Preparation and Characterization of Ti/SnO$_2$-Sb Electrode by Pechini's Method for Phenol Oxidation

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In this paper the influence of calcination temperature on the corrosion resistance of a Ti/SnO$_2$-Sb electrode prepared according to Pechini's method and its efficiency for phenol oxidation in chloride medium were investigated. When calcination was performed at 600 °C tin distribution throughout the film was more uniform, providing a more homogeneous film structure. Electrolysis of a 0.34 mol.L^{-1} NaCl solution containing 100 mg.L^{-1} phenol at 10 mA.cm^{-2} for 30 minutes lead to corrosion of the electrodes calcined at 400 and 500 °C, whereas the one calcined at 600 °C remained practically unchanged, indicating that the coating structure, which is dependent of calcination temperature, plays an important role on the structural integrity of electrode material. Phenol concentration was reduced in 90% with the Ti/SnO$_2$-Sb electrode calcined at 600 °C after 60 minutes of electrolysis at 10 mA.cm^{-2}.

Keywords: *Ti/SnO$_2$-Sb electrode, calcination temperature, corrosion, phenol removal*

1. Introduction

Several electrode materials (Ti/RuO$_2$, Ti/IrO$_2$, Pt, Ti/PbO$_2$, boron-doped diamond - BDD and Ti/SnO$_2$-Sb) have been used for the electrolytic treatment of effluents containing organic compounds[1-11]. Among them, the Ti/SnO$_2$-Sb electrode is reported to present high efficiency for the oxidation of such compounds due to its high oxygen evolution overpotential, which favors the generation of ·OH radicals that act in the indirect oxidation of the organic compounds at the electrode surface[2,6,8,12-14].

A number of process for manufacturing dimensionally stable anodes (DSA) have been reported in the literature: sol-gel[14,15], spray pyrolysis[16], electrodeposition[12,17], thermal decomposition[13,18-20] and precursor solution, known as the Pechini method[3,4,20-24]. The last one is useful to prepare electrode films with controlled stoichiometry due to the formation of hydroxicarboxylic acids allied to their ability to form chelates with many cations. When these acids are heated in the presence of polihydroxylic alcohols an esterification reaction takes place and the cations are incorporated in the polymeric net, avoiding metal losses by volatilization during film calcination[3].

Oliveira-Souza et al.[25] have shown that the Ti/IrO$_2$ electrode prepared by the Pechini's method presented a longer life than those prepared by sol-gel and thermal decomposition methods. Alves[1] studied the electrocatalytic properties of Ti/M$_x$S$_{(1-x)}$O$_2$ dimensionally stable anodes (where M is Ru or Ir; S is Ti or Sn and x is 0.3, 0.5 or 0.7) obtained by the polymeric precursor method (the inorganic precursors were dissolved in isopropanol) for the electrooxidation of ethanol in chloride media. The electrodes prepared by the polymeric precursor method presented better electrocatalytic properties for the generation of oxidizing agents[26].

Rodrigues and Olivi[3] studied the influence of two different temperatures (400 and 500 °C) on the structure of Ti/SnO$_2$-Sb electrodes prepared by Pechini's method. They observed that the film on the electrode calcined at 400 °C presented a cracked surface, while the one calcined at 500 °C, presented a less cracked surface, lower roughness and higher particle dispersion on its surface. Grimm et al.[23] used the sol-gel method to prepare a Ti/SnO$_2$-Sb electrode, which was calcined at 600 °C (with a heating rate of 1 °C/min) and observed that the antimony doping was an important feature for phenol oxidation with Ti/SnO$_2$ electrodes.

It is reported in the literature several methods and calcination temperatures employed to prepare electrode materials[8-10,12,14-16,20,27]; however, it is known that their corrosion resistance depends on the method used. Then, the objective of this paper was investigating the resistance to corrosion of Ti/SnO$_2$-Sb electrodes, for phenol oxidation in a saline medium, prepared by Pechini's method with different calcination temperatures.

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2. Experimental

2.1. Electrodes preparation

The electrodes were prepared from 1.0 mm thick pure titanium plates with 25 mm wide and 110 mm long. They were previously polished with 600-mesh emery paper and treated in a boiling solution of 10% (w/w) oxalic acid for 10 minutes[28]. Then, the plates were washed with deionized water, dried with a hot air blown and then stored in a vacuum sealed dissecator before being coated with the Sb doped SnO_2 film.

The titanium electrodes were coated with an antimony doped SnO_2 film prepared by Pechini's method[29]. The precursor solutions were obtained from the following analytically pure reagents: citric acid, ethyleneglycol, potassium antimony tartarate, tin(II) chloride dihydrate, sodium hydroxide and concentrated nitric acid. Tin citrate was prepared according to the procedure described by Besso[30]. The anhydro-citric acid:ethyleneglycol:tin citrate molar ratio for the film preparation was 3:10:1. The same ratio was adopted for the antimony precursor solution. The final precursor solution was obtained by mixing the two precursor solutions rendering a composition of 93% SnO_2 and 7% Sb. A flow sheet of the experimental procedure used for preparation of the anode film, including the calcination step, is shown in Figure 1.

The microstructure of the titanium plate and electrodes calcined at 400, 500, 600 °C, before and after electrolytical tests, were analyzed by SEM and EDS. Additionally, the detection of Sb^{3+} and Sb^{5+} species in the electrode coat was performed by classical qualitative chemical analysis[31]. The analysis by Fourier transform infrared spectroscopy (FTIR) of the films was carried out with a Nicolet spectrometer, model IR-760 using the KBr pellet technique.

The change on the films structure obtained for the different temperatures tested was verified by X-ray diffraction (XRD) with a Shimadzu diffractometer, model XRD-6000, using Cu-Kα radiation.

2.2. Electrochemical tests

An EG&GPAR model 273A potentiostat/galvanostat connected to a microcomputer with the M270 software was used in the voltammetric tests. The cell was a 250 mL beaker with an acrylic cover and the working electrode was a 4.5 cm² Ti/SnO_2-Sb calcined plate.

