



Separation of Li and Co from the active mass of spent Li-ion batteries by selective sulfating roasting with sodium bisulfate and water leaching



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ABSTRACT

This paper presents a novel approach for recovering valuable metal from spent Li-ion batteries by separating Li and Co by using selective sulfating roasting with $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$. This study focuses on the effects of the additive ratio of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ on the roasting mechanism. The occurrence evolution of the Li and Co elements during sulfating roasting and water leaching is studied by thermogravimetry–differential scanning calorimetry, X-ray diffraction, scanning electron microscopy, and inductively coupled plasma. The mixtures of spent LiCoO_2 and $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ possesses two obvious weightlessness platforms with corresponding endothermic peaks at 25–600 °C. As the proportion of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ in mixtures increases, the occurrence of the Li and Co elements evolves as follows: $\text{LiCoO}_2 \rightarrow \text{LiNa}(\text{SO}_4)$ and $\text{LiCoO}_2 \rightarrow \text{Co}_3\text{O}_4$. After being washed with deionized water, the concentrations of the Co and Li elements from the washed products in a mass ratio of 1:1.40 are 72.56% and 0.53%, respectively. The different occurrence forms of the Li and Co elements lead to their separation during sulfating roasting.

1. Introduction

The improvement in infrastructure and people's living standards has increased the consumption of electronic products. Therefore, the consumption of Li-ion batteries (LIBs) as electrochemical power sources is rapidly increasing. The main positive electrode materials that are pivotal for LIBs include LiCoO_2 , LiMn_2O_4 , LiNiO_2 , LiFePO_4 and $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (Horeh et al., 2016; Jiang et al., 2015). For consumer electronic devices, LIBs use LiCoO_2 as the cathode material; this cathode material is widely used owing to its comprehensive features, such as high energy density, high discharge capacity and charge efficiency, excellent reversibility, and good cycling performance (Nitta et al., 2015; Sita et al., 2017). Spent LIBs have been generated in quantity because of the overall world market growth of LIB products and the average service life expectancy of LIBs (LIBs in most portable devices possess a lifetime of less than three years) (Hu et al., 2017; Wang et al., 2014). On the one hand, the prices of Co and Li have been growing in recent years, and spent LIBs act as an important secondary and a low-cost mineral source of valuable metals and are even richer than natural ores (CNNMoney, 2017; Li et al., 2010; Martin et al., 2016). On the other hand, disposing spent LIBs improperly will cause serious environmental problems and pose a large hazard to human health because of their hazardous components (Kang et al., 2013; Zhu

et al., 2012). Therefore, recycling spent LIBs is necessary to relieve the pressure of resources and prevent environmental pollution and presents an obvious economic value.

At present, most works report the recovery of major valuable metals of Co and Li from spent cathode active materials mainly by traditional pyrometallurgy, hydrometallurgy and biometallurgy and a combination of two of them. Traditional pyrometallurgical processes exhibit advantages of high efficiency and high productivity in the industry, but they involve high energy consumption, high cost, loss of materials, and emission of hazardous gases and dust (Joulié et al., 2014; Pagnanelli et al., 2016). Hydrometallurgical processes are widely researched and utilized in laboratories and reprocessing plants. Before valuable metals from spent LIBs are recovered, the batteries need to be pretreated using various techniques, such as discharging, dismantling, crushing and sieving. Then, sulfuric acid (Chen et al., 2015; Jha et al., 2013; Meshram et al., 2015), hydrochloric acid (Barik et al., 2017; Guo et al., 2016), nitric acid (Ferreira et al., 2009; Lee and Rhee, 2003; Li et al., 2011), phosphoric acid (Pinna et al., 2017) and other organic acids (Li et al., 2015; Nayaka et al., 2016; Sun and Qiu, 2012) will be used as leaching agents to dissolve the cathode material. Finally, hydrogen peroxide will be added as a reducing agent to obtain high dissolution efficiency (Chen et al., 2011). However, hydrometallurgical processes that use inorganic and organic acids as working media are costly and

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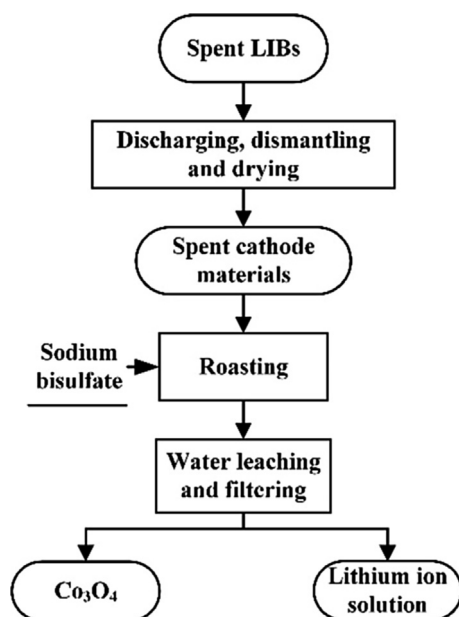


Fig. 1. Flowchart of Co and Li separation process from spent LIBs.

present high safety risk and strict operational conditions; the acid leaching process also releases and generates secondary pollutants, such as toxic gas and waste water (Babel and Del, 2007; Wang et al., 2016b; Yao et al., 2015). Currently, most biometallurgical processes are in the laboratory stage and face challenges of toxicity, long treatment period, low efficiency and competing side reactions (Ijadi Bajestani et al., 2014; Mishra et al., 2008; Zhuang et al., 2015).

