

# Nafion-Coated Mercury Thin Film and Glassy Carbon Electrodes for Electroanalysis: Characterization by Electrochemical Impedance

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## Abstract

The different behavior of Nafion-coated mercury thin-film electrodes in anodic stripping voltammetry in nitrate and acetate buffer electrolytes has been probed by electrochemical impedance studies. Investigations concerned glassy carbon electrodes, glassy carbon coated with Nafion, mercury thin film electrodes and mercury thin film electrodes deposited between the glassy carbon substrate and the polymer film, with values of applied potential similar to those employed in anodic stripping voltammetry. Comparison is made with results obtained using Nafion/5% poly(vinyl sulfonic acid) coatings. In the absence of cationic reducible species, acetate buffer leads to larger impedance values than nitrate electrolyte and correlates well with better characteristics of stripping signals at Nafion-based coatings on mercury thin-film electrodes.

**Keywords:** Electrochemical impedance, Mercury thin-film electrode, Glassy carbon, Polymer-modified electrode, Nafion, Cation-exchange polymer, Anodic stripping voltammetry

## 1. Introduction

Glassy carbon has been much used in voltammetric studies owing to its low permeability to gases, low porosity, hardness, good electrical conductivity, inertness in a number of solvents and good positive potential range [1, 2]. The kinetics of electron transfer are influenced significantly by the preparation method, surface treatment and electrochemical pretreatment, e.g. [3]. The negative potential range, which reaches to ca.  $-1.0$  V without significant hydrogen evolution in common aqueous media, can be increased by covering glassy carbon with thin mercury films [4]. This modification permits the investigation of reduction processes and the use of stripping voltammetric procedures at solid electrodes, which would not otherwise be possible without simultaneous hydrogen evolution dominating the observed currents and preventing reagents reaching the electrode surface.

A general difficulty with solid electrodes, such as the glassy carbon electrode (GCE), is a diminution in response with time due to irreversible blocking of the surface by adsorbable components of the contacting solution. However, the surfaces can be modified or protected in various ways to minimize such alterations, which allows the determination of electroactive species in complex media. One of the simplest ways is to cover the electrode with a size-exclusion or ion-exchange polymer to prevent access to the surface of unwanted components. Thus, a number of types of polymer have been investigated for this purpose, for example cellulose acetate, e.g. [5, 6], Nafion, e.g. [6–10], poly(ester sulfonic acid), e.g. [11, 12], and polyaniline, e.g. [13]. An alternative approach is to use a gel-type membrane – an agarose gel in combination with microelectrodes for in situ measurements in natural waters has been developed [14, 15].

The perfluorosulfonated polymer Nafion, a cation exchange polymer owing to the negatively charged sulfonate groups at each end of the fluoropolymer chain has also been mixed with other sulfonated polymers to improve the cation-exchange characteristics and improve discrimination against interferents [6].

Nevertheless, there is some pH and ion size-dependent permeation of inorganic anions [16].

In the case of mercury thin-film electrodes (MTFEs), the Nafion coating has been applied directly onto a glassy carbon electrode substrate and a mercury thin film is then electro-deposited between the glassy carbon substrate and the Nafion coating from a Hg(II)-containing solution [17]. Such Nafion-modified MTFEs have been used in square-wave anodic stripping voltammetry (SWASV) in conjunction with the batch injection analysis technique [6, 17, 18]. In BIA, samples of volume as small as  $50\ \mu\text{L}$ , normally without pretreatment or addition of electrolyte, are injected directly over a detector electrode immersed in electrolyte solution in the BIA cell. Adsorption and electrode blocking from interferents is minimized first by the small sample volume and secondly through protection by the polymer coating [17]. It has been shown that such mercury films consist of a large number of closely spaced tiny micrometer-sized droplets which behave as though they exist as a uniform mercury film [18]. The presence of the coating results in a reduction of signal up to 15% due to diffusion limitations, but leads to good discrimination against interferents. The coating also confers robustness to the mercury thin film, particularly important in flow or induced-flow situations such as in ultrasound-assisted anodic stripping voltammetry [18].

Potassium nitrate and acetate buffer electrolytes have been used in these studies. It has been noted that there can be significant differences in the voltammetric response in the two types of electrolyte [6]. In this article, electrochemical impedance has been employed to study and compare some of the characteristics of Nafion and Nafion-coated mercury thin film electrodes and glassy carbon electrodes, in order to throw light on the processes occurring and on the influence of the electrolyte on the electrode response. Acidified nitrate and acetate buffer electrolyte media have been employed at values of applied potential similar to those employed in anodic stripping voltammetry at mercury thin-film electrodes. Studies on Nafion/5% poly(vinyl sulfonic acid)

coated MTFEs are also presented, where differences between electrolytes are more evident in the voltammetric response.

## 2. Experimental

Electrochemical experiments were carried out using a glassy carbon electrode of diameter 6 mm, a platinum foil auxiliary electrode and a saturated calomel electrode as reference. Polymer coatings and mercury thin films were prepared as described below.

