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Research article

Recovery of lithium from the effluent obtained in the process of spent lithium-ion batteries recycling

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ABSTRACT

A novel process of lithium recovery as lithium ion sieve from the effluent obtained in the process of spent lithium-ion batteries recycling is developed. Through a two-stage precipitation process using Na_2CO_3 and Na_3PO_4 as precipitants, lithium is recovered as raw Li_2CO_3 and pure Li_3PO_4, respectively. Under the best reaction condition (both the amounts of Na_2CO_3 and Li_3PO_4 *vs.* the theoretical ones are about 1.1), the corresponding recovery rates of lithium (calculated based on the concentration of the previous stage) are 74.72% and 92.21%, respectively. The raw Li_2CO_3 containing the impurity of Na_2CO_3 is used to prepare $LiMn_2O_4$ as lithium ion sieve, and the tolerant level of sodium on its property is studied through batch tests of adsorption capacity and corrosion resistance. When the weight percentage of Na_2CO_3 in raw Li_2CO_3 is controlled less than 10%, the Mn corrosion percentage of $LiMn_2O_4$ decreases to 21.07%, and the adsorption capacity can still keep at 40.08 mg g^{-1}. The results reveal that the conventional separation sodium from lithium may be avoided through the application of the raw Li_2CO_3 in the field of lithium ion sieve.

1. Introduction

Lithium and its compounds (*e. g.* $LiCoO_2$, $LiNiO_2$, $LiMnO_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiMn_2O_4$, and $LiFePO_4$) are attractive to many fields because of the particular physical, chemical and electrochemical properties (Yang et al., 2016a,b). Since the 1990s, lithium-ion batteries (LIBs) have been widely used in energy storage including portable instruments, hybrid electric vehicles (HEVs) and electric vehicles (EVs) due to the high energy density, long cycle life and excellent storage characteristic (Senyshyn et al., 2015; Reddy et al., 2013a,b). On average, the battery performance is rarely specified over more than 1000 cycles (Li et al., 2016), which means that LIBs have a short life of 3–5 years whether they are used or not (Whittingham, 2004; Tarascon and Armand, 2001). However, the growth of energy demand for HEVs and EVs greatly increases the batteries consumption and the demand of lithium as a raw material for LIBs. Meanwhile, the impact on environment and resources are also concerned (Wang et al., 2014; Okada and Tomikawa, 2016; Singh and Lee, 2015). The typical LIBs are consisted of 5–20% Co, 5–10% Ni, 5–7% Li, 5–10% other metals (Cu, Al, Fe, Cr, et al.), 15% organic chemicals, and 7% plastics, so the value of 1 ton spent LIBs is about 7000 US dollars (Tanong et al., 2016; Wang et al., 2017; Lee and Park, 2014; Sakunthala et al., 2010; Reddy et al., 2013a,b; Prabu et al., 2013). Hence, an environmental friendly method for LIBs recycling is very important, not only to relieve the shortage of rare resources, but also to eliminate the pollution of hazardous components (Tsuchiya et al., 2002; Zazycki et al., 2017).

Some companies such as Umicore, Sony, Onto and Accurec have exploited a number of technologies to dispose the spent LIBs, which include pre-treatment process (discharging, dismantling, sorting, crush, breakdown, sieving, heat treatment et al.) (Meshram et al., 2015; Sun and Qiu, 2011; Nie et al., 2015), leaching/extraction (Dorella and Mansur, 2007; Tang et al., 2014; Yao et al., 2015), chemical precipitation (Jha et al., 2013; Xu et al., 2008; Joulie et al., 2014), and electrolytic process. At present, in the whole field of spent LIBs recycling, the overall recycling efficiencies of Fe, Cu, Al, Co, Ni, and Mn are over 50%, but the recycling efficiency of Li is still less than 1% (Chen et al., 2015a,b; Graedel et al., 2011; Reck and Graedel, 2012). Therefore, lithium recovery is an important

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challenge now. Previous methods of lithium recovery from spent LIBs are expensive and inefficient such as co-precipitation (Vayrynen and Salminen, 2012; Pasta et al., 2012), solvent extraction (Yang et al., 2016a,b; Nan et al., 2005), electrochemical process (Meshram et al., 2014). Among them, it may be a relatively simple and clean method to prepare raw Li_2CO_3 by using Na_2CO_3 as precipitant. However, the solubility of Li_2CO_3 in the aqueous solution is inversely proportional to its temperature (0.72 g per 100 g at 100 °C), so the major shortcomings of this method are low recovery, heavy energy consumption and impure product (Torrejos et al., 2015; Luo et al., 2015). Since the impurity content exerts a tremendous influence to the application of Li_2CO_3, a scrubbing step is considered as an essential purification process in order to separate sodium from lithium in almost all the previous studies (Zou et al., 2013; Wang et al., 2009; Zeng et al., 2015). However, the scrubbing step may cause a heavy loss of lithium resources and an increasing drainage of wastewater. On the contrary, it is very rare that the raw Li_2CO_3 containing Na is directly used to prepare lithium ion sieve (LIS), which is a good lithium adsorbent with large capacity and high selectivity.

