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Irena Jureviciute · Stanley Bruckenstein
Angela Jackson · A. Robert Hillman

Redox history effects accompanying the electrochemical cycling of poly(vinylferrocene)

Abstract Cyclic voltammetric studies of poly(vinylferrocene), PVF, in aqueous sodium perchlorate, sodium *p*-toluenesulfonate, and sodium naphthalenesulfonate solutions revealed unexpected history effects. The films contain redox sites in two local environments. One type of ferrocene site is in a compact, unsolvated environment; it undergoes redox switching in $NaClO_4$ with only the transfer of counter ions. The other type of ferrocene site is in a more diffuse environment; it undergoes redox switching with the transfer of perchlorate counter ion and water. Only the latter sites can accommodate large anions (toluenesulfonate or naphthalenesulfonate), and therefore undergo redox switching in such media. Upon multiple redox cycling, these large anions get progressively locked into the structure, thereby blocking the diffuse sites. Upon transfer back to $NaClO_4$ solution, only the "compact" sites are able to undergo redox switching.

Keywords Electroactive films · Poly(vinylferrocene) · EQCM · Solvation · Redox history

Introduction

In this paper we describe some unique non-equilibrium behavior involving mobile ion transfer between an

I. Jureviciute (✉)
Institute of Chemistry, A. Gostauto 9, Vilnius, Lithuania
E-mail: irjur@ktl.mii.lt

S. Bruckenstein
Department of Chemistry, University at Buffalo/SUNY, Buffalo, NY 14260, USA

A. Jackson · A. R. Hillman
Department of Chemistry, University of Leicester,
LEI 7RH Leicester, England

electroactive polymer and its bathing solution under permselective conditions. Generally, in order to explain electroactive film responses, one needs to consider the interactions between the fixed redox sites (site-site interactions) and the interactions between fixed sites and mobile ions (site-ion and site-solvent interactions). The former has been discussed extensively in the literature [1], from both theoretical and experimental viewpoints. The general thrust of these studies has emphasized *thermodynamic* effects: those that would be observed over very long experimental time-scales. On the usual potentiodynamic and chronoamperometric time-scales, the responses are usually *kinetically* controlled. The kinetic processes concerned include transfers of mobile species. Depending on the electrochemical control function and bathing solution composition, various reactions paths will be followed by the system. Different pathways will access different intermediate states whose lifetimes will depend upon site-ion and site-solvent interactions that modulate the site-site interactions under transient conditions. Undoubtedly, all of these mutual interactions play a role. Nevertheless, under the usual circumstances of kinetic control, a wide variety of metastable states may be accessed. One theoretical visualization of these states and the kinetic pathways between them is the Scheme of Cubes [2], which describes pathways between redox, solvation and configurational states. Since the kinetic significance of metastable states is largely unexplored, their importance dictates the focus of this work.

In order to provide a reference model against which our results should be compared, we first present the ideal equilibrium behavior of a permselective electroactive film, in this case a poly(vinylferrocene) – PVF – film in "dilute" electrolyte. In a previous paper [3] we reviewed the extensive early literature on this widely studied system. More recent work has explored issues of film structure [4], and ion and solvent transfers (the issue we discuss here) [5, 6, 7]; the latter has highlighted the issue of permselectivity. A quantitative discussion of permselectivity failure, in terms of a permselectively index given

elsewhere [8, 9] shows that our experiments are in the permselective regime. Then, we describe the results of the PVF film redox-switching experiments performed sequentially in sodium salt solutions of different counter-anions – first perchlorate, then toluenesulfonate, then naphthalenesulfonate, and finally once again in perchlorate. We observed a decrease in the film's electroactivity, namely less charge passage associated with smaller changes in mass. At least four possible explanations could be invoked:

- trapping of the large anions (and by implication charge and solvent trapping) so that at least part of the film is always held in the oxidized state
- a structural change in the polymer, such that electron/ion transfer transport is slowed to a time-scale longer than that of the voltammetric assay
- dissolution of the film, for unknown reasons, perhaps as a consequence of major solvent swelling needed to allow large anions into the film
- anion-driven solvation changes sufficient to trigger viscoelastic effects

We use a combination of coulometric and gravimetric data to explore these possibilities and we ultimately show that only the first of these is consistent with the data.

Experimental

The working electrodes were Au ($\sim$100 nm thick) deposited on 10 MHz AT-cut quartz crystals (International Crystal Manufacturing Co., Oklahoma City, OK), with piezoelectrically- and electrochemically-active areas of 0.21 cm^2 and 0.23 cm^2, respectively. The instrumentation and film preparation have been described previously [3, 5, 9]. PVF-modified gold electrodes in aqueous media, as here, have crystal admittance spectra characteristic of acoustically thin films [3]. Therefore, regardless of any solvent transfers that occur, at no time does the solvent population in the film reach the threshold for plasticization. The mass sensitivity of the frequency response, $-\Delta f/\Delta m$, for such an acoustically thin film is then 0.226 Hz ng^{-1} cm^2; for the piezoelectric area of the crystals used, this becomes 1.08 Hz ng^{-1}.

