



# Screen-printed carbon electrodes modified with lead film deposited using different plating methods as sensors in anodic stripping voltammetry

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## ABSTRACT

In this work a study on the preparation and characterization of the lead film in situ and ex situ plated screen-printed carbon electrodes (PbF/SPCEs) was presented, focusing in particular on their attractive stripping analytical performance. The lead film ex situ plated screen-printed carbon electrodes were prepared using methods based on: (a) the electrochemical deposition of lead film on the screen-printed carbon electrode surface and (b) the electrochemical deposition of lead into the interstitial space of a colloidal crystal template formed on SPCE. The electrodes of interest were tested as novel, potential sensors for the anodic stripping voltammetric determination of zinc traces in nondeaerated solution of 0.01 mol L<sup>-1</sup> hydrochloric acid. A comparison, of the stripping performance between a bare screen-printed carbon electrode and the PbF/SPCEs prepared with use of the investigated plating methods revealed a distinct advantage of the lead film ex situ plated screen-printed carbon electrode prepared with the use of a colloidal crystal template. This electrode shows an increase in electrochemical performance due to the porosity that gives this material a high active surface area.

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## 1. Introduction

The beauty of electrochemical techniques is to utilize a tailor made modified electrodes for sensitive and selective analytical applications. Designing new sensors has always been one the main challenges in electroanalysis. Great progress in the development of metal film modified electrodes has been made since 2000, when Wang's group introduced a novel bismuth film electrode exhibiting an impressive electroanalytical performance which compared favorably to its mercury analog [1]. Till now, many articles have been published on the procedures of preparation, properties and application of the bismuth film electrodes [2–7]. Numerous other metal film electrodes have been also suggested and studied as substitutes to mercury based electrodes, e.g. antimony film electrode [8–12], tin film electrode [13,14] and lead film electrode [15].

The lead film electrodes (PbFEs) have several attractive properties that include the simple preparation, good reproducibility and electrochemical surface renewal, mechanical stability, ability to operate in a wide range of pH media, effective preconcentration in stripping procedures, well-defined and separated stripping signals for several metal ions and organic compounds. The measurements with using PbFEs can be performed in undeaerated solutions. Thanks to their electrochemical and mechanical properties, these

electrodes have found wide application in stripping analysis [15–21].

So far, lead films have been deposited by an in situ plating method particularly on a glassy carbon [15–18], but also on a gold [19] and carbon paste [20]. Recently, an ex situ plated lead film electrode prepared with the use of a reversibly deposited mediator metal (Zn) was introduced [21]. Additionally, the microscopic characterization of lead films deposited in situ or ex situ on a glassy carbon electrode was described [21–23]. The microscopes images showed considerable variability in microstructure and compactness of the deposited lead layer depending on the selected experimental conditions, such as the concentration of Pb(II) in the plating solutions, the applied potential and time of deposition.

Screen-printed electrodes (SPEs) have been developed as single-use, disposable sensors for a variety of applications in environmental, industrial and clinical analysis [24,25]. SPEs have low unit costs and are capable of undergoing mass production, while still maintaining adequate levels of reproducibility. They also have the advantage of miniaturization. Among numerous variants of SPEs, screen-printed carbon electrodes (SPCEs) have gained great attention because of their easy-to-make modification by immobilizing a modifier on the electrode surface or adding it in the carbon ink before the electrode is made.

A recent series of papers has reported on the elaboration of porous bismuth film electrodes and porous antimony film electrodes [26–28]. The strategy to create porous electrodes is based on the replication of colloidal templates. These electrodes show an

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increase in electrochemical performance due to the porosity that gives these materials a high active surface area.

In this paper we first report on the utilization of screen-printed carbon electrode as the support for an *in situ* and an *ex situ* plated lead film. The lead film *ex situ* plated screen-printed carbon electrodes were prepared without and with the use of a polystyrene template. The colloidal crystal templating method [26–28] was adapted in order to increase an active surface area of the lead film plated screen-printed carbon electrode. In this approach, lead is electrochemically deposited into the interstitial space of a polystyrene template. After electrodeposition of lead the polystyrene spheres are removed by washing in toluene to leave a structured electrode material on the screen-printed carbon electrodes.

The aim of this paper was to present some fundamental investigations of the electrochemical properties of the lead film plated screen-printed carbon electrodes prepared *in situ* and *ex situ* without and with the use of a polystyrene template. Scanning electron microscopy with focused ion beam (SEM/FIB) and optical profilometry were applied for initial examination of the lead film *ex situ* deposited on screen-printed carbon electrodes. To show analytical potentiality of the *in situ* and *ex situ* prepared PbF/SPCEs, these sensors were tested using solutions containing 0.01 mol L<sup>-1</sup> hydrochloric acid and variable concentrations of Zn(II). Additionally, in the case of an *in situ* prepared PbF/SPCE, Pb(II) ions, were added into the supporting electrolyte. The main aim of this paper was to suggest the best plating method for fabrication of the lead film plated screen-printed carbon electrode due to its sensitivity and low experimental deviations.

