

Full Paper

Characterization and Application of Bismuth-Film Modified Carbon Film Electrodes

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Received: December 23, 2004

Accepted: February 21, 2005

Abstract

Bismuth film electrodes, formed by electrochemical deposition on carbon film resistor electrode substrates at constant applied potential, by potential cycling or at constant applied current have been investigated for the first time. The electrochemical behaviour of the films was characterised by cyclic voltammetry and electrochemical impedance spectroscopy and they were applied to the determination of Zn, Cd, and Pb by square-wave anodic stripping voltammetry. The highest sensitivities coupled with nanomolar detection limits were achieved at bismuth films formed at constant potential; however, in situ deposited bismuth films exhibited better reproducibility. Future application as small, short-term-use sensors is indicated.

Keywords: Bismuth films, Carbon film electrodes, Trace metal determination, Stripping voltammetry, Electrochemical impedance spectroscopy

Devoted to the Memory of Professor Robert (Bob) Osteryoung

1. Introduction

Since the year 2000, bismuth film electrodes (BiFEs) have become an attractive new subject of electroanalytical research as a potential replacement for mercury electrodes [1]. Bismuth films have been deposited on carbon substrates, particularly on glassy carbon [1–13], carbon fibre [1, 8], screen-printed electrodes [14, 15], carbon paste electrodes [8, 16–19], electrically heated carbon paste electrodes [20], and boron-doped diamond electrode [19], showing excellent advantages with respect to mercury films. Bismuth bulk electrodes have also been studied and compared with BiFEs [21]. The films were deposited electrochemically at constant potential either in situ (in the model or sample solution) [1, 3–5, 7, 8, 10, 14–16, 19, 22–24] or ex situ by predeposition [2, 6, 9, 11–13, 20, 25–28].

In most cases bismuth film electrodes were characterized using voltammetry [4, 13] and microscopy [1, 12, 13, 29] and the results obtained showed that the bismuth film is essentially uniform. The most common application of the bismuth film electrode has been in the determination of trace metals, in particular by anodic [1, 3–5, 8–10, 14, 17–20, 22–24], cathodic [19], adsorptive stripping voltammetry [2, 11, 13, 22, 25, 26, 28], potentiometric stripping analysis [7, 16] and chronopotentiometry [15] as well as in sonoelectroanalysis [12]. Apart from metals, some organic compounds have been analysed, such as 2-nitrophenol and bromophenoxim by cyclic voltammetry and chronoamperometry in batch [6] and flow injection mode [28].

Carbon film electrodes fabricated from carbon film electrical resistors have recently been developed and

evaluated [30–32]. They have a wider potential range than many other forms of carbon electrode, especially after surface pretreatment; other advantages are physical robustness and ease of preparation. Use as short-term or disposable sensors for trace metals [30, 33], as an ascorbate sensor [34], characterization with mediator coatings [35] and as support for enzyme biosensors [36–38] has been demonstrated.

In this work, bismuth films have been electrochemically deposited onto these carbon film resistor electrodes by different methods, in order to assess the benefits of bismuth films in the negative potential range compared to bare carbon films. Besides ex situ and in situ deposition at constant potential, electrode potential cycling in the negative potential region was used as well as ex situ deposition at constant current. The films obtained were characterized by cyclic voltammetry and electrochemical impedance spectroscopy. Square-wave voltammetry has been demonstrated to be an excellent technique for the measurement and characterization of processes involving trace metal ions [39]. At these BiFEs, the square-wave anodic stripping voltammetric response to zinc, cadmium and lead ions is successfully demonstrated and evaluated.

2. Experimental

2.1. Chemicals and Solutions

Bismuth(III) nitrate, lead(II) nitrate, cadmium(II) chloride, and zinc(II) chloride were from Sigma (Germany). Sodium

acetate and acetic acid (Riedel-de Haën, Germany) and Millipore Milli-Q nanopure water were used to prepare 0.1 M acetate buffer, pH 4.45. Stock solutions of the salts mentioned above, concentration 1 g L⁻¹, were prepared in acetate buffer and stored at room temperature. They were diluted as required before measurements. Experiments were carried out at room temperature (25 ± 1 °C).