The counter electrode was a pure titanium plate[28,32] and the reference was Ag/AgCl in saturated KCl solution ($E° = 0.198V$ vs. SHE). Unless otherwise stated all the tests were carried out at room temperature (around 25 °C) and without stirring. The electrochemical tests were carried out in 0.34 $mol.L^{-1}$ NaCl solution containing from 30 to
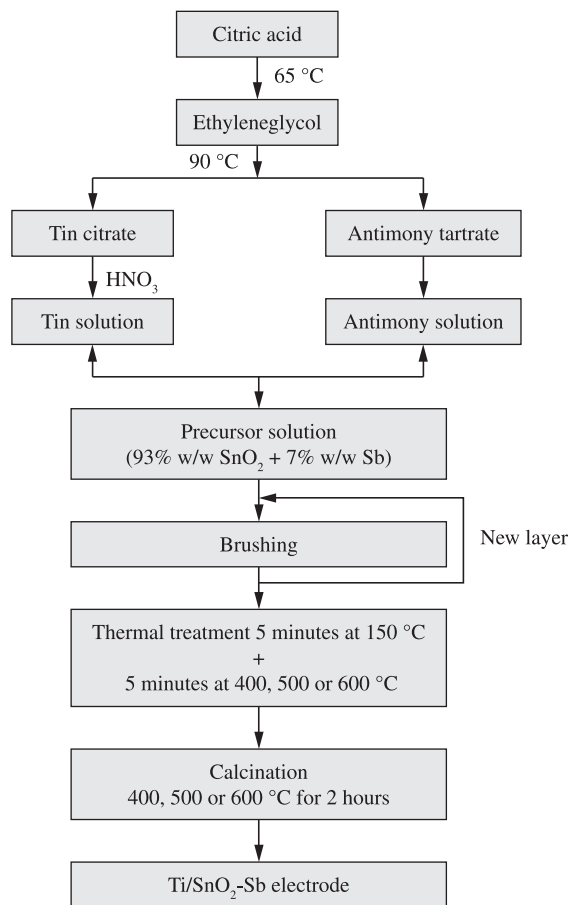

