

Binary Solvent System for Extraction of Cathode Material From Spent Li-ion Batteries

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Abstract

An effective method of water and carbon tetrachloride (CCl_4) system has been studied to recover metals ions from spent Li-ion battery cathode materials. Leaching of HCl and $\text{HCl} + \text{H}_2\text{O}_2$ has been applied individually to dissolve the collected cathode materials. Metal ions dissolved in HCl and $\text{HCl} + \text{H}_2\text{O}_2$ has been treated separately with a solution of hexadecyl amine in CCl_4 . The formation of metal ions-hexadecyl amine complex has been confirmed from UV-visible spectroscopy. Recovery of metals from the produced complex has been carried out via filtration and calcination. The calcined materials has been characterized using Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and powder x-ray diffraction (XRD).

Keywords: Spent Li-ion battery, solvent extraction, hexadecyl amine.

I. Introduction

Battery technologies have paved their applications into personal, households and industries as an energy sources¹⁻³. It can store and release energy to fulfill the purposes of heat, power, transportation on the basis of requirement⁴. Storing of energy in battery used to happen via chemical reaction of atoms, molecules and ions⁵⁻⁷. The chemical compounds stored energy is then converted to electric energy. Those are mainly electrode materials of metals. Over the last few years, the continuous advancement of information technology, energy storage systems, consumer electronics and electrically powered vehicles have been placed huge demands on electrode materials⁸⁻⁹. The growing prevalence standpoint of battery in various electronic devices and vehicles has been seen everywhere¹⁰. With the steady population increase, it is expected to raise the demand further in the future¹¹. As a result, the number of spent electrode materials will be increased dramatically¹². The direct exposure of them to the environments will raise contamination questions and toxicity issues¹³⁻¹⁵. It is therefore urgent and valuable to address the recycling processes of used battery electrode materials before exposure to environments. The recycling processes of the used battery electrode materials have been considered as a major tool to reduce the hazardous nature of discarded battery¹⁶⁻¹⁸. Accordingly, many researches focused to extract those valuable metals from the spent electrode materials. In this article, I have been described a binary solvent system to extract those valuable metals from the spent lithium ion batteries (LIBs).

II. Experiment

Reagents

The chemicals used in this study were laboratory grade and used without further purification. Millipore deionized water

used for the preparation of leaching solution. Spent LIBs (SAMSUNG, EB425161LU, 1500mAh) were taken from shops.

Pretreatment of Spent LIB Cathode

The collected spent LIBs were discharged using the discharge profile of Biologic sp 300 potentiostat. Manual methods have been done to dismantle the spent LIBs. At first the battery cover has been removed with pincers and knives. Then, cathode material pasted aluminum foil was cut into small pieces. This paste has been scratched with spatula and stored in a vial.

Acid Leaching and Amount of Reagent

HCl and $\text{HCl} + \text{H}_2\text{O}_2$ have been used as a leaching agent to decompose LiMO_2 ($M = \text{Co/Ni/Mn}$) into ions in the aqueous solution. The amounts of other reagents for the designed experiments are listed in Table 1.

Table 1. Information of the reagents used in this experiment

Experiment	Cathode materials (gm)	Conc. HCl (ml)	Distilled H_2O (ml)	Hexadecyl amine (gm)	CCl_4 (gm)
1	3	10	50	0.5	200
2	3	10	50	1.0	200
3	3	10	50	1.5	200
4	3	10	50	2.0	200

Extraction of Cobalt from Aqueous Solution Using Hexadecyl Amine

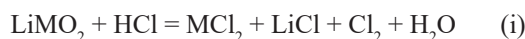
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Measured amount of the separated cathode materials were put in a beaker. Hydrochloric acid was used to dissolve them. Then, the solution was diluted to 50 mL by adding distilled water. The solution was shaken about 2 hours for hydration of the present metal ions of the cathode materials. At this stage the pH of the solution was measured. Then 1 gm hexadecyl amine was added into a

separate beaker containing specific amount of carbon tetrachloride. It was then stirred 30 mins to disperse the added hexadecyl amine into the organic phase. This solution was then poured into the aqueous solution and stirred for 24 hours. The M^{n+} ions from the aqueous solution have been transferred into the organic phase and precipitated.

