Short communication

Ti|Ir–Sn–Sb oxide anode: Service life and role of the acid sites content during water oxidation to hydroxyl radicals

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ABSTRACT

This work describes the preparation of four Ti|Ir–Sn–Sb oxide anodes by the Pechini method under different conditions and the evaluation of their service life, envisaging a future application in electrochemical advanced oxidation processes for water treatment. This was estimated by means of accelerated life tests ($1 \, A \, cm^{-2}$, 1 M $HClO_4$), which highlighted the dependence of durability on the Ir and Sn content in the mixed metal oxide (MMO) as well as on the required heat treatment time for its preparation. The best MMO anode reached up to 351 h of service life under such extreme conditions. SEM-EDS and XRD analyses were performed before and after the accelerated life tests, evidencing that the failure of the MMO coatings occurred by detachment from the titanium substrate, thus losing the anode electroactivity. Great amounts of acid sites in the range $0.21–0.26 \, meq \, g^{-1}$ were determined on the MMO surfaces by Boehm titrations. From the apparent rate constants determined for the decay of *N,N*-dimethyl-4-nitrosoaniline used as spin trap, before and after acid sites neutralization, a higher activity of adsorbed hydroxyl radicals at the MMO surface cannot be correlated with a greater amount of acid sites. The results obtained suggest that other active sites affect the formation of such radicals from water discharge.

1. Introduction

Dimensionally stable anodes (DSA®) were developed by Beer in the late 1960s. Although their primary application has been recognized in the chlor-alkali industry [1], they are widely used for the degradation of persistent organic pollutants (POPs) in water [2–15]. These works highlighted that mixed metal oxides (MMO) supported on either titanium or niobium substrates represent one of the most important categories of electrocatalysts [4–11,13–15]. In recent years, electrochemical advanced oxidation processes (EAOPs) using pure metal anodes like Pt, metal oxides (MO) such as PtO, IrO_2, RuO_2, SnO_2 and PbO_2, and MMO like SnO_2-Sb_2O_5, TiO_2-SnO_2 and IrO_2-SnO_2-Sb_2O_5, among others, have been investigated in detail for environmental preservation [13,16]. The high oxidation power of these anodes has been confirmed upon degradation of all kinds of POPs in synthetic and real water effluents.

The anode material plays a fundamental role for the development of effective electro-oxidation (EO) methods, being necessary to prevent typical surface failure and fouling that cause the anode deactivation [17,18]. At present, boron-doped diamond (BDD) anode is considered the best electrode for the EO of POPs [13,16]. Its success is attributed to the large production of physisorbed hydroxyl radicals (BDD(·OH)) via water oxidation, leading to the complete mineralization of the organic matter in most cases. However, the high cost of BDD anodes has limited its use to small devices. Hence, the design and synthesis of much less expensive MMO anodes is now attracting a lot of attention [4,6–10,14,15]. The preparation of an ideal MMO electrode must guarantee its high oxidation ability, chemical and mechanical stability based on an adequate service life, and low cost. Worth mentioning, the use of MMO for POPs degradation has only been performed at small scale due to limitations from short service life and passivation, which has impeded its industrial application so far [3,12,19].

The MMO anodes are composed of a metal substrate coated with an electrocatalytic layer. Ti, Ta, Zr, W, Nb and Bi are typical substrates, being Ti the most common, whereas Pt, Ir, Ru, Sn, Ir and Ru are used as electrocatalysts, either pure or as metal oxides. Other metal oxides such as TiO_2, Ta_2O_5, ZrO_2, Nb_2O_5 and SnO_2 are used as dispersing or stabilizing agents, and Sb is often added as a doping mediator [20]. RuO_2-

based MO anodes are suitable to evolve Cl_2, but they are stable only at alkaline conditions [20], with modest service life under acidic conditions even when a stabilizer is used [21]. In contrast, IrO_2-based anodes are typically chosen as optimum electrocatalysts to promote the O_2 evolution reaction, being stable in acid media [20], with moderate service life in alkaline media [22]. SnO_2 possesses interesting properties to produce physisorbed hydroxyl radicals ($M(\cdot OH)$) but its great drawback is the short service life [3]. MMO electrodes like IrO_2-SnO_2-Sb_2O_5 tend to increase the stability and durability, and show higher conductivity [20]. Furthermore, the IrO_2 interlayer enhances the generation of physisorbed hydroxyl radicals ($M(\cdot OH)$). Thus, IrO_2 acts as catalyst, SnO_2 behaves as dispersing agent and catalyst, while Sb_2O_5 is a dopant.

The performance of the MO and MMO electrodes depends on: (i) the preparation method of the ink to be deposited onto the substrate (sol–gel or polymeric precursor method), (ii) the coating method (immersion, painting, electrophoresis) [23], (iii) the thermal treatment to obtain the MO or MMO crystallographic phases, and (iv) the substrate pre-treatment [9]. In earlier articles, we demonstrated the good performance of a Ti|Ir–Sn–Sb oxide anode for the EO treatment of dyes like Methyl Orange [9], Indigo [10] and Acid Yellow 36 [15]. The oxidation of water to adsorbed $M(\cdot OH)$ on the Ti|Ir-Sn–Sb oxide surface may be carried out according to a mechanism that relies on the adsorption of the water molecule on the acid sites of MMO (Reaction (1)), which arise from the acid nature of the Ir-Sn-Sb oxides. This is followed by water discharge via Reaction (2). Therefore, the determination of the surface acid sites content is necessary.

$$H_2O + M \rightarrow M(H_2O) \qquad (1)$$

$$M(H_2O) \rightarrow M(\bullet OH) + H^+ + e^- \qquad (2)$$

The evidence of $M(\cdot OH)$ production at Ti|Ir-Sn–Sb oxide anode was demonstrated in previous communications of our group, using either spin-trapping with *N,N*-dimethyl-4-nitrosoaniline (RNO) [3,10] or by electron paramagnetic resonance (EPR) [15]. However, the characterization of the acid sites has not been reported yet.

