



Electrochemical oxidation of *p*-chlorophenol on SnO₂–Sb₂O₅ based anodes for wastewater treatment

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Abstract

The influence of an IrO₂ interlayer between the Ti substrate and the SnO₂–Sb₂O₅ coating on the electrode service life and on the efficiency of *p*-chlorophenol (*p*-CP) oxidation for wastewater treatment has been investigated. The results have shown that if the loading of the SnO₂–Sb₂O₅ coating relative to the IrO₂ interlayer loading (γ ratio defined by Equation 1) is high ($\gamma = 20$ –30) the service life of the electrode can be increased without modification of the ability of this electrode to perform *p*-CP oxidation. This suggests that the oxidation of *p*-CP using a Ti/IrO₂/SnO₂–Sb₂O₅ electrode with high γ ratio ($\gamma > 20$) occurs only through the SnO₂–Sb₂O₅ component of the electrode, with no interference of the IrO₂ interlayer. However, the electrode potential at a given current density is considerably lower in the case of the Ti/IrO₂/SnO₂–Sb₂O₅ electrode. In order to explain this decrease in electrode potential we speculate that water is firstly discharged on IrO₂, which is present in small amounts on the surface, forming hydroxyl radicals at a relatively low potential. These active hydroxyl radicals then migrate (spill over) towards the SnO₂–Sb₂O₅ coating, where they are physisorbed and react with *p*-CP leading to complete combustion.

1. Introduction

Wastewater containing toxic or/and non-biodegradable organic pollutants, which cannot be easily treated through biological action, has to be treated using other techniques, usually chemical oxidation. Chemical oxidation, in general, allows complete elimination of the principal organic pollutants but complete removal of total organic carbon (TOC) is a difficult task. Thus oxidation of phenol with powerful oxidizing agents such as ozone ($E^\circ = 2.07$) allows only a 30% TOC removal [1]. Similar levels of TOC removal are obtained using H₂O₂ in the presence of Fe²⁺ catalyst [2].

The electrochemical oxidation of organic compounds for wastewater treatment has attracted a great deal of attention [3–9] mainly because an appropriate choice of anode material can allow complete TOC elimination with high current efficiency. Typical examples of such materials are synthetic boron doped diamond (BDD) deposited on *p*-silicon substrate [9] and doped SnO₂–Sb₂O₅ coated on Ti base metal (Ti/SnO₂–Sb₂O₅) [4].

The main problem encountered with the BDD electrode is its high price and in the case of the Ti/SnO₂–Sb₂O₅ anode its low stability under anodic polarization.

In previous work [10] it was found that the presence of an IrO₂ interlayer between the Ti substrate and the SnO₂–Sb₂O₅ coating (Ti/IrO₂/SnO₂–Sb₂O₅) considerably increases the service life of the anode. This beneficial action of the IrO₂ interlayer was attributed to its high anodic stability and its isomorphous structure with TiO₂ and SnO₂ [10]. It was also found that the Ti/IrO₂/SnO₂–Sb₂O₅ electrode electrochemical activity for the oxygen evolution reaction (OER), lies between the Ti/IrO₂ and Ti/SnO₂–Sb₂O₅ electrodes due to the incorporation of IrO₂ in the SnO₂–Sb₂O₅ coating during electrode preparation [10].

The aim of this work is to investigate the influence of the IrO₂ interlayer between Ti and SnO₂–Sb₂O₅ coating (Ti/IrO₂/SnO₂–Sb₂O₅ electrode) on the anodic oxidation of organic compounds using *p*-chlorophenol (*p*-CP) as a model compound.

2. Experimental details

The SnO₂–Sb₂O₅ based electrodes were prepared through the decomposition of the SnCl₄ · 5H₂O and SbCl₃ precursors in alcoholic solution, directly on Ti

(18 cm²) or on Ti/IrO₂ support, using the spray pyrolysis technique. More details of the preparation of these electrodes using this technique are given elsewhere [10–12]. The Ti/IrO₂ support was prepared through deposition of IrO₂ on Ti using the thermal decomposition technique [13].

