

Development and Interfacial Properties of Novel Polymer-modified Carbon Film Electrodes

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Abstract. The surface properties of carbon film electrode sensors covered by coating with Nafion polymer film, before and after electrochemical analysis of sub-micromolar traces of lead and cadmium ions, were investigated. These protective polymer films are applied to the electrode surfaces to prevent the irreversible adsorption of chemical species, such as proteins and surfactants present in natural media, which leads to a decrease in response. Electrochemical impedance spectroscopy and voltammetric techniques were used for characterisation. The effect of non-ionic surfactant molecules in solution on the behaviour of the polymer-coated electrode was also investigated. It is shown that permanent changes to the structure and morphology of the Nafion film and of the carbon-Nafion interface occur after deposition of the trace metal ions, an effect which is lessened in the presence of surfactant.

Introduction

The importance of, and search for, novel sensor electrode materials for environmental and health applications has increased in recent years, owing to concerns with the toxicity of the traditionally-used mercury [1]. With this in mind, various forms of carbon have been developed as electrode materials, such as glassy carbon, carbon paste, boron-doped diamond and nitrogen-doped amorphous carbon [2]. Carbon film electrodes, fabricated from carbon film electrical resistors, have recently been shown to have all the necessary interfacial properties for application as sensors in the analysis of liquid environmental samples [2], besides being small and portable. Electrochemical pretreatment and conditioning of these electrodes leads to changes in the carbon surface functionalities and improved behaviour in terms of available potential window and small background currents.

In analyses of chemical species in natural media, difficulties in the use of sensors can arise owing to the irreversible adsorption of interferents. Examples of such species are proteins and surfactants, which can progressively block the surface, lead to a decrease in response and eventually to prevention of sensor functioning. For this reason, protective semi-permeable and/or selective polymer films are being developed for covering electrode surfaces.

The purpose of this work was to investigate the surface properties of these carbon film electrode sensors, coated with Nafion polymer film, before and after analysis of sub-micromolar concentrations of lead and cadmium trace metal ions by stripping voltammetry techniques. Nafion is a selective cation-exchange perfluorosulphonated polymer [3], which prevents the passage of anions and large neutral molecules owing to its reduced porosity, especially after curing. Electrochemical impedance spectroscopy and pre-concentration voltammetric techniques were used for characterisation. The effect of non-ionic surfactant molecules in solution was also investigated, using Triton-X-100 as model surfactant; their influence can be complex depending on whether they

are present in concentration below or above the critical micelle concentration and sometimes complexation with metal ions can occur. It is shown that permanent changes to the structure and morphology of the Nafion film and at the carbon-Nafion interface take place after deposition of the trace metal ions, an effect which is lessened in the presence of surfactant.

Experimental

Electrode preparation. Carbon film disc electrodes were made from carbon film resistors of 2 Ω nominal resistance, as described in [2]: the resistors are fabricated from ceramic cylinders of length 0.6 cm and external diameter 0.15 cm by pyrolytic deposition of carbon from methane in a nitrogen atmosphere. One of the two tight-fitting metal caps, which are linked to external contact wires, was removed and the other was protected by normal epoxy resin, the contacting wire being sheathed in plastic. The cylinder was then covered in epoxy resin except on the bottom surface. The final result was a disc electrode of area ca. 0.020 cm². Electrochemical pre-treatment was carried out by cycling the electrode 3 times in 1.0 M perchloric acid solution between potential limits defined by a maximum current of ± 0.1 mA (approximately -2.0 to +2.0 V vs saturated calomel electrode (SCE)) at a scan rate of 100 mV s⁻¹ to increase the width of the potential window.

Nafion-coated electrodes. A volume of 1 μ L of 0.25 wt% Nafion solution was applied to the electrochemically conditioned electrode surface followed by 1 μ L of *N, N'*-dimethylformamide, using an electronic micropipette (EDP-Plus, Rainin). Curing of the Nafion film was done with a jet of warm air for about 1 min. This Nafion coating procedure leads to a film of ca. 1 μ m thickness.

Instrumentation. Measurements were made in a three-electrode one-compartment cell containing the carbon film electrode, a platinum foil auxiliary electrode and a SCE as reference. Cyclic voltammetry was carried out using a μ Autolab potentiostat (Eco Chemie, Utrecht, Netherlands) controlled by GPES 4.9 software. Electrochemical impedance spectra were recorded using a Solartron 1250 Frequency Response Analyser coupled to a Solartron 1286 Electrochemical Interface (Solartron Analytical, UK), controlled by ZPlot software: the frequency range of 65.5 kHz – 0.1 Hz was scanned logarithmically with an applied sinusoidal perturbation of 10 mV amplitude in 10 steps per frequency decade, superimposed on the chosen applied potential. Fitting of spectra to equivalent circuits was performed with ZView software.