Figure 1. Experimental flowsheet used for the preparation of the Ti/SnO_2-Sb anode. Adapted from Rodrigues and Olivi[3].
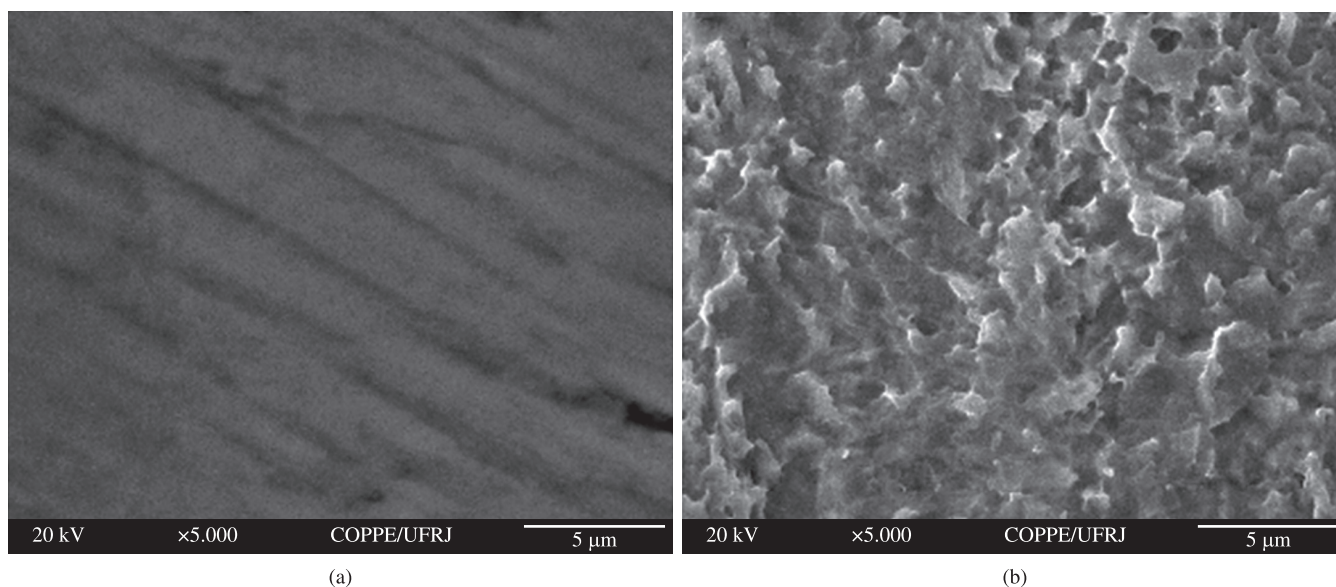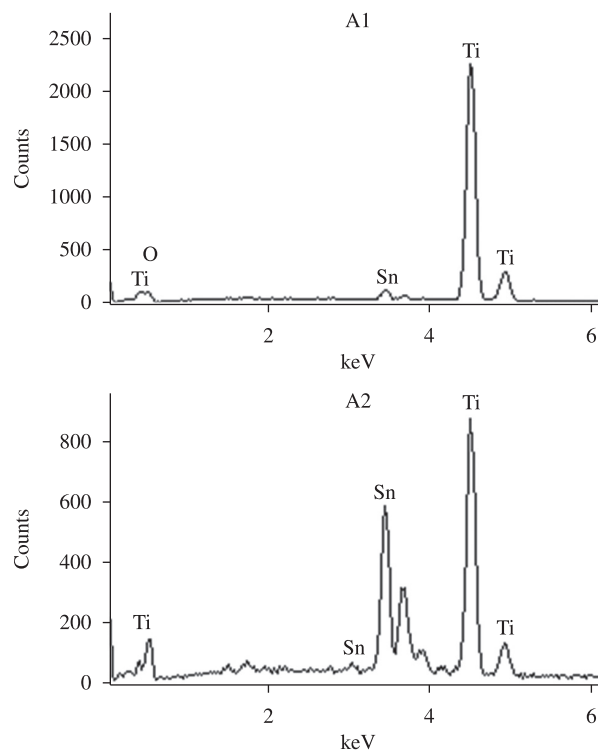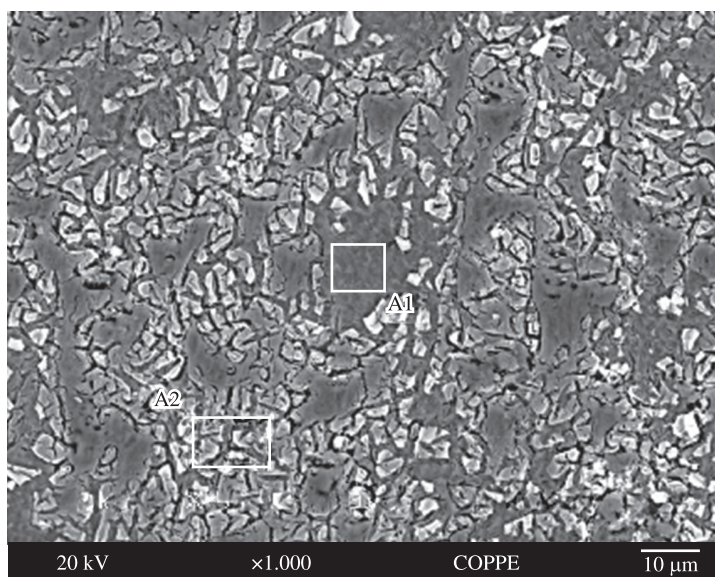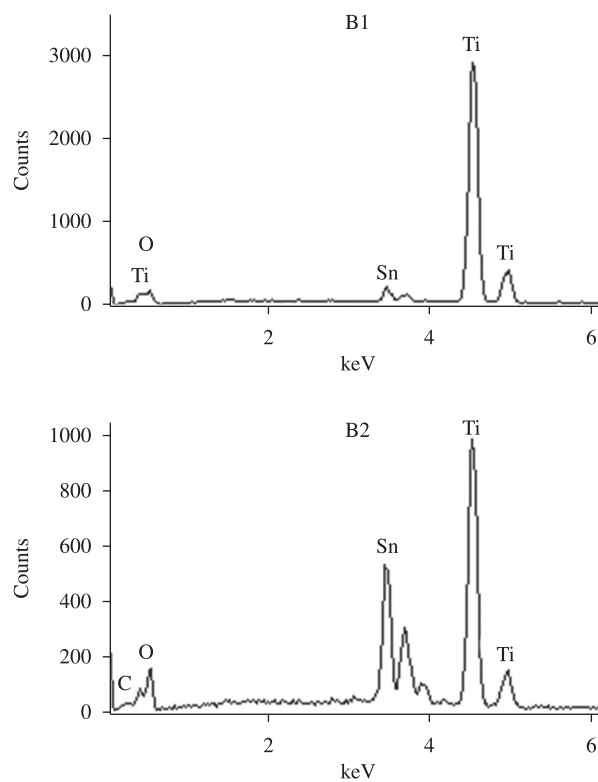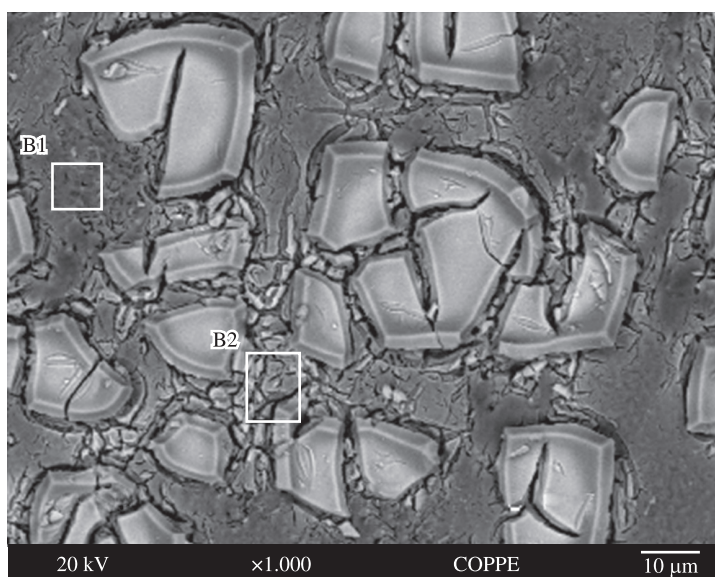

Figure 2. SEM micrographs of Ti plate. a) After grinding; and b) after treatment with hot 10 wt. (%) oxalic acid for 10 minutes.

