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Polymer Films on Electrodes. 8. Investigation of Charge-Transport Mechanisms in Nafion Polymer Modified Electrodes

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Abstract: The mechanism of charge transport through Nafion polymers coated on glassy carbon electrodes and containing Cp_2FeTMA^+, $Ru(bpy)_3^{2+}$, and $Os(bpy)_3^{2+}$ (where Cp_2FeTMA^+ is [(trimethylammonio)methyl]ferrocene, bpy = 2,2′-bipyridine) is described. The apparent diffusion coefficients, D_{app}, of polymer modified electrodes, as measured by conventional electrochemical methods and which can include contributions from intermolecular electron transfer, are compared to the diffusion coefficients of actual mass transport of the electroactive species through the polymer, D_m, as measured from the rate of permeation of the electroactive material. The results indicate that $D_{app} = D_m$ for Cp_2FeTMA^+, $D_{app} \simeq 2D_m$ for $Os(bpy)_3^{2+}$, and $D_{app} = 15D_m$ for $Ru(bpy)_3^{2+}$. These results are discussed in terms of the Dahms–Ruff model, where the observed diffusional behavior is due to both physical diffusion of the electroactive species and an electron-transfer component that can contribute to the observed behavior. The contribution of the electron-exchange mechanism toward the value of D_{app} decreases in the order of electroactive species, $Ru(bpy)_3^{2+} \gg Os(bpy)_3^{2+} \gtrsim Cp_2FeTMA^+$.

A key question in the behavior of "polymer electrodes" (electrodes coated with a thin layer of polymer[1-8]) involves the mechanism of charge transport through the layers. The rate of charge transport frequently governs the rate of electrochemical and catalytic processes at such electrodes and has been the subject of numerous recent investigations.[4,5,8-11] Charge can be transported through the layer by electron transfer between redox centers, counterion diffusion, and diffusion of the electroactive species; the relative contribution of these effects is probably different for different kinds of polymer coatings.

The relative contributions of electron transfer (electronic conduction) and diffusion to charge transport in electrochemical systems were first considered for solution processes by Dahms[13] and Ruff.[14] Similar (and equivalent) representations were later given for theoretical models of polymer electrodes.[9,10] The basic idea is that during the electrochemical reduction of a species, represented by A, at an electrode ($A + e^- \rightarrow A^-$), A can be brought to the electrode by diffusion of A^-, driven by its concentration gradient, and also by the electron-transfer reaction

$$A^- + A \rightarrow A + A^- \qquad (1)$$

(assumed to occur with a rate constant k, $M^{-1}\ s^{-1}$). A conclusion of the Dahms–Ruff (D–R) model and the polymer electrode models is that such an electron-transfer process will resemble diffusion and result in an apparent diffusion coefficient, D_{app}, composed of contributions from actual diffusion (governed by the diffusion coefficient, D) and electron transfer,

$$D_{app} = D + k\delta^2\pi C_A/4 \qquad (2)$$

where C_A is the concentration of A and δ is the distance for electron transfer. While this electron-transfer contribution usually is small in solution electrochemical processes,[13,14] it can be of importance in polymer electrodes where D values are often small. It is the purpose of this paper, as well as recent publications of Murray,[15a] Anson,[15b] and co-workers, to examine such effects for polymer-coated electrodes.

Recent reports from this laboratory[16,17] have described the preparation and behavior of electrodes modified by coating with thin films of the perfluorinated ion-exchange polymer, Nafion,[18] which can incorporate large amounts (upper limits of 0.1–1 M) of electroactive species such as $Ru(bpy)_3^{2+}$ and $Fe(tpy)_3^{2+}$ by electrostatic binding and extraction. Voltammetric studies with these electrodes often show diffusion-controlled behavior[16] (e.g., cyclic voltammetric peak currents proportional to the square root of scan rate), but the actual nature of this diffusional process

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within the polymer layer has not been determined. In this paper we examine the rate of diffusion of electroactive species into the polymer from solution and compare that rate to the apparent diffusion rates for several incorporated species within the polymer layer.

Experimental Section

Chemicals. [(Trimethylammonio)methyl]ferrocene (Cp_2FeTMA^+) hexafluorophosphate was prepared by metathesis of the corresponding iodide salt (Strem Chemicals, Inc.) with ammonium hexafluorophosphate. The resulting salt was recrystallized from acetone–ether and acetone–water to remove contaminant amines. $Ru(bpy)_3(PF_6)_2$[19] and $Os(bpy)_3(PF_6)_2$[20] (bpy = 2,2′-bipyridine) were prepared by standard laboratory methods.

Apparatus. A conventional single-compartment cell equipped with a platinum foil counterelectrode (~8 cm^2) and saturated sodium calomel reference electrode (SSCE) was employed. The working electrode was a Teflon-shrouded glassy carbon disk electrode (Atomergic; area 0.10 cm^2) polished to a mirror finish with 0.05-μm diamond paste. All measurements were performed in 0.2 M Na_2SO_4 solutions purged for at least 15 min with prepurified nitrogen. Electrochemical measurements were made with Princeton Applied Research (PAR) Model 175 universal programmer, a PAR Model 173 potentiostat, and a PAR model 179 digital coulometer and recorded on a Houston Model 2000 X–Y recorder.

Polymer Coated Electrodes. The Nafion polymer coated electrodes were prepared, as previously described,[16] by covering the glassy carbon disk electrode with a 10-μL drop of ethanolic Nafion solution (8%, equivalent weight ~970) and allowing the ethanol to evaporate. The thickness of the resulting films was determined with a Sloan Dektak surface profile measuring system. Measurements on films before and after 2-h immersion in supporting electrolyte (0.2 M Na_2SO_4) gave approximately equal thickness values, indicating very little swelling of the film. The film thickness in solution, l, was taken to be equal to the measured dry value. Various film thicknesses ranging from 0.25 to 2.0 μm were obtained by dilution of the stock Nafion solution. Cp_2FeTMA^+, $Ru(bpy)_3^{2+}$, and $Os(bpy)_3^{2+}$ were incorporated into the Nafion films by soaking the polymer coated electrode in solutions containing the respective species and supporting electrolyte (0.2 M Na_2SO_4). Electrodes prepared in this fashion are designated as GC/Nafion, electroactive species, e.g., GC/Nafion,Cp_2FeTMA^+.

