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Use of glucose as reductant to recover Co from spent lithium ions batteries

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ABSTRACT

A hydrometallurgical leaching process has been developed for recovery of Co and Li from cathode material ($LiCoO_2$) collected from spent LIBs using a mix solution of glucose and phosphoric acid. The spent $LiCoO_2$ before and after leaching process are analyzed by scanning electron microscopy. A leaching rate of about 98% Co and nearly 100% Li is presented with 1.5 mol/L phosphoric acid and 0.02 mol/L glucose at 80 °C in about 2 h. During leaching process, glucose was oxidized into monocarboxylic acid with reduction of Co(III) to Co(II). Co in solution was recovered as Co-oxalate after leaching process. Using glucose as reductant to dissolve $LiCoO_2$ with chelating agent of phosphoric acid is achieved here.

1. Introduction

Lithium ion batteries (LIBs) are widely used in portable electronic devices because of their high voltage, high energy density, low self-discharge rate and long storage life (Zeng et al., 2015; Bahaloo-Horeh and Mousavi, 2017). Consequently, a lot of spent lithium ion batteries are disposed as solid waste. Spent lithium ion batteries contain toxic organic matters and heavy metals like Co, Cu, which cause serious environmental problems (Guo et al., 2016). Meanwhile, Co, Li, Cu and Al present in spent LIBs are valuable metals and useful in industrial and military devices. Hence, it is highly desirable to recycle valuable metals from spent LIBs (Barik et al., 2016; Bertuol et al., 2016).

In order to seek a conventional process for recycling of spent LIBs, a lot of study is underway. The recycling techniques of spent LIBs mainly includes pyrometallurgy process and hydrometallurgy process. Hydrometallurgy process is more advantageous for recycling valuable metals from spent LIBs because of its low energy consumption, low hazardous gases emission, high recovery rate and simple working. Hence, most works have reported on the leaching of spent active cathode material ($LiCoO_2$) using mineral acids such as sulfuric acid, nitric acid and hydrochloric acid with hydrogen peroxide as reducing agent. However, these acids are high cost and introduce some pollutants such as SO_3, Cl_2 and NO_x, which pose serious threats to the environment or human health (Weng et al., 2013). Thus, a few studies have reported on leaching of $LiCoO_2$ materials using mild organic acids such as citric acid, malic acid, oxalic acid, aspartic acid and succinic acid (Takacova et al., 2016) with hydrogen peroxide as reducing agent. These mild organic acids provide an environmentally friendly and satisfactory result for leaching of spent active cathode material. Owing to unstability of hydrogen peroxide in acids leaching process, hence it is important and essential to found an efficient and stable alternative to hydrogen peroxide. Some alternative of hydrogen peroxide are studied recently such as sodium hydrogen sulfite (Meshram et al., 2016) and ascorbic acid (Nayaka et al., 2016a). Therefore, this study is focused on glucose as reducing agent in leaching process of spent active cathode material with phosphoric acid. With respect to the other extracting agents, glucose was a common and stable agent. It also presents a low cost from the angle of economics. There are no reports on the leaching solution of glucose and phosphoric acid. The details on behavior and condition of Li and Co leaching from spent cathode material are reported here.

2. Experimental

2.1. Materials and agents

The spent LIBs (BL-5CA, Nokia) used here were collected from the local market. Phosphoric acid was used as the leachate, mean-

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while glucose was used as the reductant. Hydrochloric acid and nitric acid were used to analyze the content of Co and Li in the cathode materials. All solutions were prepared by deionized water. Reagents used in this study were all analytically reagent.

2.2. Preparation of powder samples

The spent LIBs were discharged completely to prevent self-ignition and short-circuiting in subsequent dismantling process. Then, the spent LIBs were manually dismantled to separate the cathode, anode, plastic and steel cases. The anode was treated in ultrasonic washing machine with deionized water. All anode material was separated from Cu-foil. The cathode was uncurled to cut into small parts and leached with 5 wt.% NaOH solution at room temperature for 5 h. After Al-foil dissolving completely, the cathode material powder was collected by filtration. Based on the results of simultaneous Thermo-gravimetric and Differential Scanning Calorimetry (TG-DSC) analysis (Ordoñez et al., 2016) (shown in Fig. 1), the cathode material powder was calcined at 650 °C for 5 h in a muffle furnace to burn off the organics such as polyvinylidene fluoride (PVDF), acetylene black (AB) and carbon (C) (Hanisch et al., 2015). After calcination process, the powder was ground to fine powder and sieved through a 0.15 mm sieve prior to use in the leaching process later. The powder sample was also characterized by X-ray diffractometer (XRD, Rigaku, Japan). The flow sheet of recovery of Co and Li from spent LIBs was showed in Fig. 2.

2.3. Leaching process

The above cathode material powder ($LiCoO_2$, 0.2 g) was subjected for leaching in 100 ml mix solution of glucose and phosphoric acid. The leaching temperature was controlled using water bath. Phosphoric acid concentration was varied from 0.6 to 1.8 mol/L and glucose concentration was varied from 0.005 to 0.02 mol/L. After leaching process, the insoluble residue of cathode material powder was separated by filtration. To avoid random errors, three parallel experiments were conducted during the whole leaching experiments and the mean values were taken as the final results.

