Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Electroanalytical Chemistry 592 (2006) 113–120
Journal of Electroanalytical Chemistry
www.elsevier.com/locate/jelechem

The influence of Triton-X-100 surfactant on the electroanalysis of lead and cadmium at carbon film electrodes – An electrochemical impedance study

Carla Gouveia-Caridade, Christopher M.A. Brett *

Deopartamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal

Received 29 December 2005; received in revised form 19 April 2006; accepted 4 May 2006
Available online 12 June 2006

Abstract

The influence of the model surfactant Triton-X-100 on the electroanalysis of trace lead and cadmium ions by anodic stripping voltammetry at Nafion-coated carbon film electrodes has been studied by electrochemical impedance spectroscopy. Spectra were recorded before and after metal deposition, without and with the presence of surfactant. Plots of the imaginary part of the impedance vs. the logarithm of the frequency are shown to be particularly useful for diagnostic purposes. Results demonstrate that the effect of Triton is greatest below its critical micelle concentration and particularly at low concentrations below 100 mg dm^{-3}, the blocking of the electrode surface being reversible in these cases. Permanent changes to the structure and morphology of the Nafion film are normally less than in the absence of surfactant. Comparison with square wave stripping voltammetry data at Nafion-coated mercury thin film electrodes shows that the results obtained in this study are also applicable at such electrodes.

Keywords: Nafion coating; Carbon film electrode; Anodic stripping voltammetry; Trace cadmium and lead ions; Electrochemical impedance spectroscopy; Triton-X-100 surfactants

1. Introduction

Electroanalytical techniques are powerful for measuring trace metals in environmental samples, one of the reasons being that in many cases there is no necessity for pre-treatment or sample digestion [1,2]. To prevent surface blocking and fouling, electrodes can be covered by semi-permeable polymer films, selected so as to allow the passage of the required analytes to the electrode surface whilst preventing that of other compounds which could adsorb on the surface or undergo electrode reactions.

Polymers tested for this purpose have ranged from conducting polymers, e.g. [3], to inert cellulose-type porous membranes [4]. With regard to anodic stripping voltammetry (ASV) of trace metal ions, as well as in combination with batch injection analysis, success has been achieved with cation-exchange polymer coatings such as Nafion [5,6], model surfactants and proteins having been used to test the efficacy of the approach. During these studies it was found that the stripping signal arising from measurements with lead ions was larger than that without the coating, particularly in acetate buffer solution. In fact, in this solution lead (II) is present as acetate complexes, and cadmium remains as Cd^{2+}(aq.). Thus with a cation exchange polymer barrier, it would be expected that cadmium ions would lead to a higher response and acetate-bound lead ions would pass through the Nafion membrane to a lesser extent. Since this does not occur, there must be another, dominating, factor. It was shown in [5] that lead ions are involved in a ligand exchange reaction at the polymer–solution interface and become bound to the polymer. Cadmium ions, which have a weaker tendency to complex with acetate and a lower affinity for oxygen ligands, are not incorporated into the polymer to the same extent as lead. The results of these interactions are manifested in the size of

---

* Corresponding author. Tel./fax: +351 239835295.
E-mail address: brett@ci.uc.pt (C.M.A. Brett).

0022-0728/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2006.05.005

the peak currents in ASV, which are higher for lead than for cadmium, even in the presence of surfactant, this being equivalent to an extra pre-concentration effect. Anionic surfactants have also been used to reduce protein interferences [7] and those from cationic or neutral surfactants [8].

Mercury thin film electrodes coated with Nafion, usually on glassy carbon substrates, were developed for application in electroanalysis of environmental samples, not only to reduce the problems of electrode blocking but also to make the electrode assembly more robust in the presence of convection, such as in batch injection analysis [9] or in the presence of ultrasound [10]. Other cation-exchange polymers have also been tested and evaluated and compared with Nafion [11,12].

An important model surfactant is the highly hydrophobic non-ionic detergent Triton-X-100, formula *t*-octylphenoxypolyethoxyethanol, with an average number of ethoxy groups of 9.5 [13], leading to a molecular mass of ~625, and a critical micelle concentration of 0.30 mM at 20 °C [14]. It has a great tendency to adsorb onto surfaces, e.g. [15–19], influencing mass and energy transfer across the modified interface. With respect to ASV measurements, Triton adsorption, besides reducing the available electrode surface area, can also lead to broader peaks and shifts in peak potential, as in [20].

Recently carbon film electrodes made from electrical resistors have been developed and evaluated for use as low-cost disposable or short-term use sensors [21]; applications investigated have included sensors for trace metals without the use of mercury thin films [21,22]. Additionally, the effect of electrode pre-treatment on the available potential window has been examined and the interface characterised by electrochemical impedance spectroscopy (EIS) [23]. The influence of Nafion polymer coatings on the interfacial properties has also been probed [24].