III. Results and Discussion

The electrode materials of spent LIBs are LiCoO_2 , LiMnO_2 , LiNiO_2 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, graphite and conductive carbon materials. The extraction of metals such as Ni, Mn and Co from the electrode materials and their characterization has been the focus of this research work. Acid leaching of HCl and $\text{HCl} + \text{H}_2\text{O}_2$ aqueous solution have been used separately to remove carbon black, electrolyte and other materials from the mixed electrode materials. The leaching reaction of LiMO_2 can be written as follows:



Metals contained aqueous has been then mixed with non-aqueous solution of amine chelating agents (Q). Metals have been precipitated in the non-aqueous phase with the addition of chelating agents. The precipitation has been collected and subsequently calcined to transform them into their respective oxides. It can be represented as follows:



Those oxides have been undergone a series of characterization. The results of those characterization and respective discussion have been presented in this chapter.

Selection of Organic Solvent to Form Biphasic System with Acid Leaching

A wide variety of organic solvents such as hexane, acetone, ethanol, methanol and carbon tetrachloride were searched for investigating solubility of chelating agent's hexadecyl amine. The chelating agent has been found insoluble in hexane and acetone. It has been found soluble in polar solvents such as ethanol, methanol and carbon tetrachloride dissolved hexadecyl amine. Then, the aforementioned solvents have been checked individually about their ability of forming biphasic system with the acid leaching solution. The carbon tetrachloride has been found to form biphasic system. Biphasic system of carbon tetrachloride-water has been then

used for the extraction of metals from waste Li-ion battery. Afterwards, the complex formation reactions between metal ions and hexadecyl amine have been confirmed from the investigation of the UV-visible spectrum of the following systems (Table 2).

Table 2. Various system of investigating the complex formation reaction.

No	System
1	Acid leaching solution
2	Acid leaching solution + Hexadecyl amine
3	Acid leaching solution + Hexadecyl amine + Carbon tetrachloride
4	Hexadecyl amine + Carbon tetrachloride

The corresponding UV-visible spectra of these systems are depicted in figure 1. Spectra of Figure 1 (a) and Figure 1(b) have revealed cobalt ions UV-visible signal at 520 nm. An examination of UV-visible spectra of Figure 1 (c) and Figure 1 (d) have been supported the formation of cobalt-hexylamine complex in CCl_4 .

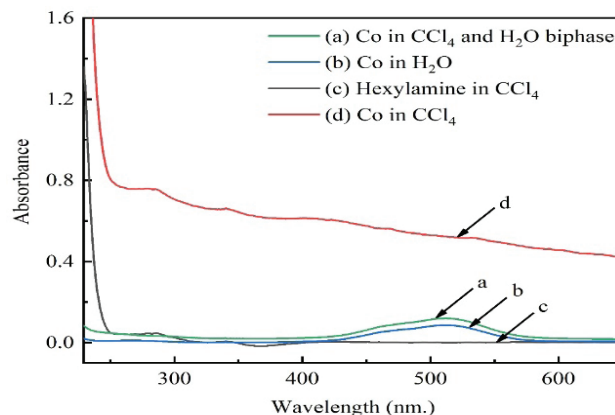


Fig. 1. UV-visible spectrum of the acid leached solution in several solvent system.

UV-visible spectrum of hexylamine in CCl_4 as shown in Figure 1 (c) basically has no peaks. Metals ions in system 3 have extracted into the organic phase. The measurement of UV-visible spectrum of the cobalt ions migrated organic phase indicates the presence of peak signals at 280, 340 and 420 nm. The appearance of peaks this position confirmed the formation cobalt-amine complexes in CCl_4 . Then hexylamine dissolved CCl_4 system has been used as organic phase throughout this study for the extraction of metal ions from the acid leached solution.

Leaching Efficiency

Metal oxides from cathode part of spent LIBs have been extracted under two leaching process. In one process metal oxides have been extracted using HCl as leaching agents. Extraction of metals has been also examined with $\text{HCl} + \text{H}_2\text{O}_2$

solution. The optimum conditions and leaching efficiency of these processes are summarized in table 3.

