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A combined process for cobalt recovering and cathode material regeneration from spent $LiCoO_2$ batteries: Process optimization and kinetics aspects

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ABSTRACT

A combined process has been developed for recovering cobalt and regenerating cathode material from leach liquor of spent $LiCoO_2$ batteries. Cobalt of 98% can be selectively separated from leach liquor using ammonium oxalate of 1.15 (mole ratio) at pH of 2.0, 55 °C, and 40 min. Kinetics analysis indicates that precipitation of cobalt is controlled by a combination of surface chemical reaction and diffusion. The E_a value of precipitation is 19.68 kJ/mol obtained from the second-order model of $(1-a)^{-1} = k't + c$. Based on the TG/DSC curves of oxidation of cobalt oxalate, it is found that formation of Co_3O_4 oxidized from cobalt oxalate is in according with the model of randomly nucleating followed by nucleus growth. The E_a value is 84.93 kJ/mol that is provided by the suitable model of $g(\alpha) = [-\ln(1-\alpha)]^{1/3}$. Then, lithium is recovered from the filtrate as Li_2CO_3 with the purity of 99.5% by precipitation method. Finally, new cathode material with a good electrochemical performance is regenerated using obtained Co_3O_4 and lithium carbonate through solid phase method.

1. Introduction

Great amounts of lithium ion batteries (LIBs) have been manufactured to meet the global demand for power source required for consumer electronics devices, electric vehicles and other applications owing to their high cell voltage, high-energy density, low self-discharge and small size (Perez et al., 2016; Barik et al., 2017). Consequently, a massive quantity of spent LIBs is discarded after several years of service lifetime (Guo et al., 2016; Pagnanelli et al., 2017). These spent LIBs cannot be disposed into landfill because it contains heavy metals and organic electrolytes such as $LiPF_6$ (Chen et al., 2017). While, valuable metals in spent LIBs are worthy of recycling due to limited natural reserves and ever-increasing demands. Hence, recycling of spent LIBs is beneficial in improving environmental and social-economic sustainability (Ku et al., 2016).

Generally, the types of LIBs used in the market include $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, $LiNi_xCo_yMn_{1-x-y}O_2$ on the basis of the types of cathode material. $LiCoO_2$ of cathode material is the first commercialized battery type and has been widely employed in most commercial LIBs of consumer electronics devices. Therefore, it has a largest of discard amount that also expected to grow in the forthcoming years. While, spent $LiCoO_2$ batteries contains significant quantities of cobalt and lithium that has a high economic value (Bertuol et al., 2016). Hence, many relevant studies for recovering cobalt and lithium from spent $LiCoO_2$ batteries have been reported.

Generally, the recycling technologies of spent $LiCoO_2$ batteries involve hydrometallurgy and pyrometallurgy method. Hydrometallurgy method is more advantageous than pyrometallurgy method because of its high recovery rate, low energy consumption and simple working. Furthermore, the hydrometallurgy method involves leaching process and recovery process. Spent $LiCoO_2$ material could be leached by inorganic acid such as HCl, H_2SO_4 and H_3PO_4 with help of H_2O_2 (Meshram et al., 2015; Pant et al., 2017). Due to potential threat of inorganic acid, leaching of spent $LiCoO_2$ material by mild organic acid such as citric acid, malic acid, succinic acid, and aspartic acid (Gu et al., 2017; Golmohammadzadeh et al., 2017) have been reported. Due to the instability of H_2O_2 in acid solution, Glucose, sodium hydrogen sulfite and ascorbic acid was used as alternative agent to H_2O_2 for leaching of spent $LiCoO_2$ material (Meng et al., 2017).

Aside from leaching process, recovery of the metals from leaching solution is also an important step for a hydrometallurgy method (Barik et al., 2017). Some studies have been reported on the recovery process, which mainly involve solvent extraction and precipitation method. Solvent extraction is a very effective method for recovery of metals from leaching solution by using a

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suitable organic solvent such as Cyanex 272, PC-88A, and D2EHPA (Chen et al., 2015c; Yang et al., 2017; Leite et al., 2017). However, solvent extraction was difficult for commercial production because of its huge investment, consumables and space. In contrast, precipitation method is best option for commercial production because of its low investment, high recovery rate and simple working. It is important and essential to find a suitable precipitating agent for recovery of metals from leaching solution (Chen et al., 2016b; Wang et al., 2016). At present, sodium carbonate (Barik et al., 2016), KOH (Pegoretti et al., 2017), NaOCl (Barik et al., 2017) ammonium oxalate and oxalate acid used as precipitating agent for cobalt have been reported. For lithium, the chemical reagent of Na_2CO_3 was used with recovery efficiency of about 90% (Pinna et al. (2017)).

To find alternative to H_2O_2, we have tried to use glucose as reductant for leaching of spent $LiCoO_2$ material in previous work (Meng et al., 2017). In this study, a process for precipitating cobalt, recovering lithium and regenerating cathode material has been proposed. Firstly, a spherical cobalt oxalate was prepared via precipitation using ammonium oxalate and cobalt oxalate also was further used for preparation of cobaltosic oxide (Co_3O_4) via oxidation process. The kinetics were studied for understanding the possible mechanism of precipitation and oxidation. And then the lithium carbonate was prepared from the filtrate. Finally, new cathode material was regenerated using Co_3O_4 and lithium carbonate through solid phase method.