The purpose of this paper is to examine the influence of the surfactant Triton-X-100 on the properties of the carbon film electrode/Nafion interfacial region, mainly by using EIS, with the particular aim of throwing light on the influence of surfactants on the efficiency and viability of the square wave ASV (SWASV) of lead and cadmium ions. The results obtained should be useful for improved understanding of the SWASV of other metal ions in natural media.

2. Experimental

2.1. Preparation of the working electrode

The preparation of Nafion-coated carbon film electrodes has been described previously [24]. Briefly, the electrodes were made from carbon film resistors of 2 Ω nominal resistance, fabricated by pyrolytic deposition of carbon from methane in a nitrogen atmosphere on ceramic cylinders of 0.6 cm length and 0.15 cm of external diameter [21]. One of the two tight-fitting metal caps was removed and the other was protected by normal epoxy resin, the contact wire being sheathed in plastic. The cylinder was then embedded in epoxy resin leaving the bottom disc surface exposed, corresponding to an electrode area of ca. 0.020 cm^2.

Prior to polymer coating, the electrode was pre-conditioned by cycling three times in 1.0 M perchloric acid solution between potential limits defined by a maximum current of ±0.1 mA, starting at 0.0 V vs. SCE in the positive direction at a scan rate of 100 mV s^{-1}.

The Nafion coating was made by placing 1 μL of 0.25 wt% Nafion, followed by 1 μL of *N*,*N*′-dimethylformamide, on the surface of the pre-treated electrode with a motorised electronic micropipette (EDP-Plus, Rainin, USA), a similar procedure to that in [24]. This procedure was used in order to obtain a film that is as uniform as possible, bearing in the mind the importance of the casting conditions [25]. After solvent evaporation, the film was cured with a jet of warm air (~ 70 °C) for about 1 min. This film had a thickness of ~1 μm.

2.2. Instrumentation

Electrochemical measurements were performed in a three-electrode system with a Nafion-coated carbon film resistor electrode as working electrode, a saturated calomel electrode (SCE) as reference and a platinum foil as counter electrode. The cell volume was ~25 cm^3.

Voltammetric experiments were carried out with a μAutolab potentiostat (Eco Chemie, Utrecht, The 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, scanning the frequency logarithmically from 65.5 kHz to 0.1 Hz, in 10 steps per frequency decade, with a sinusoidal perturbation of 10 mV rms amplitude superimposed on the chosen potential. Fitting to equivalent circuits was done with ZView software.

2.3. Reagents and solutions

Solutions were prepared from analytical-grade chemical reagents and Millipore Milli-Q ultrapure water (resistivity $\geqslant 18$ MΩ cm). Stock solutions of 10^{-3} M Pb^{2+} and Cd^{2+} were prepared and diluted as appropriate. Triton-X-100 (Sigma, USA) was used as received after appropriate dilutions. The supporting electrolyte was 0.1 M sodium acetate/acetic acid buffer (pH 4.3), a convenient electrolyte for ASV experiments, used in [23,24].

Experiments were conducted at room temperature (25 ± 1 °C) without deoxygenation.

2.4. Procedure for recording impedance spectra

Experiments were carried out in the following sequence. First, impedance spectra of the Nafion coated carbon film electrodes in acetate buffer solution at −1.0 V and −0.5 V (vs. SCE) were recorded, to check the effectiveness of the surface coating. Following this, 10^{-7} M Cd^{2+} and Pb^{2+} ions were added to the acetate buffer solution and a potential of −1.0 V vs. SCE was applied to the working electrode for 2 min in stirred solution, for metal deposition to occur. An impedance spectrum was then recorded at −1.0 V. After waiting 2 min with the electrode at open circuit for re-oxidation to occur, another spectrum was recorded at −0.5 V.

The electrode was then placed in acetate buffer solution and a "blank" SWASV experiment carried out to check the absence of metal ions. Spectra were then recorded at the same potentials of −1.0 V and −0.5 V, in order to ascertain if some permanent alteration to the polymer coating had occurred due to metal deposition.

After this, a chosen volume of Triton-X-100 was added to a solution of acetate buffer spiked with 10^{-7} M Cd^{2+} and Pb^{2+}. Metal deposition and the recording of spectra were carried out in the same way as above, first with the metal ions present and then in clean buffer solution.

For each concentration of Triton, a new electrode was employed. The concentrations of Triton were in the range 1–500 mg dm^{-3}.

