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

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

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

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

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

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

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

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

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)₃²⁺, 15158-62-0; Os(bpy)₃²⁺, 23648-06-8; Cp₂FeTMA⁺, 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)₃²⁺

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Abstract: The electrochemical behavior of Ru(bpy)₃²⁺ (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 $(5 \pm 2) \times 10^{-10}$ cm² s⁻¹. D_{app} for the 2+ form was independent of loading of Ru(bpy)₃²⁺ 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

$$-(CF_2CF_2)_x(CFCF_2)_y-$$
$$|$$
$$O-(C_3F_6)-O-CF_2CF_2-SO_3^-Na^+$$
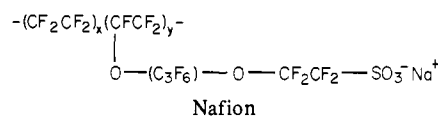
Nafion

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.

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)₃²⁺ (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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(4) (a) Nafion and Teflon are trademarks of E. I. du Pont de Nemours and Co., Inc. (b) Grot, W. *Chem.-Ing.-Tech.* **1978**, *50*, 299.

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are known to separate, on a microscopic level, into two domains or phases.[11] These are the bulk polymer phase and a much lower density ionic cluster phase. Since the counterions (in this case the electroactive ions) are present only in this low-density cluster phase and ion-pair formation usually is not significant in these polymers,[12-15] actual diffusion of the electroactive species can also occur in ion-containing polymers. Indeed, the diffusion coefficient for Na^+ in 1200 equiv wt Nafion is only slightly smaller than that in water.[14] Thus, actual diffusion of electroactive species rather than electron hopping could occur in these films. In the work described, we report results bearing on the mechanism of the redox process and the mechanism for charge transport through the polymer film. A companion paper[3] also deals with question of charge transport in Nafion.

Experimental Section

The experimental procedures generally followed those described in ref 3. Electrochemical measurements were performed in a three-electrode cell with a glassy carbon (Atomergic Corp., Plainview, NY) working electrode, a Pt flag auxiliary electrode, and a saturated mercurous sulfate reference electrode (MSE; +0.64 V vs. NHE). The area of the working electrode was 0.065 cm². The glassy carbon surface was prepared as follows: (1) grinding with 400- and then 600-grit silicon carbide grinding paper (Buehler Ltd., Evanston, IL); (2) polishing with aqueous slurries of 0.3- and then 0.05-μm alumina polishing powders (Buehler) on felt; (3) buffing on wet felt; (4) stirring in ethanol for about 2 h.

Film thickness was measured with a Sloan, Inc., Dektak surface-profile measuring system.[2] Highly polished glassy carbon rods of the same diameter as those used for electrode preparation were mounted vertically in Teflon fluorocarbon coated plates to measure the film thickness. Films were deposited on the rods as described below. After drying, the plates and rods were stored in 0.1 M H_2SO_4 overnight (electrode pretreatment procedure). The samples were removed from the solution and carefully blotted dry, and then half of the film was cut away with a razor blade. The profile measuring system was then used to measure the distance between the carbon substrate and the top of the polymer film at several points along the film edge.

About 15 min elapsed between the time the films were removed from the solution and the time when film measurement was initiated. Loss of water from the film probably occurred during this time, so that some shrinkage of the film is probably unavoidable. Note, however, that in the approximately 0.5-h period required to complete a set of measurements on a film, no further shrinkage was detected.

For measurements at bare glassy carbon, the glassy carbon rod was sealed onto the end of a glass tube by using heat-shrinkable Teflon tubing (Markel Corp., Norriston, PA). This was done after grinding but before polishing. A few drops of Hg were then placed in the tube for electrical contact. For preparing Nafion film electrodes, we slowly applied a measured quantity of a solution of Nafion polymer in ethanol to the surface of the rod with a microliter syringe. After the desired quantity of the polymer solution was applied, the ethanol was allowed to evaporate in air for about 15 min. The rod was then tightly sealed with narrow strips of Teflon tape such that only the coated surface was exposed. Prior to use, the coated electrodes were soaked overnight in supporting electrolyte. The quantity of electroactive $Ru(bpy)_3^{2+}$ introduced into the film as described below was determined by coulometry. Because oxidation of $Ru(bpy)_3^{2+}$ occurs at potentials where some water oxidation occurs, the film was quantitatively oxidized to the 3+ form and the number of coulombs required to reduce the film back to $Ru(bpy)_3^{2+}$ was measured. Positive feedback was used to compensate for solution and/or film resistance.