Figure 3. SEM micrographs and EDS spectra of Ti/SnO$_2$-Sb electrode calcined for 2 hours at different calcination temperatures. a) 400 °C; b) 500 °C; and c) 600 °C. Film composition: 93 wt. (%) SnO$_2$ and 7 wt. (%) Sb.
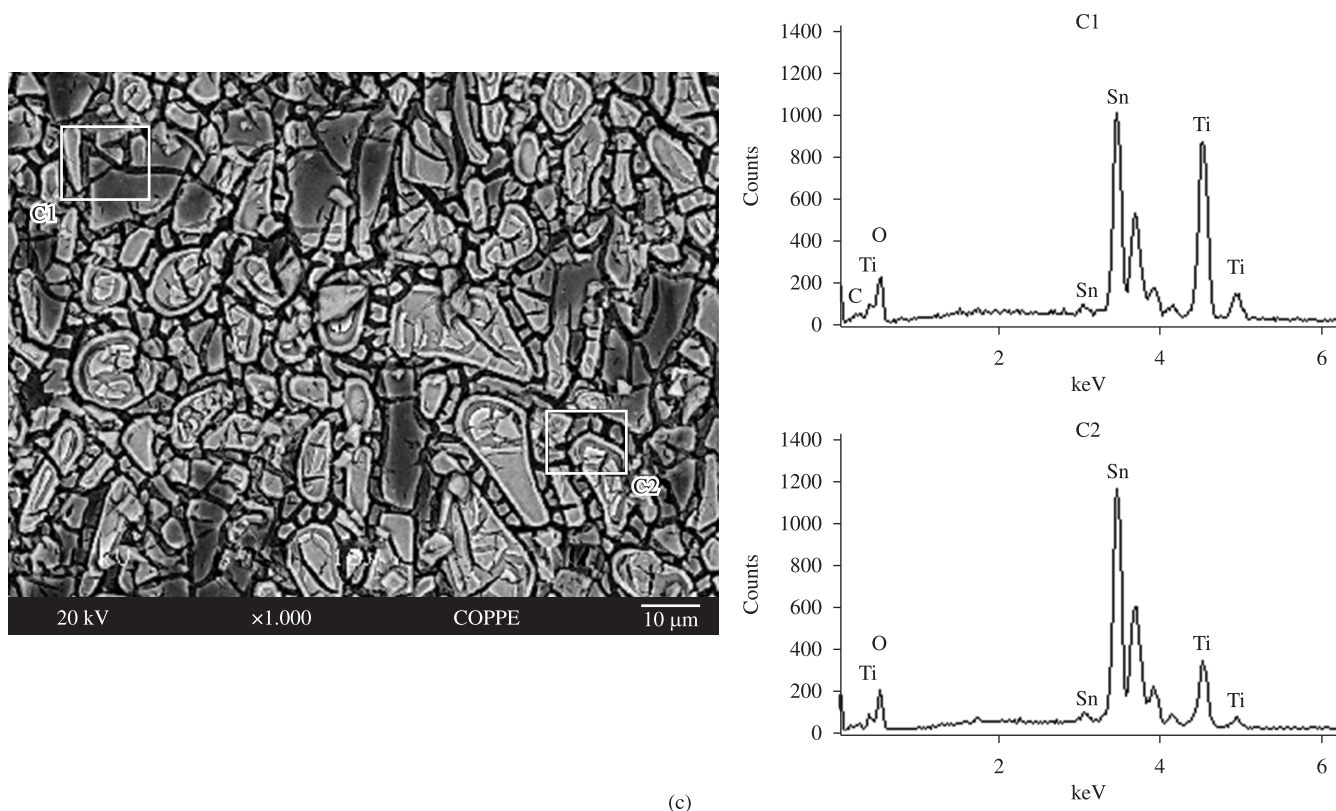
Figure 3. Continued...

100 mg.L^{-1} phenol. An initial solution volume of 200 mL was used for all the voltammetric tests. The anodic potential was measured at the beginning and at the end of each test, and the current density was set at 10 mA.cm^{-2}.

The electrolytic tests were conducted in the same cell used for the voltammetry, but under constant moderate stirring. For these tests, 230 mL of a 0.34 mol.L^{-1} NaCl solution containing 100 mg.L^{-1} of phenol was used. The anode area was 27 cm^2 and the current density was fixed at 10 mA cm^2. The anodic potential was monitored during the tests.

Samples for chemical analysis were collected periodically from 5 to 60 minutes of electrolysis. Phenol degradation was monitored by UV/Vis[28,33,34] at 269.5 nm. As hypochlorite band absorbs at the same wavelength region of phenol, its presence after electrolysis was suppressed by the addition of 0.1 mol.L^{-1} NaHSO$_3$, according to Reaction 1:

$$NaClO + NaHSO_3 \rightarrow NaCl + NaHSO_4 \tag{1}$$
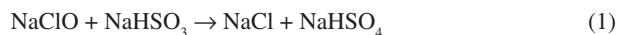
3. Results and Discussion

SEM micrographs of the titanium surface before and after treatment with oxalic acid are presented in Figure 2a and b respectively. A drastic modification of the titanium surface, due to dissolution of the titanium oxide, was observed, rendering a moderate smooth surface, which favors the film adhesion[29].

SEM micrographs along with the EDS spectra of the Ti/SnO$_2$ anode doped with 7 wt. (%) Sb and calcined at 400, 500 and 600 °C, are shown in Figures 3a, 3b and 3c, respectively. It can be observed that the surface structure presents a cracked-clay appearance. At 400 °C, this structure is composed by dispersed small blocks, while at

500 °C a smaller number of bigger blocks was observed. At 600 °C, an aspect of broken blocks was observed, possibly due to the mechanical stress caused by the different thermal expansion coefficients of the film and substrate[3], giving rise to a more homogeneous distribution of the blocks throughout the surface. Furthermore, the temperature increase led to a more homogeneous antimony-doped tin oxide distribution on titanium surface, since the presence of spots with very low tin counts was detected by EDS only at 400 and 500 °C.

The absence of antimony in the EDS spectra can be attributed to its low concentration in the precursor solution, around 7 wt. (%). Another possibility may be related to the Sn and Sb ionization energies, which are close to each other, being 3.4 keV for Sn and 3.6 keV for Sb. In this way, Sn spectrum may mask the Sb one[23].

The presence of Sb^{3+} and Sb^{5+} was identified by chemical analysis according to procedure described by Vogel[31]. The qualitative results indicate that Sb^{3+} and Sb^{5+} ions are present in all samples, regardless the calcination temperature utilized. On the other hand, it was noticed, by visual observation of the color intensity increase of the solution during the qualitative chemical analysis and also by the EDS spectra , that the amount of Sb^{3+} and Sb^{5+} in the electrode increased in the following sequence: 600 °C > 500 °C > 400 °C and 400 °C > 500 °C > 600 °C, respectively. This behavior can be attributed to decomposition of Sb$_2$O$_5$ to form Sb$_2$O$_3$ (Sb^{3+}) at temperatures above 340 °C[35], indicating that the proportion of Sb^{3+} and Sb^{5+} present in the material may be responsible for the morphological behavior of the electrode calcined at 600 °C.