2.5. Procedure for SWASV experiments

For SWASV experiments, the electrodes were immersed in an electrochemical cell containing 0.1 M acetate buffer and 10^{-7} M Cd^{2+} and Pb^{2+}. The deposition potential, −1.0 V vs. SCE, was applied to the Nafion-coated carbon film electrode for 2 min in stirred solution. The stirring was then stopped and, after 10 s, a square-wave voltammetric potential scan in the positive direction was applied to oxidise the metals, and the re-dissolution peaks were recorded. The frequency used was 100 Hz with amplitude of 25 mV and a scan increment of 2 mV. A cleaning step, applying −0.3 V in stirred solution during 10 min, was used to remove any remaining excess metal ions within the polymer film and in its vicinity prior to the next experiment. Surfactant was added after recording the voltammograms for the blank and the metal ion containing solution.

3. Results and Discussion

In this study, EIS has been the main technique used to visualise the changes occurring in the interfacial region at the carbon film electrodes as a result of the presence of Triton-X-100 surfactant. Impedance spectra obtained, in the conditions described in Section 2, with and without Triton-X-100 surfactant, are exemplified in Fig. 1 at an applied potential of −1.0 V vs. SCE and in Fig. 2 at −0.5 V vs. SCE, for concentrations of Triton of 2, 50 and 500 mg dm^{-3}.

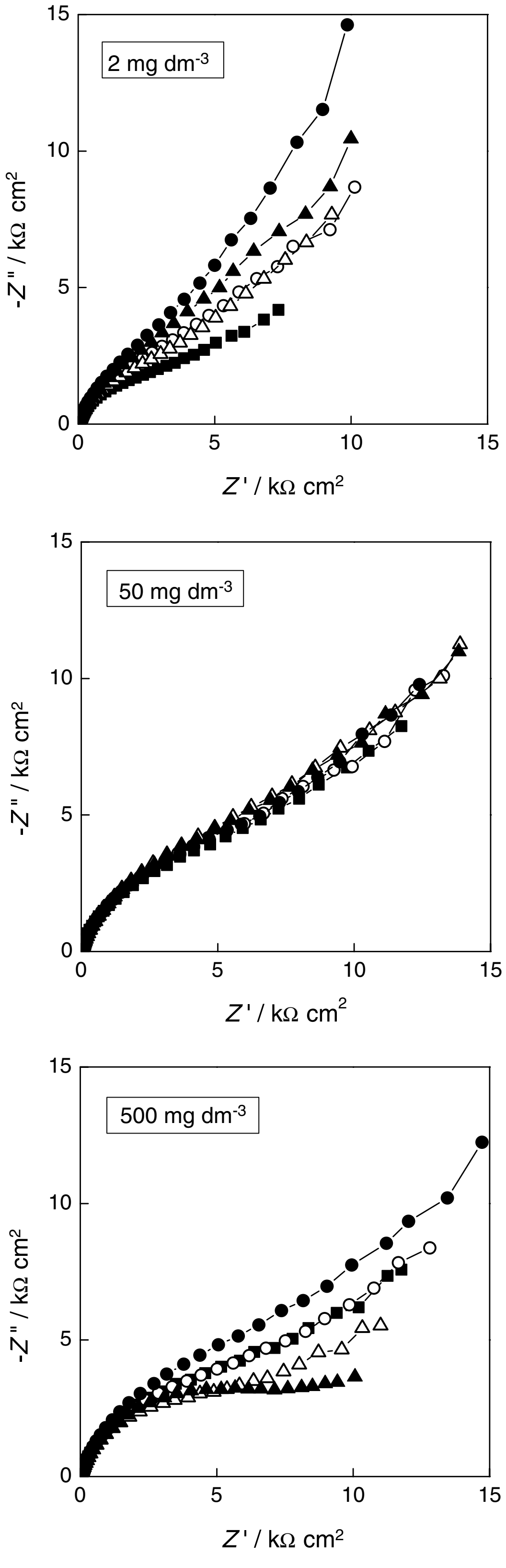

Fig. 1. Complex plane impedance plots at −1.0 V vs. SCE for Nafion-coated carbon film electrodes in pH 4.3 acetate buffer solution adding different concentrations of Triton-X-100 of 2, 50 and 500 mg dm^{-3}. Sequential spectra: (■) buffer electrolyte; (●) after deposition of Pb^{2+} and Cd^{2+}; (○) after SWASV; (▲) with Triton and (△) after electrochemical cleaning.

