



A novel screen-printed electrode modified with lead film for adsorptive stripping voltammetric determination of cobalt and nickel



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ABSTRACT

The paper presents the first report on the preparation of an in situ plated lead film screen-printed electrode (PbF-SPE) and its application for adsorptive stripping voltammetric determination of nickel and cobalt in the form of the complexes with dimethylglyoxime. The lead film was electrochemically deposited in situ on a commercially available three-electrode screen-printed electrochemical strip from a 0.2 M ammonia buffer solution (pH 8.2) containing 4×10^{-5} M $\text{Pb}(\text{NO}_3)_2$ and 1×10^{-5} M dimethylglyoxime. The composition of the supporting electrolyte and the influence of accumulation time on the stability of the lead coating and on the sensitivity and reproducibility of Ni and Co responses are discussed. The repeatability of the Ni(II) and Co(II) adsorptive stripping voltammetric signals obtained at the lead film screen-printed electrode were equal to 4% and 3%, respectively ($n=10$). The limits of detection established for simultaneous determination of Ni and Co for 90 s of accumulation time were 0.2 and $0.3 \mu\text{g L}^{-1}$, respectively. Voltammetric studies were complemented with optical and scanning microscopic observations.

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1. Introduction

Screen-printed electrodes are electrochemical sensors that are expected to be widely used in numerous real-life applications such as biology, medicine, environmental protection, and electronics [1–3]. Thanks to mass production and relatively low costs SPEs can be disposed of after a single use. Moreover, integrated screen-printed electrodes comprising 3-electrodes on one strip may be used when working with microvolumes of samples, which decreases the volume of the used solutions and generated waste. In contrast to other solid electrodes such as disk electrodes made of glassy carbon or noble metals, SPEs do not require mechanical polishing.

The application of SPEs as sensors in the stripping voltammetry of metal ions usually requires the modification of the carbon surface in SPEs with a thin metal film consisting of mercury, gold, silver, bismuth or other materials, which can improve selectivity and sensitivity of the determination. The simplest modifications of SPEs include in situ or ex situ electrochemical deposition of the metal film on the carbon SPE support. However, metal bulk-modified SPEs are also fabricated by mixing the graphite carbon ink with metal precursors (metal oxides or salts), and printing the mixture onto

the working surface of the SPE strip. The application of such an SPE sensor requires the preliminary reduction of metal ions to metallic film directly before or during the stripping voltammetric measurements. The screen-printed carbon electrode can also be modified by coating with metal nanoparticles.

Solutions of mercury ions or mercury oxides were the first ones that were used to obtain in situ, ex situ or bulk-modified SPEs [1–4]. However, the storage and utilization of SPEs modified with mercury is hazardous due to the toxicity of mercury and its salts, and consequently poses a significant threat to human and animal health and the environment. These problems were avoided by using electrodes modified with films composed of other, less volatile and less hazardous metals, mainly bismuth [5–7], antimony [6,8] and tin [9]. These metals are less toxic than mercury, and their toxicity to a large degree depends on the target organism, elements' speciation, route of exposure, and chronic or acute poisoning [10]. Based on LD_{50} values for water-soluble acetates the toxicity of the mentioned metals diminishes in the following way: $\text{Hg}(\text{II})$ (40 mg/kg) \gg $\text{Sn}(\text{IV})$ (980 mg/kg) $>$ $\text{Sb}(\text{III})$ (3730 mg/kg) $>$ $\text{Pb}(\text{II})$ (4665 mg/kg) $>$ $\text{Bi}(\text{III})$ (5000 mg/kg), indicating that Sb, Pb and Bi are two orders of magnitude less toxic than mercury [11]. The BiF-SPEs have found application mainly for the anodic stripping voltammetric determination of Cd, Pb, and Zn [for examples, see 7,12–18].

Most recently, the lead film SPE modified ex situ and in situ has been proposed for the anodic stripping voltammetric determination of zinc ions [19]. It had earlier been shown that lead film

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electrodes deposited on glassy carbon [20], carbon paste [21] or gold supports [22] could successfully be used for the determination of selected heavy metals including nickel and cobalt [19–24].

So far, only a few papers have described the application of modified SPEs for the AdSV determination of metals such as chromium [25] and nickel [26,27]. The cited procedures for nickel determination by means of AdSV at the SPEs exploited the SPEs based on dimethylglyoxime-containing carbon ink [26] or those modified with bismuth nanoparticles [27]. To the best of our knowledge, SPEs have so far not found application in the determination of Co traces.

In our work the preparation of the lead film screen-printed electrode (PbF-SPE) for adsorptive stripping voltammetric determination was undertaken. As an electrode material utilized for film generation on the surface of carbon supports lead is a less toxic substitute for mercury, and lead film electrodes have been shown to be more useful than mercury-based and environmentally friendly bismuth-based electrodes in adsorptive stripping voltammetry of Co and Ni. Furthermore, lead and inorganic lead salts are much less volatile than mercury and its salts. In laboratory practice the solutions and wastes containing lead are more controllable than the readily evaporating mercury and its salts, which makes the handling of lead compounds safer than that of mercury. The lead film was deposited in situ on the surface of the commercially available carbon SPE. The optimal conditions for the determination of Ni and Co in the form of DMG complexes, including the composition of the supporting electrolyte and the instrumental parameters, were selected. Another objective of the paper was to characterize the surface properties (topography, morphology) of the deposited lead films by means of optical and SEM microscopic techniques.