Computer-controlled impedance measurements were done using a Solartron 1250 frequency response analyzer coupled to a Solartron 1286 electrochemical interface, with Zplot software. A sinusoidal voltage perturbation of rms amplitude 10 mV was applied, scanning from 65 kHz to 0.1 Hz with 5 measurements per decade of frequency. Fitting to equivalent circuits was carried out with Zsim software.

All reagents were of analytical grade and solutions were prepared using Millipore Milli-Q ultrapure water (resistivity > 18 M $\Omega$  cm). Electrolytes employed were 0.1 M KNO<sub>3</sub>/5 mM HNO<sub>3</sub> (pH 2.4) and 0.1 M acetate buffer (pH 4.6) and experiments were done at temperatures of 25  $\pm$  1  $^{\circ}$ C without deaeration, in order to be similar to conditions used in ASV experiments [6, 17]. Experiments were also carried out in the absence of oxygen.

A solution of 5 wt% Nafion in low-molecular-weight alcohols (Aldrich) was diluted in ethanol to prepare stock solutions for formation of Nafion films.

### 2.1. Preparation of the Nafion-Coated GCE and MTFE

The procedure employed was as described previously [17]. Briefly, the glassy carbon electrode was polished with alumina polishing foils down to 0.3  $\mu$ m particle size before each experiment and washed. A volume of 5  $\mu$ L of 0.25 wt% Nafion solution was applied to the surface followed immediately by 3  $\mu$ L of *N,N'*-dimethylformamide using a micropipette. After evaporating the solvents with a jet of air at room temperature, while the electrode was rotating at 50 rpm, the polymer film was cured with a jet of warm air at 70  $^{\circ}$ C for about 1 min.

In order to prepare the Nafion-coated mercury thin film electrode (NCMTFE), the electrode coated with Nafion was placed in a batch injection analysis cell [19]. Mercury deposition was done in situ by injection of 10  $\mu$ L of 0.1 M Hg(II) in 0.1 M KNO<sub>3</sub>/5 mM HNO<sub>3</sub> directly over the center of the electrode, while applying a potential of -1.0 V during 64 s [17].

### 2.2. Preparation of the Nafion/PVSA-Coated MTFE

A solution of poly(vinyl sulfonic acid) (PVSA) in water of concentration 5 wt% was mixed with 5 wt% Nafion in alcohols in the proportion 5% PVSA/95% Nafion (v/v) and diluted with ethanol such that the final polymer concentration was 0.25 wt%. The procedures for coating the glassy carbon electrode and for preparation of the mercury thin film were the same as described above.

### 2.3. Preparation of the MTFE

The in situ electrodeposition of the mercury thin film on the glassy carbon electrode followed the same procedure as described above for electrodes with Nafion-based coatings. However, 100  $\mu$ L of 0.1 M Hg(II) in 0.1 M KNO<sub>3</sub>/5 mM HNO<sub>3</sub> was injected instead of a 10  $\mu$ L volume.

## 3. Results and Discussion

The main objective was characterization of Nafion-coated mercury thin film electrodes in nitrate and acetate buffer electrolytes, in order to distinguish the influence of these commonly-used electrolyte compositions on their behavior. An example of a BIA square-wave anodic stripping voltammetry trace obtained for the analysis of cadmium and lead ions at Nafion-coated mercury thin film electrodes is shown in Figure 1. Important parameters in a good voltammetric trace are peak height and width, with the former proportional to concentration. It is also useful for peak height determination to have a background current with as low a slope as possible.

To probe the differences and for comparative purposes, impedance spectra were recorded for bare glassy carbon electrodes, glassy carbon covered with Nafion at 0.0 V, -0.5 V and -1.0 V (vs. SCE) and for mercury thin film electrodes and mercury thin film electrodes covered by Nafion at -0.5 V and -1.0 V (vs. SCE). These values of potential were chosen to cover the range of potentials used in anodic stripping voltammetry. Results obtained in the presence of dissolved oxygen, to be the closest to the conditions employed in electroanalytical square-wave voltammetric experiments, as well as in the absence of oxygen, in order to show the influence of oxygen, are presented below. Other results obtained using Nafion/5% poly(vinyl sulfonic acid) coatings are also shown, where the differences between electrolytes become more evident. Similar effects have been found with poly(ester sulfonic acid) coatings [12].