2. Materials and methods

2.1. Materials

All the reagents (glucose, malic acid, ammonium oxalate, sodium carbonate, etc.) used in this study were all analytically reagent and all the solutions were prepared with deionized water.

The spent LIBs (battery type BL-5CA of Nokia mobile phone) used here were collected from the local mobile phone recycling market. The spent LIBs were completely discharged and manually dismantled to separate the cathode, anode, plastic and steel cases. Then, the cathode was cut into small parts and leached with 5 wt% NaOH solution at room temperature. After dissolving completely Al-foil, the cathode material was collected as powder by filtration and subsequently calcined at air atmosphere with 650 °C for 4 h in a muffle furnace to burn off the organics. And harmful gases were managed by an exhaust gas recovery unit during calcination process. The content of Co and Li in the obtained spent cathode material sample were 6.97% and 59.87%. The crystalline phase of $LiCoO_2$ was clearly identified based on the XRD data of the obtained sample (Fig. S1). Thereafter, the spent cathode material ($LiCoO_2$) was leached in solution of malic acid and glucose. Spent $LiCoO_2$ material (0.2 g) was dispersed in 20 ml mixed solution of 1.25 mol/L malic acid and 0.3 mol/L glucose at 80 °C for 180 min to leach the metal elements. The leaching efficiency of cobalt and lithium can reach 99.87% and 100%, respectively. Finally, the main metal elements contained in the leach liquor were listed in Table 1.

Table 1
The main metal elements contained in the leaching liquor.

Elements	Co	Li	Fe	Cu	Al
Content (g/L)	5.98	0.70	<0.01	<0.01	<0.01

2.2. Precipitation and oxidation studies

Cobalt was selectively precipitated from the above cobalt-enriched leach liquor. The cobalt-enriched leach liquor (10 ml) was added into a 50 ml beaker and precipitated with a predetermined dosage of ammonium oxalate at different time and temperature. The molar ratio of ammonium oxalate to cobalt was varied from 1.0 to 1.25. After precipitation, the precipitation products of cobalt were filtered, washed with deionized water and dried at 50 °C for 24 h. The concentration of residual cobalt and lithium in the filtrate was confirmed by atomic adsorption spectrophotometer (AAS). To avoid random errors, three parallel experiments were conducted during the whole precipitation experiments and the mean values were taken as the final results. The precipitation efficiency of cobalt was calculated as follows:

$$Pe = \frac{[Co]_{initial} - [Co]_{aq}}{[Co]_{initial}} \times 100\%$$

where $[Co]_{initial}$ is the initial cobalt mole in leach liquor before the precipitation and $[Co]_{aq}$ is the cobalt mole in the filtrate after the precipitation.

A simultaneous thermo-gravimetric and differential scanning calorimetry (TG/DSC) analyses instrument (Netzsch STA 449C, Germany) operated in air atmosphere (N_2/O_2 = 80/20) with a flow rate of 60 ml/min was used for oxidation analysis of the above obtained cobalt oxalate. The sample (about 4.0 mg) was heated from 35 °C to 1000 °C at five different heating rates of 5, 10, 20, 30 and 40 k/min. Based on the TG-DSC analysis, the oxidation of the cobalt oxalate (3.0 g) was performed in a muffle furnace at air atmosphere and 400 °C for 6 h. Thereafter, Oxidation product was analyzed by XRD and scanning electron microscope (SEM, TESCAN VEGA3, CZE).

2.3. Preparation of lithium carbonate and cathode material

Lithium carbonate was prepared by precipitation method. Before precipitation of lithium, the impurity in the filtrate was deeply removed by precipitation using 3 mol/L NaOH at pH = 14. The pure lithium filtrate was obtained and adjusted to the concentration of 2 mol/L through evaporation. Then, Na_2CO_3 (0.022 mol) was subsequently added to the lithium-enriched liquor (10 ml) at 80 °C. The precipitated Li_2CO_3 was washed with boiling ultrapure water and dried in a vacuum oven for 12 h.

To regenerate $LiCoO_2$ cathode material, the obtained Co_3O_4 and Li_2CO_3 was mixed together at a Li/Co molar ratio of 1.07. The mixture was sintered in air atmosphere at 900 °C for 20 h. The sintered process was conducted in a muffle furnace with the heating rate of 3 k/min. The electrochemical properties of regenerative cathode material ($LiCoO_2$) were evaluated in CR2032-type coin cells. The preparation process of the coin cells was as following. The uniform mixing of regenerative material (80%), polyvinylidene fluoride (10%) and acetylene black (10%, as the conductor) was conducted with N-methyl-2-pyrrolidinone being as the solvent. The mixture was cast onto an aluminum current collector with a coating machine. The $LiCoO_2$ laminate was received after NMP removal by vacuum drying at 120 °C for 12 h and then punched into small disks as electrodes. The coin cells were assembled in a glove box filled with Ar. Pure lithium foil served as anode material and microporous polypropylene membrane was used as separator. The electrolyte was prepared by dissolving 1 M $LiPF_6$ in the mixed solution (Molar volume ratio = 1:1) of ethylene carbonate (EC) and dimethyl carbonate (DMC).

2.4. Analytical methods

The content of cobalt and lithium in powder sample, leaching solution and the filtrate of precipitation were analyzed using atomic adsorption spectrophotometer (AAS, Thermo iCE 3000, USA). The pH values of the solutions were measured with a pH/mV meter (PHS-3C, Leici, China). For the XRD analysis, the sample

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