2.2. Instrumentation and Methods

A three-electrode cell was used for voltammetric measurements, containing a Bi-coated carbon film working electrode, a platinum foil counter electrode and a saturated calomel electrode (SCE) as reference. Preparation of the carbon film electrodes from 2 Ω carbon film electrical resistors is described in Ref. [30]. These consist of ceramic cylinders, length 0.6 cm and diameter 0.15 cm on which carbon is deposited by pyrolysis, with gold-coated metal contact caps and connecting wires at each end. One of the metal contacts with connecting wire is removed, and the other covered with a plastic sheath and epoxy resin leaving an area of ca. 0.20 cm² exposed. Electrodes were pretreated in acetate buffer by potential cycling from -1.5 to 1.5 V vs. SCE 10 times before first use.

Square-wave and cyclic voltammetry measurements were performed using a computer-controlled μ-Autolab Type II potentiostat/galvanostat with GPES 4.9 software (Eco Chemie, Netherlands). For square-wave anodic stripping voltammetry (SWASV) the frequency was 25 Hz, step potential 4 mV, and amplitude 25 mV; the potential was swept from -1.4 to -0.4 V (vs. SCE), after an equilibration time of 15 s.

Electrochemical impedance measurements were carried out in the same electrochemical cell with a PC-controlled Solartron 1250 frequency response analyzer coupled to a Solartron 1286 electrochemical interface using ZPlot 2.4 software (Solartron Analytical, UK). A sinusoidal voltage perturbation of amplitude 10 mV was applied, scanning from 65 kHz to 0.1 Hz with 10 points per frequency decade, auto-integration time 90 s. Fitting to electrical equivalent circuits was performed with ZView 2.4 software.

2.3. Formation of Bismuth Films

Bismuth films were formed by deposition onto the carbon substrate in different ways:

i) At constant applied potential. Films were deposited at -1.4 V (vs. SCE) for 300 s from a solution containing 1 mg L⁻¹ Bi(III) in 0.1 M acetate buffer, pH 4.45. The electrode was previously held at +0.3 V for 5 min to re-oxidize any heavy metal species present at the electrode surface, and the solution was stirred during conditioning and during deposition. Films were either predeposited ex situ in a different solution from that used for characterization or for measurement of trace metals or in situ together with the trace metal ions.

ii) By potential cycling in a solution containing 100 mg L⁻¹ Bi(III) in 0.1 M acetate buffer, pH 4.45. The potential was swept between -1.4 and -0.3 V vs. SCE) for 20 cycles at a sweep rate of 50 mV s⁻¹. The electrode was then taken out of the deposition solution and rinsed with distilled water.

iii) By galvanostatic deposition in 0.1 M acetate buffer solution, pH 4.45, containing 100 mg L⁻¹ Bi(III) and applying a current of -10 mA cm⁻² for 300 s.

The metals to be analyzed by square-wave anodic stripping voltammetry (SWASV) were deposited at -1.4 V (Zn), and -1.2 V (Cd, Pb) (vs. SCE) for 120 s and the electrode equilibrated after deposition for 15 s. The solution was stirred during the whole deposition time.

3. Results and Discussion

3.1. Electrochemical Characterization of the Bismuth Film Electrodes

3.1.1. Potential Window

BiFEs exhibit a wider negative potential window than carbon film electrodes in the negative range, but cannot be used in the positive potential region due to re-oxidation of Bi itself [1]. Figure 1 shows the negative limit of the potential window in pH 4.45 acetate buffer of a bare carbon film and of a bismuth-coated electrode, following deposition at a constant potential of -1.4 V for 300 s. Under these conditions, the negative potential limit of the carbon film was about -1.4 V (vs. SCE), similar to that obtained in [30, 31] after pretreatment in 0.1 M HClO₄ electrolyte. A more negative potential limit, of approximately -1.6 V, was obtained at the bismuth film. Bismuth films deposited in situ and ex situ at -1.4 V exhibit a similar potential window, as would be expected, since the only difference is the presence of Bi(III) in solution in the former case.

