



Recovery of valuable materials from spent lithium-ion batteries by mechanical separation and thermal treatment

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ABSTRACT

In this paper, a mechanical separation and thermal treatment process is developed to recover valuable metals and graphite from the –0.25 mm crushed products of spent lithium-ion batteries (LiBs). Effect of key parameters for roasting such as the temperature and roasting time are investigated to determine the most efficient conditions for surface modification of the mixed electrode materials by roasting. The roasted mixed electrode materials are separated by flotation operation to recover the cathode material and anode materials respectively. The results show that most of the organic outer layer coated on the surface of the mixed electrode materials can be removed at the temperature of 450 °C for 15 min. After roasting treatment, the original wettability of LiCoO₂ and graphite is regained. The –0.25 mm crushed products of spent LiBs can be separated into LiCoO₂ concentrate and graphite concentrate by flotation process efficiently. The enrichment ratios of Co, Mn, Cu and Al are 1.35, 1.29, 1.25 and 1.19, their recovery rates are 97.66%, 93.66%, 90.14% and 86.29%, respectively. This process proposed for the recovery of valuable materials is simple and of high efficient for the spent lithium-ion batteries recycling industry.

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1. Introduction

Lithium-ion batteries (LiBs) have been widely used in portable electronic equipment such as mobile phones, cameras, laptops, mobile power, etc., for the LiBs are of excellent performances including safe, high-energy density, long serving life, without hazardous elements (Zeng et al., 2015). In recent years, with the rapid development of electric vehicles, LiBs have been chosen to be the power sources (Hanisch et al., 2015). Therefore, the worldwide consumption of LiBs has maintained rapid growth. However, the service life of LiBs is in commonly 2–3 years, the more consumption means the more amount of scrap. Typical LiBs are generally composed of a metal shell, a cathode, an anode, organic electrolyte, and a polymer diaphragm. The anode is a copper foil coated with a mixture of graphite, conductor, polyvinylidene fluoride (PVDF) binder, and additives such as organic electrode and LiPF₆. Similarly, the cathode is an aluminium foil

coated with a mixture of LiCoO₂ (or some other kinds of cathode materials) with the other things. It has been reported that in spent LiCoO₂ LiBs, there are 17.6 wt% Co, 7.2 wt% Cu, 21.6 wt% Al (Zhang et al., 2014a, b). From the viewpoints of environmental preservation (Choubey et al., 2017), recovery of major components or valuable resources (Bahaloo-Horeh and Mousavi, 2017), the recycling of spent LiBs is quite necessary.

Recycling of spent LiBs arouses many researchers' interest, and there are many useful achievements. In general, there are three kinds of methods. They are physical method, chemical method and biological method (Ordoñez et al., 2016). In a recycling process of spent LiBs, physical method is usually applied as a pre-treatment (Chen et al., 2017) to treat the outer cases and shells and to concentrate the metallic fraction, which will be conducted to chemical method (Pinna et al., 2017) (a hydrometallurgical or a pyrometallurgical recycling process) or biological method (Horeh et al., 2016) (a biohydrometallurgy recycling process) to gain purer metal products (Zhang et al., 2013). However, in either case, the purification operation is very difficult because of the organic matter used in LiBs, such as the graphite, polymer diaphragm, electrolyte and PVDF binder, which not only increase the volume of

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the feeding, hinder the chemical reactions but also pollute the environment.

It has been proved that after crushing, the metal shell, copper foil, aluminium foil and polymer diaphragm still remained in large size, with air separation process or gravity separation, the value materials in big size could be recovered efficiently. However, electrolyte and PVDF binder following LiCoO_2 and graphite particles concentrated in small size fractions (Al-Thyabat et al., 2013). To separate the LiCoO_2 particles from graphite particles become a new problem. As the electrode materials have a very small particles size that is only 20–70 μm , though the density of LiCoO_2 particle is much higher than graphite particle, it is almost impossible to separate the mixed electrode materials with density separation. However, LiCoO_2 is hydrophilic for it is ionic crystal with strong polarity; and graphite is hydrophobic for it is nonpolar. Therefore, LiCoO_2 and graphite have opposite surface wettability (Huang et al., 2016). In theory, flotation may be a useful method for the separation of LiCoO_2 and graphite. The flotation test results showed that LiCoO_2 and graphite particles were coated by electrolyte and PVDF binder, which makes flotation result bad, to remove the organic outer layer can improve the flotation result (Zhang et al., 2014a, b).

The flotation results are totally depended on the removing of electrolyte and PVDF binder from the surfaces of LiCoO_2 and graphite particles. It was reported that the electrolyte and PVDF binder can be removed by Fenton solution (He et al., 2017), the organic materials such as electrolyte and PVDF binder were destroyed by $\cdot\text{OH}$ generated from Fenton solution. The mixed LiCoO_2 and graphite can be separated and recovered respectively and efficiently. However, Fenton solution needs Fe^{2+} reacting with H_2O_2 to produce $\cdot\text{OH}$, the introducing of Fe will make the following chemical purification more complex and expensive. In addition, the Fenton solution reacting conditions must be controlled very carefully, or the removing rate of electrolyte and PVDF binder will be very low, the flotation result would be bad. Therefore, the electrolyte and PVDF binder removing method should be easy to control, reacted fast and no more impurities introduced.

