

Electrolysis of Indium Oxide in LiCl-KCl Based Molten Salts with a Liquid Cathode

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In this work, the feasibility of extracting of metallic indium from In_2O_3 and ITO through the direct electrochemical reduction at 450°C in molten salt LiCl-KCl was studied. Cyclic voltammetry was carried out to study the behaviour of indium oxide by the liquid metal indium used as the working electrode. The reduction peak was observed in the cathodic scan for In_2O_3 . The direct de-oxidation of indium oxide and ITO were investigated by using liquid tin cathode. Constant voltage electrolysis was performed at 1.7 V for 2h. The reduction reaction occurred at the interface of the oxide pellets and the cathode. Sn-In alloy was detected after electrolysis. Liquid zinc cathode was also used as cathode taking into account the low melting points of indium and tin. Potentiostatic electrolysis was conducted for the ITO with a liquid zinc cathode. The result showed that indium could be produced at different liquid cathodes.

Keywords: Electrochemical behaviour, Indium oxide, Molten salts, Electrolysis

1. INTRODUCTION

Indium is a rare strategic resource and used in a wide range of electric and electronic applications. There is no independent indium ore deposit on the earth so that it usually is produced as a by-product of other metallurgical processes [1,2]. The largest end use for indium is in thin-film coatings as indium oxide combined with 10 percent tin oxide (ITO) [3,4]. ITO has high electrical conductivity, high transparency and high reflectivity. With these characteristics, ITO is an essential raw material and plays an important role in the production of thin-film coatings. However, due to the scarcity for the metal, the

technology for indium recovery becomes more and more important with the steady increase of indium demand.

LCD screens are a potential resource for indium recovery because the screens contain indium at up to 1400 g/ton [5]. The existing technology for recycling the waste LCD panels are mainly based on hydrometallurgical [6-10] and pyrometallurgical processes [11-14]. Hydrometallurgical treatment has typically been achieved using various solvent, which includes corrosive acid and hazardous extraction substances to increase the potential environmental risks. The pyrometallurgical route performs at high temperature with CO atmosphere or chlorine gas, so that special attention must be paid for the leakage of the reactor.

Molten salt electrolysis is already a proven technology to extract metal and form alloy [15,16]. Since the FFC process 18 published in 2000, applying this process is very attractive due to its low energy consumption and little pollution. The process is the electrolytic decomposition of a metal oxide into metal and oxygen gas, which is beneficial for reducing carbon dioxide emission and decreasing the environmental risks. It is also a suitable method for indium reduction from indium oxide or ITO because indium has low melting point. In this work, the probability and feasibility of indium reduction from its oxide is studied based on the FFC process.

2. EXPERIMENTAL

The mixture of LiCl (Sigma-aldrich, 99.0 %) and KCl (Sigma-aldrich, 99.0 %) with the eutectic composition (58.2: 41.8 mol%) was used for the electrolyte and dried in a heating cabinet at 150 °C for 24 hours before the experiments. Before melting, the salt powders were first heated at 200 °C to remove moisture under an argon flow. Then the salts were heated to 450 °C. Indium oxide (Sigma-aldrich, 99.99 %) and ITO (Sigma-aldrich, 99.99 %) powders were used as the raw materials. The In₂O₃ and ITO powders were pressed into 15 mm diameter and 5 mm thickness pellets at 60 MPa and 20 MPa respectively. Polyvinyl alcohol (PVA, 5 wt% solution) was used as the binding agent. The ITO powders (Sigma-aldrich, 99.99 %) and organic binder (5 wt% PVA solution) were mixed at a ratio of 9:1 by mass. The pellets were dried in air for 2 days and then sintered at 1273 °C for 4 hours to remove PVA and increase the strength of the pellets.

The furnace was a vertical tube furnace controlled by at Eurotherm 902 controller. The tube was made of mullite, and on the top and bottom was water-cooled lids. The experiments were performed under inert argon atmosphere. The temperature in the cell was controlled with a Pt 10% Rh vs Pt thermocouple. To minimize the temperature gradient, a total of 4 evenly spaced alumina radiation shields extended from the crucible up to the top of the tube.

