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Research paper

Preparation of porous oxide layers by oxygen bubble templated anodic deposition followed by galvanic displacement

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A R T I C L E   I N F O

A B S T R A C T

Galvanic displacement reactions between porous PbO_2, prepared by oxygen bubble templated anodic deposition, and the low-valent cations Mn^{2+}, Co^{2+} and Sn^{2+}, have been studied using electrochemical methods, SEM-EDS and XPS. These reactions occur at open circuit by immersion of PbO_2 coated electrodes in aqueous solutions of the cations and lead to the formation of outer oxide layers onto porous PbO_2, whose composition and chemical nature have been assessed by XPS. The growth of the outer oxide layers has been studied by combining Evans' diagrams with SEM-EDS and XPS results, as a function of experimental variables, such as the chemical nature of the cations, their concentration and the solution temperature. The combination of oxygen bubble templated anodic deposition and galvanic displacement provides a route for the preparation of porous low-conductivity electroactive oxides not attainable by direct electrodeposition. Deposition of Co_3O_4 thin layers by galvanic displacement results in a strong enhancement of the activity of porous PbO_2 electrodes in the oxygen evolution reaction.

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1. Introduction

During the last three decades, galvanic replacement reactions have been extensively used in the preparation of electrocatalysts based on nanostructured materials, mainly metal nanoparticles [1–7]. In those reactions, nanoparticles of a sacrificial, less noble metal undergo oxidation by the cations of a nobler metal, and are progressively dissolved, while the noble metal forms a deposit on them. The formation of an alloy between sacrificial and noble metals may be an intermediate step of the overall process that proceeds then to complete replacement of the sacrificial metal, with formation of noble metal nanoparticles. Oh et al. [8] have recently reported on the extension of galvanic replacement to the synthesis of metal oxide nanocrystals. These authors described in detail the reaction of Mn_3O_4 nanocrystals with $Fe(ClO_4)_2$ solutions, to yield Fe_2O_3 nanocages, and showed that similar processes occurred when either Mn_3O_4 or Co_3O_4 nanoparticles reacted with

$SnCl_2$ solutions. In a recent preliminary account [9], our group reported on the reaction between porous PbO_2 layers and Mn $(CH_3COO)_2$ solutions. The basic chemistry involved in this process was the same as in Oh et al. paper [8], though with different chemicals and different dimensions of the solid objects (layers some μm thick in our work, nanoparticles in theirs).

Our work described in [9] aimed at exploring a new approach to the preparation of porous oxide layers potentially interesting for electrochemical applications. Porous PbO_2 layers were prepared by oxygen bubble templated anodic deposition [10,11]. In this process, analogous to the more common hydrogen bubble templated electrodeposition of porous metals [12–16], but occurring at the anode, PbO_2 was deposited from Pb^{2+} solutions at large current densities that caused simultaneous, extensive oxygen evolution. We showed that porous PbO_2 layers prepared by oxygen bubble templated anodic deposition exchanged much larger charges than compact layers with identical mass, when cycled in H_2SO_4 solutions, due to their enhanced surface area [11]. Porous layers of other metal oxides would be interesting as electrode materials. However, the oxygen bubble templated anodic deposition of porous oxides cannot be extended to compounds whose electrical resistivity, significantly higher than that of PbO_2, prevents the use

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of large current density. Thus, we investigated a two-step process, by combining oxygen bubble templated anodic deposition and galvanic displacement. The latter step may be generally represented by equation (1)

$$PbO_2 + mM^{n+} + \frac{mn-2}{2}H_2O \rightarrow M_mO_{\frac{mn+2}{2}} + Pb^{2+} + (mn-2)H^+ \quad (1)$$
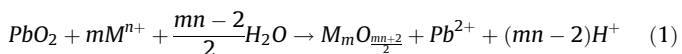
where PbO_2 represents a porous layer and M^{n+} a low-valent cation that can be oxidized to a solid oxide in a spontaneous reaction that takes place at open circuit. Our preliminary report concerned this two-step preparation route, for $M^{n+} = Mn^{2+}$ [9], and showed that an amorphous Mn oxide outer layer formed onto PbO_2. Since the PbO_2 layers were not entirely replaced by the new oxide, we preferred to call the process "galvanic displacement", rather than "galvanic replacement", and we maintain the same wording here.

In the present paper, we largely extend the scope of our preliminary study [9] by describing new results about galvanic displacement reactions between porous PbO_2 and three cations, Mn^{2+}, Co^{2+} and Sn^{2+}, focusing on the following issues:

(i) Kinetics of growth of the outer layers, studied by SEM.
(ii) Effect of experimental variables, such as M^{n+} ion nature, ion concentration and temperature.
(iii) Chemical nature of the compound(s) constituting the outer layers, studied by XPS (this information could not be achieved by XRD of amorphous layers [9]).
(iv) Partial reactions that combine in the galvanic displacement process, studied with electrochemical methods currently used in corrosion research.
(v) Electrochemical behaviour of modified PbO_2 porous layers in the oxygen evolution reaction (OER).

We show that thermodynamic considerations help in assessing the feasibility of oxide-oxide galvanic displacement reactions, but do not allow the prediction of the thickness of the outer layers that are formed. This work provides new insight on the oxides chemical nature, their growth mechanism, and their possible electrochemical activity.