Previous work showed that in the presence of Cd^{2+} and Pb^{2+} the shape of complex plane EIS spectra is not altered

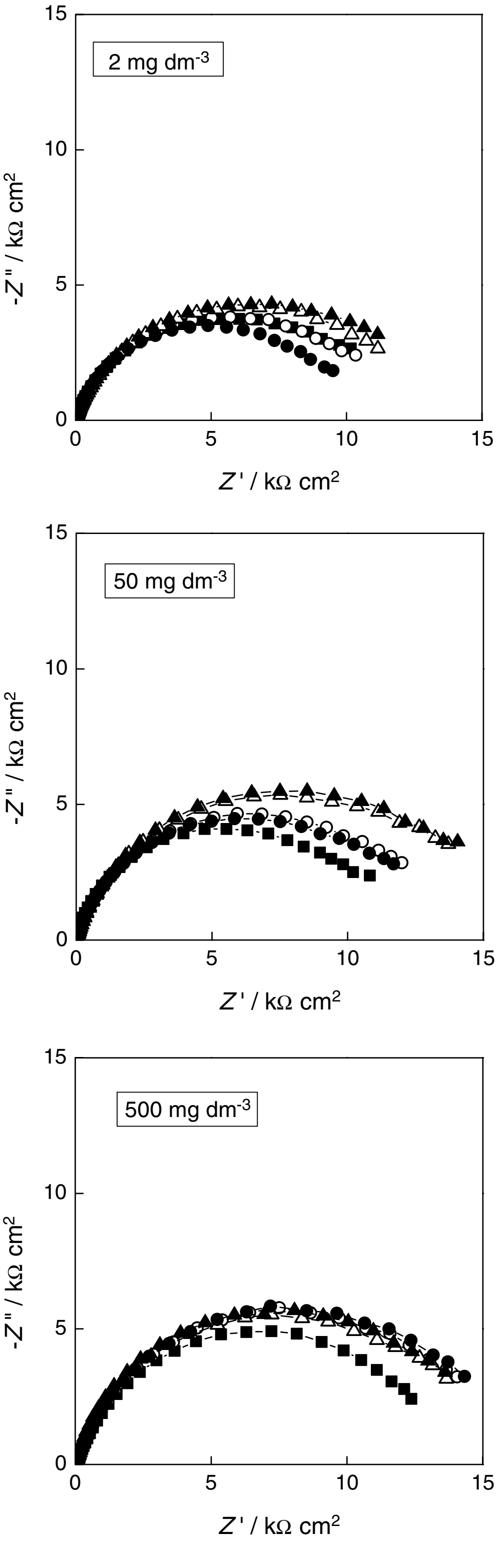

Fig. 2. Complex plane impedance plots at −0.5 V vs. SCE for Nafion-coated carbon film electrodes in pH 4.3 acetate buffer solution adding different concentrations of Triton-X-100 of 2, 50 and 500 mg dm^{-3}. Meaning of symbols as in Fig. 1.

by the presence of metal ions in solution but greater values of the impedance magnitude are obtained after metal deposition has taken place [24]. This irreversible change was attributed to distortion of the Nafion film caused by the formation of metal deposits within the Nafion pores at the electrode substrate surface. The same behaviour was observed in this study.

The spectra were fitted to an equivalent electrical circuit comprising the cell resistance, R_{Ω}, (values between 15 and 25 Ω cm^2) in series with a parallel combination of a constant phase element CPE$_1$ and a charge transfer resistance, R_1. The CPE is assumed to be a non-ideal capacitor of capacity C_1 with a roughness factor α_1, varying from 0.5 to 1, where an α value of 1 represents a perfectly smooth surface. This circuit was used for frequencies above 1 Hz at the applied potential − 1.0 V, where a high degree of reproducibility was found between different electrodes. Below this frequency, reproducibility between experiments was lower. Values obtained under the different experimental conditions lie in the range 8–17 kΩ cm^2 for R_1, 15–30 μF cm^{-2} for C_1 and 0.82–0.94 for α_1. In the chosen frequency range, the errors in the fitting of the experimental values top the equivalent circuit varied between 3% and 8% for R_1, 0.8% and 3% for C, and less than 1% for α_1.

Further diagnostic information can also be obtained from the plots of $-Z''$ vs. lg$f$, Figs. 3 and 4. These plots bring out the differences in the adsorption and charge separation of the interfacial region. Semicircles in the complex plane plots lead to peaks in the Z'' vs. lg$f$ plots, the maximum of the peak corresponding to the RC time constant. At −0.5 V, it can be seen that some changes in the time constant values occur, particularly below the critical micelle concentration (cmc). Above the cmc, the changes are much smaller. This means that adsorption is much greater below the cmc, blocking the polymer surface, whereas at higher concentrations micelles are preferentially formed such that the surface area affected by adsorption is less, and the process appears to be reversible (see, for example, 100 mg dm^{-3} Triton at −0.5 V vs. SCE (Fig. 4)). A recent study of cellulose surfaces exposed to Triton-X-100 [19] showed a complex four-region adsorption isotherm with the formation of hemimicelles and a decrease in adsorption at higher concentrations above the cmc. Our results show that Nafion polymer exhibits a similar behaviour. Nevertheless, these cases should be regarded as exceptions to the general rule in which saturation adsorption on an essentially hydrophobic surface is reached somewhat below the cmc and adsorption does not decrease with a further increase in surfactant concentration [26].

