Recovery of Cobalt and Manganese from Spent Lithium-ion Batteries using a Phosphonium-based Ionic Liquid

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A novel ionic liquid (IL) trioctyldodecyl phosphonium bis(2,4,4-trimethylpentyl)phosphinate was developed as a recovery agent for cobalt(II) and manganese(II) from spent lithium-ion batteries (LIBs). Absence of organic diluent provides an advantageous factor to IL-based extraction than the conventional one. Co(II) and Mn(II) were extracted quantitatively from the aqueous phase to the IL phase. Extracted Co(II) and Mn(II) were stripped from the IL using water and NH₄NO₃, respectively. After stripping, the IL can be reused as the extractant, facilitating the realization of a continuous extraction process. The developed hydrophobic IL shows promise as an extractant for Co(II) and Mn(II) from the spent LIBs.

1. Introduction

Lithium-ion batteries (LIBs) have become crucial components of many modern technologies. LIBs are attractive for power storage because of their high charge density, which allows them to be more compact than other rechargeable batteries [1]. The increased use of various types of portable equipment, such as mobile devices and personal computers, in recent decades, has led to huge growth in their market and greatly stimulated the production of LIBs. However, the great increase of LIB usage will be followed by the problem of spent LIBs in forthcoming years [2]. The cathodes of LIBs contain various valuable metals, such as lithium (Li), cobalt (Co), nickel (Ni), and manganese (Mn). Therefore, recycling spent LIBs is considered beneficial from both economic and environmental aspects. To date, the approaches used to recycle valuable metals in LIBs mainly involve pyrometallurgical and hydrometallurgical processes [3]. Liquid–liquid extraction is generally carried out using an inorganic acid, such as H₂SO₄, HCl, or HNO₃, as an acidic leaching agent [4].

Extracting agents, such as bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) [5], di-(2-ethylhexyl)phosphoric acid (D2EHPA) [5], bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) [6], 2-ethylhexylphosphonic mono-2-ethylhexyl ester [7], and *N*,*N*-dioctyl-1-octanamine (Alamine 336) [6] have been widely used to recover Co and Mn from not only primary ores but also secondary sources; e.g., spent LIBs. However, these conventional extractants require a large amount of solvent, such as toluene or kerosene, as a diluent. Those solvents are classified as volatile organic compounds, which have limited reusability and raise environmental concerns because of their high vapor pressure, flammability, and toxicity. Thus it is beneficial not only from economical but also from environmental viewpoint to find a suitable replacement for those solvents.

A possible alternative to organic solvents is ionic liquids (ILs). Over the past few years, ILs have been explored as a possible alternative to organic solvents and extractive agents, due to their low vapor pressure and adjustable properties. In 2012, Rybka and colleagues used phosphonium-based ILs to separate Co(II) from Ni(II) [8]. However, toluene was required as a diluent for the IL. Wellens *et al.* reported the first example of Co(II) extraction using undiluted trihexyltetradecylphosphonium chloride (P_{6,6,6,14}Cl) [9]. They found that the undiluted system provided better separation factors for Co(II) from other metals compared with those of diluted systems. Recently, trioctyl(alkyl)phosphonium chloride ILs diluted with toluene have been used for Co(II) extraction [10]. They achieved excellent Co(II) extraction performance at high HCl concentration. Only a few examples of Mn(II) extraction using ILs have been reported. Ola *et al.*, used trihexyltetradecylphosphonium bromide (P_{6,6,6,14}Br), P_{6,6,6,14}Cl, and Alamine 336 to extract and separate Mn(II) from Fe(III) [12,13]. Several conventional extractants, such as D2EHPA, Cyanex 272, and Cyanex 301 have shown excellent performance in recovering valuable metals from spent-LIBs [13,14]. However, the use of undiluted ILs to recover valuable metals from spent LIBs has seldom been explored.

Trihexyltetradecylphosphonium bis(2,4-trimethylpentyl)phosphinate (P_{6,6,614}R₂POO) has been investigated as an extractant for several kinds of metals. P_{6,6,6,14}R₂POO has also been explored as an extraction agent for Co(II) [9,12,17]. Bradaric et al. reported the synthesis and characterization of P_{6,6,6,14}R₂POO [15]. Rybka et al. achieved a good separation factor of Co(II) from Ni(II) in chloride media using P_{6,6,6,14}R₂POO [8]. Moreover, P_{6,6,6,14}R₂POO can also be used simultaneously with other immiscible ILs, such as imidazolium-based ILs. For example, a combination of P_{6.6.6.14}R₂POO and 1-ethyl-methylimidazolium chloride was able to extract Co(II) from Ni(II) with a high separation factor [13]. Previously, we synthesized trioctyldodecylphosphonium halides ($P_{8,8,8,12}X$; X = Cl, Br), which were used as extractants for valuable metals [19,20]. These ILs showed higher hydrophobicity and lower viscosity than those of their commercial counterparts. Combining the trioctyldodecylphosphonium cation $(P_{8,8,8,12}^+)$ and bis(2,4,4-trimethylpentyl)phosphinate anion (R₂POO⁻) could yield ILs with greatly enhanced performance in the recovery of valuable metals. Moreover, few studies on the extraction and separation of valuable metals from spent LIBs using phosphonium-based ILs with R₂POO⁻ have been reported. In this study, the phosphonium-based IL trioctyldodecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate $(P_{8,8,8,12}R_2POO)$ is synthesized and used as an extractant to recover valuable metals from the leachate of spent LIBs.

