Article

Production and Characterization of Ti/PbO$_2$ Electrodes by a Thermal-Electrochemical Method

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Visando obter eletrodos com alto sobrepotencial para a reação de desprendimento de oxigênio (RDO), úteis para a oxidação de poluentes orgânicos, prepararam-se eletrodos de Ti/PbO$_2$ por um método térmico-eletroquímico e compararam-se seus desempenhos com o de eletrodepositados. O potencial de circuito aberto em solução de H$_2$SO$_4$ 0,5 mol L^{-1} para esses eletrodos apresentou valores bastante estáveis, próximos entre si, na faixa de potenciais para a região de estabilidade de PbO$_2$ em diagramas de Pourbaix. Análises por difração de raios X mostraram que o óxido térmico-eletroquímico é uma mistura de ort-PbO, tetr-PbO e ort-PbO$_2$. Já os eletrodos produzidos por eletrodeposição se apresentaram mais provavelmente na forma tetr-PbO$_2$. Micrografias obtidas por microscopia eletrônica de varredura mostraram que a morfologia básica do PbO$_2$ térmico-eletroquímico é determinada na etapa térmica, sendo bem distinta da dos eletrodos eletrodepositados. Curvas de polarização, em H$_2$SO$_4$ 0,5 mol L^{-1}, mostraram que no caso dos eletrodos de Ti/PbO$_2$ térmico-eletroquímicos a RDO foi deslocada para potenciais mais positivos. Entretanto, os valores dos coeficientes de Tafel, bastante altos, indicam que possivelmente houve formação de filmes passivantes sobre os substratos de Ti, o que pode eventualmente explicar os valores de corrente algo baixos para a RDO.

Looking for electrodes with a high overpotential for the oxygen evolution reaction (OER), useful for the oxidation of organic pollutants, Ti/PbO$_2$ electrodes were prepared by a thermal-electrochemical method and their performance was compared with that of electrodeposited electrodes. The open-circuit potential for these electrodes in 0.5 mol L^{-1} H$_2$SO$_4$ presented quite stable similar values. X-ray diffraction analyses showed the thermal-electrochemical oxide to be a mixture of ort-PbO, tetr-PbO and ort-PbO$_2$. On the other hand, the electrodes obtained by electrodeposition were in the tetr-PbO$_2$ form. Analyses by scanning electron microscopy showed that the basic morphology of the thermal-electrochemical PbO$_2$ is determined in the thermal step, being quite distinct from that of the electrodeposited electrodes. Polarization curves in 0.5 mol L^{-1} H$_2$SO$_4$ showed that in the case of the thermal-electrochemical PbO$_2$ electrodes the OER was shifted to more positive potentials. However, the values of the Tafel slopes, quite high, indicate that passivating films were possibly formed on the Ti substrates, which could eventually explain the somewhat low current values for OER.

Keywords: Ti/PbO$_2$ anode, thermal-electrochemical method, oxygen evolution reaction, modified electrode

Introduction

Research on new anode materials to be used for the oxygen evolution reaction (OER) has increased in the last few years, due to conventional metallic electrodes not being stable under the operational conditions used in industrial electrolysers[1]. Furthermore, there are electrochemical processes (*e.g.*, ozone generation and oxidation of organic molecules) that require a high OER overpotential, since the occurrence of this reaction decreases the global efficiency of the reaction of interest[2]. Many electrode materials have been investigated, for example: Ti/SnO$_2$[2-6], Ti/IrO$_2$[7,8], Ti/RuO$_2$[7] and Ti/PbO$_2$[2,6,9-12]. When compared with Ti/SnO$_2$[2-6], Ti/PbO$_2$ electrodes present a low OER overpotential and, thus, a low current efficiency for the oxidation of organic molecules. Kötz *et al.*[2], based on anodic Tafel lines, showed that the OER on electrodeposited PbO$_2$ in 0.5 mol L^{-1} H$_2$SO$_4$ occurs at overpotentials higher than those on Pt but lower than on Sb-doped SnO$_2$. At 0.1 mA cm^{-2}, the OER potentials (*vs.* SCE) were 1.5 V (on Pt), 1.65 V (on PbO$_2$) and 1.95 V (on SnO$_2$). Additionaly, they reported that the SnO$_2$ electrode presented a higher efficiency for the oxidation of phenol.