The complex plane and imaginary component spectra showed the following tendencies:

1. After addition of Triton to the solution, the shape of the spectra is not altered above the critical micelle concentration (cmc ~200 mg dm^{-3} in water), either at −0.5 V or at −1.0 V vs. SCE. For frequencies below 1 Hz, in the complex plane plot an almost horizontal line was obtained, at a concentration higher than 100 mg dm^{-3}.

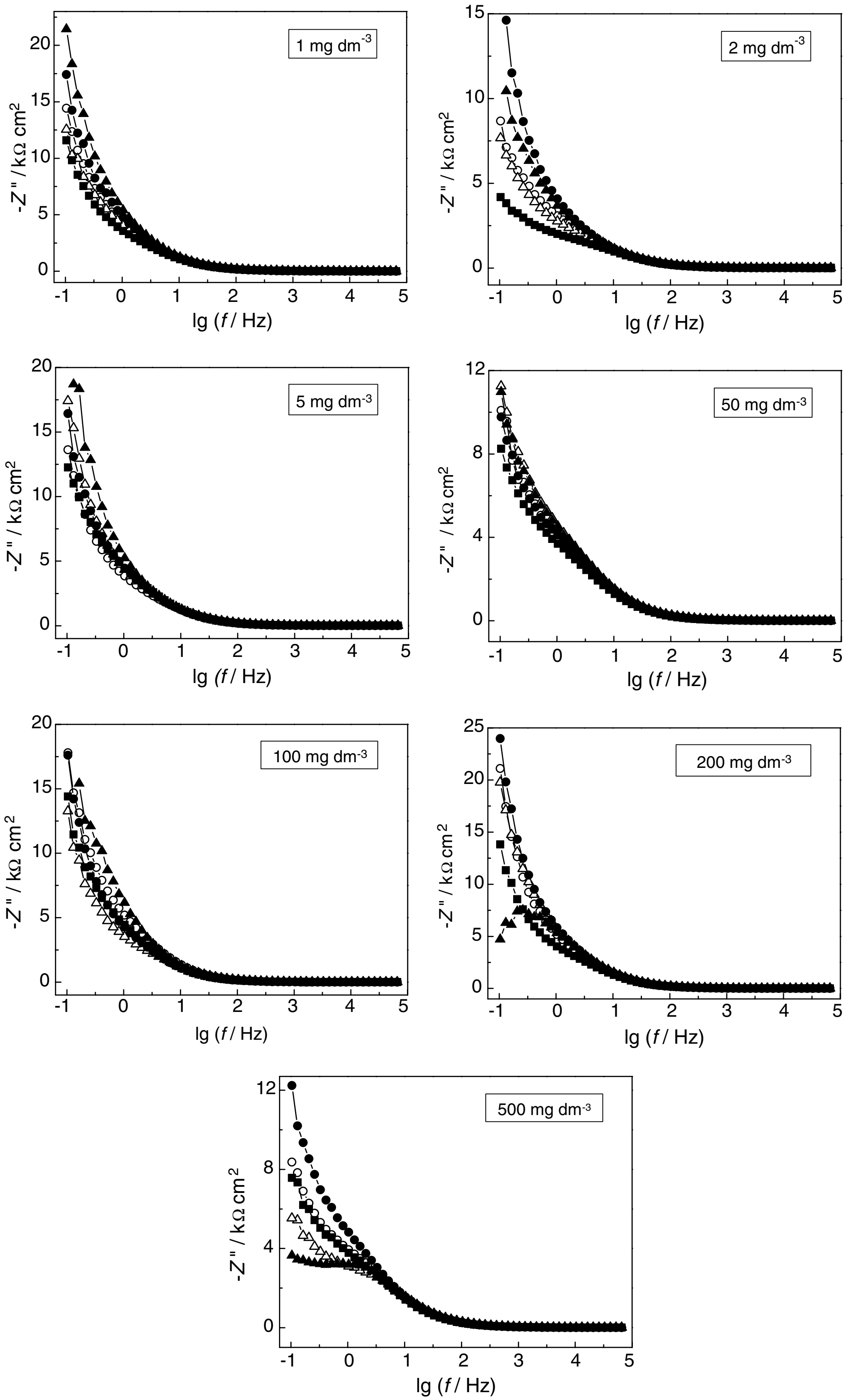

Fig. 3. Plots of $-Z''$ vs. lg(f/Hz) for Nafion-coated carbon film electrodes in pH 4.3 acetate buffer solution for different concentrations of Triton-X-100 at -1.0 V vs. SCE. Meaning of symbols as in Fig. 1.