2. Experimental

2.1 Reagents

Trioctylphosphine (97%) and 1-chlorododecane (97%), which were used as precursors for trioctyldodecylphosphonium chloride ($P_{8,8,8,12}Cl$), were obtained from Sigma Aldrich (Tokyo, Japan) and Tokyo Chemical Industry Co., Ltd (Tokyo, Japan), respectively. Bis(2,4,4-trimethylpentyl)phosphinic acid (92%), which is one of the precursors of $P_{6,6,6,14}R_2POO$ was purchased from Sigma Aldrich (Tokyo, Japan). Nitric acid (5 mol L⁻¹), HCl (5 mol L⁻¹), H₂SO₄ (5 mol L⁻¹), anhydrous Na₂SO₄ (99.9%), NH₄NO₃ (98.0%), anhydrous FeCl₃ (99.0%), CoCl₂.5H₂O (99.0%), CuCl₂.2H₂O (99.9%), and MnCl₂.4H₂O (99.0%) were purchased from Wako Pure Chemical Ltd (Osaka, Japan). (NH₄)₂FeSO₄.6H₂O (98%), NH₃OHCl (96%), formaldehyde solution, hexamethylenetetramine (99.0%), ethylenediamine tetraacetate (EDTA, 98.0%), xylenol orange disodium salt, Na₂SO₃ (98.0%), and NiCl₂.6H₂O (99.9%) were purchased from Sigma Aldrich (Singapore).

2.2 Synthesis of trioctyldodecylphosphonium chloride (P_{8,8,8,12}Cl)

 $P_{8,8,8,12}Cl$ (Figure 1a) was synthesized using a similar procedure to that described previously [17]. The synthesis process was done under nitrogen atmosphere. Chlorododecane (0.11 mol eq.) was placed into a 50 cm³ three-neck round-bottom flask with a stirring bar. Trioctylphosphine (0.1 mol eq.) was added slowly to the flask and then the flask was flushed again with nitrogen before being sealed. The synthesis was carried out at 145°C for 16 h in an oil bath. To remove the excess 1-chlorododecane, the final product was dissolved in hexane, and then extracted with water. The final product was dried using an evaporator (EYELA N-1000, Tokyo, Japan) at 40°C in vacuo for 3 h. $P_{8,8,8,12}Cl$ was obtained as a clear liquid with 98% yield (by mass) and its purity exceeded 96.0%.

P_{8,8,8,12}Cl was characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy (Bruker Bio Spin AVANCE500, Kanagawa, Japan) and elemental analysis (Yanaco CHN Corder MT-5, Kyoto, Japan). ¹H NMR (400.13 MHz in CDCl₃): δ 2.49–2.62 (8H, RCH₂P), 1.60–1.70 (8H, RCH₂CH₂P), 1.48–1.54 (8H, RCH₂CH₂CH₂P), 1.25–1.45 (40H, RCH₂R), 0.88 (12H, CH₃CH₂R). ¹³C NMR (100.54 MHz in CDCl₃): δ 33.02, 31.89, 30.76, 30.33, 23.68, 22.77, 19.38, 14.61. ³¹P NMR (161.90 MHz in CDCl₃): δ 34.20. Anal. Calcd for C₃₆H₇₆PCl: C, 74.98; H, 13.46, N, 0.00. Found: C, 74.66; H, 13.41; N, 0.01.

2.3 Synthesis of trioctyldodecylphosphonium bis(2,4,4-trimethyl pentyl)phosphinate (P_{8,8,8,12}R₂POO)

 $P_{8,8,8,12}R_2POO$ (Figure 1b) was synthesized by anionic exchange between $P_{8,8,8,12}Cl$ and bis(2,4,4-trimethylpentyl)phosphinic acid following the method reported by Dharaskar *et al.* [18]. Bis(2,4,4-trimethylpentyl)phosphinic acid (4.760 g, 0.01635 mol) was mixed with $P_{8,8,8,12}Cl$ (9.216 g, 0.1635 mol) in hexane (15 g). Then, a NaOH solution (9 mol L⁻¹) was slowly added to the mixture and stirred at room temperature for 4 h. The organic phase was then separated and washed with water several times. The residue of the aqueous phase was further removed by using anhydrous Na₂SO₄. The solvent was evaporated by a rotary evaporator (EYELA N-1000, Tokyo, Japan) for 3 h at 40°C. The yield of $P_{8,8,8,12}R_2POO$ was 95% (by mass).

 $P_{8,8,8,12}R_2POO$ was characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy (Agilent DD2, Singapore) and elemental analysis (Yanaco CHN Corder MT-5, Kyoto, Japan). ¹H NMR (500.13 MHz in CDCl₃): δ 2.49–2.62 (8H, RCH₂P), 1.70–1.40 (16H, RCH₂CH₂P; 4H, (RCH₂)₂PO₂), 1.25–0.90 (40H, RCH₂R; 6H, PO₂RCH₃; 2H, PO₂RCH; 22H, PO₂RCH(CH₃)₃), 0.88 (12H, CH₃CH₂R). ¹³C NMR (125.4 MHz in

CDCl₃): δ 13.538–55.127 (various singlets).³¹P NMR (121.49 MHz in CDCl₃): δ 33.68 (s), 34.56 (s). Anal. Calcd for C₅₂H₁₁₀O₂P₂: C, 75.30; H, 13.37, N, 0.00. Found: C, 75.01; H, 13.34; N, 0.00.



Figure 1. Structures of (a) P_{8,8,8,12}Cl and (b) P_{8,8,8,12}R₂POO.

2.4 Leaching metals from spent LIBs

A spent LIB was obtained in fine powder form with a particle size of less than 75 μ m. Initial leaching was conducted by mixing 5 g spent LIB powder with 5 mol L⁻¹ HCl solution (50 mL) in a round-bottom flask for a given time in a water bath (25°C). The mixture was then filtered and the metal concentration was measured by an atomic absorption spectroscopy (AAS).