Hence, in this paper, a novel process of lithium recovery from the effluent obtained in the process of spent LIBs recycling is developed. Through a two-stage precipitation process using Na_2CO_3 and Na_3PO_4 as precipitants, lithium is recovered as Li_2CO_3 and Li_3PO_4, respectively. Then, through heat treatment with $MnCO_3$, lithium manganese oxide ($LiMn_2O_4$, LMO) as LIS is synthesized successfully to extend the application of the raw Li_2CO_3. At last, the performance of LMO and the influence of sodium on LMO are studied systematically.

2. Experimental

2.1. Materials and reagents

The effluent (7 g L^{-1} of Li^+, 23 g L^{-1} of Na^+, 98 g L^{-1} of SO_4^{2-}, pH = 4–5) is obtained in the process of spent LIBs recycling as described in our previous research (Weng et al., 2013). Analytically pure $MnCO_3$, Na_2CO_3, LiOH and Na_3PO_4 (from the Aladdin Industrial Corporation) are employed in the experiment.

2.2. Recovery process

A flowsheet of the procedure designed for lithium recovery from spent LIBs is illustrated in Fig. 1 as follows.

2.2.1. First-stage precipitation of lithium

The first-stage precipitation of lithium as Li_2CO_3 is carried out using beakers immersed in a water bath. The solution was placed into different beakers; then, different stoichiometric rates of Na_2CO_3 (*vs.* the theoretical amount) were added to the solution slowly as precipitant. The mixtures were stirred mechanically at 40 °C for 1 h, and then filtered. At last, the precipitates of Li_2CO_3 were dried in a vacuum oven at 60 °C for 24 h. The contents of the aqueous solution and products were measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, PS-6, Baird, USA).

2.2.2. Second-stage precipitation of lithium

The second-stage precipitation of lithium as Li_3PO_4 was carried out as above. The remaining solution after the first-stage precipitation was placed into different beakers; then, different stoichiometric rates of Na_3PO_4 (*vs.* the theoretical amount) were added slowly as the other precipitant. The mixtures were stirred mechanically at 25 °C for 1 h, and then filtered. The products of Li_3PO_4 were dried in a vacuum oven at 60 °C for 24 h. At last, the filtrate containing a high concentration of raw Na_2CO_3 may be reused as precipitant in the first-stage. And the contents of aqueous solution and products were also measured by ICP-AES.

2.2.3. Synthesis of spinel LMO using the raw Li_2CO_3

Spinel LMO was synthesized via a solid state reaction using $MnCO_3$ and the raw Li_2CO_3 with different Na contents obtained from the first-stage precipitation. The molar ratio of (Li and Na): Mn was 1: 2. Prior to the heat treatment, the reactants were mixed well in the agate mortar. Then, the mixtures were placed in some ceramic boats and then heated in a tube furnace at 800 °C for 5 h under air atmosphere. At last, the crystalline forms of the obtained products were determined using X-ray diffractometer (XRD, Rigaku D/max-3C using Cu Kα radiation). And the morphology of the obtained products was examined using field emission scanning electron microscope (FE-SEM, NOVA NanoSEM 230, USA).

2.3. Adsorption experiments of spinel LMO

2.3.1. Pre-treatment of LMO

The synthesized LMO powders with various Na contents were added into 0.5 mol L^{-1} HCl solution in conical flasks, and the mixtures were kept under magnetic stirring for 24 h at 25 °C. After filtered, the hydrogen manganese oxides (HMn_2O_4, HMO) were prepared. Then, the HMO powders were washed with deionized water, and finally dried at 80 °C for 24 h. In order to analyze the corrosion resistance of LMO powders, the Mn contents in the filtrates were measured by ICP-AES. And the amount of Mn extraction (%) was calculated by the following equation:

$$R_k = \frac{n_k}{n_{k0}} \times 100\% \tag{1}$$

where R_k is the dissolved ratio of Mn; n_k is the equilibrium concentration of Mn in solution, and n_{k0} is the mass of Mn in the initial samples.

2.3.2. Adsorption experiments

To investigate the adsorption property of the prepared LIS, the prepared HMO (0.2 g) was added to 100 mL of the LiOH solution with a lithium concentration at 50 mg L^{-1} in a conical flask shaken for 24 h at 25 °C. And the lithium ion adsorption capacity was calculated by the following equation:

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \tag{2}$$

where Q_e is the lithium ion adsorption capacity; C_0 and C_e are the initial and equilibrium concentrations of lithium ion in solution, respectively; V is the solution volume; and m is the mass of HMO.

3. Results and discussion

3.1. Effect of Na_2CO_3 dosage in the first-stage precipitation

The effect of Na_2CO_3 dosage to the precipitation of Li_2CO_3 has been researched in Fig. 2. While the actual amount of Na_2CO_3 increases from 1.0 to 1.4 (*vs.* the theoretical amount), the recovery rate of lithium goes up steadily from 68.47% to 78.53%. However, the corresponding purity percentage of Li_2CO_3 decreases sharply from 70.30% to 44.13%. It is possible that the excess amount of Na_2CO_3 precipitates easily along with the formation of Li_2CO_3. In addition, the XRD patterns of the as-prepared Li_2CO_3 are shown in Fig. 3. All of the main diffraction peaks are indexed as a monoclinic phase of Li_2CO_3 (*JCPDS No.22–1141*), while the other diffraction