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Enhancement in liberation of electrode materials derived from spent lithium-ion battery by pyrolysis

Guangwen Zhang [a], Yaqun He [a, b, *], Yi Feng [a], Haifeng Wang [a], Tao Zhang [b], Weining Xie [b, d], Xiangnan Zhu [c]

[a] School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou, Jiangsu, 221116, China
[b] Advanced Analysis and Computation Center, China University of Mining and Technology, Xuzhou, Jiangsu, 221116, China
[c] College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao, Shandong, 266590, China
[d] Jiangsu Huahong Technology Stock Limited Company, Wuxi, Jiangsu, 214400, China

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ABSTRACT

In this study, pyrolysis was utilized to enhance the liberation of electrode particles in the recycling process of spent lithium-ion batteries. Pyrolysis characteristics of cathode and anode materials and the effects of pyrolysis on the liberation of electrode materials were fully investigated. Afterwards, scanning electron microscope coupled with an energy dispersive spectrometer and X-ray photoelectron spectroscopy were used to reveal the changes of mineralogical characteristics of electrode materials before and after pyrolysis. The results indicate that organic binder wrapped on electrode particles is the main reason that electrode materials are hard to liberate from foils and difficult to liberate each other. The optimum pyrolysis temperature of organic binders in electrode materials is 500 °C and the main pyrolysis products are fluorine-containing benzene and ester electrolyte. The liberation efficiency of cathode increases from 82.88% to 99.78% by pyrolysis, while that of anode increases from 88.08% to 99.60%. Meanwhile, adequate liberation of pyrolytic electrode materials requires a shorter period of time. Electrode materials from pyrolytic electrode are mainly concentrated in −0.045 mm size fraction, and they are up to 82.49% and 78.91% respectively for cathode and anode materials. 5106.

1. Introduction

Lithium-ion batteries (LIBs) have been extensively applied in electron industry, such as mobile phones, cameras, laptop computers etc., because of their high energy density, low self-discharge, long storage life, and safe handling (Bertuol et al., 2015). However, the average life time of LIBs is 2–3 years, which results in large amounts of spent LIBs are discarded into the environment (Wang et al., 2016). Generally, LIBs are mainly composed of shell, cathode, anode, electrolyte, membrane separator and the structure schematic of LIBs is shown in Fig. 1. The main anode materials are always graphite while the main components of cathode are unfixed, such as $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, as well as other lithium metal oxides (Xiao et al., 2017). Therefore, each LIB is a natural mineral that contains abundant of metals resource and it may cause serious environmental pollution if no proper disposal (Helbig et al., 2018). It has been reported that 17.60 wt% Co, 7.20 wt% Cu, 21.60 wt % Al in the spent $LiCoO_2$ LIBs. Taking one thousand kilogram spent LIBs as an example, 176 kg Co, 72 kg Cu, and 216 kg Al can be recycled, they are of great economic value. Therefore, the recycling of valuable metals, especially for cathode and anode, from spent LIBs is a significant process.

Many sophisticated technologies for the recycling of spent LIBs have been presented due to the high economic value. Chemical technology is a useful method for metals recycling because of its high purification and high efficiency, such as bio-leaching (Horeh et al., 2016), various acid-leaching (Li et al., 2015; Ferreira et al., 2009; Suzuki et al., 2012), mechanochemistry (Dorella and Mansur, 2007; Hanisch et al., 2015), and electrochemistry (Myoung et al., 2002), etc. Recently, physical methods are also proposed by many scholars, both “mechanical crushing + flotation” (Zhang et al., 2014a; He et al., 2017a) and “mechanical crushing + heated process + magnetic separation” (Li et al., 2016) are efficient physical technologies. For recycling of electrode

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* Corresponding author. School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou, 221116, Jiangsu, China.

E-mail addresses: gwzhang@cumt.edu.cn (G. Zhang), yqhe@cumt.edu.cn (Y. He).

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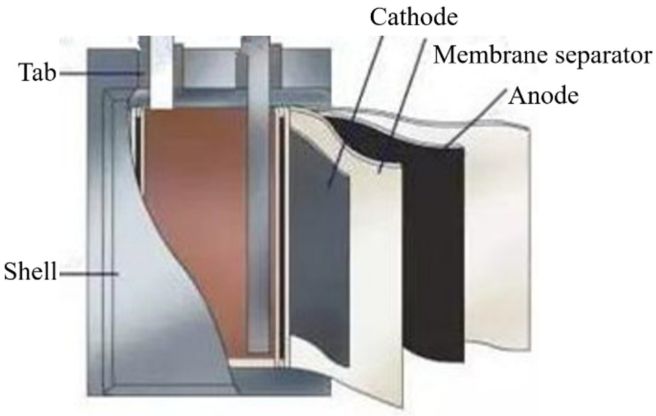

Fig. 1. Structure schematic of lithium-ion battery.

