

## Recovery of Value Metals from Waste Lithium Ion Batteries by Hydrometallurgical Process

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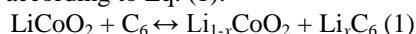
**Abstract-** In recent years, the tremendous growth of Lithium Ion Batteries (LIBs) in most of the modern electronic applications has resulted in the generation of a large amount of wastes in the form of waste LIBs. Improper disposal of these batteries may cause hazardous environment. The objective 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 (LiMnO<sub>2</sub> & LiCoO<sub>2</sub>) 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, LiMnO<sub>2</sub>, LiCoO<sub>2</sub>, 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 500 crores 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 LiCoO<sub>2</sub>, LiNiO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> and the electrolyte is an organic liquid with dissolved substances like LiClO<sub>4</sub>, LiBF<sub>4</sub> and LiPF<sub>6</sub> [5, 6, 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):



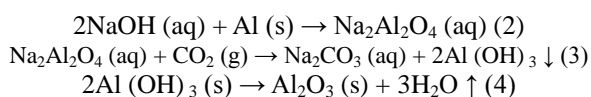
The anode is a thin copper foil coated with a mixture of carbon graphite, binder and adhesives. The heavy metals, organic chemicals and plastics are in the proportions of 5-20 % cobalt, 5-0% nickel, 5-7% lithium, 15% organic chemicals and 7% plastics, the composition varying slightly with different manufacturers [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 described a process for the recovery of cobalt oxalate from spent lithium ion batteries [12]. Sun and Qiu used organic oxalate as leachant and precipitant for the recovery of valuable metals [13], Li et al attempted recovery of cobalt and lithium using organic citric acid as leachant [14]. Pranalo et al studied recovery of metals from leach solutions with a mixed solvent extractant system. [15] Wang et al developed a process of recovery of value metals through leaching in hydrochloric acid [16] while Zhu et al

reported of investigation on the recovery of values through leaching in sulphuric acid [17].

In this study, hydrochloric acid leaching has been applied to recover cobalt and lithium from cathodic active material (LiCoO<sub>2</sub>) 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, H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>) 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 (LiMO<sub>2</sub>) on it. Al foil is dissolved in 1M NaOH solution, where Al is removed in solution as Na<sub>2</sub>Al<sub>2</sub>O<sub>4</sub> (Eq. 2). The active materials (LiCoO<sub>2</sub> or LiMnO<sub>2</sub>) 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 CO<sub>2</sub> bubbling. Eventually the solution turned white that indicates the formation of Al(OH)<sub>3</sub> precipitation (Eq. 3). It was then filtered and washed and dried at 100°C. The dried Al (OH)<sub>3</sub> was finally burned at 600°C for 4 hours to get Al<sub>2</sub>O<sub>3</sub> (Eq. 4).



The active cathode materials was leached in 3M HCl according to solid-liquid ration of 1:20 along with 3.5% H<sub>2</sub>O<sub>2</sub> and magnetic stirring at 80C. The leach liquor was treated with 4M NaOH (per 100 ml leach solution) to recover Co as Co(OH)<sub>2</sub> 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 Na<sub>2</sub>CO<sub>3</sub> and boiled for some time to get a precipitate of Li<sub>2</sub>CO<sub>3</sub> 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 Figure 1.

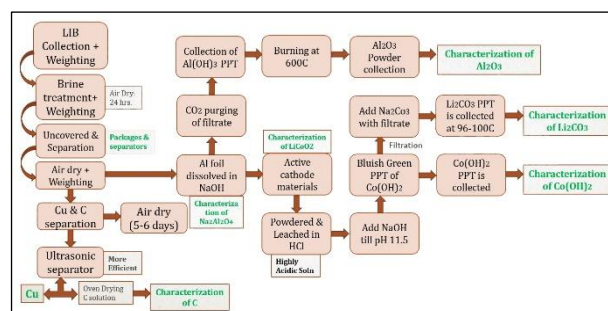


Fig.1: Flow chart for recovery process of LIBs

## 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	.245	98.53	.014	.41	.465	.225	.094	.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 <sub>2</sub> O <sub>3</sub>	A.C. M	Cu	C	Al(O H) <sub>3</sub>	Li <sub>2</sub> C O <sub>3</sub>	Co(O H) <sub>2</sub>
wt. (gm)	49.7	5.3	3.92	52.54	16.5	27.7	13.9	5.2	24.8
% wt	30.7	3.3	2.4	32.49	10.2	17.1	8.61	3.22	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. In figure 2, the peak near 27° (marked as 'C') is indicating graphite.

