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Fabrication and characterization of a porous gas-evolving anode constituted of lead dioxide microfibers electroformed on a carbon cloth substrate

Fabiano R. Costa, Leonardo M. Da Silva*,[1]

Departamento de Química, Universidade Federal dos Vales do Jequitinhonha e Mucuri, Rodovia MGT 367, km 583, 5000, Alto da Jacuba, 39.100-000 Diamantina, MG, Brazil

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ABSTRACT

Lead dioxide microfibers (MF-PbO_2) were electroformed on fibers of a carbon cloth substrate in order to obtain a porous gas-evolving anode (PGEA). A solid polymer electrolyte cell was fabricated using perforated current collectors, composed of PGEA pressed against the solid polymer electrolyte using a stainless steel fine mesh as the cathode. Ex situ characterization carried out through XRD and SEM techniques provided information about the structural and morphological properties of the MF-PbO_2, respectively. An electrochemical characterization study was carried out through analysis of the quasi-stationary polarization curves obtained for the oxygen evolution reaction (OER). Analysis of SEM images showed that the MF-PbO_2 surface is rough and uniformly distributed along fibers of the carbon cloth substrate. The formation of MF-PbO_2 occurred preferentially onto carbon fibers located near the surface of the substrate (outer fibers). The XRD study revealed a high degree of crystallinity of the beta phase (β-PbO_2), with crystals characterized by a size of 24 nm. Analysis of the Tafel plot permitted us to propose the primary water discharge as the rate-determining step for the OER. The apparent enthalpy and entropy of activation and the apparent kinetic rate constant were evaluated for the OER on MF-PbO_2. The endurance test revealed that MF-PbO_2 are resistant to wear during the intense oxygen evolution.

1. Introduction

From both fundamental and technological points of view, it is known that the fabrication of a new electrode material in order to permit a reduction in production costs and increased reactor performance constitutes a very difficult task [1–13].

Several different electrode materials presented in different geometric configurations have been proposed for different applications [1–3]. For instance, the development of porous gas-evolving electrodes (PGEEs) for applications in solid polymer electrolyte (SPE) cells has permitted carrying out the electrolysis of electrolyte-free water in order to generate oxygen, oxygen–ozone and hydrogen, as well as performing electro-organic synthesis and combustion (oxidation) of different organic pollutants in filter-press electrochemical reactors [1–4,14,15].

In addition, in some cases, it is known that a given electrode material presenting some degree of instability in acid and/or alkaline environments can present very high stability when it is used as a PGEE in an SPE cell [4,8,10,11].

In an SPE cell, the oxidation and reduction reactions are coupled and are carried out separately on porous electrodes located on different sides of the SPE [13]. In these cases, the porous electrode maintains intimate contact with the SPE (zero-gap condition) in order to permit ionic and electronic transport inside the cell, i.e., in the reaction zones of the SPE/electrode interface.

As previously discussed by Houk et al. [15], a distinct advantage of using SPE cell technology in large-scale applications toward the combustion of pollutants is the production of a final product (effluent) without the need for desalting and/or pH adjustment. However, the use of SPE cells for treating pollutants present in contaminated waters has some disadvantages, such as the excessive long periods required for decontamination due to the low ionic strength.

Therefore, the improvement of SPE cells making use of PGEE for the electrochemical combustion of emerging pollutants found in natural waters (e.g., some classes of pharmaceuticals [16]) comprises an important task from the technological point of view.

Suitable electrode materials for the fabrication of a PGEE aiming at the oxidation of organic pollutants are those presenting a high overpotential for the oxygen evolution reaction (OER), such as PbO_2, SnO_2–Sb_2O_5, boron-doped diamond (BDD), etc. [17–22]. The highest oxidation power for the combustion of pollutants is presented by PbO_2, SnO_2–Sb_2O_5 and BDD [18]. Despite its high efficiency for removing organic pollutants, doped-SnO_2 anodes have

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* Corresponding author. Tel.: +55 38 3532 6000; fax: +55 38 3532 6000.
E-mail addresses: lsilvamorais@hotmail.com, leonardo.morais@ufvjm.edu.br (L.M. Da Silva).

[1] ISE Member.

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the major drawback of a short service life at moderate and high current densities that limits their practical applications [18].

On the contrary, it is known that BDD is very stable in different environments (acid and alkaline) and presents a very good efficiency for the combustion of organic pollutants [20]. Unfortunately, the synthesis of BDD films on the surface of porous conducting substrates is not an easy task for obtaining a PGEE [7].

Even in the case of planar supports, the mechanical stability of the BDD layer is only obtained using expensive metals such as tantalum, niobium and tungsten [7,18,23]. Unfortunately, the stability of BDD films deposited on a cheaper substrate such as titanium is still not yet satisfactory, because cracks appear and then cause the detachment of the diamond film during long-term electrolysis [18].

As discussed by Sirés et al. [24], PbO_2 is widely used as an anode owing to its well-proven advantages, including its low cost compared to noble metals, ease of preparation on different substrates (planar or porous), low electrical resistivity, good chemical stability in corrosive media, relatively large surface area and high overpotential for the OER.

More recently, the fundamental and technological aspects related to PbO_2 anodes were reviewed by Li et al. [25]. As discussed by these authors, a PbO_2 anode electroformed on titanium or carbon substrates offers a cheap alternative to precious metal anodes for a number of applications and, provided it is used under controlled conditions (e.g., SPE cells [4,11]), the PbO_2 coating can have an extended lifetime with no significant contamination of the cell effluent by soluble lead species.