Considering that up to now the Ti/PbO$_2$ electrodes investigated were produced by either anodization[13] or electrodeposition[6,7,11-17], the present work concerns the preparation of Ti/PbO$_2$ electrodes through an alternative method (thermal-electrochemical) aiming to obtain electrodes with higher OER overpotentials. The obtained electrodes were characterized by X-ray diffraction and scanning electron microscopy, as well as by open-circuit potential measurements and polarization curves for the OER in 0.5 mol L^{-1} H$_2$SO$_4$.

Experimental

Production of the Ti/PbO electrodes through the thermal decomposition of Pb(NO$_3$)$_2$

First of all, the substrate Ti sheet (99.7%, Müller Metais - Brazil) was sandblasted with glass microspheres. Then, after being cut into smaller pieces (useful electrode area of ~3 cm^2), each piece was cleaned in an isopropanol ultrasound bath for 20 min and etched in boiling concentrated HCl for 60 s, washed with deionized water and dried in air. Immediately after, a Pb(NO$_3$)$_2$ coating was deposited on the substrate by repeating the following steps 25 times in order to obtain the required final PbO coating thickness (~2 μm): first, a 1.5 mol L^{-1} Pb(NO$_3$)$_2$ aqueous solution was applied on the substrate with a soft brush; then, after the water was evaporated at 60 °C for 20 min, the substrate was cooled down at room temperature for 5 min. Finally, the Pb(NO$_3$)$_2$ was decomposed[18] to PbO by leaving the substrate in an oven at 550 °C for 1 h, either in an air, O$_2$ or N$_2$ atmosphere.

Electrochemical oxidation of the Ti/PbO electrodes to Ti/PbO$_2$

This oxidation was carried out in a borate buffer (pH 9.4) in a three-electrode electrochemical cell, using an Eco Chemie Autolab/GPES potentiostat/galvanostat system. The working electrode was the ~3 cm^2 Ti/PbO electrode thermally prepared; the counter electrode was a cylindrical platinum grid placed around the working electrode, and a saturated calomel electrode (*sce*) was used as reference. Different electrolysis conditions were investigated: potentiostatic (2.0V *vs. sce* for 7 h), galvanostatic (0.5 mA cm^{-2} for 5 h) and galvanostatic in three steps (50 μA cm^{-2} for 1 h; scanning from 50 μA cm^{-2} to 400 μA cm^{-2} at v = 0.28 μA s^{-1}; then, 400 μA cm^{-2} for 5 h).

Characterizations

The Ti/PbO electrodes were qualitatively characterized by X-ray diffractometry (XRD) in a diffractometer model D5000 Siemens (CuKα radiation and Ni filter).

Their morphology was characterized by scanning electron microscopy (SEM) using a microscope model DSM 960 Zeiss.

The Ti/PbO$_2$ electrodes were also characterized through XRD and SEM, as well as through measurements of their open-circuit potential and steady-state polarization curves (from 1.6 V to 4.5 V *vs.* sce, at 0.2 mV s^{-1}) in aqueous 0.5 mol L^{-1} H$_2$SO$_4$ so as to investigate the oxygen evolution reaction (OER) on these electrodes. These curves were obtained using a potentiostat/galvanostat model 273A EG&G interfaced to a microcomputer. The characteristics and electrochemical behavior of the Ti/PbO$_2$ electrodes obtained by the thermal-electrochemical method were compared with those of Ti/PbO$_2$ electrodes galvanostatically electrodeposited (50 mA cm^{-2} for 3 h) from a 275 g L^{-1} Pb(NO$_3$)$_2$ + 25 g L^{-1} Cu(NO$_3$)$_2$ + 0.5 g L^{-1} sodium lauryl sulfate solution, as described by Bemelmans *et al.*[19].

