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Recovery of indium from TFT and CF glasses in LCD panel wastes using sub-critical water

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ABSTRACT

Indium was efficiently recovered from color filter (CF) glass in LCD panel wastes using sub-critical water, which is only harmless water, at various temperatures and reaction time. By treatment in just 5 min reaction time using sub-critical water, this work achieved an outstanding 83% indium oxide recovery from CF glass and 7% from TFT glass at 360 °C. Clean and quality glass was also simultaneously recovered from CF glass. Higher exfoliation of organic multi-layers attached together with indium oxide and tin oxide was obtained over CF glass than that over TFT glass. Furthermore, indium did not dissolve in the liquid-phase but existed as indium oxide attached with the organic multilayers that were removed from CF glass. Since indium oxide was readily separated from CF glass, it was easily recovered from the liquid-phase by filtration. The amount of indium recovered was dependent on the sub-critical water reaction temperature. Sub-CW treatment at 5 min reaction time resulted in the highest indium recovery from CF glass. Thus, it was proven that sub-critical water treatment was a promising method for indium recovery from CF glass in LCD wastes.

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1. Introduction

Efforts to recover valuable materials especially rare metal like indiums [1] from Liquid Crystal Display (LCD) wastes and indium tin oxide (ITO) targets have been investigated by many researchers. Most methods on indium recovery have concentrated via acid dissolution or acid leaching [2,3], and indium recovery has been reported. Solvent extraction [4,5], hydrometallurgical [6] and chlorination [7] methods have also been used to recover ITO from etching solutions or etching target. However all these techniques require chemical post-treatment processes to separate and treat the chemical residues after recovery of ITO. Furthermore, LCD glass substrate cannot be reused because unresolved thin films cannot be peeled from the glass surface. The glass used for LCD panel is made of high quality glass and is expensive due to the difficulty to produce high silica content, low density, large flat panels, good surface quality, high heat resistance, and dimensional stability glass panels.

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As an option to the above described process, we proposed the utilization of subcritical water as an excellent alternative. Sub-critical water (sub-CW) has been utilized for recovery and/or production of valuable resources from solid wastes and is gaining interest due to its potential as solvent with hydrolysis power and catalyst for organic reaction. This technique is based on the use of water as medium, at temperatures between its boiling point (100 °C) and its critical point (374 °C) and at pressures high enough to maintain the liquid state. Under such conditions, as the dielectric constant of water decreases, it acts as a very good solvent for hydrophobic matters. Secondly, the magnitude of ionic product of water increases three orders around 250 °C compared to room temperature. These properties are advantageous for hydrolysis and decomposition of organic compounds including polymeric materials [8]. Extensive studies led by Yoshida and coworkers [9–20] has concluded that valuable and useful substances such as organic acids, amino acids, proteins, fatty acids, oils and nutrition were made recoverable by utilizing sub-CW from wastes.

However, despite these advantages, there has been no report concerning the application of sub-CW technology in treatment of LCD wastes. The objective of the present study is to explore the

possibility of using sub-CW reaction for the recovery of indium without chemical pretreatment. At the same time, the recovery of clean glass substrate from the remaining treated LCD was also investigated.

2. Materials and methods

2.1. CF glass and TFT glass configuration

Fig. S1 (in Supplementary information) illustrates a cross-sectional view of a TFT-LCD fabricated on a glass substrate. The surface of the glass substrate is attached with polarizing films. Glass of low alkalinity and low thermal expansion coefficient is used for TFT-LCDs. Color filters (CF) are embedded in the inner side of the top substrate. The CF substrate consists of the black matrix, color pixels, overcoat layer, and ITO film in turn. Dyes of different classes are used as colorant for color filters and are printed on the LCD glass with a black matrix pattern. The liquid crystal layer is sandwiched between two ITO substrates whose inner surface is coated with a thin polyimide layer. The electrode used in TFT-LCDs comprises of tin-doped indium oxide (ITO), a mixture of 90 wt% indium (III) oxide (In_2O_3) and 10 wt% tin (IV) oxide (SnO_2) [21]. Electrodes are formed on the amorphous silicon (a-Si) layer, which typically consists of multiple layers of heavily doped n-type a-Si followed by Cr/Al [22]. The TFT in this work is categorized as an inverted staggered structure configuration.

