Surface analysis of cobalt-enriched crushed products of spent lithium-ion batteries by X-ray photoelectron spectroscopy

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ABSTRACT

In this work, detailed surface analysis on the fine crushed products of spent lithium-ion batteries is investigated by X-ray photoelectron spectroscopy. The results showed that although $LiCoO_2$ was a main composition of the fine crushed products, the surface atomic abundance of cobalt was only 1.69%, but the surface atomic abundance of organic compounds was more than 75%. During the crushing process, $LiPF_6$ decomposed and harmful and toxic substances such as HF, POF_3 were generated, it is necessary to take appropriate measures to avoid the secondary pollution in the crushing process of spent LiBs. Metallics such as Co, Cu, and Al were fluoridated and oxidized, and the organic compounds were oxidized and decomposed, too. The surface composition and microstructure of the fine particles were presented, which showed that the fine particles in the crushed products were lithium cobalt oxides and graphite cores coated inside by organic compounds. Flotation test pointed out that if the outer layer was removed, the flotation selectivity would be greatly improved: the enrichment ratio could be increased from 1.16 up to 3.24. Based on the surface analysis, potential ways for removal of the outer layer were proposed.

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1. Introduction

Lithium-ion batteries (LiBs) are widely used as power source for mobile phones, laptops and other electronic devices due to the advantages such as light weight, high energy density, high voltage, safe handling and very low self-discharge rate [1]. LiBs also have been chosen to provide power for electric automobiles [2]. In recent years, the worldwide consumption of lithium ion batteries has maintained rapid growth. The worldwide LIBs production had reached 4.6 billion in 2010. And it is estimated that the production of LiBs will be 7.0 billion in 2015 [3,4]. However, the more consumption of LiBs means the more amount of scrap. In spent LiBs, the cobalt and lithium contents are 5–15 wt.% and 2–7 wt.% respectively, which are higher than those found in natural ores or even concentrated natural ores, and also have a potential hazard to the ecosystem and human health [5,6]. From the viewpoints of environmental preservation, recovery of major components or valuable resources, and provision of raw materials, the recycling

of spent LiBs is highly desirable in either the present or the future [7–9]. Therefore, the development of recycling technologies for spent LiBs has attracted great attention.

The electrode materials are the main components for the recycling of spent LiBs due to the high value of cobalt. By now, there have been a lot of research achievements developed on the recycling technologies such as mechanical separation processes [8], thermal treatment [9–11], mechanochemical process [12], dissolution process [13], acid leaching [7,14], bioleaching [15–18], solvent extraction [19,20], chemical precipitation [12,14], electrochemical process [21] and ionic liquid separation [22]. However, most of them are still in pilot or laboratory scale. Because most acquisition of electrode materials used in the experiments was by manual dismantling method. It is obvious that in the recycling process of spent LiBs, manual dismantling is responsible for the low efficiency and high cost. Mechanical crushing and separation [23] are the key processes for industrial treatment of the other e-wastes with the purpose of obtaining liberated target products. It is, therefore, necessary to develop an effective mechanical crushing and separation method for recycling process of spent LiBs.

A LIB comprises a cathode, an anode, organic electrolyte, and a separator. The lamination of a cathode, an anode, and a separator by a pressing makes those electric contacts. The anode is a copper

plate coated with a mixture of carbon graphite, conductor, Polyvinylidene Fluoride (PVDF) binder, and additives such as $LiPF_6$. Similarly, the cathode is an aluminum plate coated with a mixture of active cathode material, electric conductor, PVDF binder, and additives. $LiCoO_2$ is commonly used as an active cathodic material for almost all the commercialized LiBs [24]. So when spent LiBs are being crushing in the crusher cavity, chemical reaction occurs on the surface of the mixed materials of spent LiBs. Previous research [25] has indicated that after crushing, the fine particles under 0.25 mm were enriched electrode materials graphite and $LiCoO_2$, which makes a good condition to meet the separation requirement for graphite and $LiCoO_2$. However, it is known that the surface properties seriously influence the separation process especially for the fine particles in such size fractions [26,27]. Thus, it is necessary to study these reactions in order to make sure whether the crushing process is environmental friendly and helpful for the following separation process or not.

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is widely used to determine the composition, and to monitor the reactivity of the very surfaces (only the top one or two atomic layers) of solid materials. Due to the chemical reaction occurs on the surface and the target product cobalt mainly enriched in the fine crushed products [25], in this paper, we report a detailed investigation of the chemical composition and the chemical states of all the elements on the surface of the fine crushed products of spent LiBs using XPS. Possible chemical reactions among these materials used in spent LiBs during crushing process were discussed. And in the end, a flotation experiment was carried out to test the impact of the surface microstructure on the separation between $LiCoO_2$ and graphite, and potential ways for improving flotation selectivity were proposed.