2.4. Analytical methods

TG-DSC analyses were performed using a TG/DSC instrument (Netzsch STA 449C, Germany) in an argon atmosphere from 0 °C to 1000 °C at a heating rate of 10 k/min. For the XRD analysis, the samples were finely powdered and then were scanned from 10° to 90° using 0.5° steps and a count time of 1 s with Cu Kα radiation (1.5418 Å) at a voltage of 40 kV, 150 mA. The content of Co and Li in powder samples and in leachate were analyzed using atomic adsorption spectrophotometer (AAS, Thermo iCE 3000, USA) (Perez et al., 2016).The surface of the residue particles was analyzed by scanning electron microscope (SEM, TESCAN VEGA3, CZE) at an accelerating voltage of 10 kV.

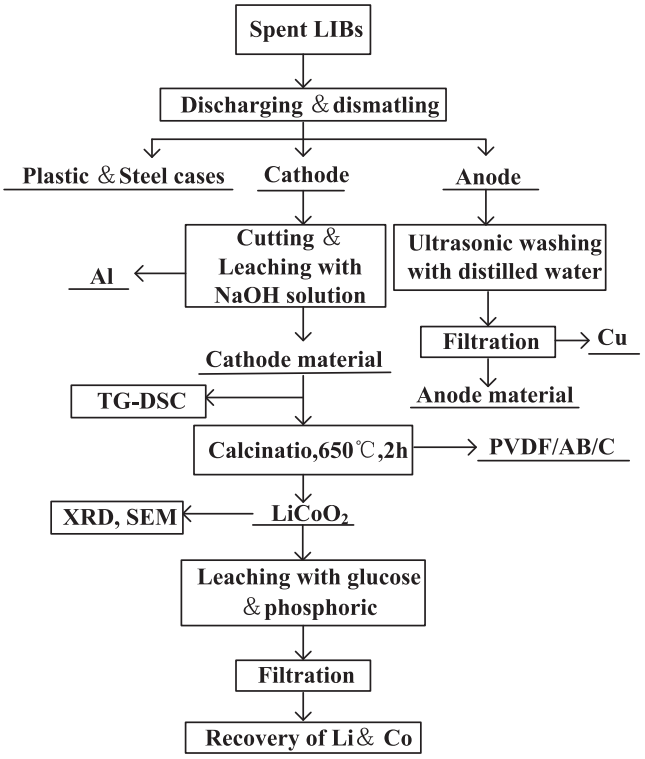

Fig. 2. Flow sheet for the recovery of Co and Li from spent LIBs.

3. Results and discussion

3.1. Characterization of the powder samples

Fig. 3 shows the XRD patterns of spent cathode materials after calcination and grinding. Based on the XRD data, the crystalline phase of $LiCoO_2$ was clearly identified. The content of Co and Li in powder samples were 5.77% and 58.03%. The main composition of the powder sample is $LiCoO_2$ (Geder et al., 2014).

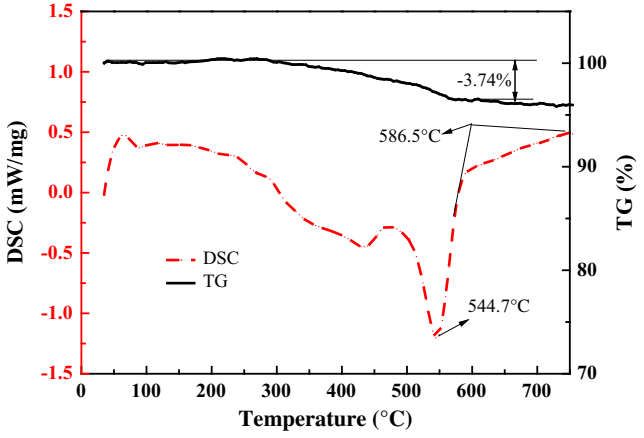

Fig. 1. TG-DSC curves for the spent cathode materials.

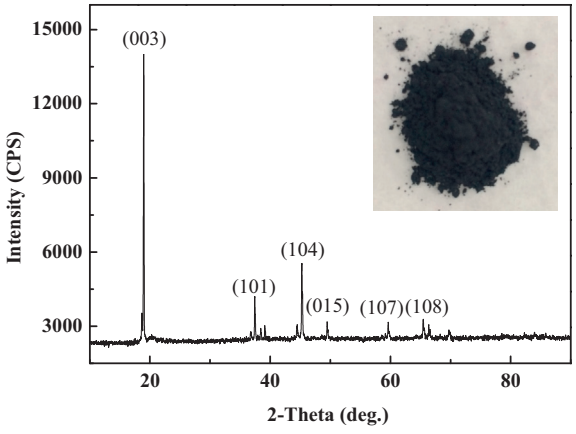

Fig. 3. XRD patterns of cathode materials after calcination and grinding.

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