2.5 Spectrophotometric determination of metals

Spectrophotometric determination of Co(II) and Ni(II) was performed by EDTA titration following the approach reported by Liu *et al.* [19]. Initially, a solution containing 100 ppm of either Co(II) or Ni(II) in HCl solution (5 mol L⁻¹) was prepared. In Ni(II) detection with EDTA, 20% hexamethylenetetramine (10 mL) and water at 70°C (50 mL) were added to the Ni(II)-containing solution to accelerate the complexation reaction of Ni(II) and EDTA. Then, both Co(II)- and Ni(II)-containing solutions were mixed with several drops of xylenol orange disodium salt indicator (5 g L⁻¹). Titration was conducted by the addition of 0.01 mol L⁻¹ EDTA until the solution changed to purplish red. The solution was heated to boiling. After adding 0.01 mol L⁻¹ EDTA, titration was continued until the solution turned bright yellow. The end point was achieved when the color did not change within 30 s.

Determination of Mn(II) was conducted using formaldoxime as the indicator, as reported by Mirea *et al.* [20]. NH₃OHCl (10 g) was dissolved in distilled water and then mixed with 35% formaldehyde solution (5 mL). A solution containing Mn(II) was mixed with 500 mg L⁻¹ (NH₄)₂Fe(SO₄)₂.6H₂O solution (1 mL) and EDTA (2 mL). Formaldoxime solution (1 mL) and 4 mol L⁻¹ NaOH solution (2 mL) were added. The solutions were mixed, rested for 10 min, and then 5 mol L⁻¹ NH₄Cl (3 mL) was added. The solution was left to stand for 1 h for color development.

The other candidate extractable metals from spent LIB leachate are Fe(III) and Cu(II). The spectroscopic determination of these metals was conducted by diluting CuCl₂ and FeCl₃ solutions to desired concentrations. Then, ultraviolet–visible (UV-vis) spectroscopic analysis was performed at 265 and 340 nm, respectively. All experiments and spectrophotometric measurements were conducted in triplicate to minimize the error, which did not exceed 4%. Spectrophotometric analysis was performed with a Jenway 7615 UV-vis split-beam enabled spectrophotometer (Cole-Parmer Co. Ltd., Birmingham, UK). The absorbance of the solutions was measured using 1 cm-thick quartz cell against double-distilled water as the blank, unless stated otherwise.

2.6 Calibration curve

Different volumes of metal-containing solutions and color-developing reagents were placed in volumetric flasks to obtain different concentrations of the metal in the range of $50 - 150 \text{ mg L}^{-1}$. The absorbance of each metal-containing solution within the range of 200 - 800 nm was measured and then a calibration curve was drawn.

2.7 Extraction procedure

The extraction operation was conducted in a similar manner to our previous report [21]. Undiluted IL was mixed with an aqueous metal solution (single metal solution/leachate). The mixture was agitated and shaken in a water bath at 25°C for a period of time. Stripping experiment was carried out in a similar manner of the forward extraction experiment. The metal concentrations in the single metal solution were measured by a spectrophotometric method. The metal concentration of the leachate was analyzed with an atomic absorption spectrometer (Agilent Atomic Absorption Systems 280FS AA, Singapore). All experiments were performed with a phase volume ratio of the aqueous phase to the IL of 2:1, unless otherwise stated. The degrees of extraction E (%) and stripping S (%) were calculated using Eqs. (1) and (2), respectively,

$$E = \frac{M_{IL}V_{IL}}{M_{IL}V_{IL} + M_{aq}V_{aq}} \times 100$$
⁽¹⁾

$$S = \frac{M_{st}V_{st}}{M_{st}V_{st} + M_{IL}V_{IL}} \times 100$$
⁽²⁾

where M (mg L^{-1}) is the concentration of the metal ion in the aqueous phase (aq), stripping phase (st) and the IL, and V (L) is the volume of each respective phases. Each experiment and measurement were performed in triplicate and the error did not exceed 5%.

3. Results and Discussion

3.1 NMR spectroscopy of P_{8,8,8,12}R₂POO

The ³¹P NMR spectra of P_{8,8,8,12}Cl and P_{8,8,8,12}R₂POO both exhibited a singlet at around 34.5 ppm, as shown in Figure 2. This signal was attributed to the quaternary phosphorus atom of P_{8,8,8,12} [18, 25]. The ³¹P NMR spectrum of P_{8.8.8.12}R₂POO also contained another peak at 33.6 ppm, as shown in Figure 2b, which could be associated with the quaternary phosphorus center atom of R₂POO in the IL [18]. Impurity peaks were also seen in the ³¹P NMR spectrum of P_{8,8,8,12}R₂POO at 46.41, 46.20, 37.99, and 34.47 ppm. These peaks were ascribed to the presence of small amounts of phosphine isomer and various phosphine oxides in the bis(2,4,4-trimethylpenthyl)phosphinic acid. The ³¹P NMR spectrum of P_{8,8,8,12}R₂POO showed a noticeable change after the extraction operation of the leachate: a new peak was observed at 47.4 ppm (Figure 2c). This peak could be associated with the center atom of bis(2,4,4-trimethylpenthyl)phosphinic acid [23]. Moreover, there was a shift of the peak at 33.6 ppm to 30.6 ppm after the extraction process, whereas the peak at 34.5 ppm was unaffected by the extraction process. bis(2,4,4-trimethylpenthyl)phosphinic acid was present after extraction because of the ion exchange process that occurred during the extraction process. As shown in the ³¹P NMR spectrum of P_{8.8.8.12}R₂POO in Figure 2d, the content of bis(2,4,4-trimethylpenthyl)phosphinic acid, which is present at 47.4 ppm decreased after

adding excess NaOH and heating the solution to 55°C. This indicates that the bis(2,4,4-trimethylpenthyl) phosphinic acid was converted back to $P_{8,8,8,12}R_2POO$, which is similar to the synthesis process of $P_{6,6,6,14}R_2POO$ [18, 27].



Figure 2. ³¹P NMR spectra of (a) $P_{8,8,8,12}Cl$, (b) $P_{8,8,8,12}R_2POO$, (c) $P_{8,8,8,12}R_2POO$ after extraction, and (d) $P_{8,8,8,12}R_2POO$ after NaOH treatment.



