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Short communication

Characteristics of wet and dry crushing methods in the recycling process of spent lithium-ion batteries

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HIGHLIGHTS

- We get the particle size distribution of crushed products of spent LIBs.
- The microscopic morphology and the composition distribution of the <0.25 mm size fractions are analyzed.
- Spent LIBs have good selective crushing property.
- Dry crushing method brings the selective crushing characteristic into full play.

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ABSTRACT

Methods of wet and dry crushing are adopted to experiment on spent lithium-ion batteries in this investigation. Particle size distribution is analyzed using the wet and dry screening respectively and fine crushed products are characterized by XRD, SEM and EDX. A comprehensive comparison of the characteristics between the two crushing methods indicates that the wet crushing results in an enrichment of each component in spent lithium-ion batteries to fine fractions because of the scouring action of water flow, which makes the fine products complicated and lost; while the dry crushing method can bring the selective crushing characteristics of spent lithium-ion batteries into full play, and in this case, lithium cobalt oxide and graphite electrode materials can be liberated from aluminum foil and copper foil without the overcrushing of the other components in spent lithium-ion batteries. Thus, the purity and dispersion of electrode materials can be improved to create favorable conditions for subsequent purification and regeneration.

1. Introduction

In virtue of the advantages such as high energy density, high battery voltage, long charging–discharging cycle, wide temperature range and safe [1,2], the lithium-ion batteries (LIBs) are extensively used in portable electronic equipments. Along with the rapidly increased use of LIBs, the annual global production of LIBs will reach 7 billion in 2015 [3]. After removing the plastic and metal casing, LIBs contain 36 ± 9 wt.% of cobalt and in which high metal content even higher than the processed mineral or ore [4]. However, because of flammable and toxic ingredients in LIBs [5], safe disposal of LIBs has become a tough issue, and thus, the recycling and harmless disposal of spent LIBs has become more and more important.

By now recycling of spent LIBs is still in its infancy. Though there are many recycling methods of spent LIBs, the vast majority of recycling methods are based on hydrometallurgical chemical process and limited to laboratory scale [6–8]. Most recycling research mainly focus on the recycling of $LiCoO_2$ [9–11], while plenty of useful materials are lost during those processes. However, most acquisition of the electrode materials used in the experiments is by manual dismantling method [12–14], and it is obvious that in the recycling process of spent LIBs whose amount are huge and the size are small, manual dismantling is responsible for the low efficiency and high cost. It is, therefore, necessary to develop an effective crushing method for recycling process of spent LIBs.

Mechanical crushing is a key link in the recycling process of E-waste [15]. The combined rate and reaction rate of followed

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chemical, biological methods, separation efficiency and even the choice of subsequent physical methods are directly influenced by the particle size distribution and liberation degree of the crushed products. Though, Shin [10] and Li [16] used crushing methods in their research of recycling process of spent LIBs, until now the research on the crushing properties of spent LIBs has not been reported in detail.

This work aimed at realizing the characteristics of wet and dry crushing methods and mechanical crushing properties of spent LIBs by analyzing the influences of wet and dry crushing methods on the efficient crushing of spent LIBs.

2. Experimental

2.1. Materials and pretreatment

Spent LIBs used in mobile phones of different manufactures and sizes were collected by Environmental Protection Association of China University of Mining & Technology for this study. In order to ensure the safety of the experiment, before crushing, samples were fully discharged for 24 h with 5% mass fraction NaCl solution and then air dried naturally. The total weight of samples was 30 kg, 165.75 g and 133.82 g crushed products of wet and dry crushing respectively were sampled representatively for instrumental analysis.

2.2. Crushing and screening

The wet crushing equipment is a blade crusher with a water medium. Its schematic representation is shown in Fig. 1. Blades are attached to rotating arms in a way that allows the blades to swing freely. As the arms rotate inside the drum the swinging blades contact the feed material at a high speed. This imparts kinetic energy from the blades to the feed, fracturing the feed in the process. High speed feed particles also fracture when they contact other particles or stationary parts of the crusher. Feed that escapes fracture after one impact is hit by the blades again. In this crusher, water is fed into an inlet. This causes the particles to form slurry that carries the broken particles through the sieve plate.