Reagents and solutions. All solutions were prepared from analytical grade reagents and Millipore Milli-Q ultrapure water (resistivity ≥ 18 M Ω cm). Stock solutions of 10⁻³ M Cd²⁺ and Pb²⁺ were prepared. Triton X-100 surfactant was used as received after appropriate dilutions. The supporting electrolyte was 0.1 M sodium acetate/acetic acid buffer (pH 4.4). All experiments were carried out at room temperature (25 \pm 1°C).

Results and Discussion

The pre-concentration technique of square wave anodic stripping voltammetry (SWASV) was used to determine sub-micromolar concentrations of trace metal ions at the electrode assemblies studied in this work. Changes to the interface and polymer coating were examined. Therefore, results obtained are presented below regarding electrochemical impedance spectroscopy of the carbon film electrodes with and without Nafion coatings, before and after SWASV experiments of cadmium and lead ions, and finally the influence of Triton-X-100 surfactant is discussed.

Anodic Stripping Voltammetry. In this technique, the metal ions are deposited on the electrode over a chosen period of time at a sufficiently negative applied potential (-1.0 V vs SCE in this case) and are then re-dissolved (stripped) by a fast square wave potential scan in the positive direction, the resulting peaks of stripping current being monitored, the height of which is proportional to concentration; their position identifies the metal ion. SWASV at Nafion-coated carbon film electrodes of lead and cadmium ions leads to voltammetric re-dissolution profiles such as those

shown in Fig. 1, demonstrating that these ions can be determined simultaneously with good peak resolution: the peak potentials were at -0.75 V for cadmium and at -0.55 V vs SCE for lead. Although both ions in solution have the same concentration of 10^{-7} M, the lead ion stripping peak is higher due to a greater tendency to interact with the Nafion coating in acetate buffer solution. Lead ions are involved in ligand exchange reactions at the Nafion-solution interface and become bound to the polymer, equivalent to an extra pre-concentration effect, resulting in a higher peak current. These exchange reactions occur less with cadmium ions due to weaker complexation reaction with acetate and lower affinity with oxygen ligands.

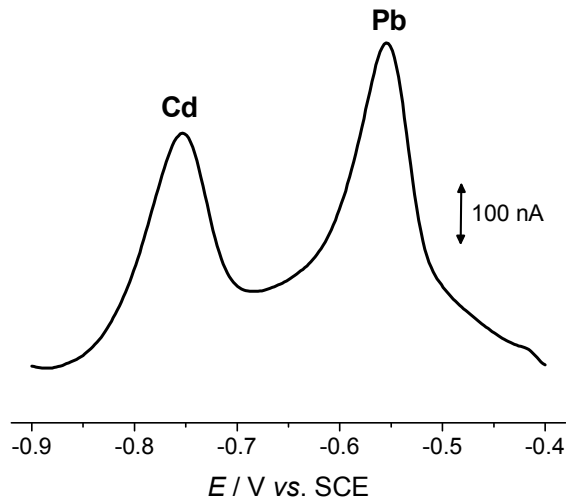


Fig.1. SWASV voltammogram of cadmium and lead in 0.1 M acetate buffer, $[Cd^{2+}] = [Pb^{2+}] = 10^{-7}$ M. Deposition potential -1.0 V vs SCE during 120 s. Square-wave scan conditions: amplitude 25 mV, frequency 100 Hz, potential increment 2 mV.

Electrochemical Impedance Spectroscopy. Typical impedance spectra obtained in acetate buffer solution for electrochemically pre-treated electrodes, before and after applying a Nafion coating, are shown in Fig.2. Spectra obtained after SWASV of lead and cadmium ions at Nafion-coated electrodes are also included. The values of applied potential chosen correspond to the metal deposition potential (-1.0 V) and a value positive of the re-dissolution peaks (-0.5 V).

