



## Synergistic extraction and separation of valuable metals from waste cathodic material of lithium ion batteries using Cyanex272 and PC-88A

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### ABSTRACT

Synergistic extraction and separation of cobalt (II), manganese (II) and lithium (I) from simulated sulfuric acid leaching of waste cathodic materials, using mixture of bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272, HA) and 2-ethylhexyl phosphinic acid mono-2-ethylhexyl ester (PC-88A, HL) in *n*-heptane have been investigated. Extraction of  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Li}^+$  follows the order as:  $\text{Mn} > \text{Co} \gg \text{Li}$  independent on taking the single Cyanex272 or PC-88A or their mixtures as extractants. The possible extracted species are  $\text{MA}_2\cdot 3\text{HA}$  or  $\text{M}(\text{OH})\text{A}\cdot 3\text{HA}$  for single extractant (PC-88A and Cyanex272 are same) and  $\text{MH}_3\text{A}_2\text{L}_3$  for the mixed-extractant ( $\text{M}^{2+}$  is  $\text{Co}^{2+}$  or  $\text{Mn}^{2+}$ ). Cyanex272 + PC-88A shows an evident synergistic effect. The maximum synergistic enhancement coefficients,  $R_{\text{max}}$ , are obtained for  $\text{Co}^{2+}$  (3.48) and  $\text{Mn}^{2+}$  (4.12) at the mole fraction  $X_{\text{Cyanex272}}$  around 0.6 at  $\text{pH}_e$  4.95. Furthermore, the separation factors ( $\text{Mn}/\text{Co}$ ) have been improved around two orders of magnitude upon adding EDTA into the synergistic extraction system. The entire stripping of Co and Mn can be achieved in one single stage when the concentration of hydrochloric acid or sulfuric acid is larger than 0.04 M or 0.01 M, respectively. Finally, a feasible process for recycling of spent cathodic materials of LIBs was proposed with industrial applications prospects.

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### 1. Introduction

Lithium ion batteries (LIBs) are widely used as electrochemical power sources in popular portable electronic devices such as cellular phones, laptop computers and camcorders. On the one hand, there are more and more electric vehicles such as bicycle and hybrid cars powered by LIBs. Nowadays, with increasing electronic equipments and electric vehicles, the amount of LIBs increases drastically. If we assume that the average lifetime of LIBs for portable electronic devices and electric vehicles are 2–3 years and 5–8 years, respectively, we can imagine how huge for this kind of electronic trash. On the other hand, in order to meet the market demand, the production of lithium ion batteries has to be scaled up, which means that more and more battery scraps are generated during manufacture. This work will aim at the recovery of valuable metals from cathodic scraps produced by LIBs' plants or from the used LIBs, which should be recycled not only for environmental reasons, but also as an important secondary source of metals, sometimes even higher grade than those found in natural ores. In addition, some metals are quite expensive such as cobalt and lithium. Lithium is being regarded as 'gold' in 21st century [1].

The cathode for LIBs is prepared by mixing the active materials with the conductive agent (carbon black) and a polymeric binder, and then pasting the mixture onto aluminum current collector. At the moment, almost all of commercialized cathodic active materials of LIBs include  $\text{LiCoO}_2$ ,  $\text{LiMn}_x\text{O}_y$  and  $\text{LiMPO}_4$  ( $\text{M} = \text{Fe}, \text{Mn}$ ) due to their favorable performances [2,3]. The waste cathodic materials of LIBs were usually leached by sulfuric acid and hydrogen peroxide [4,5]. Thus, cobalt, manganese, lithium, aluminum and iron were the main species in the residue. After the leaching step, most of aluminum and iron can be removed from the leach liquor by introducing a selective precipitation step prior to the liquid–liquid extraction step [6]. Therefore, the studies of extraction and separation of cobalt, manganese and lithium are significant for the recycling of the waste cathodic materials of LIBs.