The concentration of electroactive material incorporated into the polymer film was calculated from thickness measurements and the charge, Q, consumed in complete oxidation or reduction of the film species. The concentration of Cp_2FeTMA^+ incorporated in the polymer film was varied (7 mM to 3.8 M) by varying the concentration of Cp_2FeTMA^+ in the soaking solution (10^{-5} to 5×10^{-3} M). All electrodes were soaked 10 min in the Cp_2FeTMA^+ solution prior to use to ensure concentration equilibrium between the polymer and solution, although no appreciable change in polymer concentration was observed after 3–4 min. Incorporation of $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ required longer soaking periods (>15 min) to obtain fully loaded films. The polymer-covered electrodes containing the respective electroactive species were rinsed briefly with distilled water and placed in the electrochemical cell containing only supporting electrolyte solution.

Results

Extraction Coefficient. As described above, the concentration of Cp_2FeTMA^+ incorporated within the film was varied over 2 orders of magnitude by varying the concentration of the soaking solution. The polymer Cp_2FeTMA^+ concentration, as measured by complete coulometric oxidation of polymer-incorporated material, is a measure only of the material available to undergo electrochemical oxidation either directly at the electrode surface or through electron exchange with neighboring electroactive sites. Some Cp_2FeTMA^+ may be trapped in regions inaccessible to electrochemical oxidation, so that the concentrations reported here are probably lower than the true values. Plots of log C_p vs. log C_s (where C_p and C_s are the concentrations of electroactive species in polymer and solution, respectively) were linear over the range of solution concentration, 10^{-5} to 10^{-3} M (Figure 1). Curvature in these plots was observed at solution concentrations $>10^{-3}$ M, indicating Cp_2FeTMA^+ concentration saturation in the film. This saturation limit, ~3.5 M, is 67% larger than the calculated limit based on the available polymer sulfonate groups, 2.1 M (based on the density, 2 g cm^{-3}, and 970 equiv. wt.). The difference in the experimental and calculated limiting values of C_p may arise because some Cp_2FeTMA^+ is extracted into the film by means other than electrostatic binding. Nafion polymer films are capable of incorporating some uncharged ferrocene (Cp_2Fe) from aqueous solutions, presumably by extraction of the solution species into less polar regions of the polymer film.[16a] The fraction of total sulfonate groups utilized to incorporate Cp_2FeTMA^+, based on a 1:1 stoichiometry, over this range of solution concentration was 0.35–170% (corresponding to concentrations in the polymer of 7 mM to 3.5 M Cp_2FeTMA^+). The extraction coefficient, $K = C_p/C_s$, was determined from the slope of these plots in the linear segment to be $\sim 1.5 \times 10^3$. The relatively good correlation between solution and polymer concentrations indicates that C_p can be estimated from a knowledge of C_s within the solution concentration range 10^{-5}–10^{-3} M. However, the reproducibility of incorporating low concentrations of Cp_2FeTMA^+ (5–20 mM) was only within a factor of 2–3; therefore, the concentration of each individual film was determined by coulometry. Because K is large and the rate of equilibration of species between solution and polymer is relatively slow (several minutes), the rate of loss of electroactive species from the polymer layer is very slow. Thus, appreciable loss of electroactive species from the loaded polymer when it contacts water or supporting electrolyte solution does not occur over the time scale of the experiment (~1 h). However, when the electrode is immersed in the pure supporting electrolyte solution at open circuit for ~24 h, >90% of the Cp_2FeTMA^+ is lost from the polymer layer.

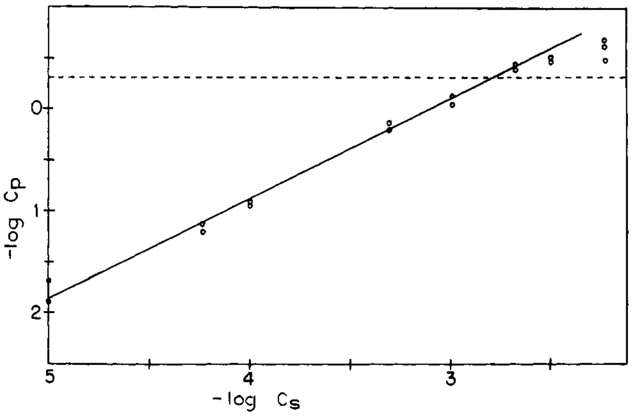

Figure 1. Concentration of Cp_2FeTMA^+ incorporated in GC/Nafion electrode, C_p (M), as a function of solution Cp_2FeTMA^+ concentration, C_s. Data for different 1-μm films. Incorporated Cp_2FeTMA^+ determined coulometrically in 0.2 M Na_2SO_4. Dashed line corresponds to a concentration based on complete utilization of all sulfonate groups.

Table I. Apparent Diffusion Coefficient, D_{app}, and Physical Diffusion Coefficient, D_m, of Nafion Polymer Modified Electrodes

GC/Nafion	$10^{10} \cdot D_{app}$,[a] cm^2/s	$10^{10} D_m$,[b] cm^2/s	$10^{10} k\delta^2 \pi C_A/4$, cm^2/s	
			exptl[c]	calcd[d]
Cp_2FeTMA^+	1.7	~1.6–1.8	<0.1	0.1–10
$Ru(bpy)_3^{2+}$	4	~0.2–0.3	~3.7	160–16 000
$Os(bpy)_3^{2+}$	0.7	~0.2–0.3	~0.4–0.5	

[a] Calculated from Cottrell slopes in loaded films. [b] From permeation chronoamperometric response (see text). [c] From eq 2 ($D_{app} - D_m$). [d] Calculated for the concentration range C_A = 1–100 mM; $\delta = 10^{-7}$ cm; $k(Ru(bpy)_3^{3/2+}) = 2 \times 10^{12}$ cm^3 s^{-1} mol^{-1} (H_2O, ref 22); $k(Cp_2FeTMA^{2+/+}) = 1.6 \times 10^9$ cm^3 s^{-1} mol^{-1} (acetonitrile, ref 23).