The FT-IR absorption spectra associated with stretching and bending vibrations at 400-4000 cm^{-1} of the powder precursor (SnO$_2$-Sb film) and its decomposition products after calcination at 400, 500 e 600 °C is shown in Figure 4. The spectra profile for the three calcination temperatures examined is similar. There are adsorption

bands at 3405 cm^{-1} (Figure 4) due to water (OH-stretching)[36,37]. The bands between 400-1300 cm^{-1} can be attributed to the formation of Sn-O and carbonate species during the calcination process[38,39]. The small peak at 1627 cm^{-1} can be ascribed to the presence of H$_2$O in the precipitated phase, as verified by Acarbas et al.[38] during preparation of nanosized tin oxide (SnO$_2$) powder by homogeneous precipitation.

The XRD spectra of the Ti/SnO$_2$ anode doped with 7 wt. (%) of Sb and calcined at 400, 500 and 600 °C are shown in Figure 5. The profile is the same for all calcination temperatures but peak intensities increased as calcination temperature was increased. This behavior suggests a better formation and growing of SnO$_2$ crystals at the more elevated temperature. Similar results were found by Ding et al.[11] with electrodes prepared by electrodeposition method. The peak at 2θ = 37.8º, which corresponds to Sb$_2$O$_3$[28], increased as calcination temperature was increased. This behavior is probably due to the decomposition of Sb$_2$O$_5$ to Sb$_2$O$_3$, suggesting that the presence of Sb$_2$O$_3$ may account for the morphology of the electrode calcined

at 600 °C, as shown in Figure 3c. The peaks at 2θ = 26.6º; 33.8º; 51.7º; 54.8º and 57.9º may be ascribed to SnO$_2$ with a cassiterite-type tetragonal structure[3,4,11,28,37,40]. The slight displacement of the peaks when compared to the standard SnO$_2$ file may be a consequence of the formation of a solid solution due to the presence of antimony[11,28].

The polarization behavior of Ti/SnO$_2$-Sb anodes in 0.34 mol.L^{-1} NaCl calcined at 400, 500 and 600 °C is presented in Figure 6. It can be observed that as the calcination temperature is increased the anodic current became higher, indicating a more intense chlorine/hypochlorite generation. The voltammetric behavior observed for the electrode calcined at 600 °C is probably, due to the morphologic characteristics of the material which presents higher superficial area, favoring the formation of oxidizing agents, when compared with the electrodes calcined at 400 and 500 °C[10,20,41].

The polarization behavior of Ti/SnO$_2$-Sb anodes in a 0.34 mol.L^{-1} NaCl with and without phenol (30 mg.L^{-1}) calcined at 400, 500 and 600 °C is presented in Figure 7. For all temperatures the presence
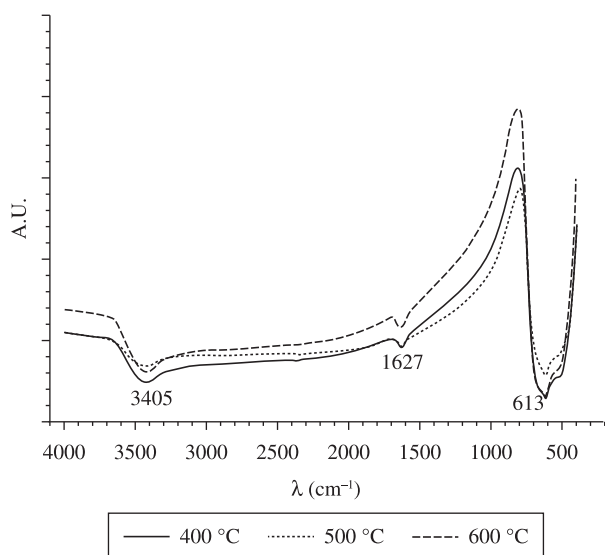

Figure 4. IR spectra obtained from precursor solution used on the SnO$_2$-Sb film calcined at 400, 500 or 600 °C for 2 hours. Film composition: 93 wt. (%) SnO$_2$ and 7 wt. (%) Sb.
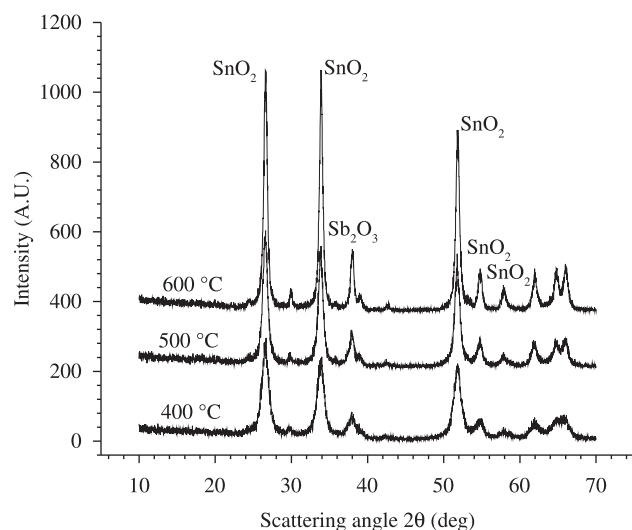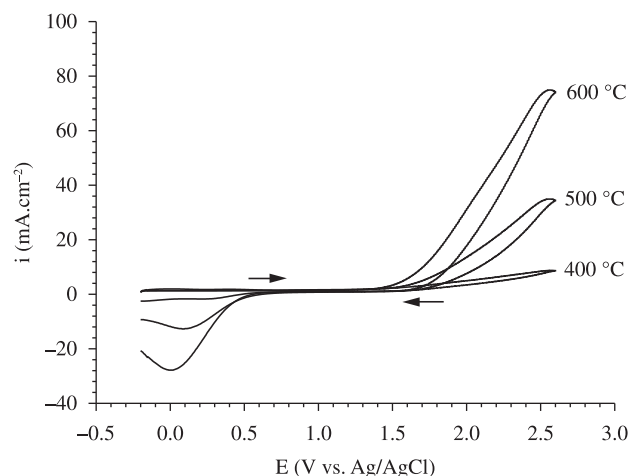

Figure 6. Cyclic voltammograms on Ti/SnO$_2$-Sb anodes, calcined at different temperatures, in a 0.34 mol.L^{-1} NaCl. ν = 100 mV s^{-1}; anodic area: 4.5 cm^2; temperature: 25 °C.

