



Preparation of porous nanostructured Ag electrodes for sensitive electrochemical detection of hydrogen peroxide



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ABSTRACT

Porous Ag layers have been prepared by hydrogen bubble templated electrodeposition from an ammonium acetate bath, under application of a large current density (-2 A cm^{-2}). SEM images of the layers show macroscopic porosity and a spongy dendritic structure, analogous to those observed for other porous metals/alloys deposited with a similar procedure. A deposition charge of 30 C cm^{-2} produces a porous deposit with a mass of ca 1.7 mg cm^{-2} . The roughness factor f_r is evaluated by impedance and from the charge density of Pb UPD; both methods provide estimates of f_r in the order of several hundreds but values obtained from impedance analysis are more than twice larger. Mass transport to the porous electrodes is studied by linear sweep voltammetry at stationary and rotating disk electrodes. In comparison with flat Ag cathodes, porous Ag electrodes show larger sensitivity, lower limit of detection and extended range of linear response in H_2O_2 reduction.

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1. Introduction

Porous electrodes have attracted much interest due to their good performances in numerous applications like reactors, fuel cells, batteries, sensors. An established preparation method is based on slow metal electrodeposition through solid templates and final removal of the latter, typically by etching or dissolution [1]. This method allows deposition of many materials including alloys and noble metals, and provides excellent control of shape, size and organisation of the deposit [2–7].

An alternative approach is the so-called hydrogen bubble templated electrodeposition of porous metals, that exploits the actions of confinement and stirring provided by gas evolution during polarisation [8]. The method may be used for the cathodic deposition of porous layers of various metals including Cu, Sn, Ni, Co, Pb, and of several alloys [8 and references therein]. The deposit morphology is less controlled than that obtained using solid templates, but is nonetheless favourable to the use as electrode, since the obtained materials show large area, hierarchical porosity and increased transport to the electrode. With this method we have recently deposited porous Cu alloys, used for cathodic

reduction of nitrate in alkaline solutions [9–12]. Furthermore, we extended the method to the symmetrical anodic process, the deposition of a porous conductive oxide (PbO_2) in a regime of vigorous oxygen evolution [13].

Cathodic electrodeposition of spongy metals is not generally applicable, and for some time it was considered impossible for noble metals [14]. Recently, Cherevko et al. have reported on the electrodeposition of Ag foams [15,16] from a bath developed for deposition of compact Ag [17,18], containing a large concentration of KSCN as complexing agent for silver ions. We propose here the deposition of porous Ag from a simpler deposition bath based on silver and ammonium acetate. Acetate is a mild complexing agent warranting the necessary solubility of Ag^+ ions and providing a stable clear bath. Porous Ag electrodes are characterized and then tested in the reduction of H_2O_2 showing, in comparison with massive flat Ag electrodes, improved performances that appear promising in the search for efficient H_2O_2 detection [19–24].

2. Experimental

2.1. Chemicals, materials and instrumentation

Deposition baths and stock solutions for electroanalysis were prepared from deionized water (Elga-Veolia Purelab Pulse system, resistivity $\rho > 15\text{ M}\Omega\text{ cm}$) and high purity chemicals (Sigma-Aldrich-Fluka), used without further purification. H_2O_2

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solutions for analytical determinations were prepared from a freshly purchased Fluka solution 30%, puriss. p.a.; H_2O_2 concentration was checked by titration with permanganate [25]. Electrochemical determinations of H_2O_2 were performed in a deaerated buffer solution containing 0.1 M KH_2PO_4 + 0.1 M K_2HPO_4 ($\text{pH} \cong 7$), henceforth called 0.2 M PBS. A stock solution containing 0.35 M H_2O_2 in 0.2 M PBS was freshly prepared daily.

Porous Ag layers were deposited on Cu and Au substrates. Deposition on Ag substrates gave poor results, not reported. Most electrodepositions were performed on Cu rotating disk electrodes (RDEs, area 0.283 cm^2), inserted in a plastic sheath and mounted on a EDI 101 rotating unit (Radiometer). Depositions aimed at the gravimetric estimate of efficiency and the recording of XRD spectra were performed on Cu sheets (area 1 cm^2). Some porous layers were deposited onto screen-printed Au electrodes (SPEs, area of 0.125 cm^2), purchased from DropSens, (Oviedo, Spain). Henceforth, we call porous Ag RDEs those deposited on Cu RDEs, porous Ag SPEs those deposited on Au SPEs. A Ag disk electrode (area 0.317 cm^2), polished with alumina down to 0.3 μm , was used for comparison in some experiments. All current densities and deposition charges refer to geometric area.

Electrochemical experiments were controlled with an Autolab PGSTAT 302N, equipped with a booster providing currents up to 10 A. EIS investigations were performed with a Solartron 1286 Electrochemical Interface and a Solartron 1254 FRA, both controlled by a ZPlot-ZView commercial software. Measurements were taken over the frequency range 10 kHz to 0.01 Hz, with 8 points per decade; the potential modulation was 10 mV rms, low enough to ensure linear response. SEM images were recorded 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. A few X-Ray Diffraction patterns (not reported) were taken as described elsewhere [11].

