

Hydrometallurgical Recovery of Value Metals from Spent Lithium Ion Batteries

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Abstract Effects of reaction variables on leaching in hydrochloric acid of LiCoO_2 contained in cathodic electrode of spent lithium ion batteries were investigated. The dissolution of LiCoO_2 was found to increase with an increase in temperature, concentration of HCl, time and solid/liquid (S/L) ratio. Li and Co from LiCoO_2 were leached around 89% with addition of 3.5 Vol% of H_2O_2 as a reducing agent. The metal values contained in the leach liquor were recovered by chemical precipitation. Cobalt was separated as cobalt hydroxide and lithium was separated as lithium carbonate. The effects of pH on the extent of recovery of metal values were investigated. The products obtained were characterised by x-ray diffraction analysis.

Keywords: Li-ion battery (LIB), leaching, spent batteries, recovery

1. Introduction

Lithium ion batteries are widely used in mobile telephones, laptops, video cameras, and other modern life appliances. Due to characteristic light weight, high energy and good performance these batteries are increasingly replacing the other types of batteries [1,2]. The life-span of a LIB is about 1-3 years. 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 comprises a cathode, an anode, organic electrolyte, and a separator. The cathode is a thin aluminium foil coated with a mixture of active cathode material, electric conductor, binder and adhesives. Most lithium systems use a material like LiXMA_2 at the positive electrode. Some materials used at the cathode include LiCoO_2 , LiNiO_2 and LiMn_2O_4 and the electrolyte is an organic liquid with dissolved substances like LiClO_4 , LiBF_4 and LiPF_6 [3,4,5]. The anode is a thin copper foil coated with a mixture of carbon graphite, conductor, 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 [6]. In 2000, the worldwide production of LIBs reached about 500 million cell and from this LIB waste is estimated at 200 to 500 MT, with a metal content of 5 to 15 wt.% Co and 2 to 7 wt.% Li [7]. 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 [8, 9]. 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_2) of spent LIBs. The cathodic active material was separated from the support substrate by dissolution in an organic solvent. Effects of temperature, time, HCl concentration, solid/liquid (S/L) ratio and hydrogen peroxide concentration on the extent of dissolution of LiCoO_2 were investigated. Cobalt and lithium dissolved in the hydrochloric acid solution was recovered by chemical precipitation. The effects of pH and concentration of sodium hydroxide on the extent of recovery was also investigated.

2. Experimental

TECNO M 660 (3.7V) type Lithium Ion Battery used in this study was collected from local vendors. Such batteries consist of a plastic casing and several cell units. The

batteries were opened by cutting the outer aluminium cases and the cathodes were separated.

The cathode (aluminium foil containing the active electrode material) was immersed in N-methylpyrrolidone (NMP) at about 100 °C for an hour [9]. This treatment allowed an effective separation of the paste containing the active electrode material from the thin foil of aluminium metal on which it was pasted. The suspension of the paste in NMP thus obtained was filtered to separate the paste containing the active material. The paste was dried in an oven at 110 °C to a constant weight and was used in all the leaching experiments. The constituents of the paste were identified by X-ray diffraction analysis. The x-ray diffraction pattern was recorded by a Bruker X-Pert diffractometer using a Cu K α ($\alpha=1.54056 \text{ \AA}$) radiation source.

Leaching was conducted in a 500-ml three necked round bottom flask with a mechanical stirrer, a temperature sensor and a refluxing condenser fitted to it. Effects of concentration of hydrochloric acid in the range 1-4M, solid-liquid ratio in the range 1:5 to 1:20, time of leaching of up to 60 minutes, temperature in the range 40-100 °C, and concentration of hydrogen peroxide in the range 0-4 percent in the leaching solution on the extent of dissolution of lithium and cobalt were studied. All leaching experiments were performed at a constant stirring speed of 400rpm.

The lithium and cobalt contents of the leach liquor were determined using an Atomic Absorption Spectroscope (Model: Varian AA240). Sodium hydroxide was used to precipitate cobalt from the leach liquor as cobalt hydroxide. After the recovery of cobalt the leach liquor was concentrated and treated with sodium carbonate to precipitate lithium as lithium carbonate. The effects of pH on the extent of precipitation of cobalt and lithium were investigated. The separated products were identified by X-ray diffraction analysis. X-ray diffraction patterns were recorded in Bruker X-Pert diffractometer using Cu K α ($\alpha=1.54056 \text{ \AA}$) radiation source.

3. Results and Discussion

3.1 Characterization of the Cathode Active Material

The X-ray diffraction analysis of the paste separated from the cathodic electrode (Figure 1) showed that Li and Co in the form of LiCoO $_2$ [marked L in the diffractogram, Figure 1] were the major constituents of the cathode active material. The most intense diffraction lines for lithium cobalt oxide occurred at near 19° and at 46°. The diffraction pattern contained some diffraction lines that could not be identified and have been marked as "U" in the diffraction pattern. These diffraction lines perhaps belong to the binders or additives that are mixed with the active cathode material to facilitate its pasting on the aluminium foil.