Table 3. Experimental condition and leaching efficiency of the studied processes.

Experimental condition		Leaching with HCl	Leaching with HCl+H ₂ O ₂
1	Time	30 min	30 min
	Temperature	25 °C	25 °C
	Volume of 1 M HCl	5 mL	10 mL
	Volume of H ₂ O ₂	0 mL	3 mL
	Efficiency	0.42%	13.02%
2	Time	2 hours	2 hours
	Temperature	25 °C	25 °C
	Volume of 1 M HCl	10 mL	10 mL
	Volume of H ₂ O ₂	0 mL	3 mL
	Efficiency	5.52%	15.32%
3	Time	24 hours	24 hours
	Temperature	25 °C	25 °C
	Volume of 1 M HCl	10 mL	10 mL
	Volume of H ₂ O ₂	0 mL	3 mL
	Efficiency	3.88%	16.65%

FTIR Spectrum of the Extracted Metal Oxides

The FTIR spectrums of HCl and HCl+H₂O₂ leaching agent's extracted metal oxides are shown in Figure 2 (a) and Figure 2 (b), respectively. Several significant absorption signals can be seen from the FTIR spectrum. Broad absorption bands in the region of 400-700 cm⁻¹ are attributed for the vibration mode of extracted several metal oxides¹⁹⁻²¹.

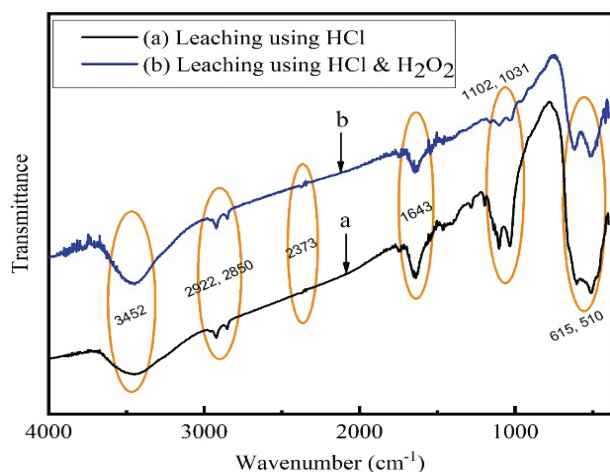


Fig. 2. FTIR spectrum of extracted compound in different leaching conditions.

Two peaks located at 510 cm⁻¹ and 615 cm⁻¹ are characteristic

for the Mn–O stretching modes of tetrahedral and octahedral coordination, respectively²². Two peaks at 510 cm⁻¹ and 615 cm⁻¹ are characteristics for the stretching modes of Co³⁺/Mn³⁺ octahedral site and Co²⁺ tetrahedral site vibrations in the Co₃O₄ spinel lattice, respectively²³. These results of FTIR spectrum are closely related to the reported value found in literature¹⁹⁻²³. A broad peak ~3452 cm⁻¹ assigned to the O–H stretching vibration of water molecules. The peaks around 2373 cm⁻¹ is responsible for the asymmetric vibration (C=O) of CO₂ which might be absorbed from air during heat treatment of metal oxides²³. Appearance of peak around 1643 cm⁻¹ corresponds to the bending vibration of water molecules. Peaks at 1102 cm⁻¹ and 1031 cm⁻¹ are assigned for the symmetric and asymmetric stretching vibrations of CO₂ molecule²¹.

FESEM Images of the Extracted Metal Oxides

Figure 3 (a) and 3 (b) show the differences offield emission scanning electron micrographs of HCl and HCl+H₂O₂ leaching agent's extracted metal oxides morphology. It is seen from the images that the particles size of HCl+H₂O₂ leached metal oxides (Figure 3 (b)) are larger than the leaching with no addition of H₂O₂ (Figure 3 (a)). The larger particle of HCl+H₂O₂ leaching may have been resulted due to the high agglomeration rate compared to the leaching without the addition of H₂O₂.