Cyclic voltammetry measurements were carried out using a three-electrode cell. Pt was used as the counter electrode, SnO₂–Sb₂O₅ based electrodes as the working electrode and Hg/Hg₂SO₄/K₂SO₄(sat) as reference. In order to increase the reproducibility of the polarization measurements, the electrodes were electrochemically preconditioned before use. The preconditioning consisted in polarizing the electrodes at 12 mA cm⁻² for 2 h [4]. The working temperature was 25 °C.

A one compartment cell of 150 mL capacity was used in electrolysis experiments. The anode was an SnO₂–Sb₂O₅ based electrode and the cathode was a zirconium plate. Stirring was provided by a magnetic bar. A 1.0 mol l⁻¹ Na₂SO₄ solution adjusted with H₂SO₄ to pH = 2 was used as supporting electrolyte. The working temperature was 30 °C. Electrolysis was carried out under galvanostatic conditions and the anode potential was measured during electrolysis using Hg/Hg₂SO₄/K₂SO₄(sat) as the reference electrode.

The disappearance of *p*-CP and the appearance of its oxidation products were monitored by HPLC (Shimadzu 8A). A Nucleosil C18 column was used with a mobile phase of acetonitrile/water 35/65 (v/v) at pH = 2 adjusted with addition of *o*-phosphoric acid at a flow rate of 0.8 ml min⁻¹. A UV detector (280 nm) was employed. The progress of the electrochemical oxidation was monitored by measuring the total organic carbon (TOC Shimadzu 5050) of the electrolysis solution.

3. Results and discussion

3.1. Electrochemical measurements

Cyclic voltammograms (CV) of the Ti/IrO₂/SnO₂–Sb₂O₅ electrodes containing different amounts of IrO₂ interlayer were obtained in 1.0 mol l⁻¹ Na₂SO₄, adjusted with H₂SO₄ at pH = 2. The results were compared to those obtained with the Ti/IrO₂ and the Ti/SnO₂–Sb₂O₅ electrodes (Figure 1). The Ti/SnO₂–Sb₂O₅ electrode has a small voltammetric charge, in the potential region of water stability, in comparison with the Ti/IrO₂ electrode. The small voltammetric charge of the Ti/SnO₂–Sb₂O₅ electrode when compared to the Ti/IrO₂ electrode can be attributed to the low rugosity/porosity of the SnO₂–Sb₂O₅ coating [10] and the absence of surface redox transitions. This morphology is related to the preparation technique. In fact, the spray pyrolysis technique (used for the preparation of the SnO₂–Sb₂O₅ coating) favors the formation of crystalline and compact coatings [10] in contrast to the thermal decomposition technique (used for Ti/IrO₂ preparation) which favors the formation of a rough/porous coating [13].

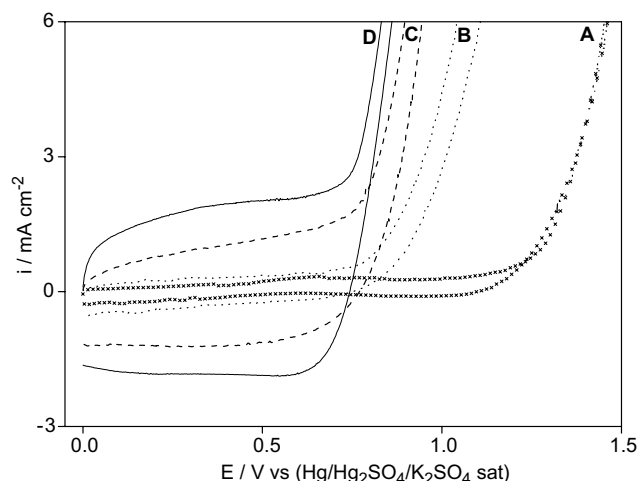


Fig. 1. Cyclic voltammograms obtained in 1.0 mol l⁻¹ Na₂SO₄; pH = 2; T = 25 °C. (A) Ti/SnO₂–Sb₂O₅ (51 g m⁻²); (B) Ti/IrO₂ (1.8 g m⁻²)/SnO₂–Sb₂O₅ (48 g m⁻²); (C) Ti/IrO₂ (10 g m⁻²)/SnO₂–Sb₂O₅ (47 g m⁻²); (D) Ti/IrO₂ (2.1 g m⁻²).

