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Pre-concentration of graphite and $LiCoO_2$ in spent lithium-ion batteries using enhanced gravity concentrator

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Abstract: The pre-concentration of electrode material of spent lithium-ion battery has great significance on the resource utilization and environmental protection. The feasibility of separation of graphite and $LiCoO_2$ based on density difference using the enhanced gravity concentrator was verified in this paper. Combustion characteristics of $LiCoO_2$ and graphite were used to propose a simple evaluation index of separation efficiency. Separation tests were carried out to specify the influence of operating parameters on the separation efficiency. Moreover, the effect of particle size on the separation performance was studied. Combustion characteristics results showed that mass loss of graphite was much greater than that of $LiCoO_2$. Thus, mass loss were used to evaluate the purity of product. Effective separation of graphite and $LiCoO_2$ was achieved by the enhanced centrifugal separator. Separation results showed that increasing centrifugal force decreased the overflow yield and increased the graphite content of the overflow stream. In addition, yield of overflow grew an increase in fluidization water pressure, while the purity of graphite in overflow decreased. The effect of particle size on the separation efficiency was also significant, the separation efficiency decreased with the decreasing of particle size.

Keywords: *spent lithium-ion batteries, electrode material, resource utilization, pre-concentration, enhanced gravity concentrator*

1. Introduction

In the commercialization of rechargeable batteries, lithium-ion batteries have a wide range of applications due to high energy density and relatively safe handling. Waste battery recycling issues have gradually been valued because the enormous production and potential environmental pollution risk (Chen et al., 2016). The recovery of valuable components in the waste battery has been studied for many years. The current techniques mainly include hydrometallurgy, pyrometallurgy and physical separation etc. The separation process is mainly comprised of crushing and liberation of various components, separation and enrichment, smelting and purification, etc.

Dismantling is the first step to fully separate the components of the waste lithium ion battery and it is often done manually (Bahgat et al., 2016; Sun and Qiu, 2011). Mechanical fragmentation was utilized for battery breaking, and the enrichment of the components has also been studied (Georgi et al., 2012; Granata et al., 2012). Blade crusher and joint two-stage crushing that consist of shear crusher and impact crusher was utilized to study the breakage behavior of spent lithium-ion batteries. The results show that the selective crushing effect caused by differences of mechanical properties of the components can enrich lithium cobalt oxide and graphite electrode materials in the -0.25 mm size range and they can be separated from other metal materials because of size difference, which provides

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favorable conditions for subsequent purification and reuse (Zhang et al., 2013). In the subsequent study, element enrichment in different particle size fractions was studied. Based on this information, flowsheet for recycling spent batteries was proposed. Results show that the surface of the particles of -0.25 mm fraction that contains lithium cobalt oxide and graphite is covered with a layer of hydrocarbon, which has a negative effect on flotation (Zhang et al., 2014a, 2014b).

The reuse of electrode materials is an important part of resource utilization. The electrode material of lithium ion battery is mainly composed of $LiCoO_2$ and graphite that is mainly concentrated in the -0.25 mm size fraction of the broken product. The valuable component can be dissolved into liquid phase by acid or alkali solution, and then the metal is separated and enriched by precipitation and extraction. The leaching of electrode materials has been studied by several authors, and the $LiCoO_2$ obtained by leaching treatment has high purity (Wang et al., 2016; Xin et al., 2016; Chen et al., 2015; Gratz et al., 2014; Joulié et al., 2014; Meshram et al., 2015). Because of the high cost of leaching treatment, it is necessary to enrich the material in advance.

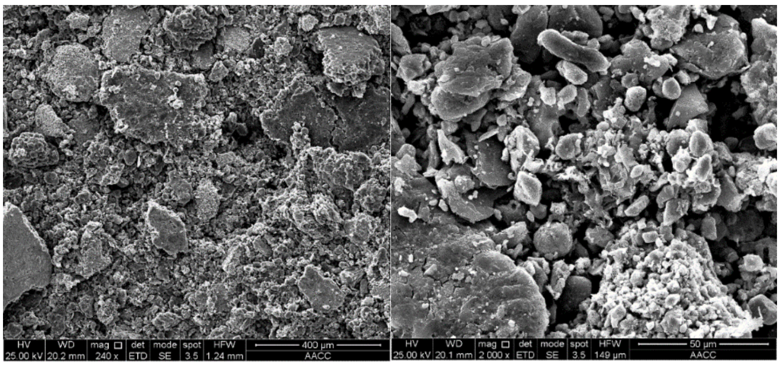
As the density of graphite is different than that of $LiCoO_2$, gravity separation is suitable as traditional equipment cannot achieve effective separation due to lower settling velocity of particles. However, the invention of the Enhanced Gravity Separator (EGS) improved the separation accuracy of fine mineral fractionss (usually -0.5 mm) (TAO et al., 2006; Batalović, 2011; El-Midany and Ibrahim, 2011; Uslu et al., 2012). The introduction of the centrifugal force field improves the stratification efficiency of the particles. Falcon concentrator and Knelson concentrator have excellent separation efficiency of fine materials with density difference (Liu et al., 2006; Greenwood et al., 2013).