The heat decomposition of sodium bisulfate ($\text{NaHSO}_4 \cdot \text{H}_2\text{O}$) can release sulfur trioxide gas at a roasting temperature greater than 500°C (Wang et al., 2016a; Wang et al., 2016b). The mixtures can transform to water-soluble sulfates when LiCoO_2 and $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ with a mass ratio of 1:4.2 are present in the roasting process. Therefore, a possible process of recovering Li and Co by separating Li and Co can be achieved by adjusting the additive ratio of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$.

This paper presents a novel process of recovering Li and Co by separating Li and Co from the active mass of spent LIBs through the selective sulfating roasting of LiCoO_2 with $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ and water leaching. The effects of the additive ratio of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ on the roasting mechanism and the occurrence evolution of the Li and Co elements during sulfating roasting and water leaching were studied by thermogravimetry–differential scanning calorimetry (TG–DSC), X-ray diffraction (XRD), scanning electron microscopy (SEM), and inductively coupled plasma optical emission spectrometry (ICP–OES).

2. Experimental

2.1. Materials and reagents

The spent LIBs were collected from a local e-waste collection center in Lanzhou, China. The cathode active material substance used in this work was separated from the spent LIBs. All other chemical reagents used were of analytical grade, and all solutions were prepared with deionized water during the experiments.

2.2. Separation procedure

The overall flow of the separation process is shown in Fig. 1. The spent LIBs were manually dismantled after discharged, the plastic and steel cases were removed, and anodes and cathodes were uncurled and separated. The cathode materials were separated from the aluminum foil, which was stripped by calcination in a muffle furnace at a required

temperature for 0.5 h (model KSL-1100X-S). This process was followed by leaching in deionized water, ultrasonic shaking (model KQ3200DE), filtering, and drying in vacuum drying oven at 80°C for 10 h (model DZF-6050). The spent cathode materials (spent LiCoO_2) were mixed completely with an appropriate ratio of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$. The mixtures were placed in a 50 mL ceramic crucible with a sealed cover. Thereafter, the ceramic crucible was placed into the muffle furnace (model KSL-1100X-S) and roasted at 600°C for 0.5 h. After the roasting process, the roasted product was naturally cooled to room temperature, leached with deionized water, and filtered.

Three parallel experiments were repeated during roasting and water leaching to ascertain the repeatability of results, and the mean values were taken as the final results of the concentrations of Co and Li.

2.3. Analytical methods

TG–DSC was used to identify the appropriate temperature interval of the roasting process, and the mixtures were heated from 20°C to 600°C at a heating rate $10^\circ\text{C}\cdot\text{min}^{-1}$ using a simultaneous thermal analyzer (model STA 449F3, Germany). The composition of the mixtures was investigated by XRD (model D/max-2400, Japan) with Co K α radiation. The operating voltage and current were 30 kV and 30 mA, respectively. The mixtures were scanned from 5° to 90° . To determine the phase transformation behavior, the morphologies before and after roasting were analyzed by SEM (model JSM-6701F, Japan). The concentrations of Co and Li in the washed products were measured using ICP–OES (Prodigy, Leeman, USA). The possible reactions of the corresponding Gibbs energies were calculated using HSC Chemistry 6.0.

3. Results and discussion

3.1. TG–DSC analysis

The TG–DSC curves of the spent LiCoO_2 and the mixtures with $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ in different mass ratios are exhibited in Fig. 2. As shown in Fig. 2(a), the mass of spent cathode materials decreased slightly in the range of $25\text{--}600^\circ\text{C}$. However, the mass loss of the mixtures at (b) 1:0.28, (c) 1:0.56, (d) 1:0.84, (e) 1:1.12 and (f) 1:1.40 was higher than that of (a) spent LiCoO_2 . Obvious exothermic peaks appeared at $100\text{--}300^\circ\text{C}$ in the DSC curve of the mixtures. This difference showed that not only physical mixing existed but also chemical reactions occurred when LiCoO_2 was roasted with $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$. As shown in Fig. 2(b), (c), (d), (e), and (f), the major mass loss of the mixtures and the corresponding DSC curves presented a strong endothermic peak at the temperature zone of $25\text{--}200^\circ\text{C}$. This peak was due to the release of adsorbed water and crystal water from the mixtures. The rate of weightlessness gradually increased with the increase in the additive ratio of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$. As temperature increased, weightlessness appeared again at $200\text{--}300^\circ\text{C}$ and the rate was lower than that at the roasting temperature within the range of $25\text{--}200^\circ\text{C}$. This finding might be related to the formation of sulfates at approximately 260°C . At $300\text{--}600^\circ\text{C}$, the sample mixtures of LiCoO_2 and $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ in mass ratios indicated in Fig. 2(a), (b), (c), (d), (e) and (f) displayed no weightlessness. Several small endothermic peaks existed on the corresponding DSC curves, and these peaks might be related to the effect of the crystal form transformation at $400\text{--}600^\circ\text{C}$.

3.2. XRD analysis

The XRD patterns of the spent LiCoO_2 and the roasted products at different additive ratios of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ are shown in Fig. 3. The XRD pattern in Fig. 3(a) indicated that the phase composition of the spent cathode materials was LiCoO_2 and a small quantity of Co_3O_4 . The comparison of Fig. 3(b–f) with Fig. 3(a) showed that a new phase of $\text{LiNa}(\text{SO}_4)$ appeared in the roasted products, and the characteristic diffraction peaks of LiCoO_2 in the roasted products completely

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