Short communication

Ion modulated electroactivity in thin-film polymers derived from bipyridyl and phenanthroline complexes of iron

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1. Introduction

Uses (or potential uses) of polymeric redox conductors [1–3] in such areas as electrochromics [4–6], diagnostic and analytical sensing [7–11], and electrocatalysis [12–15] suggest a need for a detailed understanding of mechanisms of switching as well as conduction. While it is generally acknowledged that both phenomena involve electron diffusion and that electrons diffuse through redox polymers via a series of hopping events [16], the precise role of charge compensating counter ions is unclear. Available theory implies that intrapolymer ionic and electronic motion should be strongly correlated [17–18] yet there are only a handful of experimental observations to support this contention [20–23]. In the current study, some unusual and apparently unprecedented electrochemical thermodynamic effects and redox capacity effects have been uncovered. The experiments were also initially suggestive of strong electron-ion coupling in the microscopic conductivity process. Careful evaluation has revealed, however, that the unusual thermodynamic effects are not carried over in a significant way to the conductivity process, i.e. to the kinetics of charge transport or hopping. Details of the experiments are presented below, together with preliminary explanations.

2. Experimental

Polymer films were prepared on glassy carbon surfaces via electropolymerization of either $Fe(II)(vbpy)_3](PF_6)_2$ (vbpy = 4-methyl-4'-vinyl-2,2'-bipyridine) [24,25] or $[Fe(NH_2-phen)_3](PF_6)_2$ (NH_2–phen = 5-amino-1,10-phenanthroline) [26,27]. Continuous cycling between -0.5 and -2.0 V, or $+0.3$ and $+1.9$ V (vs. SSCE), in acetonitrile solutions containing 0.1 M tetraethylammonium perchlorate (TEAP) and approximately 2 mM monomer, produced adherent red films. (Electrochemical reduction of $Fe(vbpy)_3^{2+}$ leads to polymerization based on vinyl radical generation and propylene linkage formation [24]. The chemical basis for polymer formation following $Fe(NH_2-phen)_3^{2+}$ electrooxidation is amine radical generation, followed by proton loss and diazo linkage formation [26,27].) To achieve electrolyte solubility, subsequent measurements were made in water as solvent. These measurements, as well as the initial electrochemical syntheses, were performed with a PAR 273 potentiostat by using a standard three-electrode arrangement (glassy carbon working electrode (0.07 or 0.008 cm^2 disk), platinum wire counter electrode and saturated (NaCl) calomel reference electrode). Spectroelectrochemical measurements were made with an HP Model 8452A diode array spectrophotometer by using indium–tin oxide coated glass (Delta Technologies) as the working electrode. All alkanesulfonates were purchased from Aldrich and used as received. TEAP (GFS Chemicals) was recrystallized from purified distilled water (Millipore system) and dried in vacuo. Acetonitrile (Fisher) was distilled in glass and stored over molecular sieves.

3. Results and discussion

Metal centered oxidation and reduction of thin-film polymers necessarily involves the uptake and release of charge-compensating ions from the external electrolyte solution, e.g.

$$poly\text{-}Fe(vbpy)_3^{2+} + nX^-$$

$$\rightleftharpoons poly\text{-}Fe(vbpy)_2^{3+}, X_n^- + ne^- \text{ (electrode)} \qquad (1)$$
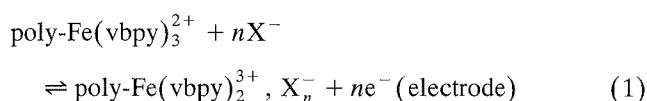
We have observed that replacement of TEAP by 1-decanesulfonic acid, sodium salt (DSA) as the electrolyte has

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enormous effects upon thin film (i.e., poly-Fe(vbpy)$_3^{m+}$ and poly-Fe(NH$_2$-phen)$_3^{m+}$) electroactivity. As shown by Fig. 1, electrolyte replacement leads to a reversible — roughly factor of four — decrease in film redox capacity or electrochemical accessibility. Related mixed electrolyte studies show that the full modulation effect can be induced by as little as 5 mM of the decanesulfonate in a 95 mM TEAP solution. We interpret the results as strong evidence for preferential partitioning of the DSA anion into the polycationic film framework — where presumably the preference reflects differential hydrophobic interactions.