2. At -1.0 V vs. SCE, addition of surfactant leads to a higher cell resistance which can be explained by its adsorption on the Nafion surface, higher values of the capacitance, and higher charge transfer resistance. After electrochemical cleaning of the electrode, the spectra in acetate buffer remain altered reflecting permanent

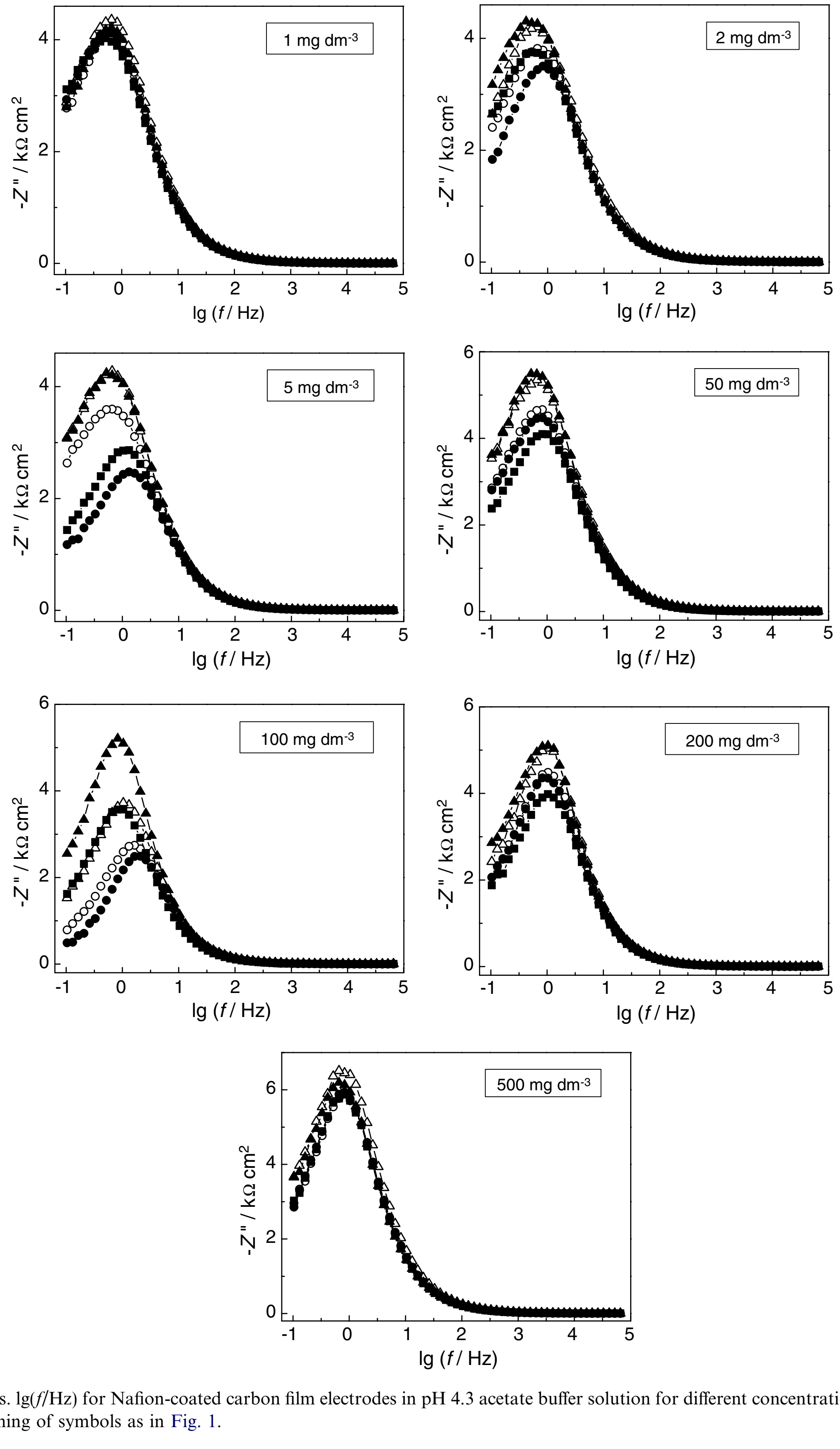

Fig. 4. Plots of $-Z''$ vs. lg(f/Hz) for Nafion-coated carbon film electrodes in pH 4.3 acetate buffer solution for different concentrations of Triton-X-100 at −0.5 V vs. SCE. Meaning of symbols as in Fig. 1.

changes to the modified electrode surface. At −1.0 V the charge transfer resistances are higher than before use and at −0.5 V they are higher.