The wet impact crusher was used for wet crushing for 20 s with 500L h^{-1} water consumption. The dry crushing was carried out by a joint two-stage way. Firstly, the spent LIBs were chopped in to pieces by shear crusher and then the products were crushed in the impact crusher for 20 s. Sieve analysis was carried out by Retsch AS-200 automatic screening instrument. Wet and dry screening were used for the Sieve analysis of wet and dry crushed products respectively.

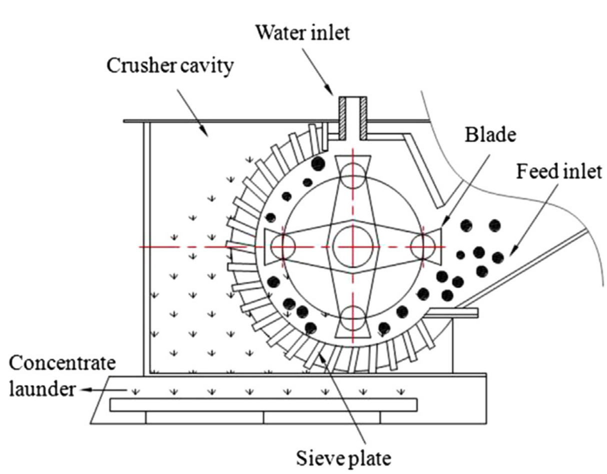

Fig. 1. Sketch of wet impact crusher.

2.3. SEM + EDX analysis

In low vacuum mode, SEM (Quanta 250, FEI, America) and EDX (QUANTAX400-10, Bruke, Germany) were jointly used to analyze the micro-morphology and composition distribution of crushed products.

2.4. XRD analysis

XRD (D8 ADVANCE, Bruke, Germany) was applied to make phase analysis of crushed products. The tube voltage of X-ray was 40 kV and the current was 30 mA. Cu was made as the anode target material. The scanning speed was 0.1 s/step and the interval was 0.019450 (step).

3. Results and discussion

3.1. Sieve analysis

The particle size distribution of crushed products by dry crushing is shown in Fig. 2. Wherein particles larger than 2 mm accounted for 27.57%. While yield of 2–1 mm, 1–0.5 mm, 0.5–0.25 mm three size fractions were only 16.21%, and the particles under 0.25 mm occupied the 56.22% of gross. In comparison, the particle size distribution of crushed products by wet crushing (Fig. 3) described that the yield of fraction larger than 2 mm reached 21.28%. 2–1 mm, 1–0.5 mm, 0.5–0.25 mm three size fractions yielded 30.46%. The total yield of fractions smaller than 0.25 mm in crushed products arrived at 48.26%. Thus it can be seen that the particle size distribution of crushed spent LIBs was not uniform. The coarse size fractions and the fine size fractions were both high while it is low with middle size fractions. That is because LIBs are complex of various materials with different crushing mechanical properties. So, under the same crushing condition, different materials have different particle size distribution. Therefore, the crushing of spent LIBs belongs to selective crushing. However, the performance of selective crushing for dry crushing is obviously better. Given that dry screening is not thorough enough, the actual effect will be better. It means different materials in the dry crushed products can be well separated only by screening.

These results all relate to the structure of spent LIBs: the outermost layer is a plastic shell. The inner core is well encapsulated by aluminum shell with roll type structure which mainly consists of the anode with lithium cobalt oxide pasted on

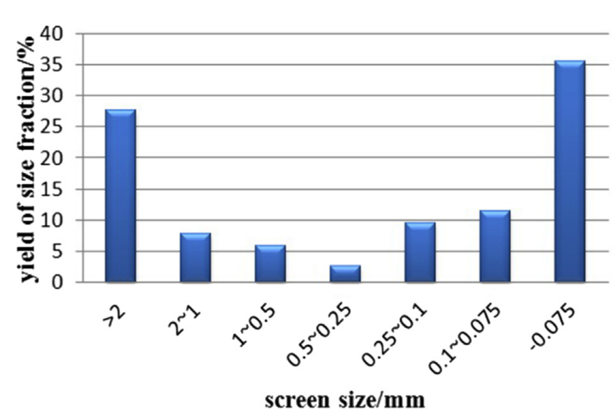

Fig. 2. Particle size distribution of dry crushed products.