Reductive acid leaching of valuable metals from mixed spent lithium-ion batteries

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Abstract

In this work the recovery of valuable metals from spent mixed-type lithium-ion batteries (LIBs) was carried out by sulfuric acid leaching coupled with reducing agents including hydrogen peroxide (H_2O_2), ascorbic acid ($C_6H_8O_6$), and glucose ($C_6H_{12}O_6$). Test specimens comprised the prismatic type and cylindrical 18650-type LIBs. The relevant leaching performance was thus compared. In this work it was found that reductive acid leaching yielded a greater leaching efficiency than that of ordinary acid leaching regardless of the reductant used. In addition, H_2O_2 was found to be the best reductant in this regard, followed by $C_6H_8O_6$ and then $C_6H_{12}O_6$. Under the optimal conditions of reductive acid leaching using H_2SO_4 and H_2O_2 , the following leaching efficiencies were yielded: Li, 100%; Co, 80%, Ni, 100%; Mn, 75%; Al, 82%; and Fe, 71%.

Keywords: Spent lithium-ion batteries, Recovery of metals, Reductive acid leaching

Introduction

Over the past 25 years, varies types of lithium ion batteries (LIB) have been widely used as electrochemical power sources in modern electronic equipment due to their high energy density, high cell voltage, long storage life, low self-discharge rate and wide temperature range of usage [1].

In view of the cathode active material, commonly used LIBs can be divided into the following types: (1) lithium cobalt oxide (LiCoO₂); (2) lithium manganese oxide (LiMn₂O₄); (3) lithium nickel manganese cobalt oxide (LiNiMnCoO₂ or NMC); (4) lithium iron phosphate (LiFePO₄); (5) lithium nickel cobalt aluminum Oxide (LiNiCoAlO₂); and (6) lithium titanate (Li₄Ti₅O₁₂) [2]. In terms of the design shape, currently, there are four configurations of LIBs: cylindrical, coin, prismatic, and thin and flat [3]. Nowadays, LIBs are one of the most commonly used batteries over the world. Their usage is expected to grow further, particularly in automotive sector of electric vehicles. Inevitably, a great quantity of spent LIBs will be generated in years to come [4]. Since LIBs are known to contain valuable metals (e.g., Co, Ni, Li, and Mn), recycling of metallic values from LIBs is preferred to simply dispose of by landfilling or incineration to alleviate or eliminate the adverse impact on the environment [5]. Common technologies

used for the recycling of metals from spent LIBs include pyrometallurgical and hydrometallurgical processes [6,7]. Generally, a pyrometallurgical process involves more energy consumption, high cost, low efficiency, loss of materials and emission of hazardous gases [8-11]. Hence, recent studies have shown that the hydrometallurgical process is preferred to recover valuable metals from spent LIBs [12,13]. Among various hydrometallurgical processes employed for metal recovery from spent LIBs, reductive acid leaching is commonly reported in the literature [4,14,15]. Many researchers also reported that such reductive acid leaching yielded a greater leached metal concentration when it was performed at elevated temperatures in the range of 60-80 °C in comparison with room temperature [8-10,14]. In the literature, several reducing agents have been tested in reductive acid leaching including hydrogen peroxide, sucrose, glucose [16], and cane molasses [17]. To the best knowledge of the present authors, however, no one has compared the performance of at least three reductants in reductive acid leaching for recycling of spent LIBs in a single study. Thus, the goal of this research was set to compare the performance of recovery of valuable metals from spent mixed-type LIBs using H_2SO_4 and various reductants. Reducing agents of interest included hydrogen peroxide (H_2O_2), ascorbic acid ($C_6H_8O_6$), and glucose ($C_6H_{12}O_6$).

Hypothesis and methodology

In this study the spent mixed-type LIBs were collected from a local battery recycling plant. The spent mixed-type LIBs are mainly composed of prismatic type and cylindrical 18650 type. Such collected spent LIBs were subjected to various pre-treatments including battery discharge, crushing, and sieving. The screen undersize (< 0.27 mm fraction), the test specimen of spent LIBs, was then subjected to roasting at 400 $^{\circ}$ C for 1 h before its acid leaching experiments.