In this work, we proposed to meet the above requirements by roasting method and recover LiCoO_2 and graphite from the mixed electrode materials by flotation respectively. The thermostability of both recovered LiCoO_2 and graphite was analysed firstly, and the effect of roasting time and temperature on the wettability of the recovered electrode materials were studied and discussed. Under the optimum condition, the recovered mixed electrode materials were roasted, and by flotation, the LiCoO_2 and graphite were separated from each other and the mechanism was discussed, too.

2. Experimental

2.1. Sampling and preparation

The graphical presentation of the experimental approach was as shown in Fig. 1. Spent LiBs used in this research were 18650 type, and the total weight was 1 kg. Before dismantling and crushing steps, in order to make the experiment process safe, the spent LiBs were discharged completely in 5 wt% sodium chloride solution for 24 h, and let them air-dry afterwards. Then, the spent LiBs were dismantled by manual work, the anode and cathode were obtained respectively.

In this research, three kinds of samples were prepared, they were the -0.25 mm crushed product only come from the anode which were the graphite concentrate, the one only come from the cathode which was the LiCoO_2 concentrate and the one come from both the anode and cathode which was mixed LiCoO_2 and graphite concentrate.

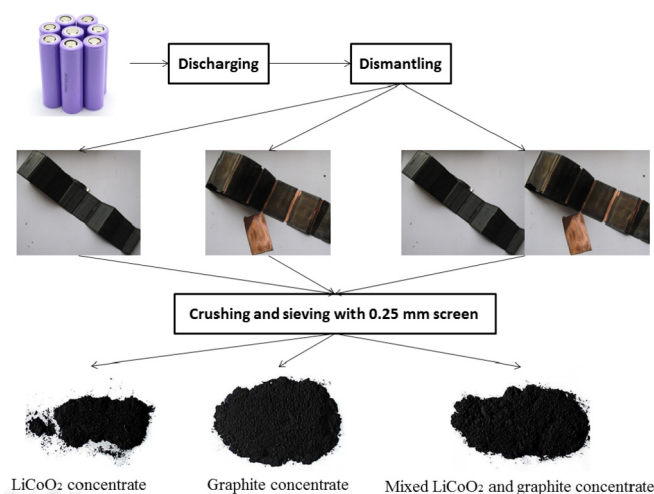


Fig. 1. Graphical presentation of the experimental approach.

2.2. Method

2.2.1. Roasting test

Graphite concentrate and LiCoO_2 concentrate were analysed by combining TG (Retsch STA-409C, Germany) and FTIR (NICOLET-Nenus 470, USA) to show ignition loss and the composition of the generated waste air from 25 °C to 900 °C. The TG test was in an air atmosphere, the airflow was 100 ml/min, the temperature range was from 25 °C to 900 °C and the heating rate was 15 °C/min. The FTIR test range was from 400 to 4000 cm^{-1} , the resolution was better than 1 cm^{-1} , the S/N was better than 6000.

All the two samples were thermally treated in muffle furnace, and the roasted samples were analysed by SEM and XPS to show the surface properties. Powder structure and particle configuration of the -0.5 mm crushed products were analysed by a scanning electron microscope (SEM, FEI quanta 250, America) equipped with a tungsten filament and coupled with an energy dispersive spectrometer (EDS, Bruker QUANTAX400-10, Germany) using a silicon drift detector.

The XPS test was carried out by an X-ray photoelectron spectrometer (XPS ESCALAB 250Xi, America) at room temperature in an ultra-high vacuum (UHV) system. The base pressure of the analysis chamber during measurements was lower than 1×10^{-9} mbar. Al K α radiation ($h\nu = 1486.6\text{eV}$) from a monochromatized X-ray source was used for the experiments. For all analyses, the take-off angle of photoelectrons was 90° and the spot size was 900 μm . Spectra were recorded with the pass energy of 20 eV, and the energy step size was 0.05 eV.

The contact angle was measured by a Contact Angle Meter (DSA100, Kruss, Germany) to show the wettability changes. The roasted sample was pressed into sheet, and a drop of distilled water was put on the surface of the sheet in six different positions. Six contact angles were got, and the average value was calculated to be the last result.

2.2.2. Flotation

Pulp density, impeller speed, pH and aeration during flotation were maintained at 40 g/L, 1800 rpm, 9 and 0.8 L/min, respectively. Methyl isobutyl carbinol (MIBC) and n-dodecane were used as frother and collector in the flotation with the dosage of 150 g/t and 300 g/t. The dry masses of the concentrates and tailings were determined and samples assayed for their elemental compositions by X-ray fluorescence (XRF, Bruker S8 Tiger, Germany) using a powder pressed method to prepare the samples.

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