### 3.1. Glassy Carbon Electrode

Complex plane impedance plots are shown in Figure 2a for the bare glassy carbon electrode in nitrate and acetate buffer electrolytes. The behavior noted at -0.5 V for both electrolytes and at

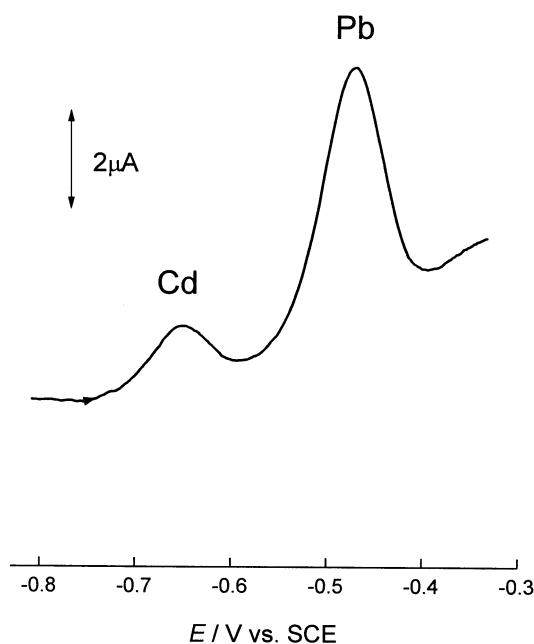


Fig. 1. Stripping voltammetric traces for BIA-SWASV of  $10^{-7}$  M Cd<sup>2+</sup> and Pb<sup>2+</sup> in 0.1 M KNO<sub>3</sub>/5 mM HNO<sub>3</sub> electrolyte. 50  $\mu$ L injection at 24.5  $\mu$ L s<sup>-1</sup> injection speed;  $t_{\text{dep}}$  = 30 s at -1.3 V (vs. SCE). Square-wave conditions: amplitude 25 mV, frequency 100 Hz, potential increment 2 mV.

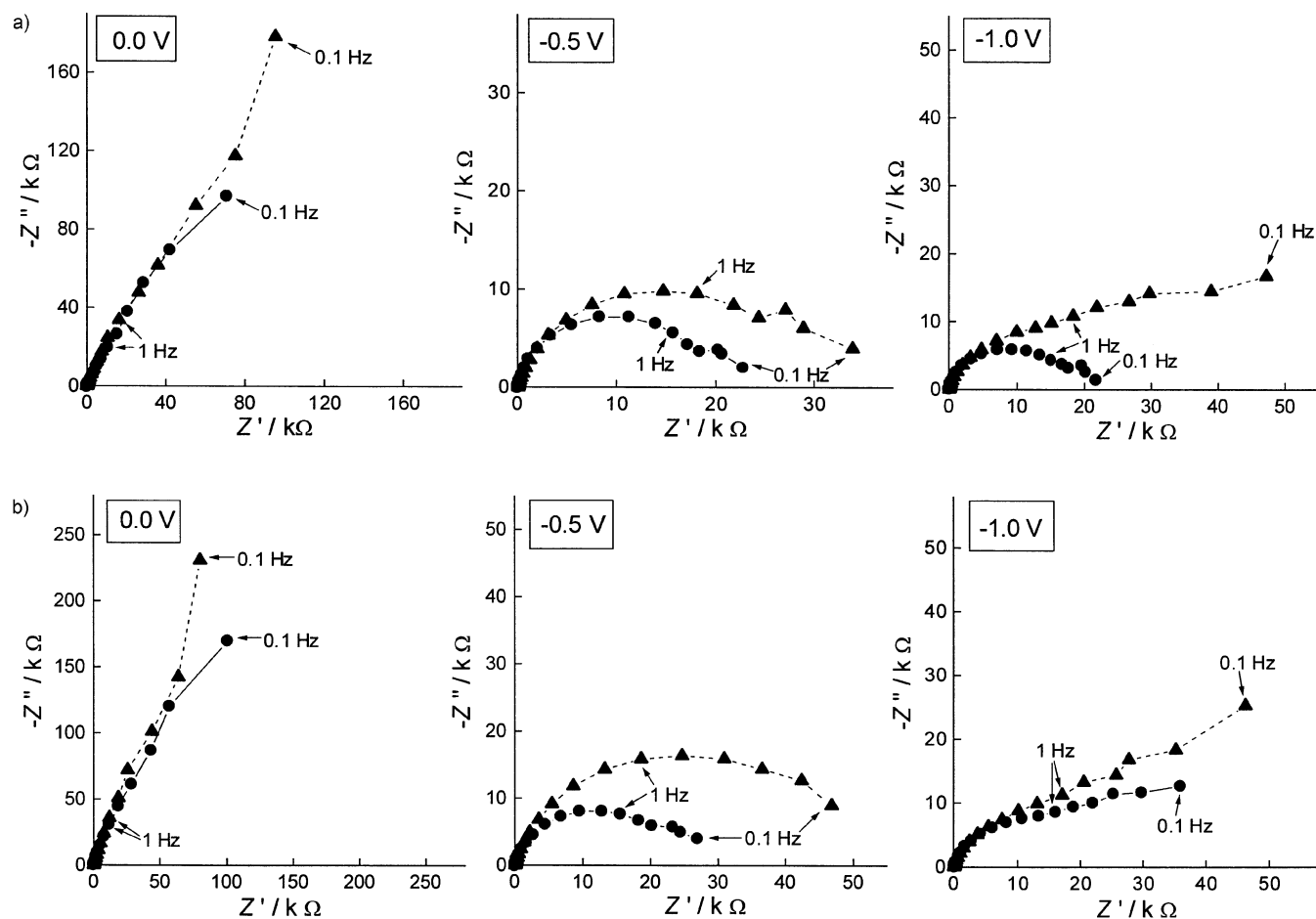


Fig. 2. Complex plane impedance plots in the presence of oxygen for a) bare glassy carbon electrode and b) Nafion-coated glassy carbon electrode: ●) 0.1 M  $\text{KNO}_3/5$  mM  $\text{HNO}_3$ , ▲) 0.1 M acetic acid/sodium acetate buffer (pH 4.6).