## 2. Experimental

### 2.1. Reagents

Lead(II) nitrate was purchased from Sigma–Aldrich. Nitric acid and hydrochloric acid (Suprapur®) were obtained from Merck. A standard solution of zinc at concentration of 1 g L<sup>-1</sup> was obtained from Fluka. Solutions with lower zinc concentrations were made daily by appropriate dilution of the standard solution. Monodisperse polystyrene spheres (diameter 500 nm) were prepared by surfactant free emulsion polymerization of styrene initiated by potassium peroxydisulfate [29]. All solutions were prepared in deionized water of resistivity not less than 18.2 MΩ cm<sup>-1</sup> at 298 K (Millipore, UK).

### 2.2. Apparatus

All voltammetric measurements were performed using μAutolab analyser made by Eco Chemie, The Netherlands. A classical three-electrode quartz cell of volume 10 mL was used throughout, consisting of a lead film modified screen-printed carbon electrode as a working electrode, with an Ag/AgCl reference electrode and a platinum wire as an auxiliary electrode. High-resolution microscope FEI DualBeam™ Quanta™ 3D FEG (scanning electron microscope (SEM) with focused ion beam (FIB)) was used for the electrode surface characterization. The electrode surface profile measurements were carried out using Veeco's Contour GT-K1 optical profilometer.

### 2.3. Preparation of screen-printed carbon electrodes

The screen-printed carbon electrodes were prepared using a commercial carbon ink (C10903D14, Gwent Electronic Materials Ltd., Pontypool, UK) by screen-printing of ink onto the ceramic supports (each 40 mm × 10 mm). Thick layers of the carbon ink were formed by brushing the ink through an etched stencil (thickness

100 μm, electrode printing area 105 mm<sup>2</sup>) with the aid of the spatula provided with the screen-printing device (UL 1505 A, Tesla, Czech Republic) onto the ceramic substrates. The printed electrodes were dried at 60 °C for 30 min and then were covered with layer of a PVC insulator, leaving a defined rectangular shaped (3 mm × 3 mm) working area and a similar area on the other side for electrical contact.

### 2.4. Preparation of lead film *ex situ* plated screen-printed carbon electrodes

The lead film *ex situ* plated screen-printed carbon electrodes were prepared using the conventional *ex situ* plating method and the colloidal crystal templating method. In the first one, the lead film was plated using galvanostatic electrodeposition from 1 mol L<sup>-1</sup> solution of HNO<sub>3</sub> containing 0.1 mol L<sup>-1</sup> Pb(NO<sub>3</sub>)<sub>2</sub> at a constant current of –1.2 mA. The second method is based on the electrochemical deposition of lead into interstitial spaces of a template formed by polystyrene spheres. Approximately 30 μL of the suspension of polystyrene spheres diluted with water to 0.5 wt% were spread over the area of the screen-printed carbon electrode surrounded by a teflon ring (0.07 cm<sup>2</sup>). Then the suspension was allowed to dry over 2 days in a humidity chamber. The lead film was then plated using galvanostatic electrodeposition from 1 mol L<sup>-1</sup> solution of HNO<sub>3</sub> containing 0.1 mol L<sup>-1</sup> Pb(NO<sub>3</sub>)<sub>2</sub> at a constant current of –1.2 mA after a 15 min waiting time to ensure penetration of the electrolyte into the whole colloidal crystal template. After the deposition of Pb atoms the electrode was rinsed with deionized water and then the polystyrene template was removed by washing in toluene.

### 2.5. Procedure of *in situ* deposition of lead film and measurements at *in situ* prepared PbF/SPCE

An aliquot of the analyzed sample was pipetted into the electrochemical cell and deionized water was added to the volume 9.825 mL. Then, 100 μL of 1 mL HCl and 75 μL of 0.01 mol L<sup>-1</sup> Pb(NO<sub>3</sub>)<sub>2</sub> were added. In the course of Zn(II) determination the potential of the electrode was changed in the following sequence: +0.5 V for 30 s and –1.4 V for 60 s. The first step was applied to clean the electrode surface after the preceding measurement. During the second step, the lead and zinc were co-deposited on the electrode. During both steps, the solution was stirred using a magnetic stirring bar. Then, after a rest period of 10 s the anodic differential pulse voltammograms were recorded between –1.4 and –0.7 V with amplitude of 50 mV and potential step of 4 mV. The measurements were carried out from undeaerated solutions.

### 2.6. Procedure of measurements at *ex situ* prepared PbF/SPCE

All voltammetric measurements at the *ex situ* lead film plated screen-printed carbon electrodes were carried out in 0.01 mol L<sup>-1</sup> HCl containing variable concentrations of Zn(II). The preconcentration potential of –1.4 V was applied for 60 s to the working electrode in order to convert the Zn(II) ions on the lead film into metal. During this step the solution was stirred using a magnetic stirring bar. Then the stirring was stopped and after 10 s equilibration time, the anodic differential pulse voltammograms were registered with amplitude of 50 mV and potential step of 4 mV. The potential was stopped at –0.7 V. This end potential was applied for 30 s between measurements for cleaning the electrode surface. All voltammetric measurements were carried out in undeaerated solutions.

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