The extraction coefficients of the $Os(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$ were not measured over as wide a range of solution concentration as those of Cp_2FeTMA^+. However, for 1 and 0.5 mM solutions of the respective electroactive species, approximately 2–3 times less $Os(bpy)_3^{2+}$ or $Ru(bpy)_3^{2+}$ was incorporated into the Nafion films compared to Cp_2FeTMA^+. Thus, the extraction coefficients

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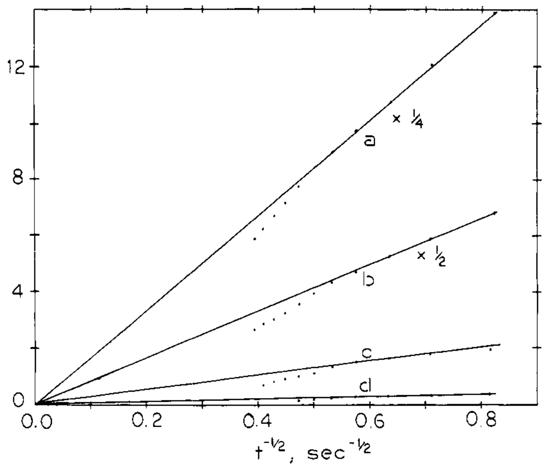

Figure 2. Cottrell plots resulting from oxidation of GC/Nafion, Cp_2FeTMA^+ in 0.2 M Na_2SO_4. Film thickness, 1 μm. Cp_2FeTMA^+ concentration: (a) 0.76 M; (b) 0.19 M; (c) 35 mM; (d) 7 mM.

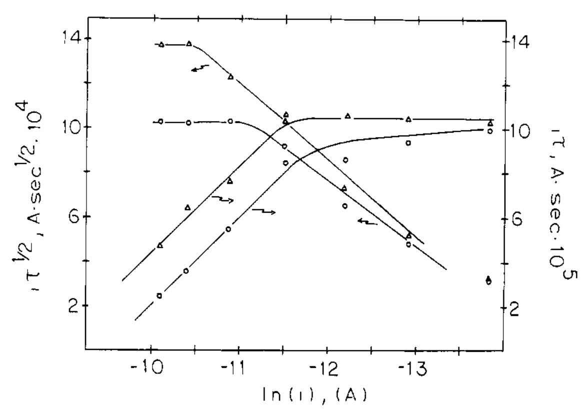

Figure 3. Chronopotentiometric results of GC/Nafion,Cp_2FeTMA^+ electrode (1-μm film thickness, polymer Cp_2FeTMA^+, 1.1 M) in 0.2 M Na_2SO_4. $i\tau^{1/2}$ and $i\tau$ as a function of applied current; (○) oxidation and (△) reduction of film.

of $Os(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$ into Nafion films are ~500–750.

Diffusion Coefficients. Values for the apparent diffusion coefficient D_{app}, of Nafion polymer electrodes containing Cp_2FeTMA^+, $Os(bpy)_3^{2+}$, or $Ru(bpy)_3^{2+}$, determined from chronoamperometric and chronopotentiometric experiments,[21] are listed in Table I. Typical plots of current (i) vs. $t^{-1/2}$ for a potential-step chronoamperometric experiment (Cottrell plots) are shown in Figure 2. For $t < 3$ s, these are linear with zero intercepts, as expected for a diffusion-controlled process:

$$i = nFAD_{app}^{1/2}C_p/\pi^{1/2}t^{1/2} \qquad (3)$$

$$C_p = N_p/Al \qquad (4)$$

where N_p is the amount of electroactive species in the polymer determined coulometrically and l is the polymer film thickness. At longer times the current decayed faster than expected from pure diffusional behavior, indicating depletion of electroactive material[4g] (thin-film behavior). Constant-current step (chronopotentiometric) experiments also showed semiinfinite, linear diffusional behavior with $\tau_F/\tau_R = 3.0$ and $i\tau_F^{1/2}$ = constant at current densities of 0.2–0.5 mA/cm², depending on film thickness, where τ_F and τ_R are the forward and reverse transition times. At lower current densities, 5–20 μA/cm², thin-film behavior was observed as expected ($\tau_F = \tau_R$ and $i\tau_F$ = constant) (Figure 3). D_{app} values determined from chronoamperometric and chronopotentiometric experiments for the same polymer coated electrode were essentially identical.

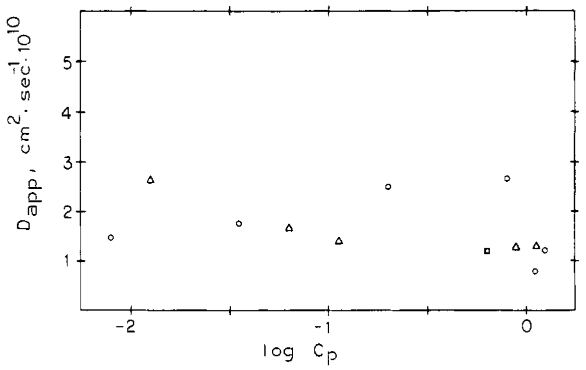

Figure 4. Diffusion coefficient, D_{app}, of GC/Nafion,Cp_2FeTMA^+ electrodes as a function of Cp_2FeTMA^+ concentration in 0.20 M Na_2SO_4. Film thickness: (△) 0.5 μm; (○) 1 μm; (□) 2 μm.

D_{app} for GC/Nafion,Cp_2FeTMA^+ as a function of Cp_2FeTMA^+ concentration is shown in Figure 4. Although considerable scatter existed in the values obtained, a D_{app} value of $1.7 \pm 0.5 \times 10^{-10}$ cm²/s, independent of the total film concentration over the range 7 mM–1.2 M, was found. A similar independence of D_{app} with concentrations has been reported for other polymer modified electrodes.[5f] Detailed measurements on the GC/Nafion,$Ru(bpy)_3^{2+}$ system have also shown a concentration-independent D_{app}.[17] The appreciable scatter in D_{app} values in Figure 4 is probably attributable mainly to uncertainties in the film thickness, l, which enters the calculation of the Cp_2FeTMA^+ concentration. The film thickness was measured for a set of samples involving a given amount of Nafion solution, and this value was then employed for all subsequent films involving this quantity of material. From these measurements on a series of Nafion films, we estimate the reproducibility of producing films of constant thickness as about ±25%. This corresponds to a scatter of ±50% in values of D_{app}.