The magnitude of the electroactivity attenuation effect is significantly dependent upon film thickness. For example, a polymer film that is grown via extensive cycling in a 2 mM monomer solution (> 50 electrochemical scans; limiting coverage of ca. 500 monolayer equivalents) exhibits a much greater change in current response than a film grown in a similar solution for only ten scans (coverage of ca. 100 monolayer equivalents). However, thinner films exhibit fewer memory and time effects than the thicker (and presumably more cross-linked) assemblies. The extent of modulation also depends upon the alkyl chain length. A series of voltammetry studies with poly-Fe(vbpy)$_3^{m+}$ and CH$_3$(CH$_2$)$_n$SO$_3^-$Na$^+$ electrolytes ($n = 0$–11; see Fig. 2) shows a systematic decrease in electroactivity with increasing chain length (where the relative magnitude of the electroactivity decrease is essentially unaffected by factor of ten changes in voltammetry sweep rate).

These experiments, as well as the mixed electrolyte measurements, are obviously suggestive of a film reaction that involves anion uptake during metal oxidation (Eq. (1)), with uptake driven, in part, by hydrophobic interactions. The unusual film-based redox effects are then reasonably ascribed to steric phenomena. Conceivably, however, if the initial hydrophobic partitioning of CH$_3$-(CH$_2$)$_n$SO$_3^-$ were sufficiently strong, subsequent ion release (during film reduction) would not occur. Electroneu-
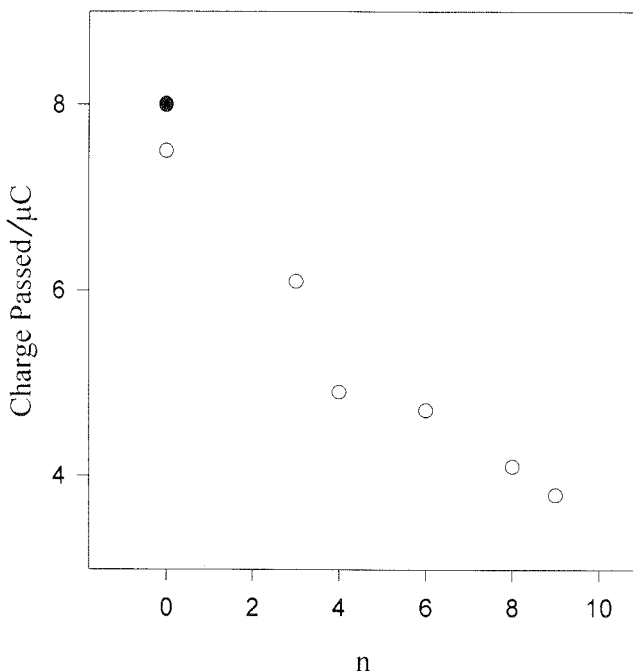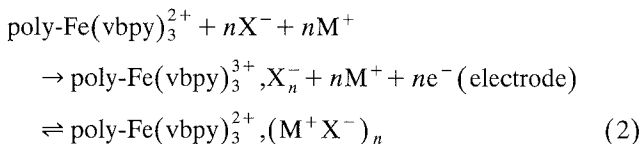
Fig. 2. Charge passed during poly-Fe(vbpy)$_3^{3+/2+}$ film electroreduction as a function of electrolyte composition: ● = 0.05 M TEAP; ○ = 0.05 M CH$_3$(CH$_2$)$_n$SO$_3^-$ Na$^+$. Electrode area: 0.008 cm^2. Sweep rate = 100 mV s^{-1}. Uncertainty is approx. ±1.5 μC. Since signal sizes also display a detectable dependance on film age, as well as history, multiple (similar) films were used to generate the charge data.