The availability and use of organophosphorus extractants has made the separation of Mn from Co feasible, and Hoh et al. [7] have reported that the separation between Mn and Co can be achieved by di-2-ethylhexyl phosphoric acid (D2EHPA). Devi et al. [8] also proved that NaD2EHPA was the most suitable extractant for this separation compared with sodium salts of PC-88A and Cyanex272. However, with the development of organophosphorus extractants, D2EHPA is gradually substituted by PC-88A and Cyanex272 since its physical–chemical phenomena are not good enough, such as easy emulsification and more loss based on relatively large solubility in the aqueous phase. After D2EHPA, PC-88A gets more and

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more researched and applied in the separation of Co from Li [9], and Co from Ni [10]. Zhang et al. [9] reported that LiCoO<sub>2</sub> active material was peeled off from aluminum substrate and leached with hydrochloric acid, and finally cobalt was recovered by solvent extraction with PC-88A, while lithium was precipitated as carbonate. In recent years, bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) attracts much attention due to a high selectivity for the separation of cobalt (II) from nickel (II) [4]. The separation of Co (II) and Li (I) using Cyanex272 from both synthetic solutions and a leach liquor of cathodic waste material has been reported in the earlier studies [11,12]. Although Cyanex272 offers good separation ability sometimes [13], the organic phase caused an increase in viscosity, a subsequent decrease in mass transfer rates. In addition, the cost of Cyanex272 is relatively high, which makes high initial plant investments.

Instead of using a single extractant, mixtures of extractants can give rise to synergistic effects and better selectivities of metal extraction/separation in solvent extraction processes. Devi et al. [14] studied the extracton of Co with D2EHPA, PC-88A, Cyanex272 and their mixtures, and found that Cyanex-272 was the best synergist. Recently, Swain et al. [15] used Cyanex272 as synergist to separate Co from Li for the recycling of LIB industry wastes. Pranolò et al. [16] studied a mixed solvent extractant system to obtain the pure cobalt and lithium products from spent lithium-ion battery leach solutions. However, the reported studies have largely focused on cobalt and lithium separation or cobalt and nickel separation, and have not referred to the separation of manganese, cobalt and lithium. In addition, few papers have reported about the systematic comparative studies of the extraction and separation of cobalt (II) and manganese (II) by Cyanex272, PC-88A and their mixtures.

Here, for the commercial application purposes, we consider the combination of PC-88A and Cyanex272 as synergistic extractants for the extraction and separation of Co, Mn and Li for the purpose of recycling active cathodic materials of spent LIBs.

In the present work, special attention was given to characterization of mixed extractant systems (Cyanex272 + PC-88A) selective towards Mn over Co from sulfate medium because Li keeps almost no extraction in this multi-metal complicated system under the current experimental conditions. Extraction mechanism, pH isotherms, separation and stripping properties have been investigated in detail as a comparison of the mixture of Cyanex272 + PC-88A with the single Cyanex272 and PC-88A. Based on this, a feasible flowsheet process for the extraction and separation of cobalt, manganese and lithium for recycling of spent cathodic materials of LIBs was proposed with possible scale-up for commercial application.

## 2. Experimental

### 2.1. Reagent

PC-88A (purity >98%) and Cyanex272 (purity >85%) were kindly supplied by Shanghai Organic Chemistry Institute and CYTEC Canada Inc., respectively, and they were used without purification. The extractants were dissolved in heptane to the required concentration. Stock solutions of metal ions were prepared by dissolving their sulfate with a purity >99% in sulfuric acid. All other reagents employed in this work were of analytical grade.

