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Electrochemical Stability of Indium-Tin Oxides

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Abstract

The electrochemical activity of mixed indium-tin oxides (ITO) at the cathode and anode treatment in various solvents was studied. It was established that in case of the anodic polarization at potentials that are more negative than the potential prior to the beginning of hydrogen evolution in appropriate solutions of ITO were reduced to the metals In and Sn followed by the formation of intermetallides. It was shown at the anodic treatment the nature of the acid and current density had a big impact on the rate of the anodic dissolution of ITO. The dissolution rate in HCl is lower than in H_2SO_4 and significantly reduced with the increase of the acid concentration due to the acceleration of the side reaction of the evolution of Cl_2. The electrochemical activity of ITO at the cathode and anodic treatment in solutions allows using electrolysis for the disposal of used magnetron targets or ITO scraps.

Key words: indium-tin oxides, ITO, cathode reduction, anodic dissolution, magnetron targets

INTRODUCTION

Mixed indium-tin oxides, known in the literature as indium-tin oxides (ITO) have a number of unique properties, such as a high electronic conductivity, high transparency in the visible part of the spectrum, high reflectivity in the infrared range. Due to this, ITO are essential in the production of transparent conductive films for liquid crystal displays, solar panels and opto-electrical devices [1−3]. Due to the depletion of primary sources of indium and its high cost, in recent years, the increasing attention is being paid to the extraction of In from secondary sources, so called ITO scraps. Films from ITO are mainly obtained by the magnetron sputtering from ceramic targets that are the subject to regeneration after the wear by 60−70 %. At the present time, reagent methods, as a rule, are used for the regeneration of waste targets and other ITO scraps. Because of a great mechanical hardness and chemical inertness of targets known methods include laborious and time-consuming crushing and grinding of targets, requires a significant consumption of concentrated strong acids and elevated temperatures [3]. For this reason, lately, a search is held for alternative methods of registration, for example, electrochemical, when goods containing ITO are exposed to the cathode or anode treatment [4, 5]. The implementation of this method depends on the electrochemical stability of ITO. The goal of the present work is the study of the behaviour of ITO at the cathode and anodic polarization in solutions of HCl and H_2SO_4.

EXPERIMENTAL

For the study of the electrochemical stability of ITO at the cathode and anodic polarization, methods of cyclic voltammetry, gravimetry, atomic adsorption and X-ray phase analysis (XRPA) were used. The phase composition of the initial sample from waste targets containing ITO and products of their electrochemical treatment was determined using the

diffractometer DRON-3 (CuK_α radiation). Gravimetric measurements were conducted using the electronic balances CAUX 220 (CAS Corp. Ltd., Korea). Cyclic voltammograms were filmed at room temperature in a three-electrode cell using a programmed potentiostat IPC Micro (the development of the Institute of Physical Chemistry of the RAS, Moscow). The working electrode is made in the form of a square rod cut from waste ITO targets. The side surface of the rod was insulated with epoxy resin, while the end ($S = 0.06$ cm^2) was refreshed by grinding. A saturated silver-chloride electrode was used as the reference electrode; a graphite rod with a large surface was used as an auxiliary electrode. The sweep rate of the potential amounted to 50 mV/s. Values of potentials including standard equilibrium ones are given relatively to saturated silver-chloride electrode.
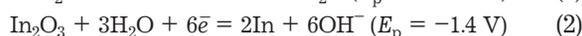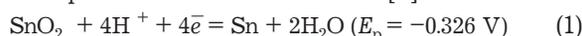
The stability of ITO in the process of the long cathode or anodic treatment was studied in the galvanostatic mode using a laboratory electrolyser, in which the plane electrode from ITO tested ($S = 0.11-0.14$ dm^2) was placed between two auxiliary electrodes of the opposite sign made from graphite or titanium. The rate of cathodic reduction and anodic dissolution of ITO was measured by the gravimetric method as the weight loss of a single surface of the electrode for 1 h of the electrochemical treat-ment. The mass of the metal reduced was determined based on decreasing the mass of the cathode after the anodic dissolution of the precipitate in 6 M HCl solution. The end of the dissolution of the precipitate is clearly recorded by a sharp jump of the anode potential from values characteristic for the dissolution of metallic In up to the potential of chlorine allocation.