3.2 Leaching

3.2.1 Effect of Hydrochloric Acid Concentration

The effect of hydrochloric acid concentration, in the range 1 to 4M, on the extent of dissolution of lithium and

cobalt from the cathode was studied. The other process parameters were kept fixed at temperature = 80 °C, stirring speed = 400rpm, time = 60min, solid/liquid ratio = 1:20 (gm/ml) and hydrogen peroxide concentration = 3%. Dissolution of lithium and cobalt was found to increase with an increase in the hydrochloric acid concentration of up to 3M (Figure 2).

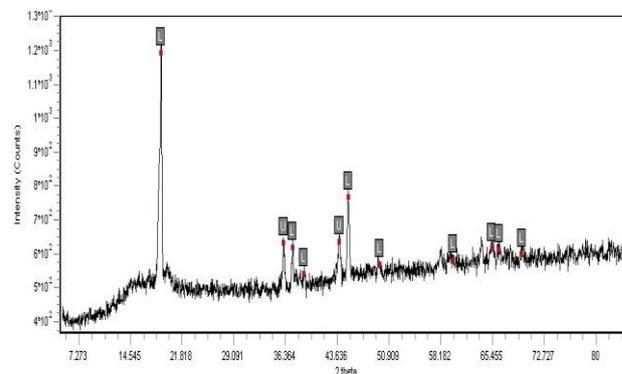


Figure 1. X-ray diffraction analysis of cathode electrode of M 660 Lithium ion Battery

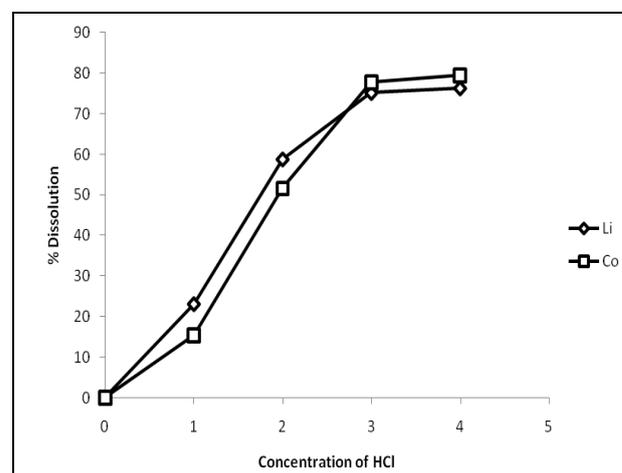


Figure 2. Effect of HCl concentration on dissolution of lithium and cobalt

3.2.2 Effect of Solid/Liquid Ratio

The ratio of solid to liquid was varied from 1:5 to 1:20 while the other parameters were fixed as: temperature = 80 °C, hydrochloric acid concentration = 3M, stirring speed = 400rpm, time = 60min and hydrogen peroxide concentration = 3%. The effect of solid/liquid ratio on the extent of dissolution of lithium and cobalt was rather intense (Figure 3). Extent of dissolution of lithium increased from about 30 percent at a solid-liquid ratio of 1:5 to 79% during leaching at a solid-liquid ratio of 1:15. The percentage dissolution of lithium was about 80% at a solid/liquid ratio of 1:20. The extent of dissolution of cobalt, at all solid-liquid ratios investigated, was slightly higher.

3.2.3 Effect of Temperature and Time

Temperature was varied from 40 °C to 100 °C, while the other variables were kept fixed at: S/L ratio = 1:20, hydrochloric acid concentration = 3M, stirring speed = 400rpm, time = 60min and hydrogen peroxide concentration = 3 percent. The extent of dissolution of both Li and Co increased with an increase in the leaching

temperature (Figure 4). The increase in the rate of dissolution was not significant at temperatures above 80 °C. Thus the optimum temperature for leaching of lithium and cobalt were taken to be 80 °C. Moreover, at temperatures above 80 °C, the cost of operation increases and hydrochloric acid poignantly evaporates resulting in the deterioration of the operation conditions.

