International Conference on Mechanical, Industrial and Materials Engineering 2017 (ICMIME2017)
28-30 December, 2017, RUET, Rajshahi, Bangladesh.

Paper ID: RT-271

Characterization of Waste Lithium ion Batteries in the Process of Recovery of Value Materials

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Abstract

Generation of waste Lithium Ion Batteries and their improper disposal at an alarming rate may cause hazardous environment. The objective of this experiment is to characterize the component parts of two different branded (Samsung & Symphony) smartphone batteries, to determine the contained amount and nature of value materials through hydrometallurgical route. The outer casing was found to be of aluminum alloy. Lithium metal oxide was the most prominent phase 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 electrodes were separated by polymeric separator. The remainder was electrolyte solvent, adhesive and other impurity elements. In this experiment, probable causes those can make impact on the yield of the recovered value materials will be revealed.

Keywords: E-Waste, Smartphone Batteries, Characterization, Waste-to-Energy, Environmental Engineering

1. Introduction

The public concern about the environment in the last decade has increased a lot and thus resulted in stricter regulations worldwide on those containing hazardous residues of heavy metals such as waste lithium metal oxide batteries. In recent times, these type of secondary batteries are widely used in most of the portable electronic appliances such as cellular phones, laptop, solar power storage, electric power train etc. Statistics show, the world demand for primary and secondary batteries is forecasted to grow by 7.7 percent annually, amounting to US$120 billion in 2019. Among all of these batteries, Li-ion is the battery of choice for portable devices and the electric powertrain and gives most revenue share (37-40%) [1]. LIBs consists of heavy metals, organic chemicals and plastics are in the proportions of 5-20% cobalt, 5-10% nickel, 5-7% lithium, 15% organic chemicals, and 7% plastics, the composition may vary slightly with different manufacturers [2]. The lifespan of LIBs is 1-3 years. After this time, these batteries are of no use may impact on environmental and health issues if they are ignored and thrown anyway. However, value materials including highly priced metals like cobalt or lithium can be recovered. Recycling of spent batteries may result in economic benefits [3, 4]. At the same time development of a suitable method for the recovery of values from spent LIBs can decrease the amount of wastes to be disposed and thus reduce the disposal and treatment problems. Many research have been done on recycling of LIBs. Most of the proposed processes are based on hydrometallurgical route [5, 6] and recovery of lithium and cobalt is one of the primary objectives in the recycling of LIBs [7, 8]. In this study, the nature and the amount of different materials contained in two commercially branded (Samsung and Symphony) smartphone batteries were determined. Results from this experiment will be useful for the development of a suitable process for extraction of the metal values contained in those batteries.

2. Experimental Procedure

Samples of spent lithium ion batteries of two commercially branded (Samsung & Symphony, six of each) were collected from various sources. The potential voltage of all the batteries was 3.8V. The chemical reagents (HCl, NaOH, H_2O_2 and Na_2CO_3) 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. At first, the batteries were brine treated so that the residual charge could be removed. The collected batteries dismantled manually. The plastic cover of the batteries were removed by using a sharp cutting edge. The metallic outside shell of the battery was removed mechanically. The different component parts were separated and grouped on the basis of appearance and information available in the published literature. The weights of the different components like casing, chips, electrodes etc. were measured and the average weights were calculated. The weight proportions of the different component parts are calculated too. The composition of external casing in the spent batteries was determined by Optical Emission Spectroscopy. Electrodes were identified on the basis of information available and they were taken through hydrometallurgical recovery process. 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).

3. Results

Identification of the structural components

Dismantled lithium ion batteries (Samsung) with its different component parts is shown in Figure 1.

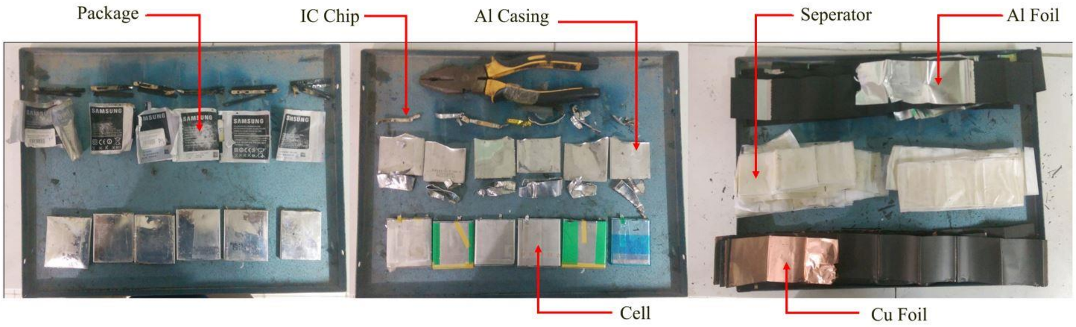

Fig. 1. Dismantled spent lithium ion batteries

Table 1 lists the materials used in the construction of the different component parts of the batteries. This was based on the appearance and information available in the published literature [9]

Table 1. Materials used in the construction of the different component parts

No.	Component Parts	Materials
1	External Case	Aluminum Alloy
2	Cathode	$LiCoO_2$
3	Anode	Graphite conductor
4	Electrolyte	$LiClO_4$, $LiPF_6$
5	Electrolyte Solvent	PC, DMC
6	Separators	Polypropylene (PP), Polyethylene (PE)
7	Current Collector	Aluminum & Copper Foil
8	Current Joining	Gold Plated Pad
9	Printed circuit board(PCB)	

Composition of the outer casing

The chemical compositions of external casing of the two types of spent lithium ion batteries selected for this investigation were determined by optical emission spectroscopy and were essentially the same (Table 2). The material may be classified as commercially pure Aluminum with the usual impurity elements.

