Removal and recovery of indium from ITO coated glass and scraps using molten salt electrolysis

Peng Cui [a], Bo Qin [a,b, z], Ana Maria Martinez [c], Geir Martin Haarberg [d],

[a] Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China;

[b] State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China;

[c] SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway;

[d] Department of Materials Science and Engineering, Norwegian University of Science and Technology, NTNU, NO-7491, Trondheim, Norway

[z] Corresponding author. E-mail: 59077730@qq.com

Abstract

Indium is an important strategic resource due to the scarcity for the metal. In the present study, molten salt electrolysis is used to reduce indium from ITO coated glass and scraps in order to seek a new way to recycle the value resource. The electrochemical behavior of indium and tin oxides was studied by cyclic voltammetry at 450 °C in molten LiCl-KCl. The reduction peaks were observed in the cathodic scan for In_2O_3 and SnO_2. Constant voltage electrolysis was performed at 1.7 V and 450 °C for ITO. The deposits between ITO layer and the cathode were collected and analyzed by XRD. The reduction reaction occurred at the interface of the oxide pellets and the cathode. Metallic indium and Sn-In alloys were detected after electrolysis. The ITO covered glass was reduced by electrochemical method in molten LiCl-KCl at 450 °C under argon with Mo wire contacting electrode. The findings, together with SEM and EDX analyses, confirmed ITO layer was removed from the glass surface.

Introduction

Indium is regarded as an important strategic resource because it is a rare metal and mainly used in electronics industry. It has no minerals of its own so that it has to be produced as a byproduct of other metallurgical processes.[1,2] The largest end use for indium is in thin-film coatings as a mixture of 80–90 wt % indium oxide (In_2O_3) and 10–20 wt % tin oxide (SnO_2).[3,4] Indium tin oxide (ITO) is

1

an essential raw material in the production of thin-film coatings due to its high electrical conductivity, high transparency and high reflectivity. This thin-film coating-technology is used in the manufacture of liquid crystal displays (LCDs), flat panel displays and touch screens. Based on the status of the scarcity of indium resource and increasing demand for the metal, it is necessary to consider possible means to separate and recycle indium from secondary sources.

LCD screens are a potential resource for indium recovery because the screens contain indium at up to 1400 g/ton.[5] Therefore, the recovery of indium from waste sputtering targets and the obsolete LCDs have become more and more important because these wastes are a valuable resource, and at the same time they are not environmentally friendly. Several processes for recycling the waste LCD panels have been proposed in the literature, and are mainly based on hydrometallurgical and pyrometallurgical processes.

The separation and recovery of indium from indium tin oxide (ITO) has been achieved using hydrometallurgy,[6-10] which involves leaching, concentration and separation, and electrorefining. Hydrometallurgical treatment has typically been achieved using solvent extraction, which is a useful metallurgical process for indium and has the high recovery rate of indium. However, the using of various solvents, including corrosive acid and hazardous extraction substances, increases the potential environmental risks. The pyrometallurgical route mainly includes vacuum metallurgy and chlorination reaction.[11-14] The indium and tin oxides can be reduced to metal state under high temperature with CO atmosphere. But the use of CO is a potential safety risk as it is asphyxiating. Chlorination process also plays an important role in the indium extraction. This process has the good effectiveness and usefulness because it has relative lower temperature. Chlorine and hydrogen chloride gases are very corrosive in nature, so that special attention must be paid for the leakage of the reactor. Therefore, in order to directly recycle metallic indium from waste LCD panel or ITO scraps, environmentally friendly methods and high efficiently methods for achieving metallic indium are desired.

Molten salt electrolysis has been used in metal extraction [15] and alloy formation [16,17] and is already a proven technology. Primary aluminium is mainly produced based on this manner all over the world. Since the FFC process [18] published in 2000, this process has the potential to drastically reduce and recovery the cost of the production of metals. The process is facilitating the extraction of metals from their oxides, and is the electrolytic decomposition of a metal oxide into metal and oxygen

gas. That is beneficial for reducing carbon dioxide emission and decreasing the environmental risks.

Both indium and tin have low melting points, thus, they are well suited for molten salt electrolysis to recycle indium and tin from waste of ITO because it is good for saving the energy. The possibilities of applying this process appear to be very attractive. The aim of this work was to study a direct electrolysis process in molten salts to recycle indium from waste of ITO.