3.2 Leaching of a spent LIB

Figure 3. Factors influencing the dissolution efficiency of Co and Mn (2.5 g of spent LIB powder in 50 mL of HCl). (a) Leaching solution (Leach solution= 5 mol L^{-1} HCl, 5 mol L^{-1} H₂SO₄, 2 mol L^{-1} HNO₃, time = 24 h, temperature = 70°C). (b) HCl concentration (time = 24 h, temperature = 70°C). (c) Leaching temperature (time = 24 h, [HCl]_{aq} = 5 mol L^{-1}). (d) Leaching time ([HCl]_{aq} = 5 mol L^{-1} , temperature = 70°C). μ XRF of 5g sample (%) Li = 3.7; Co = 11.9; Cu = 13.4; Ni = 1.1; Mn = 1.28; Al = 14.1; Fe = 1.8.

Leaching from a spent LIB was carried out using several leaching solutions. The yields of Co and Mn to the mineral acids were over 80% in 5 mol L^{-1} HCl and 5 mol L^{-1} H₂SO₄ (Figure 3a). Meanwhile, 2 mol L^{-1} HNO₃ showed the lowest dissolution efficiency for both Co and Mn. Organic acids such as 1 mol L^{-1} oxalic acid and 1 mol L^{-1} malic acid were not effective as dissolution agents for Co and Mn from spent LIBs. Thus, subsequent investigation of Co and Mn dissolution from spent LIBs was done with 5 mol L^{-1}

HCl.

Then, the effect of HCl concentration was investigated on the dissolution of Co and Mn. Co and Mn dissolution increased with HCl concentration (Figure 3b). However, considering that the leachate is subjected to an extraction procedure, it is not favorable for the HCl concentration of the feed solution to be too high. Thus, the subsequent experiment used 5 mol L^{-1} HCl as the leaching solution. Leaching temperature and time were also investigated to further improve the dissolution efficiency of Co and Mn. The dissolution of Co and Mn increased with leaching temperature (Figure 3c) up to 70°C, where the highest dissolution efficiency for Co and Mn was observed. Further increasing the temperature above 70°C did not improve the dissolution efficiency. Increasing the leaching time from 6 to 12 h had a favorable effect on Co and Mn dissolution, whereas increasing the leaching time from 12 to 24 h only slightly improved the dissolution of Co and Mn (Figure 3d). Overall, the highest dissolution efficiency of Co and Mn was achieved using 5 mol L⁻¹ HCl for 12 h at 70°C (Table 1). The leachate also contained a considerable amount of Ni, Cu, and Fe.

Table 1. Spent LIB leachate composition (5 g of sample per liter of 5 mol L^{-1} HCl)										
_	Metal	Li	Co	Cu	Ni	Mn	Al	Fe		
-	Leachate (mg L ⁻¹)	111	560	38	41	58	2.7	48		

3.3 Absorption spectral analysis

The spectra of [Co(EDTA)]²⁻, [Ni(EDTA)]²⁻ and [Mn(EDTA)]²⁻ complexes exhibited absorption peaks at 469, 380, and 448 nm, respectively. In addition, the absorption spectra of Cu(II) and Fe(III) showed distinct peaks at 265 and 348 nm, respectively. For Cu(II), the peak at 265 nm indicates the presence of CuCl₂ in the solution [28,29]. The peak at 348 nm in the UV-vis spectrum of Fe(III) was attributed to the presence of $FeCl_3$ in the solution [27]. The calibration curves of the metal complexes were linear in the designated concentration range. Furthermore, t-tests revealed that the intercepts of the calibration curves of all the metal complexes were close to zero. The linear range of Beer's law was observed at the designated wavelength for each complex.

3.4 Extraction behavior

Solutions of Co(II), Mn(II), Ni(II), Fe(III), and Cu(II) with a concentration of 100 mg L⁻¹ were equilibrated with $P_{8,8,8,12}R_2POO$ at different HCl concentrations and $V_{aq}/V_{IL} = 2$. All metals except Ni(II) showed increased extraction efficiency with rising HCl concentration, as illustrated in Figure 4a. The highest extraction efficiencies of Co(II) and Mn(II) of 99% and 98%, respectively, were achieved at an HCl concentration of 5 mol L⁻¹. Moreover, Fe(III) and Cu(II) were also effectively extracted into the IL phase, achieving highest extraction efficiencies of 85% and 96%, respectively. Figure 4b shows the time course of the extraction process of the metals from the model leachate ([HCl] = 5 mol L^{-1}). The quantitative extractions of Co(II) and Mn(II) using P_{8,8,8,12}R₂POO were achieved within 3 h. Cu(II) and Fe(II) were also extracted in considerable efficiency. Although Fe(III) required a longer operation time of 8 h to reach equilibrium. In contrast, Ni(II) was not extracted at any HCl concentration, even when the extraction period was prolonged. Thus, these results suggest that extraction for 3 h under the present experimental conditions allows the quantitative extraction of Co(II) and Mn(II) and suppresses the extraction of Fe(III).



Figure 4. Extraction of metal complexes using $P_{8,8,812}R_2POO$ with different (a) HCl concentrations ([metals]_{aq} = 100 mg L⁻¹, [HCl]_{aq} = 5 mol L⁻¹, $V_{aq}/V_{IL} = 2$, time: 12 hours) and (b) contact time ([metals]_{aq} = 200 mg L⁻¹, [HCl]_{aq} = 5 mol L⁻¹, $V_{aq}/V_{IL} = 4$).



Figure 5. UV-vis spectra of (a) Fe(III), (b) Cu(II), (c) Co(II) in IL phase. Solvent = toluene, $[HCl]_{aq} = 5 \text{ mol} L^{-1}$. (d) Co(II) in IL phase. Solvent = toluene, $[HCl]_{aq} = 0 \text{ mol} L^{-1}$ (e) Fe(III) in P_{8,8,8,12}R₂POO after extraction. $[HCl]_{aq} = 5 \text{ mol} L^{-1}$.

