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Study of the stability of SnO_2 doped anodes

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INTRODUCTION

Wastewater containing organic pollutants, which can not be easily treated by biological action, has to be treated by chemical oxidation. Chemical oxidation allows, in general, complete elimination of the organic pollutants but complete removal of total organic carbon (TOC) is more difficult [1,2]. Using the electrochemical oxidation the TOC removal is higher than that obtained by chemical oxidation [3, 4, 5]. This higher TOC removal using electrochemical oxidation has been attributed to the oxidation of adsorbed organic compounds to CO_2.

A good electrode for the elimination of organic pollutants has to have high oxygen overpotential and a good stability in the anodic work conditions. The electrode of SnO_2 doped satisfies these requeriments.

In this work, the stability of SnO_2 electrodes doped only with antimony or antimony and platinum have been studied.

EXPERIMENTAL

The SnO_2 film electrodes doped with antimony were prepared on titanium base metal by the standard spray pirolysis method. Preparation details are given in [6]. The electrolyte was 0.5M sulphuric acid (Merck suprapur) solution and the water used for its preparation was from a Millipore-Milli Q system. A counter electrode was a

platinum spiral. All potentials are referred to the reference hydrogen electrode in the same solution (RHE). The cyclic voltammograms were recorded at room temperature at a sweep rate of 50mV/s.

The reaction used to verify the stability of SnO_2 electrodes was oxygen evolution in acid media (that are the worst conditions for the electrode) and that to study the electrochemical behaviour was Fe^{3+}/Fe^{2+} couple.

RESULTS AND DISCUSSION

Figure 1, dashed line, shows the electrochemical behaviour obtained for a SnO_2 electrode doped with antimony in 0.5M H_2SO_4. This electrode has been prepared by spray pyrolisis of $SnCl_4$ 10% + $SbCl_3$ 1% in ethanol solution on a pretreated titanium substrate and five process of pyrolisis. No well defined peaks appear and the anodic evolution of oxygen is shifted about 600mV to more positive potentials with respect to platinum electrode.

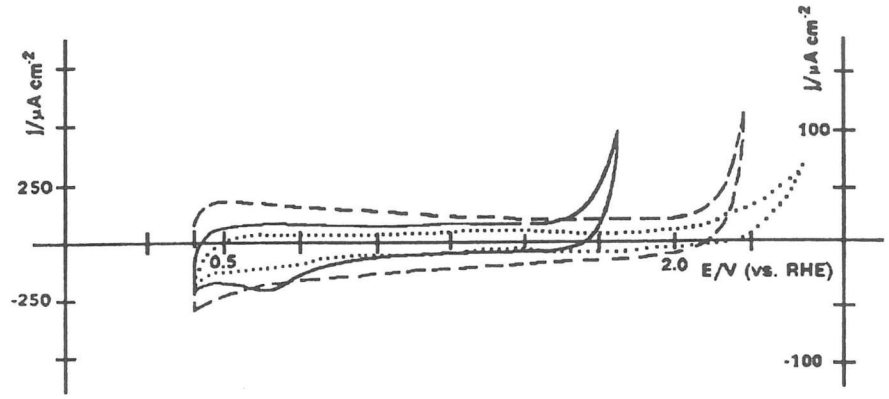

Figure 1. Voltammogram in 0.5M H_2SO_4 for: (——) SnO_2-Sb-Pt (0.2%) electrode, (— —) SnO_2-Sb electrode and (.....) SnO_2-Sb electrode before of electrolisys.

Figure 2, dashed line, shows the behaviour of this electrode with respect to the

Fe^{3+}/Fe^{2+} couple. It can be observed a better behaviour with respect to platinum electrode (ΔE_p = 104mV) obtaining a separation between peaks of 96mV.

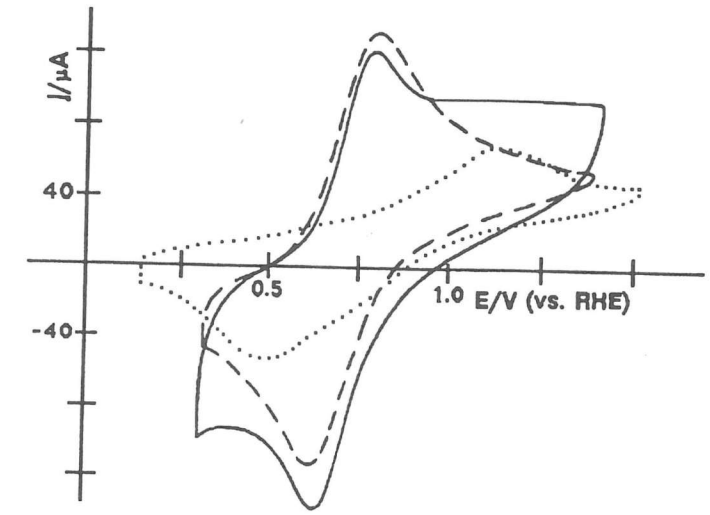

Figure 2. Behaviour with respect to the Fe^{3+}/Fe^{2+} couple (0.5M H_2SO_4, 0.05M $FeSO_4$) for: (——) SnO_2-Sb-Pt (0.2%) electrode, (— —) SnO_2-Sb electrode and (.....) SnO_2-Sb electrode before of electrolisys.