2. Experimental

2.1. Apparatus

All experiments were carried out using an Autolab PGSTAT 20 apparatus in connection with DropSens DRP 154 electrode which was covered with lead film. The GPES 4.4 software was used to record, save, and process the collected data. A magnetic stirrer and classic glass cell of volume 10 ml were used.

2.2. Reagents

All solutions were made using deionized water with a resistivity of 18.2 M Ω (Millipore, Simplicity UV). 2 M ammonia buffer (pH 8.2) was prepared by mixing the corresponding amounts of NH₄Cl and ammonia solution (Suprapur, Merck). 0.01 M dimethylglyoxime (DMG) solution was prepared by dissolving an appropriate amount in NaOH (0.1 M, analytical grade) or in ethanol. A standard solution of Ni(II) and Co(II) at concentration 1 g L⁻¹ were obtained from Merck and diluted as required. 0.01 M Pb(II) solution was prepared by dissolving an appropriate amount of Pb(NO₃)₂ in deionized water. The addition of NH₃ or HCl was used to obtain the required pH of the supporting electrolyte. The electrochemical measurements were carried out in undeaerated solutions.

2.3. Measurements procedure

2.3.1. In situ lead plating

The SPE electrode was cleaned by applying the following sequence of potentials: (a) –1.45 V for 20 s, (b) 0.5 V (1 s) and –0.5 V (1 s) potential steps applied alternately as one step; total number of steps: 30. Immediately after cleaning, the potential of –1.3 V was applied for 20 s (lead nucleation) followed by deposition of lead with simultaneous adsorption of Ni-DMG and Co-DMG complexes at –0.8 V for 60 s or 90 s. During all steps the solution was stirred

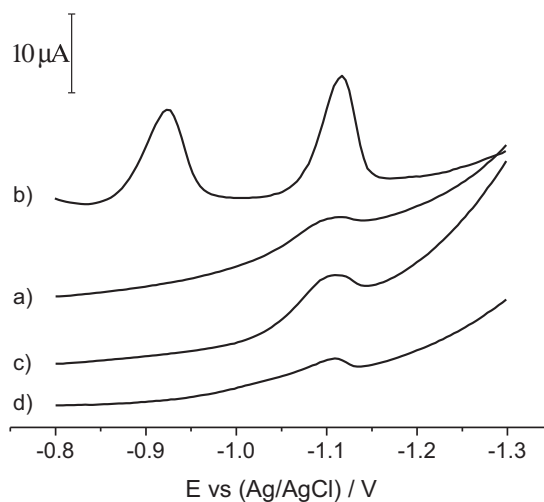


Fig. 1. Square wave adsorptive stripping voltammograms of the solutions containing: 5×10^{-7} M Ni and 5×10^{-7} M Co, 1×10^{-5} M DMG, 0.2 M ammonia buffer, pH 8.2 at the bare SPE (a), at the PbF-SPE plated in situ after an addition of 4×10^{-5} M Pb(II) to the investigated solution (b), PbF-SPE plated ex situ from 0.1 M acetic buffer (c) or 1 M HNO₃ (d), both containing 4×10^{-5} M Pb(II). SWV instrumental parameters: $E_{\text{acc}} = -0.8$ V, $t_{\text{acc}} = 60$ s, $t_{\text{eq}} = 5$ s, $f = 50$ Hz.

using a magnetic bar. The parameters of the SWV mode were as follows: $E_{\text{begin}} = -0.8$ V, $E_{\text{end}} = -1.35$ V, $\Delta E = 50$ mV, $E_s = 2$ mV, $t_{\text{eq}} = 5$ s.

2.3.2. Ex situ lead plating

PbF-SPEs plated ex situ were used only in preliminary studies. The lead film was plated at a constant potential of –0.8 V for 60 s in the stirred solution containing 4×10^{-5} M Pb in 0.1 M acetic buffer or 0.1 M HNO₃. The ex situ plated PbF-SPEs were then rinsed with water and tested in experiments performed by means of the procedure described above (excluding the cleaning procedure).

3. Results and discussion

3.1. Preliminary experiments

Metal films may be deposited on the support's surface in three main ways: in situ or ex situ procedures, or through the modification of the electrode surface with metal powder or insoluble metal compounds (e.g. metal oxides, salts). There are several advantages to forming an in situ film: (a) analysis time is decreased, because a separate deposition procedure is not needed, (b) the risk of damaging the film is reduced substantially, since the film electrode does not have to be transferred between different solutions, (c) cross contamination is less likely, and (d) a new film surface is generated for every analysis. However, in situ plating during co-deposition might also involve several issues. Sometimes the interaction between the film-forming metal and analyte results in multiple reaction pathways, so additional peaks or shoulders might be seen. During in situ plating there is also a risk that ineffective electrochemical cleaning will result in high coverage of support surface by insoluble debris impairing the electrode performance.

In the preliminary experiments the SW-AdSV measurements of Ni(II) and Co(II) signals in the solution containing 1×10^{-5} M DMG, 0.2 M ammonia buffer were carried out at a carbon SPE, first bare, and then ex situ or in situ modified with lead film (Fig. 1). The obtained adsorptive stripping voltammetric responses were compared in order to observe the effect of the lead films and the mode of their deposition. As Fig. 1 demonstrates, the formation of in situ lead deposits on the SPE surface facilitates the adsorption of both Ni(II) and Co(II) dimethylglyoximate complexes; it is also very likely that catalytic reduction of dimethylglyoxime ligands bound

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