Figure 1 clearly shows that in the presence of an IrO₂ interlayer (Ti/IrO₂/SnO₂–Sb₂O₅ electrode), the voltammetric charge increases with increasing IrO₂ interlayer loading. This contribution of IrO₂ to the voltammetric charge is certainly due to the incorporation of IrO₂ into the SnO₂–Sb₂O₅ coating by diffusion during the coating preparation.

Concerning the oxygen evolution reaction (OER) Figure 1 shows that the onset potential for this reaction on the Ti/SnO₂–Sb₂O₅ electrode is about 0.5 V higher than on the Ti/IrO₂ electrode. In the case of the Ti/IrO₂/SnO₂–Sb₂O₅ electrodes the onset potential for the OER is highly dependent on the amount of IrO₂ interlayer between the Ti substrate and the SnO₂–Sb₂O₅ coating. In other words, the thicker the IrO₂ interlayer, the lower is the onset potential for the OER. This is consistent with the proposal that IrO₂ is incorporated in the SnO₂–Sb₂O₅ during electrode preparation. In fact it seems that the amount of IrO₂ incorporated into the SnO₂–Sb₂O₅ coating and that reaches the coating surface increases with increasing IrO₂ interlayer loading, explaining satisfactorily the decrease in OER overpotential with increasing IrO₂ interlayer loading.

Figure 2 shows Tafel plots, corrected for ohmic drop that were obtained with the Ti/IrO₂/SnO₂–Sb₂O₅, Ti/SnO₂–Sb₂O₅ and Ti/IrO₂ electrodes in 0.5 mol l⁻¹ H₂SO₄. The plots have a slope of 0.12 V dec⁻¹ for all the investigated Ti/IrO₂/SnO₂–Sb₂O₅ electrodes, independently of the presence of the IrO₂ interlayer. However the Ti/IrO₂ electrode shows two linear potential regions with slopes of 0.07 and 0.12 V dec⁻¹ at low and high current densities, respectively, in agreement with the value reported previously [13].

Polarization measurements in the presence of *p*-CP (2 × 10⁻² mol l⁻¹) were obtained on both Ti/IrO₂ and Ti/IrO₂/SnO₂–Sb₂O₅ electrodes with different loadings of the IrO₂ interlayer (Figure 3). The presence of *p*-CP

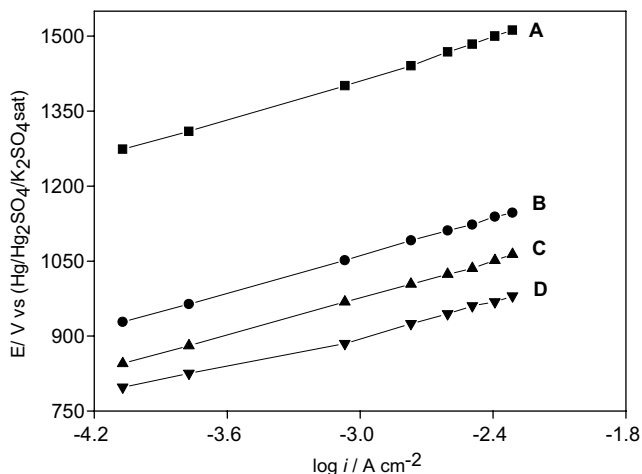


Fig. 2. Tafel plots for oxygen evolution reaction in $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$; $T = 25 \text{ }^\circ\text{C}$. (A) $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ (30 g m^{-2}); (B) Ti/IrO_2 (10 g m^{-2})/ $\text{SnO}_2\text{-Sb}_2\text{O}_5$ (30 g m^{-2}); (C) Ti/IrO_2 (10 g m^{-2})/ $\text{SnO}_2\text{-Sb}_2\text{O}_5$ (10 g m^{-2}); (D) Ti/IrO_2 (10 g m^{-2}).