The PVF film was prepared in the perchlorate-doped form in methylene chloride as solvent, and then transferred to 0.05 M sodium perchlorate aqueous solution where its current-potential and mass-charge curves were recorded. The film was then transferred successively to 0.05 M aqueous sodium salt solutions containing the following counter ions: toluenesulfonate and naphthalenesulfonate. The PVF film was then redox-cycled, as well as multiply potential-jumped, in each of these solutions. Finally, the PVF film was returned to the initial 0.05 M sodium perchlorate solution and its current potential curves and mass charge curves were again recorded.

Model system behavior

Equilibrium conditions

Film counterion content

The relationship between film redox state and mobile species transfers (under permselective conditions, equivalent to ion and solvent population changes) has

been discussed widely; for instance the historical record of early work is presented in [10]. We summarize only some relevant aspects for the surface bound redox process in which the oxidized form is assumed to have counter anions associated with it, for example:
O + ne$^-$ = R + nX$^-$.

Here, and in the subsequent analysis (Eqs. 6 to 11), we use the symbols "O" and "R" to represent the oxidized species and nX$^-$ as any counter ion(s) required to maintain electroneutrality during redox switching. This has the advantage that, by indicating only the transferred (rather than both the transferred and retained) counter ions, it represents a formalism applicable to any polymer redox site charge type, not just the PVF system studied here. The equilibrium potential for this system is then given by the expression:

$$E = E^0 + \left(\frac{RT}{nF}\right) \ln \left\{ \frac{\Gamma_O}{\Gamma_R [X^-]^n} \right\} \qquad (1)$$

where $[X^-]$ is the equilibrium concentration of the counter anion in the bathing solution, and the Γ symbols represent the populations of the subscript species in the surface film. In terms of the total population of redox sites, $\Gamma_T = (\Gamma_R + \Gamma_O)$, the Nernst expression becomes:

$$E = E^0 + \left(\frac{RT}{nF}\right) \ln \left\{ \frac{\Gamma_O}{(\Gamma_T - \Gamma_O)[X^-]^n} \right\} \qquad (2)$$

In view of the usual situation in which multilayers of the electroactive polymer film exist on the electrode surface, it is convenient to recast the Nernst expression in terms of the total charge, $Q_T = (Q_O + Q_R)$, and the distribution of charge between O and R:

$$E = E^0 + \left(\frac{RT}{nF}\right) \ln \left\{ \frac{Q_{Ox}}{(Q_T - Q_O)[X^-]^n} \right\} \qquad (3)$$

Equation 3 is generally applicable to an equilibrated film whose thickness is sufficient to exhibit bulk properties.

In an EQCM experiment, the mass changes that accompany charge flow and the associated potential changes provide the surface populations of the oxidized and reduced forms of the electroactive polymer, and also help to characterize the mobile species that transferred. A 3-D plot, such as that shown in Fig. 1, is a convenient way to visualize the relationships that exist between potential E, charge Q, and film mobile species population changes, Γ, at fixed counter ion concentration in the bathing solution. The 3-D vector Σ describes the path followed during the transformation of the film during its redox transformation between the reduced and oxidized states. The projection on the 1) E-Γ plane represents the conventional Nernst equation, 2) E-Q plane represents the potential-charge isotherm, and 3) Q-Γ plane represents the charge required to produce a particular mixture of reduced and oxidized species. Under equilibrium
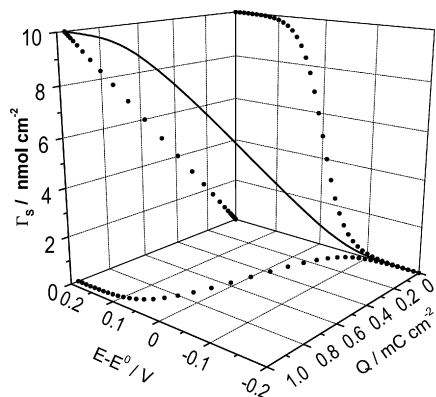
Fig. 1 Redox state Σ-vector for the equilibrium path taken upon film redox conversion. Axes x, y, z, respectively, represent the potential (E), the charge density (Q) and the film solvent population (Γ_S). A typical value was used for $\Gamma_T(10^{-8}$ mol cm^{-2}), and K_S was assigned an arbitrarily large value (1000), representative of a hydrophilic oxidized film (see Eq. 4)

conditions, only two of the three variables (E, Q, or Γ) need be known, as the system is over-determined (the value of E determines a unique value for each of Q and Γ). In the simple case of redox-induced film solvation under permselective conditions (the case relevant to the experiments described here), the only mobile species – aside from the counter ion – is the solvent, so the general population parameter Γ reduces to Γ_S.