Figure 5. XRD spectra of the SnO$_2$ film doped with 7 wt. (%) antimony and calcined at a) 400 °C; b) 500 °C; and c) 600 °C.
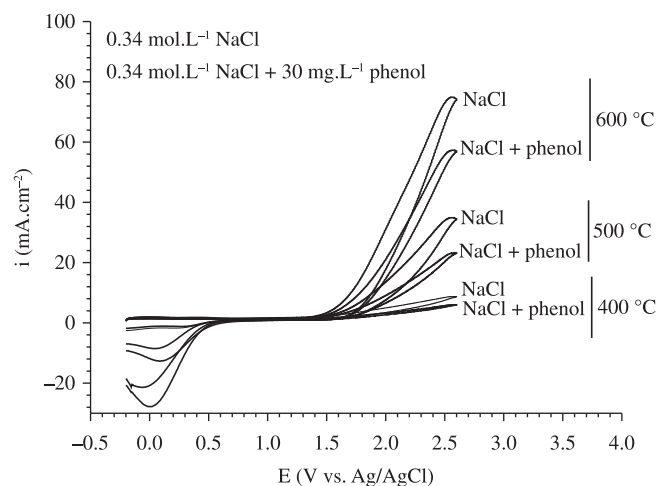

Figure 7. Cyclic voltammograms on Ti/SnO$_2$-Sb anode, calcined at different temperatures, in a 0.34 mol.L^{-1} NaCl in the absence and presence of 30 mg.L^{-1} phenol. ν = 100 mV. s^{-1}; anodic area: 4.5 cm^2; temperature: 25 °C.
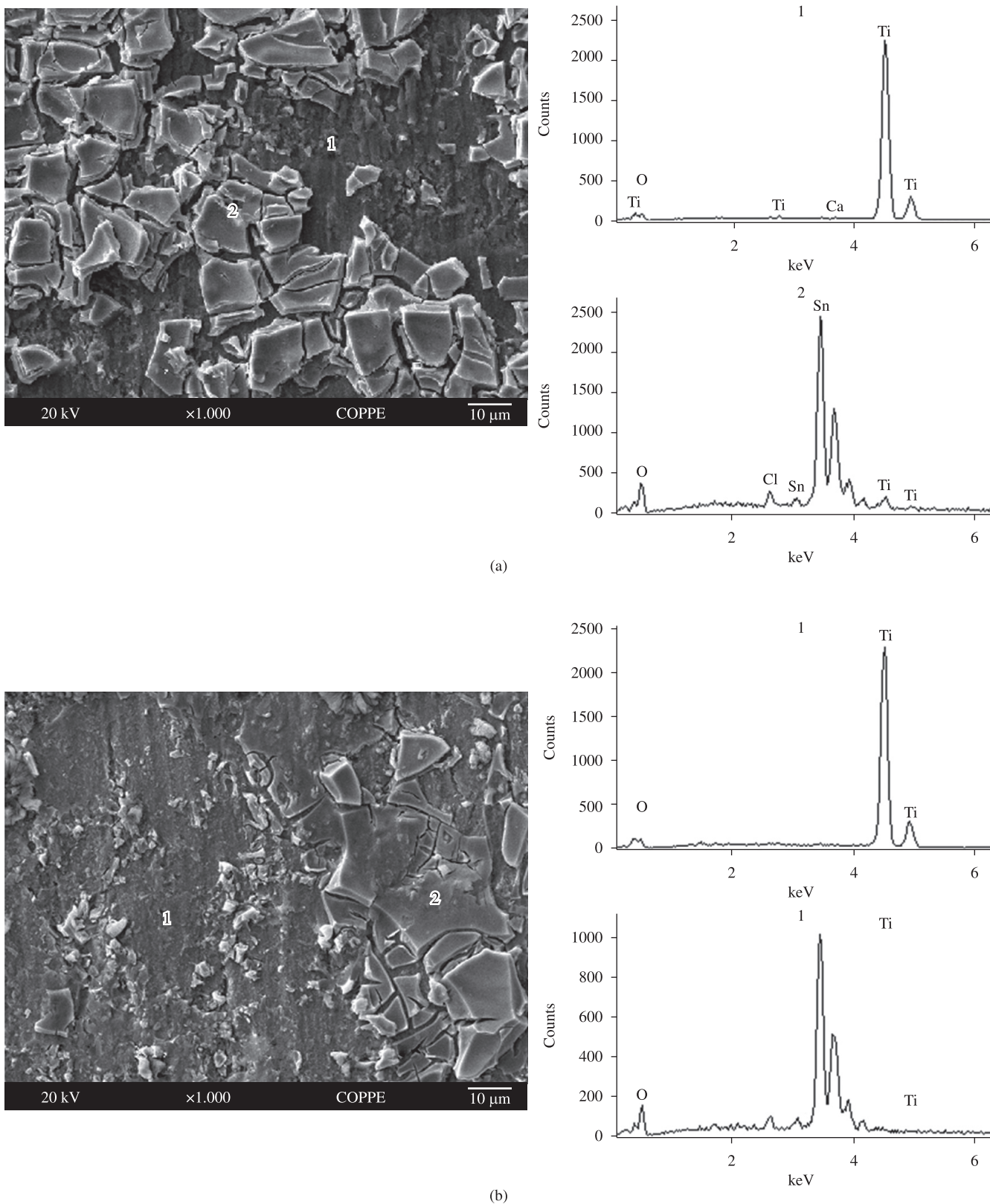
Figure 8. SEM micrographs of Ti/SnO$_2$-Sb anode calcined at different temperature, after electrolysis of a 0.34 mol.L^{-1} NaCl solution containing 100 mg.L^{-1} phenol. Anodic area: 27 cm^2; temperature: 25 °C; i = 10 mA.cm^{-2}. a) 400 °C; and b) 500 °C after 30 minutes of electrolysis; and c) 600 °C after 60 minutes of electrolysis.
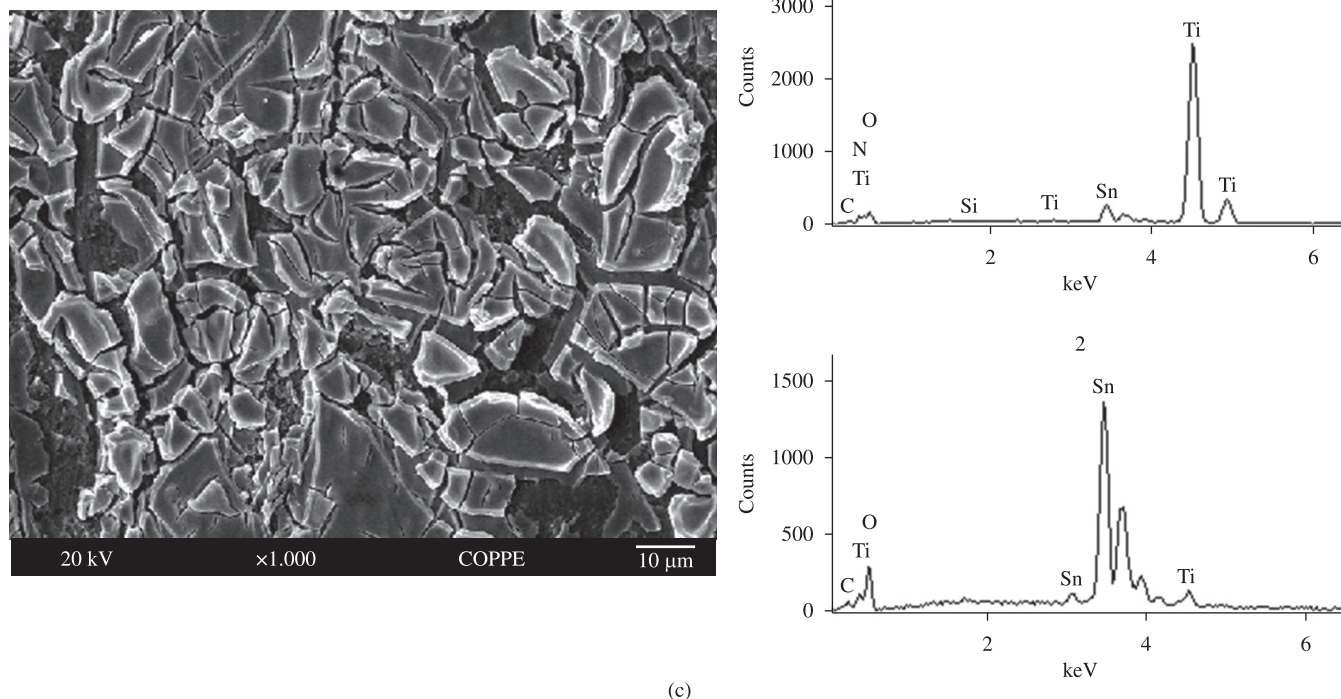
(c)