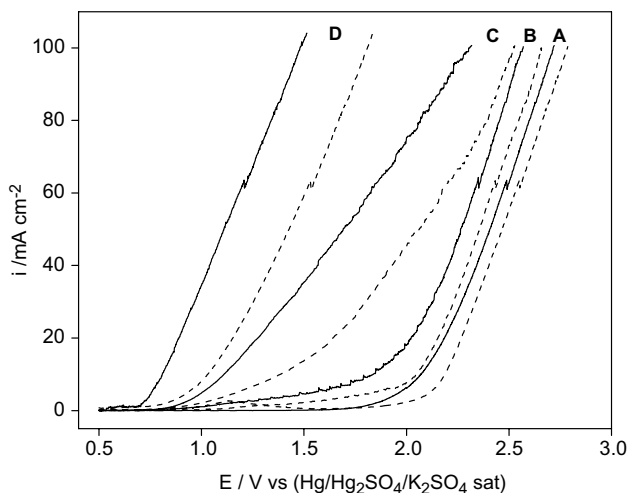


Fig. 3. Polarization curves in $1.0 \text{ mol l}^{-1} \text{ Na}_2\text{SO}_4$, $\text{pH} = 2$, $T = 25 \text{ }^\circ\text{C}$, in the absence (—) and presence (---) of $2 \times 10^{-2} \text{ mol l}^{-1} p\text{-CP}$; scan rate: 10 mV s^{-1} . (A) $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ (51 g m^{-2}); (B) Ti/IrO_2 (1.8 g m^{-2})/ $\text{SnO}_2\text{-Sb}_2\text{O}_5$ (48 g m^{-2}); (C) Ti/IrO_2 (10 g m^{-2})/ $\text{SnO}_2\text{-Sb}_2\text{O}_5$ (47 g m^{-2}); (D) Ti/IrO_2 (2.1 g m^{-2}).

in the electrolyte deactivates all the investigated electrodes (decrease in current at a given potential). However, this deactivation seems to be sensitive to the IrO_2 interlayer loading. In fact it seems that the tendency of the electrode to be deactivated increases with increasing loading of the IrO_2 interlayer and consequently with the amount of IrO_2 incorporated into the $\text{SnO}_2\text{-Sb}_2\text{O}_5$ coating. Maximum deactivation is observed for a pure IrO_2 coating. Deactivation in the presence of organic compounds from electrodes rich in IrO_2 can be associated with the formation of a polymeric film on the electrode surface which blocks the active sites. The formation of this polymeric film also depends on the experimental conditions used. Therefore, alkaline media, low current density, high temperature and high $p\text{-CP}$ concentration favors polymer film formation.

Similar behavior has been reported using Pt [14] and BDD [15] electrodes.

3.2. Electrochemical oxidation of *p*-chlorophenol (*p*-CP)

The anodic stability and the electrochemical behavior of the $\text{Ti/IrO}_2/\text{SnO}_2\text{-Sb}_2\text{O}_5$ electrodes toward *p*-CP oxidation (main reaction) and oxygen evolution (side reaction) strongly depends on the ratio between the $\text{SnO}_2\text{-Sb}_2\text{O}_5$ coating loading and the IrO_2 interlayer loading. This ratio has been defined as the γ ratio (Equation 1).

$$\gamma = \frac{\text{loading of SnO}_2 - \text{Sb}_2\text{O}_5 \text{ coating (g m}^{-2}\text{)}}{\text{loading of IrO}_2 \text{ interlayer (g m}^{-2}\text{)}} \quad (1)$$

High γ values increase the electrode service life, however, the efficiency of *p*-CP oxidation decreases with increasing γ values. In fact an optimum γ ratio must be used in order to achieve both high electrode service life and high *p*-CP oxidation efficiency. Preliminary measurements have shown that this optimum γ ratio lies between 20 and 30.

The anodic oxidation of *p*-CP has been investigated using two $\text{SnO}_2\text{-Sb}_2\text{O}_5$ based electrodes, one electrode without an IrO_2 interlayer ($\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ electrode) and another electrode having an interlayer with a γ ratio equal to 26.6 [Ti/IrO_2 (1.8 g m^{-2})/ $\text{SnO}_2\text{-Sb}_2\text{O}_5$ (48 g m^{-2}) electrode].