Cyclic voltammetry was carried out in an electrochemical cell, which is shown in Figure 1 and has a three-electrode system with a Zahner pp201 computer controlled potentiostat. The indium oxide (In₂O₃) pellets connected with a molybdenum (Sigma-Aldrich 99.99 % purity) wire dipped into the liquid metal indium were used as the working electrode. The potential is swept in the cathodic direction from the open circuit potential. The scan rates are 0.1 V/s and 1 V/s. The graphite rod (8 mm) after drying was used as the counter electrode. The AgCl | Ag reference electrode (99.99 % Ag wire with 1mm

diameter) was encased in a mullite tube, in which the LiCl-KCl eutectic salt contained 0.75 mol/kg AgCl (Sigma-Aldrich 99.998 % purity). The electrolysis part was shown in Figure 2.

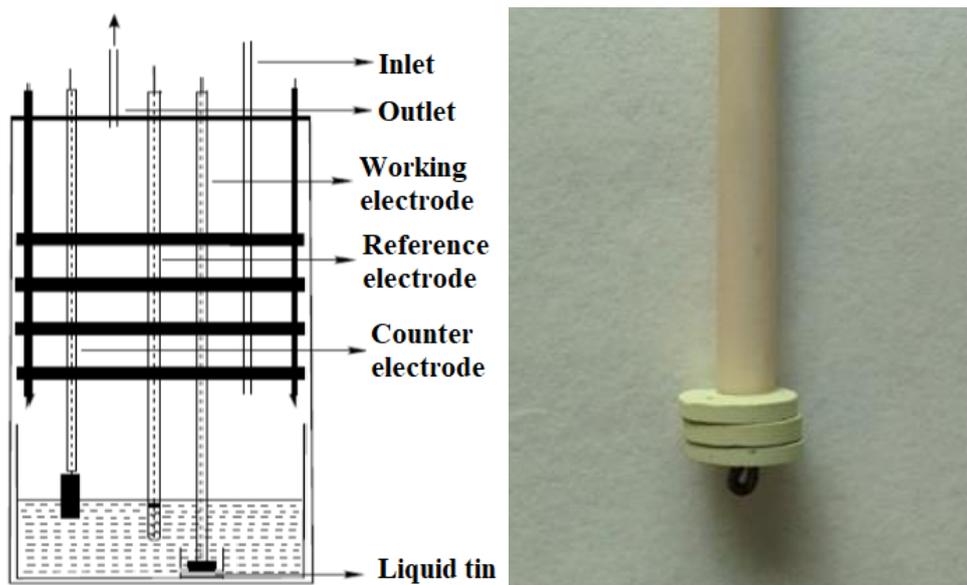


Figure 1. Schematic diagram of the electrochemical cell

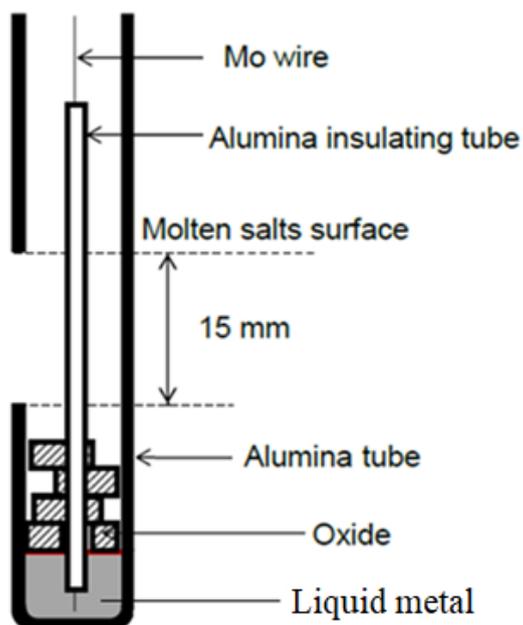


Figure 2. Schematic diagrams of the experimental set-ups for electrolysis.