Experimental

Materials. — The eutectic mixture of LiCl (Sigma-aldrich, 99.0 %) and KCl (Sigma-aldrich, 99.0 %) was used for the electrolyte. LiCl: KCl with the eutectic composition (58.2: 41.8 mol%) was dried in a heating cabinet at 150 °C for at least 24 hours respectively prior to the start of the experiments. Before melting, the salt powders were mixed and they were first heated at 200 °C, under an argon flow, for at least 12h to remove moisture. Then the salts were heated to full temperature, 450 °C. Indium oxide (Sigma-aldrich, 99.99 %) and tin oxide (Sigma-aldrich, 99.9 %) powders were used as the raw materials for indium and tin. The In_2O_3 and SnO_2 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.

Electrochemical apparatus. — 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 (Figure 1) having a three-electrode system with a Zahner pp201 computer controlled potentiostat when the oxides (In_2O_3 or SnO_2) pellets connected with a molybdenum (Sigma-Aldrich 99.99 % purity) wire (Figure 2) were used as the working electrode. 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 3. Liquid tin connected with Mo wire was used in the

3

alumina tube to replace the working electrode as the cathode in the cell. The graphite rod was used as the anode. High purity tin (Sigma-aldrich, 99.9 %) was placed at the bottom of the alumina tube. ITO pellets were placed on the top of the tin metal. Electrons are supplied from the Mo wire to the tin metal. There is a hole on the alumina tube to make the molten salt flow in. The reduction of ITO starts at the interface of ITO layer contacted with the liquid tin. The oxide pellets were stable between the salt and metal phases during electrolysis. If ITO was reduced, In will sink to alloy with Sn.

A molybdenum wire is wound around the ITO glass (one side of the glass coated by ITO) which supplies electrons to a selected region of the ITO film in Figure 4. This electrode was used for bulk reduction experiments.

Instrumentation. — The voltammetry studies were performed with a Zahner pp201 computer controlled potentiostat. 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 deposits between ITO layer and the cathode were collected to analyze by X-ray diffraction (XRD). The polished cathode and the ITO coated glass were examined with a scanning electron microscope (SEM) Hitachi S3400N LV-SEM equipped with an energy dispersive spectrometer (EDS) probe Oxford instruments.

Results and discussion

Electrochemical behavior of indium and tin oxides. — In_2O_3 and SnO_2 pellets connected with a Mo wire were used as the working electrode. Cyclic voltammetry was performed in order to investigate anodic and cathodic reactions occurring during the reduction and oxidation of In_2O_3 and SnO_2. According to the phase diagram of the In–Mo system,[19] 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.

Fig. 5 shows the results of a voltammetric study of indium deposition using a molybdenum wire working electrode. The black trace represents data obtained in the electrolyte without In_2O_3. In the anodic direction, an oxidation current is observed at potential 0.15 V and the polarization curve corresponds to the dissolution of molybdenum to form Mo^{3+}.[20,21] 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 Vijh.[22] The dissolution reaction slows gradually because of the formation of the K_3MoCl_6 salts which blocks the active sites [20]. The red trace represents data taken in the same melt where In_2O_3 pellets were connected to the Mo wire. The wave B shows reduction current on the cathodic sweep. Reduction of In_2O_3 occurs at around -1.0 V, but only a broad reduction peak was observed in the cathodic scan. In the anodic direction, waves B' and D' are related to the electrochemical dissolution of In to In^+ and oxidation of In^+ to In^{3+} respectively. Two stage anodic dissolution of indium was also observed.[23] The wave A, which can be assigned to the reduction of Mo^{3+}, was observed at the second cathodic sweep.[24] The cathodic peak C can be assigned to the reduction of Li^+ since the reduction potential of K^+ is more negative than Li^+ in the LiCl-KCl eutectic melt.