D_{app} was also investigated as a function of the ratio $(Cp_2FeTMA^{2+})/(Cp_2FeTMA^+)$. Various ratios were established within the polymer film containing a total concentration of ~1 M by holding the electrode at different potentials on either side of $E^{\circ\prime}$ (0.32 V vs. SSCE). The ratio of oxidized to reduced material was determined by integrating the charge passed on stepping the potential from 0.0 V (where the film is totally reduced) to specific E values where partial oxidation of the film occurred. The electrode was then held at this potential for 5 min to allow any concentration gradients within the film to disappear. Potential step experiments were then performed to oxidize the film completely. D_{app} was independent of $(Cp_2FeTMA^{2+})/(Cp_2FeTMA^+)$ over the investigated range of 0.0–0.9. D_{app} was also independent of film thickness for 0.25–2-μm films (Figure 4).

Polymer Film Incorporating $Os(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$. $Os(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$ were incorporated into GC/Nafion polymer electrodes by soaking the electrode in a solution containing both complexes, each at a concentration of 0.2 mM. Cyclic voltammetry of this electrode in 0.2 M Na_2SO_4 showed two well-separated waves, at $E^{\circ\prime}$ = 0.6 and 1.0 V vs. SSCE, that were diffusion controlled over sweep rates ranging from 0.1 to 0.5 V/s (Figure 5). The peak of each wave corresponded to that when each component was alone in the film at the same concentration. For the $Ru(bpy)_3^{2+}$ wave, $i_p/v^{1/2}$ vs. v was constant. This behavior, where both species are homogeneously distributed throughout the film, can be contrasted with that found for very nonuniform distributions. These latter electrodes, produced as described below, are useful in investigating the mobility of the incorporated electroactive species. The Nafion polymer electrodes were prepared as usual (0.5-μm thickness), immersed in 0.2 mM $Ru(bpy)_3^{2+}$ solution for 600 s, rinsed, and cycled briefly in 0.2 M Na_2SO_4. After a well-defined steady-state CV was obtained, (Figure 5b), the electrode was removed from the cell, rinsed with water, im-

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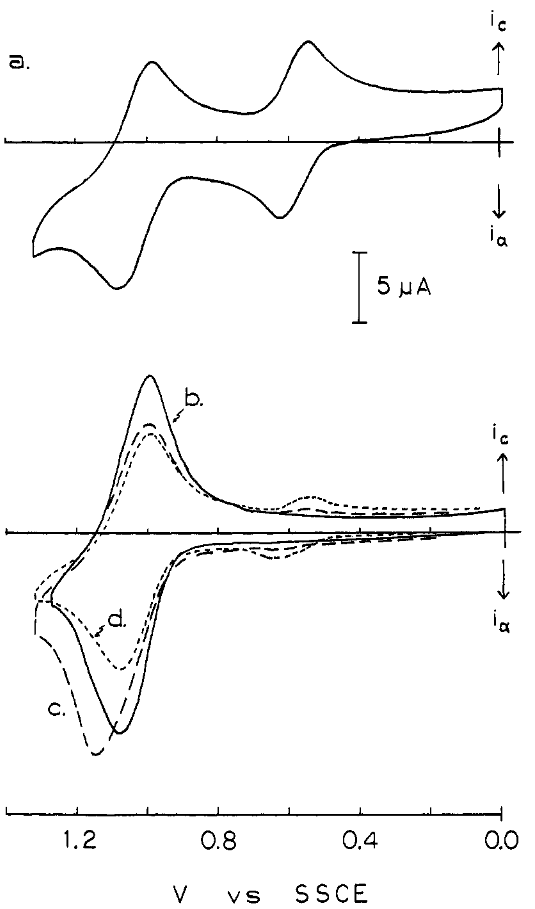

Figure 5. Cyclic voltammetric response of (a) GC/Nafion electrode incorporating homogeneous distribution of $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$; (b) GC/Nafion,$Ru(bpy)_3^{2+}$ only; (c) GC/Nafion,$Ru(bpy)_3^{2+}$, $Os(bpy)_3^{2+}$ heterogeneous electrode (see text), initial scan; (d) same as (c) except steady-state CV. Scan rate: 50 mV/s; supporting electrolyte, 0.2 M Na_2SO_4.

mersed in 0.2 mM $Os(bpy)_3^{2+}$ for 100 s, rinsed again, and placed back into the electrochemical cell. This procedure results in a polymer film with an "inner layer" (near the polymer–electrode interface) of predominantly $Ru(bpy)_3^{2+}$ and an "outer layer" (polymer–solution interface) with a relatively high concentration of incorporated $Os(bpy)_3^{2+}$ (although both complexes probably coexist in this region). Note that long immersion (1–2 h) of a Nafion $Ru(bpy)_3^{2+}$ electrode in an 0.2 mM $Os(bpy)_3^{2+}$ solution will result in essentially complete replacement of Ru by the Os species. No well-defined boundary exists between the incorporated $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ species produced by this stepwise treatment, but the initial concentration gradients within the polymer are such that the polymer–electrode interface is Ru rich and the polymer–solution interface is Os rich.

This electrode was used immediately (within 15 s) after immersion in the $Os(bpy)_3^{2+}$ solution. On the initial cycle, only a very small peak current (~1 μA) at 0.6 V was observed due to the direct oxidation of $Os(bpy)_3^{2+}$ at the electrode surface. However, there was a significant *increase* in the anodic current due to $Ru(bpy)_3^{2+}$ oxidation (relative to that observed prior to incorporation of $Os(bpy)_3^{2+}$) with a diminished re-reduction peak (Figure 5c), indicating that electron-mediated oxidation of the outer $Os(bpy)_3^{2+}$ layer occurred through the inner $Ru(bpy)_3^{2+}$ layer and that the electron-transfer reaction between the Os(II) and Ru(III) species is more rapid than the electron-exchange reaction between Ru(II) and Ru(III) species. However, with continued cycling (0.1 V/s) over the potential range 0.0–1.2 V, the $Os(bpy)_3^{2+}$ oxidation/reduction peak currents increased steadily with a concomitant decrease in the $Ru(bpy)_3^{2+}$ wave. After 6 cycles (~3 min), the steady-state voltammogram (Figure 5d) was typical of the homogeneous film. The electrode was removed from the cell and reimmersed in the $Os(bpy)_3^{2+}$ solution for 100 s. On the initial cycle, the peak currents at 0.6 V for the $Os(bpy)_3^{2+}$ direct oxidation/reduction were the same as on the final scan of the previous experiments while the $Ru(bpy)_3^{2+}$ oxidation wave again increased in height. With cycling, the $Os(bpy)_3^{2+}$ wave increased while for $Ru(bpy)_3^{2+}$ the additional (catalytic) currents and *overall* peak currents decreased. This procedure (immersion in $Os(bpy)_3^{2+}$ solution followed by cycling) was repeated two times until the peak currents due to both complexes were approximately equal.

