

Extraction and recovery of critical metals using eco-friendly processes to secure lithium- ion batteries resources

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Extraction and recovery of critical metals using eco-friendly processes to secure lithium-ion batteries resources

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Chapter 1. General Introduction

1.1 Critical metals in lithium-ion batteries

A lithium-ion battery (LIB) consists of four components: a cathode, an anode, an electrolyte, and a separator, illustrated by Fig.1.1(a). LIBs are named after the type of cathode active materials. In addition to the most used lithium cobalt oxides (LiCoO_2), there are also lithium manganese cobalt nickel oxides ($\text{LiMn}_x\text{Co}_y\text{Ni}_z\text{O}_2$), lithium nickel cobalt aluminum oxides ($\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$), and lithium iron phosphates (LiFePO_4) [1]. In a typical LiCoO_2 LIB, the cathode accounts for about 25% by weight (Fig.1.1(b)). According to reports, the weight ratio of each metal in LIBs in electronic products is: lithium 2.2%-10.3%, cobalt 15.6%-30.4%, manganese 5.2%-21.3%, nickel 2.5%-15%, copper 0.6%-8.1%, iron 0.4%-2.2%, and aluminum 0.3%-9.1% [2].

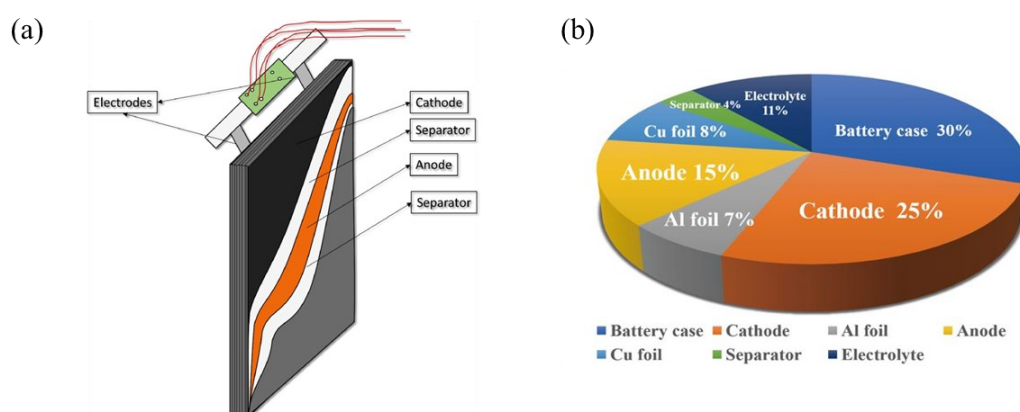


Fig. 1.1 (a) Pictorial representation of cross section of a mobile phone Li ion battery; (b) The weight of different components in a typical LiCoO_2 lithium-ion battery. (a) Reproduced with permission from ref. [2]. Copyright 2021 Elsevier; (b) Reproduced with permission from ref. [3]. Copyright 2022 John Wiley and Sons.

With the vigorous development of new energy vehicles, lithium, cobalt, nickel, and manganese, as critical metals in LIBs, are also economically valuable for their research [4]. Lithium is the most basic element of LIBs, and LIBs mainly rely on the movement of lithium ions and electrons to work [5]. According to the data of the Statista [6], the average price of battery-grade Li_2CO_3 was estimated at 17 000 dollar per metric tons in 2021, which is 3.4 times that of 2010. Cobalt is attractive due to its high price, as shown in Fig. 1.2, a pound of cobalt cost around 25 dollars in 2021 [7]. Among the metals in LIBs, nickel follows cobalt in price, rising to 9 dollars a pound in 2021. Even if the price of manganese remains flat, it is a valuable metal along with cobalt, nickel, and lithium due to their significant application in LIBs [3].

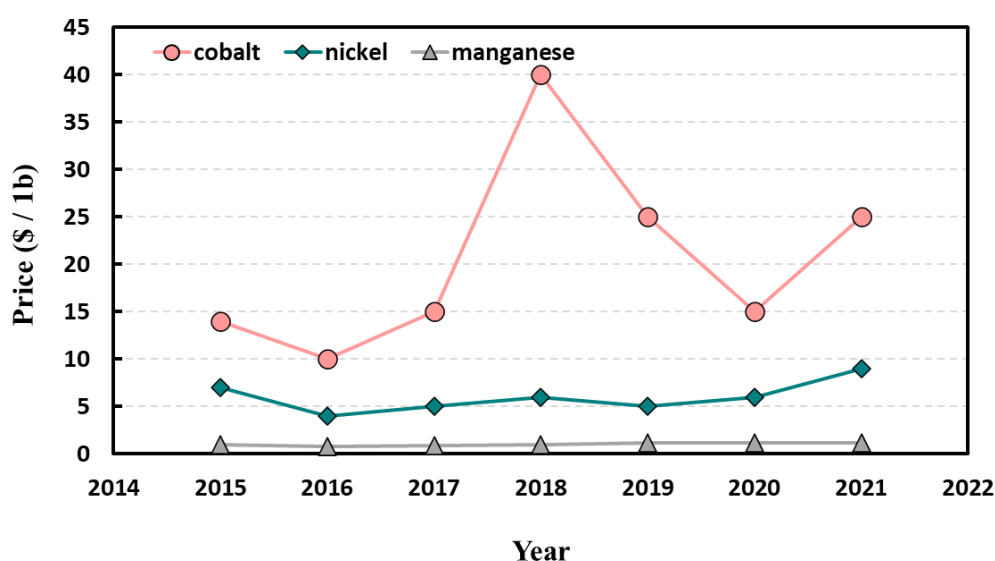


Fig. 1.2 Price trends of nickel, manganese, and cobalt from 2015-2021. Data derived from ref. [7].

1.1.1 Global demand for lithium-ion batteries

Under the background that governments around the world have set the goal of

"carbon neutrality" and designated a series of measures, the new energy electric vehicles industry has shown a vigorous development trend. LIBs have become the main driving force for electric vehicles due to their unique advantages such as high energy and power density, long cycle life, small size, light weight, and decreasing production cost year by year [8-11].

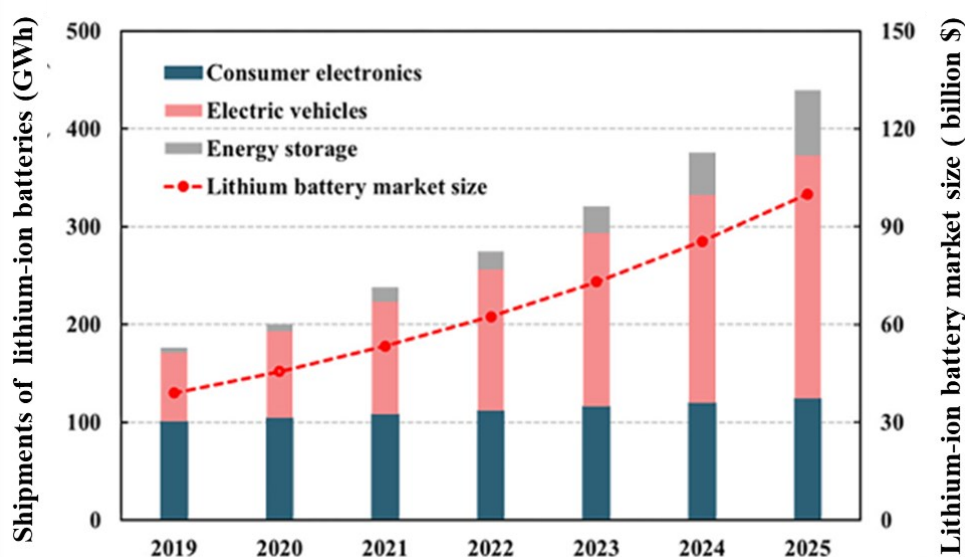


Fig. 1.3 LIBs shipments and its market size from 2019 to 2025. Reprinted with permission from ref.

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As shown in Fig. 1.3, the volume of shipments for LIBs in 2021 is 234.44 GWh and it is predicted that it will reach 439.32 GWh with a market size of \$99.98 billion in 2025 [10]. In addition to being used in the emerging electric vehicle market, LIBs are also widely applied to aerospace, medical, defense, energy storage, electronic consumption, and other fields [12]. Driven by the booming electric vehicle industry, the demand for LIBs will grow strongly and is expected to account for 70% of the global rechargeable

battery market by 2025 [13]. Due to the huge global demand for LIBs, the critical metals contained in LIBs are more attractive.

1.1.2 Critical metals in lithium-ion batteries primary resources

Lithium

The raw material used in LIBs is lithium carbonate, and the sources of lithium carbonate are mainly silicate minerals and mineral-rich brine [14]. As shown in Fig. 1.4, about 59% of lithium is distributed in brine and 25% in hard rock [15]. The global distribution of lithium deposits is uneven, with Chile, Bolivia and Argentina holding more than 70% of the world's lithium deposits [16]. Since the cost of extracting lithium from brine is lower than that from minerals, the main source of lithium in the market is brine, accounting for approximately 50%, and 40% comes from minerals [17]. According to the report by USGS in 2022 [18], currently four mining operations in Australia, two brine operations in Argentina and Chile, and two brine and one mining operations in China account for most of the world's lithium production.

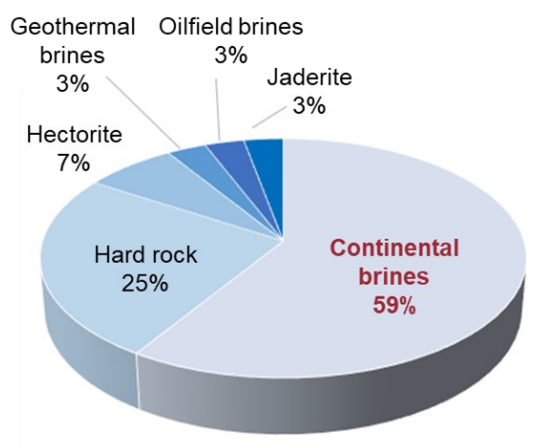


Fig. 1.4 Distribution of lithium at various natural resources. Data derived from ref. [15]

Cobalt

Cobalt is a strategic resource, and the world's terrestrial cobalt resources have been identified as about 25 million tons [19]. In 2021, the global cobalt production is estimated at 170 000 tons. Considering the high price of cobalt and the economics of extracting cobalt from the deposit, the amount of cobalt recovered from secondary resources is 2.3 times that extracted from the mineral in 2021 [19].

Nickel

The identified terrestrial nickel resources with an average nickel content of about 0.5% or more are at least 300 million tons, of which about 60% are laterite where the principal ore minerals are nickeliferous limonite and garnierite, and 40% are sulfide deposits where the principal ore mineral is pentlandite [20]. In 2021, the global nickel production is estimated at 2.7 million tons [20].

Manganese

Terrestrial manganese resources are abundant, about 1.5 million tons, but irregularly distributed. South Africa holds about 30% of the world's manganese reserves [21]. Due to the abundance of manganese resources and the relatively low price of cobalt, nickel and lithium, there are few industries that specifically recover manganese from secondary resources [22].

1.1.3 Critical metals in lithium-ion batteries secondary resources

LIB disposal was estimated to be 250 000 tones in 2020 and is expected to increase to 464 000 tones by 2025 [23]. The discarded LIBs have become a secondary resource

of critical metals (e.g., Li, Co, Ni, and Mn). Mineral resources in nature are limited. Faced with the imbalance of supply and demand [2, 4], the subject of recycling and reusing metals contained in discarded LIBs is undoubtedly strategic and urgent. The recycling of waste LIBs is necessary both from an environmental point of view and an economic point of view [24, 25].

The conventional treatment processes of waste LIBs are shown in Fig. 1.5. The recovery methods are generally divided into hydrometallurgy, pyrometallurgy and electrochemical treatment. The pyrometallurgy [26] is widely applied in industry due to its advantages of simple process and a large-scale application, but its disadvantage of excessive energy consumption cannot be ignored. Hydrometallurgy [27] has recently received extensive attention due to its advantages of low energy consumption, mature technology, and selective extraction of valuable metals. However, there are also disadvantages such as high wastewater yield and high corrosiveness. The method of electrochemical extraction [28] has low energy consumption and simple process, but it has not yet been widely used in industry.

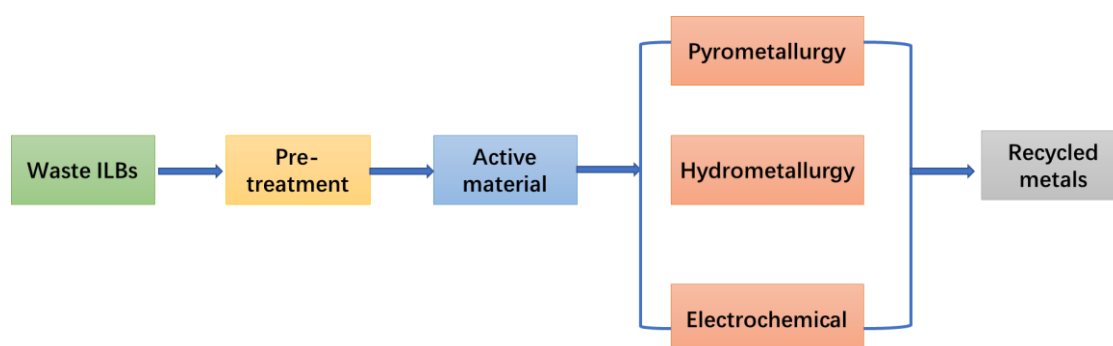


Fig. 1.5 Flow sheet of spent LIBs treatment processes.

1.2 Solution chemistry in metal extraction and recovery processes

Solvent extraction corresponds to hydrometallurgy in the field of extraction and separation. According to the type of solvent in the process, it can be roughly divided into three categories: aqueous biphasic system (ABS), liquid–liquid extraction (LLE) and solvometallurgy. An ABS—a self-separating two-aqueous-phase system comprising polymer/polymer, polymer/salt, or salt/salt—is a fully aqueous system. It utilizes that the two solutes in the system have different entropy of hydration, so that the two solutes are concentrated in different phases after salting out [29-32]. LLE [33-35] is a separation process that involves the transfer of a solute from one solvent to another, where the two solvents are immiscible or partially miscible with each other. Typically, two phases, one is an aqueous phase, and the other is an organic phase. LLE is thought to be one of the most mature and efficient methods for the industrial operation. Solvometallurgy [36] is the extraction of metals from ores or urban waste using non-aqueous solutions. To avoid definition confusion, we make a clear distinction between ABS (based on water as solvent), LLE (based on water and organic solvent as solvent) and solvometallurgy (based on non-aqueous solvent as solvent).

1.2.1 Aqueous biphasic system

The ABS (Fig. 1.6) is considered an environmentally friendly substitute for traditional LLE. The initial attempt in using the ABS for the separation and purification of biological compounds was proposed by Albertsson in 1958 [37]. He has reported the partitioning of proteins in a polymer-based ABS. For a long time after that, the

development of ABS was limited due to the problem of low extraction rate in the polymer-based ABS. It was not until Rogers and co-workers [38] created an ionic liquid (IL)-based ABS where ILs replaced polymers that ABS received attention in the field of metal extraction and separation. The first application of IL-based ABS for metal extraction and separation was Akama group [39]. The IL-based ABS composed of tetrabutylammonium bromide ($[N_{4444}][Br]$) and ammonium sulphate $[(NH_4)_2SO_4]$ was used for selective separation of cadmium from cobalt, copper, iron (III) and zinc.

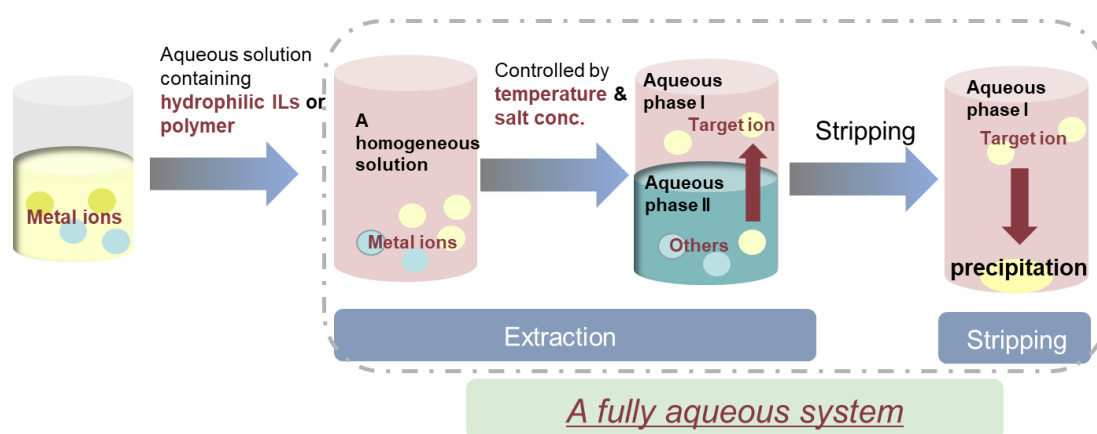


Fig. 1.6 Schematic illustration of aqueous biphasic system

Recently, many studies on the separation of metal ions using ABS techniques have been reported. Coutinho and co-workers [40] developed a remarkable separation ratio for $Co(II)$ and $Ni(II)$ using the IL-based ABS composed of tributyltetradecylphosphonium chloride ($[P_{44414}][Cl]$) and $NiCl_2$ for a spent-battery recovery. Liu and co-workers [41] reported the selectively separation of rare earths from the transition metals using a novel IL-based ABS toward efficient recycling of rare earths from the NdFeB magnets. The first application of integrated leaching and

separation of metals using the IL-based ABS consisting of IL ($[P_{44414}]Cl$) and an organic acid (CH_3COOH) was proposed by Coutinho group in 2020 [42]. ABS has great prospects for application in the field of metal extraction and it is attractive due to its environmentally friendly and simple in process.

1.2.2 Liquid–liquid extraction

The use of LLE (Fig. 1.7) in metal extraction and recovery processes could date back to the 1940s [43]. As a well-known metal separation technology, LLE has been widely used in industry. An important element in LLE is the extractant. According to the chemical properties of extractants, they can be divided into acidic extractants (i.e., DEHPA, Cyanex 272, Cyanex 301, and Versatic 10), alkaline extractants (i.e., Alamine 336, Aliquat 336, Amberlite LA-2, and Primene 81R), chelating extractants (i.e., LIX 64, LIX 54, LIX 63, and LIX-84-IC), and solvating extractants (i.e., TBP, Cyanex 923). In addition to the type of extraction agents, the pH of the solution, the type of organic solvent, and temperature are also important factors that affect the extraction efficiency.

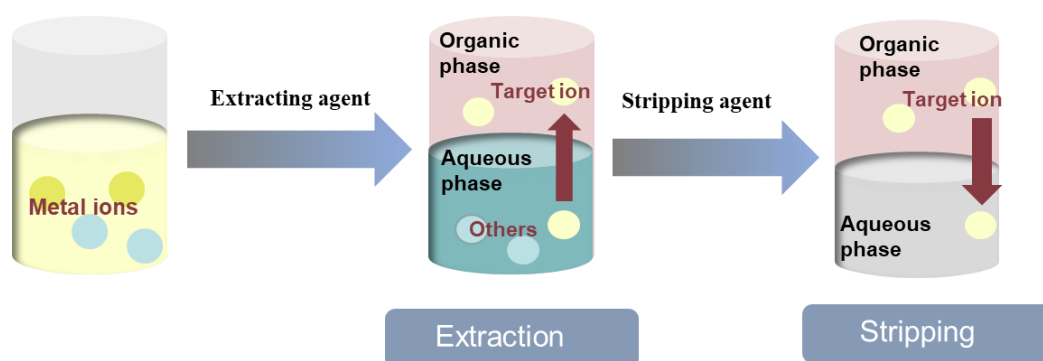


Fig. 1.7 Schematic illustration of liquid-liquid extraction

Recently, to reduce the harm of organic solvents to the environment, ILs are used to replace organic solvents. Traditional LLE is developing in the direction of combining with other new extraction technologies, such as the liquid membrane system formed by combining with membrane technology. Researchers are committed to developing eco-friendly and efficient extractants to substitute the toxic extractants. LLE is also used in the field of scrap metal recovery because it is suitable for large-scale industrial production.