Table 2. OES analysis of spent battery casing

Elements	Pb	Sn	Al	Cr	Mn	Fe	Ni	Mg	Ti	Na	P	S	Cl
Samsung	.013	.245	98.53	.014	.41	.465	.225	.094	.005	-	-	-	-
Symphony	.01	.271	98.3	.02	.72	.491	.17	.068	.032	-	-	-	-

Average Weight Analysis of Value Materials

Comparative weight analysis was performed and minor variations were found between two brands. These variations in the weight of the whole battery and in the weight proportions of the different component parts of the spent batteries. Those could be attributed to the difference in the physical condition of the battery when collected and mechanical loss and contamination during the manual dismantling of the batteries. Table 3 represents the average weight of different components of those two types of batteries.

Table 3. Average weight analysis by parts

Batch	Total Weight	Brine & Dry	Wt. (gm)									
			Pack.	Separator	Al Foil	A.C.M	Cu Foil	C	$Al(OH)_3$	Li_2CO_3	$Co(OH)_2$	Loss
Sam.	164.66	164.44	50.976	5.823	8.84	55.62	15.6	27.6	24.024	7.3	27.3	1.2
Symp.	161.69	160.75	49.7	5.37	3.92	52.54	16.5	27.7	13.919	5.2	24.8	1.7

Characterization of Recovered Materials

The recovered anode and cathode materials were characterized. Figure 2 shows the summery of it and indicates the accuracy according to the previous literature.

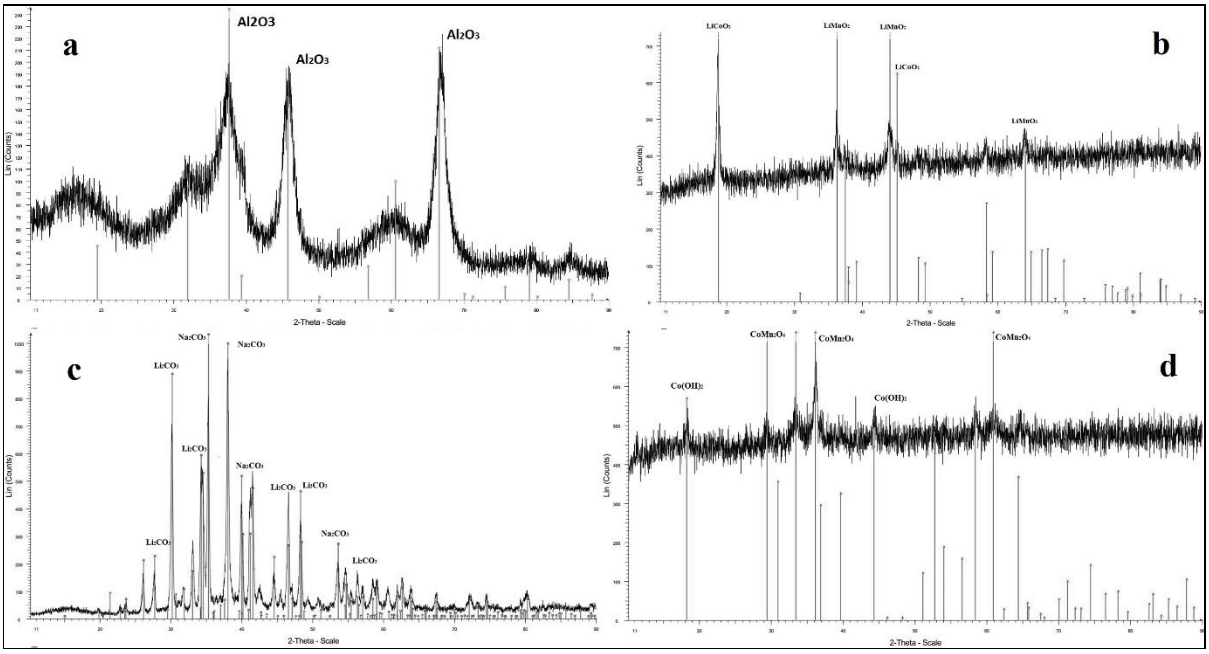

Fig. 2. Characterization of (a) aluminum oxide (b) active cathode materials (c) Li_2CO_3 (d) Co $(OH)_2$

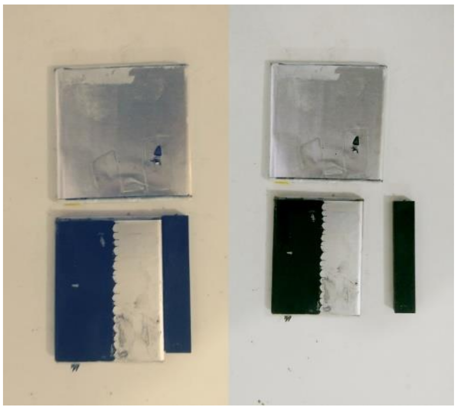

Fig. 3. Impurity like that black thin polymeric material will reduce total yield

4. Discussions

Very often manganese is used instead of cobalt due to lower cost. This will impact on recycling application that won't be much profitable. Figure 2(b) indicates the issue. Deception of manufacturing companies may also cause lower yield. Figure 3 describes the deception of Samsung. 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 gives better result than natural drying during the separation of graphite and copper foil.

5. Conclusions

This study on the characterization of spent lithium ion batteries yielded some results. Pure aluminum and copper in the form of thin foils act as current collector in cathode and anode respectively. $LiCoO_2$ was found to be the most prominent component of the active material of the cathode, while graphite was the active material of the anode. Lithium and cobalt content was 19.79 percent of the total weight. Aluminum and copper constituted about 11.64 percent and 9.8 percent of the total weight of the battery.

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