$-1.0$  V for nitrate can be modelled by an  $RC$  parallel combination with constant phase element, exponent between 0.7 and 0.8; an exponent of 1.0 representing a completely smooth surface and 0.5 a porous electrode [20]. On the other hand, in acetate buffer the form of the spectrum at  $-1.0$  V is different; it does not curve back to the real axis at low frequency, but continues in almost a straight line. This behavior can be modelled by a circuit representing diffusion through a rough surface structure, including two distributed elements in series.

As a first approximation, the observed semicircles could be attributed to the reduction of oxygen at  $-0.5$  V and of protons also at  $-1.0$  V. However, after solution deaeration (which resulted in an increase of the system impedance) they continue to be observed, which suggests that the time constant must also be related to the surface structure of the glassy carbon. This is in agreement with the observations of Heiduschka et al. [21]. When studying glassy carbon in  $\text{KCl}$  solution they observed a straight line at low frequencies and an underlying semicircle above 500 Hz. This was interpreted in terms of the distributed capacitances of exposed basal and edge planes of the glassy carbon, as well as the capacitance originating from carboxyl groups on the edge planes.

One main effect that can be noted from the impedance spectra for the two different electrolytes is the larger impedance values obtained in acetate buffer electrolyte. Approximate values of  $R$  and  $C$  in the  $RC$  parallel combination are shown in Tables 1 and 2.

### 3.2. Nafion-Coated GCE

The application of a Nafion coating using the procedure described in the experimental section leads to a film of ca.  $1 \mu\text{m}$  thickness, estimated using optical microscopy with indirect

Table 1. Data obtained from analysis of the high frequency part of the impedance spectrum for the various modified GC electrodes in 0.1 M  $\text{KNO}_3/5$  mM  $\text{HNO}_3$ .

GC electrode modified with	Presence of oxygen	$E(\text{V})$ (vs. SCE)	$R(\text{k}\Omega)$	$C(\mu\text{F})$
–	✓	$-0.5$	19	4.0
–	–	$-1.0$	18	4.1
–	–	$-0.5$	57	5.0
–	–	$-1.0$	39	4.2
Nafion	✓	$-0.5$	22	5.7
–	–	$-1.0$	27	7.3
Nafion	–	$-0.5$	46	5.6
–	–	$-1.0$	44	5.1
Nafion/Hg	✓	$-0.5$	26	7.5
–	–	$-1.0$	24	4.8
Nafion/Hg	–	$-0.5$	104	5.6
–	–	$-1.0$	44	4.9
Hg	✓	$-0.5$	140	5.6
–	–	$-1.0$	17	9.6
Nafion/PVSA/Hg	✓	$-1.0$	10	26

Table 2. Data obtained from analysis of the high frequency part of the impedance spectrum for the various modified GC electrodes in 0.1 M acetate buffer (pH 4.6).

GC electrode modified with	Presence of oxygen	$E(V)$ (vs. SCE)	$R(k\Omega)$	$C(\mu F)$
–	✓	–0.5	28	5.3
		–1.0	34	6.8
–	–	–0.5	62	5.2
		–1.0	58	4.1
Nafion	✓	–0.5	43	6.1
		–1.0	35	8.1
Nafion	–	–0.5	83	6.7
		–1.0	60	5.3
Nafion/Hg	✓	–0.5	28	8.4
		–1.0	43	5.6
Nafion/Hg	–	–0.5	97	6.6
		–1.0	66	5.6
Hg	✓	–0.5	66	6.7
		–1.0	21	6.3
Nafion/PVSA/Hg	✓	–1.0 (NaOAc)	29	28
		–1.0 (KOAc)	24	30

lighting and confirmed using known densities of Nafion films [10]. It can be expected that the main difference is increased difficulty of noncationic species reaching the substrate electrode surface. The impedance plots obtained are shown in Figure 2b. As can be seen, the impedance values have increased in relation

to the bare glassy carbon. As for bare glassy carbon, a semicircle was observed at  $-0.5$  V for both electrolytes, at  $-1.0$  V the spectra do not curve back to the real axis at low frequency, but continue in almost a straight line. This means that the Nafion polymer has altered the influence of the structural properties of the glassy carbon in some way as would be expected. Solution deaeration leads to an increase in impedance values rather than to a modification of the spectrum shape.

