Recovery of valuable metals from cathodic active material of spent lithium ion batteries: Leaching and kinetic aspects

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A B S T R A C T

This work is focussed on the processing of cathodic active material of spent lithium ion batteries (LIBs) to ensure resource recovery and minimize environmental degradation. The sulfuric acid leaching of metals was carried out for the recovery of all the valuable metals including nickel and manganese along with the frequently targeted metals like lithium and cobalt. The process parameters such as acid concentration, pulp density, time and temperature for the leaching of metals from the cathode powder containing 35.8% Co, 6.5% Li, 11.6% Mn and 10.06% Ni, were optimized. Results show the optimized leach recovery of 93.4% Li, 66.2% Co, 96.3% Ni and 50.2% Mn when the material was leached in 1 M H_2SO_4 at 368 K and 50 g/L pulp density for 240 min. The need of a reductant for improved recovery of cobalt and manganese has been explained by the thermodynamic analysis (Eh–pH diagram) for these metals. Leaching of the valuable metals was found to follow the logarithmic rate law controlled by surface layer diffusion of the lixiviant reacting with the particles. The mode of leaching of the metals from the spent LIBs was further examined by chemical analysis of the samples at various stage of processing which was further corroborated by characterizing the untreated sample and the leach residues by XRD phase identification and the SEM-EDS studies.

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1. Introduction

Lithium is an important light metal which finds application in the production of batteries, glass and ceramics, aluminium electrolytic cells, and in preparation of greases, rubbers, alloys and pharmaceuticals. The rechargeable lithium ion batteries (LIBs) are present in 60% of the cellular telephones and about 90% of laptop/-computers, and are also essential constituents of batteries for electric and hybrid vehicles (Harben, 2002; Garret, 2004; Smith, 2010). The life span of lithium ion batteries (LIBs) is about 2–3 years depending upon the usage and the quality of the batteries (Contestabile et al., 2001). The tremendous growth in the usage of LIBs has resulted in generation of a large amount of spent LIBs. These batteries contain heavy metals, organic chemicals and plastics. This includes 5–20 wt.% cobalt- a strategic metal, 5–7 wt.% lithium, 15 wt.% organics and 7 wt.% plastics (Shin et al., 2005; Fouad et al., 2007; Kang et al., 2010a). Spent LIBs cannot be disposed off due to the toxic components like organics and metals particularly the contained metallic lithium which is explosive in nature, unless they are properly removed/treated. Metallic lithium

in the used LIBs is formed on the graphite anode by overcharging and abnormal deposition as given in Eq. (1).

$$LiCoO_2 + 6C \rightarrow Li_xC_6 + Li_{(1-x)}CoO_2 \qquad (1)$$
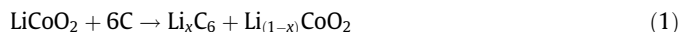
A number of technologies based on the pyro-metallurgical approach in combination with the aqueous processing are being industrially exploited by a few companies (Umicore, Sony, OnTo, Accurec, etc.) to treat the spent LIBs with the explicit aim of recovering mostly cobalt. Several processes have also been proposed to treat the spent LIBs to recover some of the valuable metals and prevent the environmental pollution. In general these are the pyro- and hydro-metallurgical processes coupled with the pre-processing steps particularly for the dismantling of the used batteries (Meshram et al., 2014). In the pyrometallurgical treatment all the acetylene black, organic electrolyte and binder are usually burnt off; these are often associated with the consumption of high energy also. Most of the other processes proposed are based on hydrometallurgical approach using both organic and inorganic leaching agents. The hydrogen peroxide is generally used as a reductant during the leaching. The purpose of adding H_2O_2 (Shin et al., 2005; Ferreira et al., 2009) and other reductants (Pagnanelli et al., 2014) during the leaching is to reduce Co^{3+} to Co^{2+} and Mn^{4+} to Mn^{2+} present in the spent LIBs, which are favourably

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solubilized than the unreduced moieties (Lee and Rhee, 2003). Leaching of the metals from the spent LIBs has been reported with mineral acids like HCl (Zhang et al., 1998; Contestabile et al., 2001), H_2SO_4 (Shin et al., 2005; Nan et al., 2005; Dorella and Mansur, 2007; Swain et al., 2007; Aktas et al., 2006; Kang et al., 2010a, 2010b), HNO_3 (Lee and Rhee, 2002, 2003), and a few organic acids like DL-malic acid (Li et al., 2010a), and citric acid (Li et al., 2010b). It may be mentioned that most investigations in the reported literature have dealt with the recovery of cobalt from the spent batteries with little or no emphasis on the extraction of lithium and other metals. Kinetic aspects of the metal leaching from such materials have also been mostly neglected, excepting a few studies which are preliminary in nature with hardly any structural/micrographic evidence to support the leaching mechanism (Lee and Rhee, 2003; Jha et al., 2013).

Considering the scanty resources of metals of interest for lithium ion batteries in general and environmental pollution associated with the disposal of the used batteries with the rapid growth of this sector in particular, it has become necessary to extract not only the cobalt but other valuable metals such as Li, Ni and Mn also while investigating the kinetics of leaching. With an objective of resource recovery and recycling, the present study is focused on the sulfuric acid leaching of all the metals present in the cathodic active material of end-of the life LIBs. Effect of temperature, time, acid concentration and pulp density has also been investigated in order to optimize the parameters for leaching. Kinetics of the dissolution of metals of importance are particularly stressed upon along with the mechanism of leaching reaction using an appropriate model, which have been confirmed through the characterization of cathode material and the leach residues generated during the process using XRD and SEM-EDS techniques.