Mo is suggested as an effective diffusion barrier against the attack of liquid tin according to the phase formation and reaction kinetics in the Mo–Sn system. Fig. 6 shows the results of a voltammetric study of tin deposition using a molybdenum wire working electrode. It was observed that in the cathodic direction, there are three reduction peaks A, B and C. The peak couples C and C' are corresponding to the deposition and dissolution of Li. The cathodic current A can be attributed to the existing surface oxides of the molybdenum wire. After the anodic oxidation of molybdenum wire, the cathodic scan appears the reduction peak of Mo^{3+}. Current wave B, and the likely anodic counterpart wave B' clearly originates from the oxide as the two waves are absent in the pure molten salt. The formation of stable metal nuclei on an inert cathode surface requires a potential more negative than the reduction of metal on its own surface. The peak B, which occurs at around -1.2 V, is related to the reduction of SnO_2. In the anodic reaction, there is a feature between -0.8 and -0.3 V. B' is related to the dissolution of tin from the Mo. The oxidation of Sn to Sn (II) was observed at -0.30 V.[25]

Electrolysis of ITO scraps. ─ Constant voltage between the anode and the cathode is applied here because of its simplicity in construction and operation. The applied potential was well below the decomposition voltage of LiCl and KCl considering the voltage losses due to the resistance of electrodes, electrolyte and other materials used in the electric circuit. Thus, Constant voltage electrolysis was performed at 1.7 V for 2h. The sample at the interface between the ITO pellets and the tin cathode was analyzed by XRD and shown in Fig. 7.

The tin liquid metal was used as the cathode in order to distinguish whether indium was reduced in the electrolysis process. The metallic indium and indium-tin alloy were detected on the sample at the interface. Although it seems that the intensity of indium is not very strong, the result indicates that

it might be possible to reduce ITO to indium and alloy with tin. $LiInO_2$ was also present in the sample. It might conclude that the indium oxide in the ITO pellets were reduced to indium and oxygen ion during the electrolysis, and then oxygen ion is involved in a further reaction with the lithium ion because oxygen ion has certain solubility in the LiCl-KCl molten salts. Lithium oxide reacts with indium oxide to form $LiInO_2$ as an intermediate. The process is as follows:

$$In_2O_3 + 6e = 2In + 3O^{2-} \qquad (1)$$

$$2Li^+ + O^{2-} = Li_2O \qquad (2)$$

$$Li_2O + In_2O_3 = LiInO_2 \qquad (3)$$

The upper part of the cathode was polished and analyzed by SEM with EDS. The compositions of three points selected are shown in Fig.8. The points 1 and 2 have the similar composition without oxygen. This shows that the reduced indium is alloyed with tin. The point 3 is in the grey region where oxygen is found to be present. This 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.

The electro-deoxidation of any oxide pellet starts by rapid reduction of the surface film according to what is known as the "thin layer three phase interline model" at the metal/oxide/electrolyte three phase interlines (3PIs).[26] When the liquid metal is used as the cathode, there are two advantages. 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 towards the center of the reactant.[27] The reduced metal covers on the reactant so that the reaction does not continue. In this case, the reduced metal will fall into the liquid cathode from the surface of the reactant so that the reaction isn't blocked.

Based on the feasibility experiments, the results are promising for the aim of extracting indium and tin from ITO scraps. The deoxidization process in molten salt is fit to deal with the scraps and to remove the metal produced from the cell without interrupting production. There will be further improvements in the electrolyte composition to decrease the electrolysis temperature, aiming at increasing current efficiency and decreasing energy consumption. Further work is required for improving the kinetics of the reaction and measuring the current efficiency.

Electrolysis of ITO coated glass. ─ The major use of ITO is in industry to manufacture of liquid crystal displays (LCDs), thus, ITO coated glass is the main source of indium recovery. Fig. 9 shows a photograph of the specimens obtained by constant potential electrolysis at -1.7 V versus reference for 30 minutes. The molybdenum wire was removed and the sample was washed in the distilled water. It can be seen that after electrolysis some electrolytic reactions happened in the molybdenum wire contacted area and the color turned black as shown. Moreover, an obvious groove was also formed.

The SEM image of the contacting region of the ITO covered glass electrolyzed for 30 minutes was shown in Fig. 10. A vertical elemental analysis was scanned on the groove by EDS line element analysis which was shown in Fig. 11. It can be seen that all the element concentrations were decreased. The contents of In (purple line) and Sn (red line) are constant in the non-contacting region of ITO layer. But they could not be found in the reaction zone after the electrolysis. The concentrations of Si and O are reduced significantly. This shows that the silicon is reduced at the applied voltage -1.7 V versus reference. Indium and tin can be removed from ITO coated glass by molten salt electrolysis. However, the disadvantage is that the reaction zone is only the contacting region of the glass with molybdenum wire. There is also the molybdenum residual on the coated glass in the contacting region.