Different forms of Co(II) chlorocomplexes are present depending on the concentration of HCl. According to several previous studies, Co(II) is present as $[CoCl_4]^{2-}$ at high HCl concentration [28]. The extraction of Co(II) using P_{8,8,8,12}R₂POO has a different mechanism depending on the HCl concentration. In 5 mol L⁻¹ HCl, the UV-vis spectrum of Co(II) loaded in P_{8,8,8,12}R₂POO showed a distinct peak within the range of 600–720 nm (Figure 5a), which corresponded to the presence of the tetrahedral Co(II) chlorocomplex [28]. Thus, the extraction process of Co(II) at such high HCl concentrations follows Eq. (3). P_{8,8,8,12}R₂POO also effectively extracted Co(II) without HCl. This performance could be explained by the formation of coordination between Co(II) and bis(2,4,4-trimethylpentyl)phosphinate from the IL [29]. The IL phase after extraction showed an absorption peak at 645 nm (Figure 5b) that corresponded to the UV-vis spectrum of Co(R₂POO)₂ [30]. This result indicates that anionic exchange occurs with P_{8,8,8,12}R₂POO to form Co(R₂POO)₂ rather than ion association to form (P_{8,8,8,12}R₂POO concentration were drawn to establish the

ratio between the metal and ILs in the complexes formed during extraction. The slope of the plot for Co was approximately two, which indicated that the formation of extractable species required two molecules of $P_{8,8,8,12}R_2POO$ per metal ion (Figure 6a). This result supports the Co(II) extraction mechanism described by Eq. (3)

$$\operatorname{CoCl}_{4}^{2^{-}} + 2\mathrm{H}^{+} + 2\overline{(\mathrm{P}_{8,8,8,12}^{+} + \mathrm{R}_{2}\mathrm{POO}^{-})} \rightleftharpoons \overline{(\operatorname{CoCl}_{4}^{2^{-}})(\mathrm{P}_{8,8,8,12}^{+})_{2}} + 2\overline{\mathrm{H}\mathrm{R}_{2}\mathrm{POO}}$$
(3)

(4)

 $\operatorname{CoCl}_2 + 2\overline{\operatorname{P}_{8,8,8,12}}^+ \operatorname{R}_2 \operatorname{POO}^- \rightleftharpoons 2\overline{\operatorname{P}_{8,8,8,12}}^+ \operatorname{Cl}^- + \overline{\operatorname{Co}(\operatorname{R}_2 \operatorname{POO})_2}$



Figure 6. Effect of $P_{8,8,8,12}R_2POO$ concentration on the extraction of (a) Co(II), (b) Mn(II), and (c) Cu(II). [metal]_{aq} =200 mg L⁻¹, V_{aq}/V_{IL} = 4, [P_{8,8,8,12}R₂POO] = 0.01 - 0.1 mol L⁻¹, solvent = toluene, [HCl]_{aq} = 5 mol L⁻¹.

In the chloride-based solution, chlorocomplexes of Mn(II) are formed such as $MnCl_2$, and $MnCl_3^-$. Either anion exchange or an association reaction pathway may be involved in the extraction of Mn(II) by $P_{8,8,8,12}R_2POO$ [12,34]. Eqs (5) and (6) describe the anion exchange and association reactions of Mn(II) from the HCl solution by $P_{8,8,8,12}R_2POO$, respectively.

$$MnCl_{3}^{-} + \overline{P_{8,8,8,12}^{+}R_{2}PO0^{-}} + H^{+} \rightleftharpoons (MnCl_{3}^{-})(P_{8,8,8,12}^{+}) + \overline{HR_{2}PO0}$$
(5)

 $Mn^{2+} + 3Cl^{-} + \overline{P_{8,8,8,12}}^+ R_2 POO^{-} + H^+ \rightleftharpoons \overline{(MnCl_3^-)(R_3R'P^+)} + \overline{HR_2POO}$ (6)

The extraction efficiency of Mn(II) showed a positive trend along with the increase of HCl concentration. This corroborates with Eq. (6), which suggests a positive effect of chloride concentration on the extraction efficiency of Mn(II). While, in Eq. (5), the chloride concentration has little effect on the extraction efficiency of Mn(II). Therefore, Eq. (6) is plausible as the solvent extraction reaction of Mn(II) with $P_{8,8,8,12}R_2POO$. The slope of logarithmic plots of IL concentration against the distribution ratio of Mn(II) was approximately one, indicating that the formation of extractable species required one molecule of $P_{8,8,8,12}R_2POO$ per metal ion (Figure 6b).

According to UV-vis analysis, the presence of FeCl₃ in the solution containing Fe(III) and 5 mol L^{-1} HCl was confirmed by the peak at 360 nm (Figure 5c) [32]. The extracted species were also determined through UV-vis spectrophotometry. The Fe(III)-loaded IL was diluted in acetone so that the Fe(III) concentration did not exceed the detection limit. The spectrum showed the typical peaks of [FeCl₄]⁻ at 248, 316, and 371 nm (Figure 5d) [27]. Thus, Fe(III) extraction could follow the ion association pathway as

presented by Eq. (7).