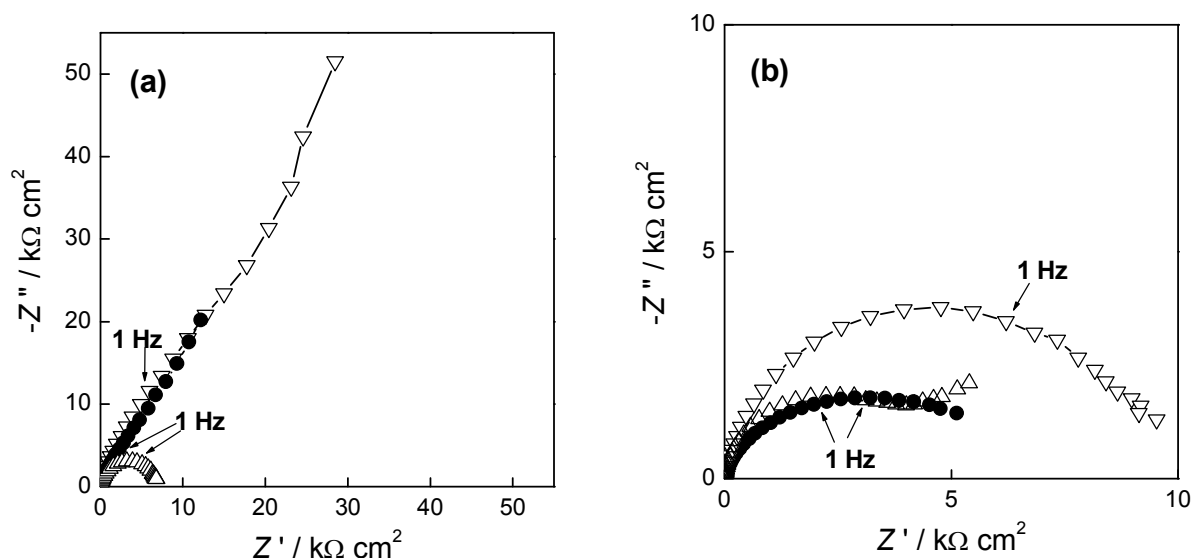


Fig. 2. Complex plane impedance plots in pH 4.4 acetate buffer at (a) -1.0 V vs SCE and (b) -0.5 V vs SCE for carbon film electrodes: (Δ) electrochemically pre-treated, (\bullet) Nafion-coated and (∇) after metal deposition from 10^{-7} M Cd^{2+} and Pb^{2+} in acetate buffer.

It can be seen that the coating significantly influences the shape of the spectra obtained at -1.0 V vs SCE, where charge separation in the Nafion/carbon film lead to the almost straight line obtained. In

the presence of metal ions, the shape of the spectrum remains similar, but the impedance magnitude is greater, which is evidence of permanent changes to the Nafion film caused by the metal deposition. Repeating the metal deposition/SWASV experiments did not lead to any further alterations to the spectra, which means that the polymer film structure does not change further. Examination of the spectra at -0.5 V also shows large differences after metal deposition experiments were undertaken. A fuller analysis of the experimental data and fitting to electrical equivalent circuits can be found in [4]. The circuit includes a resistance (representing charge movement) and non-ideal capacitor (representing charge separation) in parallel. Data analysis shows that the coating leads to larger capacitances and greater roughness, which decrease irreversibly after metal ion deposition, suggesting physical distortion of the polymer film.

Effect of surfactant. The non-ionic surfactant Triton-X-100 is a highly hydrophobic non-ionic detergent, formula *t*-octylphenoxypolyethoxyethanol, with an average number of ethoxy groups of 9.5 [5], a molecular mass of ~ 625 , and a critical micelle concentration of ~ 200 mg dm $^{-3}$ at 20°C . Various concentrations below and above the critical micelle concentration were added to the analysis solution in order to investigate possible adsorption phenomena which can arise in natural environmental media. Some typical spectra obtained are illustrated in Fig.3: the two surfactant concentrations shown correspond to a “small” concentration of 2 mg dm $^{-3}$, similar to that which could be expected in natural media, and another of 500 mg dm $^{-3}$, higher than the critical micelle concentration.