Liquid zinc and tin connected with Mo wire were used in the alumina tube to replace the working electrode as the cathode in the electrochemical cell. The graphite rod was used as the anode. High purity liquid metal (zinc or tin) (Sigma-Aldrich 99 % purity) was placed at the bottom of the alumina tube. The electrolysis experiments were performed at -1.7V (versus reference) for 2 h at 450 °C. Potentiostatic electrolysis was conducted for the In₂O₃ or ITO with liquid tin or zinc cathode. Oxide pellets were placed

on the top of the liquid metal. Electrons are supplied from the Mo wire to the liquid metal. There is a hole on the alumina tube to make the molten salt flow in. The reduction of the oxide starts at the interface of its layer contacted with the liquid metal. The oxide pellets were stable between the salt and metal phases during electrolysis. If indium was reduced, it will sink to alloy with the metal on the bottom.

The products in the alumina tube were washed with distilled water in order to remove residual salt and then dried under a vacuum after 2h of the electrolysis. And then, the polished cathode was examined with a scanning electron microscope (SEM) Hitachi S3400N LV-SEM equipped with an energy dispersive spectrometer (EDS) probe Oxford instruments.

3. RESULTS AND DISCUSSION

3.1 Electrochemical behavior of indium oxide

Table 1. Standard electrode potentials E^0 at 450 °C.

Couple/Reaction	E^0/V
K(I)/K	-2.90
Li(I)/Li	-2.71
Ag(I)/Ag	0
Cl ₂ /Cl ⁻	0.91
In ₂ O ₃ = 2In + 1.5O ₂ (g)	-1.19
In ₂ O ₃ + 1.5C = 2In + 1.5CO ₂ (g)	-0.16
SnO ₂ =Sn+O ₂ (g)	-1.12
SnO ₂ +C=Sn+CO ₂ (g)	-0.09

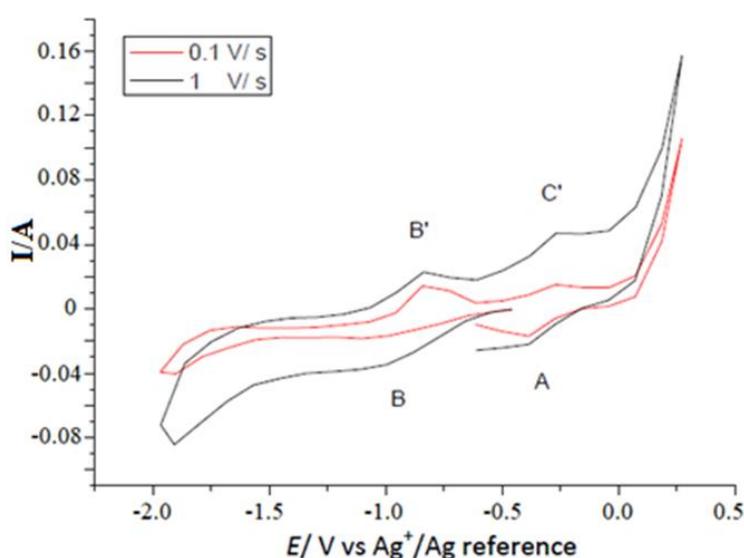


Figure 3. CVs related to the reduction of In₂O₃ in the fused LiCl-KCl with scan rates 0.1 V/s and 1 V/s at 450 °C.

Cyclic voltammetry was carried out to study the behaviour of indium oxide in molten LiCl-KCl in Fig. 3. In_2O_3 pellets connected with a Mo wire dipped into the liquid metal indium were used as the working electrode. According to the phase diagram of the In–Mo system [17], there is no intermetallic compound phase. The solubility of In in Mo is negligible at temperature lower than 1000 °C. Mo is inert with respect to indium at the working temperature. Table 1 shows standard electrode potentials E^0 versus the potential of Ag^+/Ag reference electrode and also standard decomposition voltages of oxides. The calculations were performed from known thermodynamic data at 723 K using HSC Chemistry 6.1 [18].

The wave B shows the reduction of In_2O_3 on the cathodic sweep, which occurs at a potential of around -1.0 V. In the anodic direction, waves B' and C' are related to the electrochemical dissolution of In to In^+ and oxidation of In^+ to In^{3+} respectively, while the peak at the more positive potentials showed the dissolution of Mo. Molybdenum exhibits a high degree of electrochemical stability, but its practical oxidation potential is lower than that at which chlorine is evolved. At higher potentials molybdenum gets anodically passivated in chloride media as pointed out by Vijn [19]. The wave A, which can be assigned to the reduction of Mo^{3+} , was observed at the cathodic sweep [20].