materials, it is worth noting that whether it is chemical technology or physical method, liberation i.e. anode and cathode materials are stripped off from copper and aluminum foils, is the key process. Now, main technologies for achieving the liberation between electrode materials and aluminum/copper foils are as follows: (a) mechanical crushing: in these process, the whole batteries or cathode/anode sheets are placed into mechanical crusher. Under the action of mechanical force, anode and cathode materials are stripped off from copper and aluminum foils (Ku et al., 2016; Zhang et al., 2013). Mechanical crushing may be of lower efficiency for the liberation of electrode materials, because it does not break the binding force of Polyvinylidene Fluoride (PVDF) between electrode materials and foils effectively. Studies demonstrate that removal of PVDF is an efficiency method for the liberation of electrode materials (Wang et al., 2017; Nayaka et al., 2016a); (b) ultrasonic cleaning: cathode/anode sheets are firstly cut into small parts and then put into an ultrasonic washing machine with mechanical agitation (Li et al., 2009). Anode and cathode materials will be liberated from copper and aluminum foils; (c) N-methyl-2-pyrrolidone (NMP) dissolution or ultrasonic washing with NMP: electrode materials are attached to the copper or aluminum foil by PVDF. NMP can be used to achieve the liberation between electrode materials and foils, because PVDF can be dissolved by NMP (Xin et al., 2016). Application of ultrasonic can accelerate this process (Nayaka et al., 2016b; He et al., 2017b). However, the cyclic utilization of these used solutions is very hard because some organic binders have dissolved into these solutions and then gradually reached saturation (Xu et al., 2014). It is also worth noting that the heating process is applied to accelerate the dissolution process of organic binder. But at the same time large amounts of solutions have volatilized at high temperature (Sandhya et al., 2016). Therefore, some solutions are wasted in the dissolution process. In addition, the subsequent heating process must be used to remove the organic residue in this process (Lee and Rhee, 2002). Therefore, secondary pollution may be caused in the chemical process; (d) heating process: PVDF will be decomposed at high temperature, electrode material particles will liberate from foils efficiently. Direct heating process is the simplest method, but secondary pollution may be caused (Meshram et al., 2016). Pyrolysis is a useful method to recover organic materials, and it has been used in recycling of waste printed circuit boards and waste plastics (Hao et al., 2014; Choi and Kim, 2012). Previous studies also indicate that pyrolysis can make electrode materials liberated from foils adequately with little environmental pollution (Yang et al., 2016; Sun and Qiu, 2011; Zhang et al., 2018). However, pyrolysis characteristics of electrode materials and effects of pyrolysis on the liberation of electrode materials derived from spent LIBs have not been fully characterized.

In this study, based on the liberation characteristics of electrode materials, pyrolysis was utilized to improve the liberation between electrode particles and aluminum/copper foils by removing organic binders. Pyrolysis characteristics of electrode materials were analyzed by thermogravimetry gas chromatograph-mass spectroscopy (TG-GC/MS). Advanced analysis technologies of scanning electron microscope (SEM) coupled with an energy dispersive spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS) were used to obtain the morphology, chemical composition, and chemical states of surface elements of electrode material particles before and after pyrolysis. Effects of pyrolysis on the liberation and mineralogical characteristics of electrode materials were fully investigated.

2. Experimental

2.1. Samples preparation

Spent LIBs derived from waste mobile phones were collected from the environmental protection association. Discharging process was conducted using NaCl solution with 5% mass fraction (Zhang et al., 2014b). The discharged LIBs were naturally air dried and then manually dismantled into different portions, such as shell, anode sheet, cathode sheet, and membrane separator. After discharging and dismantling, cathode and anode were pretreated. A part of cathode and anode were respectively crushed to −0.075 mm for TG analysis while others were used to analyze the effects of pyrolysis pretreatment on the liberation of electrode materials.

2.2. Pyrolysis procedures

Pyrolysis experiments were conducted in a controlled atmosphere tube furnace (MXG1200-80, Shanghai Micro-X furnace Co., Ltd.). In each experiment, one cathode (approximate 6.65 g) and one anode (approximate 4.55 g) were placed into the corundum tube and were sealed by flanges at both ends. Vacuum pump was firstly applied to provide the vacuum environment, and then the corundum tube was filled with high purity nitrogen with the air flow of 100 ml/min. Gas pyrolysis products were taken out of tube by nitrogen flow and then macromolecular organics were collected by condensation while small molecule organic gases could be treated by gas-treating system. Pyrolysis temperature increased from an initial temperature of 30 °C to terminal temperature of 500 °C at a heating rate of 10 °C/min. Samples were processed at isothermal temperature of 500 °C for 10 min. Afterwards, the samples were moved from high-temperature region to low-temperature region and then were naturally cooled to 30 °C at nitrogen atmosphere.

2.3. Crushing liberation

Raw sample and pyrolytic sample were successively crushed using a pulverizer. Each crushing time was 5 s, and then the liberated electrode materials were obtained by sieving. The coarse fractions will be returned to the pulverizer again, and the crushing process will stop when the fine fraction is less than 0.1 g. There is a significant difference of crushing property among different components of spent LIBs. After crushing, large pieces of metal shells and separator are mainly concentrated in +2 mm size fraction. −2+0.25 mm size fraction comprises aluminum/copper foils and separator with fiber shape (Zhang et al., 2014b). Therefore, particles with −0.2 mm size were collected as the electrode material concentrate in this study because electrode materials concentrated in fine particles. In addition, sieving experiments