Bismuth films deposited by cycling of the electrode potential and galvanostatically, following the procedure

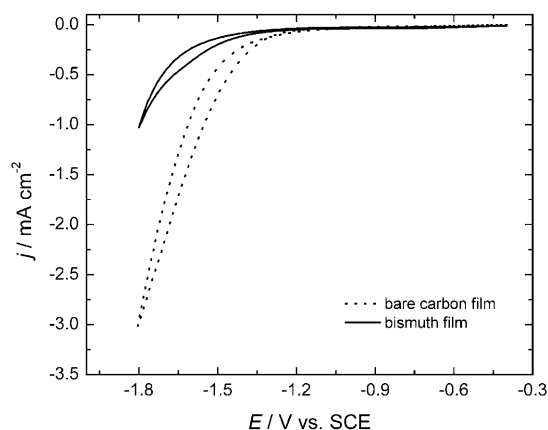


Fig. 1. Cyclic voltammograms at bare carbon film electrode and bismuth film electrode, formed ex situ at constant potential, in 0.1 M acetate buffer, pH 4.45, sweep rate 50 mV s⁻¹.

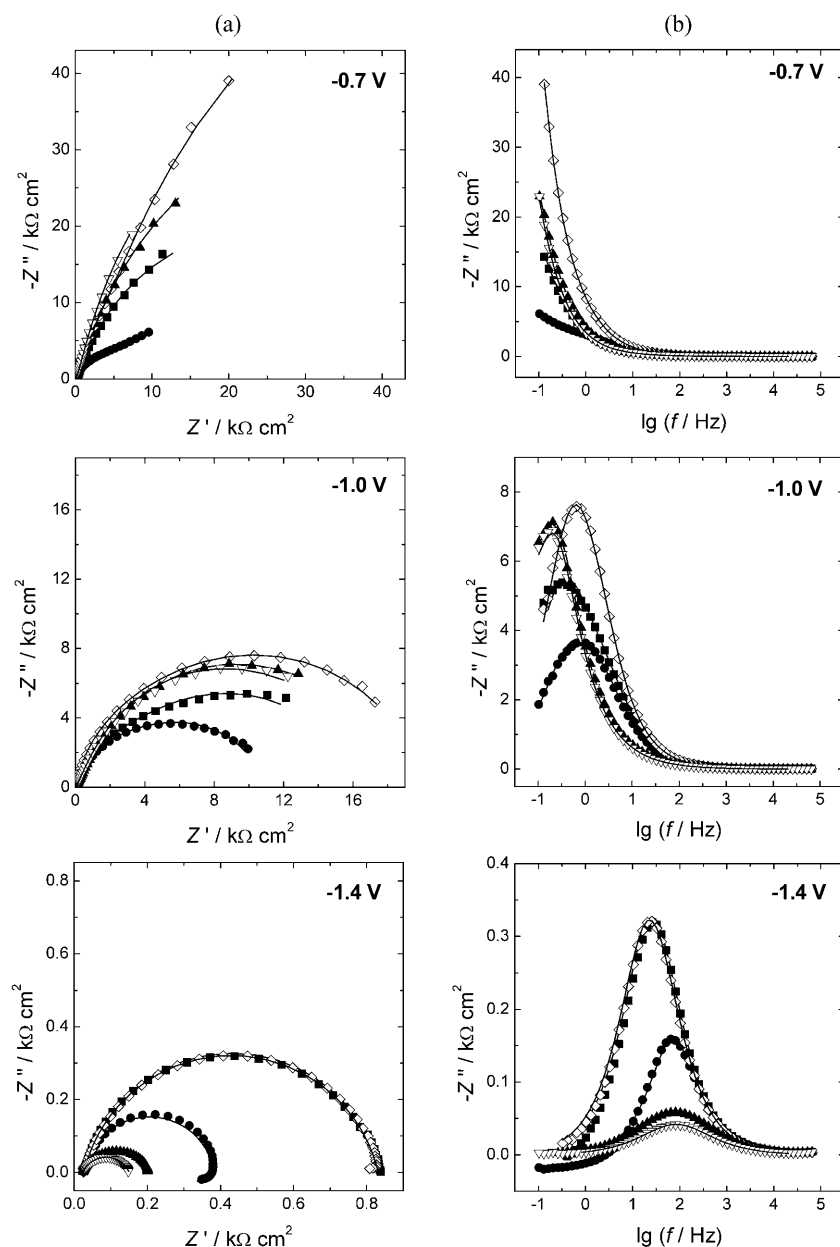


Fig. 2. Electrochemical impedance spectra: (a) complex plane (b) imaginary part vs. frequency at bare carbon film (●) and at bismuth films formed at constant potential (■) ex situ and (◇) in situ, (▽) by potential cycling and (▲) galvanostatically. The lines show the results of fitting. Supporting electrolyte 0.1 M acetate buffer, pH 4.45.

described in the experimental section, had a less wide potential window, closer to that of the bare carbon film.

The more negative potential limit obtained by constant potential deposition is better suited to the determination of zinc, as will be shown below.

3.1.2. Electrochemical Impedance Spectra

Figure 2 shows impedance spectra recorded at bare carbon electrodes and at BiFEs deposited in different ways at applied potentials of -0.7 V, -1.0 V and -1.4 V as plots (i) in the complex plane and (ii) with the imaginary part, Z'' , as a function of frequency. The latter type of plot represents a

powerful way of examining the time constants of interfacial processes, since the peaks in the plots correspond to when $\omega RC = 1$ for situations where charge separation (capacitance, C) and charge transfer (resistance, R) are in parallel, with ω the frequency of the voltage perturbation in radians.

Spectra at -0.7 V are all similar, the in situ deposited bismuth film having the highest impedance while the bare carbon film has the lowest values. Differences between film formation methods become more apparent at -1.0 V, probably reflecting the beginning of a tiny amount of hydrogen evolution.

At -1.4 V, where hydrogen evolution is beginning to become more significant in acetate buffer solution, the