### 3.3. Nafion-Coated MTFE

Mercury thin-film electrodes were then formed under the Nafion films. This has an interesting effect on the shape of the impedance plots at  $-0.5$  V and  $-1.0$  V, as seen in Figure 3a. Taking into account the roughness factor, the spectrum at  $-0.5$  V can be modelled by an  $RC$  parallel element in series with a constant phase angle capacitance, which could not be observed for bare glassy carbon or for Nafion-modified glassy carbon. The spectrum curves towards the real axis at an applied of  $-1.0$  V. In this case, the impedance values are larger than at the glassy carbon electrode; this is probably due to the fact that proton reduction does not occur at the mercury surface as opposed to the glassy carbon surface, owing to its high hydrogen overpotential. Higher impedance values were observed in acetate buffer than in nitrate. Mercury thin film electrodes without Nafion also

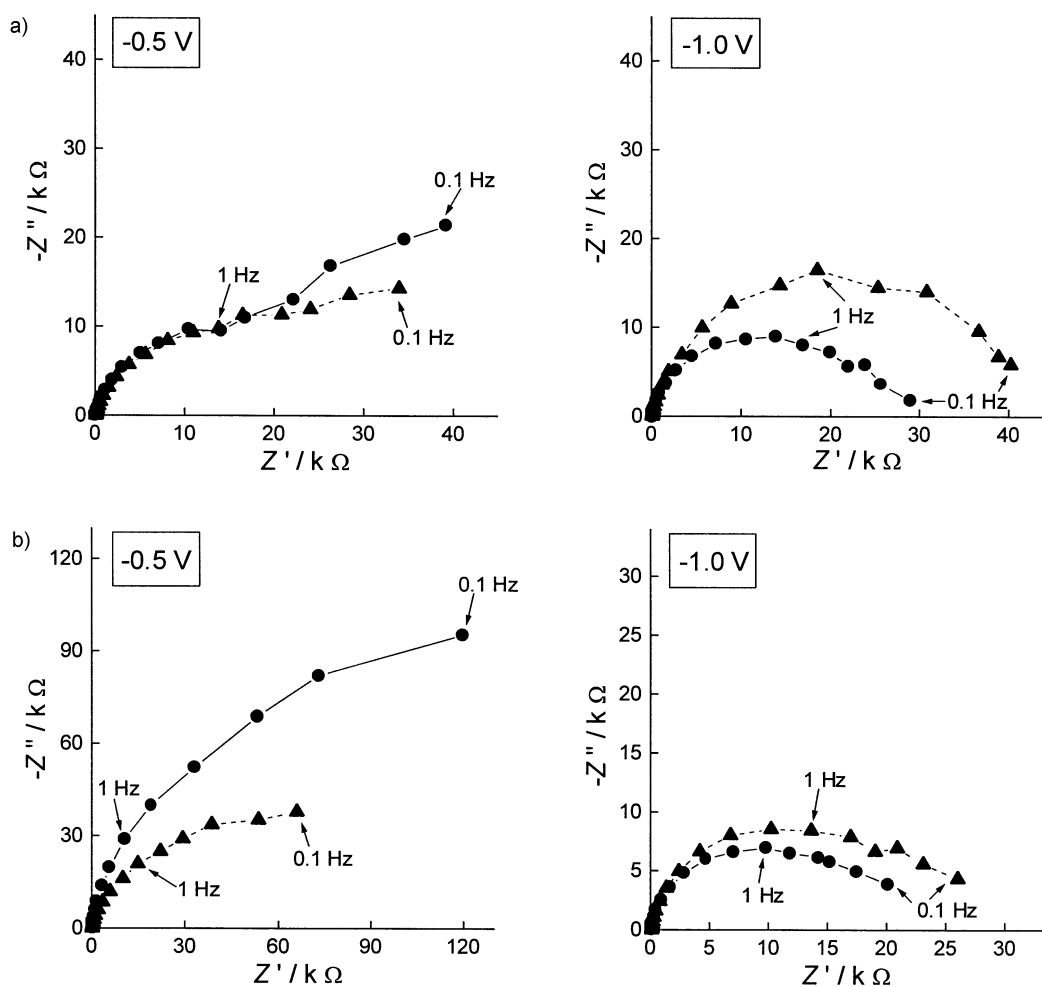


Fig. 3. Complex plane impedance plots in the presence of oxygen for a) Nafion-coated MTFE b) MTFE on glassy carbon substrate: ●) 0.1 M  $KNO_3/5$  mM  $HNO_3$ , ▲) 0.1 M acetic acid/sodium acetate buffer (pH 4.6).

presented a semicircular shape at  $-1.0$  V (Fig. 3b) the impedance values being lower than those for the Nafion-coated MTFEs.