A constant pulp density of 3.3 g/L and a constant temperature of 80 °C were maintained in all tests unless otherwise specified. H_2SO_4 (3 M or 4 M in concentration) was used as a leaching agent in the acid leaching process to which a selected reductant was also added. The reducing agents tested included hydrogen peroxide (H_2O_2), ascorbic acid ($C_6H_8O_6$), and glucose ($C_6H_{12}O_6$). Heating was provided by an external thermostatic apparatus. H_2SO_4 solution was first put inside of a reaction vessel and heated at 80°C. Then the desired weight of the test specimen of spent LIBs and the stoichiometric amount of a selected reducing agent were added to the said reaction vessel to perform reductive acid leaching for 1 h.

Presumably, the test specimen of spent LIBs contained $LiCoO_2$, MnO_2 , and Mn_2O_7 . The stoichiometric amounts of various reductants were calculated based on the following reaction equations:

$$LiCoO_2 + 1.5 H_2SO_4 + 1.5 H_2O_2 \rightarrow CoSO_4 + 0.5 Li_2SO_4 + O_2 + 3 H_2O$$
 (1)

 $20 \text{ LiCoO}_2 + 30 \text{ H}_2\text{SO}_4 + \text{C}_6\text{H}_8\text{O}_6 \rightarrow 20 \text{ CoSO}_4 + 10 \text{ Li}_2\text{SO}_4 + 6 \text{ CO}_2 + 34 \text{ H}_2\text{O}$ (2)

$$24 \text{ LiCoO}_2 + 36 \text{ H}_2\text{SO}_4 + \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 24 \text{ CoSO}_4 + 12 \text{ Li}_2\text{SO}_4 + 6 \text{ CO}_2 + 42 \text{ H}_2\text{O}$$
(3)

$$MnO_2 + H_2SO_4 + H_2O_2 \rightarrow MnSO_4 + O_2 + 3 H_2O$$

$$\tag{4}$$

$$10 \text{ MnO}_2 + 10 \text{ H}_2\text{SO}_4 + \text{C}_6\text{H}_8\text{O}_6 \to 10 \text{ MnSO}_4 + 6 \text{ CO}_2 + 14 \text{ H}_2\text{O}$$
(5)

$$12 \text{ MnO}_2 + 12 \text{ H}_2\text{SO}_4 + \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 12 \text{ MnSO}_4 + 6 \text{ CO}_2 + 18 \text{ H}_2\text{O}$$
(6)

$$Mn_2O_7 + 2 H_2SO_4 + 5 H_2O_2 \rightarrow 2 MnSO_4 + 7 O_2 + 5 H_2O$$
(7)

 $2 \text{ Mn}_2\text{O}_7 + 4 \text{ H}_2\text{SO}_4 + \text{C}_6\text{H}_8\text{O}_6 \rightarrow 4 \text{ MnSO}_4 + 6 \text{ CO}_2 + 8 \text{ H}_2\text{O}$ (8)

 $12 \text{ Mn}_2\text{O}_7 + 24 \text{ H}_2\text{SO}_4 + 5 \text{ C}_6\text{H}_{12}\text{O}_6 \rightarrow 24 \text{ MnSO}_4 + 30 \text{ CO}_2 + 54 \text{ H}_2\text{O}$ (9)

Briefly, equations 1-3 are for chemical reduction of $LiCoO_2$, equations 4-6 are for chemical reduction of MnO_2 , and equations 7-9 are for chemical reduction of Mn_2O_7 . **Table 1** presents the test conditions used in this work for various reductive acid leaching. To compare the difference in reductive acid leaching performance due to the change of H_2SO_4 concentration, Test 8 was conducted to meet this need.