trality would instead be achieved by electrolyte cation incorporation:

$$\text{poly-Fe(vbpy)}_3^{2+} + n\text{X}^- + n\text{M}^+$$

$$\rightarrow \text{poly-Fe(vbpy)}_3^{3+}, \text{X}_n^- + n\text{M}^+ + n\text{e}^- \text{(electrode)}$$

$$\rightleftharpoons \text{poly-Fe(vbpy)}_3^{2+}, (\text{M}^+\text{X}^-)_n \qquad (2)$$

To evaluate this possibility, we measured film redox potentials as a function of electrolyte concentration in each of several electrolytes (including TEAP and DSA). After correction for small liquid junction potentials associated with the SSCE reference (-13 mV per decade of electrolyte concentration [28]), we found that the poly-Fe(vbpy)$_3^{3+/2+}$ potential shifted in the negative direction by 58 to 68 mV per decade increase of electrolyte concentration (independent of electrolyte identity). (Control experiments with monomeric Fe(vbpy)$_3^{3+/2+}$ in solution revealed almost no dependence of E_f on electrolyte concentration and only a marginal dependence on electrolyte identity (i.e. slight shifts toward more positive values with increasing alkanesulfonate anion size). If the metallopolymer behaved as a perfect cation-exclusion membrane (i.e. anion uptake only), rigorous Donnan behavior (-59.2 mV per decade) would have been seen [29,30]. Our results clearly are sufficiently close to the ideal that only anions can be participating significantly in the film charging and conduction processes.
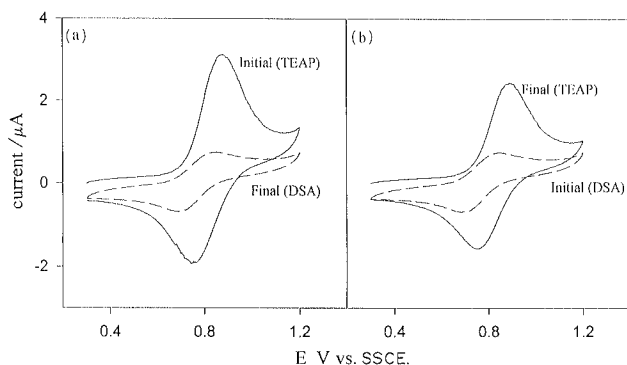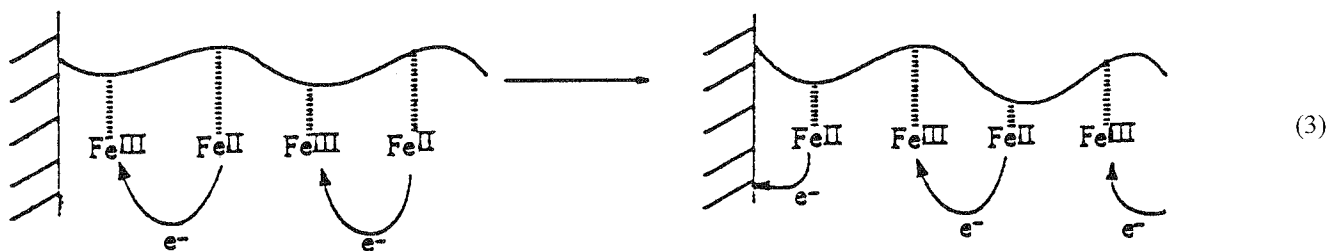
Fig. 1. Poly-Fe(vbpy)$_3^{3+/2+}$ film voltammetry (100 mV s^{-1}): (a) in 0.05 M TEAP (———), followed by 0.05 M DSA (– – – –); (b) in 0.05 M DSA, followed by 0.05 M TEAP. Electrode area: 0.008 cm^2.