The possibilities of applying the deoxidization towards the recovery of indium from ITO coated glass appear to be very difficult. Although indium and tin were removed during electrolysis, the reaction just happened in the contacting region. Thus, the major issue is the connection between electrode and oxide. The other way is to find a suitable electrolyte like aluminium production by the electrolysis of alumina in molten cryolite where In_2O_3 or ITO has some solubility in the molten salt, so that the reduction and electrowinning steps are performed simultaneously. This work would build upon attempts to develop a practical and economical process for detoxification and recycling of waste ITO coated glass. However, considerable efforts still need to be done in the future.

Conclusion

In this work, the electrochemical redox processes of In_2O_3 and SnO_2 were studied using a molybdenum rod working electrode at 450 °C in molten LiCl-KCl. Two reduction peaks were observed in the cathodic scan for In_2O_3 and SnO_2. Reduction of In_2O_3 occurs at -1.0 V. The electrolytic reduction peak of SnO_2 occurs at around -1.2 V. Another peak is considered to be the reduction of molybdenum oxide. Liquid tin was used as cathode taking into account increasing the contacting area.

Constant voltage electrolysis was performed at 1.7 V for ITO. The reduction reaction occurred at the interface of the oxide pellets and the cathode. Metallic indium and Sn-In alloys were detected after electrolysis by XRD. Electrolysis at 450 ℃ showed that indium can be produced at a liquid cathode. An ITO coated glass electrode was investigated by electrochemical means in molten LiCl-KCl at 450 °C using Mo wire current collector. The result showed ITO layer was removed from the glass surface. Further work is required for confirmation of the formation of metallic tin or indium during electrolysis process in order to demonstrate that ITO layer has been reduced.

Acknowledgements

References

1. F. Li, B. Lan, W. Z. He, Li, G. G. Li, J. W. Huang, *J. Hazard. Mater.* 299, 103 (2015).

2. K. Zhang, Y. F. Wu, W. Wang, B. Li, Y. Zhang, T. Zuo, *Resour. Conserv. Recycl.* 104, 276 (2015).

3. A.V.M. Silveir, M.S. Fuchs, D.K. Pinheiro, E.H. Tanabe, D.A. Bertuol, *Waste Manage.* 45, 334 (2015).

4. D. Fontana, F. Forte, R. D. Carolis, M. Grosso, *Waste Manage.* 45, 325 (2015).

5. K. Takahashi, A. Sasaki, G. Dodbiba, J. Sadaki, N. Sato, T. Fujita, *Metall. Mater. Trans. A.* 40, 891 (2009).

6. G. Dodbiba, H. Nagai, L.P. Wang, K. Okaya, T. Fujita, *Waste Manage.* 32, 1937 (2012).

7. H. Hasegawa, I. M.M. Rahman, Y. Egawa, H. Sawai, Z. Begum, T. Maki, S. Mizutani, *J. Hazard. Mater.* 254-255, 10 (2013).

8. T. Kato, S. Igarashi, Y. Ishiwatari, M. Furukawa, H. Yamaguchi, *Hydrometallurgy.* 137, 148 (2013).

9. E. B. Pereira, A. L. Suliman, E. H. Tanabe, D. A. Bertuol, *Miner. Eng.* 119, 67 (2018).

10. L. Rocchetti, A. Amato, F. Beolchini, *J. Clean. Prod.* 116, 299 (2016).

11. S. Itoh, K. Maruyama, *High. Temp. Mat. Pr-Isr,* 30, 317 (2011).

12. Y. He, E. Ma, Z. Xu, *J. Hazard. Mater.* 268, 185 (2014).

13. R. Lu, E. Ma, Z. Xu, *J. Hazard. Mater.* 243, 311 (2012).

14. E. Ma, Z. Xu, *J. Hazard. Mater.* 263, 610 (2013).

15. X.Y. Yan, D.J. Fray, In Electrolysis: Theory, Types and Applications, in: S. Kuai, *Molten salt electrolysis for sustainable metals extraction and materials processing - a review*, p. 255, Nova Science Publishers, Inc., New York (2010).

16. R. Bhagat, M. Jackson, D. Inman, R. Dashwood, *J. Electrochem. Soc*. 155, 63 (2008).

17. F. Meng, H. Lu, *Adv. Eng. Mater.* 11,198 (2009).

18. G.Z. Chen, D.J. Fray, T.W. Farthing, Nature. 407, 361 (2000).

19. T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kacprzak, *Binary Alloy Phase Diagrams*, *Second ed.*, ASM International, Ohio (1996).