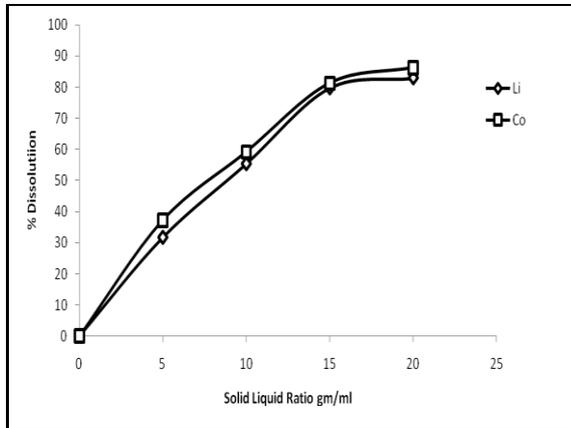


Figure 3. Effect of solid/liquid ratio on the dissolution of lithium and cobalt

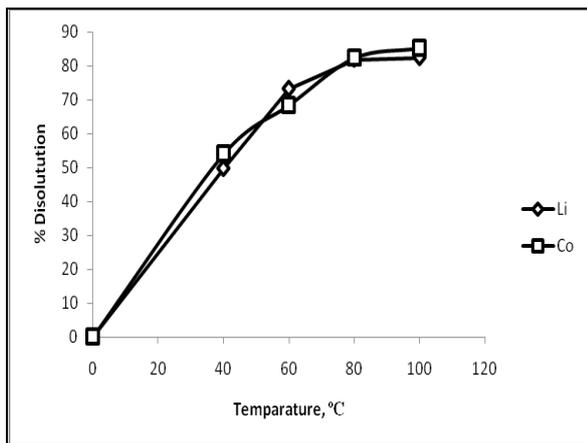


Figure 4. Effect of temperatures on dissolution of lithium and cobalt

Time of leaching was varied from 20 minute to 80 minute keeping the other variables in the leaching experiment fixed. The extent of dissolution increased with time of leaching (Figure 5). A maximum dissolution of about 83.69% could be obtained within 60 minutes of leaching.

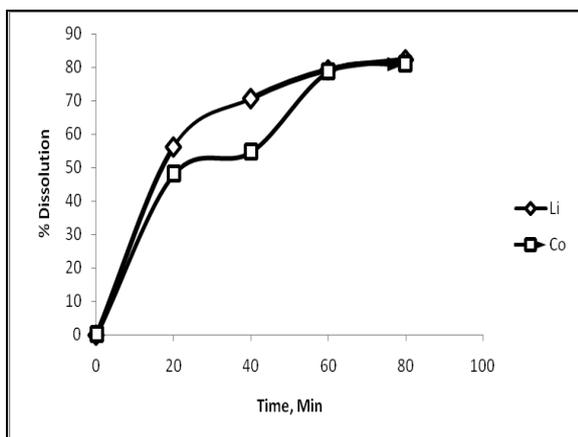


Figure 5. Effect of time on dissolution percentage of lithium and cobalt

3.2.4 Effects of H₂O₂ Concentration

To investigate the effects of H₂O₂ concentration on the extent of dissolution, the concentration of H₂O₂ was varied from 0% to 4%. The other variables were kept fixed at: temperature = 80 °C, hydrochloric acid concentration = 3M, S/L ratio = 1:20, stirring speed = 400rpm, and time = 60min). An increase in the H₂O₂ concentration increased the extent of dissolution of both lithium and cobalt (Figure 6). This increase in dissolution of cobalt has been attributed [6] to the reduction of Co³⁺ to Co²⁺ which dissolves readily. While the hydrogen peroxide helps the dissolution of cobalt, the dissolution of lithium is promoted because the two metals are contained in the same oxide compound. The optimum amount of H₂O₂ in the leach liquor was taken to be 3.5% for dissolution of lithium and cobalt.

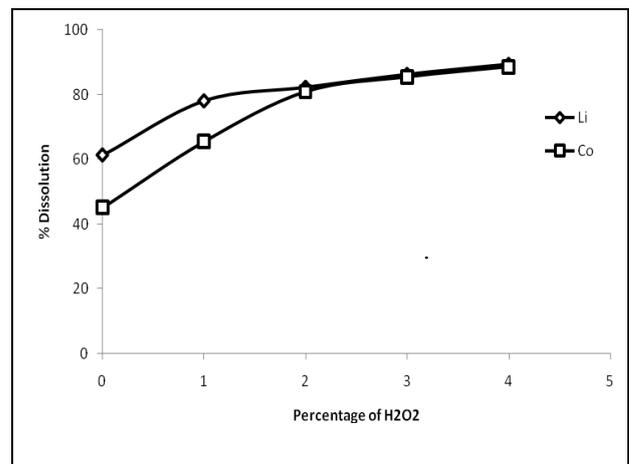


Figure 6. Effect of H₂O₂ Concentration on the Extent of Dissolution of Lithium and Cobalt

3.3 Recovery of Value Metals from Leach Liquor

3.3.1 Recovery of Cobalt

Separation of lithium and cobalt from the leach liquor was effected by employing redox reaction. Direct addition of small additions of 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. The extent of precipitation of cobalt hydroxide was found to increase with an increase in pH value (Figure 7). Over 95 percentage of cobalt could be precipitated at a pH of about 12 leaving 93 percent of lithium in the leach liquor. The extent of recovery of lithium as indicated in this figure represents the percentage of lithium in the leach liquor after the separation of cobalt hydroxide. The figure indicates that the optimum value of pH for the precipitation of cobalt hydroxide could be taken to be 11-12. The Co(OH)₂ precipitate was separated by filtration.

