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Oxygen bubble–templated anodic deposition of porous PbO_2

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ABSTRACT

The oxygen bubble–templated deposition of porous PbO_2 was realized by anodizing Pb(II) solutions (in nitrate-acetate, sulfamate or methanesulfonate media) at large current density. This process is the anodic analogue of the more common hydrogen bubble–templated electrodeposition of porous metals. The porous PbO_2 layers consisted of a mixture of α- and β-phases, in contrast to compact layers deposited at low current density (pure α-PbO_2). The void volume fraction and surface roughness factor of porous PbO_2 were estimated.

1. Introduction

The hydrogen bubble–templated electrodeposition of porous metals and alloys has been extensively investigated in recent years [1]. In this process, an electrolysis performed at high current density causes simultaneous metal ion reduction and hydrogen evolution, leading to the formation of highly porous metal films on the cathode, normally consisting of nanocrystals. Some metals, for example, Sn [2], Ru [3] and Cu [4], have been converted to their oxides through annealing steps, maintaining their original bimodal porosity. In principle, metal oxide porous films might be produced directly at the anode, by oxidation of low-valence cations, under conditions of intense oxygen evolution. To the best of our knowledge, such a process, which would be the anodic analogue of hydrogen bubble–templated cathodic deposition of metals, has never been explored. Therefore, we undertook the investigation described below, aimed at realizing the oxygen bubble–templated anodic deposition of porous PbO_2. Owing to possible uses of PbO_2 in energy storage and as inexpensive anode material, obtaining this oxide with a high surface roughness may be of practical interest [5,6]. Hu et al. [7] prepared porous ε-MnO_2 using a similar method. However, in their work, O_2 bubble formation and oxide deposition were achieved in separate, successive steps.

2. Experimental

Most PbO_2 layers were electrodeposited from a 0.20 M $Pb(CH_3SO_3)_2$, 1.1 M CH_3SO_3H electrolyte, under galvanostatic control onto Ni face-down RDEs ($0.317\ cm^{-2}$, $900\ min^{-1}$) using a single-compartment cell, with a Pb sheet counterelectrode, at 25 °C. PbO_2 layers used for the measurement of their thickness (by SEM) and in XRD experiments, were deposited onto vertical Ni sheet electrodes ($1\ cm^2$). Ahead of applying the large j_D expected to cause the growth of porous oxide, a thin PbO_2 film (deposition charge $Q_D = 1\ C\ cm^{-2}$) was deposited onto Ni electrodes, polished with abrasive paper, at low current density ($j_D = 0.02\ A\ cm^{-2}$) to improve the adhesion. Two other electrolytes were also tested: (i) 0.45 M $Pb(NO_3)_2$, 0.065 M $Pb(CH_3COO)_2$ and (ii) 0.50 M $Pb(NH_2SO_3)_2$, 0.20 M NH_2SO_3H.

Electrochemical tests were performed with an Autolab PGSTAT 302 N. The morphologies of the PbO_2 films were determined with a FEG-ESEM FEI Quanta 200F instrument, equipped with a field emission gun, operating in high vacuum conditions. X-ray diffractograms were obtained with a Philips X-PERT PW3710 diffractometer, employing a CuKα source (40 kV, 30 mA).

3. Results and discussion

Fig. 1a–b show that porous PbO_2 layers were obtained in CH_3SO_3H medium, at large current density. They adhered well to Ni and, besides pores with a mouth diameter of a few micrometres, exhibited some cracks. Comparable layers were deposited from nitrate-acetate or sulfamate baths, but using these media some detachment was observed.

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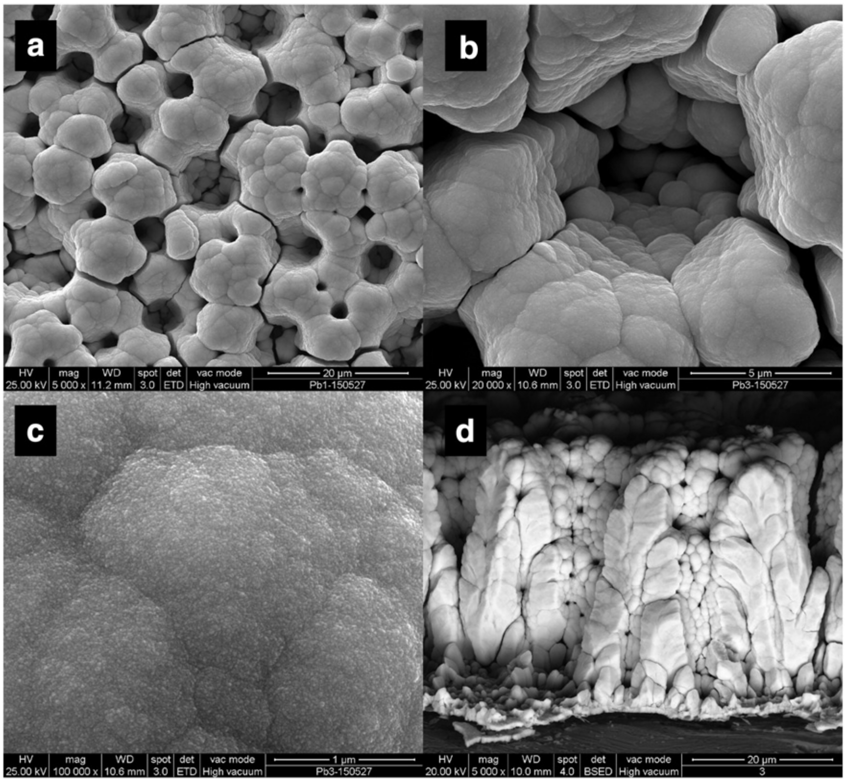