Results and Discussion

Characterization of the Ti/PbO$_2$ electrodes through their open-circuit potentials

The open-circuit potential *vs.* time behavior of the different Ti/PbO$_2$ electrodes in a 0.5 mol L^{-1} H$_2$SO$_4$ solution is shown in Figure 1. After 24 h in solution, the electrodes prepared by the thermal-electrochemical method presented almost the same open-circuit potential as the one prepared by electrodeposition; furthermore, the values were quite stable. These open-circuit potentials are in the range of the potentials for the stability region for PbO$_2$ in Pourbaix diagrams[20], indicating that the surface of the oxide film obtained by the thermal-electrochemical method is predominantly PbO$_2$.
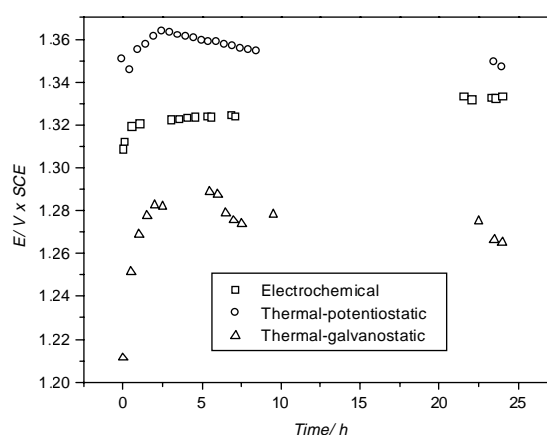

Figure 1. Open-circuit potential (*vs. sce*) as a function of time for Ti/PbO$_2$ electrodes produced by the thermal-electrochemical method and by electrodeposition, in a 0.5 mol L^{-1} H$_2$SO$_4$ solution at room temperature.

Qualitative characterization of the Ti/PbO and Ti/PbO₂ electrodes through X-ray diffractometry

Comparison of the diffraction angles for the different peaks in the X-ray diffractogram obtained for the Ti/PbO electrode with JCPDS (Joint Committee of Powder Diffraction Standards) standard data did not allow to conclude whether the PbO was in the orthorhombic or the tetragonal form. On the other hand, the diffractograms for the Ti/PbO₂ electrodes obtained by the thermal-electrochemical method did not differ very much from the one for the Ti/PbO electrode. Figure 2 shows the diffractogram for the Ti/PbO₂ electrode obtained by the thermal-galvanostatic method. The peaks at the diffraction angles $2\theta = 18.6^o$, 28.7^o, 31.8^o, 35.8^o, 40.2^o and 48.7^o, also present in the diffractogram for the Ti/PbO₂ electrode obtained by the thermal-potentiostatic method, are quite similar to the ones typical of PbO. The peak at $2\theta = 40.2^o$ is clearly due to the Ti substrate. On the other hand, only the peaks at $2\theta = 28.7^o$ and 35.8^o coincide with those of the JCPDS standard data for orthorhombic PbO₂. Thus, the X-ray diffractograms indicate that the electrode coating is a mixture of ort-PbO, tetr-PbO and ort-PbO₂. Although only two of the peaks are attributable to PbO₂, the values of the open-circuit potential in 0.5 mol L⁻¹ H₂SO₄ and the color of the electrode surface (dark gray) are typical of PbO₂; furthermore, the fact that the electrode is stable in 0.5 mol L⁻¹ H₂SO₄ also indicates that its surface is made of PbO₂ (PbO is soluble in acid media).
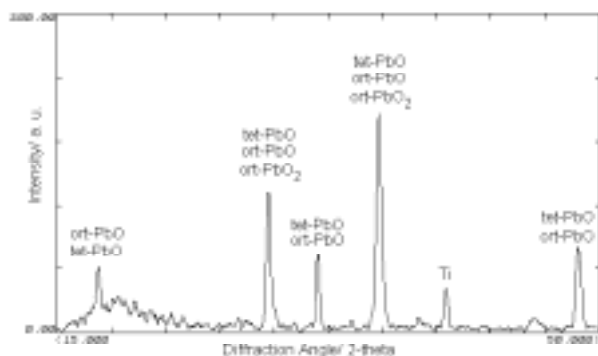

Figure 2. X-ray diffractogram of the Ti/PbO₂ electrode produced by the thermal-galvanostatic method.