1.2.3 Solvometallurgy

Solvometallurgy is a process that utilizes non-aqueous solvents. The first use of the term “solvometallurgy” was coined in his book-Ion solvation by Marcus in 1985 [44]. In this solvent extraction, it is the distribution of ions between two incompatible organic solvents [36]. In LLE, solvent extraction refers to the distribution of ions between an aqueous phase and an incompatible organic phase. In solvometallurgy, the type of non-aqueous solvent is very critical, and it should be sustainable and eco-friendly. In recent years, the application of green solvents such as ILs and deep eutectic solvents in solvometallurgy has been greatly developed [45,46].

The pioneers of this research include Binnemans and co-workers [47-49] and Goto and co-workers [50]. Solvometallurgy is a promising new approach to extractive metallurgy with several advantages such as low energy consumption, low toxicity, high selectivity, high efficiency [36].

1.3 Objectives and outline of the thesis

The main objective of the present thesis is to develop the eco-friendly and effective processes for selective extraction of the critical metal—lithium from the primary resources for production of LIBs, and selective recovery of the critical metals—cobalt, nickel, and manganese from the secondary resources—waste LIBs.

The present thesis consists of 5 chapters, i.e., the general introduction (Chapter 1), the research contents (Chapter 2-4), and general conclusions (Chapter 5). In addition, references are presented at the end of each chapter.

In the Chapter 1, a general introduction to the critical metals (lithium, cobalt, nickel and manganese) in LIBs and the solution chemistry in metal extraction and recovery processes is presented. Focusing on LIBs, the author discusses the critical metals in LIBs primary resources—Salt lakes and Minerals, and the secondary resources—waste LIBs in detail. For the application of solvent chemistry in the field of extraction and recovery, the author briefly reviewed the scientific literature on the topics, including the historical development and recent progress.

Chapter 2 discusses selective extraction of the critical metal—lithium from the primary resources—Salt lakes for production of LIBs. The author reported a feasible extraction of Li(I) from a simulated salt lake solution using a novel extraction system, in which a functionalized ionic liquid (FIL) is dissolved in a different ionic liquid diluent. As a functional extractant, 3-methyl-1-octylimidazolium thenoyltrifluoroacetone [Omim][TTA] was successfully prepared in a simple way and its extraction performance for Li(I) was evaluated. A sustainable technology for

resource extraction was demonstrated in this chapter.

Chapter 3 discusses the selective recovery of the critical metals—cobalt, nickel, and manganese from the secondary resources—waste LIBs. A novel route to recover Co, Ni, and Mn from a waste LIB cathode leachate model using the ABS consisting of fully eco-friendly components, i.e., hydrophilic ionic liquids, amino acids, and organic acids, without any hazardous reagents or organic solvents was proposed. Separation of Co, Ni, and Mn from sulfate media was successfully carried out using the ABS in a quite straightforward manner. In addition, the plausible mechanism of metal ion separation within the ABS was elucidated. A safer and cleaner technology for resource recovery was demonstrated in this chapter.

Chapter 4 discusses the integrated leaching and selective recovery of cobalt from an actual waste—a spent LIB cathode powder using an amino acid-based ABS. The amino acids efficiently leached critical metals from the cathode powder without adding any acid. Using the ABS, the integration of leaching and recycling has been successfully achieved in this chapter.

In the Chapter 5, a summary of the entire research contents was presented and future perspectives regarding the industrial interests and challenge was also discussed.

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Chapter 2. An Ionic Liquid Extractant Dissolved in An Ionic Liquid Diluent for Selective Extraction of Li(I) from Salt Lakes

2.1 Introduction

In the current pursuit of a green lifestyle and the vigorous development of electric vehicles, the demand for lithium-ion batteries has been rapidly increasing [1-4]. Therefore, securing lithium resources as fuel materials for the green revolution has become a hot topic. Approximately 59% of the lithium resources are stored in the continental salt lakes of the world [3]. Moreover, compared with extracting Li(I) by a mineral mining process, extracting it from a water solution is more environmentally friendly and leads to lower production costs [3]. Although relatively new separation methods, such as ion sieve adsorption and membrane extraction, have been developed in recent years, liquid-liquid extraction is thought to be one of the most mature and efficient methods for the industrial operation, and many studies are being conducted on Li(I) recovery [5-10]. However, liquid-liquid extraction normally requires a large amount of organic solvents, which causes an environmental problem [11]. It is essential to reduce or eliminate the use of such hazardous organic solvents. In most cases, in the process of extracting lithium ions, the pH of the raw material solutions needs to be adjusted to greater than 7, which limits the industrial application [12-14]. The currently available extractants, such as alcohols and ketones, acidic extractants, and crown ethers, for the lithium recovery form a stable complex under alkaline conditions [15]. The uses of a large amount of alkaline solution might result in a negative impact on natural

resources. Therefore, it is essential to develop a more efficient extractant for lithium ions that is applicable over a wider range of pH conditions. The types of salt lakes and brines in the world are diversified, and their pH values are also varied [3]. Therefore, the development of an extractant that functions in multiple pH ranges would be very significant.

The ketone type of extractants is an effective extractant used for lithium recovery. Great efforts have been made on their applications owing to their high selectivity for lithium ions [15-19]. For example, Kinugasa et al. [20] studied the equilibrium and kinetics of Li(I) extraction in the LIX54-TOPO system. Young-Sang et al. [13] explored the extraction of trace lithium using thenoyltrifluoroacetone (TTA) and trioctylphosphine (TOPO) as synergistic ligands. Pranolo et al. [12] used LIX54 and Cyanex 923 as extractants to separate Li(I) from Na(I). In the extraction process, a large amount of organic solvents, which are highly toxic, were required. Ionic liquids (ILs) have attracted much attention owing to the negligibly small vapor pressure, high thermal stability and low melting point to name a few, which are very promising properties for extraction operations [21, 22]. The functional group of $[TTA]^-$, as an anion of ILs, has also been studied in the field of Li(I) extraction. Wang et al. [23] investigated diketone-based ionic liquids with a trialkylmethylammonium ($[A336]^+$) cation and trialkylphosphineoxide (TRPO) to separate Li(I) from a solution of Li_2CO_3 . Although the above research achieved a high extraction rate of Li(I) under alkaline conditions, the addition of a neutral extractant for collaborative extraction is required.

Functional ionic liquids (FILs) mean that the cationic or anionic part of the ILs can

be involved in complex formation with a metal ion [14, 24-28]. Normal extraction with ILs usually proceeds by a cation exchange mechanism, which often causes the loss of extractants, thereby reducing the recycling efficiency. The extraction reaction with FILs proceeds by an ion association mechanism so that the extractant body will always remain in the extractant phase, which is conducive to recovery and reuse of extractants [28]. Yang et al. [14] reported solvent extraction using a hydroxyl functionalized ionic liquid, 1-hydroxyethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide ([OHEMIM][NTf₂]), and a neutral ligand, trialkyl phosphine oxide (Cyanex923), as the extractants to prove that the [OHEMIM][NTf₂]-Cyanex923 extraction system is promising in the recovery of lithium from an alkaline brine. Tetrabutylammonium 2-ethylhexyl hydrogen-2-ethylhexylphosphonate ([N₄₄₄₄][EHEHP]) was also studied in the extraction of Li(I) from an aqueous solution by Shi et al. [28]. A screening method, based on a computational approach with Conductor-like Screening Model for Real Solvents (COSMO-RS), and extraction experiments were carried out to demonstrate that the tetrabutylammonium mono-2-ethylhexyl(2-ethylhexyl)phosphate ([N₄₄₄₄][EHPMEH]) had a high Li(I) extraction efficiency by Zhao et al. [2]. These FILs are promising extractants for the extraction of Li(I). In these articles, the separation of Li(I) from Na(I) was also another important issue. However, the separation efficiency of Li(I) over Na(I) still needs to be improved for the construction of an efficient lithium recovery process from lithium resources.

From this point of view, we studied a feasible extraction of Li(I) from a simulated salt lake solution using a novel FIL system, namely an ionic liquid extractant dissolved

in an ionic liquid diluent, in which 3-methyl-1-octylimidazolium thenoyltrifluoroacetone [Omim][TTA] was dissolved in a different ionic liquid without using additional neutral extractants. The effects of pH and metal concentration on extraction, as well as the stripping properties, were systematically investigated. A study on the extraction mechanism was conducted by slope analysis and ultraviolet–visible (UV-vis) measurement. The thermodynamic parameters for the extraction reaction were obtained according to the Van't Hoff equation. The stripping of lithium ions from the loaded extractant phase was also investigated. The selective extraction of lithium from a simulated salt lake solution was demonstrated using a countercurrent extraction process.

2.2 Experimental

2.2.1 Materials and reagents

The ionic liquids 3-methyl-1-octylimidazolium chloride ([Omim][Cl]) and 3-methyl-1-octylimidazolium bis(trifluoromethanesulfonyl)imide ([Omim][NTf₂]), and thenoyltrifluoroacetone (TTA) were supplied by Tokyo Chemical Industrial Co., Ltd (Tokyo, Japan). An ammonia solution (NH₃, 28%) and dichloromethane (CH₂Cl₂) were purchased from Fujifilm Wako Chemical Ltd (Osaka, Japan). Lithium, and sodium and potassium salts were supplied by Kishida Chemical Co., Ltd (Osaka, Japan). Hydrochloric acid (HCl), sulfuric acid (H₂SO₄), chloroform (CHCl₃) and ammonium chloride (NH₄Cl) were also purchased from Kishida Chemical Co., Ltd. Deionized water (Milli-Q, Merck Millipore) was used to prepare the aqueous solutions used in this

study.

2.2.2 Synthesis of [Omim][TTA]

The synthesis of [Omim][TTA] was performed according to a similar study [29]. First, 50 mmol of TTA was dissolved in CH₂Cl₂, and then 50 mmol of ammonia solution was added. The TTA and ammonia solution was thoroughly shaken and mixed. Then, 50 mmol of [Omim][Cl] was added and refluxed at 313 K for 12 h. A reaction was carried out between [Omim][Cl] and [NH₄][TTA]. After rotary evaporation, stripping and drying the residue, the product [Omim][TTA] was finally obtained in a yield of 75.9%. It was observed that the resulting [Omim][TTA] was an orange viscous liquid. Figure 2.1 shows the synthetic path for [Omim][TTA]. The [Omim][TTA] was characterized by a nuclear magnetic resonance (NMR, JNM-ECZ400, JEOL Ltd.) spectrometer (Fig. 2.2), and the data from ¹H NMR were ¹H-NMR (400 MHz, CDCl₃, ppm, δ): δ 0.85 (t, 3H), δ 1.23 (m, 10H), δ 1.78 (m, 2H), δ 4.01 (s, 3H), δ 4.21 (t, 2H), δ 6.02 (s, 1H), δ 7.02 (m, 1H), δ 7.16 (s, 2H), δ 7.35 (m, 1H), δ 7.52 (m, 1H), 10.52 (s, 1H).

The purity of the product was determined by calculating the relative area of proton signals in ¹H NMR spectra, following Eq. (2.1) [30, 31]. The product purity was 95.1%.

$$Purity(\%) = [\Sigma I (product) / \Sigma I (total)] * 100 \quad \text{Eq. (2.1)}$$

(*I* : the relative area of each signal)

To further confirm the purity, elemental analysis (Yanaco CHN Corder MT-5) was carried out to quantify the amount of carbon, hydrogen and nitrogen. As shown in Table

2.1, the values of experimental data were quite consistent with those of theoretical values.

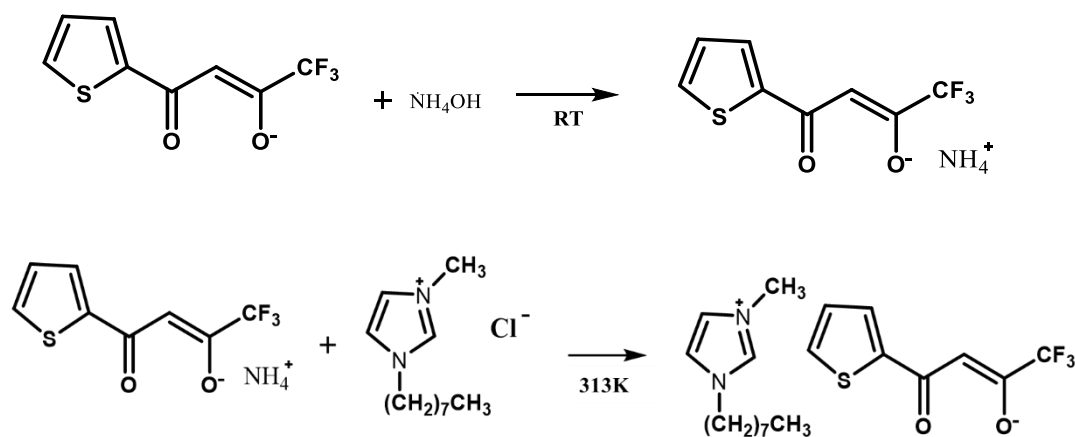


Fig. 2.1 Synthetic path for [Omim][TTA].

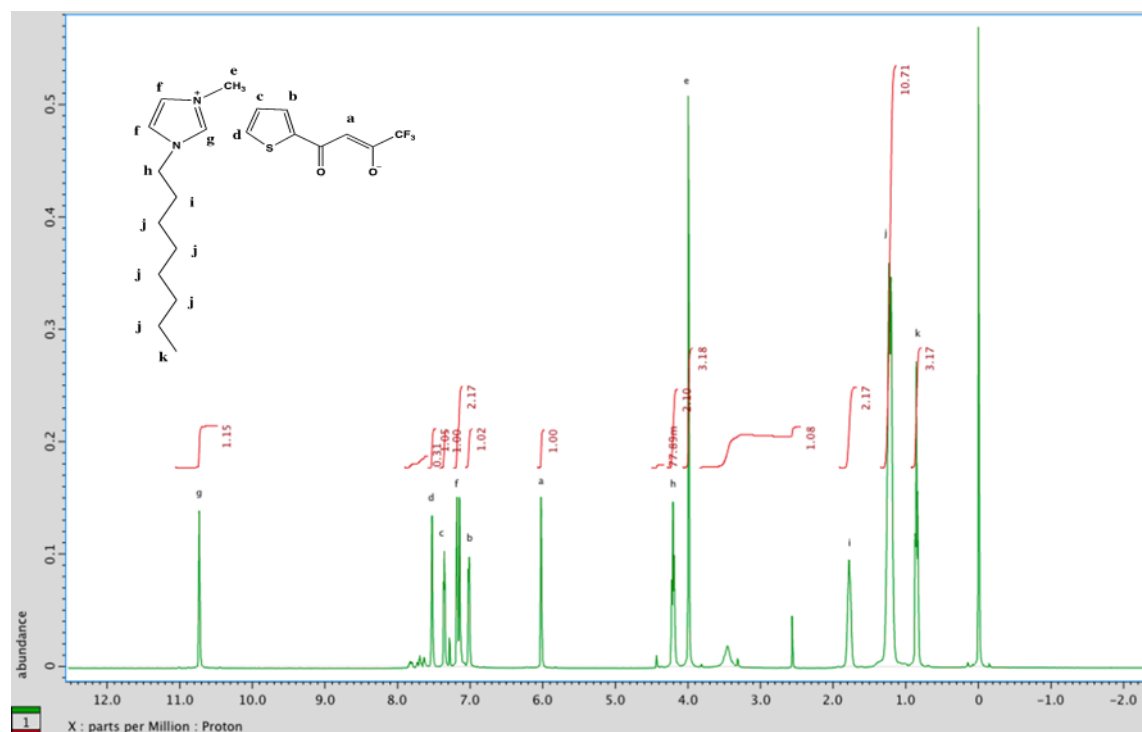


Fig. 2.2 ^1H -NMR of IL [Omim][TTA]

Table 2.1 Elemental analysis of [Omim][TTA]

	H (%)	C (%)	N (%)
Measured data	6.39	56.49	6.40
Theoretical data	6.53	57.68	6.73

2.2.3 Extraction and stripping procedures

The extraction and stripping performances were evaluated through liquid-liquid extraction. Equal amounts of organic and aqueous solutions (2 mL) were mixed and shaken in a water bath at constant temperature for approximately 2 hours to allow for the extraction equilibrium. Then, the extraction ability of the extractants for Li(I) was evaluated by the change of the Li(I) concentration in the aqueous solution before and after the extraction.

The Li(I) was stripped from a loaded extractant phase by contacting with hydrochloric acid (HCl) or sulfuric acid (H₂SO₄). The volume ratio of the aqueous to the extractant phase was 2:1. The stability test was conducted five times. After each cycle, the extractant phase was washed with an ammonia solution and deionized water for neutralization, and then was applied for the next cycle.

The extraction of lithium from a simulated salt lake solution was conducted using a countercurrent extraction process. The ionic composition of the Qarhan salt lake [32] is shown in Table 2.2. The Li(I) extraction isotherm was constructed at various phase ratios. The volume ratio of the aqueous and extractant phases ($V_a : V_o$) was 1:3, 1:2, 1:1 and 1:2, respectively.

Table 2.2 Ionic composition of the Qarhan salt lake [mmol / L]

(mmol / L)	Li(I)	Na(I)	K(I)
Concentration	32	650	360

2.2.4 Characterization

The metal concentrations in the aqueous solutions were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES) Optima 8300 (PerkinElmer). The extraction efficiency (E , %), stripping efficiency (S , %), distribution ratio (D) and separation factor (SF) were calculated using Eqs. (2.2), (2.3), (2.4) and (2.5), respectively.

$$E = 1 - [M]_e/[M]_0 \quad \text{Eq. (2.2)}$$

$$S = ([M]'_e/([M]_0 - [M]_e)) \times (V'_e/V_e) \quad \text{Eq. (2.3)}$$

$$D = ([M]_0 - [M]_e)/[M]_e \quad \text{Eq. (2.4)}$$

$$SF = D_{Li(I)}/D_i \quad \text{Eq. (2.5)}$$

where $[M]_e$ (ppm) is the equilibrium concentration of metal M in the aqueous phase, $[M]_0$ (ppm) is the initial concentration of metal M in the aqueous phase, $[M]'_e$ (ppm) is the concentration of metal M in the aqueous phase after stripping, V'_e (L) is the volume of stripping solution, and V (L) is the volume of extract. $D_{Li(I)}$ is the distribution ratio of Li(I) and D_i is the distribution ratio of the other metal ions.

UV-vis spectra of the aqueous phase were obtained by a UV-vis spectrometer (JASCO V-670) at 298 K with a 1 nm spectral resolution. The density and viscosity of [Omim][TTA] were determined by a density meter (DMA 35 Ampere, Anton Paar) and a viscosity meter (Lovis 2000M, Anton Paar), respectively. The solubility test of the

FIL into water was conducted by mixing deionized water (2 mL) and the FIL (2 mL). After shaking for a few minutes, the aqueous phase was taken out and the change in the sulfur concentration in the aqueous phase was monitored by using ICP.

2.3 Results and Discussion

2.3.1 Physical properties of [Omim][TTA]

The physical properties of the FIL are shown in Table 2.3. The density was similar to that of typical ionic liquids. The low solubility of the FIL into water indicated that it showed a high hydrophobic property that facilitated the phase separation in the liquid-liquid extraction operation. Compared with other ionic liquids containing the same cation [Omim]⁺ (Table 2.4), [Omim][TTA] was found to have a relatively low viscosity. A high viscosity of ionic liquids is not suitable for the separation process in extraction, which requires the consumption of a lot of organic diluents for practical uses. Therefore, based on the above physical properties, it was found that the newly developed FIL is suitable for application in liquid-liquid extraction.

Table 2.3 Physical properties of the FIL.

Physical properties	[Omim][TTA]
Density [g/cm ³]	1.196
Viscosity [cP]	208
Solubility in water [g/mL]	5.0×10 ⁻⁴

Table 2.4 The viscosity of ILs containing the same cation – [Omim]⁺

Name of ILs	Abbreviated	Viscosity [cP]
1-octyl-3-methylimidazolium hexafluorophosphate	[Omim][PF ₆]	682-710
1-octyl-3-methylimidazolium tetrafluoroborate	[Omim][BF ₄]	415
1-octyl-3-methylimidazolium chloride	[Omim][Cl]	337
1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[Omim][NTf ₂]	93

*Data was from Lanzhou Greenchem ILs, LICP, CAS.