The anodic oxidation of a *p*-CP ($2 \times 10^{-2} \text{ mol l}^{-1}$) aqueous solution in $1.0 \text{ mol l}^{-1} \text{ Na}_2\text{SO}_4$ was carried out at constant pH ($\text{pH} = 2$) and temperature ($30 \text{ }^\circ\text{C}$) under galvanostatic conditions (30 mA cm^{-2}). The evolution of the anode potential, *p*-CP concentration and TOC during the oxidation of *p*-CP is shown in Figure 4 for both electrodes. This figure shows that the presence of the IrO_2 interlayer decreases the electrode potential and allows operation at constant potential during almost all the process. This indicates a higher stability of the electrodic material. In fact the potential of the $\text{Ti/IrO}_2/\text{SnO}_2\text{-Sb}_2\text{O}_5$ electrode initially increases and, after the passage of an electrical charge (Q) of about 40 A h L^{-1} , it stabilizes at about 3 V. In the absence of an IrO_2 interlayer the situation is different. The anode potential of the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ electrode firstly increases, stabilizing at 4.5 V before the passage of about 40 A h L^{-1} . For $Q > 120 \text{ A h L}^{-1}$ the electrode potential rapidly increases with Q indicating deactivation of the electrode.

The rate of *p*-CP oxidation and TOC elimination also depends strongly on Q . Two regions can be distinguished. For $Q < 100 \text{ A h L}^{-1}$ both electrodes behave similarly towards *p*-CP oxidation and TOC elimination (Figure 4A and B). However, for $Q > 100 \text{ A h L}^{-1}$, the rate of TOC elimination at the $\text{Ti/IrO}_2/\text{SnO}_2\text{-Sb}_2\text{O}_5$ electrode is higher than at $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$. The decrease in the rate of TOC elimination at the latter electrode material coincides with the onset of the increase in anode potential. This behavior suggests the beginning of electrode deactivation after the passage of about

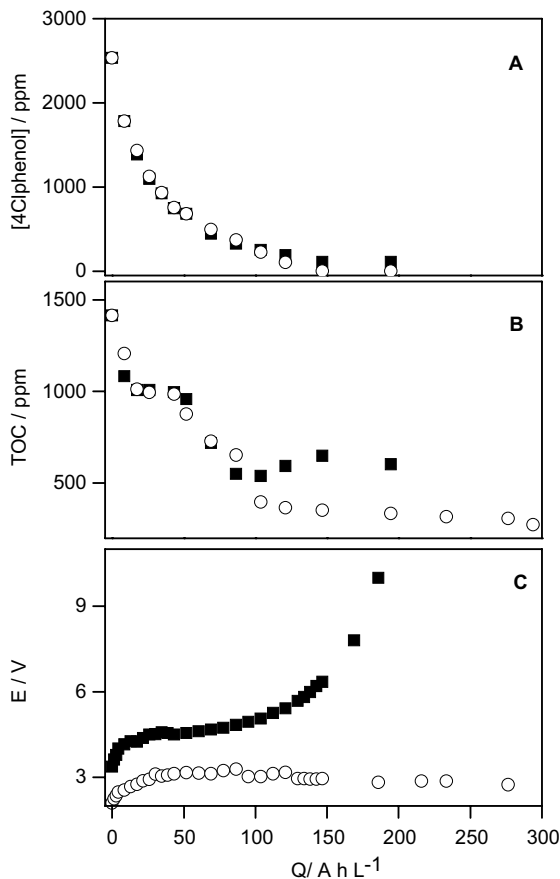


Fig. 4. (A) *p*-CP concentration, (B) TOC and (C) anode potential as a function of specific anodic charge (○) Ti/IrO₂/SnO₂-Sb₂O₅ and (■) Ti/SnO₂-Sb₂O₅. Conditions: $i = 30 \text{ mA cm}^{-2}$, $T = 30 \text{ }^\circ\text{C}$

120 A h L⁻¹. The Ti/IrO₂/SnO₂-Sb₂O₅ electrode does not give any indication of deactivation during the experiment. The high stability of the Ti/IrO₂/SnO₂-Sb₂O₅ electrode has been previously reported by Correa-Lozano et al. [10].

