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Short Communication

Evaluation of poly(sodium 4-styrenesulfonate) film coating in thin mercury film electrodes for lead determination

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ABSTRACT

In this work, polyelectrolyte coatings assembled on glassy carbon/thin mercury film electrodes, as an adsorbed layer of poly(sodium 4-styrenesulfonate) (PSS), were studied. The goal was to search for the best conditions for the production of stable PSS-coated electrodes that could present high negative charge densities within the thin polymeric film, providing a fast and significant electrostatic cation accumulation. Square-wave anodic stripping voltammetry was applied to measure the amount of incorporated lead used as the reference cation. The influence of the composition of the PSS solution, the amount of deposited PSS, molecular weight and of the ionic strength of the electrolyte solution, on the features of the PSS coatings for ion-exchange voltammetry was studied. The PSS films morphology was assessed by SEM. The best PSS coating performance was found for the electrodes prepared from water solutions with a molecular weight of at least 70,000, and a mass loading of *ca.* 8 μg mm^{-2}. In these conditions a three fold increase was observed in low ionic strength (0.0032 M) media. However, this improvement was not sufficient for the application of direct ion-exchange voltammetry, thus different strategies to obtain polymer films with higher charge densities have to be envisaged.

1. Introduction

The use of ion-exchange polymers for modification of electrodes and for developing electrochemical sensing devices is still an area of continuous interest, where the study of the adsorption features, structural architectures and molecular/ionic incorporation properties is of crucial importance [1–5].

In the specific case of metal cation determinations the use of adsorbed micrometer thick coatings of an ion-exchange polymer associated to a mercury film electrode, has been the method of choice. Those coatings have been produced by a one-step solvent evaporation procedure (volumetric deposition) usually on a glassy carbon electrode. Several polymers have been tested, such as the ionomers Tosflex [3], Nafion [4] and Eastman-AQ [6] or the polyelectrolytes poly(sodium 4-styrenesulfonate), PSS [5], poly-L-Lysine, PLL [7], poly(allylamine hydrochloride), PAH [8] and mixtures of PSS with Nafion [9]. In this context, the main advantage of ionomers over polyelectrolytes is their higher insolubility in the aqueous media generally used for the determinations. However, as a drawback the volume concentration of ion-exchange groups for ionomer coatings is much lower than in typical polyelectrolytes. Although being water soluble, PSS was successfully used to coat a glassy carbon/thin mercury electrode (GC/TMFE) and applied to the square-wave anodic stripping voltammetry (SWASV) of trace metals in estuarine waters [5,10]. No leakage of PSS was detected within a one-day work.

The objective of this work is to evaluate if the PSS coatings are able to enhance the electrostatic accumulation of cations within the films, thus enlarging the voltammetric signal. If a significant amount of charge is present in the film at a not too high ionic strength the electrostatic effect will be large and the concentration of the metal cation within the film might become orders of magnitude larger than the metal in the solution (*ca.* one order of magnitude for each 30 mV difference between the bulk solution potential and the potential inside the film). Similar behaviour was observed and modelled using Donnan potential in gel layers [11]. This constitutes effectively a pre-concentration step in the PSS film, as long as the thickness of the diffusion layer associated with the time scale of the technique does not exceed the film thickness, and would be then followed by a direct voltammetric measurement. In a previous work [9] the thickness of the PSS film of 11 μm was obtained for a loading of 8.6 μg mm^{-2} which is of the same order of magnitude of the thickness of the diffusion layer for a square wave voltammetry of lead(II) performed at 25 Hz, assuming that the diffusion coefficient of lead ions in the film is the same as in solution.

This study develops an idea which arose in a related work [9] where it was found that the lead determinations using a mixed

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Nafion/PSS film (r_m 5.3) performed in the concentration range (2.00–10.0 × 10^{-8} M) showed a 23% increase in sensitivity, compared to the Nafion–TMFE.

PSS has both hydrophilic parts (sulfonate groups and their counter-ions) and hydrophobic parts (hydrocarbon backbone and phenyl groups) [12]. Strong repulsive electrostatic interactions exist between the monomeric units and this factor leads to the decrease of the backbone flexibility, inducing a regular and linear conformation of the PSS chain in aqueous solution [13]. So, in pure water PSS has a linear conformation, but highly coiled structures are observed in ionic solutions of relatively high ionic strength e.g., 0.1–2 M [14,15].

In electrostatically self assembled monolayers of PSS or other polyelectrolytes the structure and adsorption properties can be tailored by a fine control of the polyelectrolyte solution conditions [16,17]. For instance, by addition of NaCl to the casting solution, the film thickness increase and, consequently, a decrease of the charge density can be observed [16,18]. However, one must keep in mind that the resulting structures are generally dominated by internal interfaces and local interactions, differing from the corresponding volume material [19].

For adsorbed micrometer thick polyelectrolytes/polymers coatings, an evaluation of the influence of the polymer solution characteristics on the properties of the films is still needed. Some studies appeared for Nafion [20–22] and, more recently, for PLL [7], PAH [8], PSS [5], and mixtures of PSS with Nafion [9].

The ideal PSS-coated electrode would be that with the highest density of $-SO_3^-$ groups and the lowest leakage to the test solution, in order to obtain the maximum loading of divalent cations in the film, previously to the voltammetric determination.