As generally appreciated, the approach to equilibrium for an electroactive polymer being switched from one state to another can be very slow. However, if sufficient time is allowed after charge injection into/removal from a film, equilibrium behavior can be observed. This has been reported for PVF in both sodium perchlorate and perchloric acid solutions where Nernstian behavior has been found at constant perchlorate concentration with variable charge injection, and at constant charge level and variable perchlorate concentration [5].

Solvent content of the film

Solvent is one of the mobile species that transfer during the redox switching process; quite generally, solvent population changes may be non-linearly related to the charge transferred into/out of the film [11]. At equilibrium Eqs. 1 to 3 still apply if (i) the ratio of solvent within oxidized and reduced species does not vary with total charge, and (ii) all free and bound solvent in the film is in equilibrium with solvent in the bathing solution. As a first order approximation, in effect this requires that the solvent population in the film, Γ_S, changes linearly with the film charge. In the simple case of redox-induced film solvation change, we can express this solvent population as:

$$\Gamma_S = \frac{K_S}{K_S + 1} \frac{x_Q}{F} \tag{4}$$

where K_s is the film solvation equilibrium constant, and x is the fraction of the total charge Q to oxidize the film [12].

Structural transformations of the polymer

In an earlier model [2] we assumed that the polymer film has only two configurations in a given charge state. Then the equilibrium between any pair of species in the same oxidation state is characterized by four unique equilibrium constants K_{config} between the redox states at fixed solvation, or another set of four unique equilibrium constants between solvation states at fixed redox state. The difference in standard potentials, ΔE^0, for a given pair of these eight possible states is:

$$RT \ln \left(K_{config}\right) = nF\Delta E^0 \tag{5}$$

The various equilibrium parameters relating unsolvated, solvated, and reconfigured oxidized and reduced species have been given elsewhere [2].

Generally, changes in solvation level, redox level and configuration states will be accompanied by changes in free volume. We expect that the maximum changes in free volume will occur when reconfiguration of the polymer occurs, since this process is associated with movement of the "heavy" atoms in the polymer structure.

Kinetically-controlled conditions

Kinetically-controlled conditions usually exist during the redox switching of electroactive polymers. Just as under equilibrium conditions, film ion populations can be described by $\Gamma_A = Q/nF$ and solvent population by Γ_S, both of which can be visualized using a 3-D plot of the Σ-vector. Figure 2 shows just such a plot for particular values of electron transfer rates and water
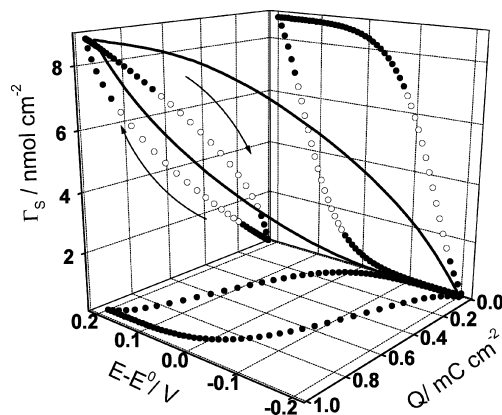

Fig. 2 Film compositional responses for a representative case of first order slow electron/ion and slow solvent transfers. Arrows indicate potential scan direction. Simulation parameters: $\kappa_e = 0.05$ V^{-1}; $K_S = 1000$; $\kappa_S = 30$ V^{-1}; equal forward and reverse solvent transfer rates (see main text and [12] for procedures)

transfer rates. The basis of this model has been recently described [12]: it involves first order rate constants k_e and k_S, respectively, for the interfacial transfers of electrons (and coupled counter ions) and of solvent. These two rate constants are normalized, to allow comparison of voltammetric data from different experiments. This is done by dividing the rate constants by the potential scan rate (v), so that the simulation parameters are κ_e and κ_S (V^{-1}).

In the general case, coupled electron/ion transfer, solvent transfer, and polymer reconfiguration may be slow on the experimental time-scale. Frequently, the rates of electron transfer, solvent transfer, and polymer reconfiguration may be sufficiently different so that only one of these processes is rate-controlling for any particular polymer state that exists during redox switching [2]. The particular state at a given time depends on the history of the polymer; in other words on its instantaneous polymer configurational state, populations of the solvent, reduced and oxidized forms, and critically upon the path followed in reaching the particular state. This situation has been discussed elsewhere in a detailed analysis of the cyclic voltammetry of PVF in a sodium perchlorate solution [13, 14].