The aim of this article is the preparation of Ti|Ir-Sn-Sb oxide anodes by the polymeric precursor method (Pechini method), which show several advantages [10], and the evaluation of their service life, as well as to ascertain the role of the acid sites in the formation of $M(\cdot OH)$ from water discharge. The service life was estimated using accelerated life tests, in strong acidic medium under galvanostatic conditions. The influence of the Ir, Sn an Sb molar percentage on service life was also addressed. The acid sites content was determined by the Boehm titration method, which consists in neutralizing the acid sites with a carbonate or hydroxide [24,25]. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to examine the morphological and structural changes of the coating.

2. Experimental

2.1. Chemicals

All solutions were prepared with deionized water. The chemicals for the MMO preparation were $H_2IrCl_6 \times H_2O$, $SnCl_4$, $SbCl_3$, citric acid and ethylene glycol of analytical grade purchased from Sigma-Aldrich. RNO and phosphate buffer used for the $M(\cdot OH)$ detection were of analytical grade supplied by Sigma-Aldrich. Perchloric acid used for accelerated life tests and other chemicals employed for the pre-treatment of the Ti surface were of reagent grade also provided by Sigma-Aldrich.

2.2. Preparation of the MMO electrodes

The Ti plates were pre-treated by consecutive immersion in concentrated HCl at 70 °C for 1 h and concentrated HNO_3 at room temperature for 20 min. Then, the plates were rinsed with distilled water

Table 1
Molar content of organic chemicals and metals in the polymeric precursor solutions employed for the preparation of different anodes.

Electrode	EG	CA	Ir	Sn	Sb
E1	16	0.12	0.0296	0.0296	0.0004
E2	3.2	0.024	0.0296	0.0296	0.0004
E3	16	12	0.0296	0.2371	0.0296
E4	16	12	0.0296	0.2371	0.0296

and dried at room temperature. This pre-treatment served to increase the surface roughness and improve the coating adhesion. Each plate was 4 cm long, 0.5 cm wide and 0.1 cm thick.

The polymeric precursor solution to perform the Pechini method was prepared by mixing citric acid (CA) and ethylene glycol (EG) at 60–70 °C, according to the molar contents summarized in Table 1. The metallic precursors ($H_2IrCl_6 \times H_2O$, $SnCl_4$ and $SbCl_3$) were added to the mixture (see Table 1), maintaining the temperature at 60–70 °C for 30 min. The resulting solutions were used to coat the pre-treated Ti substrates on both sides using a brush. To obtain electrodes E1 and E3, the coated Ti was heated at 115 °C for 15 min in a furnace to induce the polymerization of the precursor. The overall procedure was repeated until forming 32 layers and, finally, the electrodes were heated at 550 °C for 1 h. To obtain electrodes E2 and E4, the heating after the application of the solution onto the pre-treated Ti substrate was made at 550 °C for 10 min, and the overall procedure was repeated to form 32 layers. A final heating at 550 °C was performed for 1 h. The temperature was controlled to avoid the formation of TiO_2, which occurs at 600 °C, because it would cause passivation [26].

2.3. Surface characterization of the electrodes

The morphological characteristics and distribution of metal oxides of the Ti|Ir–Sn–Sb oxide electrodes were evaluated by SEM, using a Carl Zeiss EVO HD15 scanning electron microscope, coupled with an integrated energy dispersive X-ray detector. The crystal structure of the MMO was analyzed by XRD using a Rigaku Ultima IV diffractometer. The diffraction patterns were measured in the 2θ range from 20° to 70°, using Cu $K\alpha_1$ $\lambda = 1.5418$ Å.

2.4. Detection of generated hydroxyl radicals

RNO was employed as a spin trap for the detection of low concentrations of $M(\cdot OH)$ formed at the MMO surfaces. This technique is based on the analysis of the solution bleaching, which is confirmed from the absorbance decay at $\lambda_{max} = 440$ nm [3,10,17]. More details about its effectiveness are reported in previous work [3,10,27]. The absorption spectra of RNO were recorded using a Perkin Elmer Lambda UV/Vis spectrophotometer coupled to an anode half-cell for the in-situ detection of $M(\cdot OH)$. A divided three-electrode cell was employed in order to avoid cathodic interferences during the detection process. Two quartz cells typically used in UV/Vis spectrophotometry were utilized to construct the two half cells, which were connected through a saline bridge of Pyrex glass (containing phosphate buffer) and with a Pt wire welded at each extreme. An MMO anode of 0.66 cm² area in contact with 3 mL of anolyte (5.2×10^{-5} M RNO in phosphate buffer at pH = 7) and a carbon rod cathode in contact with the same volume of catholyte (phosphate buffer at pH = 7)) were used. The reference electrode was an Ag/AgCl (saturated KCl) electrode immersed in a Luggin capillary, which was carefully inserted into the anodic half-cell. The microelectrolysis tests were performed at 25 °C using a BioLogic® SP 150 potentiostat-galvanostat running with EC-Lab® software. All the electrode potentials reported in this work are referred to the standard hydrogen electrode (SHE). The oxidation of water was performed at constant anode potential of 1.3 V|SHE for 2 h, carrying out the in-situ monitoring of RNO bleaching from starting yellow solution. Note that