2. Experimental

PbO_2 porous layers were deposited onto different electrodes: (i) Ni disc electrodes (0.317 cm^2) polished with abrasive paper and used as RDE at 900 rev min^{-1}; (ii) stationary Au screen-printed electrodes (discs with a 0.125 cm^2 geometric surface area, manufactured by DropSens, Oviedo, Spain). Electrodeposition of PbO_2 was performed in 0.05 M Pb(CH$_3$SO$_3$)$_2$, 0.60 M CH$_3$SO$_3$H, with a two-electrode configuration, at 1 A cm^{-2} anodic current density (referred to the electrode geometric surface area). Other experimental details were reported in [10,11], where it was shown that PbO_2 deposits with the same morphology were obtained onto Ni or Au.

Galvanic displacement reactions were carried out by immersing the PbO_2-coated electrodes, at open circuit, in the following solutions:

for $M^{n+} = Mn^{2+}$, either 0.20 M Mn(CH$_3$COO)$_2$, 0.20 M CH$_3$COOH or 0.02 M Mn(CH$_3$COO)$_2$, 0.20 M CH$_3$COOH, 0.40 M NaCH$_3$COO (both pH 4.8 ± 0.1);

for $M^{n+} = Co^{2+}$, 0.20 M Co(NO$_3$)$_2$, 0.02 M CH$_3$COOH, 0.20 M NaCH$_3$COO (pH 4.8 ± 0.1);

for $M^{n+} = Sn^{2+}$, 0.02 M Sn(CH$_3$COO)$_2$, 0.10 M HClO$_4$. Only in this case the solution was purged with N$_2$.

The temperature of the solutions used in galvanic displacement reactions, controlled with a thermostat, was varied between 25 °C and 75 °C. The potential of the PbO_2-coated electrodes was monitored during the galvanic displacement process with respect to a mercurous sulphate electrode (MSE).

The electrocatalytic activity of pristine and modified PbO_2 porous electrodes in the OER was tested by recording linear voltammograms in 1.0 M NaOH at 25 °C, with a 1 mV s^{-1} scan rate.

Electrochemical tests were performed with an Autolab PGSTAT 302N. Pseudo-steady-state current-potential curves for both PbO_2 reduction and divalent cations oxidation were recorded with 1 mV s^{-1} scan rate. The reduction of PbO_2 was performed either in 0.20 M CH$_3$COOH, 0.4 M NaCH$_3$COO, or in 0.1 M HClO$_4$, 0.04 M NaCH$_3$COO. The oxidation of Mn^{2+}, Co^{2+} or Sn^{2+} was carried out in the same solutions used in galvanic displacement reactions, using a stationary Ni disc electrode (for Mn^{2+}, Co^{2+}, at pH 4.8) or 0.0314 cm^2 Au disc electrode (for Sn^{2+}, at pH 1.0).

SEM images and EDS analyses were obtained with a FEI Quanta 200 FEG ESEM instrument, equipped with a field emission gun, operating at an accelerating voltage variable in the range of 20–30 kV. Cross-sectional images of modified PbO_2 layers were recorded with samples obtained by fracturing Au screen-printed electrodes.

XPS analyses were performed with a Perkin-Elmer Φ 5600-ci spectrometer using Al Kα radiation (1486.6 eV). The sample analysis area was 800 μm in diameter. Survey scans were obtained in the 0−1350 eV range (187.8 eV pass energy, 0.8 eV step^{-1}, 0.05 s step^{-1}). Detailed scans were recorded for the C1s, O1s, Pb4f, Mn2p, Mn3s, Co2p and Sn3d regions (23.5 eV pass energy, 0.1 eV step^{-1}, 0.1 s step^{-1}). The standard deviation for the BEs values was ± 0.2 eV. The experimental uncertainty on the reported atomic composition values did not exceed ± 5%. The XPS spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f$_{7/2}$ line at 83.9 eV with respect to the Fermi level. The BE shifts were corrected by assigning to the C1s peak associated with adventitious hydrocarbons a value of 284.8 eV [17]. Samples were mounted on steel holders and introduced directly in the fast-entry lock system of the XPS analytical chamber. The data analysis involved Shirley-type background subtraction, non-linear least-squares curve fitting adopting Gaussian-Lorentzian peak shapes, and peak area determination by integration [18]. The atomic compositions were evaluated from peak areas using sensitivity factors supplied by Perkin-Elmer, taking into account the geometric configuration of the apparatus [19].

3. Results and Discussion

3.1. Galvanic displacement reactions between PbO_2 and low-valent cations

Porous PbO_2 layers were prepared according to the procedures described in [10,11], i.e. by galvanostatic electrolyses carried out at large current densities in Pb(CH$_3$SO$_3$)$_2$, CH$_3$SO$_3$H solutions. Anodic current density and deposition charge were fixed at 1 A cm^{-2} and 26 C cm^{-2}, respectively. The resulting porous layer thickness was between 16 μm and 18 μm.

Galvanic displacement reactions involving Mn^{2+} or Co^{2+} were carried out in moderately acid acetate solutions because both divalent cations and the Pb^{2+} ions formed by PbO_2 reduction were soluble in those media. A more acid medium, pH 1, was required for the PbO_2/Sn^{2+} reaction, to prevent Sn^{2+} hydrolysis: at that pH value, the concentration of Sn^{2+} in equilibrium with SnO was just above 0.1 M [20], ca. 5 times higher than the Sn^{2+} concentration we employed. The solution volume and the divalent cation concentrations were both large enough to allow the successive reaction of many PbO_2 samples, without significant change in Mn^{2+}, Co^{2+} or Sn^{2+} concentrations. We had no evidence that accumulation of minor amounts of Pb^{2+} in solution affected the galvanic displacement reactions.