

POTENTIAL SHIFTS AT ELECTRODES COATED WITH ION-EXCHANGE POLYMERIC FILMS

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Summary—Voltammetry at electrodes modified with ion-exchange polymers, named “ion exchange voltammetry”, has been recently developed for characterizing and determining quantitatively ionic electroactive analytes preconcentrated at the electrode surface. Like for other voltammetric techniques, characterization is based on the position of the response on the potential scale, but an appreciable difference is frequently observed between the formal half-wave potential for redox couples incorporated within ion-exchange polymeric films and those for the same redox couples in solution as measured at bare electrodes. Such a difference has been rationalized here by a generalized equation, inferred from a suitable elaboration of the Nernst equation, whose validity has been tested by a thorough investigation performed at glassy carbon electrodes modified with either cationic (Nafion) or anionic (Tosflex) polymeric films. With this purpose, the effect of both charge and concentration of the analyte and of the loading counterion, thus last introduced as the cation or anion of the supporting electrolyte, of the ion-exchange selectivity coefficients of the redox partners and of their stoichiometric coefficients, as well as of the number of electrons involved in the charge transfer has been evaluated. The results obtained agree quite well with theoretical expectations and indicate that the potential shifts found are mainly conditioned by both charge and concentration of the counterion from the supporting electrolyte and by the ratio of the ion-exchange equilibrium constants for the two redox partners involved. Other parameters considered have no influence on the potential shift or lead to negligible effects, provided that the quantities of the redox partners incorporated within the ion-exchange coating represents less than 5% of the film capacity. Again in agreement with theoretical expectations, positive shifts are found for increasing supporting electrolyte concentrations when cationic redox species incorporated within cationic films are involved, while the opposite effect is found for anionic redox species incorporated within anionic films.

Electrodes modified with ion-exchange polymers are the subject of a number of recent investigations in which they are suggested as profitable sensors for electroactive ionic species.¹⁻³ Electroanalysis by this approach, for which the name “ion exchange voltammetry” has been suggested recently,⁴ is in fact suitable for enhancing the electroanalytical sensitivity relative to any organic or inorganic ionic analyte since it permits their preliminary accumulation in the polymeric film.

In several papers concerning these electrodes it is commonplace to report that formal potentials for redox couples incorporated within the coatings are apparently coincident with those in solution as measured at bare electrodes. Otherwise, when such coincidence is not claimed, different reasons are advanced to account for

the potential shifts observed. Thus, the concentration of the supporting electrolyte,⁵ the ion-exchange selectivity coefficients of the redox partners,⁶ the number of electrons involved in the charge transfer,⁷ the analyte concentration⁸ or the charge of both the electroactive species⁸ and ions of the supporting electrolyte⁵ have been considered.

Such an ambiguity needs to be overcome since analyte characterization by ion exchange voltammetry, consistently with other voltammetric techniques, is based mainly on the position of the response on the potential scale. Consequently, we have carried out the present investigation aimed at improving understanding of the reasons causing the potential shifts observed frequently at electrodes modified with either cationic or anionic coatings, so as to

achieve a comprehensive description of this phenomenon as well as its rationalization. With this purpose, we have worked out a generalized equation able to provide the potential shift expected for any redox couple under any experimental condition concerning the ionic strength of the medium. Its reliability has been then checked by measuring voltammetrically, the formal redox potentials of a series of ionic analytes with different charge, preconcentrated at glassy carbon electrodes modified with either perfluorinated cationic (Nafion) or anionic (Tosflex) polymeric films in aqueous solutions containing variable concentrations of different supporting electrolytes whose cation and/or anion displays a different charge

EXPERIMENTAL

Chemicals and instrumentation

All the chemicals employed were of reagent grade quality and they were used without further purification. Stock solutions of the electroactive analytes Pb^{2+} , $[\text{Ru}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$ and Br^- ($10^{-3}M$) as well as of the ions Na^+ , Mg^{2+} , La^{3+} , ClO_4^- , Cl^- and SO_4^{2-} ($1M$) competing in the ion-exchange reactions, these last added as the supporting electrolytes, were prepared by dissolving suitable amounts of the corresponding salts $\text{Pb}(\text{NO}_3)_2$, $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, NaBr , NaClO_4 , $\text{Mg}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$, Na_2SO_4 and NaCl in Milli-Q reagent-grade water. The concentration of NaClO_4 , Na_2SO_4 and NaCl solutions was directly inferred from the weight of the anhydrous salts employed, while other solutions were standardized by titration with EDTA (Pb^{2+} , Mg^{2+} , La^{3+}), with thiosulphate via the iodometric method ($[\text{Fe}(\text{CN})_6]^{3-}$), by coulometric titration ($[\text{Ru}(\text{NH}_3)_6]^{3+}$) or by argentometric titration (Br^-). These solutions were diluted before use to the desired concentration with water purified by a Milli-Q system Millipore ("Milli-Q water") which was always used as the solvent.

