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Acid baking of spent lithium ion batteries for selective recovery of major metals: A two-step process

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ABSTRACT

The present work focuses on a two-step process for selective dissolution of metals from cathode active material of spent LIBs. Cathode powder baked at 300 °C using H_2SO_4 being subjected to first stage leaching with water extracted 78.6% Li, 80.4% Co in 60 min at 75 °C and 25% pulp density; recovery of Ni and Mn being low (<15%). In second stage, reductive leaching was performed using an acid mixture (H_2SO_4 and HNO_3) with glucose solubilizing 67% Ni, 64.8% Mn in 45 min. The overall recovery of the metals was 93.2% Li, 90.52% Co, 82.8% Ni, 77.7% Mn.

Introduction

Lithium ion batteries (LIBs) are widely used in portable electrical and electronic devices such as mobile phones, laptops, camcorders etc. due to their characteristics of light weight, high energy density, long storage life and other superior performance as compared to other batteries. Accordingly, the huge battery consumption brings in the generation of a large quantity of spent batteries. The life span of LIBs is 1–3 years [1]. LIBs contain high amounts of valuable metals which are present in metallic (casing and electrode foils) as well as in the form of inorganic metallic compounds (cathode active material, electrolyte). The cathode active materials in the LIBs are generally of four categories [2] cobalt type, manganese type, nickel type and ternary-type (Mn–Ni–Co). Since all such batteries have the specific chemistry which depends upon the size and type of applications as well as the manufacturer, hence it is difficult to generalize a common flow sheet to extract all the metals present in the batteries.

Most of the previous works reported the recovery of major valuable metals viz., cobalt and lithium from cathode active material mainly by pyrometallurgical and hydrometallurgical processes. These processes often include the steps such as crushing, physical separation, acid leaching, precipitation or solvent extraction to recover cobalt and lithium only. The leaching of cathode active material has been widely investigated using HCl [3,4], H_2SO_4 [5,6], HNO_3 [7,8] or other organic acids [9,10] as lixiviants in the presence of H_2O_2 [11,12], $NaHSO_3$ [13] or other reducing agents [14,15]. In a few studies, alkaline leaching followed by acid leaching is also investigated [5,16]. In the absence of such reducing agents, the recovery of metals in acids was found to be often low [6]. More than 99% of cobalt and lithium can be recovered by using more concentrated acid solutions. It is important to mention that in most acidic leaching, no selectivity of metal dissolution of the cathode material, particularly that of ternary type from the spent LIBs could ever be obtained. After the acid leaching, the recovery processes become more complex because of the presence of multi-metals like lithium, cobalt and other metal ions in the solutions. Leaching of all the constituent metals together in the mixture (especially Co and Mn) poses an issue in formulating a simple process for their separation by solvent extraction and precipitation [17]. The constituent metals in the spent batteries containing Co–Ni–Mn along with Li in the cathode active powder exist in various associations from which selective recovery becomes a challenge that can possibly be addressed by acid baking as the first step followed by leaching.

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Sulfation or acid baking results in the transformation of prominent metals to sulfate form in the presence of sulfuric acid, thereby breaking the impervious layer, making the material more active, which, if discharged into water or low concentration of acid can result in selective leaching of some metals (in transformed matrix) to the bulk solution phases [18]. Therefore, this work aims the novelty of sulfuric acid baking and water leaching of the spent cathode active material with the purpose of operating the same at comparatively lower temperature than that of the alkali roasting processes, besides ensuring lower acid consumption compared to the direct sulfuric acid leaching. Moreover, selective recovery is another merit of this work which has finally resulted in lesser metal contamination at each stage and ease in separation. Accordingly, an innovative two-step process intensification for complete recovery of all the metals is presented which involves the sulfuric acid baking to convert major components of spent battery material to water soluble phases yielding selective recovery of Li and Co over other metals (Ni and Mn) in water leach stage, followed by the dissolution of the remaining metals in the reductive acid leaching stage.

Experimental

Materials

The spent LIBs of the laptops were collected and manually dismantled after discharge. The plastic cases and outer steel cells were removed first and then anode and cathode were uncurled. The cathode active material/powder was separated from aluminum foil which was facilitated by heating the latter at 250–300 °C, and was used in the leaching studies. The particle size of the cathode powder was determined by a laser particle size analyzer (Model-Malvern®, UK); the particle size was found to be $<20\ \mu m$ and the average size being 10–12 μm. The phases present in the sample was identified by XRD (Model-Bruker® D8 Discover). Sulfuric acid used for baking/leaching and all other chemicals were of analytical grade (Make-Merck™).

