

RECOVERY OF VALUE METALS FROM WASTE LITHIUM ION BATTERIES BY HYDROMETALLURGICAL PROCESS

M. I. Noor¹, A. S. W. Kurny¹, M. R. Qadir², M. A. Gafur² and F. Gulshan^{1*}

¹Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh

²Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh

Abstract: In recent years, the tremendous growth of Lithium Ion Batteries (LIBs) in most of the modern electronic applications has resulted in the generation of a large amount of wastes in the form of waste LIBs. Improper disposal of these batteries may cause hazardous environment. The objective of this study is to recover value metals of Samsung branded smartphone LIBs through hydrometallurgical route. The outer casing was found to be of aluminum alloy. Lithium metal oxides (LiMnO₂ & LiCoO₂) were the most prominent phases in the material pasted on a thin foil of aluminum that formed the cathode. On the other hand, graphite pasted on a thin foil of copper formed the anode. The value metals contained in the leach liquor were recovered by chemical precipitation. Lithium was separated as lithium carbonate and other metals were separated as metal oxides. Separation of copper and graphite was performed by ultra-sonication.

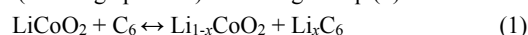
Keywords: Lithium Ion Battery, Hydrometallurgy, LiMnO₂, LiCoO₂, Recovery, Value Metal.

1. INTRODUCTION

Lithium ion batteries (LIBs) are widely used in basic or smartphones, tablets, laptops, cameras and other modern appliances. Due to light weight, high energy and good performances these batteries are increasingly replacing the other types of batteries [1]. In 2013, the worldwide production of LIBs exceeded about 700 million cells and the manufacturing industries earned a revenue of 40 billion US dollar by 2017 [2]. There are 5 billion subscribers of cellphone in 2016 [3]. The life span of a LIB is about 2.5 years. This LIBs will produce waste that's estimated at 300 to 600 MT, with a metal content of 5 to 15 wt. % Co and 2 to 7 wt. % Li [4]. The tremendous growth in the use of LIBs has also resulted in the generation of a large amount of wastes in the form of spent LIBs.

A LIB consists of a cathode, an anode, organic electrolyte, and a separator. The cathode is a thin aluminum foil coated with a mixture of active cathode material, electric conductor, binder and adhesives. Some materials used at the cathode include LiCoO₂, LiNiO₂ and LiMn₂O₄ and the electrolyte is an organic liquid with dissolved substances like LiClO₄, LiBF₄ and LiPF₆ [5–7]. The energy is stored in these batteries through the movement of lithium ions

from the cathode to the anode (charge process of the battery) or vice versa (discharge process) according to Eq. (1):



The anode is a thin copper foil coated with a mixture of carbon graphite, binder and adhesives. The heavy metals, organic chemicals and plastics are in the proportions of 5-20 % cobalt, 5-0% nickel, 5-7% lithium, 15% organic chemicals and 7% plastics, the composition varying slightly with different manufacturers [8]. Spent lithium batteries represent a valuable waste material for the recovery of the metals present (Co, Li, Mn and Ni) or their compounds and recycling of spent batteries may result in economic benefits [9]. However, these batteries contain hazardous materials and improper disposal of these batteries may cause serious environmental problems. Recovery of value metals from LIBs is thus important from the viewpoint of environmental preservation. A lot of research has been done on the development of recycling technologies of LIBs. Most of the proposed processes are based on hydrometallurgical chemistry [10, 11] and both organic and inorganic reagents have been used. Chen *et al.* [12] described a process for the recovery of cobalt oxalate from spent lithium ion batteries. Sun and Qiu [13] used organic oxalate as leachate and precipitant for the recovery of valuable metals, Li *et al.* [14] attempted recovery of cobalt and

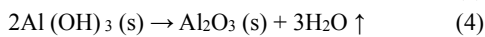
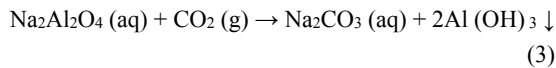
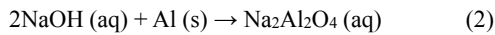
*Corresponding author: Email: fahmidagulshan@mme.buet.ac.bd

lithium using organic citric acid as leachate. Pranalo *et al.* [15] studied recovery of metals from leach solutions with a mixed solvent extraction system. Wang *et al.* [16] developed a process of recovery of value metals through leaching in hydrochloric acid while Zhu *et al.* [17] reported of investigation on the recovery of values through leaching in sulfuric acid.