The feasibility of pre-enrichment of electrode material in the waste lithium ion battery recycling by using the enhanced gravity separation technology based on density difference was verified in this paper. The effect of main operation parameters on separation efficiency were studied. In addition, the effect of particle size on the sorting process was also discussed.

2. Experimental

2.1 Materials

Spent lithium-ion batteries were manually disassembled to separate the electrode material and other components. The broken electrode material is fully mixed in order to ensure that the properties are consistent. The electrode material with mass of 60 grams was sealed in a sample bag to isolate the sample from the air. In order to observe the micro morphology of the samples, scanning electron microscope (SEM, Quanta 250, FEI, America) was adopted at high vacuum mode. Qualitative analysis of the microstructure of the samples were conducted by energy dispersive X-ray analyzer (EDX, Quantax400-10). Results are shown in Fig. 1.



(a) 240× (b) 2000×

Fig. 1. SEM images of the samples

Fig. 1 (a) shows the overall morphology of samples and it can be seen that the coarse particles in products are mainly flaky. Fig. 1 (b) illustrates how the flaky coarse particles are composed of fine grains with micrometer size. In addition, the surface roughness of the particles is high. The reason of this phenomenon is that the electrode material powder is adhered on the electrode foil by a binding agent. Fig. 2 shows that the elements composition of the materials are carbon, oxygen and cobalt. In addition, it also contains a small amount of manganese, copper and aluminum and other elements, which is mainly caused by the excessive force used in breaking the battery cover.

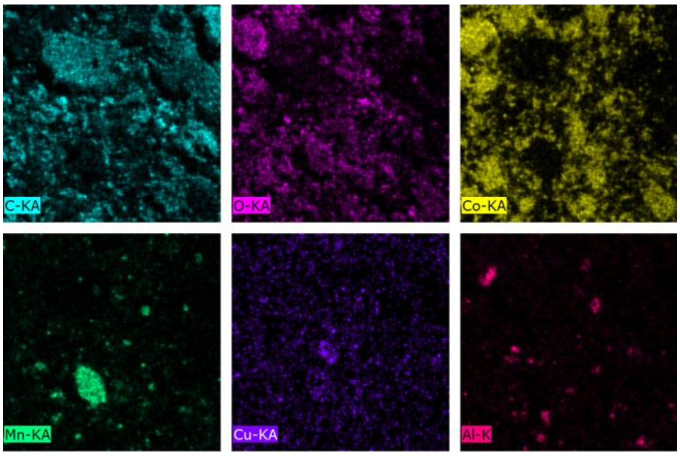


Fig. 2. Surface element distribution of Fig. 1(a)

2.2 Evaluation of separation efficiency

In order to develop simple evaluation index of separation efficiency, the combustion characteristics of pure lithium cobalt oxide and graphite were studied. Test temperature was 815 °C, and the mass loss of pure lithium cobalt oxide and graphite with mass of 1 gram using different roasting times was measured. Therefore, based on the different combustion characteristics of $LiCoO_2$ and graphite, the mass loss rate was used to evaluate the purity of the product. The lower is the mass loss, the higher is content of $LiCoO_2$:

$$\text{Mass loss} = \frac{m_0 - m_i}{m_0} \times 100\% . \quad (1)$$

In the formula (1) m_0 is the initial mass of the sample and m_i is the mass of the residue after combustion treatment.

2.3 Separation tests

Falcon concentrator (SB40) that is semi-batch unit was used for separation test. The structure of the separator is shown in Fig. 3. A sample with weight of 60 gram was mixed with water into pulp with volume of 0.5 dm^3, and then it was fully stirred evenly. Pulp was fed into the separation chamber from feed port of concentrator by peristaltic pump with flow rate of 2.4 dm^3/min. Under the combined effects of centrifugal force and fluidization water, stratification and separation of particles was achieved. The light product entered the overflow, the heavy product was enriched in the enrichment area and discharged from the discharge port at the bottom of separation chamber when the sorting process completed. The products were filtered and dried separately. The yield is the ratio of the overflow quality to the total mass of overflow and underflow.