 $\operatorname{FeCl}_{3} + \overline{(P_{8,8,8,12} + R_2 P 0 0^{-})} + \operatorname{HCl} \rightleftharpoons \overline{(\operatorname{FeCl}_{4}^{-})(P_{8,8,8,12}^{+})} + \overline{\operatorname{HR}_2 P 0 0}$ $\tag{7}$

As shown in Fig 5e, the absorption maximum at 268 nm indicates the presence of $CuCl_2$ as the dominant chlorocomplex of Cu(II). In chloride medium with high HCl concentration, $CuCl_2$ and $[CuCl_4]^-$ are stable chlorocomplexes of Cu(II) [36,37]. The slope of a logarithmic plot of the distribution ratio of Cu(II) against $P_{8,8,8,12}R_2POO$ concentration after extraction was 2 (Figure 6c). Thus, the extraction pathway of Cu(II) probably proceeded by the ion association mechanism according to Eq. (8),

$$\operatorname{CuCl}_{2}+2(\operatorname{P}_{8,8,8,12}+\operatorname{R}_{2}\operatorname{POO}^{-}) \rightleftharpoons 2\operatorname{P}_{8,8,8,12}+\operatorname{Cl}^{-}+\operatorname{Cu}(\operatorname{R}_{2}\operatorname{POO})_{2}$$
3.5 Stripping and scrubbing of metals from loaded ILs
$$(8)$$

As described above, various metals aside from the target metals were extracted from the aqueous feed solution. Therefore, crucial factors on the recycling process of Co(II) and Mn(II) are found to be the ability to recover Co(II) and Mn(II), and removing most of co-extracted metal from the IL. The stripping of the metals from metal-loaded $P_{8,8,8,12}R_2POO$ was then investigated using different stripping reagents. The results are listed in Table 2.

Table 2. Stripping of various metals from loaded P_{8,8,8,12}R₂POO using various stripping solutions.

S (%)	Co(II)	Mn(II)	Fe(III)	Cu(II)
H ₂ O	99.8	98.2	0	0
$1 \text{ mol } L^{-1} \operatorname{Na}_2 S_2 O_3$	0	90.3	92.3	0
1 mol L ⁻¹ Na ₂ SO ₃	0	4.31	89.3	0
0.5 mol L ⁻¹ Na ₂ SO ₄	0	98.2	67.9	0
1 mol L ⁻¹ NH ₄ NO ₃	0.2	82.4	0.0	0
1 mol L ⁻¹ H ₂ SO ₄	72.1	57.7	11.0	91.5
$5 \text{ mol } L^{-1} \text{ H}_2 \text{SO}_4$	83.4	90.3	23.6	94.4

As reported previously [35], 1 mol L^{-1} Na₂SO₃ was able to effectively scrub Fe(III) from the loaded P_{8,8,8,12}R₂POO. Our previous report also demonstrated that Na₂SO₃ was an efficient scrubbing agent to remove Fe(III) from the loaded P_{8,8,8,12}Cl [36]. The superior performance of Na₂SO₃ can be attributed its ability to reduce Fe(III) to Fe(II) [35]. The reduction of Fe(III) to Fe(II) was analyzed by UV-vis spectroscopy of the scrubbing solution by the addition of 1,10-phenanthroline, in which resulted to a color transition towards translucent reddish. The presence of (phen)₂Fe(II) complex was confirmed by a distinct peak at 517 nm in the UV-vis spectrum of the solution (Figure 7a) [37]. This further supported the scrubbing mechanism of Fe(III) with Na₂SO₃.



Figure 7. UV-vis spectra. (a) Fe(III). [stripping solution]_{aq} = 1 mol L⁻¹ Na₂SO₃, time = 30 min, temperature = 50°C, [1,10-phenanthroline] = 0.01 mol L⁻¹, $V_{aq}/V_{IL} = 2$. (b) Cu(II). [stripping solution]_{aq} = 5 mol L⁻¹ H₂SO₄, $V_{aq}/V_{IL} = 2$. (c) Co(II). Stripping solution = water, $V_{aq}/V_{IL} = 2$.

Efficient scrubbing of Cu(II) was achieved using H_2SO_4 . The stripping was followed by the formation of CuSO₄ in the stripping solution. An absorption maximum attributed to the presence of CuSO₄ was observed at 632 nm from the UV-vis spectrum of the stripping solution (Figure 7b). Thus, stripping of Cu(II) probably occurs according to Eq. (10),

$$\overline{[Cu(R_2POO)_2} + H_2SO_4 \rightleftharpoons CuSO_4 + 2\overline{HR_2POO}$$
(9)

In addition, 1 mol L^{-1} H₂SO₄ was also able to effectively strip Co(II). To recover Co(II) from the stripping solution, CuSO₄ can be precipitated with CaCO₃ at elevated temperature [38]. Upon addition of CaCO₃ to the solution, a light green precipitate formed. Thus, Cu(II) in the stripping solution was removed through precipitation using CaCO₃ at a pH of 2.5 and temperature of 55°C for 2 h, leaving Co(II) in the stripping solution. The precipitation reaction occurred as follows,

 $2CuSO_4 + 2CaCO_{3(s)} + 3H_2O \rightleftharpoons CuCO_3.Cu(OH)_2 + 2CaSO_{4(s)} + 2H_2O + CO_2$ (10)

The recovery of Co(II) from the loaded $P_{8,8,8,12}R_2POO$ is a crucial aspect of this study because Co(II) is an important target in the recycling process. Previous studies have shown that various stripping agents are effective to recover Co(II) from loaded ILs, such as water, H_2SO_4 and NH_3 [9–11,42]. Therefore, water, H_2SO_4 and NH_3 were tested as stripping agents for extracted Co(II) in the loaded IL phase, which was obtained after extraction from an aqueous leaching solution containing Co(II). As seen in Table 2, all stripping agents effectively recovered Co(II) from the loaded IL. Water was able to recover Co(II) quantitatively from the loaded IL as well as Mn(II). The effective stripping of Co(II) by water was possible because water washed the excess chloride from the IL phase, leading to the transformation of $[CoCl_4]^{2-}$ to $[Co(H_2O)_6]^{2+}$. While $[CoCl_4]^{2-}$ was observed in the IL phase before the stripping process, it was not detected in the water after the stripping process (Figure 7c). This is because the equilibrium between these two Co(II) complexes is easily shifted [40], following Eq. (11).

$$\overline{(\text{CoCl}_4^{\ 2^-})(\text{P}_{8,8,8,12}^{\ +})_2} + 6\text{H}_2\text{O} \rightleftharpoons \text{Co}(\text{H}_2\text{O})_6^{\ 2^+} + 2\overline{(\text{P}_{8,8,8,12}^{\ +}\text{Cl}^-)} + 2\text{Cl}^-$$
(11)

