

**ELECTROCHEMICAL BEHAVIOUR OF BaSn<sub>0.9</sub>Sb<sub>0.1</sub>O<sub>3</sub> COATED TITANIUM  
ELECTRODES**

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**Abstract**

BaSn<sub>0.9</sub>Sb<sub>0.1</sub>O<sub>3</sub> /Ti electrodes were prepared by painting a slurry containing the oxide, synthesised by high-temperature solid state reaction, and Triton X-100 on titanium supports. The electrochemical behaviour of the electrodes was studied by cyclic voltammetry. From the voltammetric data the electrodes surface roughness was estimated and it was possible to conclude that an insulating film of TiO<sub>2</sub> is formed at the support/oxide layer interface.

*Key words:* perovskite, oxide, ohmic drop

**Introduction**

The applicability of electrochemistry in environmental protection was recently described by Rajeshwar and Ibanez, who reviewed some of the recent work published on the subject [1]. Electrochemistry is mainly associated with waste treatment and development of new processes or products, which have no harmful effects on the environment. These aspects are close related with the development of new electrode materials with suitable properties.

The perovskite oxide BaSn<sub>0.9</sub>Sb<sub>0.1</sub>O<sub>3</sub> has several electrochemically desirable properties, namely metallic conductivity and resistance to corrosion in addition to a wide potential window in aqueous solutions [2-5]. These properties make this material a suitable candidate for oxidative electrochemical processes, namely the degradation of organic compounds [6].

Previous electrochemical studies performed on sintered pressed-disc electrodes showed that the voltammetric response of the sintered electrodes is dominated by the exhaustive electrolysis of

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electroactive species in the pores [3]. In order to overcome this problem new electrode types were studied.

In this work  $\text{BaSn}_{0.9}\text{Sb}_{0.1}\text{O}_3$  films were prepared on titanium supports and cyclic voltammetry was used to study the oxide electrode behaviour. The aim of the study was to investigate how the electrochemical response of the oxide, is affected by the type and preparation of the electrode, for the purpose of obtaining anodes for practical applications.

### Experimental

**Preparation of the electrodes:** The oxide was synthesised by high-temperature solid-state reaction of appropriate precursors as previously reported [5]. Stoichiometric amounts of  $\text{BaCO}_3$  (99% Merck),  $\text{SnO}_2$  (99.9% Aldrich) and  $\text{Sb}_2\text{O}_3$  (99% Merck) were ground and heated at 1173 K for 12 hours in a muffle furnace and then regrind and heated at 1523 K for 12 hours. The synthesis was routinely controlled by means of X-ray powder diffraction.

The titanium disks (99% Goodfellow, 15 mm in diameter and 0.25 mm thick) were mechanically polished with emery paper, then dipped in boiling 20% oxalic acid during 30 min and finally rinsed with purified water [7].

The coatings were obtained by painting a slurry containing the oxide and Triton X-100 (Merck) on the titanium disks and subsequent sintering in air at 400°C during 2 hours [8]. The loading of the oxide film was  $7 \pm 1 \text{ mg cm}^{-2}$  in each case.

**Electrochemical measurements:** All the electrochemical measurements were carried out in a three-compartment glass cell, at room temperature using a Tacussel potentiostat/galvanostat model PJT 35-2 Interface IMT-1. The working electrode was the  $\text{Ti}/\text{BaSn}_{0.9}\text{Sb}_{0.1}\text{O}_3$  disc, which fitted into a polypropylene holder. All potentials were measured against a commercial saturated  $\text{Ag}/\text{AgCl}$  reference electrode and the auxiliary electrode was a platinum foil. The solutions were prepared volumetrically from Millipore water and pro analysis reagents, and deaired with nitrogen, before each experiment.

**Materials characterization:** The crystal structure was determined by means of X-ray diffractometry using a Philips PW 1730 X-ray diffractometer, with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The X-ray diffraction data analysis showed that the oxide is a single phase with a cubic perovskite type structure and a cell parameter  $a = 4.117 \text{ \AA}$  [2,5].

SEM was done on a JEOL JSM 35C microscope.

### Results and discussion

The electrochemical behaviour of the coated perovskite  $\text{BaSn}_{0.9}\text{Sb}_{0.1}\text{O}_3$  electrodes was studied in  $1 \text{ mol dm}^{-3}$  KOH and fig. 1 shows a representative cyclic voltammetric curve. For comparison a curve for the Ti substrate was also included. As observed the coated perovskite electrode presents a wide range of electrochemical stability as it was previously reported for sintered pressed-disc type electrodes of the same material [2].