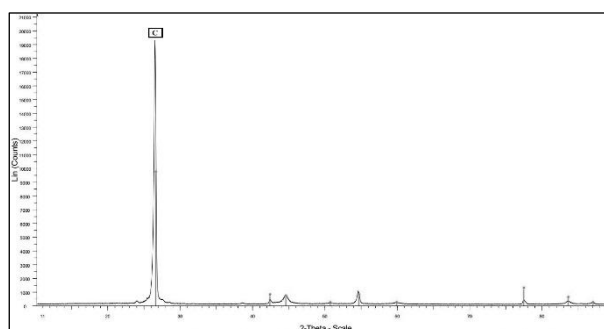


Fig.2: XRD analysis of graphite powder

### 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 ( $\text{LiMnO}_2$ ,  $\text{LiCoO}_2$ ) were found as the most prominent phases. The result is showed in Figure 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.

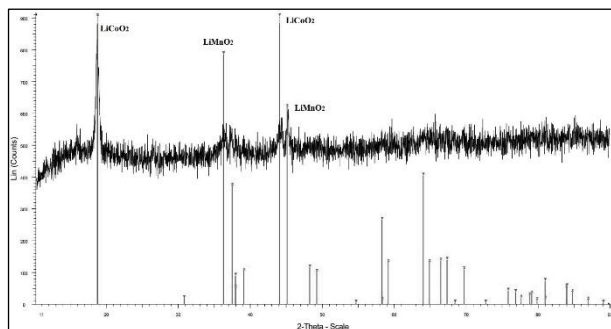


Fig.3: XRD analysis of Active Cathode Materials

### 3.5 Characterization of Aluminum Oxide

Aluminum oxides was found after burning Aluminum Hydroxide at 600C, then it was characterized. The result is showed in Figure 4. Proper purging of sodium aluminate solution should be done by  $\text{CO}_2$ , otherwise aluminum oxide will be contaminated with impurity like sodium aluminate.

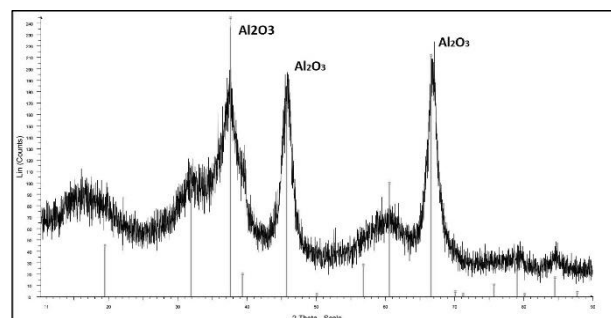


Fig.4: XRD analysis of Aluminum Oxide

### 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  $\text{NaOH}$  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 Figure 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,  $\text{CoMn}_2\text{O}_4$  may form due to chemical affinity.

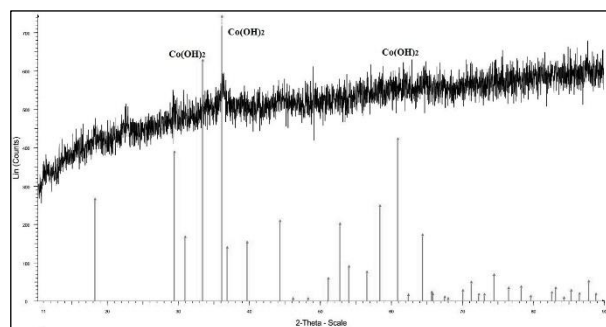


Fig.5: Characterization of Cobalt Hydroxide

#### 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 100C to precipitate lithium carbonate. After filtration and washing with hot water the solid residue was dried and characterized. The result is showed in Figure 6. Proper washing with hot water should be provided, otherwise the added  $\text{Na}_2\text{CO}_3$  solution will restrict the formation of  $\text{Li}_2\text{CO}_3$ .