On the other hand, it should be noted that, according to the obtained diffractograms, the coating in the electrodeposited Ti/PbO₂ electrodes is made most probably of tetragonal PbO₂ (actually some peaks are common to orthorhombic PbO₂). This result agrees well with those of Bemelmans *et al.*[19], who reported that the addition of sodium lauryl sulfate to the electrolyte used for the electrodepositon of PbO₂ supressed the growth of the orthorhombic phase in favor of the tetragonal phase. Furthermore, PbO traces seem to be present, since peaks also attributable to this oxide were observed.

Surface morphology characterization of the Ti/PbO and Ti/PbO₂ through scanning electron microscopy

No significant influence of the atmosphere used during the decomposition of PbO to PbO₂ on the final surface morphology of the electrodes was noticed. Figures 3 to 6 show SEM images of the surface of the Ti/PbO electrode, Ti/PbO₂ electrode obtained by the thermal-potentiostatic method, Ti/PbO₂ electrode obtained by the thermal-galvanostatic method and Ti/PbO₂ electrode obtained by electrodeposition, respectively; in all cases the decomposition of PbO to PbO₂ was carried out in a O₂ atmosphere. The comparison of Figures 3 to 5 allows one to conclude that the basic morphology of the PbO₂ surface (entangled and porous) is determined in the thermal step, *i.e.*, during the PbO formation (Figure 3). Clearly the electrochemical oxidation of PbO to PbO₂ (Figures 4 and 5) does not change the basic features of the initial morphology. On the other hand, there is a subtle difference between the Ti/PbO₂ electrodes (Figures 4 and 5), that is the presence of fibrils on top of the thermal-potentiostaic electrode (Figure 4), increasing its surface area and rugosity.
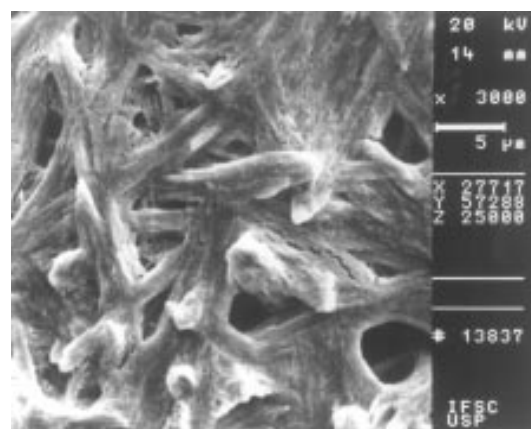

Figure 3. SEM image of the surface of the Ti/PbO electrode obtained by the thermal decomposition of Pb(NO₃)₂ to PbO. Magnification: 3,000.