2.3.2 Effect of pH in the feed solution

The pH of the aqueous phase greatly influences the extraction efficiency of the extractants for the target ions. The experimental conditions were as follows; the organic phases were prepared by dissolving 0.1 M TTA in [Omim][NTf₂] and by dissolving 0.1 M [Omim][TTA] in [Omim][NTf₂]. The main purpose here was to compare the extraction performance for Li(I) between the FIL and its corresponding extractant TTA. The aqueous phase contained Li(I), Na(I) and K(I), and their concentrations were 20 ppm. The experimental results are shown in Fig. 2.3. Li(I) was extracted at a pH greater than 7 when 0.1 M TTA was dissolved in [Omim][NTf₂] (Fig. 2.3(a)). A large amount of alkaline solution would inevitably need to be consumed, which would have a negative impact on the environment. Most of the extractants show a similar performance, which means that the extraction of lithium occurs in an alkalic condition.

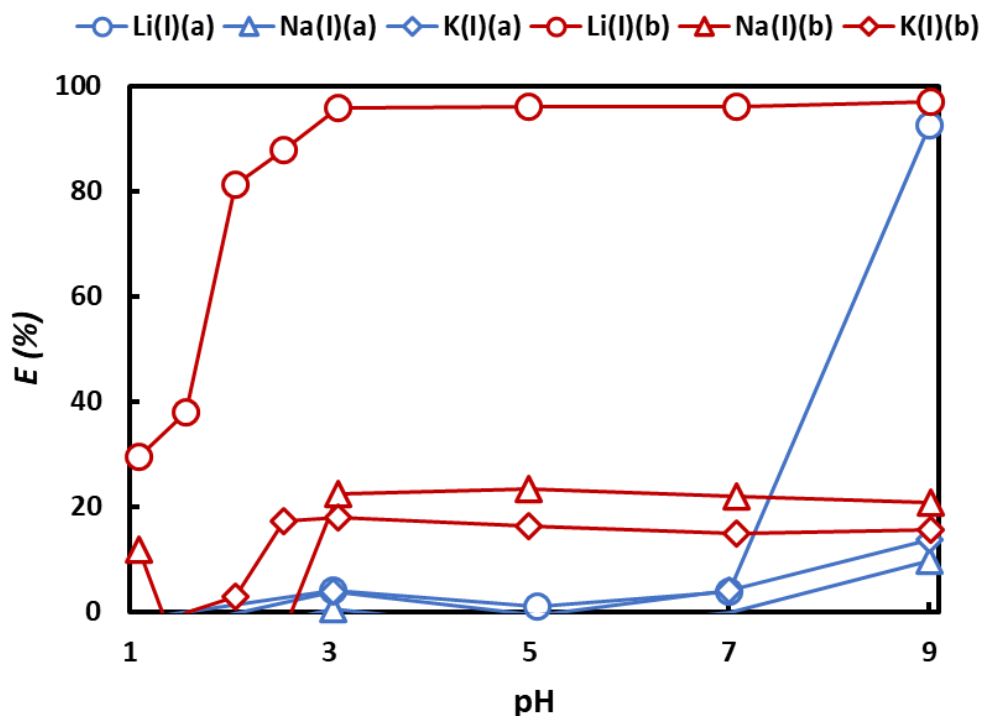


Fig. 2.3 Effect of pH of the aqueous phase on the extraction efficiency.

(a): the aqueous phase: 2 mL of 20 ppm Li(I), Na(I) and K(I); the organic phase: 2 mL of 0.1 M TTA was dissolved in [Omim][NTf₂].

b): the aqueous phase: 2 mL of 20 ppm Li(I), Na(I) and K(I); the organic phase: 2 mL of 0.1 M [Omim][TTA] was dissolved in [Omim][NTf₂].)

Using the FIL [Omim][TTA] (Fig. 2.3(b)), the FIL could, however, effectively extract Li(I) over a wide range of pH, and even under acidic environments. This indicates that an additional extractant is not required to extract Li(I) effectively. This is a major improvement compared with the previous reports [3, 15], and it also broadens the scope of applications. Moreover, the extraction efficiency could remain high and did not depend on a pH value above 3. The coordination of TTA toward Li(I) occurs in a basic

solution. The enol structure of TTA would be dehydrogenated, and then results in an adduct with Li(I) to form an enolate complex with Li(I) [13]. The anionic species in [Omim][TTA] is an enolate ion of TTA; therefore, the dehydrogenation step is not required, which enhances the extraction efficiency of the ionic liquid extractant. However, there is a competitive relationship between H^+ and Li^+ at the lower pH region. We found that the FIL extractant had a stronger extraction ability compared with that of the extractant TTA itself and a wide range of pH in the feed solution was suitable for lithium extraction.

2.3.3 Effect of diluents

To create a novel ionic liquid system without using the traditional organic diluents, we dissolved [Omim][TTA] as the extractant in another ionic liquid [Omim][NTf₂] as the diluent. According to the result in Fig. 2.4, we confirmed that Li(I), Na(I) and K(I) were not extracted at all by using the diluent [Omim][NTf₂] alone. The other ionic liquid [Omim][NTf₂] did not interfere with the extraction of Li(I). As shown in Fig. 2.5, compared with that using CHCl₃, the degree of extraction of Li(I) was strongly enhanced in the newly developed ionic liquid system. Both [Omim][TTA] and [Omim][NTf₂] are ionic liquids and have the same cation. Ionic liquids exhibit a strong electrophilicity, and this environment would be favorable for complex formation. Therefore, compared with dissolving the FIL in CHCl₃, the newly developed ionic liquid system is more suitable for lithium extraction. Moreover, an organic diluent is highly toxic and more volatile; therefore, the use of ionic liquids as diluents is more

beneficial for the environment.

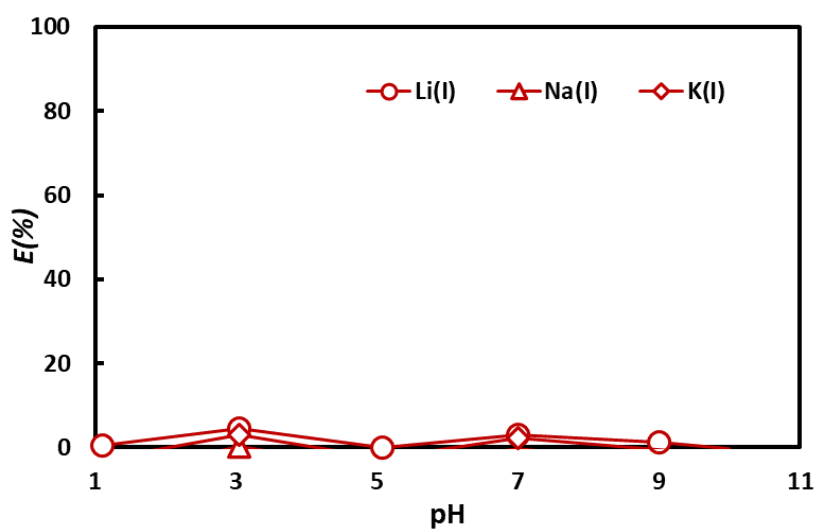


Fig. 2.4 Effect of pH in the aqueous phase on the extraction efficient

(Organic phase: 2 mL of [Omim][NTf₂], Aqueous phase: 2 mL of 20 ppm Li(I), Na(I) and K(I))

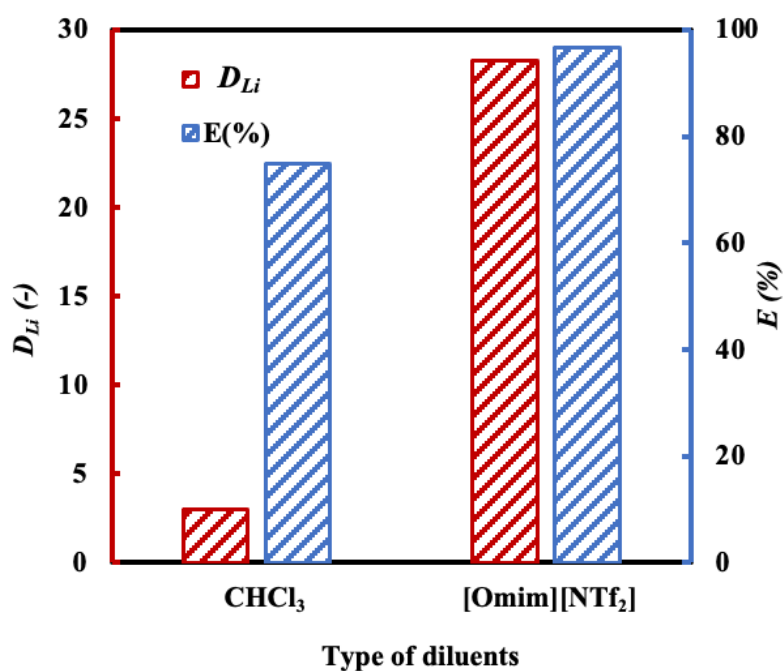


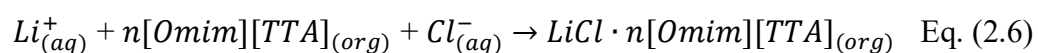
Fig. 2.5 Effect of diluents on the extraction efficiency.

(The organic phase: 2 mL of 0.1M [Omim][TTA] dissolved in [Omim][NTf₂] or CHCl₃; the aqueous phase: 2 mL of 20ppm Li(I), Na(I), and K(I).)

2.3.4 Extraction mechanism

Dietz et al. [33] proposed a triple mode for the extraction of metal ions in an ionic liquid system. The three extraction mechanisms were the ion association, the cation exchange and the special cation exchange involving hydrated ions. The extraction mechanism was dependent on the experimental conditions such as pH or hydrophobicity of the ionic liquid. In particular, the hydrophobicity of the cation in the ionic liquids had a key role in the extraction reaction. On the basis of the discussion, because the cationic part of [Omim]⁺ is very hydrophobic and does not easily enter the aqueous phase, the extraction mechanism of Li(I) using [Omim][TTA] is deduced to be proceeded by the ion association mechanism [28]. To elucidate the mechanism, slope analysis was carried out. The organic phase was prepared by dissolving 0.1 M [Omim][TTA] in CHCl₃. The concentration of Li(I) in the aqueous phase was varied to be 10, 25, 50, 75 and 100 mM.

From the results of metal extraction with FIL [1, 24], the extraction reaction equation can be expressed by Eq. (2.6). To ensure electronic neutrality, it was deduced that only one chloride anion could be involved in the extraction reaction.



By plotting $\log D$ as a function of $\log [Omim][TTA]$, a fitted straight line with an R^2 value of 0.9958 was obtained, and the slope was approximately one (Fig. 2.6). The value of n could be calculated by using Eq. (2.7).

$$\log D_{Li} = \log K + n \log [Omim \cdot TTA]_{(org)} + \log [Cl^-]_{(aq)} \quad \text{Eq. (2.7)}$$

Figure 2.6 shows that the D_{Li} increased by increasing the concentration of

[Omim][TTA] at a phase ratio (O/A) of one. The result from slope analysis indicated that a 1:1 complex of the FIL and Li(I) was formed. The ion association mechanism provides the benefit where we can maintain the extractant concentration in the extraction operation because the release of the extractant is protected and the recycling of the extractant would be easy.

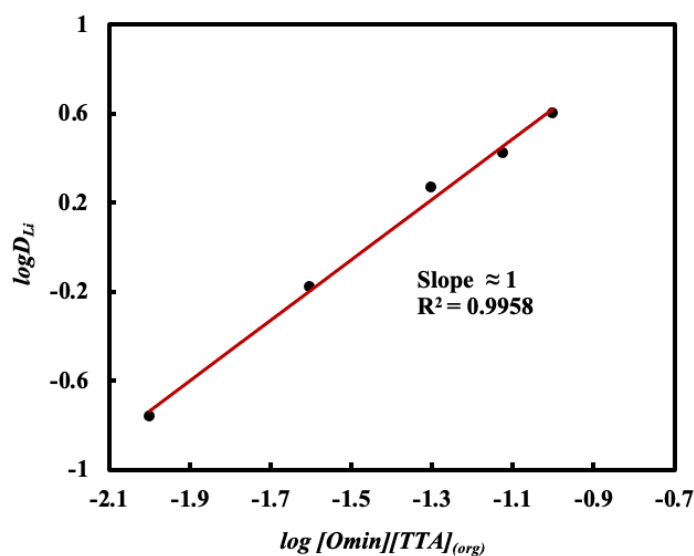


Fig. 2.6 Plot of $\log D_{Li}$ as a function of $\log [Omim][TTA]$.

To further confirm the mechanism, a comparative analysis of the aqueous phase was conducted using the UV-vis spectrometer. The experiment adopted the method of liquid-liquid extraction. Two different samples were prepared. The organic phase of both samples was where the FIL [Omim][TTA] was diluted in $CHCl_3$. Their aqueous phases were different, where one was deionized water and the other was an aqueous solution containing Li(I). We compared the changes of the UV-vis curve of the aqueous solution in each sample before and after extraction. From the result shown in Fig. 2.7, we observed that the absorbance of the aqueous solution between 200 nm and 400 nm

in each sample increased after the extraction reaction. This indicated that some substances entered the aqueous phase from the organic phase during the extraction reaction. There are two possible explanations for this. The first is that $[\text{Omim}]^+$ entered the aqueous phase owing to the cation exchange mechanism, and the other is that trace amounts of the FIL were dissolved in the aqueous phase during the reaction. Because the changes in the absorbance of the aqueous solution in the two samples were similar before and after the reaction, we inferred that a trace amount of the FIL was dissolved in the aqueous solution, and the ion exchange reaction did not occur. This result proved that the ion association mechanism plays a major role in the ionic liquid system.

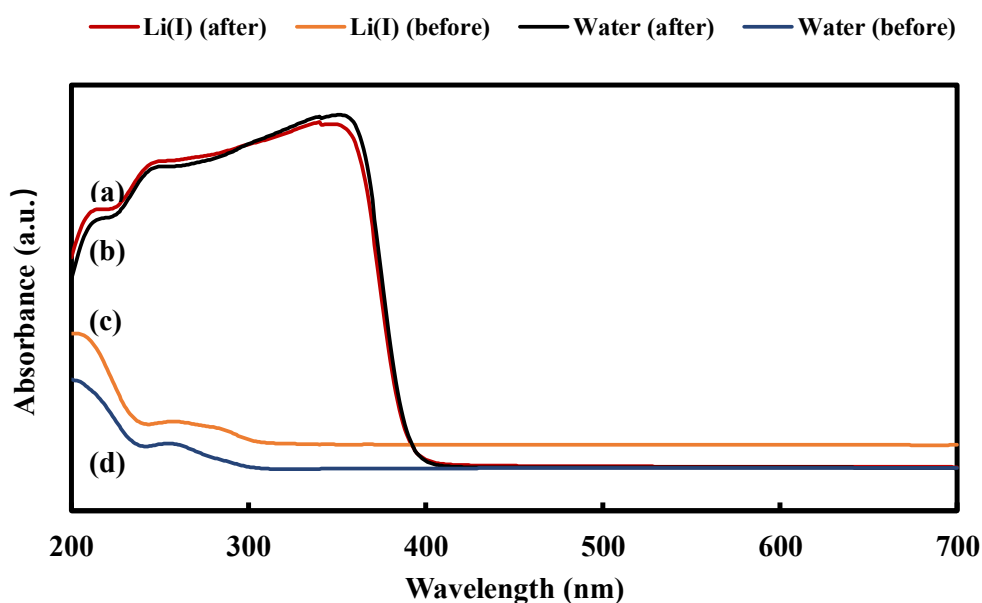


Fig. 2.7 UV-vis spectra of the aqueous phase before and after extraction.

((a) and (c): the aqueous phase: 2 mL of aqueous solution containing Li(I); the organic phase: 2 mL of 0.1 M $[\text{Omim}][\text{TTA}]$ was dissolved in CHCl_3 .

(b) and (d): the aqueous phase: 2 mL of deionized water; the organic phase: 2 mL of 0.1 M $[\text{Omim}][\text{TTA}]$ was dissolved in CHCl_3 .)

2.3.5 Determination of thermodynamic parameters

The thermodynamic property of the [Omim][TTA] extractant is very important to study the extraction behavior in the newly developed FIL system. The extractant phase was composed of 0.1 M [Omim][TTA] dissolved in [Omim][NTf₂]. The Li(I) concentration in the aqueous solution was 20 ppm. The samples were shaken for 1 hour in a water bath at a constant temperature of 298, 303, 313, 323 and 333 K. As shown in Fig. 2.8, in the temperature range of 298–333 K, the Li(I) distribution efficiency decreased as the temperature in the extraction system was increased. There was a linear relationship between $\log D$ and $1000/T$, and the slope of the fitted line was 0.9228. The enthalpy change (ΔH°) was calculated to be $-17.67 \text{ kJ}\cdot\text{mol}^{-1}$ using Van't Hoff's equation (Eq. 2.8), which indicated that the extraction of Li(I) using [Omim][TTA] was exothermic.

$$\frac{\partial \log D}{\partial (1/T)} = \frac{-\Delta H^\circ}{2.303R} \quad \text{Eq. (2.8)}$$

The Gibbs energy (ΔG°) and the entropy (ΔS°) changes were obtained as follows:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad \text{Eq. (2.9)}$$

$$\Delta G^\circ = -2.303RT \log K \quad \text{Eq. (2.10)}$$

The ΔG° and ΔS° of this extraction reaction were calculated to be $-17.02 \text{ kJ}\cdot\text{mol}^{-1}$ and $-2.18 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 298.15 K, respectively. The ΔG° was negative, which indicated that the extraction reaction of Li(I) with the FIL was spontaneous and was favorable. The value of ΔS° was also negative, which meant that the degree of freedom for the FIL decreased when the extraction reached equilibrium. This entropy value also

suggested that the mechanism of the extraction reaction was the ion association. Because the FIL formed an adduct with Li(I), the degree of freedom on the FIL was reduced.

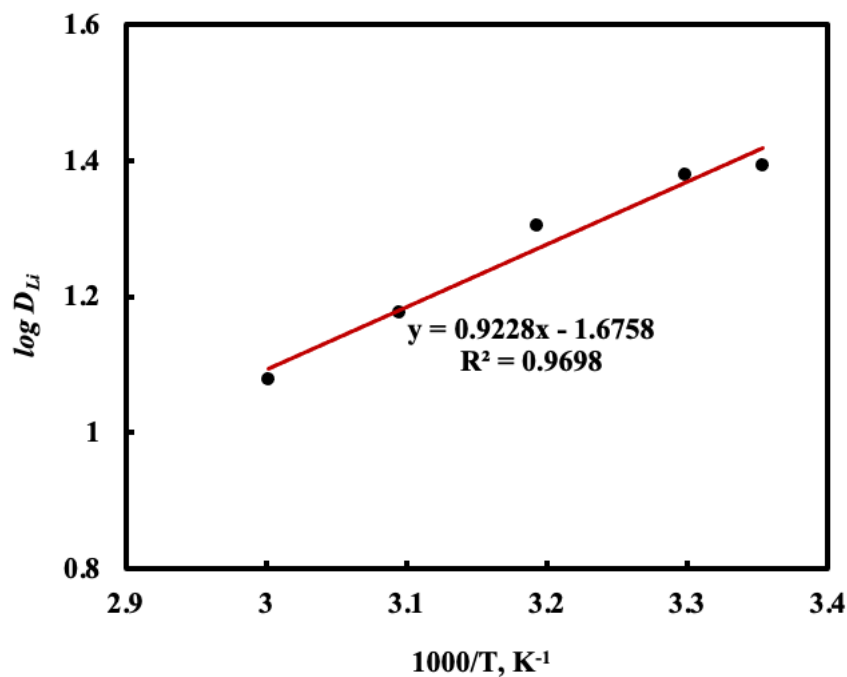


Fig. 2.8 Plot of $\log D_{Li}$ versus $1000/T$.

2.3.6 Stripping study

After quantitative extraction of Li(I), the stripping behavior was investigated using HCl or H₂SO₄. As shown in Fig. 2.9, the stripping efficiency initially increased as the acidic concentration was increased. Around 80% of the loaded Li(I) could be recovered as the acidic concentration was increased to 0.1 M. The plausible stripping mechanism could be described by Eq. (2.11).



Eq. (2.11)

The hydrogen ions dissociated the $LiCl \cdot [Omim][TTA]$ complexes [13].

The stripping efficiency showed a peak at the concentration of acid around 0.1 M. A slight decrease of stripping efficiency at higher acid concentration might be attributed to the competitive extraction reaction shown in Eq. (2.6). Consistently, the type of acid did not show a significant effect on the stripping efficiency. In addition, a lower concentration of acids would reduce the corrosion problem during the process. Therefore, 0.1 M acid was used to recover Li(I) from the extractant solution.