20. J.C. Gabriel, J. Bouteillon, J.C. Poignet, J.M. Roman, *J. Electrochem. Soc.* 141, 2286 (1994).

21. J.C. Gabriel, D. Vincent, J. Bouteillon, J.C. Poignet, V.A. Volkovich, T.R. Griffiths, *Electrochim. Acta.* 44, 4619 (1999).

22. A.K. Vijh, *Corros. Sci.* 11, 161 (1971).

23. P. Cui, B. Qin, A. M. Martinez, G. M. Haarberg, *Int. J. Electrochem. Sci*.14, 5064 (2019).

24. J.C. Gabriel, J. Bouteillon, J.C. Poignet, J.M. Roman, *J. Electrochem. Soc*. 141, 2286 (1994).

25. H. Groult, H.E. Ghallali, A. Barhoun, E. Briot, C.M. Julien, F. Lantelme, S. Borensztjan. *Electrochim. Acta,* 56, 2656 (2011).

26. G.Z. Chen, E. Gordo, D.J. Fray, Direct electrolytic preparation of chromium powder, *Metall. and Materi. Trans. B*. 35, 223 (2004).

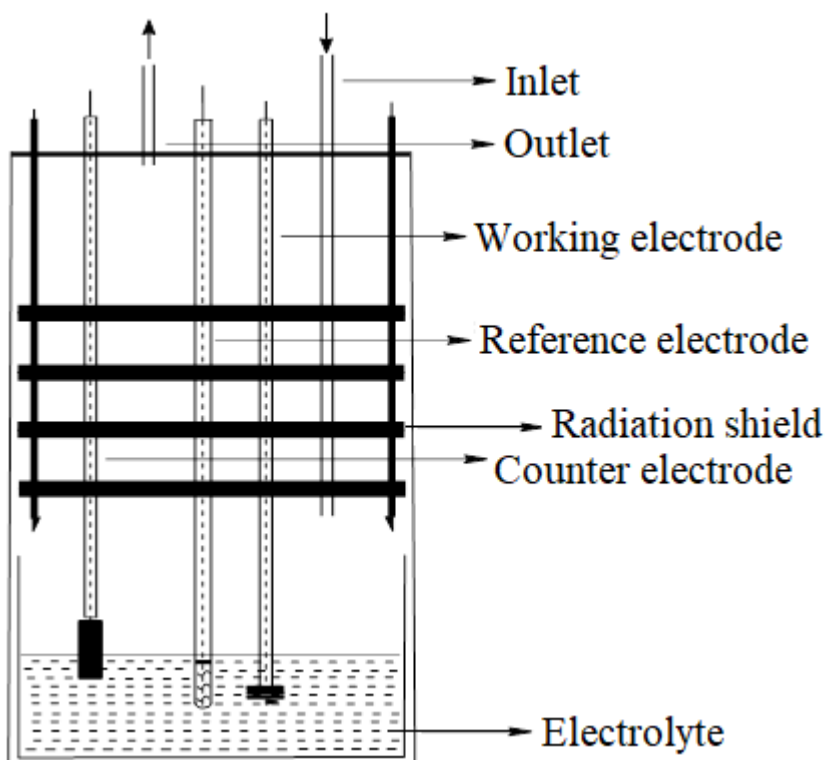27. A.M. Abdelkader, K.T. Kilby, A. Cox, D.J. Fray, *Chem. Rev.* 113, 2863 (2013).

Fig. 1. Schematic diagrams of the experimental set-ups for electrochemistry.