impedance values are, consequently, much lower. The films formed at constant applied potential, *ex situ* and *in situ*, give an almost coincident response due to their similarity and the highest impedance values. Bismuth films deposited galvanostatically or by potential cycling have spectra significantly different from the films formed at constant potential.

The plots of Z'' vs. $\lg f$ conveniently show the different time constants of the processes occurring at both -1.0 V and at -1.4 V. At -1.0 V those of the films obtained by potential cycling and galvanostatically are the same, and bismuth films formed at constant potential approximate to those of the bare carbon film. The peaks move to much higher frequency values at -1.4 V, mainly due to more facile charge transfer, being coincident at $\lg f = 1.3$ for films formed at constant applied potential and are also the same at $\lg f = 2.0$ for the other bismuth films and the bare carbon electrode. This suggests that potential cycling and galvanostatic deposition lead to bismuth films with some similar characteristics to the bare carbon film.

Equivalent electrical circuits for modelling comprised the cell resistance, R_{Ω} , which was ca. $20 \Omega \text{ cm}^2$ in all cases, in series with one or two RCPE parallel combinations. The first of these, corresponding to that at higher frequency, consists of the charge transfer resistance, R_{ct} , at the electrode-solution interface and the CPE models a non-ideal capacitor, according to:

$$\text{CPE} = 1/(C_1 \omega)^{\alpha_1} \quad (1)$$

This was sufficient to model the spectra at -1.4 V, since hydrogen evolution was the dominant process. At the more positive values of applied potential the second RCPE

Table 1. Parameters from equivalent circuit fitting of the high frequency part of impedance spectra of Figure 2. R_{ct} : charge transfer resistance, C_1 : capacitance, α_1 : roughness exponent.