Figure 3, square, shows the evolution of the increases of potential with the electrolysis time of the same electrode in an electrolysis at 10mA/cm² in 0.5M H_2SO_4. The electrode potential increases 1V from the initial value after 4 hours. After 5 hours of electrolysis, the potential reached a value of 4.5V more higher than the initial potential. After this time of electrolysis the behaviour of the electrode in sulphuric acid is shown in figure 1, pointed line. It can be observed that the voltammogram has changed and the potential of oxygen evolution have increased to more positive potentials.

The behaviour with respect to Fe^{3+}/Fe^{2+} couple indicates a more separation between peak potentials (ΔE_p = 620mV), with respect to the electrode before 5 hours of electrolysis (figure 2, pointed line). Then, it can be consider that the electrode has lost

its good electrochemical properties. A possible explanation of this feature is the formation of TiO_2 in the interphase between the film and the titanium support [6], increasing the electrode resistance. Then, the problem of these electrodes is the absence of stability in the work conditions.

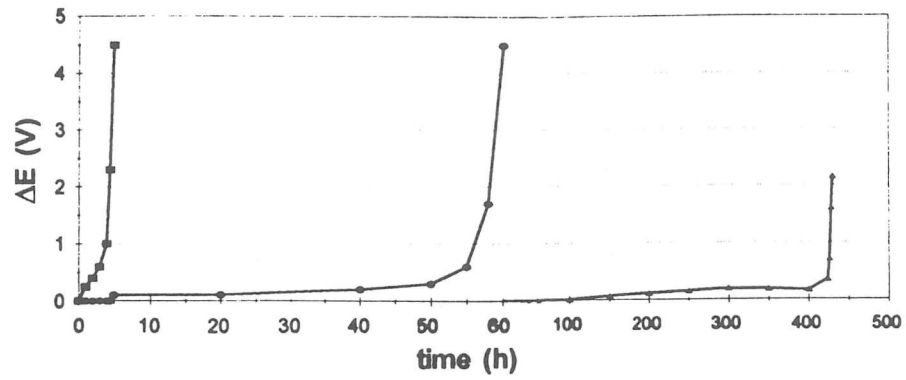

Figure 3. ΔE versus time (hours) in 0.5M H_2SO_4 for: (■) SnO_2-Sb electrode, (●) SnO_2-Sb-Pt (0.2%) electrode and (▲) SnO_2-Sb-Pt (1%) electrode.

A possible method of increases the stability, is to increase the thinkness of the SnO_2 + Sb film by increasing the number of pyrolysis process. In the case of nine process of pyrolysis, the behaviour in 0.5M H_2SO_4 and with respect to Fe^{3+}/Fe^{2+} couple of the electrode is very similar to that obtained for five process of pyrolysis. The stability of the electrode increases from 5 to 9 hours of electrolysis at $10mA/cm^2$ in H_2SO_4 0.5M.

Another possible method to obtained a better stability is doper the SnO_2 electrodes with antimonium and platinum. Figure 1, solid line, shows the voltammogram in 0.5M H_2SO_4 solution for a SnO_2 electrode doped with antimonium and platinum prepared from five pyrolysis process of a solution of $SnCl_4$ 10% + $SbCl_3$ 1% + $[PtCl_6]^{2-}$ 0.2% in ethanol. This figure shows that the oxygen evolution is shifted to less positive

potentials to the obtained with a SnO_2 electrode doped with antimonium only. Figure 2, solid line, shows a good behaviour of this electrode with respect to Fe^{3+}/Fe^{2+} couple (ΔE_p = 113mV).

The stability of this electrode in an electrolysis at $40mA/cm^2$ in 0.5M H_2SO_4 is presented in figure 3, circles. It can be observed that the potential increases only after 60 hours of electrolysis indicating a more stability than the electrode without platinum.

If the percentage of platinum is 1% and the number of pyrolysis process increases from 5 to 15, the electrochemical behaviour of this electrode is very similar to that obtained for an electrode with 0.2% and 5 pyrolysis processes electrode, but the potential of the electrode is maintained after 450 hours of electrolysis (figure 3, triangle).

The bad electrochemical behaviour of both electrodes after 60 hours and 450 hours of electrolysis are very similar to that obtained for the SnO_2 electrode doped with antimonium after 5 hours of electrolysis (figure 1 and 2, pointed line).

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