On the other hand, the comparison of Figures 4 and 5 with Figure 6 clearly shows that the Ti/PbO₂ electrode obtained by electrodeposition (Figure 6) has a distinctly different, polyhedral surface morphology, which is similar to the one reported by Bemelmans *et al.*[19]. Its formation is due to the addition of the sodium lauryl sulfate additive to the electrodeposition solution.
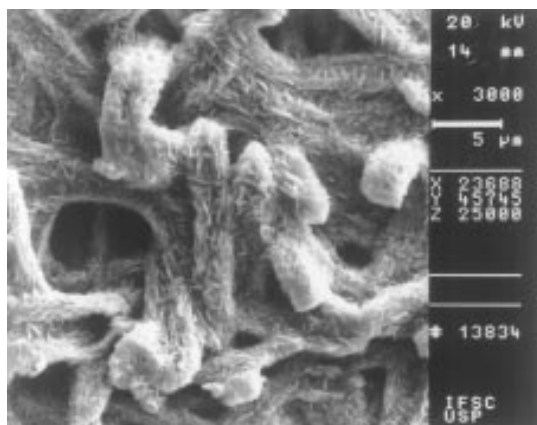
Figure 4. SEM image of the surface of the Ti/PbO$_2$ electrode obtained by the thermal-potentiostatic method. Magnification: 3,000.
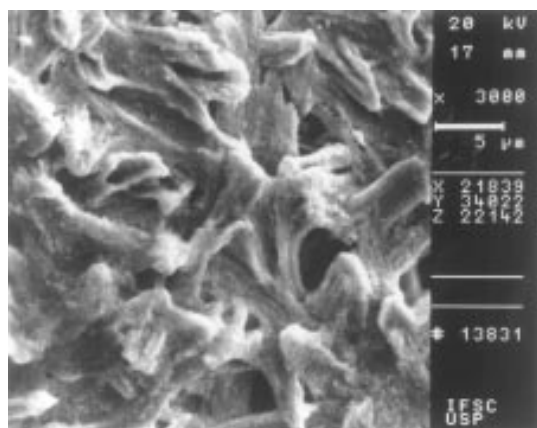

Figure 5. SEM image of the surface of the Ti/PbO$_2$ electrode obtained by the thermal-galvanostatic method. Magnification: 3,000.
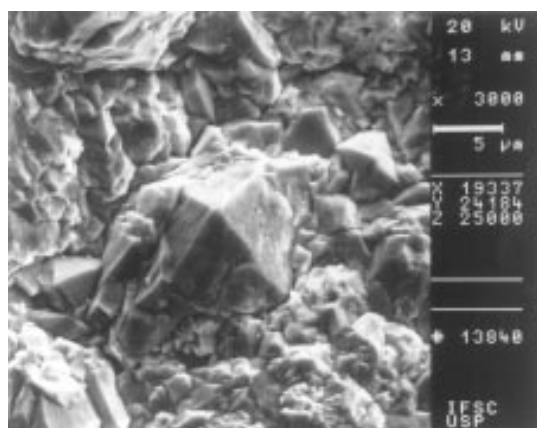

Figure 6. SEM image of the surface of the Ti/PbO$_2$ electrode obtained by electrodeposition. Magnification: 3,000.

Electrochemical characterization of the oxygen evolution reaction on the Ti/PbO$_2$ electrodes

This characterization was carried out in a 0.5 mol L^{-1} H$_2$SO$_4$ solution, at room temperature. No significant

difference was noticed between the behavior of Ti/PbO$_2$ electrodes produced by the thermal-electrochemical methods. Thus, considering that the galvanostatic oxidations of PbO to PbO$_2$ could be carried out in less time, hereinafter only electrodes thus obtained were characterized.

Figure 7 shows that the atmosphere in which PbO was decomposed to PbO$_2$ influences the efficiency of the OER on Ti/PbO$_2$ electrodes obtained by the thermal-galvanostatic (three steps) method. Clearly the reaction occurs more readily on the electrodes produced in a N$_2$ atmosphere. This may be due to the absence of O$_2$ in the oven during the decomposition of PbO to PbO$_2$ at 550 °C. It is known that when titanium is heated in air, even at temperatures smaller than 550 °C, an oxide film is formed on its surface[21]. This insulating/passivating film makes the electrode less conductive, thus leading to a decrease of the electrode efficiency for the OER. A comparison of these results with those reported by Kötz *et al.*[2] clearly indicates that the Ti/PbO$_2$ electrodes produced by the alternative method described in this paper have a much higher overpotential for the OER, which may be of interest when using the electrodes for the oxidation of organic molecules. However, it should be noticed that the Ti substrate in the Ti/PbO$_2$ electrodes studied by Kötz *et al.*[2] was platinized, which may hinder any oxidation of the titanium substrate.
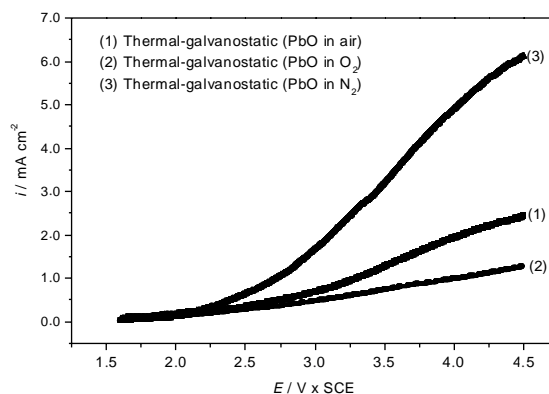