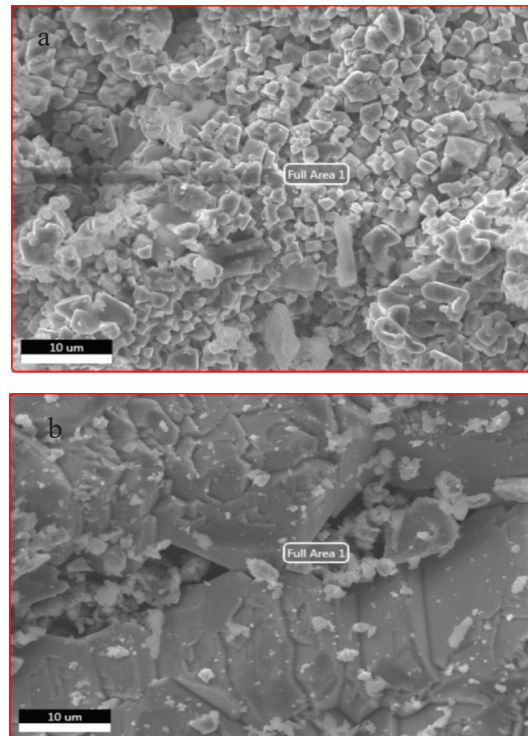


Fig. 3. FESEM image of recovered cobalt using (a) HCl as leaching agent (b) H₂O₂ and HCl as leaching agent.

EDS Spectrum of the Extracted Materials

The elemental distributions of HCl and HCl + H₂O₂ leachant assisted metal oxides have been represented in Figure 4 (a) and Figure 4 (b) respectively. In case of HCl leaching the EDS spectrum shows the presence of Mn, Ni, Co and O element. Observation of EDS spectrum of HCl + H₂O₂ leachant assisted metal oxides has been demonstrated Mn, Co and O element presence. Table 4 shows the elemental composition of the extracted metal oxides. Ni is present as the main element in case of HCl leaching of cathode materials (41.56%), followed by Mn (21.17%), Co (18.74%) and O (18.53%).

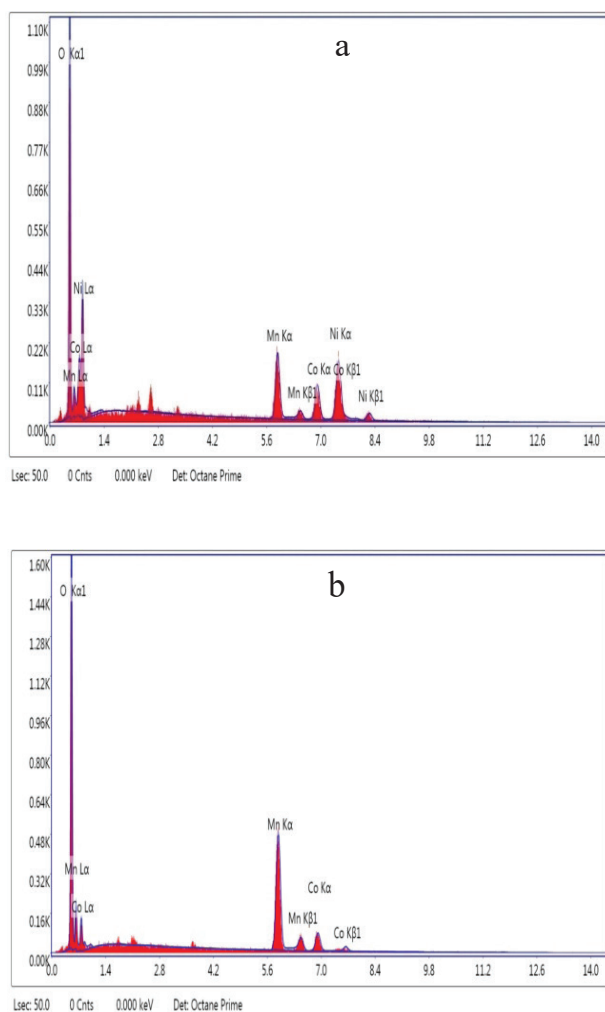


Fig. 4. EDS spectrum of the extracted metal oxides using (a) HCl (b) HCl+ H₂O₂ as leaching agents.