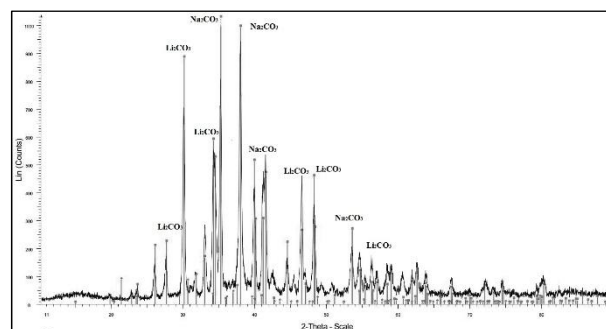


Fig.6: Characterization of Lithium Carbonate

### 4. Conclusions

1.  $\text{LiCoO}_2$  was found as the most prominent phase in active cathode materials. It contained impurities like Mn.
2. Batteries should be brine treated before dismantling. This will save the batteries from catching fire, thus will give better amount of value metals.
3. Ultrasonic separator will give better result than natural drying during the separation of graphite and copper foil.
4. 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.
5. 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.

## 5. References

- [1] Lundblad, A. and Bergman, B., "Synthesis of  $\text{LiCoO}_2$  starting from carbonate precursors II. Influence of calcination conditions and leaching," *Solid State Ionics*, 96 (3-4), 183-193, April 1997
- [2] Global Market for Lithium-Ion Batteries- Forecasts, Trends & Opportunities 2014-2020, Taiyou Research
- [3] Mobile Economy 2017, GSMA (Date of access-10.07.17)
- [4] Lee, C. K. and Rhee, K.I., "Reductive leaching of cathodic active materials from lithium ion battery wastes," *Hydrometallurgy*, 68 (1-3), 5-10, February 2003.
- [5] Bernardes, A. M., Espinosa, D. C. R. and Tenorio, J. A. S., "Recycling of batteries: a review of current processes and technologies," *J. Power Sources*, 130 (1-2), 291-298, May 2004
- [6] Wu Q., Lu W.; and Prakash J., "Characterization of a commercial size cylindrical Li-ion cell with a reference electrode," *J. Power Sources*, 88 (2), 237-242, June 2000
- [7] Chen, J. M., Yao, C. Y., Sheu S. P., Chiou, Y. C. and Shih, H. C., "The study of carbon half-cell voltage in lithium-ion secondary batteries," *J. Power Sources*, 68 (2), 242-244, October 1997.
- [8] Shin, S. M., Kim, N. H., Sohn, J. S., Yang, D. H. and Kim, Y. H. , "Development of a metal recovery process from Li-ion battery wastes," *Hydrometallurgy*, 79 (3-4), 172-181, October 2005
- [9] Kondás, J., Jandová, J. and Nemeckova, M., "Processing of spent  $\text{Li/MnO}_2$  batteries to obtain  $\text{Li}_2\text{CO}_3$ ," *Hydrometallurgy*, 84 (3-4) 247-249, November 2006.
- [10] Lupi, C. and Pasquali, M. "Electrolytic nickel recovery from lithium-ion batteries," *Minerals Engineering*, 16 (6), 537-542, June 2003
- [11] Contestabile, M., Panero, S. and Scrosati, B. "A laboratory-scale lithium-ion battery recycling process," *J. Power Sources*, 83 (1-2), 75-78, October 1999
- [12] Chen, L., Tang, X., Zhang, Y., Li, L., Zeng, Z. and Zhang, Y., "Process for the recovery of cobalt oxalate from spent lithium-ion batteries," *Hydrometallurgy*, 108 (1-2), 80-86, June 2011
- [13] Sun, L. and Qiu, K., "Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries," *Waste Management*, 32 (8), 1575-1582, August 2012
- [14] Li, L., Ge, J., Wu, F., Chen, R., Chen, S. and Wu, B., "Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant," *Journal of Hazardous Material*, 176 (1-3), 288-293, April 2010.
- [15] Pranolo, Y., Zhang, W. and Cheng, C. Y., "Recovery of metals from spent lithium-ion battery leach solutions with a mixed solvent extractant system," *Hydrometallurgy*, 102 (1-4) 37-42, April, 2010.
- [16] Wang, R. C., Lin, Y. C. and Wu, S.H., "A novel recovery process of metal values from the cathode active materials of the lithium ion secondary batteries," *Hydrometallurgy*, 99 (3-4) 194-201, November 2009.
- [17] Shu-guang, Z., Wen-zhi, H., Guang-ming, L., Xu, Z., Xiao-jun, Z. and Ju-wen, H., "Recovery of Co and Li from spent lithium ion batteries by combination method of acid leaching and chemical precipitation," *Trans. Nonferrous Met. Soc. China*, 22 (9), 2274- 2281, September 2012.

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