Figure 7. Steady-state polarization curves (v = 0.2 mV s^{-1}) in a 0.5 mol L^{-1} H$_2$SO$_4$ solution at room temperature for Ti/PbO$_2$ electrodes produced by the thermal-galvanostatic method (three steps); comparison of the performance of electrodes produced in different atmospheres during the thermal step: either air, O$_2$ or N$_2$.

Figure 8 shows that the OER on the thermal-galvanostatic Ti/PbO$_2$ electrode has a much higher overpotential than on the electrodeposited Ti/PbO$_2$ electrode. The corresponding Tafel slopes are about 240 mV/decade and 500 mV/decade, respectively. Kötz *et al.*[2] reported a slope of 120 mV/decade for Ti/PbO$_2$ and 240 mV/decade for Ti/SnO$_2$. The difference between the Tafel slopes of the electrodeposited Ti/PbO$_2$ electrodes studied by Kötz *et al.*[2]

and by us indicates that the Ti substrate may have been passivated under the polarization conditions used for PbO$_2$ electrodeposition[22]. Furthermore, the larger Tafel slope for the thermal-galvanostatic Ti/PbO$_2$ electrode indicates that the passivation of the Ti substrate may have occurred to a greater extent under the heating conditions used in the thermal-galvanostatic method (550 °C in a N$_2$ atmosphere). Although, as pointed out by Bemelmans *et al.*[19], the PbO$_2$ phase influences the polarization behavior of the electrode (PbO$_2$ exists as a different phase in each case: ort-PbO$_2$ in the thermal-galvanostatic electrode, and tetr-PbO$_2$ in the electrodeposited electrode), such a large difference in the Tafel slopes cannot be accounted for solely by this. Further studies are presently being carried out in order to confirm or not the passivation of the Ti substrate in these electrodes.
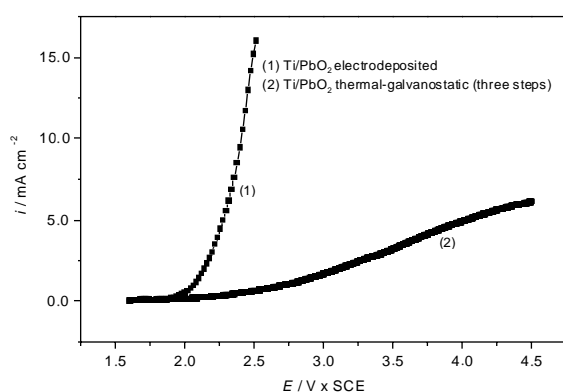

Figure 8. Steady-state polarization curves (v = 0.2 mV s^{-1}) in a 0.5 mol L^{-1} H$_2$SO$_4$ solution at room temperature for Ti/PbO$_2$ electrodes produced by the thermal-galvanostatic method (three steps) or by electrodeposition; the thermal step was carried out under a N$_2$ atmosphere.

Finally, it should be noted that although from the point of view of the OER overpotential the Ti/PbO$_2$ electrodes produced by the alternative method described in this paper are very good, the fact that the OER currents obtained are quite low is worrisome, since the electrodes may turn out not to be practical; this will be determined by the outcome of the tests of these electrodes for the oxidation of organic compounds, which will be carried out in the near future.

Acknowledgments

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