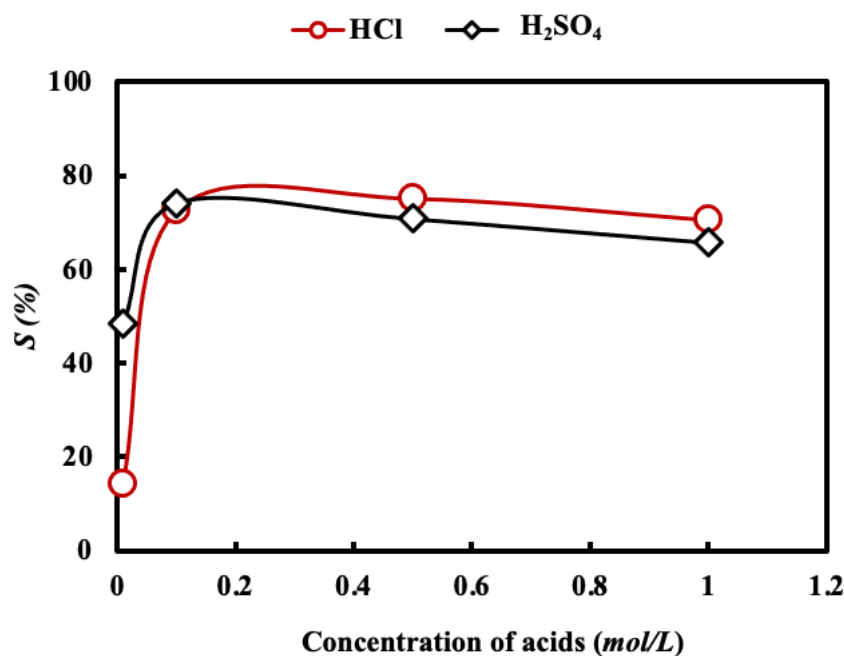
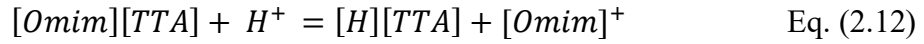


Fig. 2.9 Effect of concentration of acids on stripping behavior for Li(I).

2.3.7 Stability test

To verify the stability of the FIL, we carried out five cycles of the experiments. Figure 2.10 shows that the extraction efficiency of Li(I) did not change significantly, and was maintained at 97%. On the basis of the result obtained, the FIL extractant could be reused. A key operation was that after each cycle the extractant phase needed to be

neutralized. If the FIL was not treated with an alkaline solution and deionized water after each cycle, the result of recycling was not satisfactory so that the extraction efficiency of Li(I) dropped severely after two cycles of experiments, as shown in Fig. 2.11. The reason for this was assumed by Eqs. (2.12) and (2.13).



By comparing Eqs. (2.6) and (2.12), there was a competition between hydrogen ions and Li(I) under acidic conditions. Owing to the large amounts of acids used in the stripping process, the high concentration of hydrogen ions would combine with the anionic species of the FIL, so it requires an additional operation to neutralize the FIL after each cycle. However, as shown in Fig. 2.3, when the acid concentration is not high, that is, the pH is greater than 3, the FIL is more inclined to combine with Li(I).

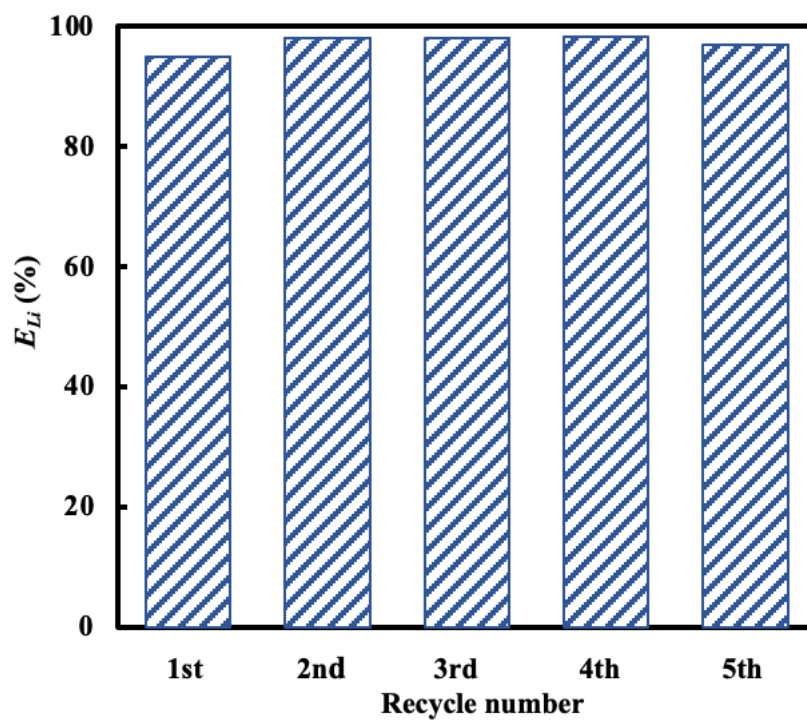


Fig. 2.10 Circulation experiment on the extraction of Li(I).

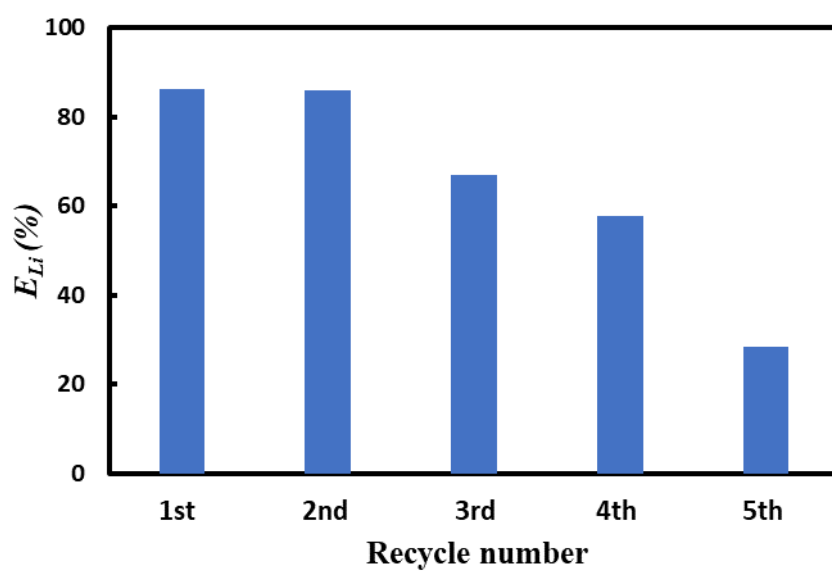


Fig. 2.11 Circulation experiment about extraction of Li(I)

(The FIL was not treated with alkaline solution and deionized water after each cycle)

2.3.8 Extraction of Li(I) from a simulated salt lake solution

The ionic liquid of 0.1 M [Omim][TTA] dissolved in [Omim][NTf₂] was used to

recover Li(I) from a simulated salt lake solution (see Table 2.2). The Li(I) extraction isotherm was investigated at various phase ratios. The degree of extraction of each metal ion is shown in Fig. 2.12. The extraction efficiency of Li(I) could maintain a high level even though the interference ion concentration was very high, which was a huge improvement. In general, the extraction efficiency of the target ions will be reduced when the concentration of interfering ions is too high. From the McCabe–Thiele diagram (Fig. 2.13), at a phase ratio of $V_o : V_a = 1 : 1$, the Li(I) recovery from the simulated salt lake solution reached 88.2% in 2-3 stages and the recovery yield of lithium reached 97.3% at a phase ratio of $V_o : V_a = 3 : 1$. In an industrial operation, the extraction stages are usually increased by one or two stages from the theoretical value [34]. The changes in ion concentration after extraction are shown in Table 2.5. The $SF_{Li/Na}$ obtained in this study was compared with that of various FILs previously reported which were used without the addition of a neutral extractant for collaborative extraction and the results are summarized in Table 2.6. The $SF_{Li/Na}$ at the phase ratio ($V_o : V_a = 1 : 1$) in the present study was 227, which is much higher than that of the previously reported FILs. The higher selectivity for Li(I) over Na(I) and K(I) could be attributed to the steric effect of TTA^- [13, 36, 37]. The FIL extractant [Omim][TTA] shows good prospects for the recovery of Li(I) from salt lakes.

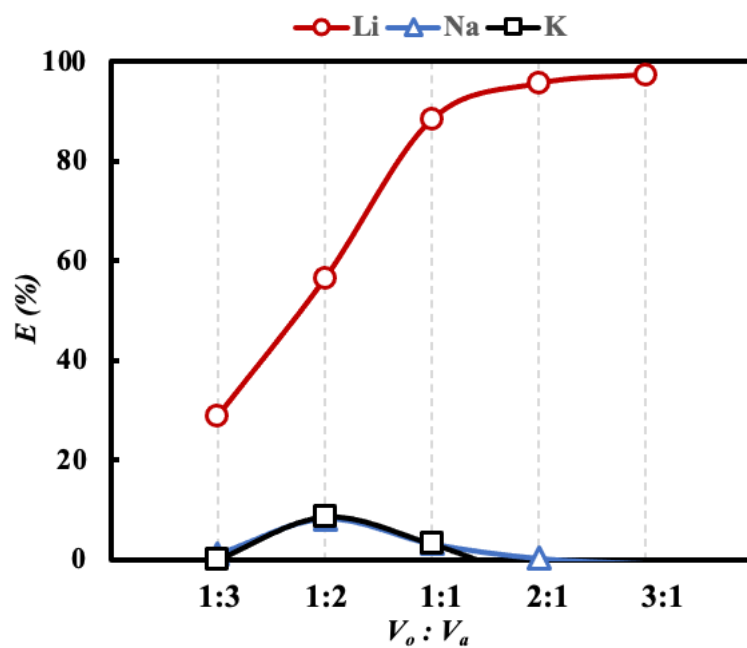


Fig. 2.12 Extraction efficiency of each metal ion at various phase ratios.

Table 2.5 Changes in ion concentration after extraction

(ppm)	Li (I)	Na (I)	K (I)
Initial	215.5	14990	13500
After Ex	25.3	14510	13330

* $V_o : V_a = 1 : 1$, pH = 10.

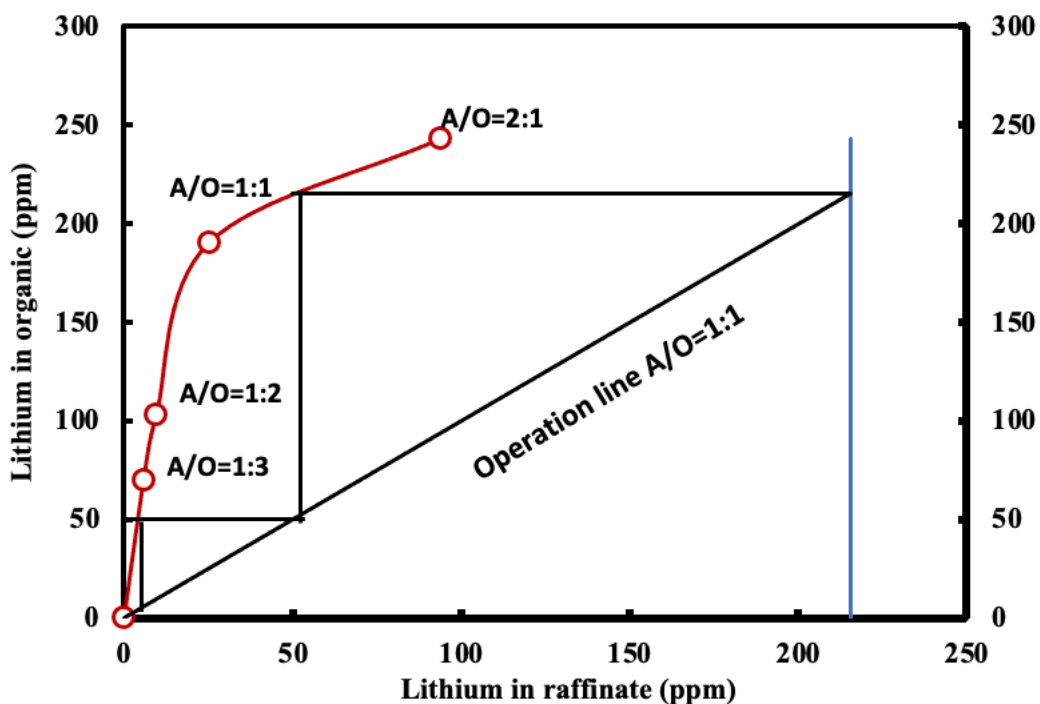


Fig. 2.13 McCabe–Thiele diagram of Li(I) extraction with [Omim][TTA].

Table 2.6 $SF_{Li/Na}$ for various FILs

Cation	Anion	$V_o:V_a$	$SF_{Li/Na}$	Ref.
[N ₄₄₄₄]	[EHEHP]	1:1	6.67 ^a	[28]
[N ₄₄₄₄]	[EHPMEH]	2:1	1.94 ^b	[2]
[N ₄₄₄₄]	[DEHP]	2:1	6 ^c	[1]
[N ₈₈₈₈]	[DEHP]	2:1	5 ^d	[1]
[Bmim] ₃	[PW ₁₂ O ₄₀]	1:1	37 ^e	[35]
[Omim]	[TTA]	1:1	227	This study

^a These data were obtained from Fig. 8 in [28].

^b These data were obtained from Fig. 6 in [2].

^{c/d} These data were obtained from Fig. 6 in [1].

^e These data were obtained from Fig. 4(b) in [35].

* FILs above were used without the addition of another extractant for collaborative extraction.

2.4 Conclusions

An environmentally friendly diketone-based ionic liquid extractant [Omim][TTA] has been synthesized. We have developed a novel extraction system by dissolving [Omim][TTA] in a different ionic liquid [Omim][NTf₂] instead of hazardous organic diluents. The newly developed FIL system shows a high extraction ability and enables the extraction of Li(I) at a lower pH condition. The extraction performance of the FIL extractant was enhanced by dissolving it in an ionic liquid diluent, because the active component TTA anion was enhanced. The extraction mechanism was examined by slope analysis and UV-vis measurement, which indicated that one molecule of FIL interacts with one Li(I) ion and forms a 1:1 complex. The extraction reaction with the FIL was found to be exothermic and spontaneous, and the degree of freedom was decreased when the extraction reaction reached equilibrium. Moreover, the FIL showed a high selectivity toward Li(I) in the presence of high concentrations of interfering ions such as Na(I) and K(I). A flow sheet was proposed for the recovery of Li(I) from a simulated salt lake solution with the FIL extractant. Using a countercurrent extraction process at a phase ratio of $V_o : V_a = 1 : 1$, the Li(I) recovery from salt lakes reached 88.2% in 2-3 stages and the extraction efficiency reached 97.3% at a phase ratio of $V_o : V_a = 3 : 1$. The $SF_{Li/Na}$ at a phase ratio ($V_o : V_a = 1 : 1$) in this study was 227, which is the highest value among the FILs previously reported which were used without the addition of another extractant for collaborative extraction. Overall, the ionic liquid extractant [Omim][TTA] shows a good prospect in the industrial operation for the recovery of Li(I) from salt lakes.

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Chapter 3. Novel Ionic Liquid-Based Aqueous Biphasic System with Amino Acids for Critical Metal Recovery from Lithium-Ion Batteries

3.1 Introduction

As the rise of the electric vehicle revolution has positioned lithium-ion batteries (LIBs) at the center of the energy industry and dramatically affected stock market movements [1-3], the amount of LIB wastes is increasing year on year. LIB disposal was estimated to be 250 000 tonnes in 2020 and is expected to increase to 464 000 tonnes by 2025 [1, 4]. As such, developing a recycling technology for spent LIBs would be beneficial from environmental and economic viewpoints. An essential step in LIB recycling is the separation of Co(II), Ni(II), and Mn(II) [5]. Use of solvent extraction is relatively mature in achieving high separation efficiency for Co(II) from Ni(II); however, the use of toxic organic reagents and excessive energy consumption have brought great harm to the environment [6], and thus this conventional hydrometallurgical technique does not comply with sustainable development goals. Therefore, development of an eco-friendly and biocompatible recycling route is required.

An aqueous biphasic system (ABS)—a self-separating two-aqueous-phase system comprising polymer/polymer, polymer/salt, or salt/salt—is considered an environmentally friendly substitute for traditional liquid–liquid extraction. The two solutes in such a system have different hydration entropies; thus, as the system separates from a homogeneous mixed solution into two aqueous phases after salting out, the two

solutes are concentrated in different phases [5, 7-11]. Table 3.1 summarizes prior studies of the separation of metal ions from batteries using ABS techniques. The phosphonium ionic liquid (IL) reported by Schaeffer et al. [5] showed a remarkable separation ratio for Co(II) and Ni(II); however, the phase separation required a high temperature for the optimum result. Moreover, Mn(II) could not simultaneously be separated because it coextracted with Co(II) to form chloro complexes; thus, additional separation steps are required, which complicates the entire recovery route. Likewise, use of a polymer-based ABS (polyethylene oxide (PEO) 1500–(NH₄)₂SO₄–H₂O) showed excellent separation of Co(II) and Ni(II) [15]; however, the addition of toxic extractants in polymer-based ABSs reduced the sustainability of this system.

Table 3.1 Summary of separations of metal ions from batteries using aqueous biphasic systems.

ABS components		Extracted metals	Reference
ILs/polymer	Salts/Acids		
[P ₄₄₄₁₄][Cl]	NiCl ₂	Mn ²⁺ , Ni ²⁺ , Co ²⁺	[5]
L35	NH ₄ SCN/NH ₄ NO ₃	La ³⁺ , Cs ⁺ , Ni ²⁺	[8]
[P ₄₄₄₁₄][Cl]	NaCl	Co ²⁺ , Ni ²⁺	[12]
L64	NH ₄ SCN	Fe ²⁺ , Ni ²⁺ , Co ²⁺	[13]
L64 (+1N2N)	Na ₂ SO ₄	Co ²⁺ , Ni ²⁺	[14]
PEO1500 (+KSCN)	(NH ₄) ₂ SO ₄	Fe ²⁺ , Ni ²⁺ , Co ²⁺	[15]
[P ₄₄₄₁₄][Cl]	CH ₃ COOH	Co, Mn, Fe, Ni, Cu, Zn, La, Cs, Y	[16]

(L35: a pluronic triblock copolymer; L64: a triblock copolymer; 1N2N: 1-nitroso 2-naphthol; PEO: polyethylene oxide)

An IL-based ABS [5, 9-12, 16-21] is a benign technology derived from the use of hydrophilic ILs. Hydrophilic ILs are generally less toxic than hydrophobic ILs [19] and thus are environmentally preferred. Moreover, the relatively low viscosity of hydrophilic IL solutions might significantly improve extraction kinetics [19]. Hydrophilic quaternary phosphonium or ammonium ILs and an organic acid are common constituents of IL-based ABSs [16]. Schaeffer et al. [22] demonstrated that the cationic structure of ILs governed their ability to form ABSs. The four butyl chains in quaternary phosphonium or ammonium ILs effectively shield the cationic charge from the solvent to generate a more neutral surface charge, thereby facilitating phase separation. In addition, the ecotoxicity of quaternary ammonium $[N_{4444}]^+$ is considered to be lower than that of the quaternary phosphonium $[P_{4444}]^+$ ion [23]. Therefore, quaternary ammonium ILs were applied in this work. In addition to using biodegradable hydrophilic ILs, we also used biocompatible amino acids in the present study. Baba et al. [24] previously proposed that an extractant with amino acid moieties could efficiently separate Ni(II) and Co(II) from Mn(II).

Herein, we present a study on the fully aqueous separation of Co(II), Ni(II), and Mn(II) from a model LIB leachate solution, with the ABS consisting of biocompatible components, i.e., hydrophilic ILs, amino acids, organic acids, and salts. Co(II) and Ni(II) are separately recovered, and Mn(II) can be separated in a straightforward way. A schematic of the process is presented in Fig. 3.1. Sulfate medium was selected as the model for the LIB leachate solution because H_2SO_4 is industrially relatively easier to handle compared with the other two primary inorganic acids, i.e., HCl and HNO_3 [25]:

HCl causes equipment corrosion and chlorine pollution and HNO₃ releases nitrogen oxides (NO_x) into the atmosphere. To the best of our knowledge, this study reports the first application of amino acids to an IL-based ABS for separation of Co(II), Ni(II), and Mn(II).