The structure of polymer-coated MTFEs should be considered [22]. The mercury film is, in fact, a collection of droplets, sufficiently closely spaced that in ASV experiments they act in the same way as a uniform film [17]. The Nafion film adheres to the glassy carbon substrate between the droplets, which is important to prevent the polymer film peeling off. Thus the mercury causes distortion of the Nafion film, which may lead to increased porosity, and helps to explain differences between the spectra for Nafion-coated GCEs and Nafion-coated MTFEs.

### 3.4. Nafion/PVSA-Coated MTFE

The reason for introduction of 5% PVSA into the Nafion matrix was to improve the cation-exchange properties of Nafion by increasing the concentration of sulfonate groups. This approach has had some success [11], and suggests that structure modifications had occurred. Differences between electrolytes should thus be more clearly demonstrated.

The effect of the introduction of PVSA is to decrease the impedance values at  $-0.5$  V; at  $-1.0$  V there is little change (see Fig. 4). It can be deduced that distortion of the polymer film after mercury plating reduces the effect of the introduction of PVSA. The observed alteration in cation-exchange properties [6] can thus be ascribed primarily to the higher concentration of sulfonate groups.

The effect of both the anion and the cation of the electrolyte solution on Nafion/PVSA films from impedance experiments in pH 4.6 sodium and potassium acetate buffers as well as the potassium nitrate electrolyte are also shown in Figure 4. The differences between the various electrolytes are evident at both  $-0.5$  V and  $-1.0$  V. The main influence on the shape of the spectra is from the anion, with little cation effect.

### 3.5. Comparison of Different Electrode Materials and Coatings

As mentioned above, the spectra were fitted using an equivalent circuit which consists of an RC parallel distributed element, necessary due to the depressed semicircle character of the responses, in the frequency range 1 to 10 000 Hz. Results from modelling the high frequency data at  $-0.5$  V and  $-1.0$  V (a typical metal ion deposition potential in stripping voltammetry) are shown in Tables 1 and 2. This circuit, although not leading to perfect fitting, was the best that can be used for the large majority of the spectra. In any case, the variability of the polymer film characteristics, exemplified by variations in current of up to 10%, precludes the obtaining of exact data. For this reason each experiment was tested for reproducibility. Thus, the form of the spectra is always the same for each case and the values of  $R$  and  $C$  in Tables 1 and 2 have a maximum error of 10%. In all the fitting procedures, the high frequency intercept was in the range 40–50  $\Omega$  for nitrate electrolyte and 70–80  $\Omega$  for acetate buffer, which reflects the different ionic strengths. The roughness factor, where a value of 1 represents a completely smooth surface and 0.5 a porous surface [20], varied between 0.7 and 0.9.

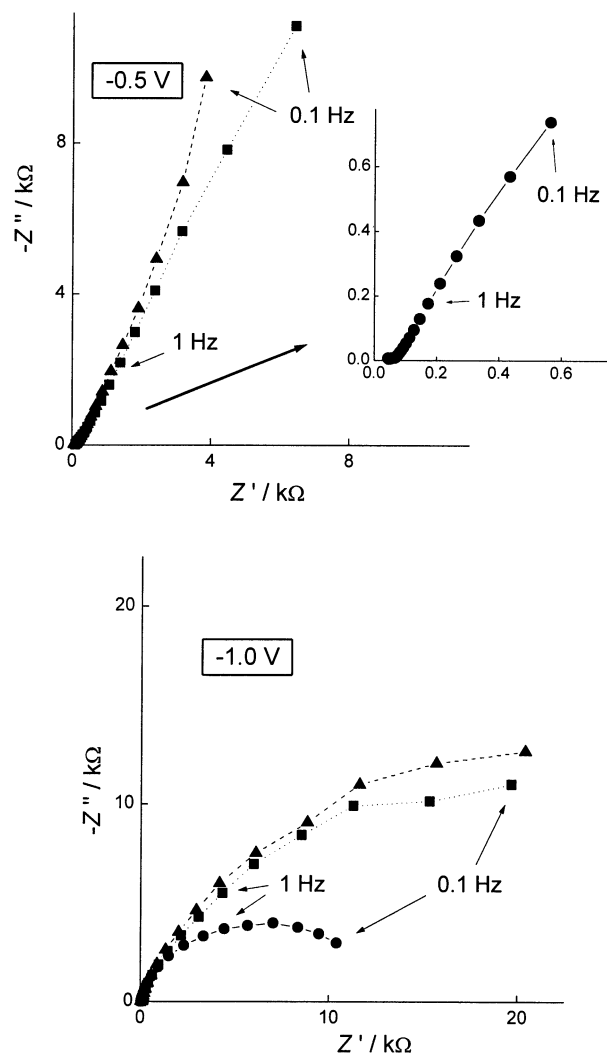


Fig. 4. Complex plane impedance plots in the presence of oxygen for Nafion/PVSA covered MTFE. (●) 0.1 M  $\text{KNO}_3/5$  mM  $\text{HNO}_3$ , (▲) 0.1 M acetic acid/sodium acetate buffer (pH 4.6), (■) 0.1 M acetic acid/potassium acetate buffer (pH 4.6).