In this study, hydrochloric acid leaching has been applied to recover cobalt and lithium from active cathode material (LiCoO₂) of Samsung branded smartphone LIBs. Cobalt and lithium dissolved in the hydrochloric acid solution was recovered by chemical precipitation.

2. EXPERIMENTAL

Six Samsung branded (3.8V) Lithium ion batteries were used in this study. Those were collected from local retailers. The potential voltage of all the batteries was 3.8V. The chemical reagents (HCl, NaOH, H₂O₂ and Na₂CO₃) used in this study were of analytical grades (Merck, Germany and Scherlue, Spain). For all purposes de-ionized water (pH 6.5 - 7.5) was used. For completion of discharging, those batteries were brine treated for 24 hours and then dried for another 24 hours. The plastic packages were separated and the casing were cut. The casing was based on Aluminum alloy and that was confirmed by optical emission spectroscopy. The electrodes and separators were separated and dried for 24 hours. Anode (copper foil and graphite layer) were taken to the ultrasonic separator and then dried. This process perfectly separated copper and graphite. On the other hand, Cathode contains aluminum foil and active cathode material like lithium metal oxides (LiMO₂) on it. Al foil is dissolved in 1M NaOH solution, where Al is removed in solution as Na₂Al₂O₄ (Eq. 2). The active materials (LiCoO₂ or LiMnO₂) was found by filtering. It was dried, weighed, powdered and further taken to leaching for elementary separation. On the other hand, the filtrate was treated with dry CO₂ bubbling. Eventually the solution turned white that indicates the formation of Al(OH)₃ precipitation (Eq. 3). It was then filtered and washed and dried at 100°C. The dried Al (OH)₃ was finally burned at 600°C for 4 hours to get Al₂O₃ (Eq. 4).



The active cathode materials was leached in 3M HCl according to solid-liquid ration of 1:20 along with 3.5% H₂O₂ and magnetic stirring at 80C. The leach liquor was treated with 4M NaOH (per 100 ml leach solution) to recover Co as Co(OH)₂ precipitates at pH 11.5-12. The remaining solution was condensed to one third of the initial volume by heating. Later it was treated with 2M Na₂CO₃ and boiled for some time to get a precipitate of Li₂CO₃ as Zabuyelite at 100C.

The phases present in the electrodes were identified by x-ray diffraction analysis (Phase identification data of several intermediate products and raw materials were obtained using

XRD (Brand: Bruker, Model: D8 Advance, Origin: Germany). A flow chart of recovery process is shown in Fig. 1.

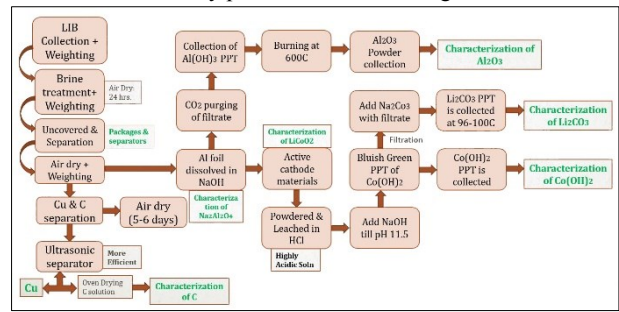


Fig.1 Flow chart for recovery process of LIBs.

