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PVD fabrication of lead film electrodes and their catalytic adsorptive stripping voltammetric performance in the presence of oxidants

Andrzej Bobrowski[a], Agnieszka Królicka[a,*], Julia Śliwa[a], Jerzy Zarębski[a], Marta Januś[b], Karol Kyzioł[b]

[a] Department of Building Materials Technology, Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Mickiewicza 30, 30-059 Krakow, Poland

[b] Department of Physical Chemistry and Modelling, Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland

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ABSTRACT

For the first time, lead film electrodes resistant to the action of oxidants commonly used to enhance the catalytic electrochemical response were deposited physically from a gaseous phase on thick film gold substrates and applied in catalytic adsorptive stripping voltammetry (CAdSV). The newly developed multilayer electrodes comprising a glass slide, an adhesive layer of titanium, a gold layer and finally, the working layer of lead were characterized by excellent CAdSV performance. Their sensitivity and reproducibility improved further after thermal pretreatment. The proposed sensor was sensitive (LOD = 0.002 μg L^{-1}; t_{acc} = 30 s) and the cobalt response was very reproducible (2.3%) and depended linearly on cobalt concentrations within the range of 0.06–1.05 μg L^{-1}.

1. Introduction

In recent years, electrochemical sensors have been a field which has experienced very rapid development. The general trend, which is related to the ongoing process of reducing the impact of scientific activity on the environment, seems to be the production of miniaturized, integrated multi-electrode planar devices working with portable potentiostats [1]. Such electrodes (individual working electrodes or integrated three-electrode devices) may be fabricated using several methods. Of these, screen printing physical vapor deposition (PVD) seems to be the most significant. Screen-printed electrodes (SPEs) are constructed by depositing various conducting and insulating inks on the surface of an inert substrate (preferably polymeric or ceramic materials) [2–7]. The particles of noble metals or carbon are dispersed in selected solvent-dispersant-binder mixtures [8]. The insufficient resistance of the binders to the action of various chemicals is often responsible for the progressive deterioration of the cohesion of the printed layers and their adhesion to the substrate. In the case of layers deposited by means of PVD methods [9], there is no need to apply organic binders, solvents or adhesion promoters, which is desirable, since they may interact with certain chemicals. Before PVD, the support is cleaned and roughened via plasma etching. Occasionally, to provide good adhesion before the deposition of the final layer (e.g. gold), the deposition of one or more intermediate metallic layers is needed (Ti or Cr). If this is performed correctly, the auxiliary layers do not hinder the performance of the final layer. PVD-manufactured electrodes were applied for the stripping voltammetric determination of metal ions in both anodic [10–24] and adsorptive stripping modes [9,13,14,25–29], using films composed of bismuth [10–13,15,17–19,23–28], antimony [16,29], tin [14,21,22], platinum [30] and gold [31] deposited on oxidized silicon wafers [10–14,16,22,25,26], chromatography paper [21,35], or carbon tape [20] supports. Laboratory-made as well as commercially available electrodes comprising a bismuth layer sputtered on aluminum oxide have also been used [15,17–19,29]. The voltammetric applications of PVD electrodes have not been limited to metal ions, but also allowed the determination of hydrogen peroxide [30], uric acid [32], pesticides [33], bisphenol A [34] and DNA [35].

The use of catalytic action induced in the presence of oxidants (e.g. nitrates, iodates, bromates) to amplify the analytical signals is widely appreciated among electroanalysts [36–39]. Although SPEs and electrodes produced via PVD have been successfully applied in stripping voltammetry, so far none of them have been applied in catalytic adsorptive stripping voltammetry (CAdSV), the technique renowned for its extraordinary sensitivity. This might be due to the fact that – according to our unpublished research – the oxidants present in solutions have a tendency to damage the active layer of the working electrode,

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[*] Corresponding author.
E-mail address: krolicka@agh.edu.pl (A. Królicka).

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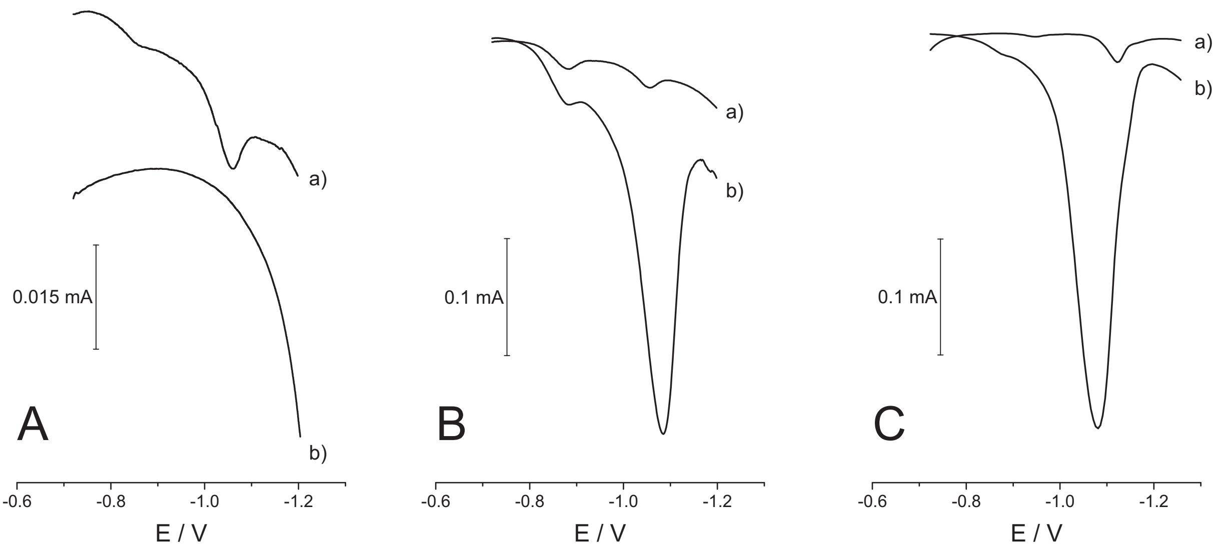