The key to analyzing the electrochemical kinetic behavior of electroactive polymers is recognizing that the instantaneous rate controlling step in the redox switching of an electroactive polymer is determined by its starting state and that the rate-controlling step can change at each step of the switching process.

Results and discussion

Figure 3 shows the cyclic voltammetric curves for the PVF film at two potential scan rates in 0.05 M NaClO$_4$ solutions. They were obtained before and after potential cycling in different bathing solutions. Current-potential curves obtained initially at scan rates of 0.004 V s^{-1} and 0.050 V s^{-1} are given in panels A and C, respectively. The film is electrochemically irreversible since the oxidation and reduction cycles are not mirror images of each other about the potential axis. However, at the 0.05 V s^{-1} scan rate the second potential cycle does not completely coincide with the first cycle, unlike the result at 0.004 V s^{-1}. This difference in shapes of the cathodic and anodic half cycles, and the behavior between the two voltage scan rates, is characteristic of a change in kinetic pathways. In this case, the change is described by a scheme-of-cubes redox cycle [10] (see Fig. 4).

The scheme-of-cubes is a method for visualizing EC-type processes, based upon geometrical figures (here, obviously cubes). Corners of the figure (cube) are used to represent the species, and edges connecting these corners to represent the elementary steps involved. The elementary steps we consider are coupled electron/ion transfer, solvent transfer and polymer reconfiguration; these correspond to translations in x, y and z directions in a 3-D figure, a cube.
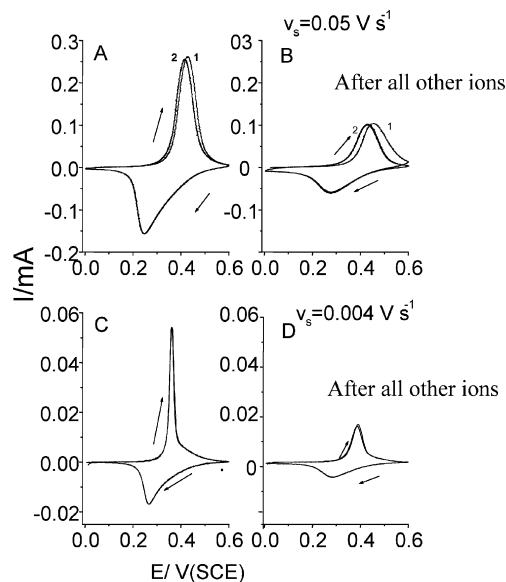

Fig. 3 Voltammetric response curves for a PVF film in 0.05 M NaClO$_4$ solution at $v_s = 0.05$ V s^{-1} (panels A, B) and $v_s = 0.004$ s^{-1} (panels C, D), made on the fresh film (panels A, C) and after the experiments with the large anions (panels B, D)
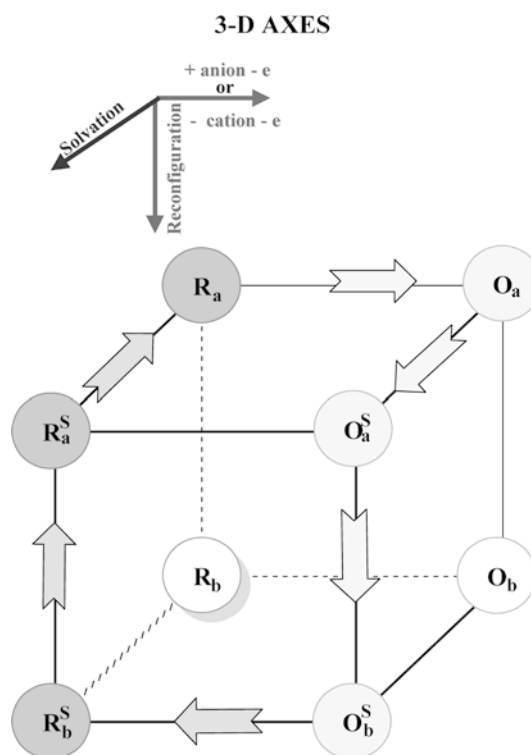

Fig. 4 Representation of the scheme-of-cubes pathway for Eqs. 6, 7, 8, 9, 10, 11

Each of the eight cube corners represents one of the four reduced or four oxidized species; the four reduced states make up a cube face opposite to a cube face representing the four oxidized species. The four species in a given oxidation state denote two possible solvated

species, each of which can have one of two different configurations. Here, this model is organized so that two solvation levels correspond to opposing cube faces connecting the opposing faces of the reduced and oxidized species of different configurations. Therefore, the cube faces represent species that have one of the two allowed levels of fixed charge, solvation or configuration. A cube edge represents one kind of elementary step with the other two fixed (kinetically "frozen"), while a cube face represents two kinds of elementary steps with the third process fixed.

