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Synthesis of porous thin silver films and their application for hydrogen peroxide sensing

Elżbieta Kurowska-Tabor[a], Karolina Gawlak[a], Katarzyna Hnida[b,1], Marian Jaskuła[a], Grzegorz D. Sulka[a,*,1]

[a] Department of Physical Chemistry and Electrochemistry, Faculty of Chemistry, Jagiellonian University in Krakow, Ingardena 3, 30060 Krakow, Poland
[b] AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, A. Mickiewicza 30, Krakow, Poland

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ABSTRACT

Porous thin silver films were fabricated by electrochemical deposition of Ag-Zn alloys followed by a selective dealloying of zinc component. The Ag-Zn alloys were synthesized at various operating conditions including: different Ag^+/Zn^{2+} molar ratio in the electrolyte (1:1 and 1:3), current density (0.2–20 mA cm^{-2}), and time of electrodeposition (5–60 min). The deposited thin alloy films were characterized with scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The effect of dealloying time on morphology of resulting films was studied. The formation of alloys and their chemical composition were confirmed by XRD and EDS spectra. The developed porous thin Ag film electrode showed good electrocatalytic activity toward reduction of hydrogen peroxide. The influence of interfering compounds such as ascorbic acid, uric acid and glucose was studied. The proposed method with amperometric detection was applied with success, satisfying accuracy and precision to determination of hydrogen peroxide in real samples.

1. Introduction

In recent years, there has been a renewed interest in porous materials for use as catalysts [1], gas sensors [2], heat exchangers [3], supercapacitors [4], and membranes in fuel cells [5]. Porous materials offer a broad spectrum of applications due to their remarkably physical, chemical, biological and mechanical properties resulting from high surface to volume ratio, low density, controlled active sites morphology and size distribution, as well as better control over the pore physical, chemical and hydrothermal stability [6]. Principally, nanostructured metallic electrodes, offering excellent thermal conductivity, catalytic recyclability, high mechanical rigidity and chemical stability, are widely used in electrocatalysis [7]. Moreover, the direct formation of porous metal films on the electrode surface is advantageous for a rapid transfer of electronic response from the surface to the substrate in comparison with electrodes consisting of current collector coated with nanostructured materials [8,9].

Among different methods used for synthesis of porous metallic materials, a dealloying process seems to be the most straightforward and effective approach. In general, it is based on selective chemical etching of alloys, e.g., porous silver was formed from Au-Ag alloys [10,11]. The dealloying of Ag-Zn alloys is not broadly reported in the literature, however some reports can be found. In the literature, the dealloying by a simple immersion in 1 M HCl for 45 days and electrochemical polarization in 3.5 wt.% NaCl at a critical potential were reported for Ag-Zn alloys formed by sintering of silver and zinc powders [12]. Using 5 wt.% H_2SO_4, Jia et al. performed the chemical dealloying of the Ag-Zn alloy obtained by thermal alloying of the silver foil with the electrodeposited thin Zn layer [9]. On the other hand, the electrochemical dealloying of Ag-Zn alloys by anodic polarization of alloyed electrodes at critical potentials in H_2SO_4 solutions [13] and ionic liquids [14] was also described. In these cases, the Ag-Zn alloy electrodes were obtained by induction melting from zinc granules and silver plates [13] or by electrodeposition performed in a zinc chloride-1-ethyl-3-methylimidazolium chloride ionic liquid [14].

Over the last decade, a considerable interest in the accurate and rapid determination of hydrogen peroxide (H_2O_2) has been risen notably due to the fact that it is an essential mediator in food, pharmaceutical, clinical and environmental analyses [15,16]. Moreover, hydrogen peroxide is a common end product in many enzymatic reactions, thus its concentration may be used as a direct indicator of the reaction progress. The sensitive and selective

* Corresponding author.
E-mail address: sulka@chemia.uj.edu.pl (G.D. Sulka).
[1] ISE member.

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determination of H_2O_2 is of greatly practical importance, and many research groups have been working on development of new methods for its determination. Numerous analytical strategies have been used for this purpose. Among them, the use of electrochemical techniques that employ simple and inexpensive electrodes, seems to be the most promising strategy for the reliable and accurate determination of hydrogen peroxide. These methods give results very quickly and can be used in direct and real-time measurements [17,18]. On the other hand, relatively inexpensive metallic electrodes provide a long time stability of electrochemical sensors. In addition, the presence of nanosized objects (pores, particles and wires) in the structure of metallic electrodes offers a new basis to electrochemical sensors. Such optimized unmodified catalytic electrodes decrease the overpotential for the desired reaction path of many analytes. Moreover, noble metal nanopore, nanowire or nanoparticle array structures improve electrochemical properties of electrodes and sensitivity of the electroanalytical method, due to their large specific surface areas, nano confined spaces (nano-confinement effect), and excellent electrical conductivity [19–22].

According to the available literature, the electrochemical deposition of silver-zinc alloys was not extensively studied, and there are only a few papers reporting this process [23–28]. In the present work we described initially the preparation of silver-zinc alloys by electrodeposition from an aqueous solution, and then their chemical etching resulting in porous thin Ag layers. We evaluated also the analytical performance of the prepared porous thin Ag films and used them as new electrodes for the electrocatalytic determination of hydrogen peroxide.

