

# Role of acidic and basic electrolytes on the structure and morphology of cathodically reduced indium tin oxide (ITO) substrates



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## ABSTRACT

In this report we track the structural changes suffered by ITO along galvanostatic polarization at different current densities by X-ray diffraction and SEM micrographs. The XRD shown that cathodic treatment induces structural change in ITO, characterized by appearing peaks set distinct from ITO original structure associated to metallic phase of the solid solution of In–Sn. It is interesting to note that although the different ions present in the solution are not, at least to a noticeable degree, incorporated in the metallic phase, the SEM images show that they do influence its formation, pointing to some type of adsorptive mechanism of the inert ions during the lateral diffusion of the metallic ions.

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## 1. Introduction

Thanks to its highly praised electrical and optical properties and widespread use in optoelectronic devices such as flat panel displays and photovoltaics, ITO ( $\text{In}_2\text{O}_3:\text{Sn}$ ) is now being regarded as a practical and reliable substrate that may be used in many other applications. Among others, glass or plastic-based ITO thin films are being used as substrates in electrochemical deposition of metals [1,2], electrosynthesis of ceramics [3–5], electrophoresis [6], amperometric and optical biosensors [7,8], total internal reflection fluorescence, electroporation [9] and electrical stimulation of cultured cells.

These applications involve the use of cathodic polarization in aqueous electrolytes and demand electrochemical stability of the ITO electrode under the applied conditions. The first investigations on the electrochemistry of conductive oxides date back to 1968 and were firstly performed on  $\text{SnO}_2$  [10,11] and  $\text{In}_2\text{O}_3$  electrodes [11] and later on, in tin-doped indium oxides [12]. Those first studies determined the available electrochemical window under specific conditions and mentioned irreversible damage to the electrode when exposed to potentials beyond those limits. The stability of ITO electrodes in aqueous electrolytes was revisited many times throughout the 90s in studies that addressed some very specific topics of technological interest like the etching behavior of ITO in concentrated acids or bases for micropatterning, device

instabilities caused by Al corrosion of ITO contacts in alkaline solutions [13], degradation mechanisms in oLEDs [14] and in solid state polymeric electrochromic cells [15]. The partial reduction of ITO substrate was also explored in the improvement in adhesion during copper plating [16,17]. In the next decade there were some studies specifically devoted to the electrochemical behavior of ITO [18–23]. Huang et al. [18] focused on the morphological changes suffered by ITO substrates upon cathodic treatment and reported the appearance of spherical particles of a metallic In–Sn solid solution after polarization at  $-0.8\text{V}$  ( $\text{Ag}/\text{AgCl}$ ,  $0.3\text{M}$  HCl). Senthilkumar [21] showed that voltage cycling in the cathodic region beyond  $-0.8\text{V}$  ( $\text{Ag}/\text{AgCl}$ ) at  $\text{pH} < 6$  increased electrical resistance and decreased optical transparency. Concurrently, other authors interpreted the loss of transparency in terms of an electrochromic effect caused by hydrogen intercalation in ITO [24,25].