In SWASV experiments the Nafion-coated carbon film electrodes, Fig. 5, display well-defined cadmium and lead peaks in the absence of surfactant, with peak potentials

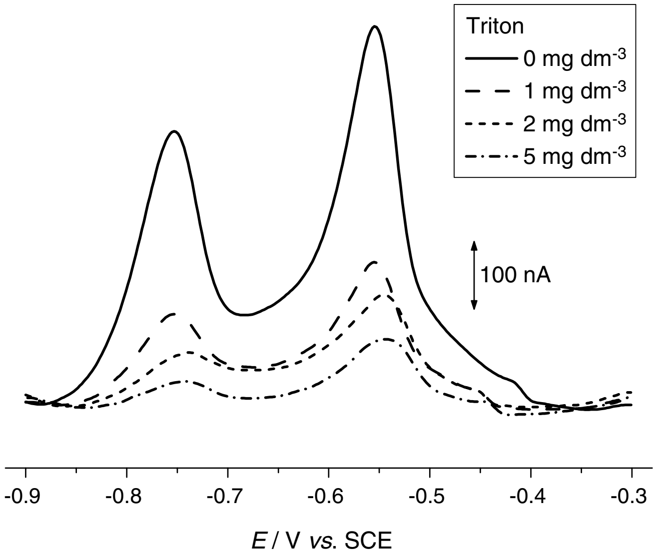

Fig. 5. SWASV of 10^{-7} M Cd^{2+} and Pb^{2+} in 0.1 M acetate buffer (pH 4.3) at a Nafion-coated carbon film electrode in the presence of increasing concentrations of Triton-X-100. Experimental conditions: $t_{\text{dep}} = 120$ s at −1.0 V vs. SCE and square wave amplitude 25 mV, frequency 100 Hz, potential increment 2 mV.

of −0.75 V for cadmium and −0.55 V for lead. The higher peak current for lead suggests a greater tendency for incorporation within and/or transport through the Nafion coating in acetate buffer solution. The apparent diffusion coefficient, D_{app}, was determined for these two ions in the same 0.1 M acetate buffer solution at Nafion modified carbon film electrodes from cyclic voltammetry, as described in [27]. Plots of peak current vs. the square root of scan rate were linear and led to D_{app} values nearly 10 times higher for lead (D_{app} (Pb^{2+}) $= 2.5 \times 10^{-6}$ cm^2 s^{-1}) than for cadmium (D_{app}(Cd^{2+}) $= 3.3 \times 10^{-7}$ cm^2 s^{-1}). A higher apparent rate of diffusion therefore appears to be the main factor contributing to the higher ASV response for lead ions.

The addition of the surfactant leads to a shift of the peak potentials and to a decrease in peak currents, normally referred to as electrode fouling. The normalised changes in peak current obtained at the electrodes studied here are summarised in Table 1. As can be seen, the cadmium peak decreases in the presence of Triton even for low surfactant concentrations, reaching almost 90% for 5 mg dm^{-3} Triton. In the presence of higher concentrations of surfactant the voltammogram does not show the characteristic peak for cadmium. A similar behaviour as described here was also found at Nafion-coated mercury thin film electrodes [11].

Table 1
Normalised peak currents from SWASV of 10^{-7} M Cd^{2+} and Pb^{2+} at Nafion-coated carbon film electrodes as a function of Triton-X-100 concentration

	[Triton]/mg dm^{-3}							
	0	1	2	5	50	100	200	500
Cd^{2+}	1.00	0.33	0.16	0.11	–	–	–	–
Pb^{2+}	1.00	0.39	0.29	0.20	–	–	–	–

For lead, the peak current also decreases in the presence of surfactant. This decrease in peak current is less, but again at higher concentrations of Triton the characteristic peak for lead disappeared. At the Nafion coated MTFE, the Pb^{2+} peak current increases for small concentrations of Triton-X-100 and then does not change further [11].

Although the lead and/or cadmium ion containing system normally recovers completely from the adsorption of surfactant, after being exposed to a concentration of 500 mg dm^{-3} and cleaning in acetate buffer (10 min at −0.3 V vs. SCE) recording of another voltammogram in fresh acetate buffer solution shows evidence of irreversible changes to the electrode and retention of metal ions, i.e. a memory effect. This is corroborated by EIS measurements, in Fig. 1, for a higher concentration of Triton.