In a cyclic voltammetric experiment, reduced PVF species are converted most easily to the corresponding oxidized species with similar heavy atom arrangements (Franck-Condon principle). The particular mechanism depends on the pseudo equilibria that exist among the four reduced species and among the four oxidized species, and the details of the electrode kinetics between the corresponding reduced and oxidized species. We define pseudo equilibrium to signify that every intermediate species has existed long enough to attain a steady state concentration. As the cyclic voltage scan rate increases, this may not be the case, and the reaction pathway will change as one or more of the species in a particular reaction cycle are no longer at steady state.

We now propose a specific scheme-of-cubes model to rationalize the differences (i) in the shape of the voltammetric curves observed between anodic and cathodic half cycles at fixed scan rate, and (ii) for the observed difference between the responses in the first and second potential along the reaction direction for the two species defining the edge.

Starting from a reduced, hydrophobic state of configuration, R_a, the film is oxidized to an oxidized, hydrophobic state of the same configuration, O_a:

$$R_a \rightleftarrows O_a + ne \tag{6}$$

Then the film rapidly converts to an oxidized, hydrophilic state (denoted by a superscript S) of the same configuration, O_a^S.

$$O_a + water \rightleftarrows O_a^S \tag{7}$$

Next, the film changes to an oxidized, hydrophilic state, having a second configuration b, O_b^S.

$$O_a^S \rightleftarrows O_b^S \tag{8}$$

When the scan direction is reversed, O_b^S is converted to the corresponding hydrophilic, reduced species, R_b^S,

$$O_b^S + ne \rightleftarrows R_b^S \tag{9}$$

which reconfigures to the hydrophilic species R_a^S

$$R_b^S \rightleftarrows R_a^S \tag{10}$$

that then loses water to form R_a, the starting hydrophobic reduced starting state.

$$R_a^S \rightleftarrows R_a + water \tag{11}$$

Equations 6 to 11 summarize the proposed mechanistic path for the redox cycle when R_a and O_b^S are the most stable reduced and oxidized species, respectively.

When Eqs. 7 and 8 are fast compared to Eq. 6 on the time-scale of both of the cyclic voltammetric experiments in Fig. 3, panels A and C, the concentrations of O_a and O_a^S will be small. Consequently, the first and subsequent voltammetric responses will superimpose at both scan rates. If either Eq. 7 or 8 were detectably slow at the fast scan rate, the first and second voltammetric responses would show differences at the faster scan rate. The distinction between the two would be based on whether a change in the amount of water transferred or a change in peak potential existed on the second cathodic potential half cycle. If there was a decrease in water transfer, the slow step would be Eq. 7, while if there was a shift in peak potential, the slow step would be Eq. 8.

Equations 6 and 9 give the electron transfer steps during the anodic and cathodic potential cycles. They involve different redox couples and therefore predict the absence of mirror image symmetry about the potential axis.

Panels C and D in Fig. 3 show dramatically different current-potential curves at both voltage scan rates. The results demonstrate that the film undergoes irreversible changes after earlier cycling in solutions of the toluenesulfonate and naphthalenesulfonate anions. The corresponding 3-D representations of these data are given in Figs. 5a and 5b. The projections on the m-Q plane in Fig. 5a shows hysteresis and non-linearity during the anodic scan for the voltammogram in Fig. 3, panel A, as would be expected from the previous discussion of Fig. 3. The m-Q data at 0.004 V s^{-1} are consistent with predictions drawn from Eqs. 6 to 8 in our proposed
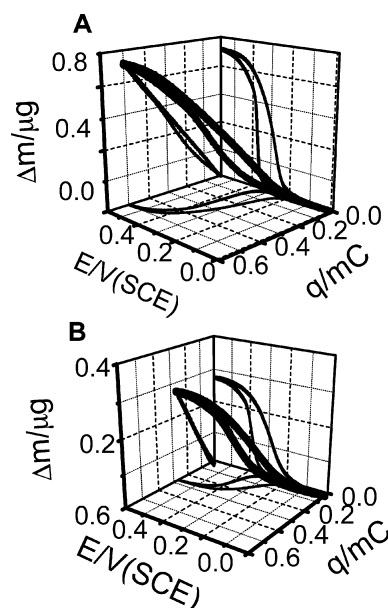

Fig. 5 3-D $(E, Q, \Delta m)$ plots of EQCM data for a voltammetric experiment at $v_s = 0.004$ V s^{-1} at fresh PVF film (A) and after the large anion experiments (B) in 0.05 M NaClO$_4$ solution

model. The projection on the m-Q plane in Fig. 5b shows no hysteresis, but has a lower slope and shorter trajectory in Σ-space than in Fig. 5a.