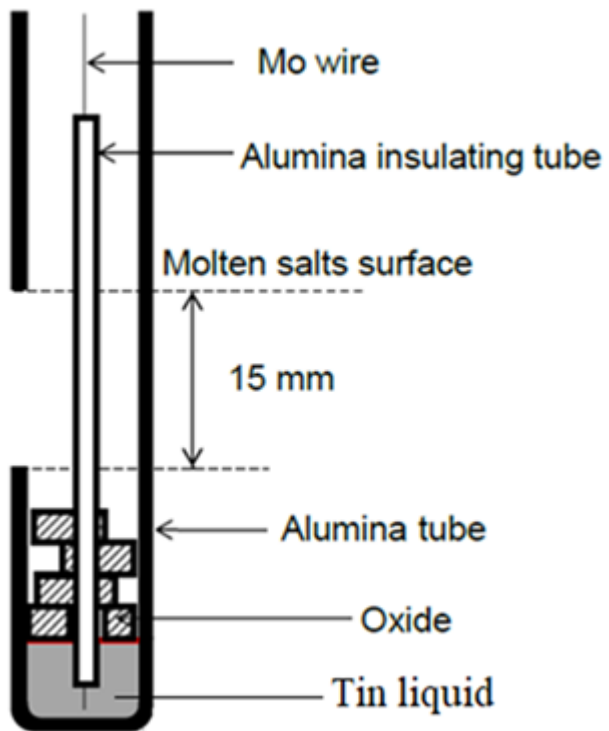Fig. 2. Photo of the oxides working electrode

Fig. 3. Schematic diagrams of the experimental set-ups for electrolysis.

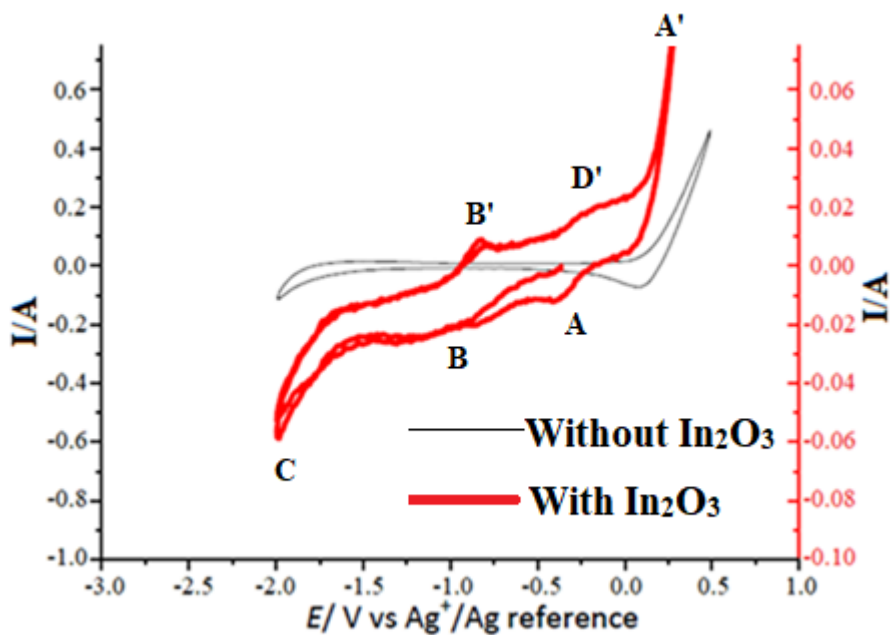Fig. 4. Photograph of the contacting electrode

Fig. 5. Cyclic voltammograms of a Mo working electrode in molten LiCl-KCl with and without In_2O_3 with a scan rate of 100 mV/s at 450 °C. The potential is swept in the cathodic direction from the open circuit potential.
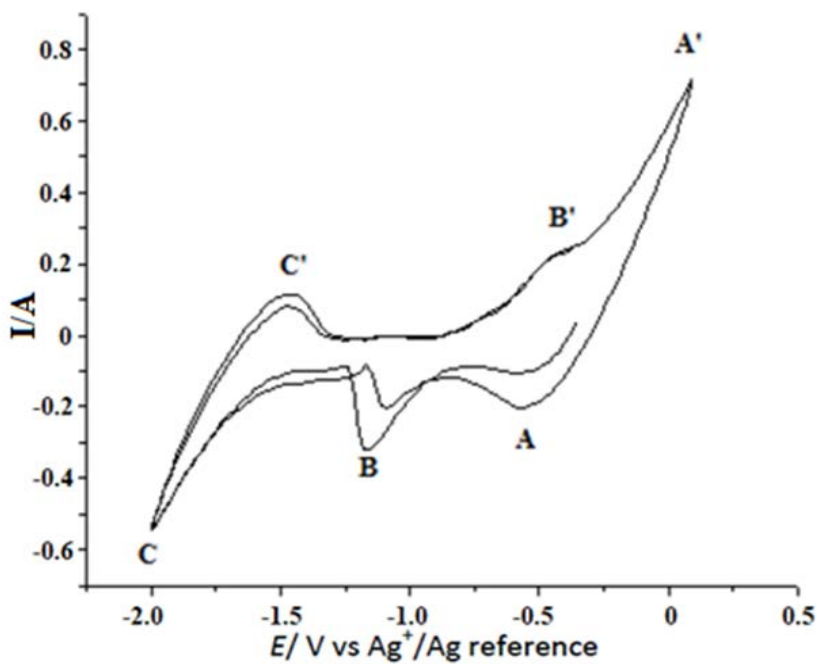