All electroanalytical measurements were performed by an EG&G-PARC model 273 potentiostat driven by a software package installed on an ASEM 386E computer.

Procedure

The working electrodes employed were glassy carbon disks (geometric area 0.07 cm^2) previously mirror polished by graded alumina powder, followed by washing with Milli-Q

water in an ultrasonic bath. They were coated with perfluorinated anionic (Tosflex) or cationic (Nafion) polymeric films. Their preparation was performed by droplet evaporation of known volumes of either 5% (w/v) Nafion solutions (Aldrich) or a 1.2% (w/v) Tosflex (Tosoh) solution, the latter was prepared according to the literature.⁹ The thickness of wet films ($1\ \mu\text{m}$) was estimated by using 1.58 g/cm^3 and 1.70 g/cm^3 , respectively, as the density of the wet Na^+ form of Nafion¹⁰ and of the wet perchlorate form of Tosflex, this last roughly estimated by weighing a piece of a Tosflex IE SA48 membrane with known thickness and carefully measured area.¹¹

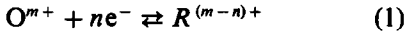
Before use, any modified electrode was equilibrated by dipping for 5 hr into a stirred solution of a suitable supporting electrolyte enabling the ion-exchange film to become loaded with the desired counter-ion. It was then inserted, together with a bare glassy carbon electrode, a Pt-wire counter electrode and a saturated calomel reference electrode (SCE), into a single-compartment cell filled with a suitable volume (30 ml) of solution containing both the assayed electroactive analyte and the desired supporting electrolyte also used in the equilibration step mentioned above. After a fixed preconcentration time (usually 15 min), cyclic voltammograms were recorded at 20 mV/sec and formal half-wave potentials were equated with the average of the anodic and cathodic peak potentials found when the analyte was either $[\text{Ru}(\text{NH}_3)_6]^{3+}$ or $[\text{Fe}(\text{CN})_6]^{3-}$. For Pb^{2+} and Br^- such a procedure can lead to misquoted values owing to the asymmetry of either the anodic stripping peak (Pb^{2+}) or the overall cathodic-anodic picture (Br^-). Consequently, the formal half-wave potential for these species was calculated by adding 28.5/2 mV to the negative cathodic-peak potential for Pb^{2+} ^{12,13} and subtracting 18 mV from the positive anodic-peak potential for Br^- .^{13,14} This entire procedure was repeated for different concentrations of both the same analyte ($10^{-4} - 10^{-2}M$) and the same supporting electrolyte ($10^{-3} - 1M$) and any formal half-wave potential thus found was then compared with that measured in the same cell at the bare electrode for the same analyte in the same samples.

All measurements were carried out on samples (30 ml) which had been deaerated with nitrogen and thermostated at 20°C . During the preconcentration step the sample was stirred at a controlled constant rate of 800 rpm.

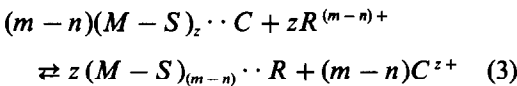
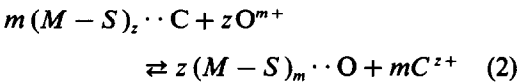
RESULTS AND DISCUSSION

Theoretical considerations

For the sake of simplicity, we consider at first the following simple generalized redox reaction:



where both the oxidized and reduced partner is a cationic species exhibiting a unity stoichiometric coefficient. When this cationic redox couple is incorporated within a cation-exchange polymeric film coating the electrode surface, the following exchange equilibria take place:



where M is the polymeric matrix, S is the anionic exchange site and C^{z+} is the original counterion from the supporting electrolyte. Under these conditions, the concentrations of the redox partners present in the usual form of the Nernst equation written for reaction (1) can be replaced by their expression drawn from the following equilibrium constants relative to the exchange reactions (2) and (3), respectively:

$$K_0 = (x_{(M-S)_m} O)^z [C^{z+}]^m / (x_{(M-S)_z} C)^m [O^{m+}]^z \quad (4)$$

$$K_R = (x_{(M-S)_{(m-n)}} R)^z [C^{z+}]^{(m-n)} / (x_{(M-S)_z} C)^{(m-n)} [R^{(m-n)+}]^z \quad (5)$$

where $x_{(M-S)_m} O$, $x_{(M-S)_{(m-n)}} R$ and $x_{(M-S)_z} C$ represent the fraction of exchange sites within the polyelectrolyte coating loaded with O^{m+} , $R^{(m-n)+}$ and C^{z+} , respectively.