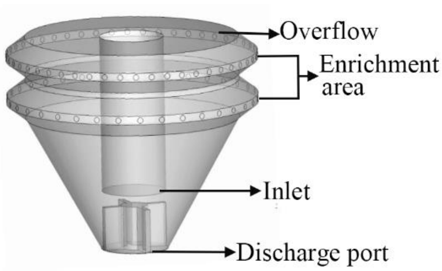


Fig. 3. Structure of the Falcon concentrator

2.4 Influence of particle size on separation efficiency

For the study of separation efficiency difference of narrow size particles, namely the effect of particle size on the separation efficiency, products of overflow and underflow were sized by standard screening procedure, and grade (mass loss) of narrow size products were analyzed under optimal experimental conditions.

3. Results and discussion

3.1 Analysis of the combustion characteristics of electrode material

Test results of combustion characteristics of pure $LiCoO_2$ and graphite at 815 °C under different time conditions are shown in Fig. 4. With the increase of roasting time, the mass losses of $LiCoO_2$ are almost unchanged and they are less than 1%. It is clear that the mass loss of graphite is much greater than that of lithium cobalt oxide, ignition loss rates of graphite are 33%, 58% and 100% at the roasting time of 20 min, 40 min and 60 min. Mass loss became relatively constant when the roasting time is more than 60 minutes. This shows that the thermal stability of $LiCoO_2$ is much greater than that of graphite. Therefore, the mass loss can be used to evaluate the content of $LiCoO_2$ and graphite. High mass loss rate means high graphite content.

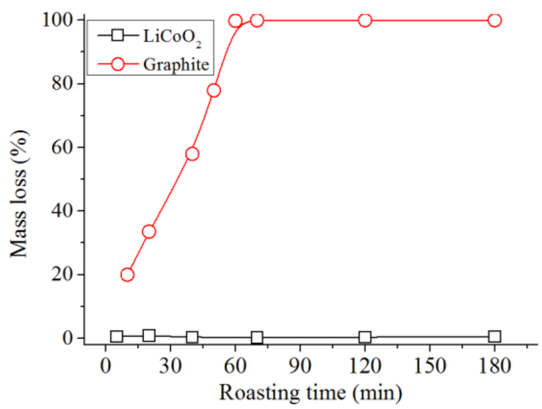


Fig. 4. Mass loss of electrode materials under different roasting time

3.2 Separation results of enhanced gravity concentrator

Separation results of electrode materials of spent lithium-ion batteries at different centrifugal force and fluidization water pressure are shown in Fig. 5 and Fig. 6.

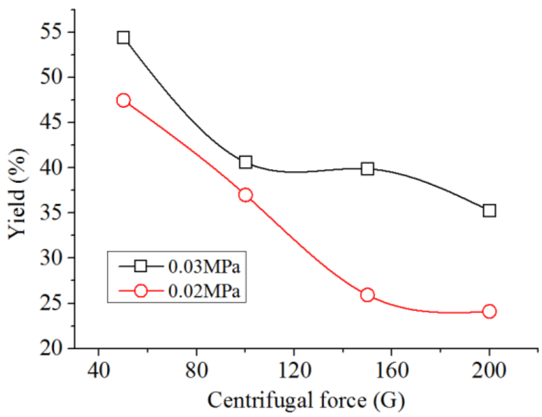


Fig. 5. Influence of centrifugal force and fluidization water pressure on the yield of overflow

As shown in Fig. 5, centrifugal force and fluidization water pressure have great influence on the yield of overflow. With the increase of centrifugal force, the yield of overflow (low density products) decreased gradually. The explanation of this phenomenon is that the settling effect of particles in the radial direction, namely the separation direction, is enhanced by the increasing centrifugal force. That is, the function of centrifugal force is to capture the particles with greater density into enrichment groove. The greater the centrifugal force, the more obvious the capture effect is.

In addition, the increasing fluidization pressure provides greater fluid resistance for the settling of particles, so the particle is difficult to settle. Thus, the yields of overflow increase with the increase of fluidization pressure. However, the grade of the heavy fraction would be improved with an increase in fluidization water.

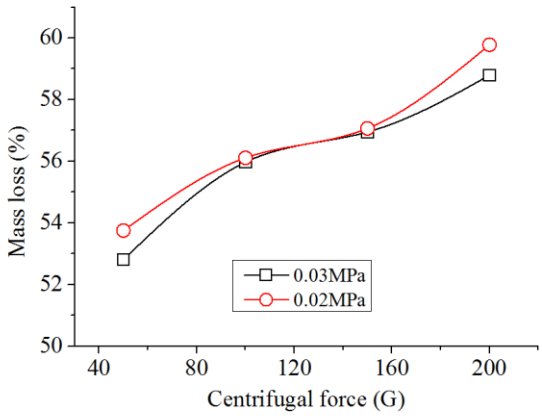


Fig. 6. Influence of centrifugal force and fluidization water pressure on the mass loss of overflow.

