acids to bind Co. The extraction efficiency of Co was only 3.4% when no organic acid was added. The addition of organic acid TA increased the extraction efficiency to 96.6%. This is because TA contains more carboxyl groups, as demonstrated in Figure 6, which is favorable for binding with Co ions. According to Figure 11, when KSCN was added to the system, almost all of the Mn, Co, Cu, and Fe ions were combined with thiocyanate ions and transferred to the PPG400-rich phase. However, only Co and Cu ions were transferred to the PPG400-rich phase when $[\text{N}_{4444}]\text{SCN}$ was added to the system. In addition, in the leaching stage, a small amount of Cu (Figure 4) exists in the solution; therefore, the purity of Co in the PPG400-rich phase is very high, $\sim 95.1\%$. Regarding this selectivity, we supposed that it is an effect of the quaternary ammonium group, which forms stable complexes with Co together with thiocyanate ions.³⁴

4. CONCLUSIONS

In this study, we successfully integrated the leaching and separation of metals from spent LIB cathode powders using biocompatible amino acids alone. Without using any toxic and volatile organic solvents in the whole process, this newly proposed recycling system satisfies the sustainable and eco-friendly goals that the current industry pursues. The ABS (Ser-PPG400- H_2O) was first applied to the recovery of metals from waste batteries. Under a relatively mild temperature ($70\text{ }^\circ\text{C}$) and an S/L ratio of 10/1 (g/L), the leaching efficiency of each metal is higher than 80%. The leaching efficiency of Co reached 98%. The mechanism of Ser leaching for metals from the waste LIB cathode was discussed. The Co was selectively extracted with an extraction efficiency of 97% and a purity of over 95% by adding thiocyanate ions to the ABS system. The amino acids have excellent prospects in the

field of spent-battery recycling because of their eco-friendly and relatively low-price advantages.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c06654>.

Structure of the amino acids; effects of the concentration of the Ser, leaching temperature, and time on the leaching efficiency of the LIB cathode; and effects of the concentration of the Ser, leaching temperature, and time on the leaching efficiency of the LiCoO_2 (PDF)

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Notes

The authors declare no competing financial interest.

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