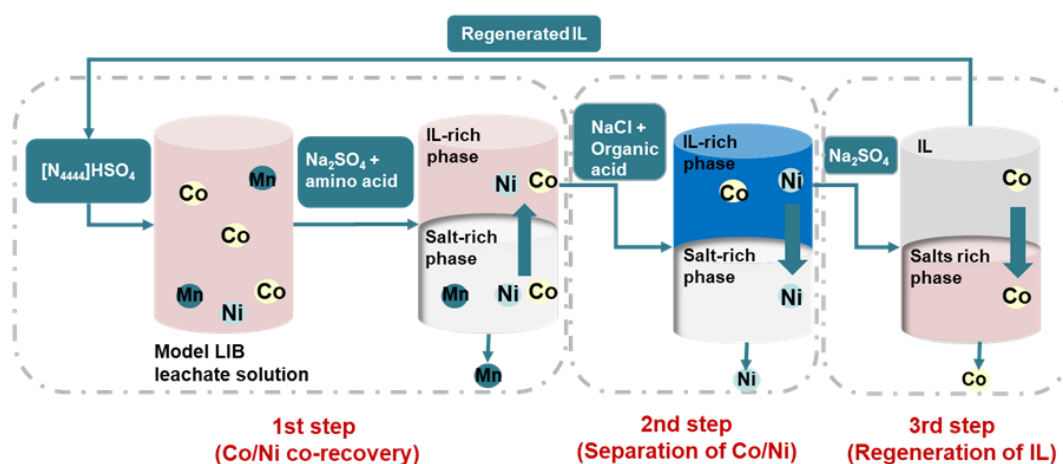


Fig. 3.1 Schematic illustration of process for aqueous separation of Co(II), Ni(II), and Mn(II) from a model lithium-ion battery leachate solution

3.2 Experimental

3.2.1 Materials

The tetrabutylammonium ILs (tetrabutylammonium bisulfate ([N₄₄₄₄]HSO₄), tetrabutylammonium acetate ([N₄₄₄₄]CH₃COO), and monobasic tetrabutylammonium phosphate ([N₄₄₄₄]H₂PO₄)) were purchased from Sigma-Aldrich Co. Tetrabutylammonium bromide ([N₄₄₄₄]Br) and tetrabutylammonium nitrate ([N₄₄₄₄]NO₃) were supplied by Fujifilm Wako Chemical Ltd. The amino acids, i.e., glycine (Gly), phenylalanine (Phe), serine (Ser), glutamine (Gln), and glutamic acid (Glu), were purchased from Kishida Chemical Co., Ltd. Sodium salts (NaCl,

NaH₂PO₄, Na₂HPO₄, Na₂SO₄) were supplied by Kishida Chemical Co., Ltd. Cobalt, nickel, and manganese sulfates were supplied by Fujifilm Wako Chemical Ltd. Acetic acid (AcOH), citric acid (CA), and sodium hydroxide (NaOH) were purchased from Kishida Co., Ltd. *p*-Toluenesulfonic acid (PSTA) was supplied by Tokyo Chemical Industry Co., Ltd. Methanesulfonic acid (MSA) was purchased from Sigma-Aldrich Co. Deionized water (Milli-Q, Merck Millipore) was used in this work.

3.2.2 Methods

To determine the phase diagram of the ABS used in this work, the binodal curves were determined by a previously reported turbidimetric titration method [21, 26]. The binodal curve of the [N₄₄₄₄]HSO₄–Na₂SO₄–H₂O ternary system was measured at 25 °C under agitation. An IL stock solution of [N₄₄₄₄]HSO₄ (70 mass%) and saturated salt stock solution (Na₂SO₄) were prepared. In accordance with the amount of titrant added until turbidity was observed, indicating formation of an ABS, the system composition for each point on the binodal curve was calculated by analytical mass balance.

In the first step (extraction of Co and Ni), a specific concentration (50 mass%) of IL stock solution and different salt solutions close to saturation were mixed in a particular proportion to detect the formation of a two-phase system. Detail of the experimental conditions is shown in Table 3.2. After selecting the system composition, as demonstrated in Table 3.3, different amino acids (0.1 M) were added to study their effect on the extraction efficiencies of Co(II) and Ni(II). The structures of the amino acids are shown in Fig. 3.2. Different NaOH concentrations (1–8 M) with the same

volume were used to adjust the basicity of the system. The experiments were carried out at room temperature (25 °C) and the reaction equilibrium time was 5 min.

Taking Co(II) as the model, the reaction mechanism between the amino acid and the metal ions was investigated. The salt stock solution contained 15 mM Co(II), 20 mass% Na₂SO₄, and different concentrations of Phe (10, 25, 50, 75, 100 mM). An ABS formed using a combination of the salt stock solution, 50 mass% [N₄₄₄₄]HSO₄ IL stock solution, and 8 M NaOH stock solution in a volume ratio of 4:5:1.

In the second step (separation of Co and Ni), several types and volumes of organic acids (20, 30, 40, 50 µL) and NaCl were added to the IL-rich phase (200 µL) obtained from the first step. A new ABS ([N₄₄₄₄]HSO₄–NaCl–acid–H₂O) subsequently formed to selectively separate Co(II) and Ni(II), in which Ni(II) was transferred from the IL-rich to the salt-rich phase.

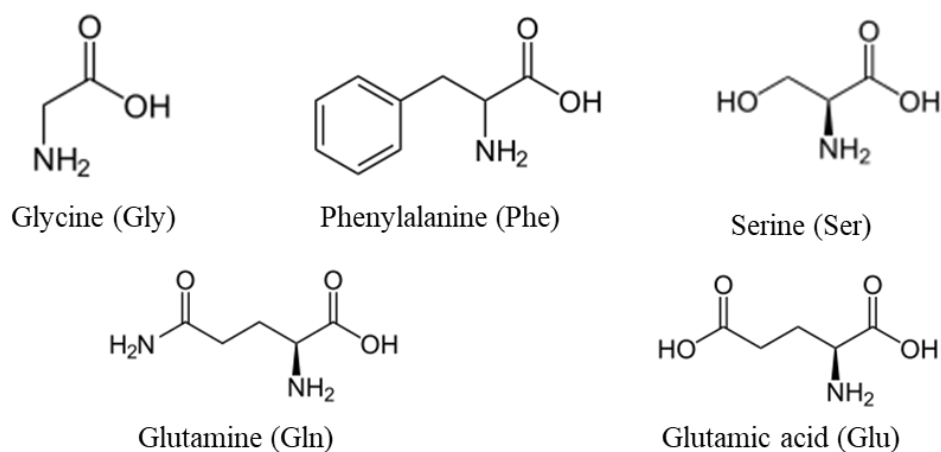
For regeneration of the [N₄₄₄₄]HSO₄ IL, Co(II) was recovered from the IL-rich phase and the IL was regenerated by adding Na₂SO₄ (24 mass%) solution to the IL-rich phase obtained in the second step, which induced a new phase separation. Three experimental cycles were carried out using the regenerated IL to explore the reusability of the IL.

Table 3.2 Experimental conditions of the ABS formation.

Experimental conditions	
IL-stock solution (70w wt%)	[N ₄₄₄₄]Br, [N ₄₄₄₄]HSO ₄ , [N ₄₄₄₄]CH ₃ COO, [N ₄₄₄₄]NO ₃ , [N ₄₄₄₄]H ₂ PO ₄
Salt-stock solution (Saturated)	NaCl, NaH ₂ PO ₄ , Na ₂ HPO ₄ , Na ₂ SO ₄
V _{ILs} :V _{salts} =1:1, 25°C, react 5 min	

Table 3.3 Experimental conditions of the first step

Experimental conditions	
Salt-stock solution	1000 mg/L CoSO ₄ /MnSO ₄ /NiSO ₄ ; 20 wt% Na ₂ SO ₄ ; 0.1M amino acid (Gly, Phe, Ser, Gln, Glu)
IL-stock solution	50 wt% [N ₄₄₄₄]HSO ₄
NaOH-stock solution	1~8 M
Volume ratio ($V_{\text{salt}} : V_{\text{IL}} : V_{\text{NaOH}} = 4:5:1$)	

**Fig. 3.2** Structures of the amino acids.

3.2.3 Evaluation

Determination of metal concentrations in each phase after achieving reaction equilibrium was conducted using an inductively coupled plasma optical emission spectrometer (Optima 8300, PerkinElmer). For each sub-step, the extraction efficiency (E , %), stripping efficiency (S , %), distribution ratio (D), purity (P , %), and separation factor (SF) of the metal ions were calculated using Eqs. (3.1), (3.2), (3.3), (3.4), and (3.5), respectively. For the entire process, the recovery efficiency (R , %) of each ion is represented by Eq. (3.6).

$$\%E = n_M^{TP}/n_M^T \times 100 \quad \text{Eq. (3.1)}$$

$$\%S = n_M^{BP}/n_M^T \times 100 \quad \text{Eq. (3.2)}$$

$$D_M = [M]_{TP}/[M]_{BP} \quad \text{Eq. (3.3)}$$

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

$$\%P_M = [M]_{BP}/([M]_{BP} + [N]_{BP}) \times 100 \quad \text{Eq. (3.4)}$$

$$SF_{M/N} = D_M/D_N \quad \text{Eq. (3.5)}$$

$$\%R = n_M^e/n_M^{ini} \times 100 \quad \text{Eq. (3.6)}$$

where n_M^{TP} is the moles of metal M in the top or IL-rich phase, n_M^{BP} is the moles of metal M in the bottom or salt-rich phase, n_M^T is the total of moles of metal M; $[M]_{TP}$ (mg/L) is the equilibrium concentration of metal M in the top phase, $[M]_{BP}$ (mg/L) is the equilibrium concentration of metal M in the bottom phase; D_M is the distribution ratio of metal M and D_N is the distribution ratio of metal ions (N) other than M in the aqueous phase; n_M^{ini} and n_M^e indicate the initial and finally recovered moles of metal M, respectively.

The metal complex species formed in the second step were investigated by measuring ultraviolet–visible (UV–vis) spectra of the IL-rich phase after Ni(II) stripping to the salt-rich phase using a UV–vis spectrometer (JASCO V-670) at 25 °C with 1 nm spectral resolution. Fourier transform infrared (FT-IR) spectra of the stock and regenerated IL were performed using an FT-IR spectrometer (Spectrum Two, PerkinElmer).

3.3 Results and Discussion

3.3.1 Investigation of ABS compositions

Experiments were undertaken to investigate the ability of various hydrophilic tetrabutylammonium ILs ([N₄₄₄₄]Br, [N₄₄₄₄]HSO₄, [N₄₄₄₄]CH₃COO, [N₄₄₄₄]NO₃, and [N₄₄₄₄]H₂PO₄) and several sodium salts (NaCl, NaH₂PO₄, Na₂HPO₄, Na₂SO₄) to form a two-phase system at room temperature. The results of the ABS formation are shown in Table 3.4. The [N₄₄₄₄]Br, [N₄₄₄₄]HSO₄, and [N₄₄₄₄]NO₃ ILs could form two-phase systems with most sodium salts. The choice of salt type seemed to follow the principle of the Hofmeister series: the possibility of inducing phase separation for the salt series with a common cation followed the order $SO_4^{2-} > HPO_4^{2-} > C_2H_3O_2^- > Cl^- > Br^- > NO_3^-$ [27, 28]. The molar entropy of hydration of strong water-coordinating ions is the primary driving force for ABS formation. Early members of the above series incline toward hydration complex formation, which increases the solvent surface tension and induces dehydration of the solutes [27]. Na₂SO₄ was therefore selected as the salting-out agent for this system. [N₄₄₄₄]HSO₄ was selected as the IL to minimize the impact of ion exchange between the salt and the IL. Based on the results, the [N₄₄₄₄]HSO₄–Na₂SO₄–H₂O system was chosen as the ABS composition.

The aqueous phase diagram of the [N₄₄₄₄]HSO₄–Na₂SO₄–H₂O system is presented in Fig. 3.3. This shows the influence of salt concentration on the formation of two phases: in the low-salt concentration area, the system comprises a homogeneous monophasic; in the high-salt concentration area, there is a large area representing the immiscible

biphasic zone. The salt concentration should be greater than 10 mass% when the IL concentration is 25 mass%. As the salt concentration increases, salt ions compete with the solute to combine with water molecules, thereby destroying the solute's hydration layer, reducing its solubility, and forming two phases [27].

Table 3.4 The results of the ABS formation using various components

ILs \ Salts	NaCl	NaH ₂ PO ₄	Na ₂ HPO ₄	Na ₂ SO ₄
[N ₄₄₄₄]Br	✗	✓	✓	✓
[N ₄₄₄₄]HSO ₄	✓	✓	✓	✓
[N ₄₄₄₄]CH ₃ COO	✗	✓	✗	✗
[N ₄₄₄₄]NO ₃	✓	✓	✓	✓
[N ₄₄₄₄]H ₂ PO ₄	✗	✓	✗	✗

(✓: ABS formation; ✗: ABS cannot be formed.)

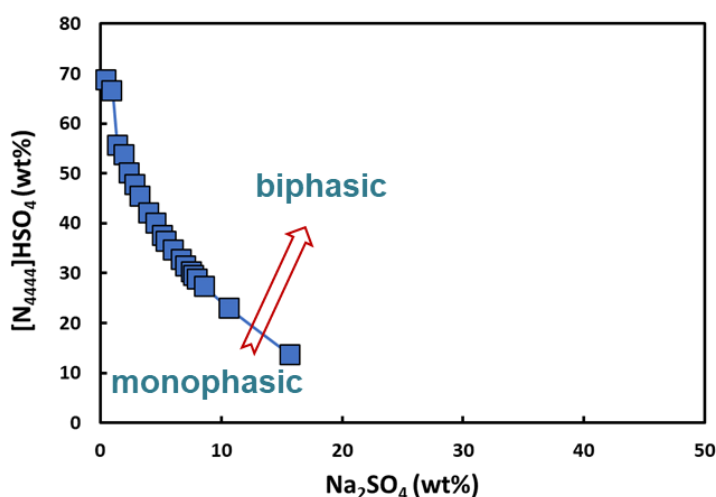


Fig. 3.3 Phase diagram of the [N₄₄₄₄]HSO₄–Na₂SO₄–H₂O system

(IL stock solution: [N₄₄₄₄]HSO₄ (70 mass%); Titrant: saturated Na₂SO₄ solution; 25 °C under agitation)

3.3.2 First step: Co/Ni recovery

Amino acids have good prospects in industrial applications because of their high biocompatibility, low price, and excellent availability [29]. The high selectivity of amino acids for Co(II) and Ni(II) over Mn(II) might be attributed to the presence of the amino group ($-NH-$). Co(II) and Ni(II) are softer acids than Mn(II), and thus have higher affinity toward the nitrogen atom according to the hard and soft acids and bases (HSAB) theory [30, 31]. The presence and type of amino acid are particularly significant for the recovery of metal ions. As shown in Fig. 3.4, no metal ions were extracted into the IL-rich phase without amino acids in the system. Of the five amino acids investigated in this study, Phe showed the highest distribution ratio (D) for Co(II) and Ni(II) over Mn(II). Phe is more hydrophobic than the other amino acids (Gly, Ser, Glu, and Gln), which facilitates dehydration of their metal complexes, thereby enhancing the distribution of their metal complexes into the less polar phase: addition of Phe maximized the extraction efficiencies of Co(II) and Ni(II).

The extractions of Co(II) and Ni(II) in the presence of Phe were strongly influenced by the pH of the system. As shown in Fig. 3.4(c), the distribution ratios of Co(II) and Ni(II) were dependent on the concentration of NaOH added to the ABS. As the NaOH content in the system exceeded 0.7 M, extraction of Co(II) and Ni(II) occurred. The distribution ratios of Co(II) and Ni(II) reached their maxima when the concentration of NaOH increased to 0.8 M (an approximate pH of 8.7 of the aqueous system); however, these metal ions precipitated when the concentration of NaOH was further increased. Similar distribution ratios for Co(II) and Ni(II) indicated that they were co-extracted

into the IL-rich phase. The extraction efficiencies (%*E*) were 98.4% and 98.7%, respectively. Mn(II) was solely concentrated in the salt-rich phase and could easily be recovered.

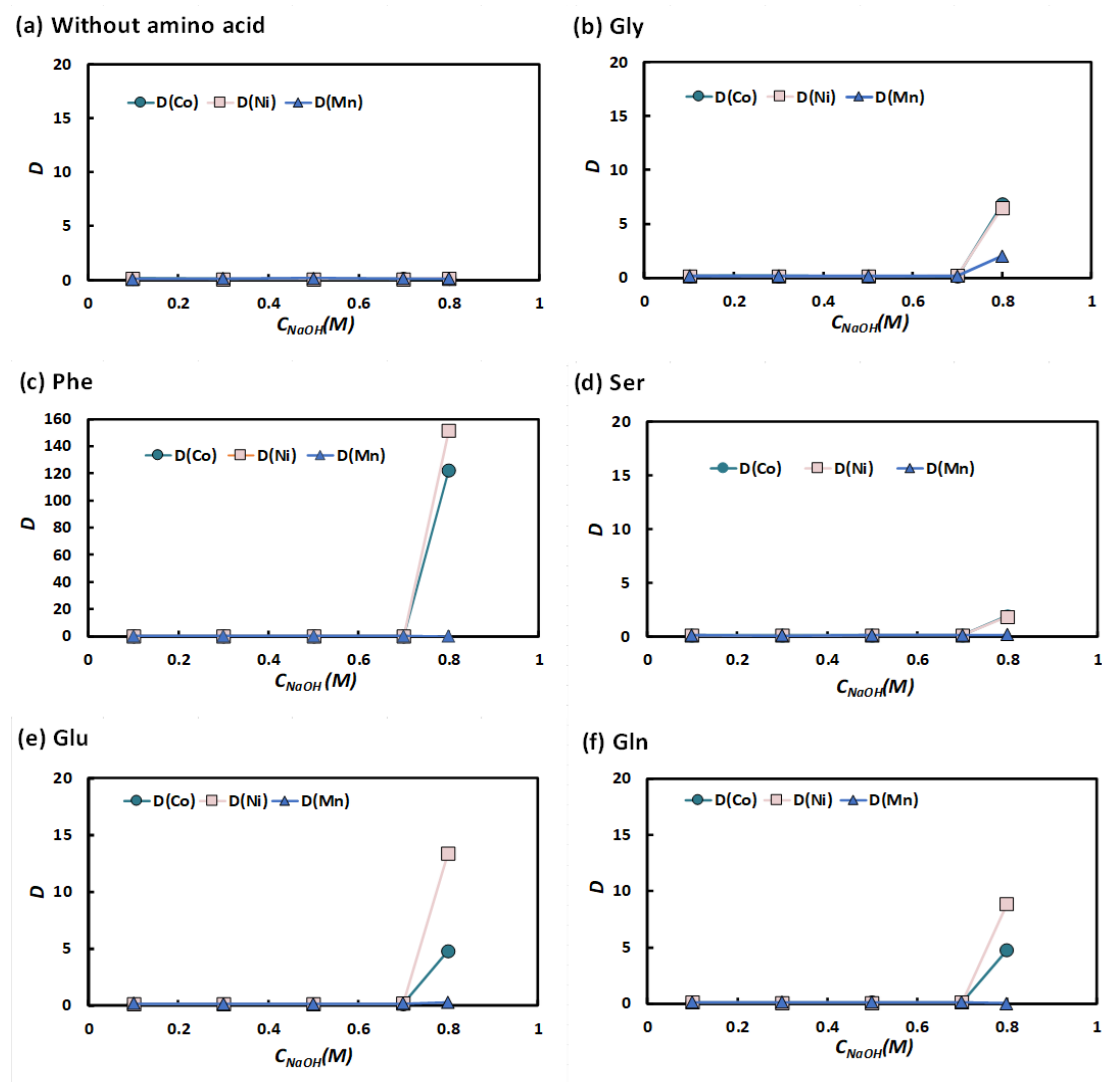
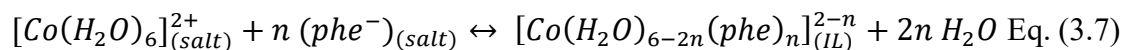


Fig. 3.4 Variation of distribution ratios (*D*) of metal ions with NaOH concentration in the presence of different amino acids in the first step