Figure 8. Continued...

of phenol inhibited the anodic current density and displaced the curves to slightly higher potentials. This behavior can be attributed to the formation of chlorophenols via organic intermediate products reactions with the hypochlorite ions generated on the anode; the chlorophenols tend to adsorb on the anode surface, blocking it partially and causing a decrease on the current density[19].

The anodic potential of the Ti/SnO$_2$-Sb anodes calcined at 400, 500 and 600 °C rose from 2.0 to respectively 9.8 V, 12.8 V and 2.4 V, vs. Ag/AgCl (E° = 0.198V in saturated KCl solution) after 30 minutes of electrolysis, indicating a strong degradation of the anodes calcined at 400 and 500 °C, while the anode calcined at 600 °C remained almost unattacked. This behavior can be better understood when the anodes surface micrographs before (Figure 3) and after (Figure 8) electrolysis are compared. In Figure 8a (anode calcined at 400 °C), after the electrolysis, the aspect was changed due to the loss of SnO$_2$-Sb coating in some spots, which is corroborated by the EDS microanalysis, where no Sn was detected after electrolysis. A similar behavior can be observed in Figure 8b, for the sample calcined at 500 °C; however, the coating loss was more severe. Probably, the absence of tin can also be associated to the anodic growth of the insulating TiO$_2$ layer. When the anode was calcined at 600 °C less coating loss was observed after 30 minutes of electrolysis, and the aspect is similar to the electrode presented in Figure 3c. Furthermore, the EDS microanalysis did indicate the presence of tin, which did not occur on most of the electrodes surface calcined at 400 and 500 °C. The more intense coating loss may be associated to the less uniform structure of the anodes calcined at 400 and 500 °C and also to the pH raise during the electrolysis, which can bring the anode to the domain of tin corrosion in the E$_h$ vs. pH diagram[42]. Moreover, the cracked clay structure of the electrodes can allow the penetration of the electrolyte, which allied to anodic gases evolution, may favor

the coating erosion. As the electrode calcined at 600 °C presents a more uniform cracked clay structure, it seems to be less affected by the aggressive conditions necessary to phenol oxidation in chloride solutions. However, for electrolysis time longer than 60 minutes (Figure 8c), under a current density of 10 mA.cm^{-2} a slight loss of the SnO$_2$-Sb coating was detected.