In general, the capacitance values are higher in acetate buffer than in nitrate. This can be related to the higher ionic strength of the potassium nitrate electrolyte, leading to a more compact electric double layer and consequently resulting in lower values of capacitance.

The electrolyte type and applied potential exert a significant effect on the shape of the impedance spectra at bare glassy carbon. Nafion-coated glassy carbon, for both electrolytes, presents higher values of capacitance and resistance than that of bare glassy carbon. The higher resistance values can be explained by the increased difficulty of the charge transfer processes at glassy carbon due to the limitations imposed by the polymer coating. The larger capacitance values are probably related to charge separation through the Nafion layer.

The results obtained at  $-1.0$  V for Nafion-coated MTFEs are of particular interest, given that these are the conditions that mimic best the preconcentration step in anodic stripping voltammetry. Unlike Nafion-modified GC, a semicircle is observed at this potential in the presence of both electrolytes, although higher impedance is clearly seen in the presence of acetate buffer. This response is attributed to the presence of the mercury thin film, which is corroborated by the semicircle

observed at the same conditions for a mercury thin film electrode on glassy carbon substrate. However, the Nafion coating leads to higher impedance values due to the resistance to species movement and charge separation it causes.

The absence of oxygen in the solution causes a systematic increase of the electrode impedance values rather than altering the shape of the impedance spectra. This increase can be attributed to the fact that, after solution deaeration, oxygen reduction no longer contributes to the charge transfer processes occurring at the potentials investigated.

With respect to electrolyte identity, it is clear that the impedance values are higher and there is much less evidence of any charge transfer process in acetate media. This is true even at bare glassy carbon electrode, so that pH effects or a lower permeation of acetate ion through the Nafion film [13] cannot be invoked as the only explanation. A likely effect at bare glassy carbon is a stronger interaction of the acetate ion with hydroxyl and carboxylate groups at the electrode surface [2, 23], which will not occur in the same way with nitrate ion. Also, the form of the impedance spectra in acetate buffer solution changes less over the potential range studied, which can be linked to a lesser change in the values of the background current.

A probable explanation of the behavior with Nafion/PVSA film coatings has to do with the swelling of the polymer film on placing in electrolyte. It is clear that there will be some

incorporation of electrolyte ions as well as solvent. Nitrate would result in more opening up of the structure than acetate, in line with the discussion presented in [13]. These deductions corroborate those from Nafion thin film coatings. Once again, there is a lesser change in impedance.

Although the influence of the electrolyte and Nafion coating has been shown above, some further experiments were carried out to examine if there are alterations in the behavior in the presence of metal ions used in anodic stripping voltammetry. For these experiments, "high" concentrations of  $10^{-7}$  M  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were added to the electrolyte solutions. After deposition at  $-1.0$  V for 10 min, spectra were recorded at  $-1.0$  V and at  $-0.5$  V (after waiting a further 10 min for reoxidation). The spectra obtained are shown in Figure 5a and b shows voltammetric traces obtained from SWASV at these electrodes. Table 3 shows the results obtained from fitting of the spectra. In relation to the data in Tables 1 and 2 it can be seen that the capacitance values are similar whereas differences appear in the charge transfer resistance. In particular, the values of  $R$  at  $-1.0$  V are lower than at  $-0.5$  V, which can be attributed to passage of cations through the Nafion film and their reduction (at  $-0.5$  V neither cation is reduced). Nevertheless, at  $-0.5$  V (after the spectra recording at  $-1.0$  V) there is a significant difference between the results in the two electrolytes, with a higher value of  $R$  in nitrate than in acetate buffer electrolyte. Differences between