RESULTS AND DISCUSSION

Cathode treatment of ITO

At the cathode treatment of ITO both their direct electrochemical reduction and chemical reduction by hydrogen released on the cathode [1] are possible. If the direct reduction is implemented, the process should proceed at certain potentials of the cathode [6]:

$$SnO_2 + 4H^+ + 4\bar{e} = Sn + 2H_2O \quad (E_p = -0.326 \text{ V}) \quad (1)$$
$$In_2O_3 + 3H_2O + 6\bar{e} = 2In + 6OH^- \quad (E_p = -1.4 \text{ V}) \quad (2)$$

If the chemical variant is implemented, the potential of the start of reduction of ITO, at which products of this reaction are registered, will be determined by the potential of evolution of H$_2$ that is shifting to negative side at the increase of pH.

To determine the field of potentials of the start of cathodic reduction of ITO and identify reduction products, cyclic voltammetric mea-
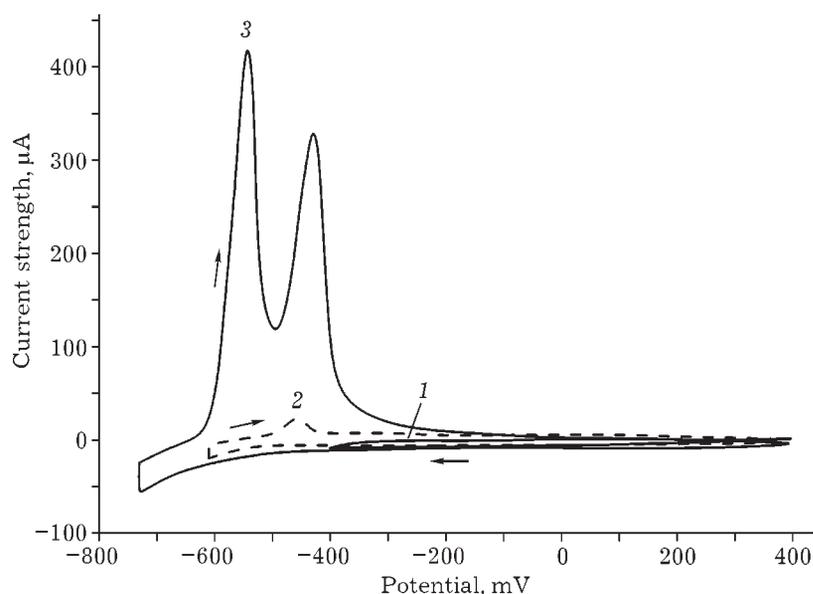

Fig. 1. Cyclic voltammograms of ITO at various final potentials of the cathode (mV): -400 (*1*), -600 (*2*), -700 (*3*). 0.1 M H$_2$SO$_4$ solution, $S = 0.06$ cm^2.

surements were carried out in acidic and alkaline solutions: H_2SO_4 (0.1 and 1 mol/L), HCl (0.1 and 3 mol/L) and KOH (1 mol/L). At that, the cathodic schedule of the cycle was carried out from the initial no-current potential $E = 0.3-0.4$ V to final values with a subsequent keeping for 1 min and scanning in the opposite (anodic) direction. The anodic scan revealed products of the cathode reaction, since on the fact of the appearance of the anodic current and position of its peaks, the amount and nature of the reaction product can be judged about.

Characteristic cyclic cathode voltammograms (on the example of 0.1 M H_2SO_4) are presented in Fig. 1, and processing voltammograms obtained in ITO in solutions of a various composition are given in Table 1.

The analysis of the results obtained shows that there is a sufficient wide area, dependent on the value of pH and solution nature, where ITO is electrochemically inert. For example, in 0.1 M H_2SO_4 solution ITO are quite stable up to the potential of -0.4 V, there is no increase of the cathode current in this diapason of potentials (see Fig. 1, curve *1*). However, at potentials that are more negative than 0.6 V, the current strength increases observed and peaks of the dissolution of the precipitate appear at the reverse anodic scan. Distinctive peaks of products of reduction of ITO are fixed at cathode potentials starting approximately with $E = -0.65$ V. In alkaline solutions, products of the cathode reduction appear at potentials that are more negative than -1.3 V.

The fact that the potential of the start of the formation of cathode products on ITO depends on the pH and with its increase shifts to the cathode direction in parallel with the shift of the start of H_2 evolution from the solution, apparently, indicates the close connection of the cathode reduction of ITO with the process of H_2 evolution from the solution. Any anomalies in the field of the potential of the direct reduction of In_2O_3 (~1.4 V) are not observed.