Important findings about the fabrication of PbO_2 deposits onto carbonaceous materials were reported recently by different authors [26,27].

Sáez et al. [26] studied the dependence on chemical and electrochemical variables of lead dioxide electrodeposition on glassy carbon and demonstrated that the lead dioxide electrodeposition follows a complex mechanism and depends on several factors such as initial surface state, pH, applied potential, coverage of PbO_2, and convective conditions, some of which can even change in the course of a single experiment.

Recio et al. [27] reported the formation of PbO_2 onto reticulated vitreous carbon (RVC), with description of good nanostructured coatings on the fibers of RVC. It was also verified by these authors that all the coated RVC electrodes exhibited excellent long-term stability and remained unaltered after prolonged electrolysis.

The scope of the present work is the fabrication and characterization (ex situ and in situ) of lead dioxide microfibers (MF-PbO_2) electroformed on fibers of a carbon cloth substrate. Electrochemical studies involving the OER were carried out in electrolyte-free water using an SPE cell.

2. Experimental

2.1. Anode preparation

MF-PbO_2 supported on fibers of a carbon cloth substrate were prepared by electrodeposition in a 0.5 dm^3 single-compartment cell equipped with a concentric cylindrical counter-electrode made of carbon cloth presenting a geometric area of 251 cm^2. The solution was magnetically stirred during electrodeposition. The carbon cloth CCS200 (serge-type and $\varepsilon = 0.34$ mm) furnished by Maxepoxi Co. (Brazil) used as the substrate was previously treated using isopropanol as described previously [28]. A fine insulating layer ($\varepsilon \approx 0.1$ mm) was applied on the edges of the substrate using silicon glue (Tekbond, Brazil) in order to avoid damages for the serge-type weaving during the cutting process using a scissor. In addition, this procedure minimized the “edge effect” that leads to a preferential electrodeposition of the lead dioxide on the edges of the substrate. A mold made of Teflon ($\varepsilon = 0.5$ mm and 2.5 cm × 2.5 cm) was used during application of the insulating layer in order to delimitate the electrodeposition area for each side of the substrate (see Fig. 1). After the careful removal of the Teflon mold, the sample was left in air for 24 h at 25 °C. This procedure was repeated for the other side of the substrate. After that, the portion of the substrate devoted to electrodeposition (2.5 cm × 2.5 cm) was totally immersed in the electrodeposition solution. MF-PbO_2 presenting a geometric area for each side of 6.25 cm^2 was prepared by electrodeposition using a 0.1 mol dm^{-3} $Pb(NO_3)_2$ + 0.01 mol dm^{-3} HNO_3 solution at 50 °C, applying a constant apparent current density of 40 mA cm^{-2} for 8.4 min. After the electrodeposition, the uncovered part of the carbon cloth used for the electric contact was removed resulting in the final configuration of the anode used in the SPE cell. Three samples were prepared in order to check reproducibility of the experimental findings. Electrodes were rinsed thoroughly with deionized water to remove any traces of Pb^{2+} ions and then air-dried and stored appropriately. The average mass obtained for MF-PbO_2 was 48 ± 3 mg cm^{-2}. Vetec (Brazil) “purum p.a.” products were used throughout.

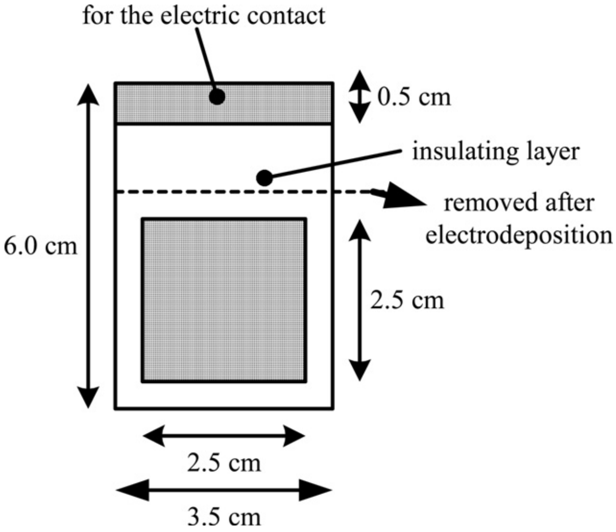

Fig. 1. Configuration of the carbon cloth substrate used for the electrodeposition of lead dioxide.

2.2. Cathode preparation

A stainless steel fine mesh (AISI-304: $A_G = 6.25\,cm^2$, Ø = 0.05 mm × 0.05 mm and $\varepsilon = 0.05$ mm) furnished by Steel Mesh Co. (Brazil) was used as the cathode.

2.3. Membrane electrode assembly

A stainless steel mesh (AISI-304: $A_G = 6.25\,cm^2$, Ø = 0.2 mm × 0.2 mm and $\varepsilon = 0.2$ mm) was placed between the electrodes (anode and cathode) and perforated current collectors made of stainless steel (AISI-304) were used to ensure the uniform distribution of the pressure applied onto the SPE using springs fixed at the edges of the current collectors. The configuration of the membrane electrode assembly (MEA) fabricated in the present study is presented in Fig. 2.

The electrochemically active centers of an SPE cell using electrolyte-free water are formed only in those regions of the electrode surface which maintains an intimate contact with the SPE [1,2,4]. Therefore, a pressure of 0.5 kgf cm^{-2} was applied by fastening spring-loaded screws (a clamping system) fixed in the current collectors in order to promote adequate mechanical/electrical contact at the porous electrode/SPE interface. This procedure ensured