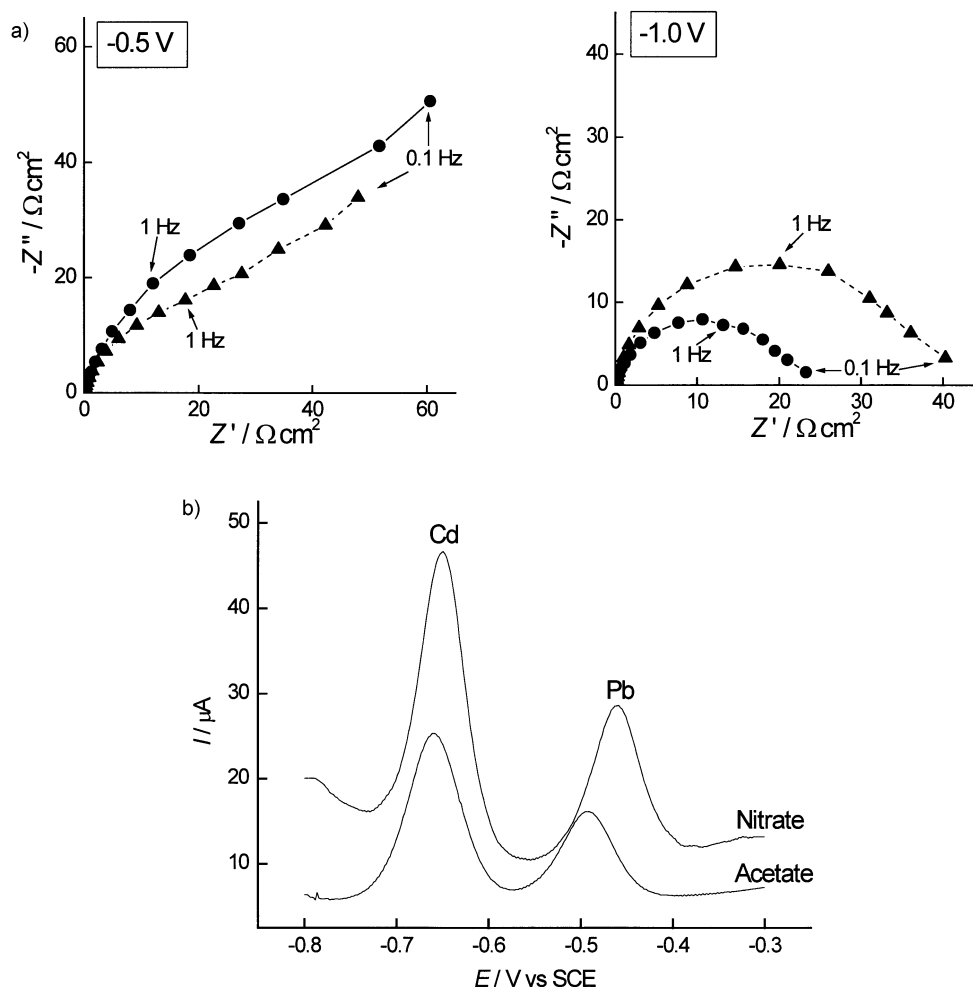


Fig. 5. Experimental results obtained in electrolyte containing  $10^{-7}$  M  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in: (●) 0.1 M  $\text{KNO}_3$ /5 mM  $\text{HNO}_3$ , (▲) 0.1 M acetic acid/sodium acetate buffer (pH 4.6). a) Complex plane impedance spectra in the presence of oxygen obtained after applying the specified potential for 10 min. b) Square-wave anodic stripping voltammetry after 10 min. deposition at  $-1.0$  V (vs. SCE), other conditions as Figure 1.

Table 3. Data obtained from analysis of the high frequency part of the impedance spectrum for the Nafion-coated MTFE in electrolyte +  $10^{-7}$  M  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  after 10 min conditioning at the spectrum recording potential.

Electrolyte	$E(V)$ (vs. SCE)	$R$ (k $\Omega$ )	$C$ ( $\mu\text{F}$ )
Acetate buffer	-1.0	35	4.5
	-0.5	48	6.9
Nitrate	-1.0	20	6.6
	-0.5	80	8.5

the electrolytes are also manifested in Figure 5b: note the higher background currents in nitrate electrolyte, the higher noise level, and the shift in the lead peak to more positive potentials. The conditions for these experiments were not those of BIA, which explains the different relative heights of the stripping peaks, also linked with the solubility of the ions in mercury. A detailed discussion of this phenomenon is beyond the scope of this article.

A complete investigation of the interfacial region would include a study of the variation of impedance with electrolyte concentration and with pH. Experiments undertaken in potassium nitrate electrolyte at pH 4.6 [24] have shown that the behavior of the glassy carbon electrode is completely different than at pH 2.4 and from acetate buffer although the differences are less for the Nafion-coated mercury electrode. Thus, although part of the difference of behavior can be ascribed to the ionization of surface groups on the glassy carbon surface the identity of the electrolyte also has an important role. For these reasons, the work described has concentrated on electrolytes as used in anodic stripping voltammetry [6].

In summary, there is a correlation between the impedance values in acetate buffer electrolyte, together with a lesser influence of applied potential on the spectra, and the often superior results – definition of stripping peaks, lower background current with lower slopes – obtained in acetate buffer electrolyte in stripping voltammetry experiments, particularly noted using the batch injection analysis technique.

#### 4. Conclusions

Several conclusions can be taken from this work, regarding the behavior of Nafion-coated electrodes and the influence of the electrolyte solution as examined by electrochemical impedance. First, the cation-exchange film itself alters the impedance characteristics of the glassy carbon electrode, and they are further changed on creating a mercury thin film between the glassy carbon substrate and the polymer film.

Secondly, there is evidence for the pronounced influence of the identity of the electrolyte, which is often neglected. It is shown

here that acetate buffer leads to larger impedance values than nitrate electrolyte in the absence of cationic reducible electroactive species in the potential range of interest.

For anodic stripping voltammetric experiments using cation-exchange polymer coated mercury thin-film electrodes, where it is preferable to minimize any contribution from the electrolyte medium, it is suggested that acetate buffer be employed.

#### 5. Acknowledgements

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