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Correlation between the plating regime of lead film deposition and electrode response after accumulation of organic compound. Microscopic study

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ABSTRACT

The properties of the lead film electrode designed for adsorptive stripping voltammetric measurements of organic compounds were examined by electrochemical and microscopic techniques. The effect of Pb(II) concentration, the influence of deposition potential and time of the lead film formation on the determination of bleomycin at an in situ lead-coated glassy carbon electrode have been studied. Atomic force microscopy (AFM) was used to characterize the Pb crystallite growth on the glassy carbon surface. The morphology of the deposits was evaluated and its influence on the bleomycin responses was discussed.

1. Introduction

Stripping voltammetry is a well-established electroanalytical technique, providing an efficient, versatile and highly sensitive method for detecting a wide range of inorganic and organic substances to concentrations as low as 10^{-10} mol L^{-1} [1]. The proper choice of the working electrode is crucial for the success of the stripping operation. The ideal working electrode should offer effective preconcentration, a favorable redox reaction of the target metal or organic compound, a reproducible and renewable surface, and a low background current over a wide potential range [2].

In the last six decades mercury electrodes have been the most extensively used for electrochemical stripping analysis of several metal ions and some selected organic compounds [3–6]. However, the toxicity and volatility of the mercury and mercury salts are the greatest drawback in the practical application of these electrodes. In addition, due to the low mechanical stability of mercury electrodes, they require special handling and their application to flow analytical systems is severely limited. Future regulations and occupational health considerations may severely limit (and even ban) the use of mercury as an electrode material. This has encouraged researchers to design new, mercury-free metallic film electrodes which could replace not only the mercury film but even the standard liquid mercury electrodes.

Great progress in the development of such a type of film electrodes has been made since 2000, when Wang's group introduced the bismuth film electrodes (on glassy carbon and carbon fiber substrates) for anodic stripping voltammetric measurements of heavy metals [7]. They have been presented in different configurations, e.g., as an in situ and ex situ bismuth film electrode (BiFE) [7–9], a bismuth bulk electrode (BiBE) [10], a bismuth powder modified carbon paste electrode (Bi-CPE) [11], etc. Recently, the antimony film electrode (SbFE) was suggested as another alternative that approaches the electroanalytical performance of mercury- and bismuth-based electrodes [12–15].

In 2005, a new type of electrode, the lead film electrode (PbFE), was proposed for the determination of inorganic ions [16–18] and organic compounds [19–25]. The proposed electrode exhibited interesting characteristics, such as lower toxicity compared to the mercury electrodes, a wide potential window and the ability to operate in a wide range of pH media, simple preparation, good reproducibility and a simple way of electrochemical surface renewal. The measurements with using PbFE can be performed in undeaerated solutions. The organic compounds accumulated at a lead film electrode can be reduced or oxidised in the stripping step. Additionally, the lead film electrode was used for the determination of organic substances in pharmaceutical formulations and human urine samples, directly without any separation steps. In the proposed procedures the time needed for sample preparation was considerably reduced, because the determinations can be performed in the presence of insoluble matter. The lead film electrode can be applied as a detector in flow-injection analysis.

Recently, microscopic and electrochemical characterization of lead film deposited in situ on a glassy carbon electrode in ammonia buffer solutions, the media typically used in adsorptive stripping voltammetric measurements carried out to quantify Co and Ni,

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was described [26]. In the case of determination of organic compounds at the lead film electrode an acetate buffer is usually used as a supporting electrolyte. It is obvious that the knowledge of the surface characteristics of an electrode is the crucial point for successful research work in both theoretical electrochemistry and applied electroanalysis. Due to those facts, the aim of this paper was the application of atomic force microscopy (AFM) to obtain information about the morphology of the lead film deposited in situ in mild acidic media. In this work special attention was paid to show the influence of the plating regime of lead film deposition on the structure of the deposited layer and on the electrode response after accumulation of the organic compound.

2. Materials and methods

2.1. Reagents

An acetate buffer, used as a supporting electrolyte for the proposed method, was prepared from CH_3COOH and NaOH obtained from Merck. The standard of bleomycin was obtained from Fluka. A stock standard solution of bleomycin (7.06×10^{-4} mol L^{-1}) was prepared by dissolving the reagent in deionized water (Millipore quality) and stored at 4 °C in the dark until used. Deionized water (Millipore quality) was used for further dilution.

2.2. Apparatus

All voltammetric measurements were performed using a μAutolab analyser made by Eco Chemie, the Netherlands. A classical three-electrode quartz cell of volume 10 mL was used throughout, consisting of a modified glassy carbon (LF/GCE) working electrode, with an Ag/AgCl reference electrode and a platinum wire as an auxiliary electrode. The homemade working electrode included an easy to take out disk (diameter 10 mm, thickness 5 mm) with a glassy carbon surface (diameter 1 mm). The PEEK housing was equipped with a stainless steel piston to make electrical contact with the disk. The GC electrode was polished daily using 0.3 μm alumina slurry on a Buehler polishing pad. The pH measurements were made on an Elmetron pH meter CI-316.