2. Materials and method

2.1. Dismantling spent lithium batteries and separation of cathode active material

Nearly 100 spent LIBs of various make used in laptops, weighing 20 kg were kindly supplied by a local e-waste collection center. These batteries were first discharged before dismantling them manually while removing the plastics and steel case mechanically. Anode and cathode were uncurled manually, and the cathode active material in the form of powder was separated from Al foil by heating the latter at 250–300 °C for 30 min which facilitated the detachment of the powder; this material was stored for leaching studies. The particle size of the cathode powder was determined by a laser particle size analyzer-(Malvern®, UK); the particle size was found to be <20 μm and the average size being 10–12 μm. The powder sample was analyzed for the phase identification by XRD (Bruker D8 Discover). All the chemicals used were analytical grade reagents.

2.2. Leaching of cathode active material

All the leaching experiments were performed in a temperature controlled three necked round bottom flask (cap. 500 mL) fitted with a reflux condenser to avoid the loss due to evaporation. To a known volume of the diluted sulfuric acid solution at a fixed temperature the desired amount of the cathodic active material was charged and the slurry was agitated with a magnetic stirrer. Effect of varying the concentration of sulfuric acid in the range 0.5–3 M, pulp density (5–100 g/L), time of leaching (up to 300 min) and temperature (308–368 K) during the leaching of metals was examined. While varying the stirring speed (200–600 rpm) the leaching of metals (data not included) was found to be nearly

constant at and above 500 rpm. The preliminary experiments thus showed that the liquid film boundary diffusion surrounding the solid particles can be minimized at 500 rpm; hence all the experiments were performed at this stirring speed. The progress of leaching was monitored by taking out samples at different time intervals and analyzing the metal contents after filtration. Upon completion of the leaching experiments, slurry was filtered and the residue was dried overnight at 353 K.

Based on the analysis of the leach solution the recovery of metals was determined. In a few set of experiments, the mass balance was checked by computing the metal contents in the leach liquor and the residue. The metal concentrations in the leach solutions were determined by using Atomic absorption spectrometer (GBC-980™) and ICP-OES (Varian, VISTA- MPX™) after necessary dilution. The XRD phase identification in the dried leach residues compared to the untreated sample could be used to understand the progress of leaching of the metals. The surface morphology of the samples pasted on the brass stub after gold coating and their elemental composition were determined by SEM attached with EDS (FEI-Quanta™).

3. Results and discussion

The chemical composition of the cathode active material given in Table 1 shows the presence of 35.8% Co along with 6.5% Li, 11.6% Mn and 10.6% Ni. Other metals such as copper, aluminium and iron are in smaller amounts (analyzed by ICP-OES). The XRD analysis (Table 2) shows the presence of $LiCoO_2$, $Li_2CoMn_3O_8$ (JCPDS file: 480261) and $(Li_{0.85}Ni_{0.05})(NiO_2)$ as the major constituents in the material. The presence of LCM based phase viz., $Li_2CoMn_3O_8$, with a distorted spinel structure might have formed as a result of heat generated during the use with a rise in temperature as high as 150 °C (Julien et al., 2014) and also due to the pre-treatment step (at 250–300 °C) followed in the present study. Besides this, lithium–nickel oxide of lower Li–Ni contents, $(Li_{0.69}Ni_{0.01})(NiO_2)$ (JCPDS file: 85-1970) and CoF_4 (JCPDS file 35-1314) were also present as the minor phases.

3.1. Thermodynamic aspects of the metals

In order to understand the extraction behavior of metals by the hydrometallurgical process, examining the thermodynamic aspects particularly the stability regions of different phases in the aqueous solutions would be useful. The Eh–pH diagrams of lithium and nickel under normal conditions are available in

Table 1
Chemical composition of cathode active material.

Element	Li	Co	Mn	Ni	Cu	Al	Fe
Wt. %	6.5	35.8	11.6	10.06	0.005	0.58	0.06

Table 2
XRD phase analysis of cathode powder and the leach residues at different time interval [Conditions: 1 M H_2SO_4, 368 K and 50% PD].

Sample	Major phase	Minor phase
Cathode active material	$LiCoO_2$, $Li_2CoMn_3O_8$ $(Li_{0.85}Ni_{0.05})(NiO_2)$	$(Li_{0.69}Ni_{0.01})(NiO_2)$, CoF_4
Leach residue in 60 min	$LiCoO_2$, $(Li_{0.65}Ni_{0.05})(NiO_2)$, NiO_2	$(Li_{0.49}Ni_{0.01})(NiO_2)$
Leach residue in 120 min	$LiCoO_2$, $(Li_{0.65}Ni_{0.05})(NiO_2)$, NiO_2	$CoFeF_5.7H_2O$, $(Li_{0.55}Ni_{0.05})(NiO_2)$, MnO_2
Leach residue in 240 min	$LiCoO_2$, $(Li_{0.09}Ni_{0.01})(NiO_2)$	$Li_{0.06}NiO_2$, $CoFeF_5.7H_2O$, MnO_2