3.2 Electrolysis of indium oxide and ITO with the liquid tin electrode

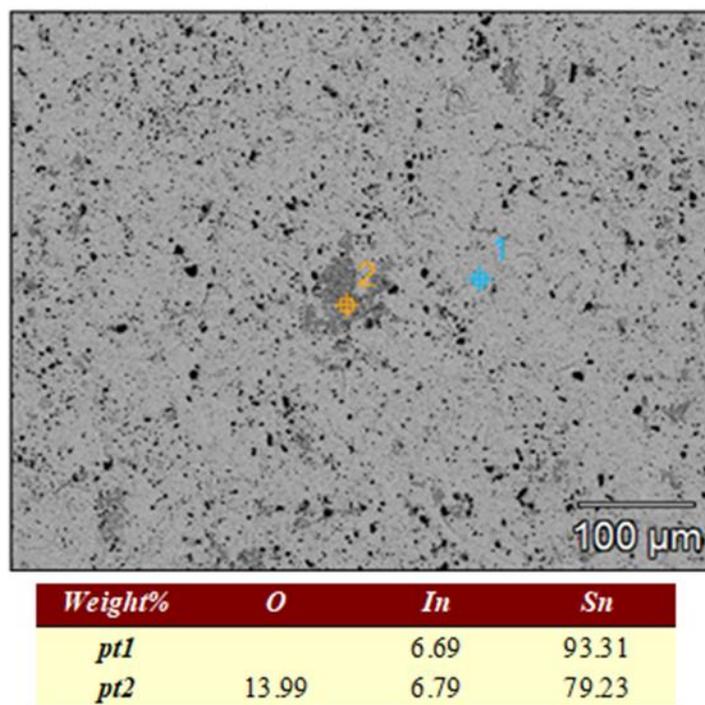


Figure 4. The SEM of tin matrix after In_2O_3 electrolysis combined EDS of the cathode deposit for the parts

Potentiostatic electrolysis was conducted for the In_2O_3 at -1.7 V (versus reference) for 2 h and liquid tin metal was used as the cathode. Well beneath the decomposition voltage of LiCl-KCl considering the voltage losses due to the resistance of electrodes, electrolyte and other materials used in the electric circuit. The applied potential is lower than the decomposition voltage of the electrolyte,

meaning that the major part of the current has been used for the metal oxide direct reduction. Because of the immiscibility of the salt and metal phases, they will form two layers. The oxides pellets were stable between the two liquid layers during electrolysis. Constant voltage between the anode and the cathode is applied here because of its simplicity in construction and operation. The electrochemical and electrolytic experiments were performed at 450 °C under argon gas atmosphere. The liquid tin metal was used as the cathode in order to distinguish whether indium was reduced in the electrolysis process. After the electrolysis of the In_2O_3 and ITO, the upper part of the cathode was washed, polished and analyzed by SEM with EDS.

The compositions of two parts selected are shown in Fig.4 after the electrolysis of In_2O_3 . The indium-tin alloy was detected on the cathode at the interface. Oxygen is not be found in the part 1, which shows that the reduced indium is alloyed with tin. The part 2 is in the grey region where oxygen is found to be present. This might be explained by the unreduced indium oxide. Electrolysis through the direct electrochemical reduction at 450 °C showed that indium could be produced at a liquid cathode.

