

Pulsed Electrodeposition of Rhenium – Rhenium Oxide on Tin-doped Indium Oxide

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Rhenium oxides exhibit interesting properties due to their catalytic activity and in the case of rhenium trioxide, its capability of intercalating ions in its crystalline structure [1]. This paper reports work aimed at synthesizing rhenium and rhenium oxide on Tin-doped Indium Oxide (ITO) from an aqueous electrolyte consisting of ammonium perrhenate dissolved in sodium hydroxide and sulphuric acid. A first attempt was made at understanding the electrodeposition mechanism of Re oxide on ITO through cyclic voltammetry as shown in Figure 1. ITO is an active electrode material in the cathodic range; it does not allow a clear observation of the reduction reaction, however, the presence of perrhenate ions in the electrolyte caused a decrease in the observed cathodic peak current as shown in Figure 2. Reverse pulse current was used to electrodeposit rhenium oxide on ITO substrates. Deposits of rhenium and rhenium oxides were obtained and observed with scanning electron microscopy as shown in Figure 3. Energy dispersive spectrometry (EDS) data was collected over the same regions; Table 1 shows the average content of rhenium (Re), tin (Sn), indium (In), and oxygen (O) in the deposit. Results showed a decrease in rhenium content with the use of a higher forward-pulse current and an increase in rhenium content with an increase of perrhenate ions concentration in solution. Grazing Incidence X-ray Diffraction (GIXRD) analysis of the deposit showed the possible formation of two basic crystalline compounds on the ITO substrate: rhenium oxide hydrate ($H(ReO_4)(H_2O)$) and hydrogen rhenium oxide ($H_{0.57}ReO_3$). Our previous transmission electron microscopy observations showed the formation of rhenium and rhenium oxides on copper substrates from alkaline aqueous electrolyte [2].

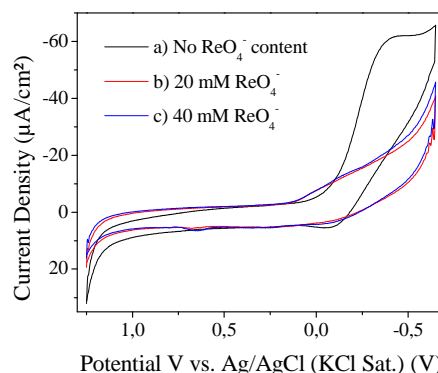


Fig 2. Voltammograms measured a) in the absence of ReO_4^- ions, (b) 20 mM ReO_4^- and c) 40 mM ReO_4^- solutions. Scan rate = 200 mV s⁻¹.

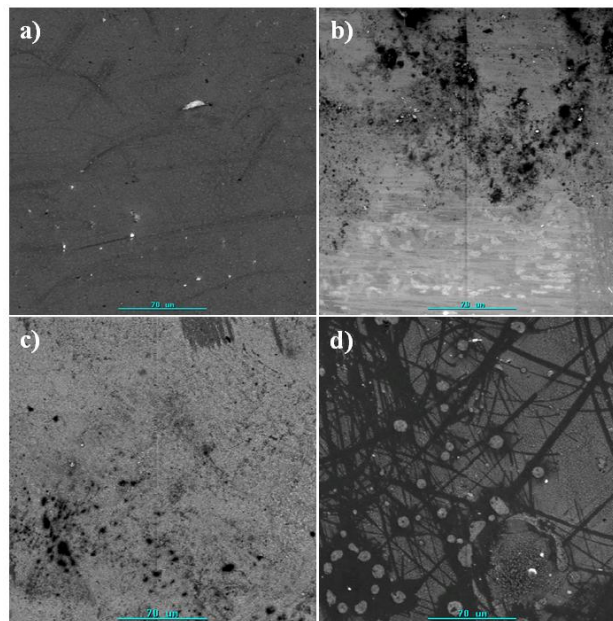


Fig 3. SEM images of electrodeposits obtained at: a) 20 mM ReO_4^- and 11 A/m² forward-pulse density current, b) 20 mM ReO_4^- and 55 A/m² forward-pulse density current, c) 40 mM ReO_4^- and 11 A/m² forward-pulse density current and d) 40 mM ReO_4^- and 55 A/m² forward-pulse density current. The scale bar equals 70 µm.

Table 1. EDS analysis of surface composition of samples shown in figure 1 (average concentrations), wt%.

Image	Re	Sn	In	O
a)	6.37	12.94	70.86	9.83
b)	2.27	10.92	72.64	14.17
c)	11.27	11.75	68.29	8.69
d)	4.43	10.95	72.14	12.48
ITO (*)	---	13.75	72.11	14.15

(*) Previous to processing.

[1] E. Cazzanelli et al. J Appl Phys 2009; 105:114904.

[2] A. Vargas, E. Mosquera, L. Cifuentes. Mater Lett.; Submitted, September 2012.

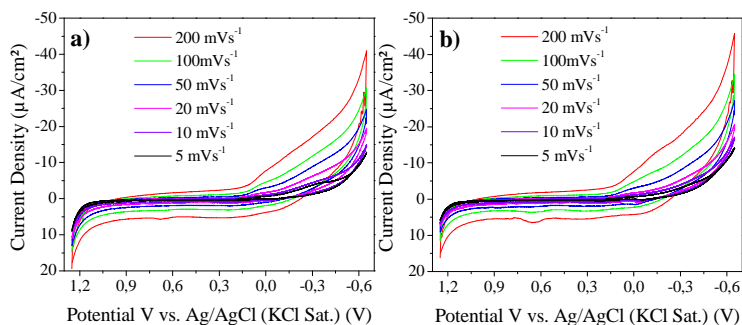


Fig 1. Voltammograms measured in a) 20 mM ReO_4^- and b) 40 mM ReO_4^- solutions on an ITO substrate at various scan rates.