



Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Recovery of value-added products from cathode and anode material of spent lithium-ion batteries

Subramanian Natarajan, Arvind B. Boricha, Hari C. Bajaj*

Inorganic Materials and Catalysis Division (IMCD), CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific and Industrial Research (CSIR), G. B. Marg, Bhavnagar 364 002, Gujarat, India

ARTICLE INFO

Article history:

Received 20 December 2017

Revised 23 February 2018

Accepted 22 April 2018

Available online xxxxx

Keywords:

Spent LIBs

Acetic acid

Graphite

Lithium Carbonate

Recycling

Green solvents

ABSTRACT

Herein we report a low cost and eco-friendly approach for the recovery of metals from cathode and anode materials of mobile phone spent lithium-ion batteries (LIBs). Li-based metal oxide and graphite were efficiently separated from their respective foils and used for lixiviation. Acetic acid (CH_3COOH) and water were used as lixiviants for the recovery of metals from cathode and anode materials respectively. It was found that with 3 M Acetic acid and 7.5 vol% H_2O_2 as reducing agent 99.9% Li, 98.7% Co, and 99.5% Mn were leached out from cathode material in 40 min at 70 °C and a pulp density of 20 g/L. Besides the cathode leaching, Li was also extracted from anodic material graphite using water as a solvent and further recovered as solid Li_2CO_3 (99.7% Li). The kinetic evaluation of the cathode lixiviate process was studied using three different shrinking-core kinetic Models and established that the reaction follows the product layer diffusion controlled mechanism. From the cathode leach liquor, 99% Co was recovered as metal sulfide by controlled sulfide precipitation with 99.2% purity, and subsequently, MnCO_3 and Li_2CO_3 were obtained with the purity of 98.7% and 99.4%, respectively. The purity of the salts revealed that these products recovered from spent LIBs might be utilized in the electrochemical energy-storage applications. In addition, this recycling process would promote the sustainable development of the battery industry.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

The role of lithium-ion secondary batteries (LIBs) as electrochemical power sources is dominating immensely in portable batteries segments such as mobile phones, laptop, video cameras and electric vehicles, etc., as it offers high energy density, high operating voltage and good electrochemical performance over other rechargeable batteries (Scrosati et al., 2011; Dunn et al., 2012; Kang et al., 2013; Ordonez et al., 2016). The LIBs consist of cathode, anode, and separator in which the cathode is in the form of Li-based metal oxide paste coated on the aluminium foil. The anode is made up of graphite coated on the copper foil. The separator is mainly used to separate the cathode and an anode to avoid the short circuit. Since a long time, layered LiCoO_2 is the most widely used cathode material for all commercial LIBs. Progressively, various other types of cathode materials (LiMnO_2 , LiFePO_4 , and $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O})_2$) are being used in Li-ion cells due to their low cost, high abundance in nature and battery lifetime etc. As a result of their growing applications in modern life appliances,

consumption of LIBs is also constantly increased, thus being responsible for the generation of a significant amount of spent LIBs (Etacheri et al., 2011; Contestabile et al., 2001).

An increasing number of these consumer appliances are constantly expanding their share market on rechargeable lithium-ion batteries (Zhang et al., 2013). The global market for LIBs was \$8.6 billion in 2014 and is estimated to reach \$46.21 billion by 2022 (Allied Market Research, 2016). In India, mobile phones manufactured in 2014–2015 was 5.4 crores (worth Rs.18,900 crore) whereas it was raised to 11 crores (worth Rs.54,000 crore) in 2015–2016 (Arakali, 2016). As a result, India became the second largest smartphone market in terms of active unique smartphone users (220 million users), after the US in 2016 (Special correspondent, 2016). Moreover, the shift to the 4G network from 2G and 3G network is driving the demand and replacement of the feature phones by smartphones in the Indian market lead to generate an enormous amount of spent lithium-ion batteries. Further, ~50 million lithium-ion laptop batteries have been discarded every year reflecting the e-waste growth, and thereby leading to pollution in developing countries like India (Mujtaba, 2016).

In general, spent LIBs are discarded as environmentally unacceptable domestic waste. After the end of their lifecycle, these

* Corresponding author.

E-mail address: hcbajaj@csmcri.res.in (H.C. Bajaj).

are disposed of as waste, dumped into the environment which causes serious concerns due to its toxic materials. For example, solvent electrolyte lithium hexafluorophosphate (LiPF_6) used in lithium-ion batteries, undergo hydrolysis with either atmospheric moisture or water will form toxic hydrogen fluoride (HF) among other products (Xu, 2004). Therefore recycling of these spent batteries is an environmentally viable option to avoid adverse environmental impacts and the major waste of resources (Chen et al., 2015; Zeng et al., 2014; Zeng et al., 2015a). Besides this, recycling process of spent LIBs has become complicated in the waste stream due to its cathode active material composition for their renovation (Gratz et al., 2014; Vanitha and Balasubramanian, 2013; Li et al., 2016). Typically, the anode material which is pasted as graphite paste on a copper foil also contained lithium, an unfocused part during recycling process of spent LIBs. Therefore, the recovery of metals required to recycle both cathode and anode materials in view of the sustainable management of natural resources.

Several methods have been proposed to treat spent LIBs for the recovery of valuable metals. Technologically existing processes for recycling spent LIBs can be categorized into pyrometallurgy, hydrometallurgy, and biohydrometallurgy. For the pyrometallurgical process, high energy consumption is required and also it contains emission of toxic gases. The long treatment period and the toxicity of metals (high concentration) with microorganisms are influencing the limitation of recovery of metals in the biohydrometallurgy process even it has lower cost, environmentally friendly, and fewer industrial requirements. Among these, hydrometallurgy is an advantageous process in the viewpoint of environmental conservation for the separation and recovery of metal ions with such benefits like the complete recovery of metals, low energy requirements and minimization of wastewater (Jha et al., 2013; Meshram et al., 2014).