E (V vs. SCE)	R_{ct} ($\text{k}\Omega \text{ cm}^2$)	C_1 ($\mu\text{F cm}^{-2}$)	α_1
Carbon film			
-0.7	3.21	43.0	0.87
-1.0	3.20	27.7	0.88
-1.4	0.34	17.4	0.85
Bi film – constant potential <i>ex situ</i>			
-0.7	47.1	130	0.85
-1.0	2.46	24.6	0.93
-1.4	0.81	15.2	0.87
Bi film – constant potential <i>in situ</i>			
-0.7	10.5	41.1	0.79
-1.0	18.3	17.4	0.86
-1.4	0.82	17.2	0.86
Bi film – potential cycling			
-0.7	102	187	0.62
-1.0	11.6	114	0.66
-1.4	0.13	75.6	0.74
Bi film – constant applied current			
-0.7	82.1	128	0.63
-1.0	13.2	92.6	0.66
-1.4	0.18	60.2	0.72

parallel element was necessary, since the properties of the carbon/bismuth film were comparable with those of the interface. Table 1 shows data from the “high frequency” loop. The more negative potential leads to lower values of capacity as well as to lower charge transfer resistances. Of particular interest is the CPE exponent α , which is much lower for the films formed by potential cycling and galvanostatically or the bare carbon film. It suggests that the surface is rougher and may not be completely covered by bismuth, as also indicated from the Z'' vs. $\lg f$ plots – this would explain the less negative potential limit. Impedance is thus an extremely useful tool for aiding in elucidating these phenomena.

3.2. Determination of Zn, Cd, and Pb by Anodic Stripping Voltammetry

The bismuth film electrodes prepared by different ways developed in this work were evaluated for the measurement of zinc(II), cadmium(II) and lead(II) by SWASV. An example of typical experimental traces is given in Figure 3 and a summary of the calibration plot data obtained is in Table 2.

It has been found by other authors [1, 3, 4, 8, 10, 16] that *in situ* deposited bismuth films are more sensitive to some heavy metals than films of mercury or bismuth deposited *ex situ*. In order to increase the sensitivity of *ex situ* deposited films, bromide ion, which increases the homogeneity of the bismuth film according to [29], was added to the deposition solution in [11, 13]. However, with carbon film substrates it was found that *ex situ* deposited bismuth films had almost the same sensitivity as the *in situ*, as shown in Table 2, and thence essentially the same homogeneity. This occurred despite the fact that a lower Bi^{3+} concentration was used for *in situ* deposition, following the optimized procedure described in [1], than in the predeposition case which used a >2 times higher bismuth concentration and a deposition time ca. 3 times longer.

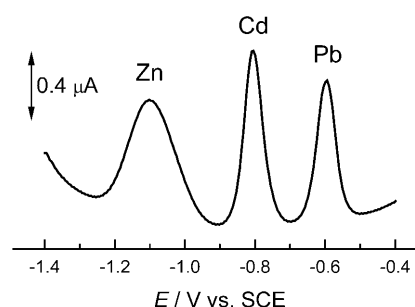


Fig. 3. Square-wave anodic stripping voltammograms of $10 \mu\text{g L}^{-1}$ metal ions (154 nM Zn , 89 nM Cd , and 48 nM Pb) at bismuth film deposited *in situ*. Preconcentration potential -1.4 V, preconcentration time 120 s. Supporting electrolyte $0.1 \text{ M acetate buffer}$, $\text{pH } 4.45$. Measurement conditions: frequency 25 Hz , step potential 4 mV , amplitude 25 mV , equilibration time 15 s .

Table 2. Calibration plot data from SWASV experiments of Cd(II), Zn(II) and Pb(II) at in situ and ex situ deposited bismuth films.