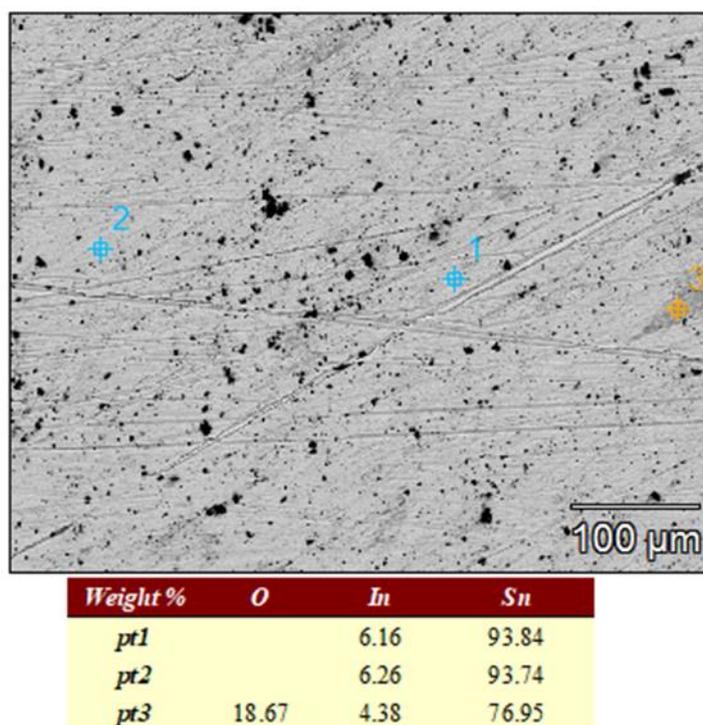


Figure 5. The SEM of tin matrix after ITO electrolysis combined EDS of the cathode deposit for the parts

The compositions of three parts selected are shown in Fig.5 after the electrolysis of ITO. The parts 1 and 2 have the similar composition without oxygen. The part 3 is in the grey region where oxygen is found to be present, which might be explained by the unreduced indium oxide or tin oxide. Owing to the low content of tin oxide in ITO pellets, the focus is on recycling indium oxide. It is hard to judge whether tin oxide is reduced during the electrolysis because tin is used to the cathode. In fact, there is no tin oxide and the other intermediate product found towards tin in the sample at the interface after the electrolysis. There is a rapid reduction of the surface film when the electro-deoxidation of any oxide pellet starts at the metal/oxide/electrolyte three phase interlines (3PIs) [21]. There are three steps for the

3PIs [22]: (1) the metal oxide which is next to the current collector is reduced firstly to the metal at the 3PIs, (2) the reduced metal on the pellet then works as a current collector, and (3) the 3PIs move to the boundary of the reduced part. The rate of the reduction process is dependent on the movement of the 3PIs. The reduction rate on the surface layer is much faster than that within the pellet core.

There are two advantages when the liquid metal is used as the cathode. Firstly, the interface area increases dramatically between the metal and the oxide compared to the oxide pellet wound by the metal wire. It is beneficial to increase the interface and the reaction rate. Secondly, the reaction rate decreases with an increasing in the depth direction of the pellet [23]. The metal is reduced and then covered on the oxide pellet leads to blocking the reaction going on. The reduced indium or tin from the surface of the oxide pellet will be as the cathode to promote the reaction.

3.3 Electrolysis of ITO with the liquid zinc electrode

In the experiments, liquid zinc was used as cathode material. The phase diagrams of the In-Zn [24] or Zn-Sn [25] system show no existence of any intermetallic compounds. The density of In or Sn is a bit larger than that of Zn. If ITO was reduced to metallic In or Sn, metallic In or Sn or In-Sn alloy will sink to the bottom of the crucible to alloy with Zn.

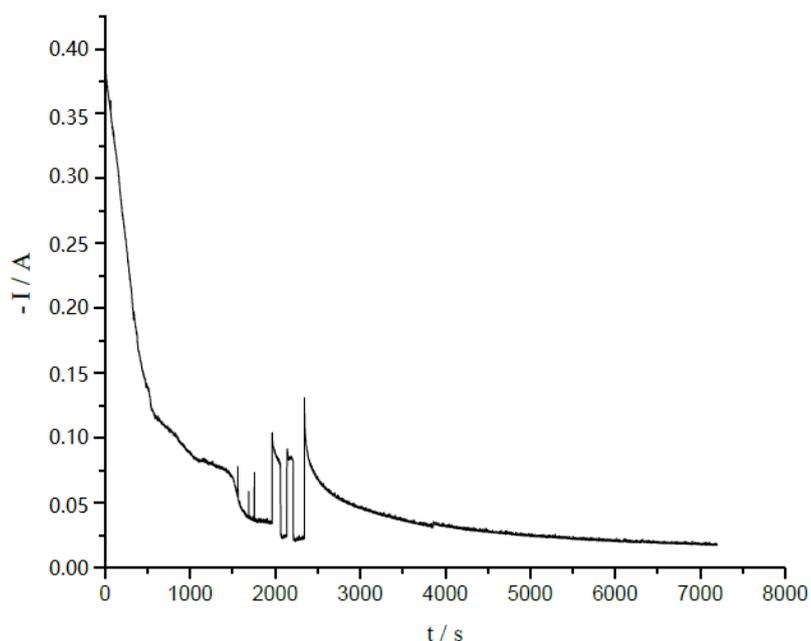


Figure 6. Current with time of ITO during constant potential electrolysis at -1.7 V for 2 h