(3)

With the identity of the charge compensating ion now more satisfactorily established, it is appropriate to consider the dynamics of Eq. (1). For all but the first "monolayer" of the metallopolymeric film, oxidation and reduction must occur by a site-to-site hopping process such that the interior of the film mediates the electrochemical transformation of the exterior layers (see Scheme 1).With fixed redox sites, the hopping-based film oxidation (or reduction) process can be viewed as an electron diffusion process. The hopping kinetics can then be described phenomenologically by a charge transfer diffusion coefficient, D_{ct} [1,16,31–33]. Transient measurements (chronoamperometry) of electron diffusion initially seemed to indicate a substantial electrolyte anion dependence. For example, a conventional analysis of current transients [$I(t)$; Cottrell equation (Eq. (4))]

$$I(t) = FAD_{ct}^{1/2}c/\pi t^{1/2} \qquad (4)$$

yielded a D_{ct} value of $\sim 3 \times 10^{-8}$ cm^2 s^{-1} in 50 mM aqueous TEAP solutions, but an apparent value of only $\sim 1.5 \times 10^{-9}$ cm^2 s^{-1} in 50 mM aqueous DSA [1]. (In Eq. (4), F is the Faraday constant, A is the electrode area, c is the molar concentration of redox active species and t is time.) Further studies with other $CH_3(CH_2)_nSO_3$ species revealed that the apparent value of D_{ct} systematically decreases as the alkyl chain length increases (with the most pronounced effects found for $n > 4$). These findings seemingly point to strong kinetic coupling of ionic and electronic motion. Careful consideration of the data in Figs. 1 and 2, however, indicates that this is not the case. From the figures (and related unpublished data) the charge passed during metal oxidation or reduction in DSA-containing films is only 20%–35% of that passed for equivalent perchlorate-containing films. It necessarily follows that the Fe(II), Fe(III) and X$^-$ concentration gradients created in DSA-containing films (i.e. effective chemical potential gradients for directional diffusion) can be only 20%–35% as large as those created in perchlorate-containing films. Accounting in Eq. (3) for the diminished concentration gradients (by simply diminishing c by 65%–80%) then leads to a ca. 9–25-fold correction in the D_{ct} estimate for the DSA system. With this correction, D_{ct}

values for the two types of films ultimately agree within experimental error.

Fig. 3 shows that the ion modulation effects extend to the polymer-film redox thermodynamics. The apparent formal potential (E_f) for (metal-based) polymer oxidation (determined from cyclic voltammetry peak potentials at limiting low sweep rates) exhibits a systematic negative shift with increasing n, for $n = 5–11$, but essentially no dependence for $n = 0–4$. The shifts imply an increasing preference for alkanesulfonate incorporation in film (Fe) oxidation state III vs. II, with increasing alkane size. (There is, of course, a compelling electrostatic basis for enhanced partitioning of counter anions into poly-Fe(III)(vbpy)$_3^{3+}$ vs. poly-Fe(III)(vbpy)$_3^{2+}$; the formal potential shifts simply indicate that the extent of the enhancement increases as n increases.) While these types of effects appear to be largely unprecedented for fixed-cation frameworks, they have been encountered previously with a fixed-anion system (specifically, the nickel/ferrocyanide polymer developed by Bocarsly and coworkers [21,22]). In
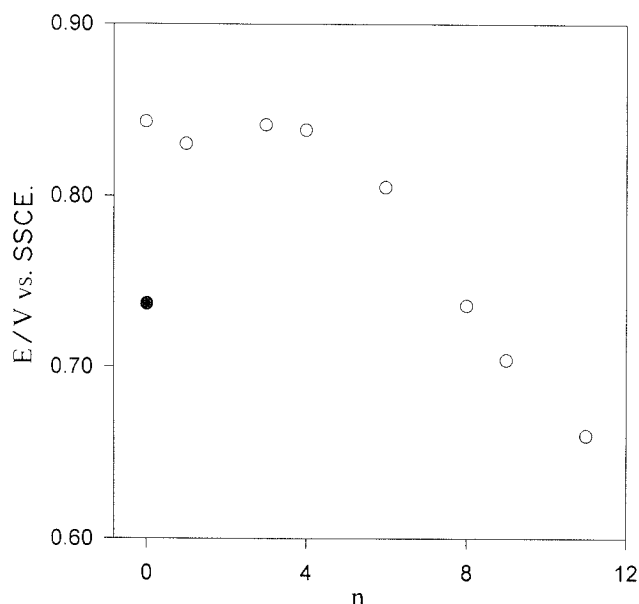

