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Enrichment of indium tin oxide from colour filter glass in waste liquid crystal display panels through flotation

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ABSTRACT

Flotation is used to enrich indium tin oxide from the colour filter glass of waste liquid crystal display panels. Contact angle measurement and infrared spectroscopy analysis indicated that colour filter contained hydrophobic methyl groups and aromatic ring. Crushing experiment and backscatter imaging analysis revealed that the colour filter with indium tin oxide almost separated from the glass substrate with size fraction of −0.032 mm. The proportion of particles in the −0.032 mm fraction increased with increasing grinding time. A sufficient dissociation was found between the colour filter with indium tin oxide and the glass substrate, and the indium content in the fine size fraction also increased. Moreover, the indium content, indium tin oxide concentrate yield and indium tin oxide recovery increased with decreasing feed size. The indium content of the indium tin oxide concentrate reached 0.61%, the indium tin oxide recovery peaked at 85.21% and the enrichment ratio was 16.6 in particles with size below 0.025 mm. Furthermore, the indium content, indium tin oxide concentrate yield and indium tin oxide recovery increased with increasing grinding time. After 80 min of grinding, the indium tin oxide recovery peaked at 92.51%, the indium content of the indium tin oxide concentrate reached 0.60% and the enrichment ratio was 18.4.

1. Introduction

Indium is widely used in radio-electronic and semiconductor industrial technologies because of its unique physical and chemical properties (Boundy et al., 2017). Indium has become an important strategic resource in modern industrial development (Zhuang et al., 2012). More than 80% of indium produced worldwide is applied to indium tin oxide (ITO) coatings for liquid crystal display (LCD) panels (Pa, 2009). ITO is a sintered alloy coating and contains a large portion of indium oxide (90%) and a small portion of tin oxide (10%) (Inoue et al., 2008). With the increasing demand for LCD devices, indium has been depleted and rarer (Rocchetti et al., 2016). LCD devices with obsolete technology are discarded yearly, and these wastes should be urgently disposed (Zhang et al., 2015).

The configuration of LCD panel is shown in Fig. 1. Which is composed of two polarizing films, two glass substrates coated with ITO film, a colour filter layer and a liquid crystal layer. Considering the significant indium content in the ITO film, waste LCD represents a potential source of secondary indium. Although the indium is the main metal in the ITO film, this element is present with low concentrations of about 0.03% (Wang et al., 2017). Indium is difficult to recover from LCDs because the impurities and harmful components such as plastic and mercury will enter crushed LCD particles in the process of crushing (Savvilotidou et al., 2014).

Up to now, existing studies about recovery of indium from waste LCD panels mainly focused on the hydrometallurgical process. Li et al. (2009) studied the leaching efficiency of indium from waste LCD panels by mixed acid. The results indicated that in total 92% (wt %) of indium could be dissolved into acid liquid under the conditions at mixed acid solution of nitric acid and hydrochloric acid (HCl:HNO3:H2O = 45:5:50, volume ratio), preservation time of 30 min, and temperature of 60 °C. Lee et al. (2013) studied the leaching efficiency of indium from waste LCD panels by hydrochloric acid after high energy ball milling, and 86% of indium which exists in raw materials was recovered about in a very short time. Ruan et al. (2012) recycled indium from waste TFT-LCDs by solvent extraction which was based on a system of H_2SO_4 acid leaching-D2EHPA extraction-HCl back extraction. The results showed that

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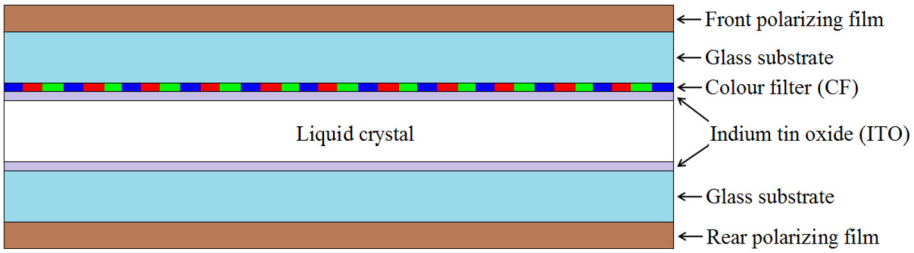

Fig. 1. Configuration of the LCD panel.