Table 1

Test conditions employed in reductive acid leaching of spent mixed-type LIBs using various reductants

Test No.	Temperature	H_2SO_4 conc.	Reductant added	Reductant conc.
	(°C)	(M)		(M)
1	80	3	None (Blank test)	0.0000
2	80	3	Hydrogen peroxide (H ₂ O ₂)	1.8659
3	80	3	Ascorbic acid (C ₆ H ₈ O ₆)	0.1866
4	80	3	Glucose ($C_6H_{12}O_6$)	0.1555
5	80	3	Hydrogen peroxide (H ₂ O ₂)	5.9189
6	80	3	Ascorbic Acid (C ₆ H ₈ O ₆)	0.5919
7	80	3	Glucose ($C_6H_{12}O_6$)	0.4932
8	80	4	Hydrogen peroxide (H ₂ O ₂)	5.9189

All leaching tests were carried out in a temperature controlled three necked flat bottom borosilicate glass flask (500 mL) and a reflux condenser to avoid the loss due to evaporation. At the end of each leaching experiment, the pulp was filtered. The filtrate was used for the analysis of metal concentrations in the leached solution by inductively coupled plasma coupled with atomic emission spectroscopy (ICP-AES). As for the solid residue, it was dried in the convection oven at 70 °C for 24 h, followed by analysis via scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS). In addition, analytical grade reagents and deionized water were used throughout this study.

Results and discussion

At the very early stage of this study, a preliminary test was conducted for acid leaching of the test

specimen of spent LIBs using 3 M H_2SO_4 alone at room temperature. The following leaching efficiencies were obtained: Li, 80%; Co, 38%, Ni, 81%; Mn, 61%; Al, 85%; and Fe, 70%. Among these metals, cobalt (Co), lithium (Li), nickel (Ni), and manganese (Mn) are selected as the target metals for recovery in this study.

Table 2 shows the experimental results for Tests1-8. Test 1 was the blank test without addition of a reductant to the leaching system performed at 80 °C. The following leaching efficiencies were obtained: Li, 86%; Co, 27%, Ni, 81%; Mn, 39%; Al, 100%; and Fe, 86%. As compared with the results of the preliminary acid leaching test, among the target metals the leaching efficiency increased for Li, Ni, Al, and Fe while decreased for Co and Mn. However, when reductive acid leaching was conducted at 80 °C, it yielded a greater leached metal concentration as compared with that of the preliminary test and Test 1. A greater leached metal concentration obtained for reductive acid leaching performed at elevated temperatures might be partly due to the endothermic dissociation of leaching agent rendering a greater acid dissolution and increased reaction rates at elevated temperatures [18]. After a series of tests, the best leaching performance was yielded using 3 M H₂SO₄ and 10 vol% reductant of interest at 80°C. Among three reductants tested, hydrogen peroxide was found to yield the highest leaching efficiency, followed by ascorbic acid $(C_6H_8O_6)$, and glucose $(C_6H_{12}O_6)$ the lowest. It was also noticed from Table 1, a much higher concentration (i.e., 5.92 M) of hydrogen peroxide was used rather than 0.592 M for ascorbic acid and 0.49 M for glucose. This is because that H_2O_2 has the lowest oxidation number among these three reductants tested. Such a high concentration of H_2O_2 had to be added to H_2SO_4 solution so that a high leaching of manganese form Mn_2O_7 could be obtained. Comparing the results of Test 8 and Test 5, it seemed that a higher concentration of H₂SO₄ did not yield an overall higher leaching performance.

Table 2

Reductive acid leaching performance for the specimen of spent LIBs under various operating conditions

Test	Leaching efficiency (%)						
No.	Al	Fe	Ni	Co	Mn	Li	
1	100	86	85	27	39	86	
2	98	61	94	72	59	90	
3	94	84	79	80	56	89	
4	98	59	77	62	55	84	
5	100	73	95	89	100	98	
6	91	68	87	83	100	89	
7	88	64	84	77	100	87	
8	82	71	100	80	75	100	

The results obtained in this work were also compared with that of reported in the literature as presented in Table 3. Overall speaking, the leaching performance resulted from Test 5 and Test 8 is comparable with that of reported by others even though the specimen of spent mixed-type LIBs was tested in this work.