(Salt-stock solution: 1000 mg/L CoSO₄/MnSO₄/NiSO₄; 20 mass% Na₂SO₄; addition of 0.1 M of different amino acids: Gly (b), Phe (c), Ser (d), Glu (e), Gln (f), or without amino acid (a). IL stock solution: 50 mass% [N₄₄₄₄]HSO₄. NaOH stock solution: 1, 3, 5, 7, 8 M. Volume ratio ($V_{salt}:V_{IL}:V_{NaOH}$ = 4:5:1). Reaction for 5 min at 25 °C)

As amphoteric substances, amino acids exist as anions, cations, or neutral molecules, depending on their isoelectric points and the solution pH [32]. The isoelectric point of Phe is 6.0 and the solution pH was approximately 9.0 after extraction; thus, the Phe species would be negatively charged. Using this assumption, the reaction mechanism between the amino acid and metal ions could be deduced using a slope-analysis method. Taking Co(II) as the model, the extraction reaction equation could be presented by Eq. (3.7) based on a previous study [33]. Co(II) generally exists in the form of hexahydrate compounds in aqueous solutions because of the nature of its electron configuration. Phe contains two ligands, i.e., the nitrogen in the amino group and the oxygen in the carboxylic acid group, and thus one mole of the amino acid would replace two moles of water in the compound $[Co(H_2O)_6]^{2+}$:



Using Eq. (3.8), a fitted line with a slope of approximately 3 was obtained (see Fig. 3.5). To investigate if most amino acid molecules had been transferred into the IL-rich phase when the reaction reached equilibrium, UV-vis measurements of the salt-rich phase after Co(II) extraction into the IL-rich phase were performed. The characteristic UV-vis absorption of Phe could be clearly observed at approximately 257 nm using a 10-times dilution of the stock solution (Fig. 3.6(a)). The spectrum of the stock solution differed completely from those acquired from the salt-rich phase solution at reaction equilibrium. As shown in Fig. 3.6(b), an almost flat UV-vis spectrum was observed, indicating that most Phe was transferred into the IL-rich phase. Therefore, the reaction

mechanism between Phe and Co(II) could be expressed as shown in Eq. (3.9). The $[Co(phe)_3]^-$ complex might be transferred from the salt-rich to the IL-rich phase because of electrostatic interaction with the IL cations.

$$\log(D_{Co}) = \log K + n \log[phe^-] \quad \text{Eq. (3.8)}$$

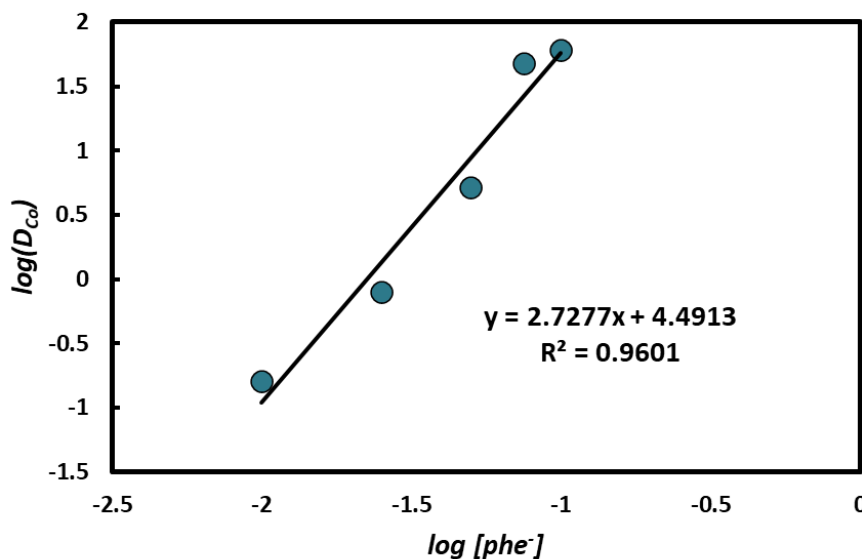
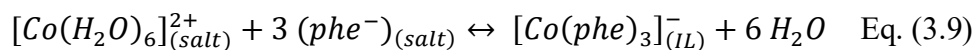


Fig. 3.5 Plot of $\log(D_{Co})$ as a function of $\log [Phe^-]$

(Salt stock solution: 15 mM $CoSO_4$; 20 mass% Na_2SO_4 ; addition of different concentrations of Phe:

10, 25, 50, 75, 100 mM. IL stock solution: 50 mass% $[N_{4444}]HSO_4$. NaOH stock solution: 8 M.

Volume ratio ($V_{salt}:V_{IL}:V_{NaOH} = 4:5:1$). Reaction for 5 min at 25 °C)

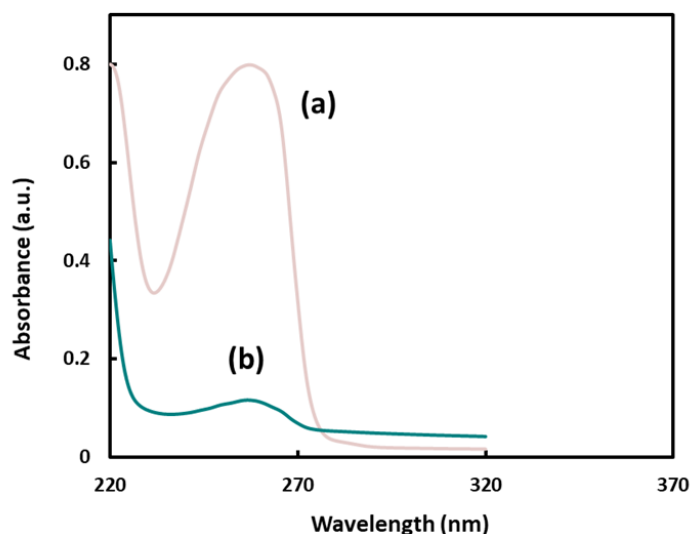


Fig. 3.6 UV–visible spectra of (a) 10-times diluted Phe stock solution and (b) 4-times diluted salt-rich phase from first step after reaction reached equilibrium

3.3.3 Second step: Co/Ni separation

In the second step, NaCl salt and different organic acids were added to the IL-rich phase obtained from the first step. As a result, a new ABS ($[N_{4444}]\text{HSO}_4\text{--NaCl--acid--H}_2\text{O}$) was formed, which could selectively separate Co(II) and Ni(II) by transferring Ni(II) to the salt-rich phase while Co(II) stayed in the IL-rich phase. The separation factor of Co over Ni ($SF_{\text{Co/Ni}}$) was approximately 1.0 and the stripping efficiency was 2% when the system did not contain an organic acid (Fig. 3.7), indicating that the presence of the acid was essential. Four types of organic acids, i.e., PTSA, CA, AcOH, and MSA, were employed in the system.

As shown in Fig. 3.7, Ni(II) could be stripped to the salt-rich phase by addition of an organic acid, with the value of D being highly influenced by the acid type. The deprotonation constants ($\text{p}K_{\text{a}}$) of the tested acids rank as follows: PTSA (-2.8) < MSA

(-0.6) < CA (3.09) < AcOH (4.75). The distribution ratio of Ni(II) was lowest (negative value) when CA was added. This might be attributed to the fact that CA has good chelating ability toward metal ions [34]. In general, the distribution ratio of Ni(II) increased with increasing value of the pK_a . In contrast, Co(II) mainly stayed in the IL-rich phase, with the highest D value obtained when MSA was added to the system. MSA is considered to be a ‘green’ acid owing to its low toxicity and high biodegradability [35, 36], which is compatible with the aims of the present study. Considering these results, MSA was selected for the system ($[N_{4444}]\text{HSO}_4\text{--NaCl--MSA--H}_2\text{O}$). With an increase in the MSA concentration, the stripping efficiencies of both Co(II) and Ni(II) also increased, as shown in Fig. 3.8. Optimum separation of Co(II) and Ni(II) was reached when the volume ratio of the IL-rich phase obtained from the first step and the MSA solution ($V_{\text{IL}}:V_{\text{MSA}}$) was 10:1. Under this condition, purities of Co (84.23%) in the IL-rich phase and Ni (85.85%) in the salt-rich phase were obtained.

A possible reaction mechanism was investigated by measuring the UV–vis spectra of the IL-rich phase after Ni(II) was stripped into the salt-rich phase. As shown in Fig. 3.9, three peaks were observed, at 631 nm, 666 nm, and 690 nm, which were attributed to the $[\text{CoCl}_4]^{2-}$ complex species [5]. Thus, the reaction mechanism could be described as shown in Eq. (3.10). The blue color of the $[\text{CoCl}_4]^{2-}$ complex [37, 38] was also identified by physical observation. In addition, it could be pointed out that the reason that stripping efficiency of Ni(II) increased with an increase in the acid concentration is that an increase in H^+ concentration causes the reaction equilibrium to shift to the right, as expressed by Eq. (3.11):

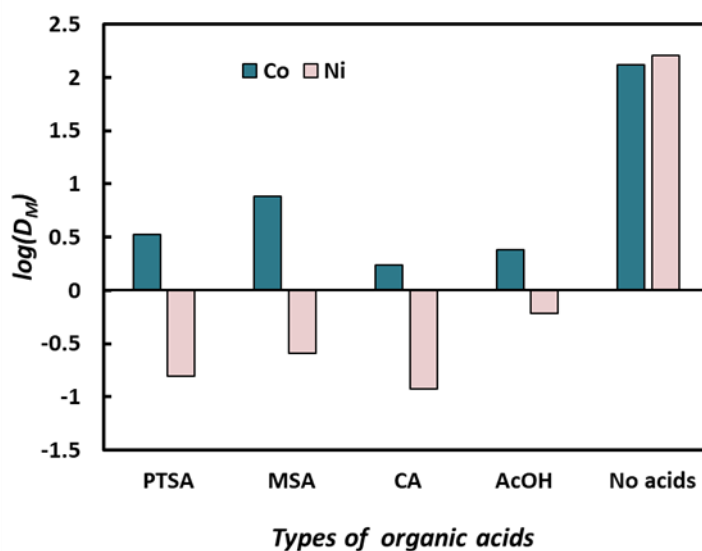
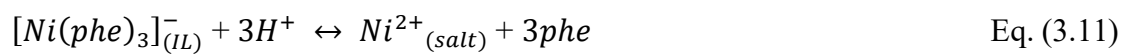
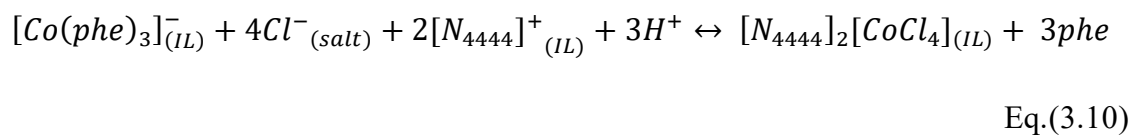


Fig. 3.7 Variation of distribution ratios (*D*) of metal ions with type of organic acid in the second step

(The 200 μ L IL-rich phase obtained from the first step was mixed with 20 μ L organic acid and 20 mass% salt (NaCl). The organic acids were PTSA, MSA, CA, and AcOH.)

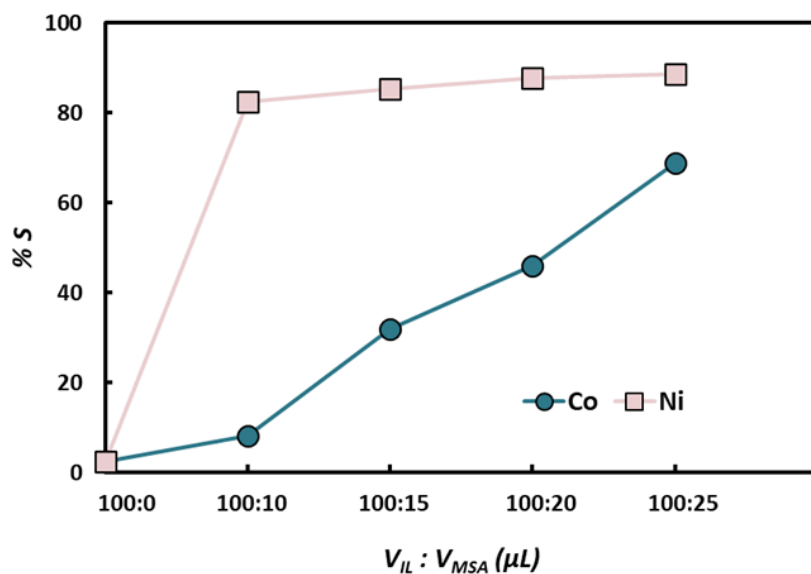


Fig. 3.8 Variation of stripping efficiency of metal ions with volume ratio of IL-rich phase obtained from the first step and MSA

(The 200 μL IL-rich phase obtained from the first step was mixed with MSA in different volumes (0, 20, 30, 40, 50 μL) and 20 mass% salt (NaCl).)

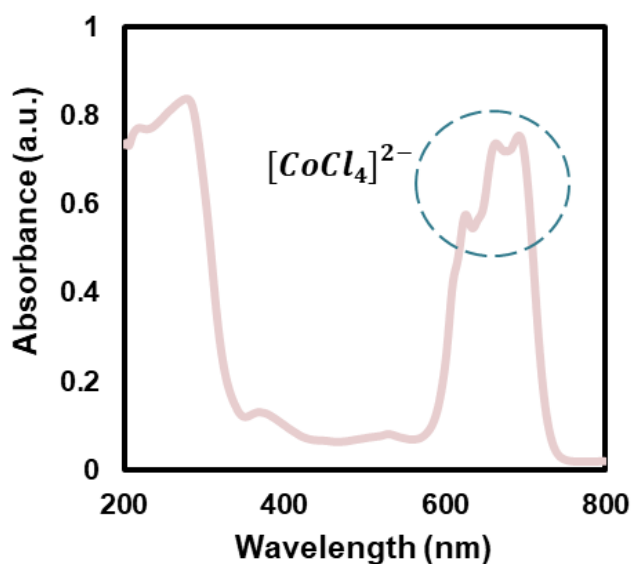
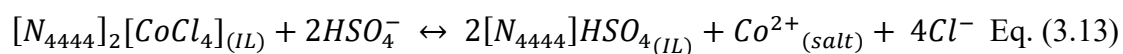


Fig. 3.9 UV-visible spectra of IL-rich phase in $[N_{4444}]\text{HSO}_4\text{-NaCl-acid-H}_2\text{O}$ system after Ni(II) stripping to salt-rich phase

3.3.4 Regeneration of ionic liquid

Co(II) was recovered from the IL-rich phase and the IL could be regenerated in a single step by adding Na₂SO₄ (24 mass%) to induce a new phase separation. As the concentration of SO_4^{2-} increases, the equilibrium (see Eq. (3.12)) shifts to the right, thereby increasing the concentration of HSO_4^- . At the same time, the volume of the system increased because of addition of the Na₂SO₄ solution, resulting in a decrease in the concentration of chloride ions. The $[CoCl_4]^{2-}$ complex consequently dissociated and the Co(II) species were transferred to the salt-rich phase. Finally, the [N₄₄₄₄]HSO₄ IL could be regenerated, as shown in Eq. (3.13). Figure 3.10 shows the FT-IR spectra of the stock and regenerated IL. The spectra are quite similar, indicating successful regeneration of the [N₄₄₄₄]HSO₄ IL. Asymmetrical C–N stretching and C–H stretching vibrations of the –CH₂ and –CH₃ groups are observed at 1021 cm^{–1} and at 2955–2872 cm^{–1}, respectively [39].



Three cycles of experiments were sequentially carried out using the regenerated IL. The recovery efficiencies of Co(II), Ni(II), and Mn(II) were monitored in each cycle. As shown in Fig. 3.11, there was no significant change in the recovery efficiencies of these metal ions within the three cycles, thereby demonstrating that the IL could be reused multiple times.

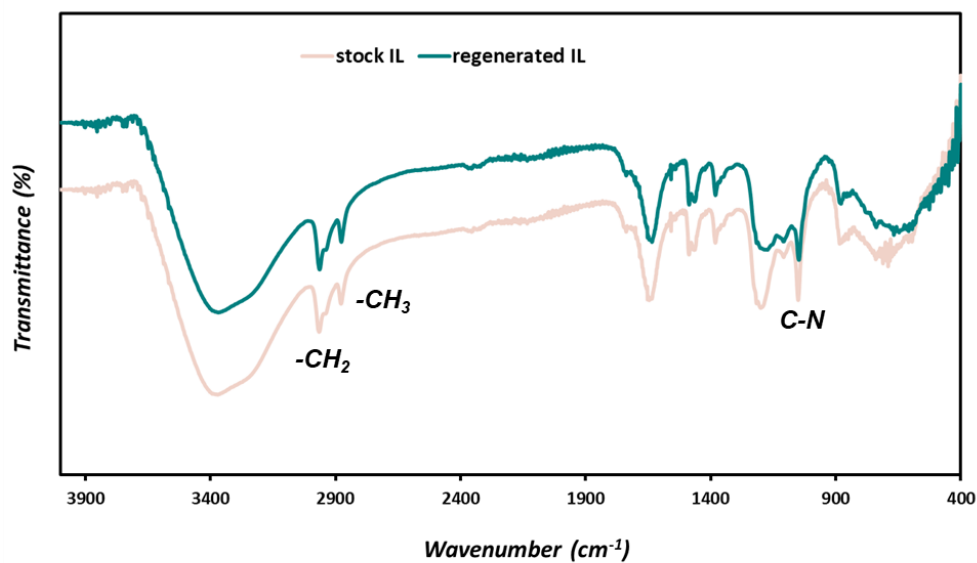


Fig. 3.10 Fourier transform infrared spectra of stock IL and regenerated IL

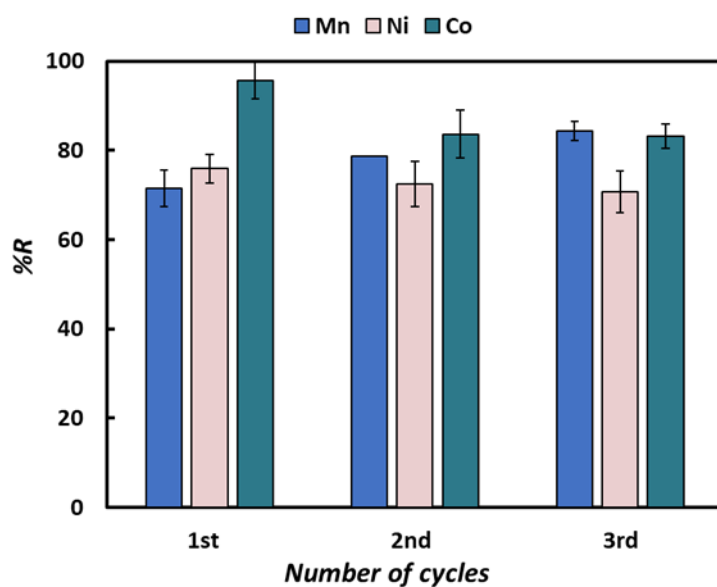


Fig. 3.11 Recovery efficiencies of metal ions in three sequential cycles

(Each cycle consists of the following three steps:

1st step: Salt-stock solution: 1000 mg/L CoSO₄/MnSO₄/NiSO₄; 20 mass% Na₂SO₄; addition of 0.1

M Phe. IL stock solution: 50 mass% [N₄₄₄₄]HSO₄ (1st cycle); the regenerated IL obtained from last

cycle (2nd cycle and 3rd cycle). NaOH stock solution: 8 M. Volume ratio ($V_{\text{salt}}:V_{\text{IL}}:V_{\text{NaOH}} = 4:5:1$).

Reaction for 5 min at 25 °C.

2nd step: The IL-rich phase obtained from the first step was mixed with MSA in a volume ratio of 10:1 and 20 mass% salt (NaCl). Reaction for 5 min at 25 °C.

3rd step: The Na₂SO₄ (24 mass%) solution was added to the IL-rich phase obtained from the second step in a volume ratio of 3:4. Reaction for 5 min at 25 °C.)