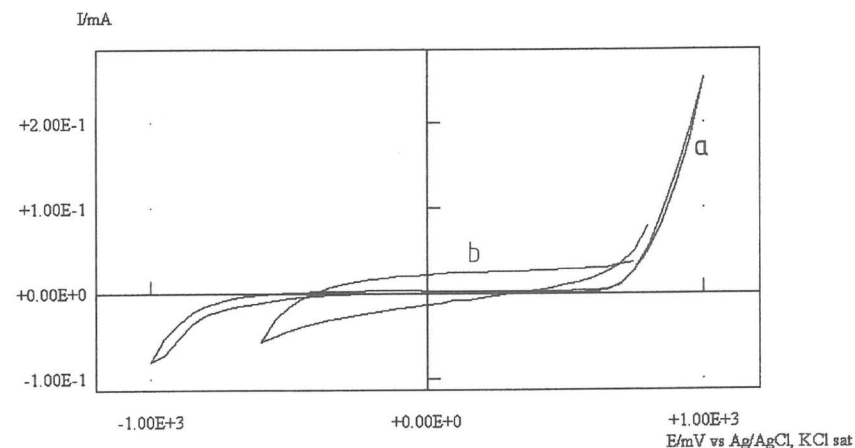


Fig. 1- Cyclic voltammograms for a) Titanium electrode and b) Titanium coated perovskite  $\text{BaSn}_{0.9}\text{Sb}_{0.1}\text{O}_3$  electrode in  $1 \text{ mol dm}^{-3}$  KOH. Sweep rate is  $50 \text{ mVs}^{-1}$ . Electrode geometric area  $1.3 \text{ cm}^2$ .

The electrochemical active surface area of the oxide coating, was estimated from double-layer charging curves, using a cyclic voltammetric technique [2] as it was done previously for the sintered pellet electrodes. The current - potential curves are given in fig 2 for a number of sweep rates.

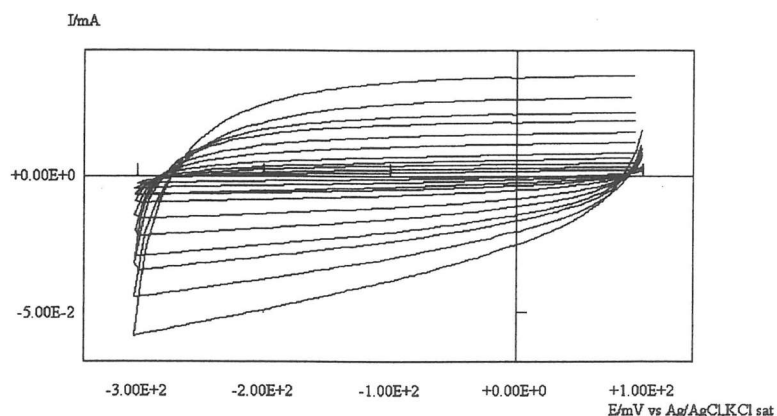


Fig. 2- Cyclic voltammograms obtained in the double layer region, for a titanium coated perovskite  $\text{BaSn}_{0.9}\text{Sb}_{0.1}\text{O}_3$  electrode in  $1 \text{ mol dm}^{-3}$  KOH. Sweep rates 2, 4, 6, 8, 10, 15, 20, 25, 30, 40 and  $50 \text{ mVs}^{-1}$ . Electrode geometric area  $1.3 \text{ cm}^2$ .

It is clear that the contribution from faradaic processes is small in the selected potential region of  $-0.300$  to  $+0.100 \text{ V}$  vs  $\text{Ag}/\text{AgCl}$  and an approximate symmetry of the anodic and cathodic currents is observed around  $-0.100 \text{ V}$ .

The voltammograms are characterised by a sluggish current switching when the sweep is reversed, with a rise time of several seconds which is associated with the time constant of the series combination due to the ohmic resistance of the oxide/titanium and the electrode capacitance.

A plot of the double-layer charging current obtained at  $E = -0.100 \text{ V}$  vs sweep rate is presented in fig. 3.

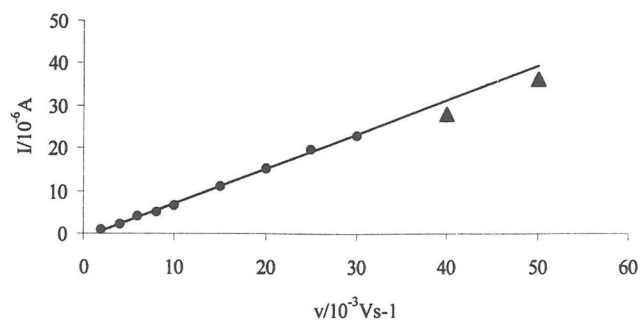


Fig. 3 - Double-layer charging currents as a function of sweep rate for a titanium coated perovskite  $\text{BaSn}_{0.9}\text{Sb}_{0.1}\text{O}_3$  electrode at  $-0.100 \text{ V}$  vs  $\text{Ag}/\text{AgCl}$ . Electrode geometric area  $1.3 \text{ cm}^2$ .