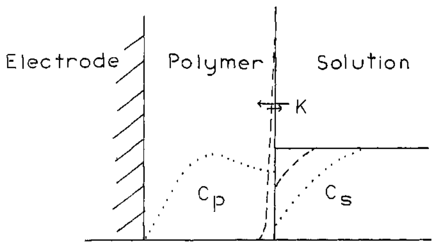

Figure 6. Schematic concentration profiles during permeation chronoamperometric experiment. (—) Initial profile at $t = 0$; (---) profile after electrode immersion in solution at relatively short times; (···) profile at longer time.

Qualitatively, several conclusions may be drawn from these experiments. The initial increased (catalytic) current for the oxidation of $Ru(bpy)_3^{2+}$ indicates that electron transfer between incorporated species is a possible charge-transport mechanism in Nafion polymer (heavily favored in this case by the large driving force of $Ru(bpy)_3^{3+}/Os(bpy)_3^{2+}$ reaction). However, the steady increase in the $Os(bpy)_3^{2+}$ waves clearly indicates that physical diffusion of this complex also occurs. Quantitatively, the rate at which either of these processes occurs (electron transfer vs. physical diffusion) is not readily determined due to the inexact nature of the initial concentration profiles. However, clearly both mechanisms of charge transport within the polymer are demonstrated. A recent investigation by Facci and Murray[15a] describes similar experiments with mixed electroactive species ($IrCl_6^{3-}$ and $Fe(CN)_6^{3-}$) incorporated in a polycationic polymer film. In their experiments, actual diffusion of the species was not seen, but pre-peaks and accelerated charge transport due to cross-reactions between the electroactive species were observed during steady-state voltammetry. Neither of these phenomena were observed with Nafion electrodes incorporating mixtures of electroactive species, probably because of the higher mobility of redox species or slower electron-transfer rate in the Nafion matrix.

Permeation Current Transients. To evaluate the diffusion coefficient of actual mass transport of ions in the Nafion-modified electrodes, we measured the rate of incorporation of electroactive species into the polymer layer. This determination of D by measurement of the rate of permeation of electroactive ions through Nafion polymers initially devoid of any electroactive species rests on the assumption that a finite period of time, characteristic of the actual diffusion coefficient, D_m, is required for the ions to permeate a polymer of known thickness and reach the substrate where the flux is conveniently measured by monitoring the current response. Consider an electrode coated with a polymer film of thickness l (initially containing no electroactive material) immersed in a solution containing the reduced form of an electroactive species (Figure 6). We assume the polymer film to be a homogeneous membrane into which the electroactive species diffuses with a characteristic diffusion coefficient, D_m, different from that in solution, D_s. An equilibrium extraction constant, K, is ascribed to the partitioning of the electroactive species between the solution and polymer. If the solvent–polymer extraction is fast at all times, then the concentration of the electroactive species at the polymer–solution interface is described by $C_p(l,t) = KC_s(l,t)$ where $C_p(l,t)$ and $C_s(l,t)$ are the concentrations of electroactive species in the polymer layer (p) and solution (s), respectively. If a potential is applied to the anodic plateau of the wave simultaneously with immersion of the electrode ($t = 0$), then the initial conditions under consideration are

$$C_p(x,0) = 0 \qquad 0 < x < l$$

$$C_s(x,0) = C_s^* \qquad l < x < \infty$$

The final chronoamperometric equation for this case is

$$i(t) = \frac{2\gamma nFAC_s^* K D_m^{1/2}}{(\gamma + K)(\pi t)^{1/2}} \sum_{j=0}^{\infty} \left(\frac{1 - K/\gamma}{1 + K/\gamma} \right)^j \exp[-(j + 1/2)^2 l^2 / D_m t] \quad (5)$$

where $\gamma = (D_s/D_m)^{1/2}$ (see Appendix).

At short times, $i(t) \rightarrow 0$ since the electroactive species has not yet permeated the polymer film from the polymer–solution interface to the electrode–polymer interface. At long times, i.e., as $t \rightarrow \infty$, the diffusion layer is confined to the solution phase and $i(t)$ approaches the i–t response of a bare electrode. Of particular interest to our investigation is the current–time response at relatively short times when the electroactive material initially permeates the film and diffuses to the electrode surface. In this short time region the i–t response will be primarily due to physical diffusion of the electroactive species through the film. Any contribution to the observed current response via an electron-transfer mechanism will be small, since only the reduced form of the electroactive species exists at any appreciable concentration at these times. Experimentally, the initial condition $C_p(x,0) = 0$ can be realized by applying the potential step prior to immersion of the electrode into the solution containing the electroactive species. The chronoamperometric response due to Cp_2FeTMA^+ (C_s = 1 mM) permeation through Nafion films of several thicknesses along with predicted responses from eq 1 are shown in Figure 7. The value of D_m (1.7×10^{-10} cm²/s) used in calculating the theoretical response has been taken from i–t response of fully loaded polymer films in 0.2 M Na_2SO_4, D_{app}, Table I. The value of the partitioning constant, $K = 1.5 \times 10^3$, used in the calculation was the value determined from bulk extraction experiments. The reasonable fit of experimental results to the theoretical curves with no adjustment of parameters obtained from earlier experiments indicates that D_{app} of fully loaded films is approximately equal to the actual diffusion coefficient of mass transport, D_m, of Cp_2FeTMA^+ in the film. The transient shape of the i–t curve was also found to be independent of solution concentration, C_s, while the current magnitude was directly proportional to C_s as predicted by eq 5.