The anode degradation can be minimized by keeping pH between 7 and 10, through controlled HCl additions, avoiding the domain of soluble tin species in the E$_h$ vs. pH diagram[42]. However, anode degradation still persists due to electrolyte penetration and gas evolution, especially for the anodes calcined at 400 and 500 °C, which do not present a very uniform and adherent coating. The aspect of the SnO$_2$-Sb coating of the anodes calcined at 400, 500 and 600 °C, after 60 min of electrolysis under a current density of 10 mA.cm^{-2}, with pH kept in the range of 7 to 10, is presented in Figure 9. In this way, a smaller coating loss was observed for the anodes calcined at 400 and 500 °C, while no coating loss was detected in the anode calcined at 600 °C.

The influence of electrolysis time on the phenol removal in chloride medium using the anode calcined at 600 °C is presented in Figure 10. Phenol removal increased with the increase of electrolysis time[43]. The low phenol removal in the first minutes can be attributed to the formation of organic intermediate compounds, such as chlorophenols. During electrolysis, the hypochlorite concentration increased due to the NaCl oxidation, after which phenol removal rate increased substantially. When most phenol was oxidized, its removal rate remains constant because phenol concentration was lower and the effect of the excess of hypochlorite used in the indirect oxidation mechanism was less noticeable. The phenol removal after 60 minutes of electrolysis with current densities of 10 mA.cm^{-2} reached 90%.
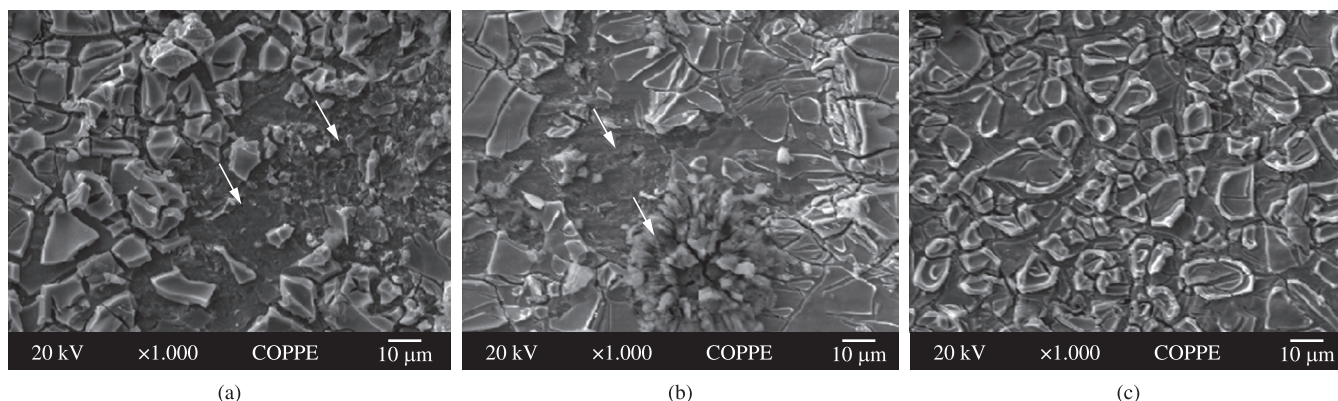
(a)   (b)   (c)

Figure 9. SEM micrographs of a Ti/SnO$_2$-Sb calcined at different temperatures, after 60 minutes of electrolysis of 0.34 mol.L^{-1} NaCl solution containing 100 mg.L^{-1} phenol, and pH between 7 and 10: a) 400 °C; b) 500 °C; and c) 600 °C. Anodic area: 27 cm^2; temperature: 25 °C; i = 10 mA cm^{-2}.
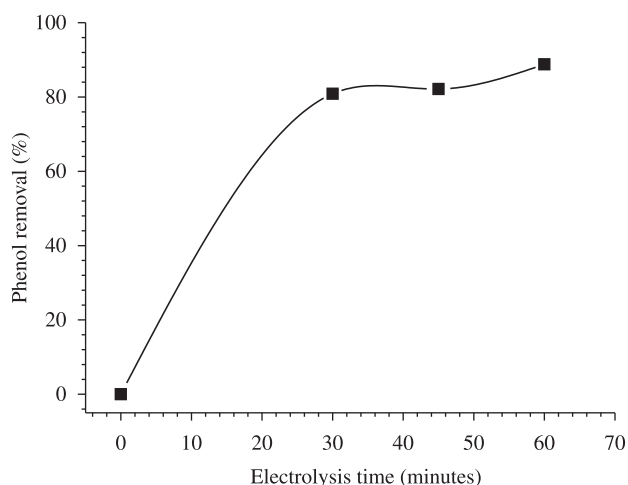

Figure 10. Influence of electrolysis time on the phenol removal using Ti/SnO$_2$-Sb calcined at 600 °C. Solution: 100 mg.L^{-1} phenol, 0.34 mol.L^{-1} NaCl; anodic area: 27 cm^2 i: = 10 mA cm^{-2}; temperature: 25 °C. Phenol UV absorbency wavelength: 269.5 nm.x

4. Conclusions

The efficiency and resistance of the Ti/SnO$_2$-Sb anode prepared according to Pechini's method for phenol oxidation in chloride environment depend strongly on its calcination temperature. SEM micrographs allied to EDS spectra indicated that calcination at 600 °C led to a more uniform tin distribution throughout the film, rendering a more homogeneous film structure.

After a 30 min-electrolysis of a 0.34 mol.L^{-1} NaCl solution, containing 100 mg.L^{-1} phenol at 10 mA.cm^{-2}, the anodes calcined at 400 and 500 °C were corroded, while the anode calcined at 600 °C remained practically unchanged.

Results indicated that the Pechini's method seem to be appropriate for the manufacturing of the Ti/SnO$_2$-Sb electrode. It was necessary to keep the pH between 7 and 10 to avoid tin dissolution and consequent film degradation. Results also indicated that the coating structure, which depends on the calcination temperature, play an important role on its integrity. By keeping the pH between 7 and 10, a reduction of 90% of the phenol concentration was obtained after a 60 minutes of electrolysis, at 10 mA.cm^{-2}, with the Ti/SnO$_2$-Sb anode calcined at 600 °C.

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