Table 3

Comparison of reported performance for reductive acid leaching of spent lithium-ion batteries

Spent LIBs	Leaching media	Temp., time &	Leaching efficiency	Reference
material		pulp density		
LiCoO ₂	4 M H SO ± 10 vol% H O	85 °C, 120 min,	060/ L; 8-050/ Co	[8]
	$4 \text{ W H}_{2}^{3} \text{ SO}_{4}^{3} + 10 \text{ VOL}_{0}^{3} \text{ H}_{2}^{3} \text{ O}_{2}^{3}$	solid/liquid = 100 g/L	90% LI & 95% CO	
LiCoO ₂	$2 \text{ M} \text{H} \text{SO} \pm 5 \text{ yol}\% \text{H} \text{O}$	75 °C, 60 min,	000/ I; & 700/ Co	[10]
	2 IVI II 30 + 3 VOI / 0 II 0 = 2 2 2	solid/liquid = 100 g/L	99% LI & 70% CO	
LiCoO ₂	$2 \text{ M H}_2 \text{SO}_4 + 6 \text{ vol}\% \text{ H}_2 \text{O}_2$	60 °C, 60 min,	> 00% C-	[14]
		solid/liquid = 100 g/L	> 99% C0	
LiCoO ₂	1.9 M H ₂ SO ₄ +	80 °C, 120 min,	000/ L: & 880/ C-	[16]
	50 g/L $C_{6}H_{12}O_{6}$	solid/liquid = 35 g/L	92% L1 & 88% C0	
LiCoO ₂		70 °C, 20 min,	000/ 1: 0 050/ 0	[18]
	$1.25 \text{ WC}_{6}^{11} \text{ C}_{6}^{10} \text{ C}_{6}^{10}$	solid/liquid = 25 g/L	98% L1 & 95% C0	
Mixed	2 M H SO + 10 wo 10/ H O	80 °C, 60 min,	000/ 1: 0 000/ 0	This study.
	$5 \text{ IVI } \Pi_2 SO_4 + 10 \text{ VOI}\% \Pi_2 O_2$	solid/liquid = 33 g/L	98% L1 & 89% CO	

In this work the solid residues obtained after the said leaching tests were further examined and analyzed by SEM-EDS. As shown in **Fig. 1(a)**, the solid residue obtained from Test 1 (i.e., ordinary acid leaching using H_2SO_4 alone) appeared to in micro chunks. However, the solid residue obtained from Test 5 appeared to become much smaller particles as shown in **Fig. 1(b)**.



Fig. 1. SEM-EDS results for the solid residues obtained from acid leaching tests: (a) Test 1, and (b) Test 5

Also presented in **Fig. 1(a)** and **Fig. 1(b)** are the semi-quantitative contents of major elements analyzed by SEM-EDS. Obviously, the detected contents for Co and Mn in solid residue obtained from Test 5 were lower than that of Test 1. This further confirmed the reductive acid leaching would leach out more metallic values from spent LIBs than the ordinary acid leaching.

Conclusions

This study has again confirmed that reductive acid leaching yielded a much better recovery for valuable metals contained in spent mixed-type lithium-ion batteries (LIBs) as compared with acid leaching by H_2SO_4 alone. When LIBs are leached by an acid, generally, high valent cobalt ions and manganese ions will be generated in the leached solution. As considered in this study, the oxidation number of the selected reducing agent has to be taken into account so that a proper reductant concentration can be used in reductive acid leaching. Like reported by many researchers, H_2O_2 was found to be the best reductant in this work to enhance the leaching of valuable metals from spent mixed-type LIBs. In this study, the test results showed that the optimum leaching efficiencies for cobalt (Co), lithium (Li), nickel (Ni), and manganese (Mn) were 89%, 98%, 95%, and 100%, respectively. To improve the leaching efficiency for Co, further studies are needed.

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