Fig. 1. DP-AdSV curves of Co(II) recorded in solutions containing equal concentrations of both Co(II) and Ni(II) ions without (a) and after the addition of 0.2 M $NaNO_2$ (b), using: (A) 20 μg L^{-1} and Pb/C-SPE, (B) 20 μg L^{-1} and Pb/Au-SPE, and (C) 0.75 μg L^{-1} and thermally treated Pb/Au/Ti-glass electrodes. Supporting electrolyte: 0.2 M ammonia buffer, $5·10^{-5}$ M nioxime. Accumulation potential: (A) −0.72 V or (B,C) −0.65 V. Accumulation time: (A) 120 s or (B,C) 30 s.

preventing a catalytic signal from being recorded. Consequently, the presented study was aimed at investigating the possibility of using lead films deposited on carbon and gold supports via PVD to determine cobalt by means of a CAdSV procedure [40–42] involving the presence of nioxime (DMG) as a ligand and nitrite as an oxidant.

2. Experimental

2.1. Apparatus and instrumentation

Electrochemical measurements were performed using an Autolab PGSTAT204 (Nova 1.10.1.9 software) potentiostat with a standard three-electrode configuration. Screen-printed electrodes (DRP-C110 carbon electrode and DRP-C220AT gold electrode – both 4 mm in diameter) were provided by Dropsens, Spain. The morphology of the deposits was evaluated using a Nova NanoSEM 200 (FEI, USA) scanning electron microscope (SEM).

2.2. Chemicals

All solutions were prepared using deionized water with a resistivity of 18.2 MΩ (Millipore, Simplicity UV). A 2 M ammonia buffer with a pH of 8.7 was prepared by mixing an appropriate amount of NH_4Cl with a 25% ammonia solution (Suprapur, Merck). A 0.01 M nioxime solution was prepared by dissolving an appropriate amount of the reagent in 0.1 M NaOH. $NaNO_2$ (analytical grade, POCH, Poland) was crystallized twice from water. Standard solutions of Co(II) and Ni(II) at a concentration of 1 g L^{-1} (Merck) were diluted as required. The metallic coatings were deposited using targets of pure Ti, Au and Pb (99.99%).

2.3. PVD lead deposition on different substrates

In all experiments, the PVD procedure was used for lead film deposition.

2.3.1. C-SPE and Au-SPE

The lead layers were deposited on the surface of the carbon SPE and Au-SPE (working electrode only) without any pretreatment, via magnetron sputtering physical vapor deposition (MS PVD) in an argon atmosphere. A vacuum apparatus (Elettorava S.p.A., Turin, Italy) operating at a constant current of 2 kW was used in this procedure.

2.3.2. Au/Ti/Glass

As the second type of substrate, BK-7 optical glass (25x75x1mm) slides were used. The slides were grooved (0.7 mm in depth) to obtain 25 × 10 × 1 mm electrodes using a precision dicing saw (DAD 2H6T, Disco, The USA). First, a thin layer of titanium (ca. 20 nm thick) was deposited, and then titanium layer was coated with gold, using electron-beam physical vapor deposition (Integrity 29, Denton Vacuum, The USA), until the total thickness of ca. 120 nm was obtained. Finally, the glass slides covered with titanium and gold were coated with lead using resistive thermal evaporation (NA 501 P, ZAP Bolesławiec, Poland).

2.3.3. Voltammetric procedure

Prior to the electrochemical tests, the lead-coated electrodes were immersed in the tested solution for 1 min. The accumulation potential of −0.65 V or −0.72 V was then applied for 120 s or 30 s and a voltammogram was recorded starting at the accumulation potential and up to −1.2 V. During accumulation, the solution was stirred using a magnetic stirrer.

The electrochemical investigations were carried out by means of differential pulse adsorptive stripping voltammetry (DP-AdSV). The parameters of the DPV mode were as follows: modulation amplitude, 50 mV; modulation time, 50 ms; potential step, 4 mV; equilibration time, 5 s; interval time, 0.5 s.

3. Results and discussion

3.1. Electrochemical properties of lead-coated electrodes depending on type of substrate

Lead layers were deposited via PVD on three different types of substrates: carbon screen-printed electrode (C-SPE), gold screen-printed electrode (Au-SPE) and a glass slide coated with titanium and gold (Au/Ti/glass). All examined lead film electrodes performed well when tested as working electrodes in the adsorptive stripping voltammetry of Co-nioxime and Ni-nioxime systems (Fig. 1A–C, curves (a)), with results comparable to electrochemically deposited lead films [43,44]. To evaluate the performance of the investigated Pb film electrodes in catalytic adsorptive stripping voltammetry, $NaNO_2$ was added to the supporting electrolyte and voltammograms were recorded. Fig. 1A shows that when using the Pb/C-SPE, the Co and Ni signals observed