Fig. 6 shows the effect of centrifugal force and fluidization water pressure on the mass loss of products in overflow. The mass loss increases with the increase of centrifugal force, and shows that increasing centrifugal force contributes to the high density materials enrichment in the enrichment area and only let light particles into the overflow. Although the yield of overflow is reduced, the proportion of graphite in the overflow is gradually increasing, that is, the large centrifugal force is helpful to increase the purity of graphite in the condition of loss of graphite recovery. Increasing centrifugal force can increase the velocity gradient of the particle group in the separation region, and strengthen the Bagnold shear loose effect dominant by density. Moreover, fluidization water pressure also has influence on the grade of the product. The mass loss rate of the product at fluidization water pressure of 0.02 MPa is greater than that of the 0.03 MPa. This phenomenon shows that increasing fluidization water pressure can improve the yield of overflow, but it has an adverse effect on the purity of the overflow product.

In summary, the increase of centrifugal force can reduce the yield of overflow, but increase the purity of the overflow product. Meanwhile, the increase of fluidization pressure is helpful to increase the yield of overflow, however, the purity of the overflow product is reduced. Therefore, the centrifugal force and the fluidization water pressure need to be integrated to achieve the best separation effect.

3.3 Separation efficiency of different particle sizes in separation process

Separation performance of certain size fraction was analyzed by screening test of products that achieved at centrifugal force of 100 G and fluidization water pressure of 0.03 MPa. Results are shown in Fig. 7. Mass loss was used as the evaluation index.

As can be seen in Fig. 7, the materials with different size in both overflow and underflow have different mass loss. In underflow, the mass loss of different size fractions show only slight change. In overflow, the mass loss rate change is relatively significant and it decreased with the decrease of particle size. It is also clear that the mass loss rate difference of materials with same size in overflow and underflow decreased with particle size, which illustrates that the separation efficiency is gradually reduced with the decrease of particle size.

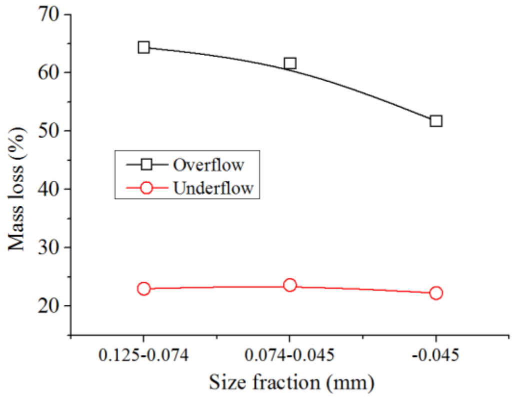


Fig. 7. Separation performance difference of narrow size fraction

4. Conclusions

Because of the existence of the valuable metals and the potential environmental pollution risk, the resource utilization of the spent lithium ion battery has been gained more importance. Electrode active materials mainly include $LiCoO_2$ and graphite, which is in the presence of powder form. In this study, enhanced gravity separation of electrode materials base on density difference was proposed to separate $LiCoO_2$ and graphite.

Combustion characteristics of pure $LiCoO_2$ and graphite were studied. Results show that mass loss rate of graphite is much greater than that of $LiCoO_2$. When the roasting time is 60 minutes at 815 °C, the mass loss of the $LiCoO_2$ is less than 1%, but the mass loss of graphite is 100%. Therefore, the mass loss of the product can be used to evaluate the graphite content. That is, the greater the mass loss, the higher the graphite content.

Separation experiments were carried out by Falcon SB40 concentrator. The influence of key operating parameters on the separation efficiency was discussed. Separation results show that yield of overflow decreases with the centrifugal force and increase with fluidization water pressure. In addition, mass loss rates increase with centrifugal force and decrease with fluidization water pressure. There is an inverse relationship between the yield and the product purity.

The influence of particle size on the separation efficiency was also studied. Results show that the separation efficiency decreases with particle size under the same operating parameter. Enhanced gravity separation is an effective method to pre-concentration of graphite and $LiCoO_2$ in spent lithium-ion batteries.