Similar permeation experiments were performed with $Os(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$ as the diffusing species (Figure 8). The experimental i–t curves, however, did not correspond to the theoretical curves computed from eq 1 with values of D_{app} and K (Table I). The best fit of the experimental data was obtained by using a value of D_m equal to 0.2–0.3 × 10^{-10} cm²/s, considerably smaller than the D_{app} values of 4×10^{-10} and 0.7×10^{-10} cm²/s for the Ru and Os complexes, respectively. Inspection of Figures 7 and 8 reveals that for a 1-μm-thick film, Cp_2FeTMA^+ permeates the polymer at a significantly faster rate than either $Ru(bpy)_3^{2+}$ or $Os(bpy)_3^{2+}$. With Cp_2FeTMA^+ the current increases rapidly and reaches a maximum at approximately 20 s, while for $Ru(bpy)_3^{2+}$ a significant increase in current was observed only after about 40 s. Although some deviation of theoretical curves from experimental permeation curves was observed by using unique D_m values, the large differences in the permeation current transients demonstrate an order of magnitude difference in the physical diffusion coefficient for Cp_2FeTMA^+ as compared to that for the Ru or Os complexes. At longer times, after the initial current increase, the permeation current transient may include contributions from electron-transfer reactions since the oxidized form is being produced at the surface. While the current transients (Figures 7 and 8) observed for Cp_2FeTMA^+ (where $D_m = D_{app}$) and $Os(bpy)_3^{2+}$ ($2D_m \simeq D_{app}$) have a similar shape and magnitude as predicted by eq 5 with D_m values listed in Table I, the current transient obtained for $Ru(bpy)_3^{2+}$ (where $D_{app} \simeq 15D_m$) rises much faster than predicted by using, for instance, a value of $D_m = 1 \times 10^{-11}$ cm²/s, although at short times (<50 s) this value of D_m yields the best fit. The difference between the D_{app} and D_m values for the Os and Ru complexes clearly indicates that the actual physical diffusion of the electroactive species occurs at a slower rate (particularly in the case of $Ru(bpy)_3^{2+}$) than the apparent diffusion of charge in fully loaded films. Further evidence of this

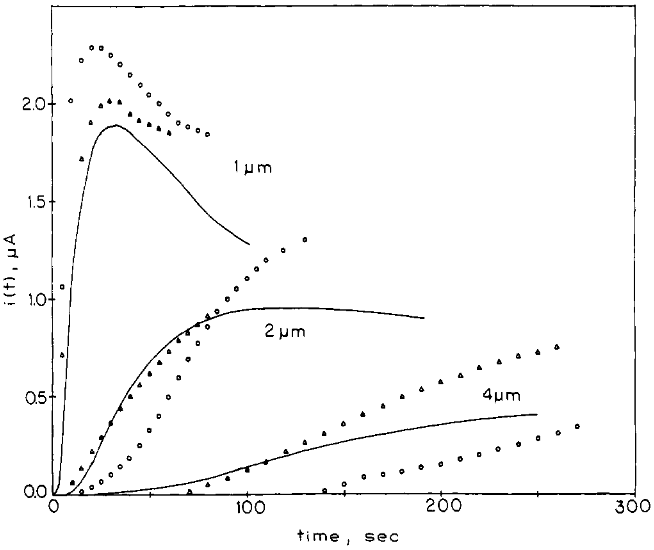

Figure 7. Chronoamperometric response of GC/Nafion electrodes immersed in 1.0 mM Cp_2FeTMA^+ (0.2 M Na_2SO_4); (○ and △), representative experimental responses. Theoretical values (—) obtained from eq 3 by using $K = 1500$, $D_m = 1.7 \times 10^{-10}$ cm²/s, and $D_s = 0.8 \times 10^{-5}$ cm²/s. Film thicknesses are indicated.

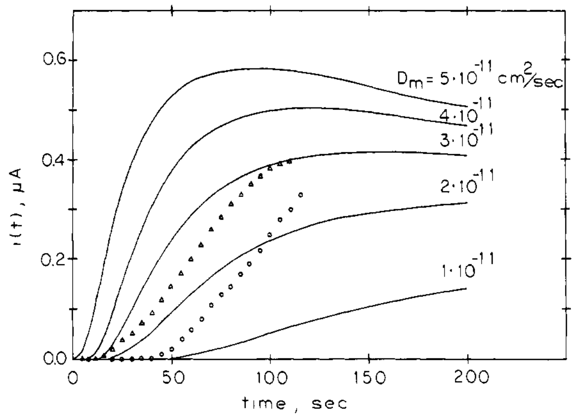

Figure 8. Chronoamperometric response of GC/Nafion electrodes immersed in (○) 1.0 mM $Ru(bpy)_3^{2+}$ and (△) 1.0 mM $Os(bpy)_3^{2+}$ (0.2 M Na_2SO_4). (—) Theoretical curves obtained by using $K = 750$, $l = 10^{-4}$ cm, C_s = 1.0 mM and $D_s = 0.5 \times 10^{-5}$ cm²/s. Values of D_m are indicated for each curve.

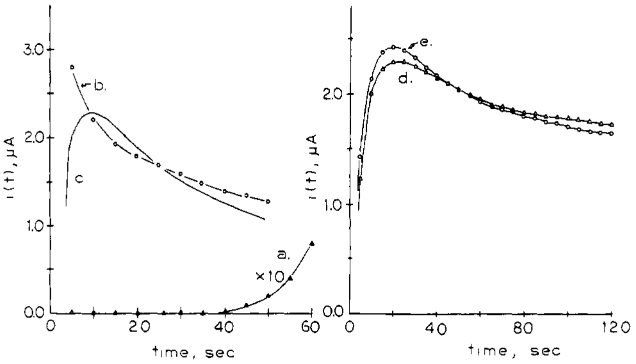

Figure 9. (a) Chronoamperometric response of GC/Nafion electrode (△) and (b) GC/Nafion,$Ru(bpy)_3^{3+}$ (0.2 M) electrode (○) immersed in 1.0 mM $Ru(bpy)_3^{2+}$ (0.2 M Na_2SO_4). (c) Theoretical curve (—) obtained with $K = 750$, $l = 10^{-4}$ cm and $D_m = 5 \times 10^{-10}$ cm²/s. (d) Chronoamperometric response of GC/Nafion electrode (△) and (e) GC/Nafion,Cp_2FeTMA^{2+} (0.4 M) (○) immersed in 1.0 mM Cp_2FeTMA^+ (0.2 M Na_2SO_4).

difference in D_{app} and D_m is found by repeating the above permeation experiments with films containing a high concentration of the oxidized form of the electroactive species. The chronoamperometric response in this case should yield a much larger value of diffusion coefficient for $Ru(bpy)_3{}^{2+}$ permeation, since the solution species can now reduce the film by electron mediation. Figure 9 shows the chronoamperometric response of such an experiment with both $Ru(bpy)_3{}^{2+}$ and Cp_2FeTMA^+. Clearly, in the case of $Ru(bpy)_3{}^{2+}$, the diffusion of this species into the Nafion film containing ~0.1 M $Ru(bpy)_3{}^{3+}$ is apparently much faster than diffusion into the bare polymer. A closer fit to this current transient can be made by using $D = 4 \times 10^{-10}$ cm^2/s, in excellent agreement with the value of D_{app} (Table I) for $Ru(bpy)_3{}^{2+}$. The chronoamperometric response of Cp_2FeTMA^+, however, was not affected by the presence of Cp_2FeTMA^{2+} in the film, as expected when physical diffusion is the rate-limiting process of charge transport.