In such a way, the Nernst equation becomes expressed as follows.

$$E = E_0 + (RT/nF) \ln(x_{(M-S)_m} O / x_{(M-S)_{(m-n)}} R) - (RT/zF) \ln(x_{(M-S)_z} C) + (RT/znF) \ln(K_R/K_0) + (RT/zF) \ln[C^{z+}] \quad (6)$$

For equal values of $x_{(M-S)_m} O$ and $x_{(M-S)_{(m-n)}} R$ this equation gives the formal half-wave potential for the redox couple incorporated within the ion exchange coating, $(E_{1/2})_{ie}$, which can easily be compared with the corresponding formal half-wave potential measured

at a bare electrode, $(E_{1/2})_{sol}$, thus providing the following equation for the potential shift expected:

$$(E_{1/2})_{ie} = (E_{1/2})_{sol} - (RT/zF) \ln x_{(M-S)_z} C + (RT/znF) \ln(K_R/K_0) + (RT/zF) \ln[C^{z+}] \quad (7)$$

Of course, this equation modifies if redox couples different from that considered in reaction (1) are taken into account. Thus, when one of the redox partners is an uncharged species, regardless of its solubility, equation (7) holds, but a unity value must be assigned to the relevant ion-exchange equilibrium constant. Moreover, different stoichiometric coefficients for the redox partners result in the sole modification of the logarithmic term containing the equilibrium constants which becomes $(RT/znF) \ln[(K_R)^y/(K_0)^x]$, where x and y are the stoichiometric coefficients for the oxidized and reduced species, respectively.

As a matter of fact, equation (7), suitably modified, requires in this last case some additional considerations since when x and y are not coincident the concentrations of the oxidized and reduced partners are not equal each other at the formal half-wave potential, so that the logarithmic term containing these concentrations does not cancel in the Nernst equation written at $E_{1/2}$. In addition, under this condition, formal half-wave potentials cannot be equated from cyclic voltammograms with the average of the anodic and cathodic potentials.¹²⁻¹⁴ However, these difficulties may be easily overcome by considering that when the simple procedure adopted above is also followed for asymmetric redox couples, strictly equal errors are introduced both in the case of their incorporation within the ion-exchange coating and when they are dissolved in solution, so that these errors cancel out when the difference $(E_{1/2})_{ie} - (E_{1/2})_{sol}$ is equated.

Finally, if the redox partners are both anionic species able to be incorporated within an anion-exchange polymeric film modifying the electrode surface, equation (7) requires only that the signs of both the second and fourth terms are changed.

As a consequence of all these statements, the following comprehensive equation can be written for the formal half-wave potential of a

generalized redox couple incorporated within an ion-exchange coating:

$$\begin{aligned} (E_1)_{ie} &= (E_1)_{sol} \\ &\mp (RT/zF) \ln x_{(M-S)_2, c} \\ &+ (RT/znF) \ln [(K_R)^y / (K_0)^x] \\ &\pm (RT/zF) \ln [C^{\pm}] \end{aligned} \quad (8)$$

where upper signs refer to the use of cationic membranes as coatings for the electrode surfaces, while lower signs refer to the use of anionic membranes

Check of theoretical expectations

The redox couples investigated have been chosen with the aim of considering quite a wide set of variables contained in the comprehensive equation (8). Thus, both cationic ($[\text{Ru}(\text{NH}_3)_6]^{3+}/[\text{Ru}(\text{NH}_3)_6]^{2+}$) and anionic ($[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$) redox couples have been examined, together with redox systems involving an uncharged species as one of the redox partners (Pb^{2+}/Pb and $2\text{Br}^-/\text{Br}_2$). Moreover, some of these couples are simply characterized by n values equal to one ($[\text{Ru}(\text{NH}_3)_6]^{3+}/[\text{Ru}(\text{NH}_3)_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$) or two (Pb^{2+}/Pb) while in one case ($2\text{Br}^-/\text{Br}_2$) different stoichiometric coefficients for the redox partners are involved.