2. Materials and methods

2.1. Sampling and preparation

Spent LiBs with different manufacturers and sizes chosen in our study were kindly donated the environmental protection association at China University of Mining & Technology. In order to make the experiment process safe, 10 kg spent LiBs were discharged in the water with NaCl of 5 wt.% for 24 h and air-dried afterwards. Shear crusher was used to cut the spent LiBs into pieces, and then comminution was carried out by an impact crusher. After crushing, the fine powder under the size of 0.25 mm was chosen in this research, and was measured by XPS using powder pressed method to prepare the samples. With the help of an X-ray fluorescence spectrometer (XRF, Bruker S8 Tiger, Germany), the element composition of the fine powder under 0.25 mm is listed in Table 1.

2.2. XPS analysis

The XPS experiments were carried out at room temperature in an ultra-high vacuum (UHV) system with the surface analysis system (ESCALAB 250Xi, America). The base pressure of the analysis chamber during the measurements was lower than 1.0×10^{-9} mbar. Al Ka radiation ($h\nu$ = 1486.6 eV) from a monochromatized X-ray source was used for XPS. For all analyses, the take-off angle of the photoelectrons was 90° and the spot size was 900 μm. The

spectra of survey scan were recorded with the pass energy of 100 eV, the energy step size was 1.00 eV. High resolution spectra were recorded with the pass energy of 20 eV, and the energy step size was 0.05 eV. The data processing (peak fitting) was performed with the Avantage (version 5.41) software provided by Thermo Fisher Scientific Corporation, using a Smart type background subtraction and Gaussian/Lorentzian peak shapes. The binding energies were corrected by setting the C 1s hydrocarbon (—CH_2—CH_2— bonds) peak at 284.8 eV.

2.3. Flotation test

There were two kinds of flotation feeds for this test. Sample 1 was the cobalt-enriched crushed products recovered from spent LiBs, and sample 2 was prepared by mixing commercialized $LiCoO_2$ and graphite together, the weight proportion was 1:1. Pulp density, impeller speed, pH and aeration during conditioning and flotation in the cell were maintained at 75 g/L, 1800 rpm, 9 and 0.8 L/min, respectively, for all experiments. Kerosene and sec-octyl alcohol were used as collector and frother in the flotation with the dosage of 360 g/t and 40 g/t. The dry masses of the concentrates and tailings were determined and samples assayed for their elemental compositions by XRF.

3. Results and discussion

3.1. Chemical composition

The XPS survey spectra (Fig. 1) show element composition detected from surface of the fine crushed products, the elements are Cu, Co, F, O, C, P, Al and Li. The atomic percentage of the elements in the sample is also listed in Table 1. Compared to the results obtained by XRF, it was obvious that the content of each element detected from the surface was very different. The contents of C, F, Cu, Al and P were much higher, while, the contents of Co and O were much lower. $LiCoO_2$ and graphite were both the main materials in the fine crushed products, but there were some other chemical forms of carbon. Cobalt only came from $LiCoO_2$, therefore, the distribution of cobalt could reflect that of graphite. The content of cobalt on the surface was very low, it was confirmed that there must be something else on both the surfaces of $LiCoO_2$ and graphite powders.

3.2. Chemical state analysis

High-resolution XPS was adopted to study chemical states of the elements detected from surface of the sample in detail, and binding energy (BE), full width at half maximum (FWHM) and atomic percentage of each element are listed in Table 2 [28].

In LiBs, lithium is from the cathode active materials $LiCoO_2$ and electrolyte $LiPF_6$. The Li 1s spectrum (Fig. 2) level region shows the presence of two peaks, the first one at 56.4 eV is assigned to LiF, the second one at 54.5 eV is assigned to Li_2CO_3 and $LiCoO_2$. The analysis of Li 1s core peaks confirms that LiF seems to be the major chemical state of Li detected from the surface, and the atomic percentage is as high as 2.85%. $LiPF_6$ has been reported that has two disadvantages [29]. One is its thermal stability and the other is its reactivity with water. During the crushing process, high temperature can be produced in the crushing cavity [23], and indeed the crushing environment is not absolutely dry. So, $LiPF_6$ was decomposed during the crushing process, and LiF was one of the decomposition products. New generated HF could react with $LiCoO_2$, and more LiF was generated.

Phosphorus used in LiBs also comes from the electrolyte $LiPF_6$. Fig. 3 shows the P 2p spectrum made of two doublets (2p3/2 and

Table 1
Atomic percentage of the elements detected by XRF and XPS.

Element (at.%)	C	O	F	Co	Cu	Al	P	Li
XRF	54.16	30.29	3.85	9.51	0.22	1.58	0.38	–
XPS	61.91	18.77	7.5	1.69	0.89	4.02	1.18	4.04