The recovery pattern of the metals has been significantly changed with the addition of H₂O₂. In that case Ni lost from the residue and Mn become the major element (59.79%), followed by O (24.69%) and Co (15.52%). The use of H₂O₂ as reducing agent may have been dissolved Ni into the solution.

Table 4. Percentage of elemental distribution of the extracted metal oxides from EDS.

Leaching using HCl			Leaching using H ₂ O ₂ and HCl		
Element	Weight %	Atomic %	Element	Weight %	Atomic %
O K	18.53	45.07	O K	24.69	53.30
Mn K	21.17	15.00	Mn K	59.79	37.60
Co K	18.74	12.38	Co K	15.52	9.10
Ni K	41.56	27.55			

XRD Spectrum of the Extracted Materials

Figure 5 (a) and Figure 5 (b) represent the XRD data of HCl and HCl + H₂O₂ leachant assisted metal oxides. The recorded XRD spectrum consists of major diffraction peaks at 18°, 33°, 36°, 38°, 44°, 48°, 58°, 64° and 67°.

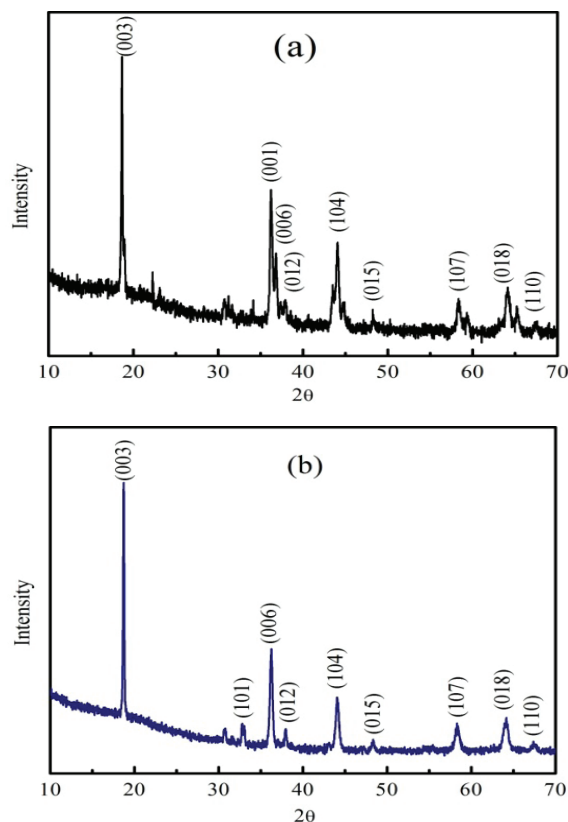


Fig. 5. XRD spectrum of the extracted materials using (a) HCl (b) HCl + H₂O₂ as leaching agents.

All of the peaks have been matched well with the XRD pattern of LiNi_xCo_yMn_zO₂²⁴. Thus, the extracted metals have been formed layered structured with R3m space group. In addition, the splitting of peaks in the 2θ region at 18 and 43 also indicates the formation of layer structure of NCM. The knowledge of crystallographic information confirmed the formation of NCM of the extracted metals during calcination

at 700 °C. The appearance of small amount impurities has been also observed in the XRD pattern²⁵. It might have been resulted due to non-stoichiometric distribution of the extracted metals from the spent LIBs.

IV. Conclusion

In this paper we have been developed a noble recycling process of reverse micelle manner to extract valuable metal ions from spent Li-ion batteries. It has been observed that the addition of H₂O₂ with HCl solution increased the leaching efficiency about 6 times because of the conversion of insoluble Co (III) to soluble Co (II). The optimum leaching conditions for cobalt leaching was found to be hydrochloric acid concentration 1 M, temperature 25° C, leaching time 2 hours, hydrogen peroxide 30-35% and stirring speed 350 rpm. Cobalt has been extracted using CCl₄ in water binary solvent system. Hexadecyl amine, soluble in CCl₄ media but insoluble in water media has been found as the suitable amine compound that might extract metals in a reverse micelle manner.

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