### 2.2. Apparatus

A HANNA pH211 digital pH meter (Italy) was used for pH measurements. OPTIMA 7000DV inductively coupled plasma-optical emission spectrometer (ICP-OES, PekinElmer, USA) was used for

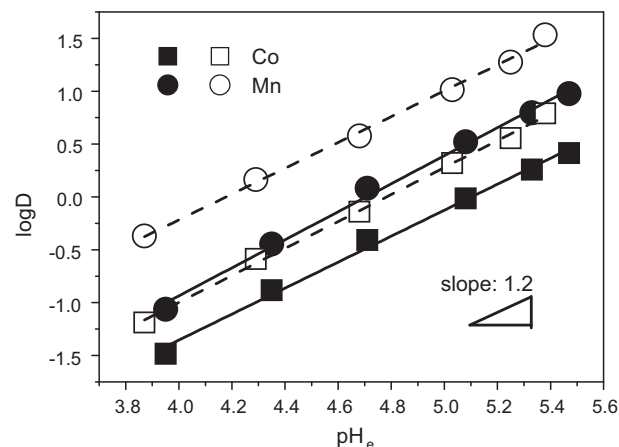


Fig. 1. Effect of pH<sub>e</sub> on the extraction of Co<sup>2+</sup> and Mn<sup>2+</sup> with Cyanex272 (solid) or PC-88A (open) at concentrations of 0.10 M extractant. [M<sup>2+</sup>] = 4 × 10<sup>-3</sup> M.

measurements of individual concentration of mixed metal ions solution.

### 2.3. Extraction and analytical procedure

Liquid–liquid extraction was performed by shaking an equal volume (10 mL) of aqueous and organic phases in centrifuge tubes using a mechanical shaker for 30 min at 303 ± 1 K although it was demonstrated that the extraction equilibrium was achieved within 5 min. After phase separation, the concentration of metal ions in the aqueous phase was determined by ICP-OES. The concentration of metal ions in the organic phase was determined by mass balance. The concentration of the extracted metal ions was fixed at 4 × 10<sup>-3</sup> M for all the extraction experiments. The distribution coefficient (*D*) was taken as the ratio of the concentration of metal ions in the organic phase to that in the aqueous phase. pH<sub>1/2</sub> means the equilibrium pH value for the extraction of one metal ion when *D* equals to 1. Normally ΔpH<sub>1/2</sub> (pH<sub>1/2(A)</sub> – pH<sub>1/2(B)</sub>) can be used to explain the separation possibility of one metal over the other one.

## 3. Results and discussion

Under the present experimental conditions, data show that lithium remains almost unextracted when Li<sup>+</sup>, Co<sup>2+</sup> and Mn<sup>2+</sup> coexist in the same system. Therefore, as far as extraction mechanism is concerned, we only focused on the distribution behavior of cobalt and manganese in the following discussion. For elucidating the extraction mechanism with Cyanex272 or/and PC-88A, the conventional slope analysis method has been introduced.

### 3.1. Extraction Co<sup>2+</sup> and Mn<sup>2+</sup> with Cyanex272 and PC-88A alone

As shown in Fig. 1, for the metal ions Co<sup>2+</sup> and Mn<sup>2+</sup>, the plots of log *D* vs. pH<sub>e</sub> gave straight lines with a slope of about 1.0 for both Cyanex272 and PC-88A, suggesting the totally released protons included one molecule of H<sup>+</sup> for Cyanex272 or PC-88A during extraction. Similarly, the Cyanex272 or PC-88A concentration effect on the Co<sup>2+</sup> and Mn<sup>2+</sup> extraction was also plotted. As shown in Fig. 2, the plots of log *D*–pH against log[HA]<sub>o</sub> or log[HL]<sub>o</sub> were straight line with a slope about 2 both for Cyanex272 and PC-88A, which is indicative of two molecules of extractant involved in the extraction reaction whether for Cyanex272 or PC-88A. According to charge balance, M<sup>2+</sup> may be also combined with SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup> or anion of the acidic extractant A<sup>-</sup> or L<sup>-</sup>. Experiments have confirmed that none of SO<sub>4</sub><sup>2-</sup> was detected from the hydrochloric acid stripping solution of the organic phase loaded with Mn and Co. Since

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