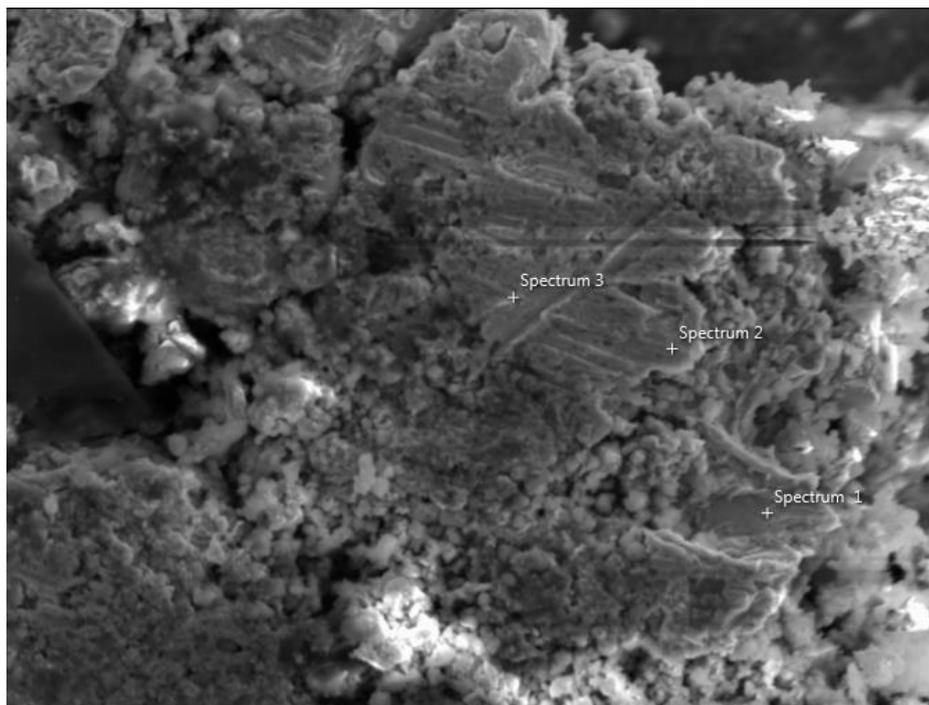


Figure 7. The SEM of zinc matrix after ITO electrolysis

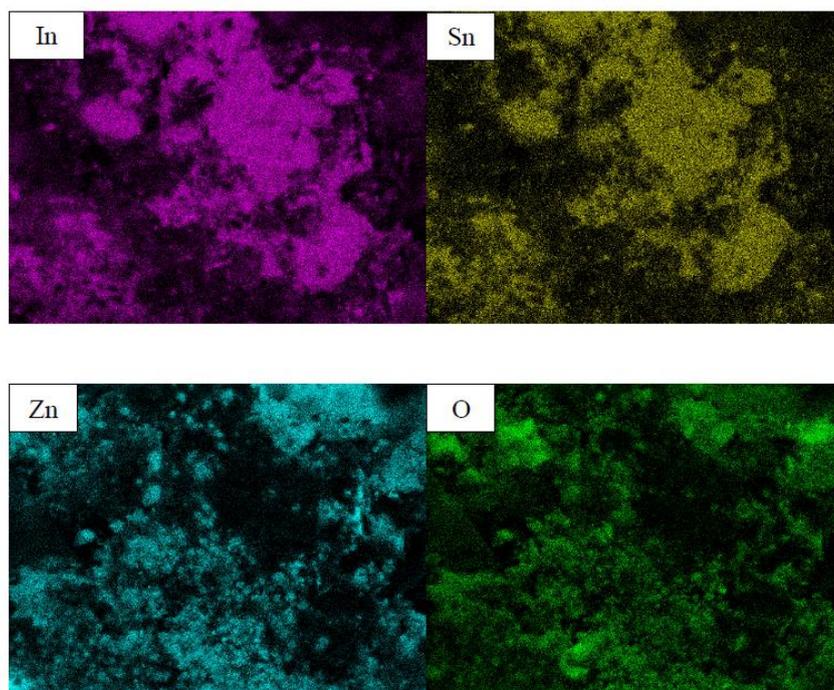


Figure 8. EDS element distribution maps after ITO electrolysis

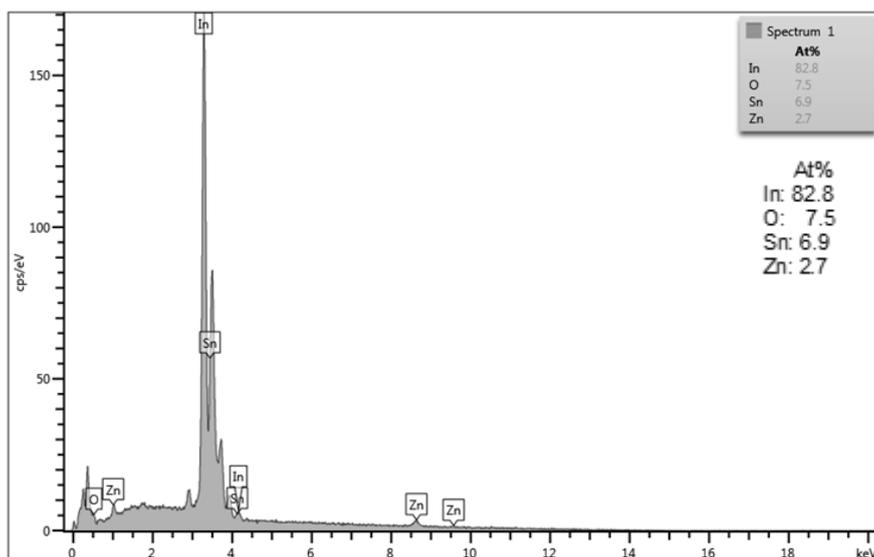


Figure 9. EDS of the cathode deposit for part 1

Potentiostatic electrolysis was conducted for the ITO at -1.7V (versus reference) for 2 h. Fig. 6 shows the current transient curve during the electrolysis. The cathodic current decreased about 300 mA during the first 10 min of the experiment, and after some fluctuation the current stabilized.

After electrolysis of the ITO, the SEM of zinc matrix was shown in Fig. 7 A lot of indium and tin intensive areas were found from the EDS element distribution maps (Fig. 8). This purple area is indium-intensive and the yellow area is tin. In the indium and tin intensive areas, little of zinc and oxygen exist. The atomic ratios of In, Sn, O and Zn in the indium and tin intensive areas are 82.8: 6.9: 7.5: 2.7 (Fig. 9). ITO was almost completely reduced.

It can be found that Indium was detected after the electrolysis of In_2O_3 and ITO with tin and zinc cathode. In fact, zinc is not a good choice for the cathode material because it increases the difficulty of separating indium from In-Sn alloy. However, it is hard to judge whether tin is reduced with both of cathodes during the electrolysis. It is necessary to use indium liquid metal as the cathode in order to distinguish whether tin is reduced in the following work.

4. CONCLUSIONS

The electrochemical redox processes of In_2O_3 was studied using a liquid indium working electrode at $450\text{ }^\circ\text{C}$ in molten LiCl-KCl. Two reduction peaks were observed in the cathodic scan for In_2O_3 . Reduction of In_2O_3 occurs at -1.0 V . Another peak is considered to be the reduction of molybdenum oxide. Liquid tin and zinc metals were used as cathode taking into account increasing the contacting area. Constant voltage electrolysis was performed at 1.7 V for 2h. The reduction reaction occurred at the interface of the oxide pellets and the cathode. Sn-In alloys were detected after the electrolysis of In_2O_3 and ITO with the tin cathode. The result showed that indium can be produced at a liquid cathode. ITO was reduced strongly when liquid zinc was used as the cathode. Based on the

feasibility experiments, further work is required for improving the kinetics of the reaction and measuring the current efficiency.

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