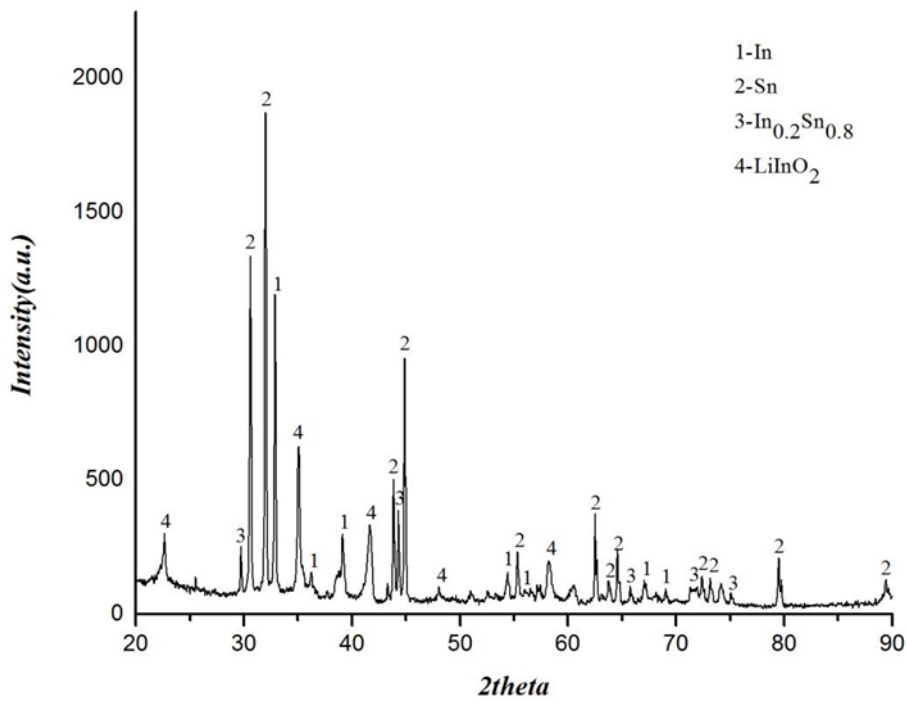Fig. 6. CV of a Mo working electrode with SnO_2 in molten LiCl-KCl with a potential scan rate of 100 mV/s at 450 °C. The potential is swept in the cathodic direction from the open circuit potential.
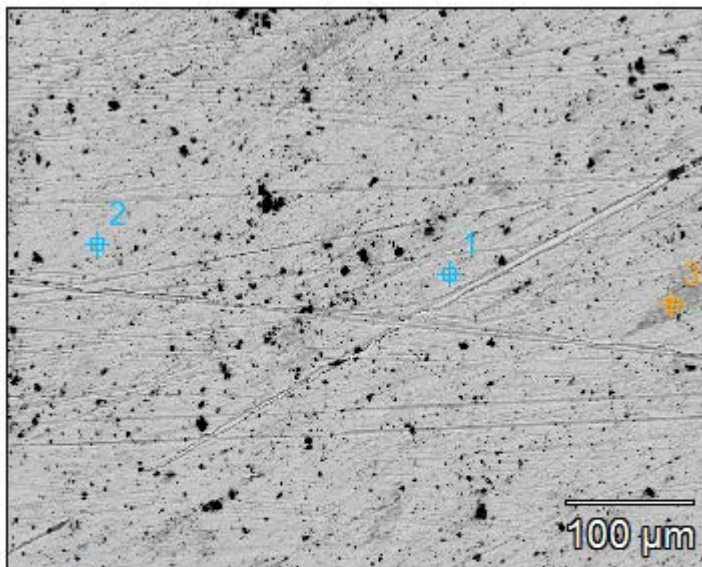
Fig. 7. X-ray diffraction pattern of the deposited indium (after washing by distilled water)