Fig. 3. Dependence of E_f for poly-Fe(vbpy)$_3^{3+/2+}$ films on electrolyte composition: ● = 0.05 M TEAP; ○ = 0.05 M CH$_3$(CH$_2$)$_n$SO$_3^-$ Na$^+$ (except 0.01 M for $n = 11$, due to solubility limitations). Electrode area: 0.07 cm^2. Sweep rate = 100 mV s^{-1}. Uncertainty is approx. ±15 mV. Limiting slow sweep rates (1 mV sec^{-1}) produce nearly identical results.

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[1] Apparent D_{ct} diminution is also observed in mixed electrolytes (TEAP + DSA).

the anionic system, E_f was found to be tremendously sensitive to the size of the charge-compensating cation (typically an alkali metal ion). The sensitivity was attributed, in part, to the potentially extreme lattice structural demands associated with cation incorporation in the semicrystalline film assembly [21,22]. In view of the greater linkage lengths, enhanced linkage flexibility and apparently greatly decreased crystallinity of poly-Fe(vbpy)$_3^{m+}$ films, a similar explanation is probably not applicable here. As an (admittedly speculative) alternative, we propose that uptake of longer chain alkanesulfonates by poly-Fe(vbpy)$_3^{2+}$ creates an increasingly lipophilic film environment (perhaps, in part, by physical displacement of water molecules). The increased lipophilicity then offers a progressively more inviting environment for an additional (hydrophobic) anion when the framework is oxidized. Presumably, systematic studies of solvent swelling would offer at least qualitative indications of the validity of the explanation.

Finally, spectroelectrochemical experiments provide compelling evidence that the observed ion-induced losses of film electroactivity are related to reversible trapping of the polymer in a mixed valence form. Spectral interrogation of polymer metal-center oxidation-state distribution is possible when film growth is carried out with a conductive glass electrode. Particularly instructive are optical measurements at 500–540 nm, where Fe(II)L$_3^{2+}$ (but not Fe(III)L$_3^{3+}$) absorbs strongly. As expected, the absorbance in this range [2] (in TEAP as electrolyte) is maximized (see Fig. 4(a)) when the film is held at potentials significantly negative of the formal potential (i.e., at strongly reducing potentials), but is minimized — and indeed, completely bleached — when the film is subjected to oxidizing potentials. In striking contrast, the bleaching process, as well as the subsequent recovery, is substantially inhibited (Fig. 4(b)) for a film equilibrated in a DSA-containing solution (2.5 mM DSA + 47.5 mM TEAP). (Equilibration, as indicated by an unchanging spectral response, was achieved after four oxidation/reduction cycles.) Thus, the metallopolymer becomes trapped in a largely mixed-valent form with changes in the external electrochemical potential causing only modest excursions away from mixed-valency. (It is worth noting that mixed valency persists even when the film is held at net oxidizing (or reducing) potentials for 30 min or more.) Nevertheless, the full spectroelectrochemical response (Fig. 4(a)) can be restored (or nearly
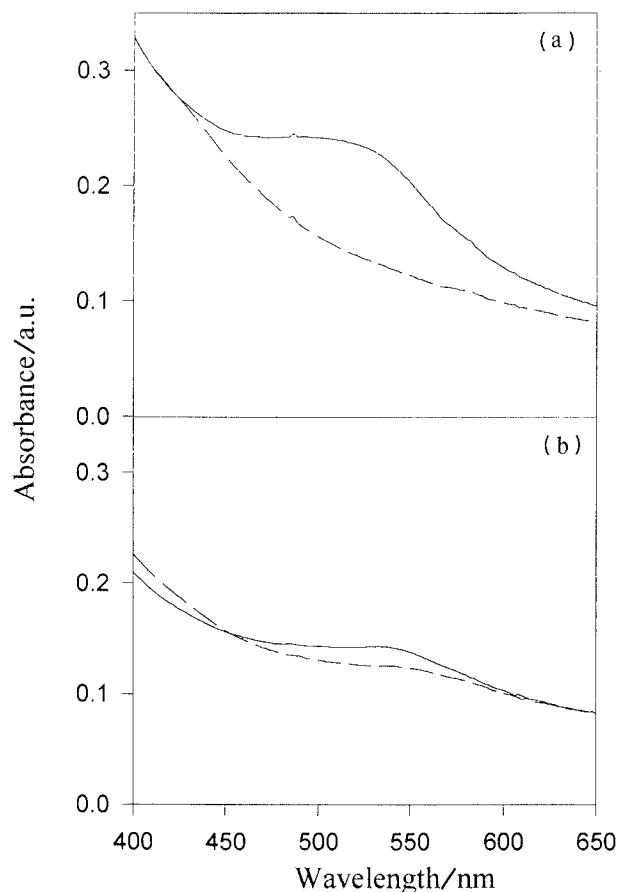