Furthermore, supporting electrolytes containing differently charged cations (Na^+ , Mg^{2+} , La^{3+}) or anions (Cl^- , ClO_4^- , SO_4^{2-}) have been employed to monitor the effect of their concentration on the formal half-wave potentials for the redox couples incorporated within the ion-exchange coating. In this connection, we wish to remark that, in agreement with the literature,¹⁵ the La^{3+} hydrolysis turns out to lead only to negligible amounts (from about 10% for a 10^{-3}M La^{3+} concentration to 0.5% for a 1M La^{3+} content) of the dicationic species $[\text{La}(\text{OH})_2]^{2+}$.

All tests have been conducted under experimental conditions assuring that the quantities of the redox couples incorporated in the ion-exchange coatings represents less than 5% of the film capacity. In such a way, $x_{(M-S)_2, c}$ is always very close to unity so as the second term in equation (8) can be ruled out since it attains zero.

The results obtained in these tests are summarized in Fig. 1 and Table 1 both showing an excellent agreement with the expectations based on equation (8). In all cases, in fact, the poten-

tial shifts $(E_1)_{ie} - (E_1)_{sol}$ are found to depend linearly on the logarithm of the supporting electrolyte with a slope very close to that theoretically expected.

As to the dependence of the potential shift on the ion-exchange equilibrium constants, also expected from equation (8), it has been checked by exploiting the plots in Fig. 1 to extrapolate the relevant intercept which enable indeed these constants to be evaluated. The constant values thus found are listed in Table 2 which shows a quite good agreement with literature values. This table does not report the constants relative to the ferricyanide/ferrocyanide redox couple as well as those referred to the lanthanum cation and to the sulphate anion since to our knowledge ion-exchange equilibrium constants for these cases are not available in the literature. On the contrary, such a table also compares some

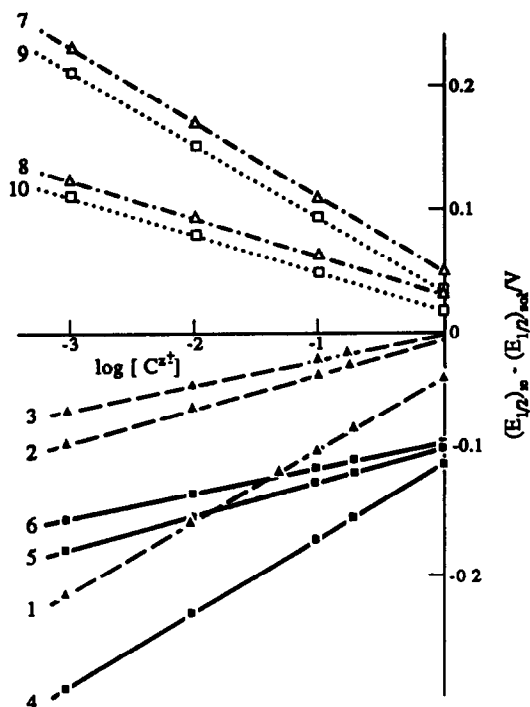


Fig. 1. Dependence on the supporting electrolyte concentration (C^{\pm}) of the formal half-wave potentials measured by cyclic voltammetry at glassy carbon electrodes coated with Nafion (lines 1–6) or Tosflex (lines 7–10) films in aqueous solutions containing the following analytes and supporting electrolytes: line 1, 10^{-5}M Pb^{2+} – NaClO_4 ; line 2, 10^{-5}M Pb^{2+} – $\text{Mg}(\text{NO}_3)_2$; line 3, 10^{-5}M Pb^{2+} – $\text{La}(\text{NO}_3)_3$; line 4, 10^{-5}M $[\text{Ru}(\text{NH}_3)_6]^{3+}$ – NaClO_4 ; line 5, 10^{-5}M $[\text{Ru}(\text{NH}_3)_6]^{3+}$ – $\text{Mg}(\text{NO}_3)_2$; line 6, 10^{-5}M $[\text{Ru}(\text{NH}_3)_6]^{3+}$ – $\text{La}(\text{NO}_3)_3$; line 7, $7.5 \times 10^{-5}\text{M}$ $[\text{Fe}(\text{CN})_6]^{3-}$ – NaClO_4 ; line 8, $7.5 \times 10^{-5}\text{M}$ $[\text{Fe}(\text{CN})_6]^{3-}$ – Na_2SO_4 ; line 9, $5 \times 10^{-4}\text{M}$ Br^- – NaCl ; line 10, $5 \times 10^{-4}\text{M}$ Br^- – Na_2SO_4 . Preconcentration time 15 min, film thickness $1\ \mu\text{m}$.