2.2. Methods and procedures

Electrodeposition of porous Ag layers was performed from a bath containing 30 mM Ag acetate + 2 M ammonium acetate ($\text{pH} \cong 7$). The single compartment cell was equipped with a Pt wire counter electrode wound as a spiral and fixed to the inner cell wall. All depositions were made under galvanostatic control, with an optimal current density of -2.0 A cm^{-2} . RDEs were rotated at 900 rev min^{-1} ; when stationary electrodes were used, solutions were stirred with a magnetic bar. Deposition charges were varied in the range 10–45 C cm^{-2} .

EIS, voltammetric and chronoamperometric experiments were performed under potentiostatic control, using a saturated calomel reference electrode (SCE, $E = 0.241 \text{ V}$ vs NHE, normal hydrogen electrode), placed in a bridge connected to the working compartment by a Luggin capillary or a glass frit. All potentials are referred to SCE.

For the estimation of roughness factor, the response of porous and flat polished Ag electrodes was compared for two types of data: i) EIS spectra, recorded in deaerated 0.1 M NaOH ($E = -0.4 \text{ V}$ vs SCE); ii) charges of Pb UPD measured during cyclic voltammeteries (CVs), performed in a deaerated electrolyte with 12 mM Pb (NO_3)₂ + 0.1 M HCl.

The reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ was investigated by linear sweep voltammetry (LSV) in neutral deaerated 1 M KCl at (stationary) flat Ag disk and porous Ag SPEs. H_2O_2 reduction was studied by LSV and chronoamperometry (CA), at controlled temperature (20 °C), in deaerated 0.2 M PBS. In CAs, the electrode was polarised in deaerated 0.2 M PBS ($E = -0.9 \text{ V}$), and the current was recorded while making multiple additions of H_2O_2 stock solution with a micropipette.

3. Results and discussion

3.1. Electrodeposition of porous Ag layers. SEM characterization

Electrodeposition of porous metals by the hydrogen bubble templated method is normally performed from acid solution. When a neutral pH is required for the stability of the bath, a large NH_4^+ concentration is frequently necessary to obtain a spongy deposit. In their work, Cherevko et al. have reported deposition of porous Ag from a thiocyanate bath [15,16], showing that $c_{\text{NH}_4^+} \geq 0.5 \text{ M}$ was necessary to warrant good results. We took this finding as a starting point and aimed at obtaining the deposition from a simpler bath. Use of nitrate baths was discarded because nitrate reduction causes a large local production of OH^- and suppression of H_2 evolution. The use of perchlorate baths (30 mM Ag perchlorate, 2 M ammonium perchlorate) was explored but produced deposits with unsatisfactory morphology. Good results were obtained using a bath containing 30 mM Ag acetate + 2 M ammonium acetate ($\text{pH} \cong 7$), henceforth named “acetate bath”.

Concerning the choice of substrates, attempts with Ag failed as the deposits showed low porosity. Good results were obtained on

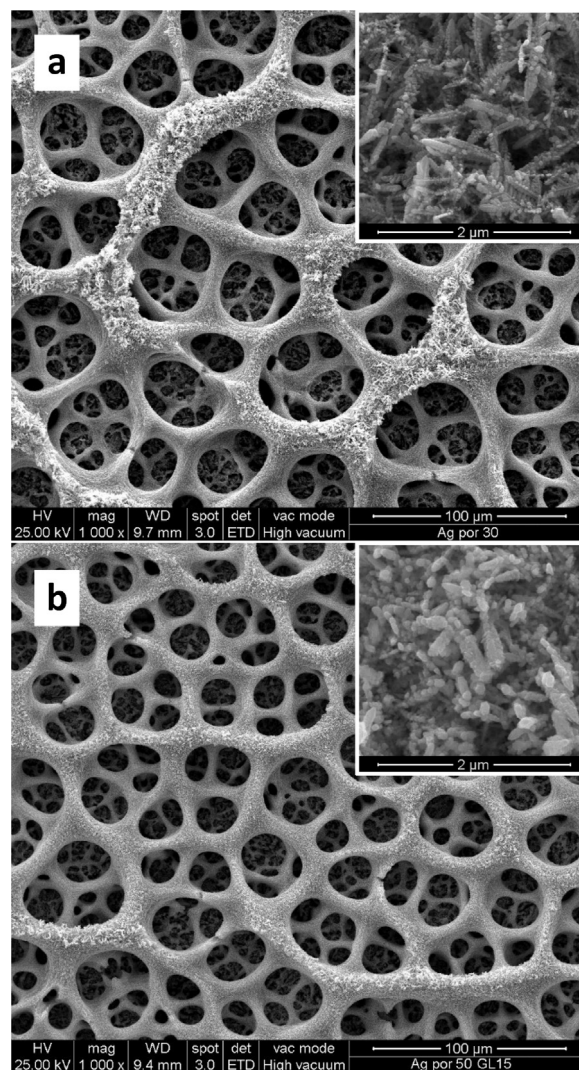


Fig. 1. SEM images of porous Ag films deposited under galvanostatic polarisation on Cu RDEs ($j = -2 \text{ A cm}^{-2}$, 900 rev min^{-1}) from: a) 30 mM Ag acetate + 2 M ammonium acetate, deposition charge 30 C cm^{-2} , efficiency about 5%; b) 30 mM Ag acetate + 2 M ammonium acetate + 15% w/w glycerol, deposition charge 50 C cm^{-2} , efficiency about 3%. Insets show details of the regular spongy structures.

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