Fig. 1. SEM images of porous PbO_2 deposited in 0.20 M $Pb(CH_3SO_3)_2$, 1.1 M CH_3SO_3H electrolyte, at $j_D = 3$ A cm^{-2}.

The formation of powders was negligible in all media. Fig. 1c, obtained with a larger magnification, reveals a microcrystalline structure of PbO_2 without a nano-scale porosity comparable to that of metal deposits. This result is ascribed to different electrocrystallization kinetics of PbO_2, as compared to metals, and to its lower tendency to undergo dendritic growth. The cross-sectional image in Fig. 1d shows pores as deep as the layer thickness and somewhat branched. According to Hu et al. [7], the growth of thick MnO_2 layers caused the disappearance of O_2 bubble–induced macropores when bubble formation and oxide deposition were separate steps. This SEM study suggests that PbO_2 has a lower void volume fraction and less strongly interconnected neighbouring pores than most porous metal layers described in the literature [1–4]. Some nano-scale porosity was visible in the SEM images of porous ε-MnO_2, reported by Hu et al. [7].

The void volume fraction, computed from the deposit mass (M) and volume (V) as

$$f_V = 1 - \frac{M}{\rho V} = 1 - \frac{M}{\rho A d} \tag{1}$$

where A is the electrode area, d the layer thickness and $\rho = 9.38$ g cm^{-3} the PbO_2 density, was in the range from 0.52 to 0.56, for j_D between 1.0 and 3.0 A cm^{-2}. Typical values found for porous metals were 0.8 to 0.9 [8].

To evaluate the current efficiency of the process, PbO_2 layers were cathodically stripped in the CH_3SO_3H solution where they had been grown. Fig. 2a shows the stripping voltammetries of layers deposited at $j_D = 0.02$, 0.50 and 3.0 A cm^{-2} (with $Q_D = 30$ C cm^{-2}). The onset potential of PbO_2 reduction was more positive when j_D was large enough to cause the growth of porous layers. At the end of the cathodic scan, minor residual deposits were still detected on the Ni surface, in agreement with Li et al. [9]. The stripping charge was used to calculate the j_D dependence of the current efficiency of the deposition/stripping cycle, as shown in Fig. 2b (full symbols). The empty symbols in the same figure, corresponding to efficiencies calculated from Q_D and M, show efficiencies systematically higher by a few percent. The efficiency decline at larger j_D was obviously due to the stronger contribution of oxygen evolution. SEM images, see insets, showed that PbO_2 was compact

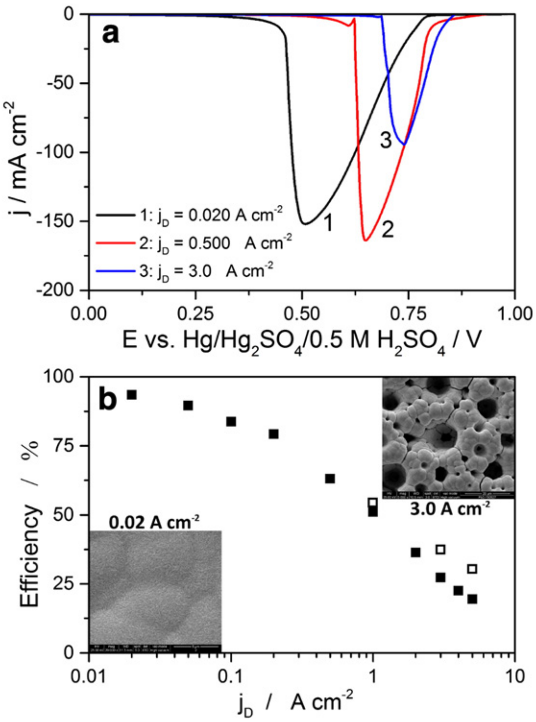

Fig. 2. (a) Stripping voltammograms of PbO_2 deposits in CH_3SO_3H medium. Scan rate 1 mV s^{-1}. (b) Dependence of the current efficiency of PbO_2 deposition on j_D, measured from stripping (full symbols) or gravimetric data (empty symbols). The insets show SEM images of layers deposited at $j_D = 0.02$ or 3.0 A cm^{-2}.