There are two separate peaks at $E = -0.5...-0.6$ V and $E = -0.4...-0.3$ V (see Fig. 1) on anodic branches of cyclic voltammograms in solution of H_2SO_4 or HCl, where the both metals form soluble salts. The first value is close to the equilibrium potential for the system In/In^{3+} ($E_{eq} = -0.565$ V), and the second one is close to the equilibrium potential of the system Sn/Sn^{2+} ($E_{eq} = -0.358$ V). The shift of peaks of dissolution of In and Sn in the cathode direction ($150-200$ mV) in HCl with an increase of its concentration from 0.1 to 3 mol/L is apparently due to the formation of chloride complexes of indium and tin (the logarithms of instability constants is ~1.5 for In^{3+} and 2.25 for Sn^{2+} [6]).

Only one peak of the dissolution at the potential of -1.17 V in a solution of alkali branch of the sequence diagram is observed what can be explained by close values of potentials of processes of the dissolution of In and Sn for the system $Sn/HSnO_2^-$ ($E_p = -1.13$ V) and $In/In(OH)_3$ ($E_p = -1.22$ V) [7].

Thus, it follows from the data of voltammetry that as a result of the cathode reduction of ITO, In and Sn are most likely formed, since the position of the peaks on the curves of anodic dissolution is close to table values of equilibrium potentials for these elements. This conclusion agrees well with data of XRPA obtained at the study of the initial material, as

TABLE 1

Potentials of the beginning for the formation of products of cathode reduction of ITO and peaks for their anodic dissolution in H_2SO_4 and HCl

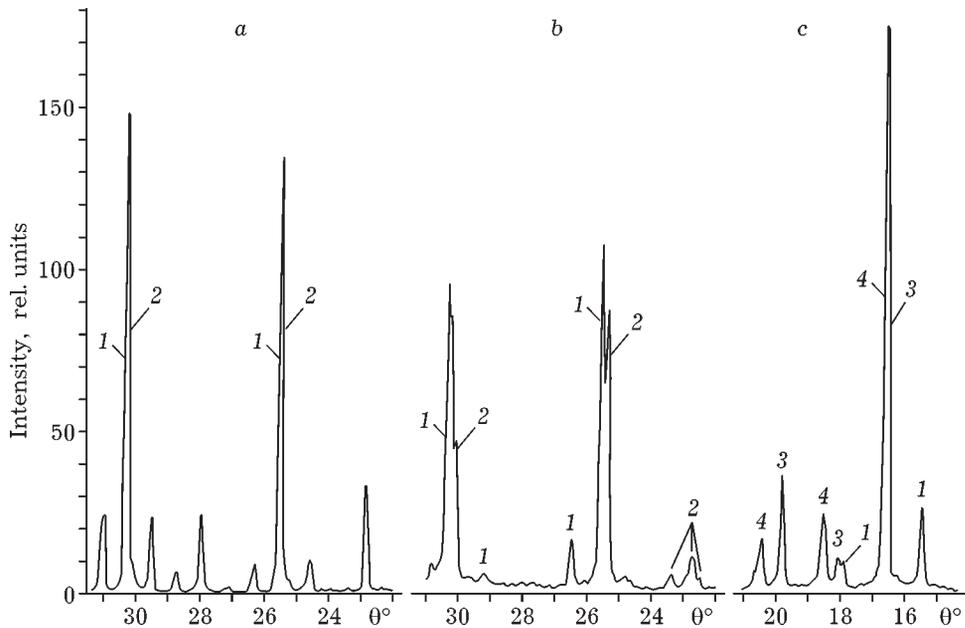| Solutions	Potential of the beginning of the formation of the cathodic product, V	Peaks potentials of dissolving products, V	
		Peak I	Peak II
0.1 M H_2SO_4	−0.61	−0.54	−0.42
1 M H_2SO_4	−0.60	−0.54	−0.43
0.1 M HCl	−0.85	−0.50	−0.35
3 M HCl	−0.75	−0.65	−0.55
1 M KOH	−1.30	−1.17	

Fig. 2. Diffraction patterns of ITO after different treatment stages: a − the initial sample, b − after the anodic etching of the surface layer (0.1 M H_2SO_4 solution, $i = 5$ A/dm^2), c − after the cathode reduction (6 M HCl solution, $i = 4$ A/dm^2, $t = 6$ h). Phases: In_2O_3 (*1*), $In_4SnO_3O_{12}$ (*2*), In (*3*), In_3Sn (*4*).

well as of products of cathode and anode processing ITO.