A good linear relationship is observed for sweep rates  $\leq 30 \text{ mVs}^{-1}$  (correlation coefficient 0.9982), and a deviation is observed for higher sweep. Similar results have been reported by Baronetto et al [9] for the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrodes and the deviation was attributed to the formation of an insulating barrier at the support/oxide layer interface.

From the slopes of the linear region of the plots, double-layer charging current vs sweep rate, the capacitance of the oxide/solution interface ( $C = dq/dE = dI/dv$ ) was calculated. The capacitance per  $\text{cm}^2$  of geometrical surface area was found dividing the capacitance value by the electrode geometric area. The value of  $643 \pm 44 \mu\text{F cm}^{-2}$  was obtained.

Our previous data report double layer capacitance 10 times higher for perovskite  $\text{BaSn}_{0.9}\text{Sb}_{0.1}\text{O}_3$  sintered pressed-disc type electrodes. It can be concluded that coated electrodes present lower double-layer capacitances than the sintered pressed-disc type and consequently lower real surface areas.

Although this method does not give absolute values for the real electrode area, since the precise "capacitance" of the oxide surface is unknown [10], a relative magnitude can be obtained by assuming the value of  $60 \mu\text{F cm}^{-2}$  usually taken for the capacitance of a smooth oxide surface [11].

In order to estimate the roughness factor  $R_f$ , defined as the ratio between the real and the geometric surface areas, the estimated capacitance value obtained for the perovskite electrode was divided by  $60 \mu\text{F cm}^{-2}$ .

Table I shows the capacitance and roughness factor values for the  $\text{BaSn}_{0.9}\text{Sb}_{0.1}\text{O}_3$  perovskite coated electrodes. Values earlier obtained in our laboratory for sintered pressed-disc type electrodes were also included [2]. These results show clearly the influence of the electrode type on the surface area/roughness values.

Table I

Capacitance and average roughness factor values for the  $\text{BaSn}_{0.9}\text{Sb}_{0.1}\text{O}_3$  perovskite electrodes.

Electrode type	$C/\mu\text{F cm}^{-2}$	$R_f$	Reference
Sintered pressed-disc	6429	107	2
Coating	643	11	This work

The morphology of the coating was examined by SEM. Fig. 4 presents a typical electrode surface where the rough and porous nature of the coating is clearly seen. These observations are consistent with roughness factor values greater than 1.

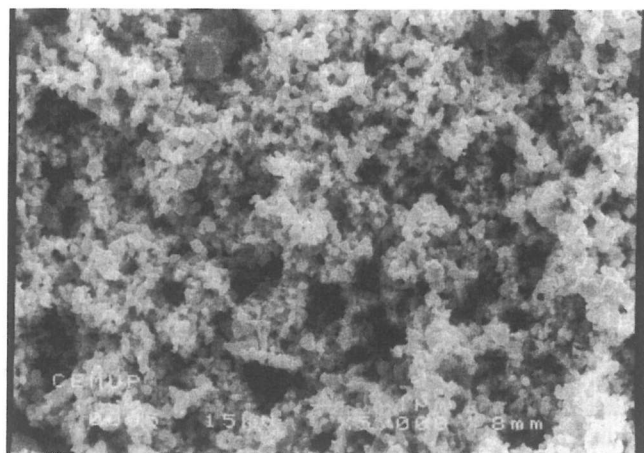


Fig. 4 - SEM of surface of Ti/ BaSn<sub>0.9</sub>Sb<sub>0.1</sub>O<sub>3</sub> perovskite electrodes.

The main problem in the preparation of coated Ti electrodes is to ensure a good electrical contact between the Ti substrate and the coating. For the perovskite coated electrodes the voltammetric results indicate that high ohmic losses occur. In order to quantify these losses, the voltammetry of the Fe(CN)<sub>6</sub><sup>4-</sup>/ Fe(CN)<sub>6</sub><sup>3-</sup> couple at the BaSn<sub>0.9</sub>Sb<sub>0.1</sub>O<sub>3</sub> coated Ti electrode was investigated in 1.0 moldm<sup>-3</sup> KNO<sub>3</sub>. As expected, the separation of the anodic and cathodic peak potential ( $\Delta E_p$ ) was greater than 59mV, the predicted value for a reversible one-electron process and increases with sweep rate, as it is shown in fig. 5.