2. Experimental

2.1. Chemicals and materials

A copper foil (0.5 mm thick, 99.9%) was used as a substrate for the fabrication of porous thin silver films. A commercially available solution containing 28.7 g dm^{-3} Ag^+ (Alfa Aesar, the main component $KAg(CN)_2$) and $Zn(CN)_2$ (98%, POCh S.A.) were used for the synthesis of thin silver-zinc alloyed films. The following reagents and chemicals were used for other measurements: H_3PO_4 (85 wt.%, POCh S.A.), H_2SO_4 (96 wt.%, Merck), H_2O_2 (30 wt.%, Chempur), Na_2HPO_4 (POCh S.A.), $NaH_2PO_4{\cdot}2H_2O$ (Chempur). All chemicals and solvents were analytical grade (unless it is otherwise noted) and all the solutions were prepared with fourfold distilled water.

2.2. Fabrication of porous thin silver films

2.2.1. Polishing of copper specimens

Prior to electrodeposition of Ag-Zn alloys, copper specimens were electropolished in a mixture of 250 cm^3 85 wt.% H_3PO_4 and 100 cm^3 distilled water at the current density of 100 mA cm^{-2} for 120 s, and then chemically polished in 0.5 mol dm^{-3} H_2SO_4 for 60 s. The electropolished Cu samples with working surface area of 0.5 cm^2 were coated with a 40 nm thick Ag layer by sputter deposition (2 min, 25 mA, Sputter Coater Emitech K575x). Next, the Ag layer was thickened (to about 400 nm) by electrodeposition for 1 min in a typical three-electrode system with a counter Pt electrode and a reference Pt electrode at the constant potential of −0.9 V. The SEM image of thickened Ag layer is shown in Fig. S1A (Supplementary content).

2.2.2. Electrodeposition of thin silver-zinc films

The electrodeposition of Ag-Zn alloys was carried out using the electrolyte prepared by dissolving an appropriate amount of $Zn(CN)_2$ in a commercially available Ag^+ solution in order to achieve a desired molar ratio of Ag^+/Zn^{2+} (1:1 or 1:3). The pH of the solution to the value of 13.2 was adjusted by adding 65 g dm^{-3} NaOH. As substrates for electrodepositions polished and then Ag-covered Cu specimens were used. The Ag layer was sputtered on Cu specimens in order to avoid a displacement of silver on copper (cementation process). The use of non-covered Cu specimens is not recommended because the displacement process might occur after immersing specimens into the electrodeposition bath. To find the optimal conditions of Ag-Zn alloys electrodeposition, different parameters such as the applied current density (0.2–20 mA cm^{-2}), deposition time (5–60 min) and the electrolyte composition were examined. The thickness of thin Ag-Zn films electrodeposited from the electrolyte with the Ag^+/Zn^{2+} molar ratio of 1:3 at −12 mA cm^{-2} was about 4 μm (Fig. S1B and S1C, Supplementary content).

2.2.3. Chemical etching of silver-zinc films

The deposited thin Ag-Zn films were subjected to selective dealloying of zinc in 5 wt.% H_2SO_4 at room temperature. To determine the effect of etching time on porosity of resulting thin films, the deposited Ag-Zn alloys with the molar ratio of Ag^+/Zn^{2+} of 1:3 were dealloyed for 0–80 min at the time interval of 20 min.

2.3. Apparatus and measurements

The morphology and chemical composition of silver-zinc alloys and porous thin silver films were characterized by using a field-emission scanning electron microscope (FE-SEM/EDS, Hitachi S-4700 with a Noran System 7).

The electrodeposition of Ag-Zn alloys was carried out at room temperature by using the EG&G 273A potentiostat/galvanostat (Princeton Applied Research).

The electrochemical measurements were performed with a potentiostat/galvanostat (Reference 3000, Gamry) using a conventional three-electrode cell consisting of the porous Ag electrode as the working electrode, a Pt counter electrode, and a saturated calomel reference electrode (SCE). During undepotential deposition (UPD) measurements, cyclic voltammograms for as-deposited and dealloyed samples were recorded at a scan rate of 100 mV s^{-1} in the electrolyte containing 0.1 M HCl and 0.1 mM Pb$(NO_3)_2$ at the potential range of −0.6 to 0 V vs. SCE. To determine the electrochemically active surface area of electrodes, linear voltammetric scans with 5 mV s^{-1} were performed between −0.48 and −0.2 V vs. SCE. Charges obtained for lead stripping were corrected by subtracting the charge associated with any background process in the absence of lead ions in solution. The amperometric response of the porous Ag electrode to hydrogen peroxide was investigated at room temperature by successive addition of 0.5 mM H_2O_2 to a continuous stirred 25 cm^3 of 0.01 M phosphate buffer solution (pH 7.4) at −0.2 V vs. SCE. Before experiments the solution was deaerated by bubbling with argon for 20 min and argon atmosphere maintained during the whole measurements.

3. Results and Discussion

3.1. Electrodeposition of Ag-Zn alloys

It is widely recognized that cyanide baths are the most promising for deposition of finely crystalline coherent both Ag and Zn thin layers [29]. Therefore, cyanide-based electrolytes were used for the codeposition of zinc with silver. In order to increase dissolution of zinc cyanide in the aqueous solution, NaOH was added to the electrolytes [29]. This process involves shifting the equilibrium towards the reduced amount of cyanide zinc complex and increased concentration of zincate ion. Achieving a relatively high zinc content in Ag-Zn alloys is crucial for obtaining porous Ag