In the present study, the incorporation features of such adsorbed PSS coatings towards lead(II) were correlated to the effects of the PSS mass loading, PSS molecular weight and concentration of the casting solution. The effect of the ionic strength of the supporting electrolyte for ion-exchange voltammetry was also analysed. The morphology of the PSS coatings was screened by scanning electron microscopy (SEM).

2. Experimental

2.1. Apparatus and electrodes

Voltammetric measurements were performed with a BAS 100B/W electrochemical analyser connected to a Cell Stand BAS-C2 (Bioanalytical Systems). The PSS coatings were prepared onto a glassy carbon disc (3 mm diameter, BAS, MF-2012). The auxiliary and reference electrodes were a Pt wire and a Ag/AgCl (sat. KCl), respectively.

Scanning electron microscopy (SEM) was conducted on an Analytical FE-SEM SU-70 Hitachi, UHR 1.0 nm/15 kV (1.6 nm/1 kV).

2.2. Reagents and solutions

Poly(sodium 4-styrenesulfonate), PSS, monomer mass: 206.20, p*Ka* = 1 [12] (M_W = 150,000; 70,000; 32,000), was purchased from Aldrich and used as received. All chemicals were of analytical reagent grade and all solutions were prepared with ultra-pure water (Direct-Q3 UV system, Millipore). Sodium chloride (Merck, Suprapur), phosphate buffer solution (0.026 mol dm^{-3} KH_2PO_4/0.041 mol dm^{-3} Na_2HPO_4, pH 7.4, ionic strength 0.14$_9$ mol dm^{-3}, Merck, Suprapur) and 1000 ppm AA-Spectrosol metal ion (Hg, Pb) standards (BDH) were also used. Stock solutions of PSS (7.0, 15, 34, 60 e 119 mM in monomer units) were prepared in pure water (absence of added electrolyte) or in phosphate buffer of different ionic strengths.

2.3. Preparation of the PSS-modified electrodes

Prior to coating, the GCE was pre-conditioned as described before [9]. The coatings were prepared by solvent evaporation placing a 5 μL microdroplet of the selected PSS solution directly on the glassy carbon surface. Then, the solvent was evaporated under a low flux air stream (*ca.* 60 °C for ~10 min). When required, the utilized polymer layer was wiped off with a wet tissue and the GC surface was re-conditioned.

For ion-exchange voltammetry, thin mercury film electrodes (TMFE) were *ex situ* plated through the PSS coating at −1.3 V for 20 s with stirring (BAS-C2 stand, position 3) in 0.12 mM mercury(II) nitrate/0.01 M nitric acid (pH *ca.* 1.9). Conventional TMFE were prepared using the same experimental conditions. The thickness of the *ex situ* plated mercury film was calculated from the charge corresponding to the deposited mercury using the Faraday law [23] and the Hg atomic radius (1.44 Å) [24]. The average charge was 219 μC (RSD 3.2%; N = 12), resulting in an estimated thickness of 1.3 nm, corresponding to a very thin mercury film [23,25].

Unless otherwise stated, all peak currents quoted are mean values of three replicate measurements at each of two different TMFE or PSS-coated electrodes.

2.4. Voltammetric procedures

Ion-exchange voltammetry (SWASV mode) were carried out in 10 mL NaCl electrolyte solutions of different ionic strength (0.50 and 0.0032 M), spiked with lead(II) as reference metal ion (concentration 6.00 × 10^{-8} M). The deposition step lasted 20 s at −0.8 V with stirring (BAS-C2, position 3). The SW stripping step was from −0.8 to −0.15 V (equilibration period 5 s). The SW parameters were: amplitude 25 mV, frequency 50 Hz and step potential 5 mV. Except otherwise stated, a 10 s cleaning step (E_{clean} = −0.2 V) between scans was used. All solutions were purged with nitrogen for 5 min prior to the voltammetric experiments and blanked although. Measurements were carried out at room temperature (18–20 °C).

3. Results and discussion

3.1. Behaviour of PSS-modified electrodes in lead determinations

An important issue to be evaluated for modified electrodes is the integrity of the mercury film and the mechanical and physical stability of the polyelectrolyte coatings itself, when immersed in the working solution.

Previous work [10] has shown that PSS coatings (M_W 70,000; mass loading 4.8 μg mm^{-2}) prepared from 0.15 M phosphate buffer and used in 0.50 M NaCl medium were mechanically stable. As a first test, forty consecutive determinations of the lead SW peak current ($I_{p(Pb)}$) were done for similar electrodes and the results confirm those from Monterroso et al. [10].

The performance of the modified TMFE using a PSS polymeric coating prepared from water was also evaluated. In what concerns the stability of these modified electrodes, there was no significant change of the lead analytical signal over the 40 consecutive measurements. In fact, there was an improvement in the mechanical stability of the PSS–TMFE prepared from water, since there was a decrease in the RSD values from 5.3%, for those recasted from 0.15 M phosphate buffer, to 1.9%. Additionally, these experiments also prove the great mechanical and physical integrity of the PSS film itself, adsorbed at the glassy carbon surface, in neutral medium. Therefore, the same PSS–TMFE (prepared from water and 0.15 M phosphate buffer) can be used for at least 40 consecutive stripping experiments with no significant variation of the lead(II) analytical signal.