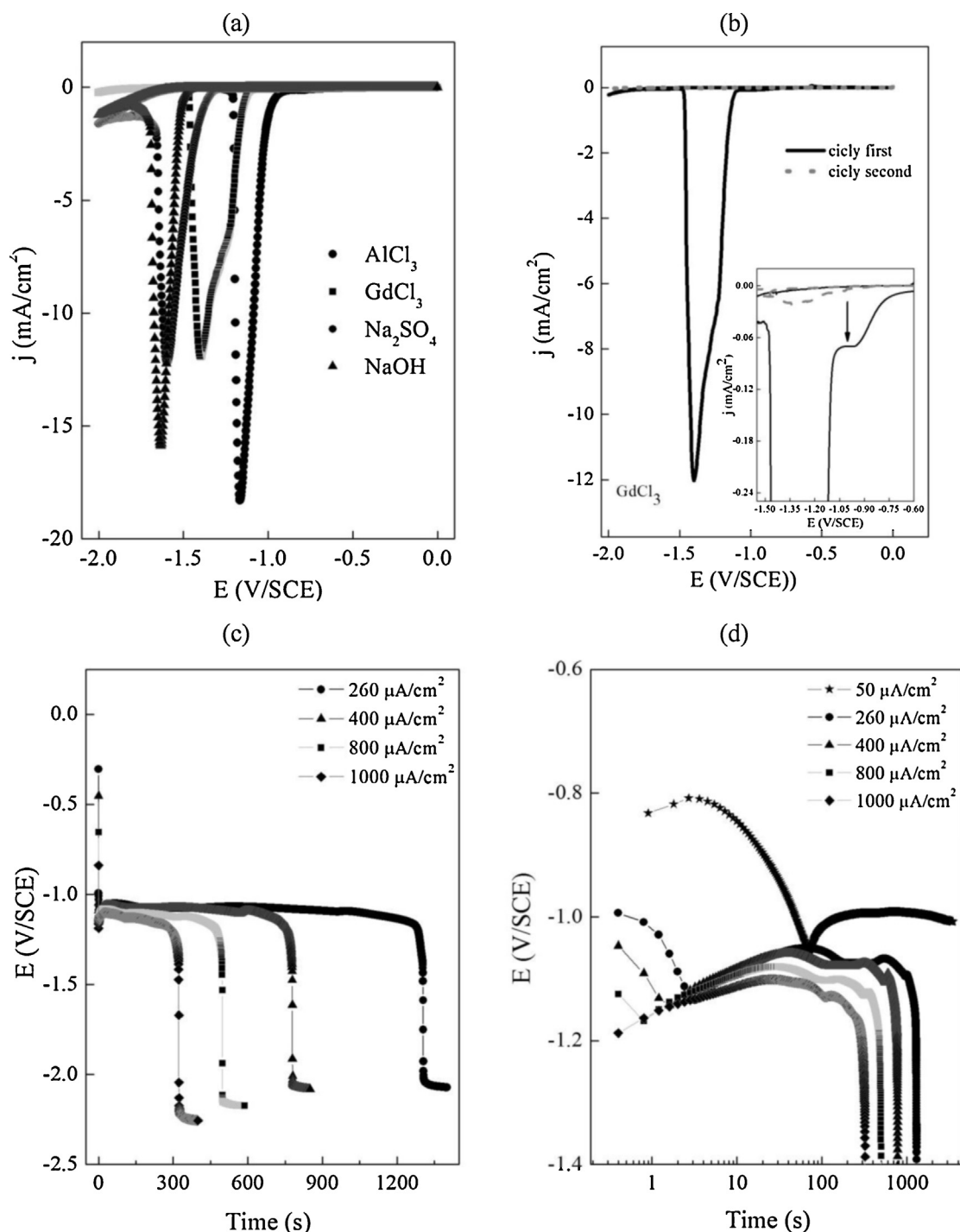
In this report we track the structural changes suffered by ITO along galvanostatic polarization at different current densities by X-ray diffraction and SEM micrographs. We show that the irreversible changes suffered by ITO occur irrespective of electrolyte composition, in a large range of pH. On the other hand, we show that the final morphology attained by the reduced film depends on the electrolyte.

## 2. Experimental procedure

ITO coated glasses were purchased from Delta Technologies Ltd., with nominal coating thickness between 150 and 200 nm and resistance varying from 4 to  $8\ \Omega\text{cm}$ . The nominal composition

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**Fig. 1.** (a) The obtained voltammograms for the electrolytes used. (b) The voltammetric curves of two consecutive scans for the electrolyte with 0.3 mol/l GdCl<sub>3</sub> (pH 4.6). (c) Potential versus time curves obtained for ITO substrates and electrolyte 0.3 mol/l GdCl<sub>3</sub> (pH 4.6), submitted at current density constant of 260, 400, 800 and 1000  $\mu$ A/cm<sup>2</sup>. (d) Potential versus logarithm of time curves obtained for ITO substrates and electrolyte 0.3 mol/l GdCl<sub>3</sub> (pH 4.6), submitted at current density constant of 50, 260, 400, 800 and 1000  $\mu$ A/cm<sup>2</sup>.

is 10% Sn. ITO substrates were submitted to cathodic potentials in aqueous supporting electrolytes of the following salts: 0.3 mol/l AlCl<sub>3</sub> (pH 2.5), 0.3 mol/l GdCl<sub>3</sub> (pH 4.6), 0.3 mol/l Na<sub>2</sub>SO<sub>4</sub> (pH 7.0), 0.3 mol/l NaOH (pH 13.1). The values in parenthesis refer to the natural pH of the electrolyte. Cyclic voltammograms and potentiometric curves were carried out in a conventional three-electrode cell using an Autolab PGSTAT302 N Potentiostat. The reference electrode was a calomel electrode (SCE) and a

large area Pt electrode was used as counter electrode. The area of the ITO electrodes was delimited in 0.5 cm<sup>2</sup>. X-ray diffraction (XRD) analysis was used to track the changes in film structure after cathodic treatment. The XRD experiments were performed at room temperature using a Panalytical X'Pert Pro MPD diffractometer model, with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in a  $\theta$ - $2\theta$  configuration with  $2\theta$  varying between 20° and 70°.

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