Discussion

The results establish that both electron transfer and actual diffusion contribute to the conduction processes in Nafion films; the relative contributions depend upon the nature of the incorporated electroactive ion. Thus, for Cp_2FeTMA^+, the actual diffusion coefficient (from permeation studies), D_m, and the apparent one, D_{app}, are essentially the same. For $Ru(bpy)_3{}^{2+}$ and $Os(bpy)_3{}^{2+}$, however, both processes contribute, with the electron-transfer mode especially important for $Ru(bpy)_3{}^{2+}$. In a recent study comparing the behavior of $Ru(bpy)_3{}^{2+}$ and $Co(bpy)_3{}^{2+}$ in Nafion films, Buttry and Anson reach a similar conclusion and find that electron transfer is of major importance for the Ru species in Nafion.[15b] Similarly, the study of Facci and Murray[15a] demonstrates the importance of cross electron transfer when two different species are incorporated into a polymer film.

Although there have been a few studies attempting to measure electron-transfer rates in solutions with electrochemical methods by applying the D–R model and eq 2,[13,14] in general, the contribution of the electron-transfer term is very small. For example, for $C_A = 0.1$ M, $\delta = 10^{-7}$ cm, $k = 10^9$ cm^3 mol^{-1} s^{-1} (10^6 M^{-1} s^{-1}), the electron-transfer term is 8×10^{-10} cm^2 s^{-1} as compared to usual D values in aqueous solutions of ~10^{-6} cm^2 s^{-1}. However, because D values in polymers are several orders of magnitude smaller than in solution, if the rate constant for electron transfer, k, is large enough, this can make an appreciable contribution to charge transport in the polymer. The estimated magnitudes for the electron-transfer terms obtained by subtracting D_m from A_{app} are given in Table I. For comparison, calculated values of the electron-transfer term based on solution electron-transfer rate data are also given in Table I.

An important consequence of the D–R model and eq 2 is that diffusion via electron transfer should become more important with increasing concentration. That D_{app} for GC/Nafion,Cp_2FeTMA^+ is independent of the loading concentration clearly supports the conclusion that electron transfer does not contribute significantly to the charge transport. However, a similar independence of D_{app} with concentration was observed for $Ru(bpy)_3{}^{2+}$ incorporated in Nafion,[15,17] in contradiction to expectations about the importance of electron transfer in this polymer. Thus, D_{app} values for both $Ru(bpy)_3{}^{2+}$ and $Ru(bpy)_3{}^{3+}$ were essentially equal and independent of concentrations between loadings of 0.7–70% of total sulfonate groups in the Nafion films (and corresponding to concentrations of ~3–300 mM).[17] This lack of concentration dependences might be attributed to a nonuniform distribution of $Ru(bpy)_3{}^{2+}$ within the polymer film, so that the homogeneous D–R model does not apply.[13,14] An alternative is that the "cross-linking" induced by the introduction of the $Ru(bpy)_3{}^{2+}$ introduces a compensating effect that decreases motion of the polymer chains and the electron-transfer rate as the concentration increases. Because of the uncertainties in the quantitative applicability of eq 2, we will not attempt to estimate electron-transfer rate constants for the incorporated species. However, the larger contribution (>40×) of electron transfer to the apparent diffusional rate (eq 2) for $Ru(bpy)_3{}^{2+}$ as compared to Cp_2FeTMA^+ in Nafion is in qualitative agreement with reported solution self-exchange electron-transfer rate constants, 2.0×10^9[22] and 1.6×10^6 M^{-1} s^{-1},[23] respectively.

Conclusion

The diffusional behavior of electroactive cations incorporated in Nafion polymers results from both physical diffusion and an apparent diffusion due to electron-transfer reactions. The occurrence of either or both charge-transfer mechanisms is dependent on the electroactive species. Permeation current transient experiments allow separation of these two components of diffusion and should be useful in investigations concerning other polymer modified electrodes where the redox ion is not tightly bound to the polymer lattice.

Acknowledgment. We are indebted to D. A. Buttry and F. C. Anson for making their paper available to us before publication and for helpful discussions and suggestions. Samples of $Ru(bpy)_3(PF_6)_2$ and $Os(bpy)_3(PF_6)_2$ were prepared and generously donated by John Gaudiello. This work was supported by grants from the National Science Foundation (CHE 7903729) and the Robert A. Welch Foundation.

Appendix

Derivation of Equation 5: Potential-Step Chronoamperometry for Permeation of a Solution Electroactive Species into a Polymer Modified Electrode. The model presented below is an extension of a previous model[12] modified for zero initial concentration of the electroactive species in the polymer.

The system we are considering consists of two phases, the polymer and the solution. For mass transfer by diffusion in both phases:

$$\text{for the polymer} \quad \frac{\partial C_p(x, t)}{\partial t} = D_m \frac{\partial^2 C_p(x, t)}{\partial x^2} \tag{A1}$$

$$\text{for the solution} \quad \frac{\partial C_s(x, t)}{\partial t} = D_s \frac{\partial^2 C_s(x,t)}{\partial x^2} \tag{A2}$$

where C_p and D_m, and C_s and D_s, are the concentrations and diffusion coefficients in the polymer and solution phases, respectively. x is the coordinate normal to the electrode surface. Initially, the concentration of the electroactive species in the solution phase is $C_s{}^*$, and the polymer concentration is 0. The thickness of the polymer is defined as l. This yields the initial conditions

$$C_p(x,0) = 0 \qquad 0 < x < l \tag{A3}$$

$$C_s(x,0) = C_s{}^* \qquad l < x < \infty \tag{A4}$$

The system is semiinfinite in the solution phase, and the potential step is to the diffusion-limited plateau. This generates the boundary conditions:

$$\lim_{x \to \infty} C_s(x,t) = C_s{}^* \tag{A5}$$

$$C_p(0,t) = 0 \tag{A6}$$

Using the flux of material across the polymer–solution interface and assuming rapid extraction with a constant, K, we obtain

$$D_m \frac{\partial C_p(x,t)}{\partial x}\bigg|_{x=l} = D_s \frac{\partial C_s(x,t)}{\partial x}\bigg|_{x=l} \tag{A7}$$

$$C_p(l,t) = K C_s(l,t) \tag{A8}$$

The current $i(t)$ is given by the flux at the membrane–substrate interface:

$$\frac{i(t)}{nFA} = D_m \frac{dC_p(x,t)}{dx}\bigg|_{x=0} \tag{A9}$$

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[22] Young, R. C.; Keene, F. R.; Meyers, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2468–2473.

[23] Yang, E. S.; Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1980**, *84*, 3094–3099.

With conditions (A3), (A4), and (A5), the Laplace transformation of (A1) and (A2) yields

$$\bar{C}_p(x,s) = A\exp(\sqrt{s/D_m}x) + B\exp(-\sqrt{s/D_m}x) \tag{A10}$$

$$\bar{C}_s(x,s) = G\exp(-\sqrt{s/D_s}x) + \frac{C_s^*}{s} \tag{A11}$$

where the barred values represent the Laplace-transformed concentrations and A, B, and G are coefficients to be evaluated by using the remaining conditions. Evaluation of the constant yields

$$\frac{\bar{i}(s)}{nFAKC_sD_m^{1/2}} = \frac{2\exp(-\sqrt{s/D}l)}{\sqrt{s}(1 + K/\gamma)[1 - \omega\exp(-2\sqrt{s/D_m}l)]} \tag{A12}$$

where $\gamma = (D_s/D_m)^{1/2}$. This can be expanded as a power series to give (A13) and (A14) The inverse transform of (A14) yields

$$\frac{\bar{i}(s)}{nFAKC_s^*D_m^{1/2}} = \frac{2\exp(-\sqrt{s/D_m}l)}{\sqrt{s}(1 + K/\gamma)}\sum_{j=0}^{\infty}\omega^j\exp(-2j\sqrt{s/D_m}l) \tag{A13}$$

$$= \frac{2\gamma}{\sqrt{s}(\gamma + K)}\sum_{j=0}^{\infty}\omega^j\exp[-(2j + 1)\sqrt{s/D_m}l] \tag{A14}$$

eq 5. This equation yields the expected limiting behavior

$$\lim_{t\to 0} i(t) = 0 \qquad \lim_{t\to\infty} i(t) = \frac{nFAC^*D_s^{1/2}}{(\pi t)^{1/2}}$$

(the Cottrell equation for an uncoated electrode).

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Os(bpy)_3^{2+}$, 23648-06-8; Cp_2FeTMA^+, 33039-48-4; C, 7440-44-0; Nafion, 39464-59-0.

Polymer Films on Electrodes. 9. Electron and Mass Transfer in Nafion Films Containing $Ru(bpy)_3^{2+}$

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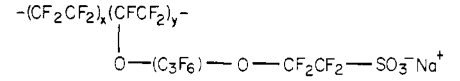
Received December 21, 1981

Abstract: The electrochemical behavior of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) contained in 2-μm-thick films of the perfluorosulfonate polymer Nafion on glassy carbon is described. The apparent diffusion coefficient, D_{app}, for the 2+ and 3+ forms was determined by potential-step chronoamperometric measurements to be $(5 \pm 2) \times 10^{-10}$ cm^2 s^{-1}. D_{app} for the 2+ form was independent of loading of $Ru(bpy)_3^{2+}$ in the film. The shapes of the cyclic voltammetric (current–potential) waves for the system were fit by digital simulation techniques with a model involving interactions between the electroactive groups as well as interconversions of different forms of the 2+ and 3+ species.

Recent reports from this laboratory[1–3] have described polymer electrodes based on the ion-containing polymer Nafion.[4] Because of the fluorocarbon backbone, these polymers are thermally and chemically very stable. The Nafion (NAF) used in this study (and in previous studies[1–3]) is a low-equivalent-weight (970 g/equiv of proton) polymer and is soluble in ethanol but insoluble in water. This material can be coated on an electrode surface by evaporation of an EtOH solution. The dissociable proton allows incorporation of electroactive cations from a contacting solution phase via ion exchange.[1–3] Such electrostatic binding of ions into polymers such as poly(vinylpyridine) (PVP) has also been reported by Anson and co-workers.[5] Interest in such polymer layers on electrodes derives not only from possible applications (e.g., electrochromic, electrochemiluminescent, or analytical devices) but also because electrochemical measurements can be used to probe transport and electron-transfer processes as well as provide information about the environment within the polymer.



$$-(CF_2CF_2)_x(\underset{\displaystyle |\atop \displaystyle O-(C_3F_6)-O-CF_2CF_2-SO_3^-Na^+}{CF}CF_2)_y-$$

Nafion

Previous investigations of the electrochemical properties of electroactive cations in Nafion films coated onto electrode surfaces have raised several questions concerning the mechanisms and rates of charge transport through the polymer film. First, the difference in potential between the anodic and cathodic peaks in cyclic voltammograms, ΔE_p, for the $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) couple in thick (10–15 μm) films[1] was large, even at moderate (<100 mV s^{-1}) scan rates. Indeed, the apparent heterogeneous rate constant for electron transfer (k°_{app}) for this couple in a polymer film was estimated to be about 1×10^{-5} cm s^{-1}, which is much lower than the heterogeneous rate constant (k°) in aqueous solution, ~0.07 cm s^{-1}.[6] It appeared worthwhile to examine other factors[7–9] that could contribute to the observed ΔE_p.

A second question concerns the mechanism by which charge is transported through the film. In these multilayer films, charge transport can occur via electron hopping,[3,7,10] in which electrons are transferred from reduced to oxidized sites in the film. This mechanism has been proposed for polymers containing electroactive sites along the polymer backbone as well as for redox reactions in PVP films[5] that coordinately bind electroactive metal complexes. However, ion-containing polymers (such as Nafion)

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