It is worth mentioning that during the oxidation of *p*-CP, a yellow polymeric material was formed on the anode surface.

The influence of *p*-CP concentration on its oxidation rate and TOC elimination is shown in Figure 5. For dilute *p*-CP solution 95% TOC elimination can be achieved using the Ti/IrO₂/SnO₂-Sb₂O₅ electrode with a ratio between the SnO₂-Sb₂O₅ coating loading and the IrO₂ interlayer loading equal to 26.6 ($\gamma = 26.6$). For more concentrated *p*-CP solution, about 80% of TOC is eliminated. This shows the applicability of Ti/IrO₂/SnO₂-Sb₂O₅ electrodes in technological electrochemical treatment mainly for solutions containing low concentrations of hazardous compounds.

3.3. General discussion

It has been previously reported that IrO₂ in SnO₂-Sb₂O₅ based electrodes behaves differently toward O₂ evolution and organic oxidation [16]. At an SnO₂-Sb₂O₅ based anode, a non-active electrode, the oxidation of organic

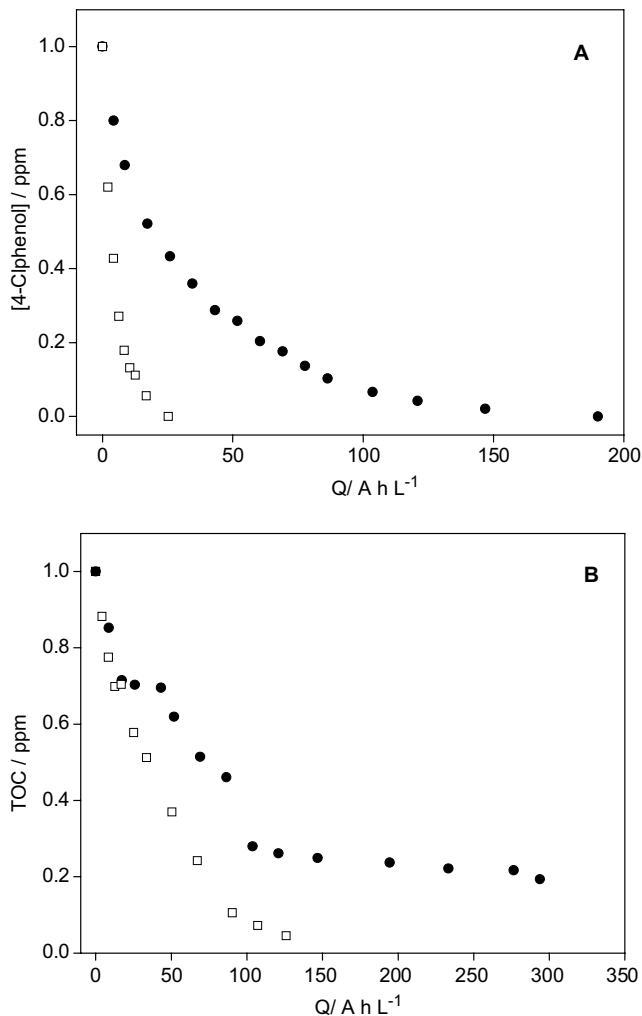


Fig. 5. Influence of initial *p*-CP concentration on the rate of: (A) *p*-CP oxidation; (B) TOC elimination at Ti/IrO₂/SnO₂/Sb₂O₅ electrode with $\gamma = 26.6$: (●) 20 mmol of *p*-CP l⁻¹; (□) 3.9 mmol l⁻¹ of *p*-CP. Conditions: $i = 30 \text{ mA cm}^{-2}$, $T = 30 \text{ }^\circ\text{C}$.

compounds occurs through physisorbed hydroxyl radicals generated from water oxidation. These active hydroxyl radicals can lead to the complete combustion of the organic compounds (step 5, Figure 6). At an IrO₂