indium could be selectively extracted from its H_2SO_4 solutions by 30% D2EHPA with O/A ratio of 1:5 within 5 min, and be completely stripped by 4M HCl from D2EHPA with A/O ratio of 1:5, the final extraction efficiency achieved more than 97%. Hsieh et al. (2009) studied the hydrometallurgical method to obtain indium metal from ITO waste liquid, and a slag-making process during hot immersion is proposed and above 99% pure indium was obtained. Except hydrometallurgical process, chlorination, vacuum carbon reduction, sub-critical water etc. were also studied. Ma and Xu (2013) studied the vacuum chlorinated separation method for the indium recovery from waste LCD panels. The results indicated that the indium recovery rate was 99.97% when the particle size is less than 0.16 mm, the weight percentage of NH_4Cl to glass powder is 50 wt% and temperature is 450 °C. Park et al. (2009) studied the indium recovery from LCD powder via chloride volatilization process using polyvinyl chloride (PVC) as the chlorination agent. The degree of In recovery at a Cl/In molar ratio of 11 and a temperature of 350 °C was 66.7% and 54.1%, for N_2 and air, respectively. He et al. (2014) investigated the recovery of indium from waste LCD panels using vacuum carbon-reduction. The recovery rate of indium from LCD powder could reach to 90 wt% under the optimum conditions at 1223 K and 1 Pa with 30 wt% carbon addition for 30 min. Yoshida et al. (2014) studied the indium recovery from colour filter (CF) glass in waste LCD panel using sub-critical water. The results indicated that the indium oxide recovery rate reach 83% from CF glass at 360 °C in just 5 min. Zhang et al. (2017) studied the indium recovery from waste LCD panels by mechanical stripping process and indium is enriched from 0.02 wt % to 7.95 wt %. Higashi et al. (2011) studied the microbial adsorption method for the indium recovery from waste LCD panels. The results indicated that 10–100 ppm indium (III) ions were completely collected into the gram-negative bacterial cells within 30 min at room temperature over the pH range 2.3–3.5.

In the above methods, wet recovery has attracted widespread attention because of its mild reaction conditions; however, this method exhibits high-energy consumption and serious secondary pollution, which restrict its large-scale application (Kaya, 2016). Hence, low-cost, highly efficient and environment-friendly recovery methods must be developed. Physical separation, especially flotation, is used to recycle valuable components such as printed circuit board, fluorescent lamp and lithium ion battery, from solid wastes. Hirajima et al. (2005) studied the recovery of rare earth phosphors from waste fluorescent lamps by flotation and the recovery were about 70–90% under the conditions at pH 2.5 using dodecyl ammonium acetate as collector. Mallampati et al. (2016) studied the separation of hazardous chlorinated plastics from E-waste plastics using hybrid method of nanometallic Ca/CaO treatment and froth flotation. The results showed that the total recovery of PVC-free plastics in E-waste reached nearly 100%. He et al. (2017) studied the recovery of LiCoO2 from spent lithium-ion batteries by fenton reagent-assisted flotation. In LiCoO2 concentration, the content of cobalt was as high as 39.91 wt%, and the recovery rate was 98.99% under the condition that the Fe^{2+}/H_2O_2 ratio was 1:120, and the liquid-solid ratio was 75:1. Although high-purity products are difficult to obtain, the target element can be enriched greatly in advance to satisfy subsequent smelting condition.

In this study, flotation was used to investigate the separation of ITO and glass for indium recycling. Although ITO is the target product, colour filter (CF) is the key medium because the ITO adheres to the CF, which can be easily fallen off from the glass through crushing. Mineralogical characteristics, including elementary composition and liberation property, of the crushed products from CF glass were analysed. Differences in floatability among particles with different sizes and among products with ground for different durations were investigated to confirm the feasibility of ITO recovery from waste LCD panels through flotation.

2. Materials and methods

2.1. Sampling and preparation

LCD panels from waste 12-inch notebook computers were cleaned using an ultrasonic cleaner to remove liquid crystal; the polarizing film was stripped after thermal–shocked treatment at 230 °C for 10 min (Li et al., 2009). The remaining panels were ground in a ball mill. The particle size of the feed ranges from 1 mm to 0.5 mm, and the ball-loading rate is 35%. The particle sizes of the products were analysed by wet-sieving method using sieve shaker (AS200, Retsch, Germany) after grinding for 20, 40, 60, 80 and 100 min, and the sieve size are 0.5, 0.25, 0.1, 0.075, 0.032 and 0.025 m. After sieving, the products in screen were dried and weighed to calculate the particle size distribution.

2.2. Contact angle measurement

The CF with ITO and glass particles were ground into powder below 0.075 mm and then they were made into pellets by press machine, the pressure was 400 KN, the dwell time was 40 s and the boric acid was used as binder. The contact angles of the pellets were measured using a drop shape analyzer (DSA100, Kruss, Germany). The pellet was put on the sample stage and the droplet was dripped on the sample completely, the volume of droplet and the titration speed were 5 μL and 100 μL. min^{-1}, respectively. The image size and definition of the droplet were adjusted, then the baseline was determined and the contact angle was calculated automatically.

2.3. Infrared spectroscopic analysis

Functional groups in the CF with ITO were determined using a Fourier transform infrared spectrometer (FT-IR, Vertex 80v, Bruker, Germany). Samples were prepared into pellets with KBr (the ratio of the sample to KBr is 1–100). A Perkin Elmer Spectrum 2000 model spectrometer was used, and the spectrum was recorded at 2 cm^{-1} resolution between 4000 and 400 cm^{-1}.