According to the data of XRPA, oxide In_2O_3 (cubic structure, card number 6-416, sp. gr. (S. G.) Ia-3 (according to 206) and a double oxide $In_4Sn_3O_{12}$ (rhombic structure, PDF N88-773, S. G. R-3 (according to 148) are included in the surface layer of the starting used magnetron targets of ITO as the main phase (Fig. 2, *a*). The absence of the phase SnO_2 is logical to explain by the occurrence of tin in the composition of the double oxide $In_4Sn_3O_{12}$ that is formed on the stage of the thermal synthesis of ITO. It is problematic to quantify the content of phases starting in the material, since all general reflexes of In_2O_3 and $In_4Sn_3O_{12}$ overlap. Numbers *1* and *2* indicate positions of general reflexes of these phases, respectively. If the surface of used targets of ITO is the exposed to etching (see Fig. 2, *b*), a good splitting of reflexes of the both oxides is observed, what allows us to state with confidence the presence of oxide In_2O_3 and double oxide $In_4Sn_3O_{12}$ in the starting product.

Products of cathode reduction of ITO, according to results of XRPA, generally consist of metallic In (tetragonal structure, card number 5-642, S.G. I 4/*mmm* (according to 139) and

intermetallide In_3Sn (tetragonal structure, PDF N7-345, S.G. P 4/*mmm* (according to 123). A small amount of indium oxide in the form of In_2O_3 (see Fig. 2, *c*) is probably captured from the starting material at scraping with it the precipitate for analysis.

During the prolonged cathodic treatment of samples from ITO H_2 is released on the cathode and the sample itself undergoes a significant change. From very solid and fragile ceramics of the blue purple colour it converts into a soft material of the grey colour with the metallic shine. At electrolysis, especially in the initial period, a small sludge (10 % from the reacted ITO), the composition of which is analogous to that of the starting material, is formed. The formation of sludge may be due to the uneven reduction, as well as to the mechanical stresses between grains of the oxide and grains of the product that are registered up to the appearance of a solid metal sponge on the surface of the cathode hindering the process of sludge formation.

It has been established that a higher rate of the cathode reduction of ITO is characteristic for a 6 M solution of HCl. At the initial stage, the reduction process proceeds with the maximal rate, then it is markedly slowing down
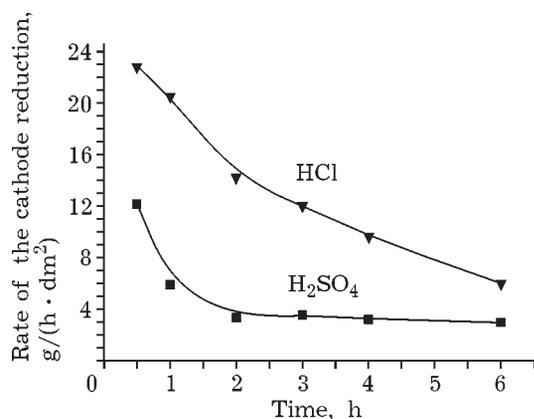
Fig. 3. Dynamics of the cathode reduction of ITO in solutions of 6 M HCl and 1 M H_2SO_4. $i = 8$ A/dm^2.

Fig. 4. Anodic voltammograms of ITO in solutions of 3 M HCl (1), 1 M HCl (2) and 1 M H_2SO_4 (3).

as the reaction of boundary is moved from the surface in the depths of electrode, particularly in sulphuric acid solutions (Fig. 3). This may be due to the gradual fusion of grains of the cathode product and formation a solid layer of the reduced metal in the form of a sponge that hinders the access of electrolyte to the oxides.

Thus, at the cathodic action on ITO, at potentials, that are more negative than the start of H_2 release mixed indium and tin oxides are reduced to appropriate metals. Metallic In and Sn are easily soluble chemically and anodically, therefore, this process can be used for processing of used targets and scraps containing ITO, as well as for preparing technological "windows" in layers of ITO. The disadvantage of the cathode way of targets utilization is its periodicity that is due to the fact that it is necessary to remove periodically the formed metal coating.

