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Electrochemical Behaviour of Porous PbO_2 Layers Prepared by Oxygen Bubble Templated Anodic Deposition

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ABSTRACT

Porous PbO_2 layers were produced from methanesulfonic acid or perchloric acid media, through an oxygen bubble templated anodic deposition process, i.e. by oxidizing Pb^{2+} ions at large current densities, with simultaneous oxygen evolution. The effect of deposition current density, Pb^{2+} concentration and nature of the acid on the deposit porosity (assessed through number of pores per unit surface area, average pore diameter, and void volume fraction) were investigated. Porous PbO_2 deposits obtained from both media consisted of the same mixture of α- and β-phases, although the corresponding compact deposits had significantly different structures (pure α-PbO_2 from methanesulfonic acid, a mixture of α- and β- PbO_2 from perchloric acid). The cycling behaviour of compact and porous PbO_2 layers in 1.0 M H_2SO_4 was compared. During the first cycle, the reduction charge was much higher for porous than for compact layers, as a consequence of the different electrochemically active areas. For the former it depended on the layer thickness, while it was independent of it for the latter. Upon cycling, the charges exchanged by compact layers steadily increased, whereas those of porous layers, after an initial increase, slowly declined, but remained markedly higher.

1. Introduction

In a recent communication [1], our group has reported the oxygen bubble templated anodic deposition of porous PbO_2. In this process, large anodic currents were imposed to the working electrodes, immersed in acid Pb^{2+} solutions, causing the simultaneous occurrence of two electrochemical reactions: Pb^{2+} ions were oxidized to PbO_2 at their diffusion limited current density and oxygen was vigorously evolved. Under appropriate conditions, the PbO_2 deposits grew around the O_2-bubble template and became significantly porous. Thus, the oxygen bubble templated deposition of porous PbO_2 was the anodic analogue of the more common hydrogen bubble templated electrodeposition of porous metals, recently reviewed by Plowman et al. [2], in which the morphology of the metal layers was governed by cathodically generated hydrogen bubbles. An advantageous feature of gas bubble templated deposition processes over methods employing solid templates was that no action was needed to remove the template, once the deposition was completed.

The size of the pores caused by the gas bubbles in both PbO_2 and metal/alloy deposits was markedly distributed, both across their surface and along their thickness. Therefore, the PbO_2 layers described in [1] had a much less regular morphology, and globally larger pores, than those prepared by Bartlett et al. [3] using self-assembled polystyrene spheres (500 to 750 nm diameter) as templates. A major difference between porous PbO_2 and most H_2-templated porous metals/alloys was that the former exhibited only the micron-scale porosity induced by oxygen bubbles, but not the nano-scale porosity currently observed with the latter. This difference was probably caused by different nucleation and growth modes of metals/alloys and oxides, the former being more prone to undergo dendritic growth at high current density. Due to the absence of nano-scale porosity, the void volume fraction of porous PbO_2 was only slightly higher than 0.5 [1], as compared to 0.85–0.90 for metals [4]. Analogously, their surface roughness factor was estimated in the range 15 to 20, comparable to that obtained by electrodeposition of PbO_2/PbO_2 composites [5], and well below the typical values of metal/alloy layers with comparable thickness (100-300) [4].

Some recent reports [6–9] on the indirect preparation of porous oxides demonstrate the widespread interest in these materials. Porous SnO_2 [6] and CuO [7] were prepared by annealing the corresponding electrochemically deposited porous metals. Porous

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hydrous ruthenium oxide was obtained by electrodepositing porous Cu-Ru alloys, selectively dealloying Cu and then annealing the resulting porous Ru [8]. In a two-step process, conceptually similar to oxygen bubble templated anodic deposition, Hu et al. [9] prepared porous ε-MnO_2. In the first step, O_2 bubbles formed and remained attached to the electrode surface; in the second step, oxide deposition occurred around the gas bubbles, at a lower potential. However, the MnO_2 layers acquired a compact morphology when their electrodeposition was protracted.

Among the metal oxides, PbO_2 is especially interesting for electrochemical applications, e.g. in energy storage, as inexpensive anode material, or as versatile matrix for oxide-oxide composites [10–13]. Therefore, the work preliminarily described in [1] was extended, with two main aims: achieving a better control on the properties of the deposits and investigating the cycling behaviour of porous PbO_2 in 1.0 M H_2SO_4, in the potential range where the $PbO_2/PbSO_4$ interconversion takes place. In the present paper we report on results achieved by using methanesulfonic acid media, deeply investigated in recent years [14–18], and perchloric acid media which were shown to produce PbO_2 deposits with large surface area at low anodic current densities [19,20], and were used for depositing H_2-templated porous Pb [21].

2. Experimental

The electrodes used as anodes for PbO_2 deposition were: (i) Ni rotating disc electrodes (RDE 0.317 cm^2, 900 rev min^{-1}); (ii) Au rotating disc electrodes (0.0314 cm^2, 900 rev min^{-1}); (iii) Ni sheets (1 cm^2); (iv) Au sheets (1 cm^2). The current densities reported in this paper always refer to the geometric area of the electrodes. The Ni electrodes were polished with abrasive paper; Au electrodes were polished with 1 μm Al_2O_3. Au was preferred to Ni in long cycling experiments involving oxidation of $PbSO_4$ to PbO_2, to minimize side reactions, e.g. oxygen evolution. In all other experiments, the same results were obtained with Au and Ni electrodes.