Consequently, configurational kinetics (Eq. 8) is not a slow step at 0.004 V s^{-1} even though the total mass of the transferring mobile species has decreased, as has the total charge to convert the film from a totally reduced to a totally oxidized state and back compared to the original film. Also, in agreement with our model, none of the Eqs. 6 to 11 are slow in a film that has been exposed to the large ions.

However, the decrease in slope shows that less water transfers into the film along with the counter anion. Also, the decrease in total available redox charge shows that the number of redox sites capable of accepting a perchlorate anion has decreased to ∼52–58% of its original value, depending on the voltage scan rate. However, the smaller mass changes we report are a consequence of progressively increasing reduced film mass at constant oxidized film mass. As discussed below, this is consistent with big anion trapping. Conversely film dissolution by itself would require progressive decreases of both reduced and oxidized forms of the film; this is at variance with the observations.

The plots in Fig. 6 show the potential dependences that relate to perchlorate ion and water transfers, resulting from prior, successive potential cycling in bathing solutions containing toluenesulfonate and naphthalenesulfonate counter ions. In Fig. 6 the ratio Δ[13] of the flux of water to flux of counter ions is plotted against charge. These plots illustrate the remarkable effect on water and charge transport of prior redox cycling of a PVF film in solutions of the large ions.
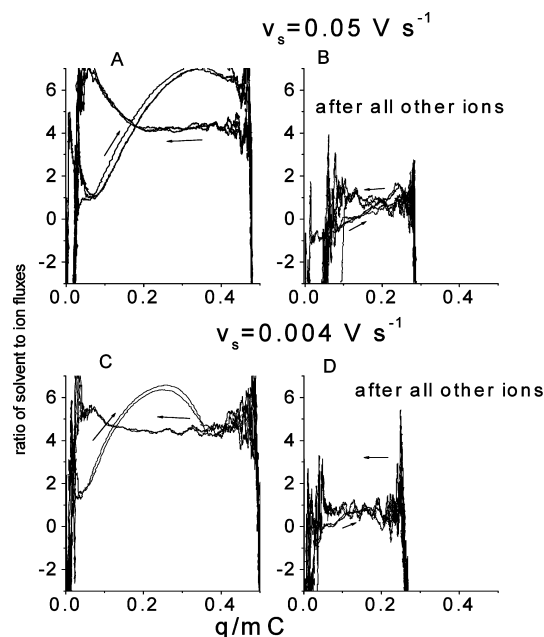

Fig. 6 Curves of flux of water per ion at a PVF film in 0.05 M NaClO$_4$ solution at $v_s = 0.05$ V s^{-1} (panels A, B) and $v_s = 0.004$ V s^{-1} (panels C, D), made on the fresh film (panels A, C) and after the large anion experiments (panels B, D)

As seen in Fig. 6, panels B and D, after the treatment of the film with the large anions, Δ is between ∼0.35–0.40 over most of the potential range. These values are to be compared to the initial Δ-values of 4–5 (in panels A and C) that existed before this treatment. In addition to the dramatic decrease in Δ, there is a corresponding decrease in available switching charge of ∼42–48%.

Panel A, at a scan rate of 0.05 V s^{-1}, shows from the values of Δ that water transport in the original perchlorate film increased rapidly during film oxidation, demonstrating the changing hydrophilicity of the PVF film (Eq. 7) and implicitly its reconfiguration (Eq. 8). Over most of the charge range during the film's reduction, Δ is constant and is hardly different at the two scan rates, ∼4.0 at 0.05 V s^{-1} and ∼4.5 at 0.004 V s^{-1}. This suggests that reduction of the terminal reconfigured, oxidized hydrophilic state converts it to a reconfigured, reduced hydrophilic state (Eq. 9). The latter then changes configurational state (Eq. 10), that expels water to regenerate the starting hydrophobic state with the starting configuration (Eq. 11).

We interpret the results in Figs. 5 and 6 by first eliminating two possibilities. Firstly, we reject any explanation that requires major loss of PVF film from the electrode surface because the Δ/charge plots are different in the fresh and multiple cycled films. Such a major film loss would decrease the switching charge and mass changes proportionately, and therefore not alter the values of Δ. The key observation in this respect is that the decreased switching charge in the large anion solutions is accompanied by an increase in film mass; dissolution would be accompanied by a mass decrease. Secondly, we note that PVF is a glassy (high G) material when a perchlorate ion is the initial counter ion. Since our rationalization of the experimental results given below assumes a decrease in the film's free volume, the film would remain glassy under this assumption. Therefore, we rule out the possibility that the experimental results reflect a change of PVF to a rubbery (low G) material (to a semi rigid or viscoelastic material). Our rationalization follows.