Table 1 Effect of the supporting-electrolyte concentration on the formal half-wave potentials for the listed redox couples incorporated within the ion-exchange coating

Redox couple	Supporting electrolyte	Line in Fig 1	Slope (mV/decade)	
			Found‡	Expected
*Pb ²⁺ /Pb	NaClO ₄	1	59.0 (±0.9)	59.1
	Mg(NO ₃) ₂	2	28.2 (±1.4)	29.5
	La(NO ₃) ₃	3	20.4 (±0.8)	19.7
*[Ru(NH ₃) ₆] ^{3+/2+}	NaClO ₄	4	60.0 (±1.0)	59.1
	Mg(NO ₃) ₂	5	28.5 (±1.1)	29.5
	La(NO ₃) ₃	6	17.3 (±2.0)	19.7
†[Fe(CN) ₆] ^{3-/4-}	NaClO ₄	7	-57.9 (±1.5)	-59.1
	Na ₂ SO ₄	8	-30.1 (±0.9)	-29.5
‡2Br ⁻ /Br ₂	NaCl	9	-60.0 (±1.2)	-59.1
	Na ₂ SO ₄	10	-30.0 (±0.8)	-29.5

*Nafion coating

†Tosflex coating

‡Standard deviations in parentheses

of the constants found with literature values for Dowex 50 (4% DVB) and Amberlite 400 (8–10% DVB) polymers, *i.e.* two ion exchangers characterized by the same exchange sites present also in Nafion and Tosflex, respectively, as well as by a comparable cross linking.

The overall agreement ascertained between experimental results and theoretical expectations allows one to conclude that the potential shifts found at electrodes coated with ion-exchange polymeric films are mainly conditioned by the ratio of the ion-exchange equilibrium constants for the two redox partners as well as by both charge z and concentration of the counterion from the supporting electrolyte. On the contrary, our results point out that the charge and concentration of the electroactive species are unable to affect the potential shift, provided that the quantities of the redox couples incorporated in the ion-

exchange coating represents less than 5% of the film capacity so that the effect of $x_{(M-S)} c$ can be neglected since it always attains unity. Moreover, only an insignificant effect of both the number n of electrons transferred in the redox reaction and the stoichiometric coefficients x and y is found in agreement with our expectations based on equation (8).

Remarkable enough is that the positive or negative slopes can be obtained according to the sign of the analyte charge. In fact, a positive potential shift is caused by an increase of the supporting-electrolyte concentration when cationic species incorporated (of course) within cationic films are involved, while the opposite effect is observed for anionic analytes incorporated within anionic films.

These different trends, expected from equation (8), can be easily accounted for on considering that the reduction of a cation bound

Table 2 Comparison between the ion exchange constants found and the corresponding literature data

Ion-exchange substitution*	Constant value		
	Found†	Literature	Ref
O/C = Pb ²⁺ /Na ⁺	22.67 (±3.63)	21.10‡	16
		24.90§	17
O/C = Pb ²⁺ /Mg ²⁺	2.70 (±1.01)	2.22§	17
R/C = Br ⁻ /Cl ⁻	3.78 (±0.45)	4.16	17
(R/C)/(O/C) = (Ru ^{II} /Na ⁺)/(Ru ^{III} /Na ⁺)	0.014 (±0.002)	0.020‡	18

*O, R and C have the meaning defined for equations (1)–(3)

†Range in parentheses.

‡On Nafion 117

§On Dowex 50 (4% DVB)

||On Amberlite 400 (8–10% DVB)

to an ion-exchange polymer requires the entrance of a cation from the supporting electrolyte to restore electroneutrality, while during the reduction of an anionic analyte electroneutrality is continuously restored through the release of anionic species (*i.e.* the competing anion from the supporting electrolyte). Consequently, the reduction process is favoured in the former case by an increase of the supporting-electrolyte concentration, while such an increase causes the opposite effect in the latter case.

All these outcomes must be carefully considered when the inspection of ion-exchange voltammograms is performed with the aim of assigning correctly the peaks found in order to avoid unreliable analyte identifications. In particular, our results point out unambiguously that analyte characterization based on a simple comparison with formal half-wave potentials of redox couples in solution as measured at bare electrodes could be strongly misleading.

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