Various types of stripping agents, including reductive (Na₂SO₃ and Na₂S₂O₃) or oxidative (NH₄NO₃

and HNO₃) agents, were investigated to remove Mn(II) from the loaded IL, as shown in Table 2. Since Mn(II) can either be oxidized or reduced, both oxidants and reductants were effective as the stripping agent for Mn(II) from $P_{8,8,8,12}R_2POO$. However, a white precipitate was formed at the interface between the IL and NH₄NO₃ solution, which hindered the separation of the phases and limited the IL reusability. The lower stripping percentage of Mn(II) using Na₂SO₃ compared to the case for Na₂S₂O₃ probably is caused by its lower reduction potential. Stripping of Mn(II) using Na₂S₂O₃ also resulted in the stripping of Fe(III) because of the reduction of Fe(III) to Fe(II). Moreover, stripping of Mn(II) from P_{8,8,8,12}R₂POO was also effectively achieved by water and Na₂SO₄. Thus, water was able to effectively recover both Co(II) and Mn(II) from the IL. Low stability of [MnCl₃]⁻ was largely influenced the capability of Na₂SO₄ to recover Mn(II) from loaded IL. Thus, 0.5 mol L⁻¹ Na₂SO₄ was chosen as a suitable stripping solution to recover Mn(II) from loaded P_{8,8,8,12}R₂POO.

$$(MnCl_{3}^{-})(P_{8,8,8,12}^{+})+Na_{2}SO_{4}\rightarrow 2(P_{8,8,8,12}^{+}Cl^{-})+MnSO_{4}+2NaCl+2Cl^{-}$$
3.6 Recovery of Co(II) and Mn(II) from spent LIB leachate
$$(12)$$

A solution of metals leached from a spent LIB was analyzed using AAS. A recovery process for Co(II) and Mn(II) from the spent LIB leachate was developed according to the results obtained using the single metal solutions, as summarized in Scheme 1. Figure 8 presents the metal concentrations in the solution after each process. Initially, extraction of Co(II) and Mn(II) was carried out by mixing the leachate with $P_{8,8,8,12}R_2POO$. Co(II) and Mn(II) were almost quantitatively extracted, followed by Cu(II) (approximately 90%), and then Fe(III) (approximately 52%), as shown in Figure 8a.



Scheme 1. Flow chart summarizing the separation and recovery process of Co(II) and Mn(II) from a spent LIB leachate. $V_{aq}/V_{IL} = 2$, [HCl]_{aq} = 5 mol L⁻¹.



Figure 8. Analysis of the extraction process of spent LIB leachate, $V_{aq}/V_{IL} = 2$. (a) Initial extraction process. [HCl]_{aq} = 5 mol L⁻¹, time = 3 h. (b) Fe(III) scrubbing. [Na₂SO₃] = 1.0 mol L⁻¹, temperature = 30°C, time = 30 min. (c) Mn(II) stripping. [Na₂SO₄] = 0.5 mol L⁻¹. (d) Co(II) stripping. Stripping solution = water. (e) Cu(II) washing. [H₂SO₄] = 1 mol L⁻¹.

Then, the metal-loaded IL was subjected to scrubbing with 1 ml L⁻¹ Na₂SO₃ for 30 min at 30°C, in which was able to almost completely removed Fe(III) from the loaded IL, while leaving Co(II), Mn(II), and Cu(II) in the IL (Figure 8b). Then, recovery of Mn(II) from the IL was done by using 0.5 mol L⁻¹ Na₂SO₄ (Figure 8c). However, this was also accompanied by the stripping of a considerable quantity of Fe(III). Then, the stripping solution containing Mn(II) was purified from Fe(II) through precipitation using CaCO₃ at pH 2.5 and 85°C for 2 h, which achieved almost quantitative removal of Fe(II) from the stripping solution containing Mn(II) recovery was then conducted with water. Co(II) was efficiently recovered and because a small amount of Mn(II) remained in the IL, the purity of Co(II) in the stripping solution was high (98%) (Figure 8d). Lastly, Cu(II) was washed from the loaded IL with 1 mol L⁻¹ H₂SO₄, which achieved almost quantitative removal of Co(II) in the stripping solution was then subjected to precipitation with CaCO₃, which left Co(II) in the stripping phase (1 mol L⁻¹ H₂SO₄).

4. Conclusion

The novel IL $P_{8,8,8,12}R2POO$ was synthesized with a purity of 98%. This hydrophobic IL was found to be an effective extractant for Co(II) and Mn(II) from chloride medium. $P_{8,8,8,12}R2POO$ effectively extracted Co(II) and Mn(II) at high levels of 99% and 98%, respectively, regardless of the HCl concentration of the medium. The metal extraction to the IL phase proceeded through an anion-exchange mechanism. In the presence of other metals, $P_{8,8,8,12}R_2POO$ also extracted substantial amounts of Fe(III) and Cu(II). Effective separation of Co(II) and Mn(II) and the removal of impurities such as Fe(III) and Cu(II) were achieved by scrubbing, washing, and precipitation steps. $P_{8,8,8,12}R_2POO$ shows potential for use as an extraction solvent for Co(II) and Mn(II) from spent LIBs. Our results illustrate that the performance of ILs for target metals can be readily tuned by changing their molecular structure.