2.2. Preparation of LCD glass sample

The LCD panel received from the manufacturer and used as the sample in this work was a 40-inch TFT type LCD panel. The polarizing films on both the outer sides of the LCD were stripped off. The panel was then separated into CF glass and TFT array by cutting the panel edge using a glass cutter (Toshin-Riko). Liquid crystals on both glass surfaces were washed away twice by acetone. Thereafter, the glass was broken into about 5–10 mm sizes, small enough to fit and freely move in the reactor. From here onwards, CF glass and TFT glass denote glass specimens without liquid crystal layer and polarizing films.

2.3. Sub-critical water treatment

The batch reactor was a stainless steel pipe (SUS316, 16 mm diameter, 150 mm length, $30 \times 10^{-6} \text{ m}^3$) with stainless steel tube end-locks (Swagelok) for both sides. First, one side of the tube was tightly sealed with the Swagelok cap. After filling pure water (Millipore, $< 0.05 \mu\text{Scm}^{-2}$) about 20 cm^3 together with 6 g of either CF glass or TFT glass into the reactor, the air gap was purged with argon gas. Thereafter, the reactor was sealed with the Swagelok cap and was then weighed. It was then immersed quickly into a preheated molten salt bath (Celsius, Thomas Kagaku Co. Ltd., Tokyo) containing a mixture of potassium nitrate and sodium nitrate at a stabled reaction temperature. The reactor was shaken in the molten salt. As the inside temperature of the reactor increased very rapidly, the reaction temperatures can be assumed to be equal to the salt bath temperature as previously demonstrated by Abdelmoez et al. [23,24]. After a period of time, the reactor was taken out from the salt bath and immediately quenched by running tap water at room temperature. We assumed that the pressure inside the reactor was vapor pressure of water at the subsequent reaction temperature. The reaction time was defined as the period of time from immersing the reactor into the salt bath until transferring it into tap water.

After cooling, the specimens were transferred from the reactor to a beaker and their physical changes were observed. The solid

residues (mainly substrate glass) were separated from the aqueous phase by means of vacuum filtration through a $1 \mu\text{m}$ pore-sized membrane filter (Advantec, cellulose acetate). To ensure no product leftover, the reactor tube and cap were rinsed with water and filtered together with the aqueous phase. The filters were dried at room temperature and weighed using an analytical balance.

2.4. Measurement and analysis

After sub-CW treatment, metal content in each medium was determined as follows: indium was extracted by soaking the remaining glass and the membrane filter in a known amount of 7% HCl aq. solution, respectively according to the following equation:



Then they were sonicated for 1 h at 50°C . This method was found to be sufficient enough to extract indium from LCD panels [5]. The indium concentration in the HCl aq. solution was measured using a plasma atomic emission spectroscopy ICP (Shimadzu, ICPE-9000) and the amounts of indium in the remaining glass substrate (W_g), filter (W_f) and liquid-phase (W_l) were determined. The material balance of indium between before reaction (W_{init}) and after the reaction was confirmed. The recovery of indium (η_{In}) was defined by the percentage of indium available on the filter to that of the fresh LCD:

$$\eta_{\text{In}} = \frac{W_f}{W_{\text{init}}} \times 100 \quad (2)$$

Total organic carbon content in the liquid-phase was measured using a TOC analyzer (Shimadzu, TOC-Vcph/cpn). The metallurgical microstructure images of the glass surface were obtained using an optical fluorescence microscope (BX51 Olympus Corp.).

3. Results and discussion

3.1. Layers of the LCD

A direct ashing method was applied to measure the amount of organic matter on the CF glass and TFT glass without the polarizer. Accurately weighed sample was placed in a crucible and was annealed in an electric furnace for 4 h at 800°C . As shown in Table 1, weight loss of the CF and TFT glasses was 0.22% and 0.18%, respectively. ITO was not removed from the LCD surface during annealing because it was reported to volatilize at 850°C [25]. Those small weight decreases suggest that an extremely thin organic multilayer film comprised of alignment and protective layers are present as in Fig. S1. Furthermore, the amount of organics in TFT glass is found to be smaller than that in CF glass. This is because CF glass consists of the black matrix, red, green, and blue sub-pixel patterned between black matrix and polyimide overcoat, and alignment layer made of organic materials [26–28] with thickness around 2–3 μm [29].

Table 1
Weight fraction and the amounts of organic matter and indium in LCD panel.

	Fraction in LCD panel (%)	Weight loss after washing by acetone (%)	Weight loss after ashing at 800°C for 4 h in air (%)	Indium amount (W_{init}) (mg/kg-GL)
CF glass	43.97	0.078	0.222	395
TFT glass	43.08	0.070	0.176	321
Polarizer	12.95	Not performed	Not performed	Not performed

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