Bismuth film preparation	Analyte	Linear range (nM)	Slope (nA nM ⁻¹)	Intercept (nA)	LOD (nM)
Constant potential in situ	Zn(II)	40–600	2.41 ± 0.11	-4.77 ± 2.74	1.30
	Cd(II)	50–350	0.42 ± 0.02	-3.06 ± 0.54	7.31
	Pb(II)	20–200	3.74 ± 0.12	-5.10 ± 0.94	0.79
Constant potential ex situ	Zn(II)	70–600	0.23 ± 0.02	10.5 ± 6.9	2.12
	Cd(II)	40–350	3.04 ± 0.08	18.2 ± 9.3	1.05
	Pb(II)	20–200	3.74 ± 0.15	-26.9 ± 9.8	0.63
Potential cycling	Zn(II)	–	–	–	–
	Cd(II)	15–75	1.98 ± 0.18	-16.9 ± 7.7	1.67
	Pb(II)	10–50	4.62 ± 0.23	-2.85 ± 0.64	0.71
Galvanostatic	Zn(II)	750–4600	0.78 ± 0.20	-46.6 ± 14.6	138.5
	Cd(II)	90–2500	0.32 ± 0.01	-4.20 ± 1.13	41.1
	Pb(II)	50–1500	0.15 ± 0.02	-2.61 ± 0.23	18.8

Both the peak current and potential vary with concentration for Zn, Cd and Pb at bismuth film electrodes. At low concentrations, the peak current increases proportionally with concentration up to 40 µg L⁻¹ of each metal ion (i.e., 615 nM Zn, 357 nM Cd, and 192 nM Pb) and the peak potential does not change for Zn (-1.06 V), but shifts to less negative potential values for Cd (from -0.81 to -0.79 V) and Pb (from -0.63 to -0.60 V vs. SCE). Other data in these linear ranges are presented in Table 2. At higher concentrations the calibration plot slope increased and a second linear range was found up to 300 µg L⁻¹ of each metal ion. However, this part of the analytical plots was not of primary interest and had a large non-zero intercept. As can be deduced from the shift of the peak potential and the slightly negative intercepts in the calibration plots (Table 2), all three metals form a kind of intermediate intermetallic complex compound, as previously found at Bi₂O₃ modified carbon paste electrodes [18]. The weakest of these occur with Pb and the strongest with Zn as deduced from the dependence of the peak potential shift on metal ion concentration.

Surprisingly, a high sensitivity was obtained at bismuth films deposited by cycling of the applied potential, see Table 2, although they exhibited non-zero intercepts and this film gave no response to Zn(II), presumably owing to competitive hydrogen evolution.

The reproducibility of SWASV at a particular carbon film electrode was determined by forming a bismuth film and applying it to the anodic stripping analysis of the metals mentioned above, repeating the whole process five times. The results obtained ($n = 5$) were better at bismuth deposited in situ (except for Zn), where the reproducibility was 96.9–98.8% than at the ex situ deposited films where it was 87.4–95.4%. The least good reproducibility was for Zn at in situ deposited films, probably caused by some small hydrogen evolution at the preconcentration potential, -1.4 V (vs. SCE); at the bismuth films deposited ex situ reproducibility was much better since the hydrogen overpotential was higher such that hydrogen evolution was negligible.

Detection limits at these electrodes were lower than or similar to those obtained at bismuth films deposited at

constant potential reported in the literature, e.g., [10, 12, 16]. Additionally, most of them used a longer preconcentration time. Except for galvanostatically-formed BiFEs these were of the order of 1 nM, which makes the method a useful tool for application in natural samples, even after sample dilution with electrolyte. This is promising for future application of these robust and cost-effective electrodes outside the laboratory.

4. Conclusions

Bismuth film electrodes, formed by bismuth deposition in different ways on carbon film resistor electrodes, were characterized voltammetrically and by electrochemical impedance spectroscopy. Bismuth films deposited galvanostatically and by potential cycling were studied for the first time. BiFEs prepared in different ways were applied to the determination of trace Zn, Cd, and Pb ions. The in situ deposited films exhibited the best reproducibility, except for Zn determination, than the predeposited ones, and sensitivity was similar at both in situ and ex situ deposited bismuth films. The highest sensitivity for lead together with a low sub-nanomolar detection limit was found at bismuth films deposited by cycling of the applied potential. These results point to future application of these bismuth film sensors for disposable or short-term use.

5. Acknowledgements

Financial support from Fundação para a Ciência e a Tecnologia (FCT), ICEMS (Research Unit 103), Portugal, is gratefully acknowledged. R. Pauliukaite thanks FCT for a postdoctoral fellowship (SFRH/BPD/14518/2003).

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