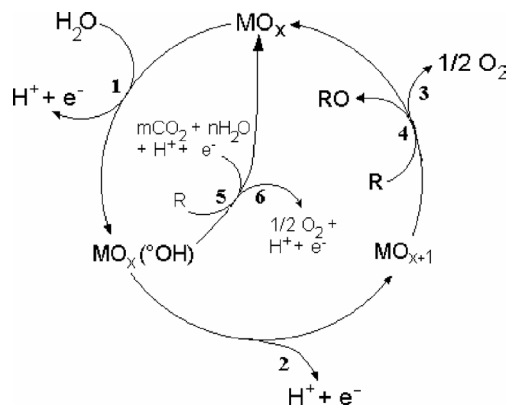
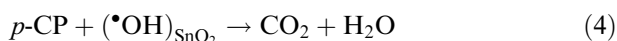
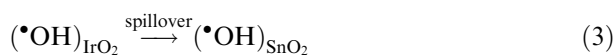


Fig. 6. Scheme of oxidation of organic compounds with simultaneous oxygen evolution at metal oxide anodes.

based anode, known as an active electrode, the reaction occurs through a higher oxidation state of the metal oxide surface sites, generally resulting in a partial oxidation of the organic compounds (step 4, Figure 6). It has also been demonstrated that the presence of an IrO₂ interlayer (Ti/IrO₂/SnO₂-Sb₂O₅ electrodes) strongly increases the electrode service life [10].

In this work we have shown that the activity of Ti/IrO₂/SnO₂-Sb₂O₅ electrodes toward the OER and *p*-CP oxidation lies between the results obtained with Ti/IrO₂ and the Ti/SnO₂-Sb₂O₅ electrodes. This is attributed to the incorporation of IrO₂ in the SnO₂-Sb₂O₅ coating during preparation. However, the effect of the IrO₂ interlayer in the SnO₂-Sb₂O₅ coating can be strongly decreased by increasing the loading of the SnO₂-Sb₂O₅ coating relative to the IrO₂ interlayer loading (γ ratio defined by Equation 1), i. e., $\gamma > 20$.

The fact that we did not observe a significant change in the behavior of *p*-CP oxidation using low loadings for the IrO₂ interlayer ($\gamma = 26$) suggests that *p*-CP oxidation at the Ti/IrO₂/SnO₂-Sb₂O₅ electrode occurs mainly through the SnO₂-Sb₂O₅ component. In other words, it occurs through physisorbed hydroxyl radicals on SnO₂-Sb₂O₅. However, the electrode potential is considerably lower than in the case of Ti/SnO₂-Sb₂O₅ electrodes. In order to explain this decrease in electrode potential, one can speculate that •OH radicals formed on IrO₂ by primary water discharge (Equation 2) spill over toward SnO₂-Sb₂O₅ (Equation 3), were they are physisorbed and react with *p*-CP (Equation 4) leading to complete combustion of the organic compound.



4. Conclusion

The influence of an IrO₂ interlayer between the Ti substrate and the SnO₂-Sb₂O₅ coating on the anodic oxidation of *p*-CP has been investigated and the results have shown that:

- (1) The presence of an IrO₂ interlayer strongly increases the service life of the Ti/SnO₂-Sb₂O₅ electrode due to its high anodic stability and its isomorphous structure with TiO₂ (formed on the Ti substrate).
- (2) The voltammetric behavior indicates that incorporation of IrO₂ into the SnO₂-Sb₂O₅ coating occurs.
- (3) If the loading of the SnO₂-Sb₂O₅ coating relative to the IrO₂ interlayer loading (γ ratio defined by Equation 1) is high ($\gamma = 20\text{--}30$) the service life of the electrode can be increased without significant affect on the ability of the electrode to carry out *p*-CP oxidation. This suggests that oxidation of *p*-CP at the Ti/IrO₂/SnO₂-Sb₂O₅ electrode with $\gamma = 20\text{--}30$ occurs only through the SnO₂-Sb₂O₅ component without any interference of the IrO₂ interlayer.
- (4) More than 95% TOC elimination can be achieved during the treatment of dilute *p*-CP solutions using the Ti/IrO₂/SnO₂-Sb₂O₅ electrode with a γ ratio equal to 26.6.

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