3.4 Conclusions

This study demonstrated the selective recovery of Co(II), Ni(II), and Mn(II) from a spent LIB model solution using novel ABSs comprising biocompatible components. In the first step, an ABS of [N₄₄₄₄]HSO₄, Na₂SO₄, and H₂O mixed with Phe successfully transferred Co(II) and Ni(II) to the IL-rich phase while Mn(II) stayed in the salt-rich phase. In the second step, the IL-rich phase was mixed with MSA and NaCl to form a new ABS ([N₄₄₄₄]HSO₄–NaCl–MSA–H₂O), which enabled effective separation of Co(II) and Ni(II): Ni(II) was stripped to the salt-rich phase and Co(II) was enriched in the IL-rich phase as $[CoCl_4]^{2-}$. Finally, Co(II) was stripped from the IL-rich phase by adding Na₂SO₄ and simultaneously regenerating the ([N₄₄₄₄]HSO₄) IL. A reusability test showed that the performance of the regenerated IL was relatively stable over a three-cycle experiment. An eco-friendly ABS with remarkable metal separation performance was developed in the present study without using any hazardous reagents or toxic organic solvents. The insights might further be explored to recover critical metals from an actual LIB waste.

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Chapter 4. Integrated Leaching and Selective Recovery of Cobalt Using an Amino Acid-Based Aqueous Biphasic System from Spent Li-ion batteries

4.1 Introduction

In the past two centuries, behind the prosperity of the world economy, it is the predatory consumption of natural resources, resulting in the risk of energy depletion [1]. The emission of greenhouse gases in the process of mineral resource mining industry and the exponential growth of urban wastes has 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]. 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 imminent. Lithium-ion batteries (LIBs), due to their high energy density, are the most important power source for these electronics including electric vehicles (EVs), energy storage devices and various electrical appliances [4]. In addition, the EVs industry has presented a booming scene in the context of governments of all countries pursuing new energy sources to achieve “carbon neutrality” goals [5, 6]. However, LIBs in EVs have a lifespan of only 5-10 years [7], and the generous LIBs will be scrapped in the near future. 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

valuable metals in the spent LIBs include lithium (Li), cobalt (Co), manganese (Mn), nickel (Ni), copper (Cu), aluminum (Al), and iron (Fe) [9]. Co has received more attention due to its high price among them. The price of a pound of Co is about \$25, 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 approximately 15.6%-30.4% [11-13]. Therefore, the recovery of Co from spent LIBs becomes more 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 of researches have focused on recycling the cathode materials. The recovery methods are generally divided into hydrometallurgy, pyrometallurgy and electrochemical treatment [14]. Hydrometallurgy [15] has recently received extensive attention due to its advantages of the low energy consumption, the mature technology, the high recovery rate, the high purity of recovered metals, and the selective extraction of valuable metals. However, there are also disadvantages such as extensive use of toxic organic solvent and high concentration of acids, and complicated recovery steps.

The aqueous biphasic system (ABS) [16] technology is considered to be an environmentally friendly substitute for traditional hydrometallurgy, which is a fully aqueous system. Two solutes in the system with different entropy of hydration are concentrated in two different phases after salting out [17]. Recently, many studies on the separation of valuable metals using the ionic liquid (IL)-based ABS [18] were reported. Coutinho and co-workers [19] showed a remarkable separation ratio for Co(II) and Ni(II) using the IL-based ABS composed of tributyltetradecylphosphonium

chloride ($[P_{44414}]Cl$) and $NiCl_2$ for a spent-battery recovery. The conventional hydrometallurgy for spent LIBs recycling is divided into the pretreatment, leaching of active materials including the anode and the cathode materials, and metal separation and recovery [15]. These complex processes often lead to increased production costs. This study devoted to optimizing the process route and integrating leaching and ion recovery. The first application of integrated leaching and separation of metals using the IL-based ABS consisting of IL ($[P_{44414}]Cl$) and organic acid (CH_3COOH) was proposed by Coutinho group [20] in 2020.

This study proposed a special biocompatible ABS, that is amino acids-based ABS [21, 22]. 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 due to its zwitterionic identity. In addition, the amino acids have good prospects in industrial applications because of their high biocompatibility, low price, and excellent availability [23].

In this thesis, we report for the first time the leaching by an amino acid alone for the LIB cathode material that is lithium manganese cobalt nickel oxides ($LiMn_xCo_yNi_zO_2$). The effects of amino acid types, temperature, extraction time, and solid-liquid ratio on leaching was discussed. In addition, we investigated the leaching mechanism using the typical cathode active material lithium cobalt oxide ($LiCoO_2$). Ultraviolet–visible (UV–vis) spectra and Fourier transform infrared (FT-IR) spectra were measured to verify the leaching mechanism. Then the polypropylene glycol 400 (PPG400) was added to the leaching solution to form the biphasic system. By adding different thiocyanates, the

selective separation of Co was verified. We integrated the leaching and the selective recovery of Co using this amino acids-based ABS in this thesis. A schematic illustration of the process is presented in Fig. 4.1.

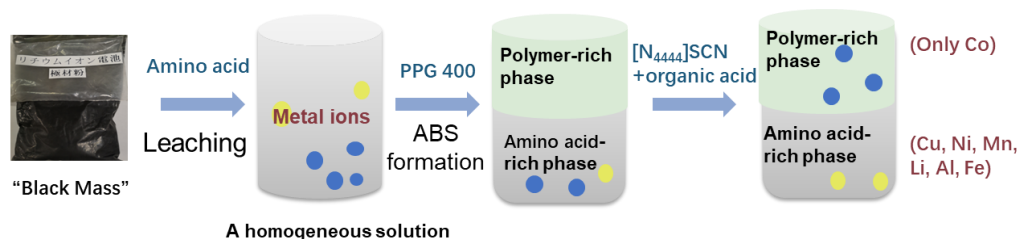


Fig. 4.1 Schematic illustration of process for integrated leaching and selective recovery of Co from an actual lithium-ion battery cathode material

4.2 Experimental

4.2.1 Materials

The powder of spent LIB cathode materials was supplied by Matsuda Sangyo Co., Ltd. The LiCoO_2 and the tetrabutylammonium thiocyanate ($[\text{N}_{4444}]\text{SCN}$) were purchased from Sigma-Aldrich Co. Potassium thiocyanate (KSCN) and the polymer PPG400 were supplied by Kishida Chemical Co., Ltd. Amino acids, i.e., glycine (Gly), proline (Pro), serine (Ser), asparagine (Asn), histidine (His), cysteine (Cys), and glutamic acid (Glu), were purchased from Kishida Chemical Co., Ltd. Ascorbic acid (Ascor) and tartaric acid (TA) were supplied by Fujifilm Wako Chemical Ltd. Acetic acid (AcOH) and formic acid (HCOOH) were purchased from Kishida Co., Ltd. *p*-Toluenesulfonic acid (PSTA) was supplied by Tokyo Chemical Industry Co., Ltd. Methanesulfonic acid (MSA) was purchased from Sigma-Aldrich Co. Deionized water

(Milli-Q, Merck Millipore) was used in this work.

4.2.2 Methods

To determine the formation of a two-phase system used in this work, different specific concentration (0.2 M) of amino acid stock solutions and a PPG400 solution were mixed by a previously reported turbidimetric titration method [24].

In the first step (leaching of LIB cathode material), leaching experiments were conducted to evaluate the leaching efficiencies of Ni, Li, Mn, Al, Cu, Fe and Co using various 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 shaken under 400 rpm. The effects of the amino acid type (Gly, Pro, Ser, Asn, His, Cys, and Glu), extraction time (0.5, 1, 3, 6, 12, 18, and 24 h), and solid-liquid ratio (5, 7.5, 10, 12.5, 15, 20 g/L) on leaching was discussed.

The leaching efficiency of various metals was calculated using Eq. (4.1).

$$L\% = C_{M(leaching\ solution)} / C_{M(HCl\ and\ H_2O_2)} \times 100\% \quad \text{Eq. (4.1)}$$

Where C_M is the concentration of metal M in the spent LIB cathode material. $C_{M(HCl\ and\ H_2O_2)}$ indicates the concentration of each metal in the powder material determined by using hydrochloric acid (HCl) and hydrogen peroxide (H₂O₂) as the leaching agent. $C_{M(leaching\ solution)}$ expresses the concentration of each metal in this material determined by using other leaching agent.

In the second step (selective recovery of Co), the polymer PPG400 was added to the leachate in a volume ratio of 1:1, and the system would form two separated phases.

Then, the effects of the addition of different types of SCN^- salts ($[\text{N}_{4444}]\text{SCN}$ 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.

4.2.3 Evaluation

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 extraction efficiency (E , %), the stripping efficiency (S , %), the distribution ratio (D), the purity (P , %), and the separation factor (SF) of the metal ions were calculated using Eqs. (4.2), (4.3), (4.4), (4.5), and (4.6), respectively.

$$\%E = n_M^{TP}/n_M^T \times 100 \quad \text{Eq. (4.2)}$$

$$\%S = n_M^{BP}/n_M^T \times 100 \quad \text{Eq. (4.3)}$$

$$D_M = [M]_{TP}/[M]_{BP} \quad \text{Eq. (4.4)}$$

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

$$\%P_M = [M]_{BP}/([M]_{BP} + [N]_{BP}) \times 100 \quad \text{Eq. (4.5)}$$

$$SF_{M/N} = D_M/D_N \quad \text{Eq. (4.6)}$$

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

than M in the aqueous phase.

The valence state of Co in this spent LIB cathode powder material was investigated by measuring X-ray photoelectron spectrometer (XPS) spectra using a XPS (AXIS-165). The appearance changes of this material before and after leaching were measured by a Scanning Electron Microscope (SEM-SU3500). The valence state change of Co during leaching was investigated by measuring ultraviolet–visible (UV–vis) spectra of the leaching solution in various time using a UV–vis spectrometer (JASCO V-670) at 25 °C with 1 nm spectral resolution. Fourier transform infrared (FT-IR) spectra of the amino acid before and after leaching were performed using an FT-IR spectrometer (Spectrum Two, PerkinElmer).

4.3 Results and Discussion

4.3.1 Characterization of spent LIB cathode powder material

With 4 M hydrochloric acid and 5% hydrogen peroxide as the leaching agent, the composition of the spent LIB cathode material is shown in Table 4.1. It shows that in this material, the content of Co is the highest, accounting for about 55% of the total metal content, followed by Mn. Fe, Al and Cu contents are very low, and iron in particular is negligible small.

Table 4.1 Composition of the spent LIB cathode material

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

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

In addition, the composition of the spent LIB cathode powder is very complex due to the countless charging and discharging of the battery and a series of pretreatments. To determine the valence state of the Co, we have tested the XPS spectrum (Fig. 4.2). In the spectrum of the material, the characteristic photoelectron spectra of Co, O, C and F can be 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 $LiCoO_2$ could be demonstrated by the two peaks locating at binding energies of 54 and 60 eV (Fig. 4.2(b)), corresponding to Li_{1s} and Co_{3p} , respectively. In addition, we also measured the XRD pattern. Except the $LiCoO_2$ binding state, Co also exists in CoO , Co_3O_4 and other combined states.

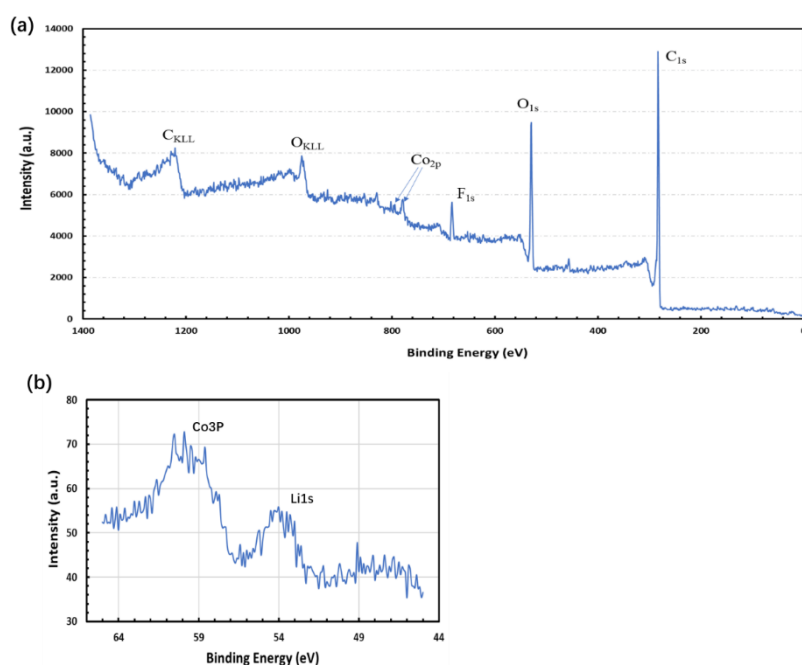


Fig. 4.2 XPS spectra of spent LIBs cathode material. (a) Full spectrum of the material (b) 1s orbital of Li and 3p orbital of Co

4.3.2 Effect of amino acid types on leaching

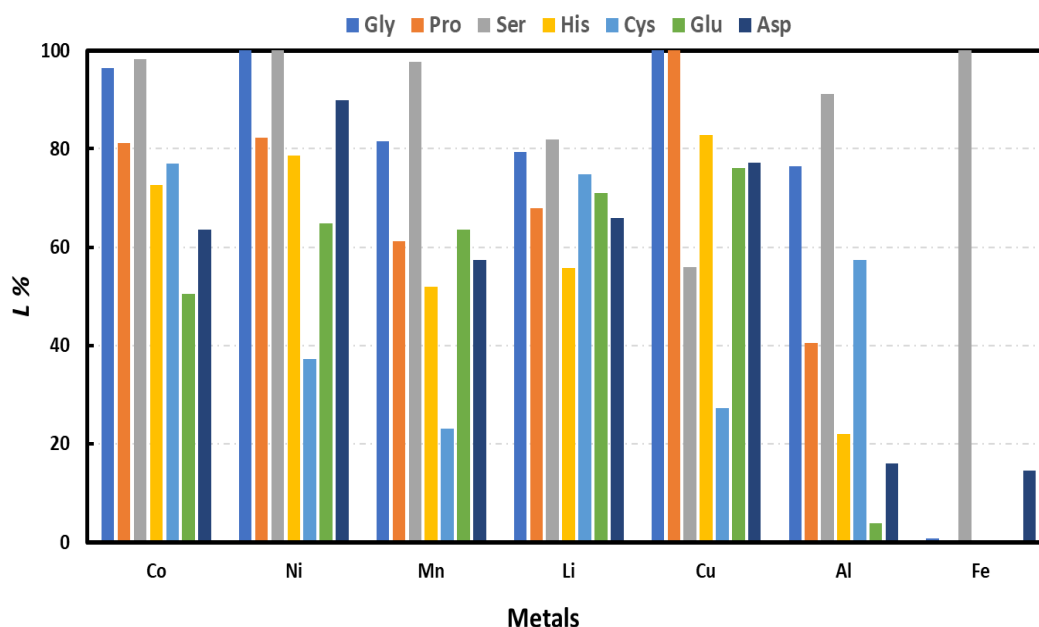


Fig. 4.3 Effect of various amino acids on leaching efficiency

Seven amino acids were chosen based on the nature of their side chains, i.e., the Pro is hydrophobic, the Ser is nucleophilic, the Asp is amide type, the Glu is acidic, the Gly belongs to the small molecular weight representative, the His is basic, and the Cys has special sulfur groups (-HS). The experimental results are shown in Figure 4.3. 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%. Overall, Ser exhibits excellent leaching ability for all metals except Cu. However, since Cu and the target ion Co belong to the transition element, they interfere with each other in the field of ion separation due to the structural similarity. In addition, the content of Cu in the material is around 1/14 of that of Co. Therefore, the

low leaching efficiency of Cu is beneficial to the subsequent selective extraction of Co. The high leaching efficiencies using amino acids for metals might be attributed to the presence of the amino group ($-NH-$) [25]. The transition elements have high affinity toward the nitrogen atom according to the hard and soft acids and bases (HSAB) theory. Based on the result, we choose the Ser as the most suitable leaching agent.

4.3.3 Effect of solid-liquid ratio on leaching

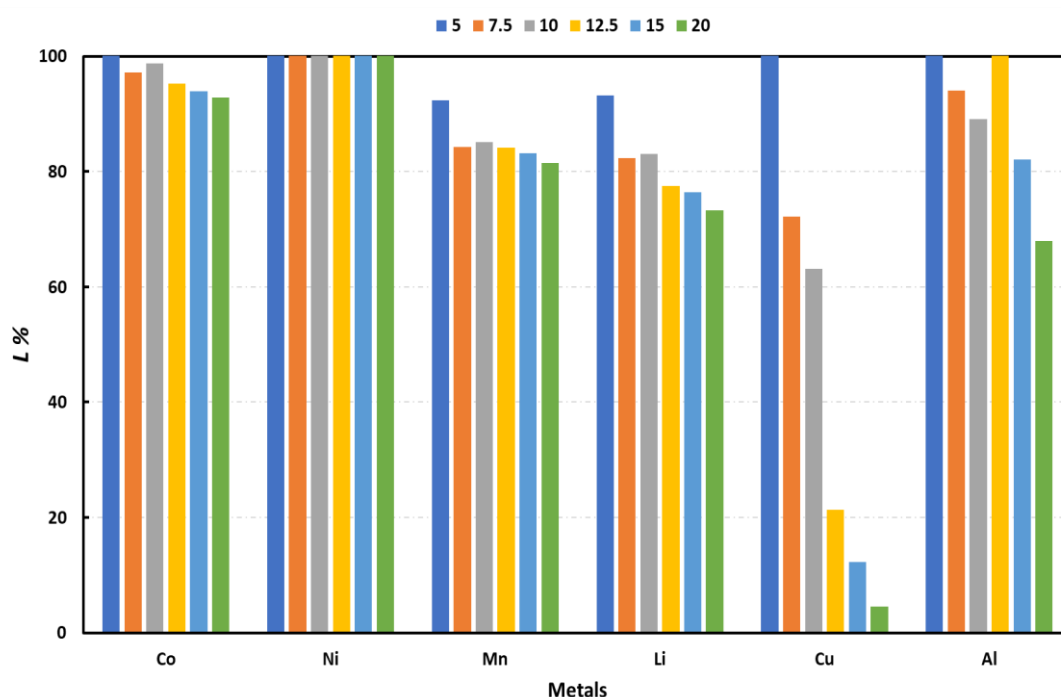


Fig. 4.4 Effect of various S/L (g/L) on leaching efficiency

The solid-liquid ratio (S/L) has a significant impact on the leaching efficiency. As shown in Figure 4.4, when the value of S/L 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. Due to the extremely low content of Fe

(around 1/300 of the Co content), there is a large error in the leaching process, which will not be discussed here. However, as the value of S/L increases, the leaching efficiency for Cu decreases significantly. This suggests that Ser hinders copper leaching. It was deduced that the copper oxide was reduced to copper by Ser and remained in the residue instead of entering the solution. Considering the scale requirements and economic benefits in the industrial production, a S/L of 10/1 is found to be optimal.

4.3.4 Leaching mechanism

In this work, 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 clear the leaching mechanism is important for establishing battery cathode recycling using amino acids.

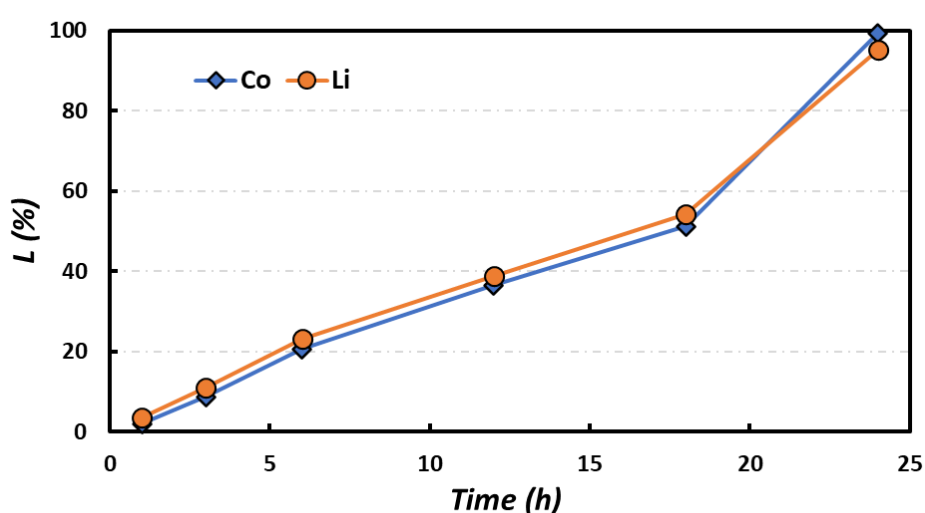


Fig. 4.5 Variation of leaching efficiency of LiCoO_2 over time

As shown in the Figure 4.5, 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 is also constantly changing, from bright purple to dark red (Fig. 4.6). To verify the change of Co valence, the UV-vis spectrum was investigated, as shown in Figure 4.6. The UV spectrum of the leachate taken out at the 24 h changed significantly. Figure 4.6 clearly shows the reduction of Co(III)-serine to Co(II)-serine. The observed absorption maxima around 375 nm and 520 nm are attributed to Co(II)-serine and Co(III)-serine, respectively [26]. We can find that with the leaching time increasing from 1 h to 18 h, the intensity of the leaching solution is also increasing, which is attributed to the continuous entry of Co into the solution. In addition, another obvious behavior is that a clear absorption peak broadening between 210 nm 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, and the other two absorption peaks of Co(II)-serine merged, indicating that Co(III)-serine in the solution was completely reduced to Co(II)-serine.