Fig. 4. Spectroelectrochemical response of a poly-Fe(NH$_2$-phen)$_3^{3+/2+}$ film at 0.0 V (———) and 1.5 V (— — —) in: (a) 0.05 M TEAP; (b) 0.05 M TEAP + 0.0025 M DSA electrolyte solutions.

restored) by re-equilibrating the film with a DSA-free solution.

The observation of nearly complete mixed-valence confinement in DSA-containing solutions is consistent with the almost complete loss of cyclic voltammetric response in the same solutions (Fig. 1). Furthermore, the observation indicates that the voltammetry effect is not merely the result of a short timescale kinetic phenomenon. Indeed, the persistence of the mixed-valence state suggests that it may be related in a fundamental way to the overall steric limitations presumably imposed by the cationic polymer film on the anion uptake process. Perhaps more intriguing are the implications of mixed valency for steady-state film conductivity. The presence of both donor (Fe(II)) and acceptor (Fe(III)) sites at potentials far removed from E_f suggests that DSA-containing films may be conductive over a very wide potential window and that it may be possible to drive conduction by electric field gradients (as in many organic conducting polymers), rather than by chemical potential gradients (i.e. donor and acceptor concentration gradients) as in conventional redox polymers [1,16]. Experiments designed to evaluate these unusual possibilities are currently underway. (Electric-field driven

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[2] Close inspection of Fig. 4 shows that the DSA-containing film absorbs at longer wavelength (lower energy) than the perchlorate-containing film. The difference persists even after correction for baseline absorption effects. Chemically, a decrease in metal-to-ligand charge transfer absorption energy implies either a negative shift in formal potential for the metal center or a positive shift in formal potential for the ligand (or both). Fig. 3 confirms that the former indeed does occur after replacement of ClO$_4^-$ by DSA (albeit not to a great enough extent to account fully for the spectral observations).

conductivity has been observed previously with redox polymers at very low temperatures (in the absence of solvent) [20] and under unusual circumstances where counter cations are physically excluded from a formally mixed-valent assembly [34].)

4. Conclusions

The substantial changes in polymer film electroactivity (i.e. redox capacity and electrochemical thermodynamics) induced by counter-ion size manipulation are unusual and, apparently, largely unprecedented. The microscopic origin of the changes may lie in ion trapping effects, hydrophobic/hydrophilic effects or, perhaps more likely, some combination of these and other effects. Further studies (in particular, electrochemical quartz crystal microbalance measurements) should eventually resolve the remaining mechanistic questions.

Acknowledgments

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