3.3.2 Recovery of Lithium

After the separation of cobalt as cobalt hydroxide, the leach liquor was concentrated and treated with sodium carbonate solution to precipitate lithium as lithium carbonate. The precipitation process was performed at approximately 100 °C. The lithium carbonate was

separated by filtration and washed with hot water to remove the residual liquor.

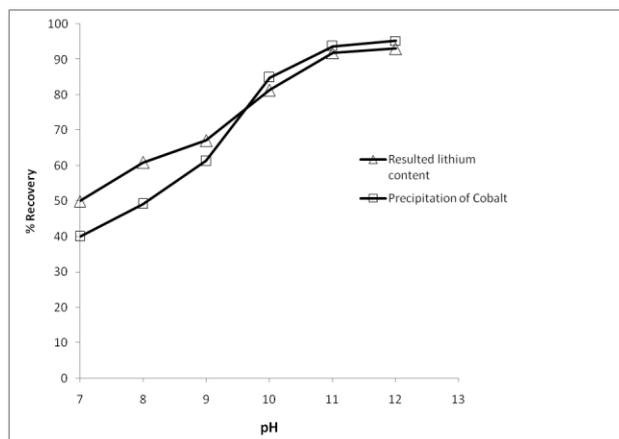


Figure 7. Effect of pH on Precipitation of Cobalt and resulting Lithium content of Leach Liquor

3.3.3 Characterisation of Recovered Products

The two products separated from the leach liquor were dried in an oven and subsequently subjected to x-ray diffraction analysis. The diffraction lines belonging to lithium carbonate in Figure 8 has been marked as “LC” and cobalt hydroxide in Figure 9 has been marked as $\text{Co}(\text{OH})_2$. It can be seen that the both the patterns contain diffraction lines that could not be identified. It has already been mentioned that the LiCoO_2 subjected to leaching contained some unidentified impurities and lines might belong to these impurities (binders, adhesives, etc).

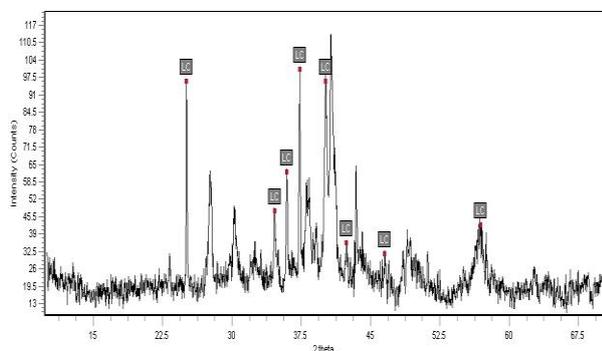


Figure 8. X-ray diffraction analysis of recovered lithium carbonate

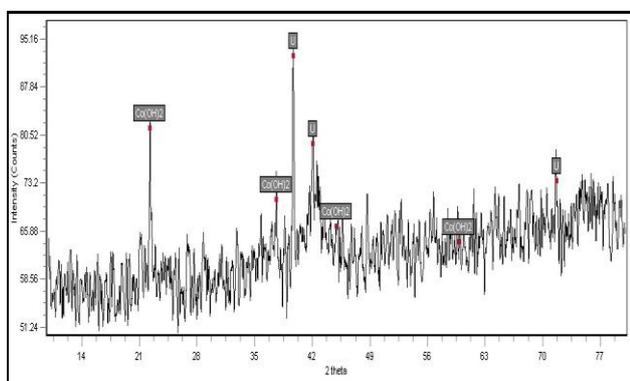


Figure 9. X-ray diffraction analysis of recovered cobalt hydroxide

4. Conclusions

1. LiCoO_2 was the most prominent phase in the positive electrode. It also contained unidentified impurities.

2. The optimum conditions for leaching of lithium and cobalt from the cathode active material of spent lithium ion battery was found to be hydrochloric acid concentration = 3M, solid-liquid ratio = 1:20 (gm/ml), Temperature = 80 °, time=60 minute, hydrogen peroxide = 3.5% and stirring speed = 400rpm.

3. A maximum of 89% LiCoO_2 could be leached at the optimised conditions.

4. Over 95% cobalt could be precipitated from leach liquor at pH a value of 11-12, leaving 93 percent lithium in the leach liquor.

5. The results obtained suggest that good recovery of metal values from spent lithium ion batteries could be obtained through easily performed operations. The method is of practical interest and may be tried on a larger scale.

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