In this work, Ser exhibits its potent reducibility, which is an attractive finding. As a zwitterionic species, Ser exhibits a negative charge when the pH of the solution is higher than its isoelectric point (IP), that is, the carboxylic acid group is converted from -COOH to -COO⁻, and its electron donating ability will increase significantly. The IP

of Ser is 5.68, and after the reaction, the pH of the solution is about 7.0. The -OH group of Ser is also oxidized to an aldehyde group [27] when it reduces Co(III) to Co(II). The reaction mechanism is shown in Figure 4.7. Figure 4.8 shows the FT-IR spectrum of Ser before and after leaching. For FT-IR spectrum of pure Ser, the band at 1217 cm^{-1} was assigned to C-OH rocking. However, after leaching, this band disappeared. And the intensity of the band (around 1571 cm^{-1}) increased, indicated that the -OH group was oxidized to C=O during the leaching [27]. Figure 4.9 shows the change of surface morphology the LIB cathode before and after leaching. After leaching, the size of the particles becomes smaller, indicating that the metals were leached into the solution, leaving only carbon and other residues. In addition, Ser has good industrial application prospects due to its low price.

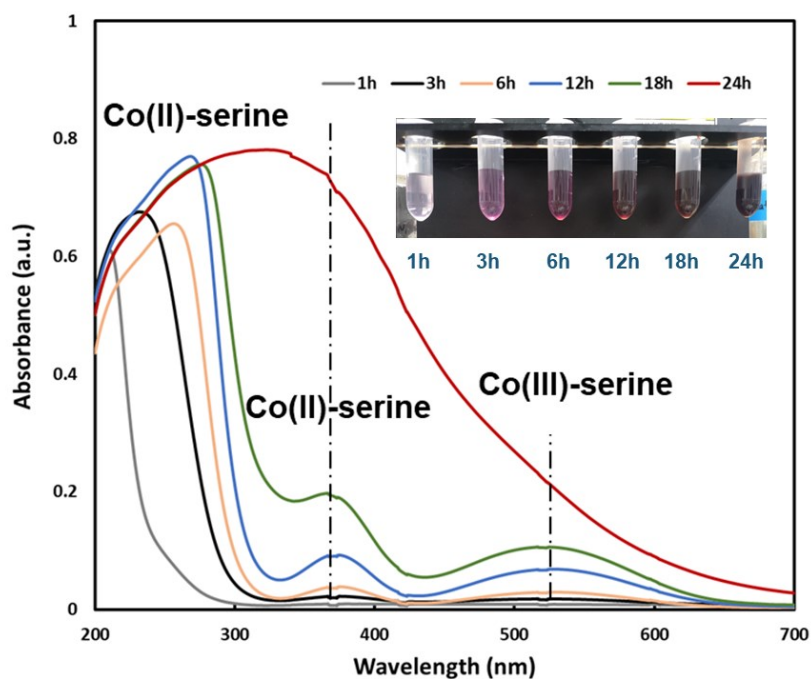


Fig. 4.6 UV-vis spectra of the leaching solution at different interval of time

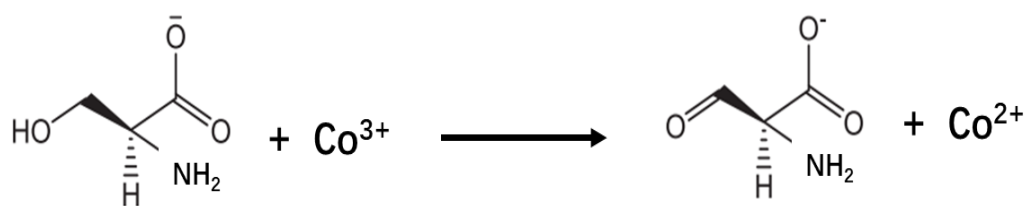


Fig. 4.7 Mechanism of Serine's reduction of Co(III) to Co(II)

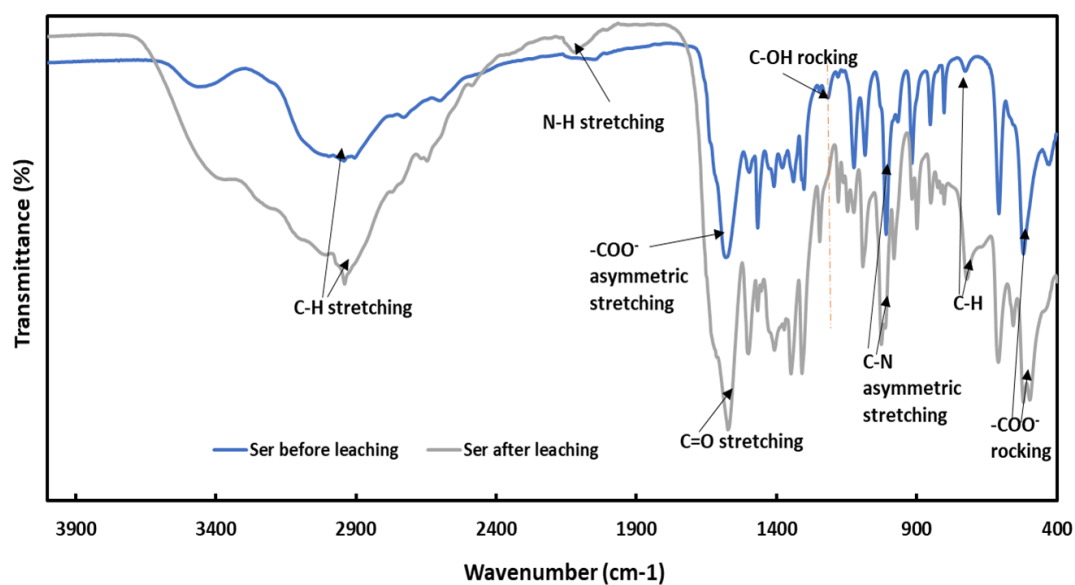


Fig. 4.8 FT-IR spectrum of Ser before and after leaching

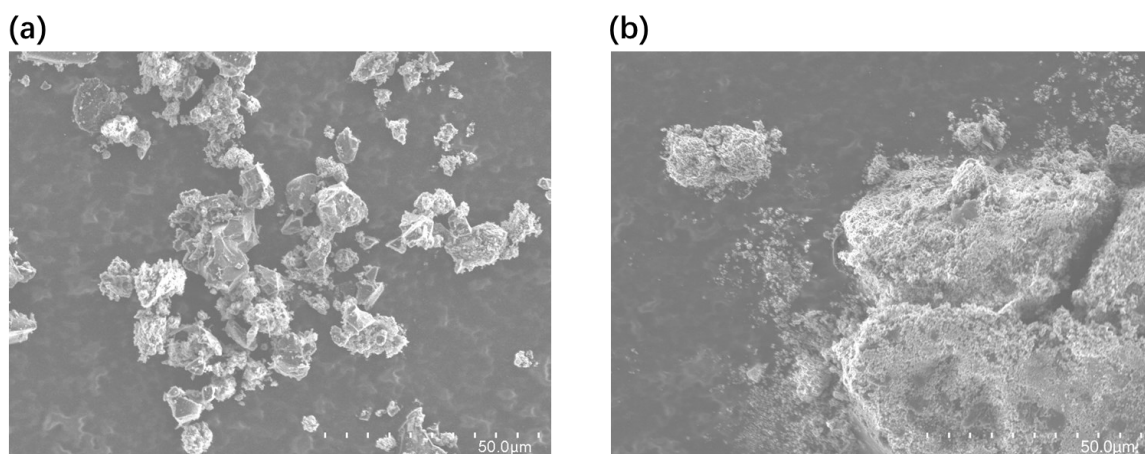


Fig. 4.9 SEM spectrum of the spent LIB cathode before (a) and after (b) leaching.

4.3.5 Selective extraction of Co in Ser-based ABS

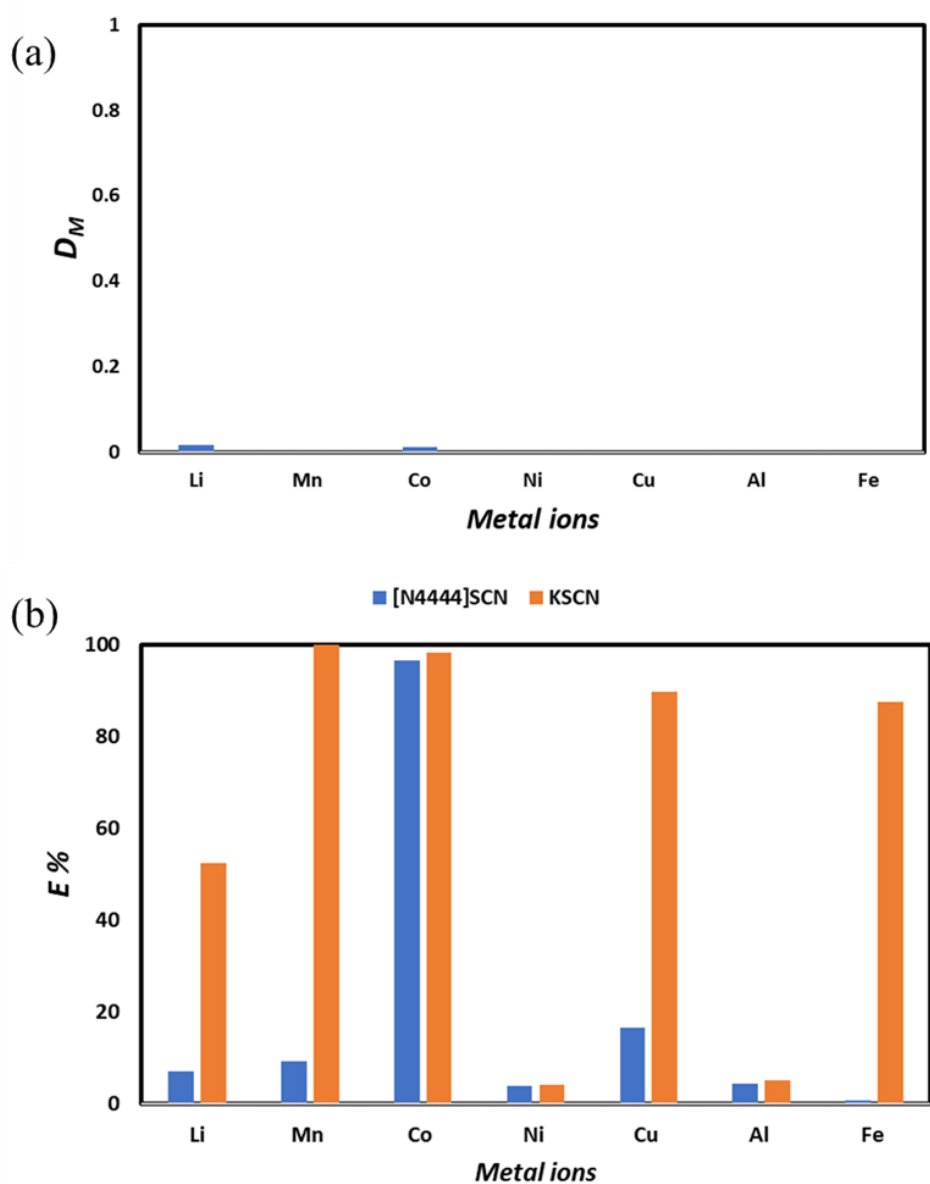


Fig. 4.10 (a) Distribution ratio of metals without adding any thiocyanate; (b) Effect of two thiocyanate on extraction efficiency of metals

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 (Fig. 4.10(a)). Since thiocyanate can form complexes with copper, cobalt,

and manganese, etc. [28], two different thiocyanates (KSCN and $[N_{4444}]\text{SCN}$) were tested in this experiment. Since Ser was complexed with Co, to improve the extraction efficiency, we added a little organic acid (0.01M) to the system. As shown in the Figure 4.11, the type of organic acid has a significant effect on the extraction efficiency of Co with the addition of $[N_{4444}]\text{SCN}$. 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 could make the extraction efficiency reach 96.64%. According to Fig. 4.10(b), when KSCN was added to the system, almost all the Mn, Co, Cu, and Fe ions were combined with thiocyanate and transferred to the PPG400 rich phase. However, only Co and Cu ions were transferred to the PPG400 enriched phase when $[N_{4444}]\text{SCN}$ was added to the system. In addition, in the leaching stage, a small amount of Cu (Fig. 4.4) exists in the solution, therefore the purity of Co in the PPG400 rich phase is very high, about 95.13%. Regarding this selectivity, we thought that it is effect of the quaternary ammonium group, which forms stable complexes with Co and Cu together with thiocyanate.

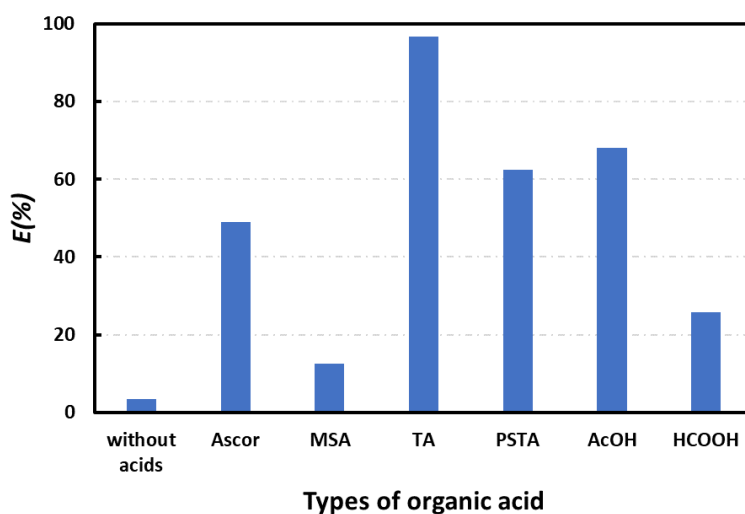


Fig. 4.11 Variation of extraction efficiency of Co over types of organic acid

4.4 Conclusion

In this thesis, we successfully integrated the leaching and separation of metals from spent LIBs cathode materials using biocompatible amino acids. 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 - PPG 400- H₂O) was first applied to the recovery of metals from waste batteries. Under a relatively mild temperature (70 °C) and a solid-liquid 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 the extraction efficiency of 97% and the purity of over 95% by adding thiocyanate to the ABS system. The amino acids have excellent prospects in the field of spent battery recycling due to their eco-friendly and low-price advantages.

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Chapter 5. General Conclusion

5.1 Summary

The demand for the critical metals (Li, Co, Ni, and Mn) has been continuously growing in recent years. Especially, the EVs industry has presented a booming scene in the context of governments of all countries pursuing new energy sources to achieve “carbon neutrality” goals. LIBs, as the main battery type for EVs, have unprecedented attractive. The prosperity of the LIBs industry has also led to the development of its upstream resources (primary mineral resources) and downstream resources (secondary resources—waste LIB). Prices of Co and Li_2CO_3 have been rising sharply in the past several years. However, around the entire battery industry, whether extracting these critical metals from its upstream resource—minerals or recovering these critical metals from its downstream resource—waste LIBs, an eco-friendly, sustainable, and economical technology is a challenging issue. To address this problem, the present thesis is devoted to the development of eco-friendly processes in the field of separation chemistry to extract and recover these critical metals required for LIBs.

In the Chapter 2, a novel extraction system by dissolving [Omim][TTA] in a different ionic liquid [Omim][NTf₂] instead of hazardous organic diluents was developed to selectively extract the critical metal—Li(I) from salt lakes (primary resources). The newly developed FIL system shows a high extraction ability and enables the extraction of Li(I) at a lower pH condition. The extraction performance of the FIL extractant was enhanced by dissolving it in an ionic liquid diluent, because the active component TTA

anion was enhanced. The extraction mechanism was examined by slope analysis and UV-vis measurement, which indicated that one molecule of FIL interacts with one Li(I) ion and forms a 1:1 complex. Moreover, the FIL showed a high selectivity toward Li(I) in the presence of high concentrations of interfering ions such as Na(I) and K(I). Using a countercurrent extraction process at a phase ratio of $V_o : V_a = 1 : 1$, the Li(I) recovery from salt lakes reached 88.2% in 2-3 stages and the extraction efficiency reached 97.3% at a phase ratio of $V_o : V_a = 3 : 1$. The $SF_{Li/Na}$ at a phase ratio ($V_o : V_a = 1 : 1$) in this study was 227, which is the highest value among the FILs previously reported which were used without the addition of another extractant for collaborative extraction. Overall, the ionic liquid extractant [Omin][TTA] shows a good prospect in the industrial operation for the recovery of Li(I) from salt lakes.

The Chapter 2 is about the successful extraction of Li from the primary resource—salt lakes. In Chapters 3 and 4, we recovered critical metals such as Co, Ni and Mn from secondary resources—waste LIBs using eco-friendly and efficient ABS technology.

In the Chapter 3, the selective recovery of Co(II), Ni(II), and Mn(II) from a spent LIB model solution using novel ABSs comprising biocompatible components was demonstrated. In the first step, an ABS of $[N_{4444}]\text{HSO}_4$, Na_2SO_4 , and H_2O mixed with Phe successfully transferred Co(II) and Ni(II) to the IL-rich phase while Mn(II) stayed in the salt-rich phase. In the second step, the IL-rich phase was mixed with MSA and NaCl to form a new ABS ($[N_{4444}]\text{HSO}_4\text{--NaCl--MSA--H}_2\text{O}$), which enabled effective separation of Co(II) and Ni(II): Ni(II) was stripped to the salt-rich phase and Co(II) was

enriched in the IL-rich phase as $[CoCl_4]^{2-}$. Finally, Co(II) was stripped from the IL-rich phase by adding Na_2SO_4 and simultaneously regenerating the $([N_{4444}]HSO_4)$ IL. A reusability test showed that the performance of the regenerated IL was relatively stable over a three-cycle experiment. An eco-friendly ABS with remarkable metal separation performance was developed in this chapter without using any hazardous reagents or toxic organic solvents. The insights might further be explored to recover critical metals from an actual LIB waste.

In the Chapter 4, we integrated the leaching and separation of Co from an actual spent LIBs cathode materials using biocompatible amino acids. The new ABS (Ser - PPG 400- H₂O) was first applied to the recovery of metals from waste batteries. Under a relatively mild temperature (70 °C) and a solid-liquid ratio of 10/1 (g/L), the leaching efficiency of each metal (Co, Ni, Mn, Li, Al, Cu and Fe) is higher than 80%. The leaching efficiency of Co reached 98%. The mechanism of Ser leaching for the metals from the waste LIB cathode was also discussed. The Co was selectively extracted with the extraction efficiency of 97% and the purity of over 95% by adding thiocyanate to the ABS system. The amino acids have excellent prospects in the field of spent battery recycling due to their eco-friendly and low-price advantages.

5.2 Outlook

These technologies developed in the thesis could simplify the process, reduce the cost input, have efficient extraction and separation rates, do not use toxic and volatile organic solvents and meet the goals of sustainable development, which provide the

possibility for an industrial large-scale production.

Amino acids are attractive as amphoteric substances that exhibit excellent reducing properties at a certain pH. For different types of amino acids, the reaction mechanisms showed differences, which needs to be further explored. Coupled with the biocompatibility of amino acids, non-toxic and harmless, and low price, its industrial application has a very broad prospect. In addition, the replacement of traditional liquid-liquid extraction technology, ABS technology, has not yet been applied on a large scale in industry. The water pollution, relatively low ion extraction efficiency, and the loss of ionic liquid are urgently needed to be solved. The green solvent-deep eutectic solvent (DES) has not yet been applied to the ABS field for metal recycling. DES has an extremely simple preparation method and a high selective extraction efficiency, therefore, a new ABS using DES will be a further attractive candidate for metal recycling methods.

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