3. RESULTS AND DISCUSSIONS

3.1 OES Analysis of Outer Casing

The chemical compositions of external casing of the batteries were determined by optical emission spectroscopy and they were almost same. The average values are listed in Table 1.

Table 1 OES analysis of spent battery casing

Pb	Sn	Al	Cr	Mn	Fe	Ni	Mg	Ti
.013	.24	98.5	.014	.41	.47	.23	.09	.005

3.2 Average Weight Analysis

Weights of batteries and their components were taken at different stages. Total weight of six batteries was 161.69 gm and after brine treatment it was 160.75 gm. From this analysis, it was found that, after slight loss, lithium and cobalt can be recovered by 18.55% as lithium carbonate and cobalt hydroxide. 11% of a battery is aluminum that can be recovered. Weight percentage of value materials are listed in Table 2.

Table 2 Average weight analysis of LIBs

	Pack	Sepa rator	Al ₂ O ₃	A.C. M	Cu	C	Al(OH) ₃	Li ₂ C O ₃	Co(OH) ₂
wt. (gm)	49.7	5.3	3.92	52.5 4	16.5	27.7	13.9 2	5.2	24.8
%wt	30.7	3.3	2.4	32.4 9	10.2	17.1	8.61	3.2	15.3

3.3 Characterization of Graphite

The separation of graphite from copper anode was found more efficient in ultrasonic separator than the air drying process. It took lower time as well. The characterization showed perfect separation of graphite and no sign of copper. Fig. 2, the peak near 27° (marked as ‘C’) is indicating graphite.

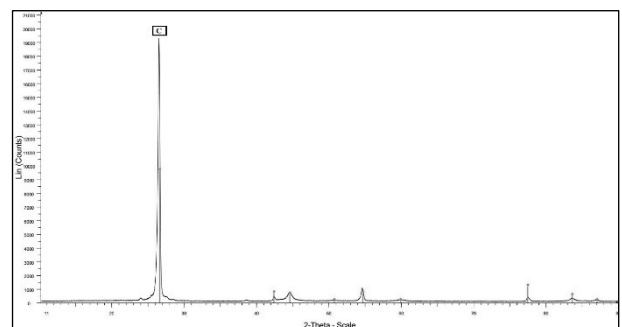


Fig. 2 XRD analysis of graphite powder.

3.4 Characterization of ACM

The composition of the paste on the cathode could not be determined by the X-ray fluorescence analysis as lithium was present as compound. The X-ray diffraction analysis was performed and the active cathode materials (ACM) like Lithium metal oxides (LiMnO_2 , LiCoO_2) were found as the most prominent phases. The result is showed in Fig. 3. For better current density, lithium cobalt oxide should be used. But, in market, as Mn is less costly than Co, the manufacturing companies use Mn mostly. Such cases will decrease the yield of recycled outcome.

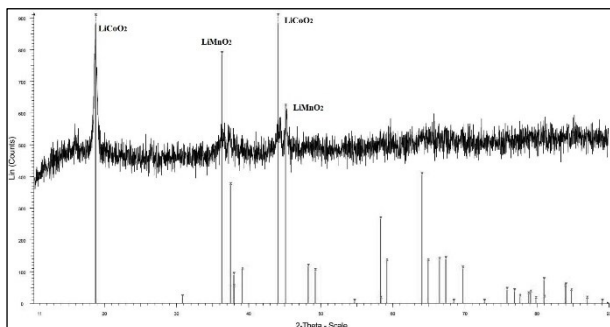


Fig. 3 XRD analysis of Active Cathode Materials.

3.5 Characterization of Aluminum Oxide

Aluminum oxides was found after burning Aluminum Hydroxide at 600°C , then it was characterized. The result is showed in Fig. 4. Proper purging of sodium aluminate solution should be done by CO_2 , otherwise aluminum oxide will be contaminated with impurity like sodium aluminate.