Methods

Baking tests were carried out in a temperature controlled electrically operated muffle furnace (Model-Naskar and Co.™, India). In each experiment, a known weight of cathode active material of spent LIBs was thoroughly mixed with a suitable amount of concentrated sulfuric acid (98%) in a porcelain crucible (boat type). The crucible was weighed and transferred to the muffle furnace, which was preheated to the desired temperature. After a certain time, the crucible was taken out of the furnace, cooled to room temperature and weighed. The baked material quite friable was removed from the crucible and ground using a mortar-pestle. Various baking parameters such as baking temperature and time, and acid concentration were optimized for maximum solubility of metal values. All leaching tests were carried out in a temperature controlled three necked flat bottom borosilicate glass flask (cap. 500 mL) on hotplate cum magnetic stirrer (IKA®) at a fixed shaking speed (500 rpm) and a reflux condenser to avoid the loss due to evaporation. At the end of each leaching experiment, the pulp was filtered. The solid residue was rinsed with deionized water and dried in an electric oven at 70 °C overnight. The residue was then weighed and sampled for XRD/SEM analysis. The filtrate was subjected to pH and E (redox potential) measurements (measured against SCE). The liquid sample taken from the filtrate was also analyzed to determine the concentration of metals by atomic absorption spectrometer (GBC-980™) and/ICP-OES (Varian™, Model: VISTA-MPX) after required dilution. Each solution was analyzed three times and the average value was taken as the concentration in subsequent calculations. The leach residues were characterized for phase identification by XRD (Bruker™) and morphology/metal distribution by FEG-SEM/EDS (FEI™). Each experiment was performed two times, and the average of two replicates was considered for computing the final metal recovery.

Results & discussion

Characterization of the cathode active material powder

The cathode active material was analyzed for the metals with composition as: 35.8% Co, 6.5% Li, 11.6% Mn and 10.06% Ni along with trace amounts of Al, Cu and Fe. The X-ray diffraction analysis (Table 1) of the material shows the presence of $LiCoO_2$, $Li_2CoMn_3O_8$ and $(Li_{0.85}Ni_{0.05})(NiO_2)$ as the major constituents [6].

Sulfuric acid baking and water leaching

The cathode active material (powder) was initially leached at 95 °C, 20 g L^{-1} pulp density and 500 rpm for 240 min yielding 90%

Table 1
XRD analysis of cathode active material before and after processing.

Sample		Major phases		Minor phases	
		Phases	JCPDS file no.	Phases	JCPDS file no.
Cathode active un-reacted material		$LiCoO_2$	77-1370 75-0532	$(Li_{0.69}Ni_{0.01})(NiO_2)$	85-1970
		$Li_2CoMn_3O_8$	48-0261	CoF_4	35-1314
		$(Li_{0.85}Ni_{0.05})(NiO_2)$	85-1982		
Baked cathode material (300 °C, H_2SO_4)		$Li_2Co(SO_4)_2$	48-0868	$NiMnO_3$	12-0269
		Li_2MnO_3	84-1634	$NiSO_3 \cdot 2H_2O$	34-0315
		Co_3O_4	78-1969 80-1541		
Leach-I residue after water leaching (75 °C, 60 min, 25% PD)		$Li_2NiO_{2.88}$	75-0634	$Li_{0.115}MnO_2$	82-2168
		$Li_2NiO_{2.91}$	31-0733	Co_3O_4	78-1969
		$NiMnO_3$	12-0269		
		$LiNi_{0.5}Mn_{1.5}O_4$	32-0581		
2nd stage acid leaching with mixed acid and glucose (50 °C, 45 min, 10% PD)	Leach-II residue in 60 min	MnO_2	42-1169	$(Li_{0.19}Ni_{0.01})(NiO_2)$	85-1975
		$Li_{0.115}MnO_2$	82-2168		
	Leach-II residue in 120 min	MnO_2	42-1169	$(Li_{0.19}Ni_{0.01})(NiO_2)$	85-1975
				$Li_{0.115}MnO_2$	82-2168

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