The PbO_2 layers were electrodeposited from a perchloric acid medium, 0.05 M $Pb(ClO_4)_2$, 0.6 M $HClO_4$, and from two methanesulfonic acid media with different Pb^{2+} concentrations, i.e. 0.05 M $Pb(CH_3SO_3)_2$, 0.6 M CH_3SO_3H, or 0.20 M $Pb(CH_3SO_3)_2$, 1.1 M CH_3SO_3H. Electrolyses were performed under galvanostatic control using a Pb sheet counterelectrode in a single-compartment cell. The electrolytic solutions were either quiescent or magnetically stirred when RDEs or sheet electrodes were respectively used, and were maintained at 25 °C with a thermostat. The deposition current density j_D was varied in a wide range to obtain layers with different porosities. As reported in [1], ahead of applying the large j_D necessary to cause the growth of porous oxide, thin PbO_2 films (deposition charge 1.0 C cm^{-2}) were deposited onto the electrodes, at low current density (j_D = 0.01 or 0.02 A cm^{-2}), to improve the adhesion.

The current efficiency of the PbO_2 deposition (ε) was measured with both RDEs and sheet electrodes. For the former it was obtained from the Q_{Red}/Q_D ratio, where Q_{Red} was the reduction charge of PbO_2 to a soluble Pb^{2+} species measured in the same electrolyte used for the electrodeposition, and Q_D the charge spent for deposition (including contributions of Pb^{2+} oxidation and oxygen evolution). For the latter it was obtained gravimetrically, i.e. as the ratio between the measured PbO_2 mass and the theoretical mass calculated assuming 100% efficiency for Pb^{2+} oxidation to PbO_2.

Voltammetries aimed at measuring the charge for the reduction of PbO_2 in CH_3SO_3H or $HClO_4$ solutions were performed in a two-compartment cell, using a Pt wire as counter electrode and an Hg/Hg_2SO_4/0.5 M H_2SO_4 reference electrode, inserted in a separate compartment, filled with CH_3SO_3H or $HClO_4$ solutions, connected to the main one through a glass frit. A similar arrangement, with the reference electrode directly inserted in the main compartment, was used for repetitive reduction/oxidation cycles in 1.0 M H_2SO_4.

An Autolab PGSTAT 302 N was used to perform all electrochemical tests. It was equipped with a booster, used for electrodepositing PbO_2 onto sheet electrodes, at high current density. The morphologies of the PbO_2 layers, either as-prepared or after cycling in H_2SO_4, were determined with a FEG-ESEM FEI Quanta 200 F instrument, equipped with a field emission gun, operating both in high and low (120 Pa) vacuum conditions. SEM images were analysed with the Genesis Particles Analysis 6.0 software (EDAX Inc., 2008) to obtain information on the number and dimension of the pores. Using images with an enhanced contrast, the pores, which appeared dark on the images, were approximated with circles. The analysis yielded the number of pores per unit surface and the average pore diameter.

X-Ray diffractograms were obtained, using PbO_2 coated sheet electrodes, with a Philips X-PERT PW3710 diffractometer, with a Bragg-Brentano geometry, employing a CuKα source (40 kV, 30 mA). The PbO_2 phases were identified and, when possible, the crystallite dimensions were estimated by Rietveld analysis, performed through the Maud software [22].

3. Results and Discussion

3.1. Preparation and characterization of porous PbO_2

Methanesulfonic acid and perchloric acid solutions were chosen as PbO_2 deposition baths after an initial screening that included other acid media, like nitrate/acetate or sulphamate [1], and concentrated alkali. Porous PbO_2 layers were obtained from all acid media, however their adhesion to the Ni or Au substrates was much better when CH_3SO_3H and especially $HClO_4$ were used. Porous deposits were not obtained from basic media, under the conditions that we explored.

Fig. 1 shows linear sweep voltammograms recorded with an Au RDE (at two rotation rates: ω = 900 or 3600 rev min^{-1}) in a 0.05 M $Pb(CH_3SO_3)_2$, 0.6 M CH_3SO_3H solution at a low scan rate (1 mV s^{-1}). For comparison, a curve obtained in 0.6 M CH_3SO_3H with a PbO_2-coated RDE is also shown; an almost identical curve was obtained with bare Au in the Pb^{2+}-free solution. In the potential range from

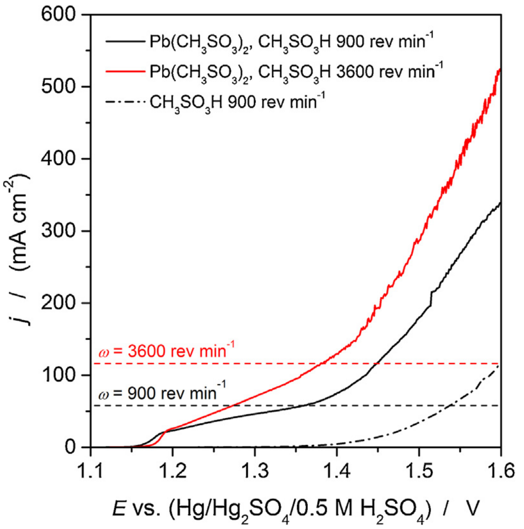

Fig. 1. Linear sweep voltammograms recorded with an Au RDE in 0.05 M $Pb(CH_3SO_3H)_2$, 0.6 M CH_3SO_3H (solid lines) or with a PbO_2 coated Au RDE in 0.6 M CH_3SO_3H (dash-dot line) with a 1 mV s^{-1} scan rate. Rotation rates are indicated on the figure. The horizontal dashed lines show calculated limiting current densities for Pb^{2+} diffusion at 900 or 3600 rev min^{-1}.