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References

- 1) S. Castillo, F. Ansart, C. Laberty-Robert, J. Portal, J. Power Sources, 112, 247-254 (2002).
- 2) B. Scrosati, J. Garche, J. Power Sources, 195, 2419-2430 (2010).
- 3) A. Chagnes, B. Pospiech, J. Chem. Technol. Biotechnol., 88, 1191-1199 (2013).
- 4) T. Georgi-Maschler, B. Friedrich, R. Weyhe, H. Heegn, M. Rutz, J. Power Sources, 207, 173-182 (2012).
- 5) N. B. Devi, K. C. Nathsarma, V. Chakravortty, *Hydrometallurgy*, 49, 47-61 (1998).
- 6) I. Y. Fleitlikh, G. L. Pashkov, N. A. Grigorieva, L. K. Nikiforova, M. A. Pleshkov, Y. M. Shneerson, *Solvent Extr. Ion Exch.*, **29**, 782-799 (2011).
- L. Luo, J. H. Wei, G. Y. Wu, F. Toyohisa, S. Atsushi, *Trans. Nonferrous Met. Soc. China (English ed.)*, 16, 687-692 (2006).
- 8) P. Rybka, M. Regel-Rosocka, Sep. Sci. Technol., 47, 1296-1302 (2012).
- 9) S. Wellens, B. Thijs, K. Binnemans, Green Chem., 14, 1657-1665 (2012).
- 10) D. E. Chaverra, O. J. Restrepo-Baena, M. C. Ruiz, ACS Omega, 5, 5643-5650 (2020).
- 11) P. D. Ola, Y. Kurobe, M. Matsumoto, Chem. Eng. Trans., 57, 1135-1140 (2017).
- 12) P. D. Ola, M. Matsumoto, K. Kondo, Desalin. Water Treat., 75, 325-330 (2017).
- 13) S. Wellens, B. Thijs, C. Möller, K. Binnemans, Phys. Chem. Chem. Phys., 15, 9663-9669 (2013).
- R. Torkaman, M. Asadollahzadeh, M. Torab-Mostaedi, M. G. Maragheh, Sep. Purif. Technol., 186, 318-325 (2017).
- 15) C. J. Bradaric, A. Downard, C. Kennedy, A. J. Robertson, Y. Zhou, Green Chem., 5, 143-152 (2003).
- 16) A. T. N. Fajar, F. Kubota, M. L. Firmansyah, M. Goto, Ind. Eng. Chem. Res., 58, 22334-22342 (2019).
- 17) M. L. Firmansyah, A. T. N. Fajar, W. Yoshida, T. Hanada, M. Goto, J. Chem. Eng. Jpn., 53, 1-8 (2020).
- 18) S. A. Dharaskar, K. L. Wasewar, M. N. Varma, D. Z. Shende, K. K. Tadi, C. K. Yoo, *Fuel Process. Technol.*, **123**, 1-10 (2014).
- N. Liu, R. A. Senthil, Y. Man, J. Pan, X. Jin, Y. Sun, X. Liu, *Int. J. Electrochem. Sci.*, 13, 11568-11579 (2018).
- 20) C. M. Mirea, I. Diaconu, E. A. Şerban, E. Ruse, UPB Sci. Bull., Ser. B, 77, 103-114 (2015).
- 21) M. L. Firmansyah, F. Kubota, W. Yoshida, M. Goto, Ind. Eng. Chem. Res., 58, 3845-3852 (2019).
- 22) G. Adamová, R. L. Gardas, L. P. N. Rebelo, A. J. Robertson, K. R. Seddon, *Dalton Trans.*, 40, 12750-12764 (2011).
- 23) D. Cholico-Gonzalez, A. Chagnes, G. Cote, M. Avila-Rodriguez, J. Mol. Liq., 209, 203-208 (2015).
- 24) J. Sun, P. C. Howlett, D. R. MacFarlane, J. Lin, M. Forsyth, *Electrochim. Acta*, 54, 254-260 (2008).
- 25) S. W. Ju, N. Zhang, Z. Q. Wang, R. T. Zhang, D. W. Zeng, X. P. Shao, K. Lin, *Chin. J. Chem. Phys.*, 30, 657-663 (2017).
- 26) H. R. Ong, M. M. R. Khan, R. Ramli, Y. Du, S. Xi, R. M. Yunus, RSC Adv., 5, 24544-24549 (2015).

- 27) L. Cui, Z. Zhao, Y. Guo, F. Cheng, Sep. Purif. Technol., 199, 304-310 (2018).
- 28) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, J. Am. Chem. Soc., 83, 4690-4699 (1961).
- 29) I. Van de Voorde, L. Pinoy, E. Courtijn, F. Verpoort, Solvent Extr. Ion Exch., 24, 893-914 (2006).
- 30) N. B. Devi, K. C. Nathsarma, V. Chakravortty, Hydrometallurgy, 34, 331-342 (1994).
- 31) M. S. Lee, M. Filiz, Mater. Trans., 49, 2642-2647 (2008).
- 32) L. Cui, F. Cheng, J. Zhou, Ind. Eng. Chem. Res., 54, 7534-7542 (2015).
- 33) B. Pospiech, J. Solution Chem., 44, 2431-2447 (2015).
- 34) B. Pospiech, Hydrometallurgy, 154, 88-94 (2015).
- 35) K. Xiang, H. Liu, B. Yang, C. Zhang, S. Yang, Z. Liu, C. Liu, X. Xie, L. Chai, X. Min, *Environ. Sci. Pollut. Res.*, 23, 8113-8119 (2016).
- 36) M. L. Firmansyah, F. Kubota, W. Yoshida, M. Goto, Ind. Eng. Chem. Res., 58, 3845-3852 (2019).
- 37) C. Vakh, E. Freze, A. Pochivalov, E. Evdokimova, M. Kamencev, L. Moskvin, A. Bulatov, J. *Pharmacol. Toxicol. Methods*, **73**, 56-62 (2015).
- 38) X. Li, Z. Lei, J. Qu, Z. Li, Q. Zhang, Sep. Sci. Technol., 51, 2772-2779 (2016).
- 39) B. Onghena, S. Valgaeren, T. Vander Hoogerstraete, K. Binnemans, RSC Adv., 7, 35992-35999 (2017).
- 40) N. M. Barrera, J. L. McCarty, V. Dragojlovic, Chem. Educ., 7, 142-145 (2002).