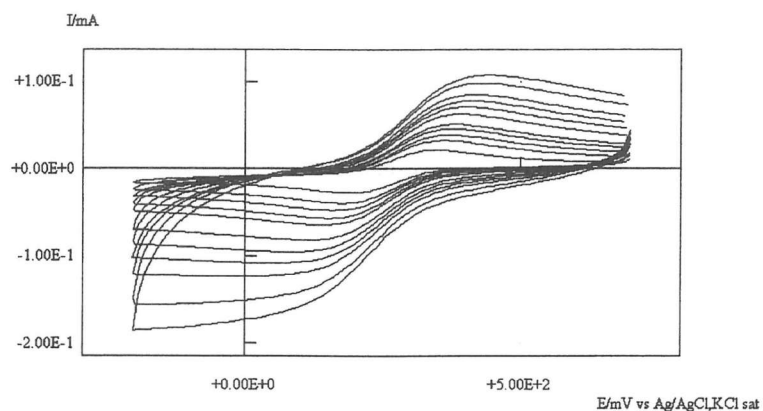


Fig. 5 – Family of cyclic voltammograms for a titanium coated perovskite BaSn<sub>0.9</sub>Sb<sub>0.1</sub>O<sub>3</sub> electrode in 1.0 moldm<sup>-3</sup> K<sub>3</sub>Fe(CN)<sub>6</sub> + 1.0 moldm<sup>-3</sup> KNO<sub>3</sub>. Sweep rates 2, 4, 6, 8, 10, 15, 20, 25, 30, 40, 50 mVs<sup>-1</sup>. Electrode geometric area 1.3 cm<sup>2</sup>.

Values of 300 mV were obtained at sweep rates of 50 mVs<sup>-1</sup>. It is interesting to note that values much lower were obtained for the sintered pressed-disc electrodes of the same material [3]. Considering that the specific resistance of the sintered perovskite oxide determined at room temperature by the four probe method is 0.15  $\Omega$  cm [2,5], the main component of the ohmic drop comes from the TiO<sub>2</sub> insulating film formed at the support/oxide layer interface. Peak separations greater than the expected were also reported by Vicent et al. for doped Ti/ SnO<sub>2</sub> electrodes [7].

Preliminary studies on the oxygen evolution reaction in the potential range between 0.800V and 1.200 V showed a single Tafel region and from the analysis of the steady-state polarisation curves a Tafel slope of ca 600 mV was calculated. This value is higher than the one earlier obtained for the sintered pressed-disc electrodes and is in accordance with the assumption that a high resistive film of TiO<sub>2</sub> is formed. Values of the same order have been reported by Rojas et al. [12] for the oxygen evolution reaction on anodic titanium oxide. These high values were also attributed to the titanium oxide film that behaves as a barrier for the charge transfer.

### Conclusions

In this study the preparation of BaSn<sub>0.9</sub>Sb<sub>0.1</sub>O<sub>3</sub> coated titanium electrodes has been developed leading to stable electrodes with high surface area. Voltammetric and kinetic data clearly show that an insulating barrier is formed at the Ti/ BaSn<sub>0.9</sub>Sb<sub>0.1</sub>O<sub>3</sub> interface giving rise to ohmic drop. Therefore the use of these perovskite oxide for technological purposes needs a deeper study into the titanium pre-treatment and/or the use of other supports.

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## PERFORMANCE OF POLYANILINE COATINGS ON STAINLESS STEEL FOR SILVER RECOVERY

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### Abstract

In this study, conducting polymer films were synthesised by electrochemical polymerisation of aniline on the stainless steel substrates, and such films were employed for the process of electroless precipitation of silver. The electropolymerisation mode and conditions were carefully selected to provide films displaying structure and electroactivity appropriate to the process. The influence on the metal recovery efficiency of the both PANI surface area and electrolyte composition was also analysed.

**Keywords:** Polyaniline, stainless steel, electroless precipitation, silver

### Introduction

The progress-of technology in the last two decades led to a search for new materials with good chemical stability, high electrical conductivity, low cost and ease of preparation. Due to these properties, electronically conducting polymers such as polyaniline, polypyrrole and polythiophene have been used in varied applications: electrochromic devices [1], secondary battery electrodes [2], electronic displays [3], effluents treatment methods [4], corrosion protection coatings [5, 6].

One of the important applications of electronically conducting polymers is for precious metal recovery [7]. The process consists in spontaneous reduction of metallic ion with simultaneously increase of the oxidation state of the polymer [8].

It is well known that the polymer morphology and structure depend on polymerisation route [9, 10]. For successful metal recovery it is important to obtain polymer with a large surface area. These facts considered, this paper is devoted to the study of the conditions for electropolymerisation of aniline on stainless steel substrates and to the influence of the electrochemical parameters on the employment of such films for the electroless precipitation of silver from acid solutions.