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Reference

BAHGAT, M., FARGHALY, FE., BASIR, SMA., FOUAD, OA., 2007. *Synthesis, characterization and magnetic properties of microcrystalline lithium cobalt ferrite from spent lithium-ion batteries*. J Mater Process Tech, 183(1), 117-121.

BATALOVIĆ, V., 2011. *Centrifugal separator, the new technical solution, application in mineral processing*. Int J Miner Process, 100(3-4), 86-95.

CHEN, X., FAN, B., XU, L., ZHOU, T., KONG, J., 2016. *An atom-economic process for the recovery of high value-added metals from spent lithium-ion batteries*. J Clean Prod, 112, 3562-3570.

CHEN, X., XU, B., ZHOU, T., LIU, D., HU, H., FAN, S., 2015. *Separation and recovery of metal values from leaching liquor of mixed-type of spent lithium-ion batteries*. Sep Purif Technol, 144, 197-205.

EL-MIDANY, AA., IBRAHIM, SS., 2011. *Does calcite content affect its separation from celestite by Falcon concentrator?*. Powder Technol, 213(1-3), 41-47.

GEORGI-MASCHLER, T., FRIEDRICH, B., WEYHE, R., HEEGN, H., RUTZ, M., 2012. *Development of a recycling process for Li-ion batteries*. J Power Sources, 207, 173-182.

GRATZ, E., SA, Q., APELIAN, D., WANG, Y., 2014. *A closed loop process for recycling spent lithium ion batteries*. J Power Sources, 262, 255-262.

GRANATA, G., PAGNANELLI, F., MOSCARDINI, E., 2012. *Simultaneous recycling of nickel metal hydride, lithium ion and primary lithium batteries: Accomplishment of European Guidelines by optimizing mechanical pre-treatment and solvent extraction operations*. J Power Sources, 212, 205-211.

GREENWOOD, M., LANGLOIS, R., WATERS, KE., 2013. *The potential for dry processing using a Knelson Concentrator*. Miner Eng., 45, 44-46.

JOULIÉ, M., LAUCOURNET, R., BILLY, E., 2014. *Hydrometallurgical process for the recovery of high value metals from spent lithium nickel cobalt aluminum oxide based lithium-ion batteries*. J Power Sources, 247, 551-555.

LIU, Q., CUI, Z., ETSELL, TH., 2006. *Pre-concentration and residual bitumen removal from Athabasca oilsands froth treatment tailings by a Falcon centrifugal concentrator*. Int J Miner Process, 78(4), 220-230.

MESHRAM, P., PANDEY, BD., MANKHAND, TR., 2015. *Hydrometallurgical processing of spent lithium ion batteries (LIBs) in the presence of a reducing agent with emphasis on kinetics of leaching*. Chem Eng J, 281, 418-427.

SUN, L., QIU, K., 2011. *Vacuum pyrolysis and hydrometallurgical process for the recovery of valuable metals from spent lithium-ion batteries*. J Hazard Mater, 194, 378-384.

TAO Y, LUO Z, ZHAO Y, TAO D., 2006. *Experimental Research on Desulfurization of Fine Coal Using an Enhanced Centrifugal Gravity Separator*. Journal of China University of Mining and Technology, 16(4), 399-403.

USLU, T., SAHINOGLU, E., YAVUZ, M., 2012. *Desulphurization and deashing of oxidized fine coal by Knelson concentrator*. Fuel Process Technol, 101, 94-100.

WANG, M., ZHANG, C., ZHANG, F., 2016. *An environmental benign process for cobalt and lithium recovery from spent lithium-ion batteries by mechanochemical approach*. Waste Manage, 51, 239-244.

XIN, Y., GUO, X., CHEN, S., WANG, J., WU, F., XIN, B., 2016. *Bioleaching of valuable metals Li, Co, Ni and Mn from spent electric vehicle Li-ion batteries for the purpose of recovery*. J Clean Prod, 116, 249-258.

ZHANG, T., HE, Y., GE, L., FU, R., ZHANG, X., HUANG, Y., 2013. *Characteristics of wet and dry crushing methods in the recycling process of spent lithium-ion batteries*. J Power Sources, 240, 766-771.

ZHANG, T., HE, Y., WANG, F., GE, L., ZHU, X., LI, H., 2014a. *Chemical and process mineralogical characterizations of spent lithium-ion batteries: An approach by multi-analytical techniques*. Waste Manage, 34(6), 1051-1058.

ZHANG, T., HE, Y., WANG, F., LI, H., DUAN, C., WU, C., 2014b. *Surface analysis of cobalt-enriched crushed products of spent lithium-ion batteries by X-ray photoelectron spectroscopy*. Sep Purif Technol, 138, 21-27.