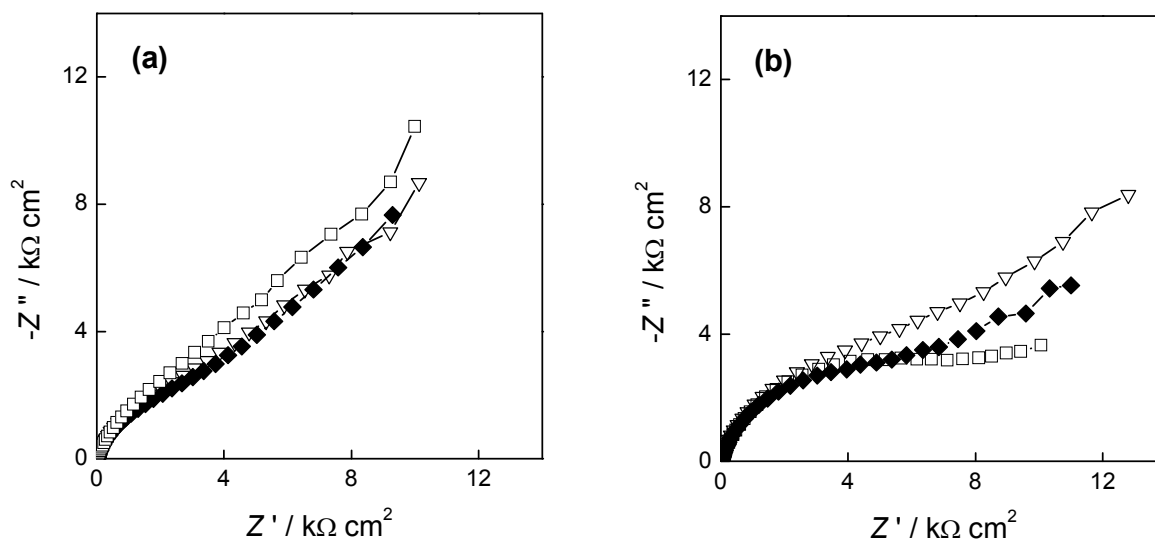


Fig.3. Complex plane impedance plots for Nafion-coated carbon film disc electrodes at -1.0 V vs SCE in: (∇) pH 4.4 acetate buffer solution, (\square) 10^{-7} M $[\text{Pb}^{2+}]$ and $[\text{Cd}^{2+}]$ + Triton in acetate buffer and (\blacklozenge) acetate buffer after SWASV. Concentrations of surfactant: (a) 2 (b) 500 mg dm $^{-3}$.

The spectra clearly demonstrate that there is an influence of the presence of surfactant in solution on the interfacial region – compare with Fig.2. At the lower concentration it can be seen that the assembly reverts to its initial state after the removal of Triton, which suggests that the electrode sensor is only influenced temporarily by the presence of surfactant and can be fully regenerated. At the high concentration of 500 mg dm $^{-3}$, the “cleaning” of the Nafion membrane appears not to be completely effective, which means that there will be permanent effects and structural changes, as happens in the absence of surfactant. Fortunately, since this situation is not encountered in natural media except in strong detergent solutions, any problems for application of SWASV analysis can be neglected. Thus, it is convincingly demonstrated that low surfactant concentrations do not lead to permanent inhibition of the height of voltammetric stripping peaks, in accordance with [6], which

means that these polymer-coated sensors can be used for long periods of time without blocking of the electrode surfaces. Such characteristics are important for field and for remote sensing applications.

Conclusions

Nafion-coated carbon film disc electrodes for application in the anodic stripping voltammetry of trace metal ions have been characterised, mainly by electrochemical impedance spectroscopy. Differences in behaviour between Nafion-coated and uncoated electrodes have been shown. Coated electrodes show an increase in magnitude of impedance at negative potentials, with a higher capacitance value and greater roughness, compared with pre-treated uncoated carbon film electrodes.

Irreversible changes to the polymer coating of the Nafion-coated carbon film electrodes caused by metal deposition when used in anodic stripping voltammetric analysis for the determination of cadmium and lead ions, have been demonstrated. These permanent changes to the structure and morphology of the Nafion film and at the carbon-Nafion interface are less in the presence of surfactant.

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References

- [1] C.M.A. Brett: *Electroanalysis* Vol. 11 (1999) p. 1013.
- [2] C.M.A. Brett, L. Angnes and H.-D. Liess: *Electroanalysis* Vol. 13 (2001) p. 765.
- [3] M.W. Epenscheid, A.R. Ghatak-Roy, R. B. Moore III, R.M. Penner, M.N. M.N. Szentirmay and C.R. Martin: *J. Chem. Soc. Faraday Trans. I* Vol. 82 (1986) p. 1051.
- [4] C. Gouveia Caridade and C.M.A. Brett: *Electroanalysis*, in press.
- [5] C.J. Biozelle and D.B. Millar: *Biophys. Chem.* Vol. 3 (1975) p. 355.
- [6] C.M.A. Brett, D.A. Fungaro, J.M. Morgado and M.H. Gil: *J. Electroanal. Chem.* Vol. 468 (1999) p.26.