Weight %	O	In	Sn
pt1		6.16	93.84
pt2		6.26	93.74
pt3	18.67	4.38	76.95

Fig. 8. The SEM of tin matrix after ITO combined EDS of the cathode deposit for the points

Fig. 9. Photograph of the contacting electrode after electrolysis
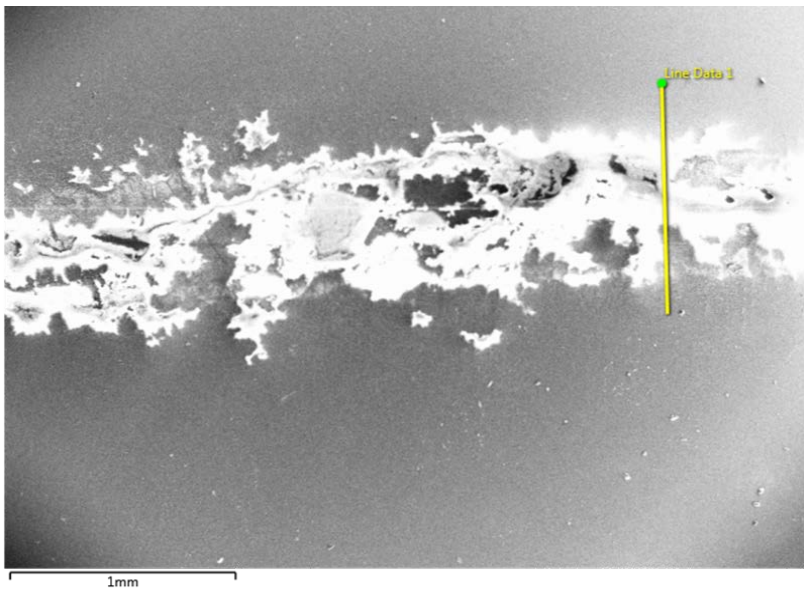

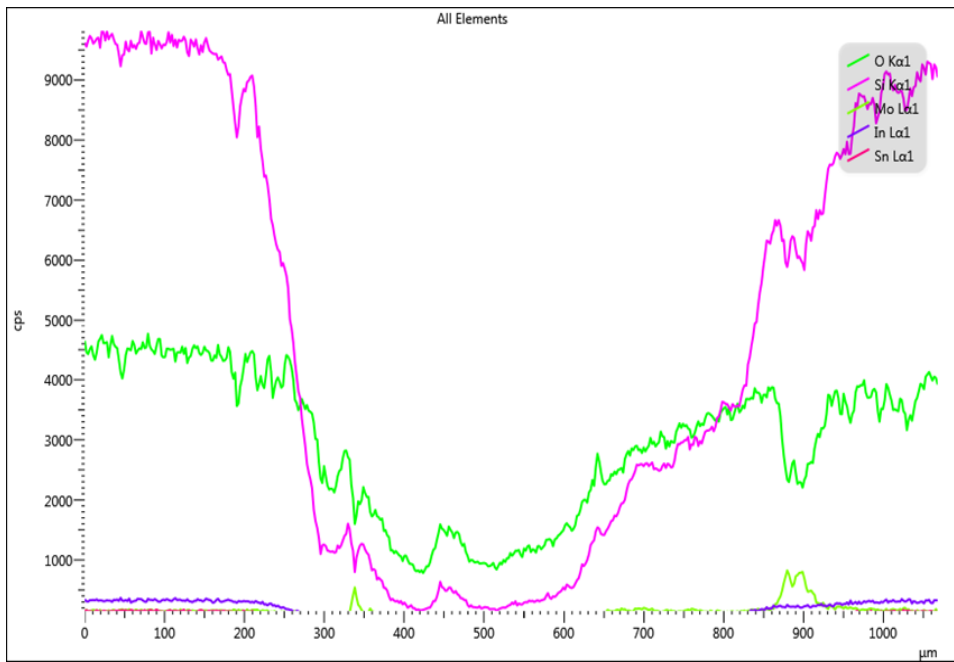Fig. 10. SEM image of the contacting region of the ITO covered glass electrolyzed for 30 minutes

Fig. 11. EDS element line distribution maps for the contacting region