Atomic force microscopy (AFM) measurements were performed using a Digital Instruments NanoScope III (USA, 2001). Contact mode topographic images were recorded using Si_3N_4 probes with a spring constant of 0.05 N/m and a nominal radius of curvature 20 nm (NANOPROBE^{TM} SPM Tips, type NP-1). The images were recorded at scan areas of 10 μm × 10 μm for three randomly chosen places (512 × 512) and with the scan rate of 1 Hz. The software used in data acquisition and analysis was the NanoScope version 5.12 (Digital Instruments, Veeco Metrology Group, CA) and the Scanning Probe Microscopy Software (WSxM 4.0 Develop 8.0 June 2005, Nanotec Electronica S.L.). The composition of the samples was studied by Raman spectroscopy (Reflex inVia Raman microscope, Renishaw, UK).

2.3. Procedures

2.3.1. Deposition of lead films and accumulation of bleomycin

In voltammetric experiments the glassy carbon electrode was exposed to the test solutions containing: 0.05 mol L^{-1} acetate buffer as the supporting electrolyte, from 0 to 1.25×10^{-4} mol L^{-1} of $Pb(NO_3)_2$ and bleomycin as the organic analyte in the concentration range from 0 to 5×10^{-8} mol L^{-1}. The electrode was cleaned electrochemically after the preceding measurement by cycling 5-time of the potential between −0.53 and +0.5 V with the scan rate of 0.1 V s^{-1}. After cleaning the potential in the range from −1.0 to −1.4 V was applied to plate a lead film on a glassy carbon electrode. During the next step at potential −0.7 V for 60 s the bleomycin was accumulated by adsorption on the electrode. During all three steps the solution was stirred using a magnetic stirring bar. Then after a rest period of 5 s a square-wave voltammogram was recorded at a frequency of 200 Hz, while the potential was scanned from −0.7 to −1.5 V. The amplitude was 50 mV. The measurements were carried out in undeaerated solutions.

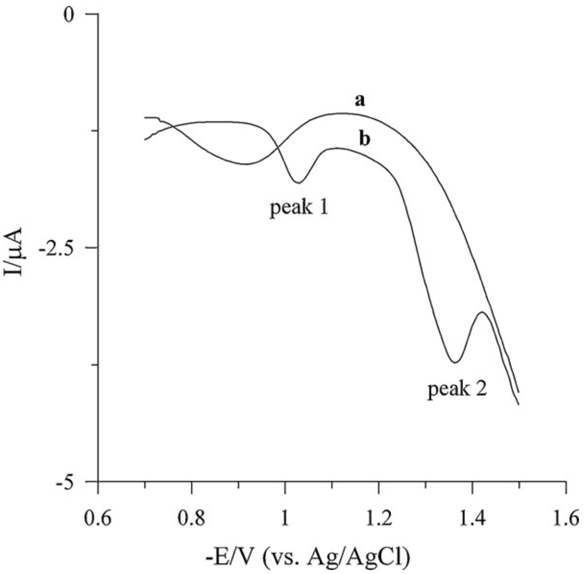

Fig. 1. Square-wave voltammograms obtained at (a) GCE and (b) PbF/GCE in a 0.05 mol L^{-1} acetate buffer (pH = 4.6) in the presence of 3×10^{-8} mol L^{-1} bleomycin. The lead film was deposited for 30 s at −1.25 V. Bleomycin was accumulated for 120 s at −0.7 V. Concentration of $Pb(NO_3)_2$ 5.0×10^{-5} mol L^{-1}. Stripping parameters: frequency 200 Hz, step height 2 mV, amplitude 50 mV.

2.3.2. Preparation of samples for microscoping

The rinsed PbF/GC working electrode was turned upwards and a disk with lead-coated surface was taken out from the housing. This sample was carefully placed in the detection chamber of the microscope.

3. Results and discussion

Preliminary electrochemical measurements were carried out in order to identify the general behaviour of bleomycin (BLM). BLM is a member of a family of structurally similar glycopeptide antibiotics recognised as antitumour drugs used in the treatment of Hodgkin's lymphoma and carcinomas of the testis, head, skin and neck [27]. Fig. 1 shows square-wave voltammograms obtained at a plain GCE and a LF/GCE in a 0.05 mol L^{-1} acetate buffer (pH = 4.6) in the presence 3×10^{-8} mol L^{-1} bleomycin, while scanning in the negative direction. At the lead film electrode two adsorptive stripping voltammogram peaks at −1.0 and −1.36 V were observed (peak 1 and peak 2). At the GCE no reduction peak of BLM was observed. The above experimental results indicate the advantages of using a lead film as a modifier of a glassy carbon electrode for determination of bleomycin. Due to this fact, this organic compound was used in further measurements to show correlation between the plating regime of lead film deposition and the electrode response and the structure of the deposited layer.

3.1. Effect of pH values of the supporting electrolyte

For determination of organic compounds at the lead film electrode an acetate buffer is usually used as the supporting electrolyte, so $CH_3COONa + CH_3COOH$ was chosen for this study. Concentrations of the acetate buffer and $Pb(NO_3)_2$ were 0.05 mol L^{-1} and