Other EIS experiments with Triton present in solution together with cations, such as Fe^{3+}, that are not reduced to metal (although they can be incorporated within the Nafion layer), showed some change to the interfacial properties of the coating even without the formation of a metal deposit.

Fortunately, in practical cases, the situation of high surfactant concentrations is unlikely to arise, since in environmental media the maximum concentration of surfactant that can be expected is around 2 mg dm^{-3}.

4. Conclusions

The use of electrochemical impedance spectra has been explored in order to follow the changes occurring at Nafion-modified carbon film electrodes in the presence of non-ionic surfactants during anodic stripping voltammetry experiments – it is found that these changes are similar to those occurring at Nafion-coated mercury thin film electrodes. It is demonstrated that plots of the imaginary part of the impedance vs. the logarithm of the frequency are particularly valuable for visualising any changes occurring to the electrode assembly. Such alterations owing to metal ion deposition or surfactant adsorption have been seen and it is shown that the system can completely recover after adsorption. Nevertheless, at high surfactant concentrations these changes are irreversible, possibly through blocking of the pores in the polymer coating such that the assembly cannot recuperate its original form. This could have important implications for the use of these electrodes in media exposed, transitorily, to high concentrations of surfactant.

Acknowledgements

Financial support from Fundação para a Ciência e Tecnologia (FCT), ICEMS (Research Unit 103), is gratefully acknowledged. C.G.C thanks FCT for a PhD Grant (SFRH/BD/18659/2004).

References

[1] C.M.A. Brett, Electroanalysis 11 (1999) 1013.
[2] C.M.A. Brett, Pure Appl. Chem. 73 (2001) 1969.
[3] Y.C. Tsai, J. Davis, R.G. Compton, S. Ito, N. Ono, Electroanalysis 13 (2001) 7.
[4] B. Hoyer, N. Jensen, Talanta 42 (1995) 767.
[5] M.E.R. Dam, K.N. Thomsen, P.G. Pickup, K.H. Schrøder, Electroanalysis 7 (1995) 70.
[6] B. Hoyer, N. Jensen, Talanta 41 (1994) 449.
[7] B. Hoyer, N. Jensen, Electrochem. Commun. 5 (2003) 257.
[8] B. Hoyer, N. Jensen, Electrochem. Commun. 5 (2003) 759.
[9] C.M.A. Brett, A.M. Oliveira Brett, F.-M. Matysik, S. Matysik, S. Kumbhat, Talanta 43 (1996) 2015.
[10] F.-M. Matysik, S. Matysik, A.M. Oliveira Brett, C.M.A. Brett, Anal. Chem. 69 (1997) 1651.
[11] C.M.A. Brett, D.A. Fungaro, J.M. Morgado, M.H. Gil, J. Electroanal. Chem. 468 (1999) 26.
[12] C.M.A. Brett, D.A. Fungaro, J. Braz. Chem. Soc. 11 (2000) 298.
[13] C.J. Biaselle, D.B. Millar, Biophys. Chem. 3 (1975) 355.
[14] E.A. Dennis, A.A. Ribeiro, M.F. Roberts, J. Robson, in: K.L. Mittal (Ed.), Solution Chemistry of Surfactants, Plenum, NY, 1979, pp. 175–194.
[15] C.M. González-Garcia, M.L. González-Martín, V. Gómez-Serrano, J.M. Bruque, L. Labajos-Broncano, Carbon 39 (2001) 849.
[16] W.W. Kubiak, E. Niewiara, Electroanalysis 14 (2002) 1169.
[17] H. Sawamoto, Anal. Sci. 19 (2003) 1381.
[18] B. Gašparović, D. Risović, B. Ćosović, Electrochim. Acta 49 (2004) 3383.
[19] S. Paria, C. Manohar, K.C. Khilar, Coll. Surf. A: Physicochem. Eng. Aspects 252 (2005) 221.
[20] J. Wang, R.P. Deo, S. Thongngamdee, B. Ogorevc, Electroanalysis 13 (2001) 1153.
[21] C.M.A. Brett, L. Angnes, H.-D. Liess, Electroanalysis 13 (2001) 765.
[22] O.M.S. Filipe, C.M.A. Brett, Talanta 61 (2003) 643.
[23] O.M.S. Filipe, C.M.A. Brett, Electroanalysis 16 (2004) 994.
[24] C. Gouveia-Caridade, C.M.A. Brett, Electroanalysis 17 (2005) 549.
[25] B. Hoyer, N. Jensen, L.P. Busch, Electroanalysis 13 (2001) 843.
[26] R.J. Hunter, Foundations of Colloid Science, second ed., Oxford University Press, Oxford, 2000.
[27] P. Ugo, L.M. Moretto, Electroanalysis 7 (1995) 1105.