We assume that freshly-prepared PVF has considerable free volume, though not enough to render it viscoelastic. Consequently, when PVF is initially redox-cycled in aqueous sodium perchlorate, in a half cycle we expect that significant transport of water is possible. In agreement, we find that, experimentally, an average of 4–5 molecules of water transfer per perchlorate ion is transferred. Also, little charge and mass trapping occurs [14]. When the PVF film is subsequently cycled in bathing solutions of the two large ions, considerable charge and mass trapping of these ions and water occurs, thereby using up most of the free volume initially present in the film. The trapped mass is the sum of the masses of water and the large anions, and the trapped charge is due to the trapped anions. Therefore, as a result of the decreased free volume, we predict (as found) that the charge required to transfer counter (perchlorate) ions will be diminished for a cyclic voltammogram in the
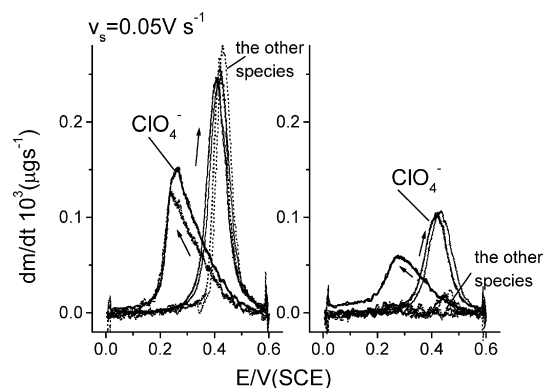
Fig. 7 Fluxes of water and ions calculated from the EQCM data obtained during the redox switching of fresh PVF film in 0.05 M NaClO$_4$ solution at $v_s = 0.05$ V s^{-1}(panel A) and after the large anion experiments (panel B)

Fig. 8 $\Delta m_{solvent}$ versus q curves obtained for redox cycling of a PVF film in aqueous 0.05 M NaClO$_4$ solution. Scan rate v_s:0.004 V s^{-1} (panel A); 0.05 V s^{-1} (panel B). In each panel, responses (as marked) are shown before and after redox cycling in sodium toluenesulfonate and sodium naphthalenesulfonate solutions

final perchlorate bathing solution. Analogously, the amount of water that can transfer between the film and the bathing solution should be – and is – decreased.

Another significant result emerges from Fig. 7. It is a plot of the rate of change of moles of water and perchlorate ion with respect to electrode potential for the PVF film at a potential scan rate of 0.050 V s^{-1}. Before and after treatment with the large anions, the fluxes of water and of perchlorate transferring between the film and the bathing solution of 0.1 M sodium perchlorate are partially decoupled. This phenomenon is clearest during the oxidation half cycle, where the peak flux of water lags behind the peak flux of the anion. In other words, at least two kinds of water enter the film, one that is not water of hydration of the anion, while the other kind could be water in the primary hydration layer of the counter anion.

Figure 8 shows the solvent component of the mass change as a function of charge passed during redox-cycling of a PVF film immersed in 0.05 M Na-ClO$_4$solution before and after "large anion treatment" (redox cycling in toluenesulfonate and naphthalene-sulfonate solutions). Since there is very little scan rate dependence (compare panels A and B), the effects are clearly not time-scale related in a simplistic sense; as we shall show, the effects are a consequence of the film redox history. Table 1 summarizes the overall mass and charge changes, and the resultant apparent molar
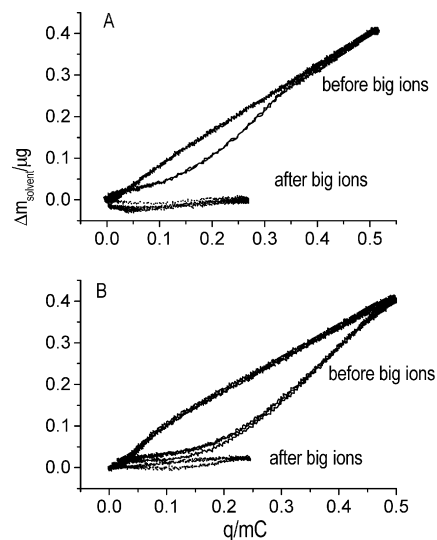
masses, before (first two rows) and after (next two rows) this "large anion treatment". The first two rows, which differ only in the potential scan rate used, yield mean molar masses of 178 g mol^{-1}. This corresponds, on average, to the entry of one perchlorate counter ion and $\sim$4–5 water molecules per ferrocene redox site upon its oxidation. The next two rows yield a mean molar mass of 98 g mol^{-1} which is, within experimental error, the same as the molar mass of a perchlorate anion (no solvent is transferred). However, in the latter case, the charge data show that only 58% of the sites remain electroactive.