Anode treatment of ITO

The anodic stability of ITO has been studied in solutions of H_2SO_4 and HCl of various concentrations in the galvanostatic electrolysis mode. The anodic voltammograms obtained indicate the stability of ITO in a fairly wide range of potentials (up to 2.6 V in H_2SO_4 and up to 1.5−2 V in solutions of HCl of various concentrations). Increasing the strength of the anode current at higher values of potentials is accompanied by the emission of gaseous products (O_2 and Cl_2, respectively) and simultaneous
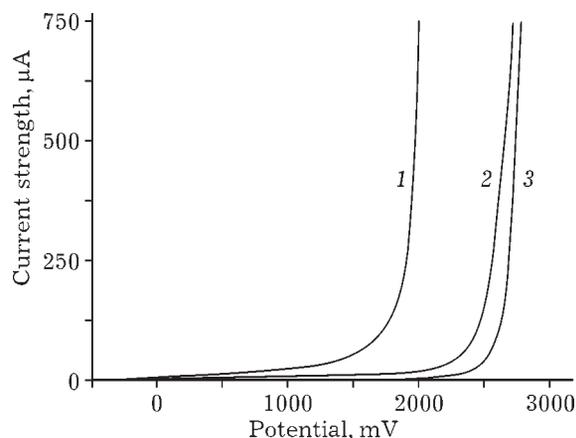
decrease of the weight of the anode. By analogy with the chemical dissolution of ITO in solutions of acids [8], the anodic dissolution of ITO is also due to the action of radical particles formed on the anode and other forms of active oxygen [9]. The direct oxidation of O_2^- ions included in the crystal lattice of oxides of ITO is not excluded [10]. The released cations In^{3+} and Sn^{4+} in the acidic medium give soluble compounds and pass into the solution, thereby increasing the concentration of metal ions. This is confirmed by the results of the analysis of the solution by the method of atomic absorption.

Unlike the cathode reduction, the rate of which decreases with time, the anodic dissolution process of ITO in acids proved to be practically stable. The current density has a strong
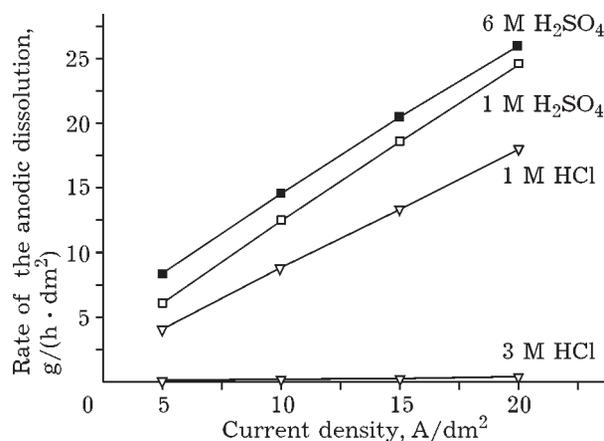

Fig. 5. Dependence of the rate of the anodic dissolution of ITO on the current density in solutions of HCl and H_2SO_4. Electrolysis duration is 1 h.

effect on the anodic dissolution of ITO. Thus, in the diapason of values of the current density of $5-10$ A/dm^2 a linear dependence of the rate of dissolution on the current density (Fig. 5). Besides, the dissolution of ITO depends on the nature and concentration of the acid. In solutions of sulphuric acid, the rate of the anodic dissolution of ITO is higher, in comparison with solutions of hydrochloric acid and it is weakly dependent on the acid concentration. On the contrary, in solutions of hydrochloric acid a strong and anomalous dependence of it on the concentration: the increase of the concentration of HCl from 1 to 3 mol/L decreases sharply the rate of the dissolution of ITO (see Fig. 5). Most likely, this is due to the increase of the side reaction of Cl$_2$ evolution at high concentrations of the acid. In favour of this along with the odour of chlorine, the shift of the beginning of rise of the anode current power to the field of lower potentials at the transition to concentrated solutions of HCl (see Fig. 4). Apparently, at the concentration of HCl ≥ 1 mol/L almost the entire anode current is consumed on the parallel process of Cl$_2$ evolution. On this reason, it is to use concentrated hydrochloric solutions for purposes of the anode treatment of ITO.

CONCLUSION

The study of the electrochemical stability of ITO at the cathode and anodic treatment in solutions of HCl and H$_2$SO$_4$ has shown that despite a high chemical stability of ITO, their electrochemical stability depends directly on treatment conditions. In case of the cathode treatment at the potentials that are more negative than potentials of H$_2$ evolution oxides are reduced to metals In and Sn and their intermetallic compounds. The rates of reduction achieved in this case are low and they decrease markedly with time because of shielding the reaction zone with a layer of products and of parallel gassing of hydrogen gas.

At the anodic treatment of ITO in sulphuric acid solutions the dissolution process proceeds with a higher rate. In hydrochloric solutions, the rate of dissolution of ITO is lower, than in sulphate and it reduces significantly with the growth of the acid concentration, apparently, due to the acceleration of the side reaction of the release of chlorine.

Acknowledgement

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