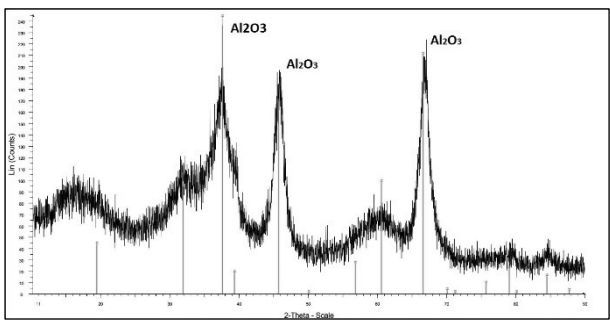


Fig. 4 XRD analysis of Aluminum Oxide.

3.6 Recovery of Value Metals

3.6.1 Recovery of Cobalt

Separation of lithium and cobalt from the leach liquor was effected by employing redox reaction. Small addition of strong base like sodium hydroxide to the leach liquor gave no precipitate, because the leach liquor was excessively acidic. The pH of the solution had to be controlled by the addition of NaOH to effect precipitation of cobalt hydroxide. In this study precipitation of cobalt hydroxide was collected at pH 11.5-12. The precipitation was collected by filtration and then dried. Characterization of cobalt hydroxide was executed and the result is given in Fig. 5. Characterization of hydroxide elements is a complex one because it won't show too many sharp peaks. As

the batteries contained Mn along with Co, CoMn_2O_4 may form due to chemical affinity.

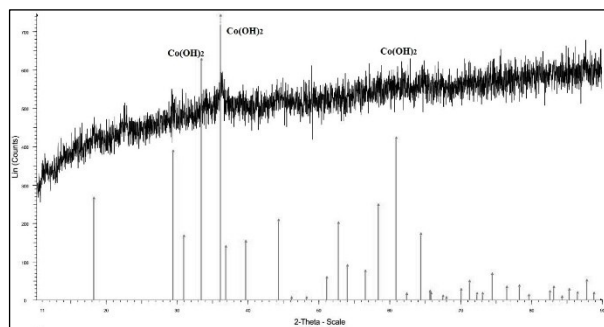


Fig. 5 Characterization of Cobalt Hydroxide.

3.6.2 Recovery of Lithium

After the separation of cobalt as cobalt hydroxide, the leach liquor was concentrated and treated with sodium carbonate at 100°C to precipitate lithium carbonate. After filtration and washing with hot water the solid residue was dried and characterized. The result is showed in Fig. 6. Proper washing with hot water should be provided, otherwise the added Na_2CO_3 solution will restrict the formation of Li_2CO_3 .

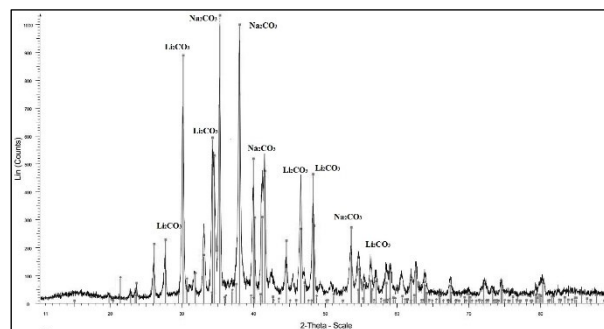


Fig. 6 Characterization of Lithium Carbonate.

4. CONCLUSIONS

- LiCoO_2 was found as the most prominent phase in active cathode materials. It contained impurities like Mn.
- Batteries should be brine treated before dismantling. This will save the batteries from catching fire, thus will give better amount of value metals.
- Ultrasonic separator will give better result than natural drying during the separation of graphite and copper foil.
- Lithium and cobalt can be recovered (18.55%) as lithium carbonate and cobalt hydroxide. 21.2% of a battery is aluminum and copper which can be recycled.
- The results obtained by this hydrometallurgical method suggest that good recovery of metal values from spent lithium ion batteries could be possible through more accurate implementation of those steps. Thus larger scale application of this method can bring massive 3R (Reduce, Reuse, Recycle) practice.

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