We therefore propose that there are two types of ferrocene sites, both of which are initially electroactive and only one of which is electroactive after the large anion treatment. Therefore, the final response is characteristic of one type of site. Since only electrons and counter ions transfer for redox switching of these sites, we deduce that their local structure is very compact; we therefore denote them "compact" sites. The initial response (see Table 1, rows 1–2) is a weighted average of

Table 1 Voltammetrically-driven changes in mass and charge upon redox cycling of a PVF film exposed to 0.05 M NaClO$_4$

Sample 101	v(V s^{-1})	Total mass change (mg)	Total charge change (mC)	Molar mass (g mol^{-1})	Interpretation
Before large ion exposure	0.004	0.867	0.473	177	ClO$_4^-$ + 4H$_2$O transfer
	0.050	0.890	0.479	179	
After large ion exposure	0.004	0.279	0.270	99.7	ClO$_4^-$transfers
	0.050	0.286	0.285	96.8	
Trapped in large ion experiments[a]	0.004	0.588	0.203	279.5	Large ion(s) trapped;
	0.050	0.604	0.194	300.4	decreased ClO$_4^-$ + H$_2$O transfer

[a] Calculated as the difference between responses in 0.05 M NaClO$_4$ just before and just after large ion treatment (previous rows)

the "compact" and other sites; given their larger solvation changes, we denote the latter as "diffuse" sites. Simple difference between the initial and final responses (the last two rows in Table 1) yields the result that the "diffuse" sites undergo redox switching via coupled electron/ion transfer and solvent transfer, to the extent of ~10–11 water molecules per redox site.

The above model immediately poses two questions. What justification is there for postulating two types of site? What process could block the electroactivity of one of them? The answer to the first question is provided by recent neutron reflectivity studies on PVF films [15], which show the presence of compact and diffuse regions within the film. (We do not attempt to pursue this quantitatively, since the films studied here and by neutron reflectivity were prepared by different means.) The answer to the second question is, we postulate, based upon trapping of anions (particularly naphthalenesulfonate) within the film. This idea is suggested by the observed progressive accumulation of film mass at the negative ends of consecutive redox cycles in naphthalenesulfonate media (data not shown).

Pursuing this approach further, we suggest that the amount of solvent transfer associated with switching of each of the two types of site is an indicator of the amount of free volume. Therefore, the "compact" sites are unable to accommodate the large anion, so they are electrochemically silent in solutions containing naphthalenesulfonate. Only the "diffuse" sites can undergo redox switching in this solution, since only they have the free volume (space) to accommodate the large anion. However, even here, the entry and exit of the large anion is rather difficult and there is progressive trapping of the large anion (and the associated charge). Therefore, the effect of cycling in the large anion solution is to progressively block all the "diffuse" sites (trap them in their oxidized form, with naphthalenesulfonate) and to leave the "compact" sites in their initial composition. Upon transfer back to NaClO₄, the large anions remain trapped, so that the diffuse sites are now electrochemically silent. Only the compact sites are electrochemically active, by means of coupled electron/perchlorate ion (but no water) transfer.

Conclusions

Solvation populations and dynamics of the redox switching of poly(vinylferrocene) are governed by chemical interactions between the components of the system, specifically the characteristics of the counter anion and the solvent. These are amenable to manipulation by deliberate alteration of the PVF film's redox history, in particular the nature of the counterions to which the film has been exposed. Redox cycling of PVF in sodium toluenesulfonate and sodium naphthalenesulfonate produced profound changes in the film's redox switching characteristics.

We can describe the initial redox response in terms of two constituent sites. One type (comprising ~58%) of ferrocene sites occupies a compact, unsolvated environment. They undergo redox switching in NaClO₄ with only the transfer of counter ions required by electroneutrality; they are sufficiently compact that this is only possible for small anions. The remaining (~42%) of the ferrocene sites are in a more solvated environment. Initially, they undergo redox switching with the transfer of perchlorate counter ion and ~10–11 water molecules per site. Upon transfer to a solution containing large anions (toluenesulfonate or naphthalenesulfonate), their relatively open local environment allows access to the large anions, which progressively get locked into the structure, with the eventual result that the electroactivity of the diffuse sites diminishes to effectively zero. Upon transfer back to the NaClO₄ solution, the "compact" sites are now once more able to undergo redox switching (involving solely perchlorate ion transfer), but the "diffuse" sites are locked (by the trapped large anions) in their oxidized state.

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