In recent years, numerous researcher has developed the dissolution of metals using strong acids like H_2SO_4 (Shu-guang et al., 2012), HCl (Wang et al., 2009) and HNO_3 (Castillo et al., 2002) as leaching reagents, and H_2O_2 as reducing agent. Furthermore, some researchers have sought to leach out the metals using organic acids such as citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (Chen and Zhou, 2014; Li et al., 2010b; Chen et al., 2016), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) (Chen et al., 2011; Zeng et al., 2015b), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) (Li et al., 2012), DL-malic acid ($\text{C}_4\text{H}_5\text{O}_6$) (Li et al., 2010a; Sun et al., 2018), succinic acid ($\text{C}_4\text{H}_6\text{O}_4$) (Li et al., 2015), L-aspartic acid ($\text{C}_4\text{H}_7\text{NO}_4$) (Li et al., 2013), L-tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) (He et al., 2017), acetic acid (CH_3COOH) (Golmohammadzadeh et al., 2017), mild phosphoric acid (Chen et al., 2017) and iminodiacetic acid ($\text{C}_4\text{H}_7\text{O}_4\text{N}$) (Nayaka et al., 2016) to avoid the use of strong mineral acids, on account of reducing their environmental pollution. Table S1 summarized the leaching protocol and recovery of metals from spent LIBs. To accomplish the viewpoints of valuable metal recovery and environmental conservation, it is necessary to recycle and separate the metals present in the all parts (cathode and anode) of the spent LIBs.

We have previously demonstrated the synthesis of reduced graphene oxide (rGO) and its application in supercapacitor (Natarajan et al., 2018), MnCo_2O_4 for electrocatalytic oxygen evolution reaction (OER) in alkaline medium (Natarajan et al., 2017), dye adsorption (Natarajan and Bajaj, 2016) and polymer-graphite nanocomposite thin films synthesis (Natarajan et al., 2015) using recovered materials of mobile phone spent LIBs. Herein easily bio-degradable acetic acid (CH_3COOH) was used to leach out the metals from cathode material and it was recovered as value-added products. Furthermore, water was used to separate the graphite from Cu foil and for lithium recovery, which is an environmental and economic benefit. This simple process is easy to set-up and can be applied at large scale to utilize the resource of metals from the mobile phone spent LIBs. An important novelty of the work is the separation of metals for producing commercial

grade products from the cathode and anode parts of mobile phone spent LIBs.

2. Experimental section

2.1. Materials and reagents

Approximately 150 mobile phones spent LIBs of different manufacturers were collected from local market of Bhavnagar, Gujarat, India. All the collected spent batteries were opened manually to separate the cathode, anode, and separator parts. The spent LIBs cathode material was recovered and used for the leaching studies using acetic acid (CH_3COOH) and hydrogen peroxide (H_2O_2). Leaching studies of lithium from graphite were conducted using de-ionized water. All chemical reagents employed were of analytical grade and all solutions at required concentrations were diluted with deionized water.

2.2. Analytical procedures

In order to quantify the concentration of the metal ions, the recovered cathode material and graphite were digested in aqua-regia separately for prolong time and analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES Optima 2100 DV, Perkin Elmer instruments, U.S.A.) after diluting appropriate solutions. The phase of the materials before and after leaching was determined by X-ray diffractometer with $\text{Cu K}\alpha$ ($\alpha = 1.54 \text{ \AA}$) radiation operated at 40 kV and 30 mA. The data was collected in 2θ angle ranged from 5° to 90° . The scan step size and step time were 0.01° and 18 S respectively. The morphologies of the cathode and anode active material were analyzed by scanning electron microscope (FE-SEM) using JEOL JEM-2010 electron microscope equipped with energy dispersive system (EDX). The leaching efficiency of metal contents from the cathode and anode material was also determined by ICP-OES, using the calculation formula represented as follows,

$$LE = \frac{C_f}{C_i} \times 100\% \quad (1)$$

where LE is the leaching efficiency (%), C_f is the amount of metal ions in the solution after leaching (mg/L) and C_i is the total amount of metal ions in their respective active materials (cathode or anode) from spent LIBs.

2.3. Leaching process

2.3.1. Discharging and dismantling process

The collected mobile phones spent LIBs were immersed in NaCl solution for 24 h to discharge the batteries before dismantling the components. Then these batteries were washed with de-ionized water and dried at 70°C for 12 h in an oven. The weight of lithium-ion battery used in the mobile phone is $\sim 20.5 \text{ g}$. Out of which 9.2 g is plastics and steel casing materials, $\sim 5 \text{ g}$ of cathode and the remaining parts containing anode, separator and base metals. The quantification of the electrolyte is not possible because it is dispersed between the cathode and anode. Table 1 detailed the components with its weight percentage of spent LIBs acquired in this study.

2.3.2. Metals leaching procedure from cathode material

Li-based metal oxide was separated from the aluminium (cathode) foil by immersing them in dimethylformamide (DMF, Fischer scientific) under sonication, filtered and collected. The recovered solid product was further calcined at 700°C for 5 h to remove the polyvinylidene fluoride binder and carbon black materials.

Download English Version:

<https://daneshyari.com/en/article/8869550>

Download Persian Version:

<https://daneshyari.com/article/8869550>

[Daneshyari.com](https://daneshyari.com)