Results and Discussion

General Electrochemical Characteristics of the $Ru(bpy)_3^{2+/3+}$ Couple in the Polymer Film. The conversion of a film to the $Ru(bpy)_3^{2+}$ form is illustrated by the results in Figure 1. When

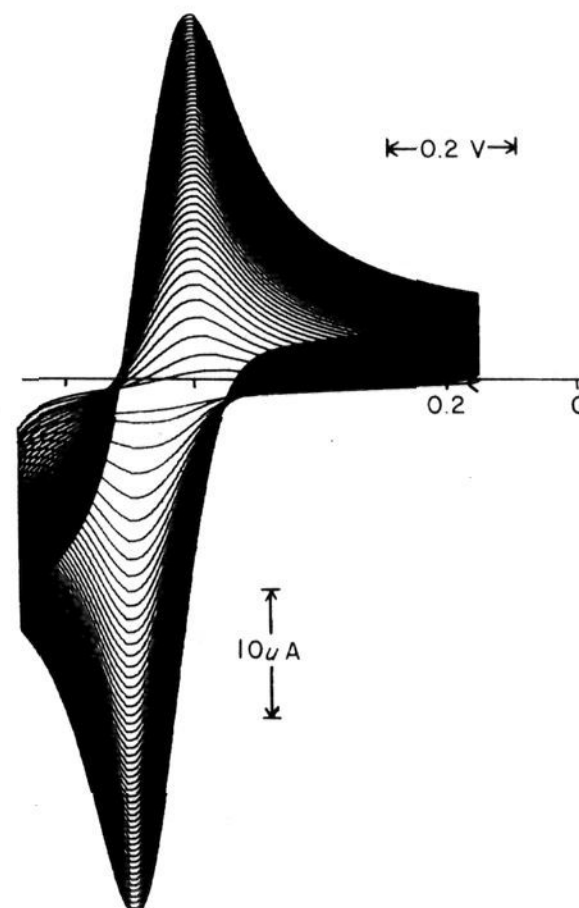**Figure 1.** Voltammograms for a glassy carbon electrode coated with a film containing 1.9×10^{-7} mol cm^{-2} of sulfonic acid groups (2.0 μm thick) cycled for ~10 min in 1 mM $Ru(bpy)_3^{2+}$. Supporting electrolye: 0.1 M H_2SO_4. Scan rate: 0.1 V s^{-1}.

a film about 2 μm thick and initially in the proton form is immersed in 10^{-3} M $Ru(bpy)_3^{2+}$ in 0.1 M H_2SO_4, the cyclic voltammograms grow with immersion time as the electroactive species is incorporated into the film. The rate of permeation of $Ru(bpy)_3^{2+}$ into the film has been estimated by potential-step experiments.[3]

After about 20 min of cycling, a steady-state voltammogram was obtained. When the electrode was removed, rinsed, and cycled in pure supporting electrolyte, the peak currents were about 30% lower than the previous steady-state currents. This has also been observed for an electrode coated with PVP$^+$, which electrostatically binds $Fe(CN)_6^{3-}$;[5c] this was attributed to the mediated reduction of solution complex by reduced species in the film. The decrease in current also can be caused by an initial rapid loss of complex from the film. However, unless the complex in the film was quantitatively oxidized to the 3+ form, no further loss was observed. If the film was stored in supporting electrolyte, about 70% of the theoretical maximum quantity of $Ru(bpy)_3^{2+}$ (based on 2:1 stoichiometry between the complex and the calculated number of sulfonate groups) was retained by the film for at least several days. This lifetime for the complex in this film is much longer than lifetimes reported for either electrostatically or coordinately bound complexes incorporated in other polymer films.[5,16]

$Ru(bpy)_3^{3+}$ is not held as strongly in the polymer as $Ru(bpy)_3^{2+}$. When the potential of NAF/$Ru(bpy)_3^{2+}$ was stepped to about 0.86 V vs. MSE, where $Ru(bpy)_3^{2+}$ is oxidized to the 3+ form, for 0.5 h and then stepped back to 0.15 V (3+ to 2+) for 0.5 h, the voltammogram demonstrated that a large portion of the complex was lost from the film. A possible explanation for the decreased binding of the more highly charged form is that solvation of the hydrophobic parts of the complex by the organic chain material is a major factor in determining the affinity of Nafion for the complex ion. Evidence for such interaction has been observed for 1200 equiv wt Nafion.[17,18] Because of the higher dielectric constant of the chain material and higher charge density in PVP$^+$, this type of interaction is presumably much less significant in this polymer and more highly charged species are held more strongly.[5a] The peak potentials for $Ru(bpy)_3^{2+}$ in the

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Table I. Effect of Quantity of $Ru(bpy)_3^{2+}$ Incorporated on Magnitude of $D_{app}{}^a$

	D_{app}, cm² s⁻¹ ^{c}			D'_{app}, cm² s⁻¹ ^{d}		
% loading^b	0-10 ms^e	0-50 ms^e	0-7 s^e	0-10 ms^e	0-50 ms^e	0-7 s^e
70	4.0×10^{-10}	4.0×10^{-10}	4.0×10^{-10}	4.0×10^{-10}	3.2×10^{-10}	4.0×10^{-10}
51	5.8×10^{-10}			6.8×10^{-10}		
28	3.2×10^{-10}		2.6×10^{-10}	4.0×10^{-10}		4.0×10^{-10}
4		4.8×10^{-10}				
2		2.8×10^{-10}			4.0×10^{-10}	
0.7		7.8×10^{-10}				

^{a} 2-μm-thick film containing 1.9×10^{-7} mol cm⁻² sulfonate groups. ^{b} Percent of maximum stoichiometric amount. ^{c} Apparent diffusion coefficient for $Ru(bpy)_3^{2+}$. ^{d} Apparent diffusion coefficient for $Ru(bpy)_3^{3+}$. ^{e} Time interval over which data were taken.
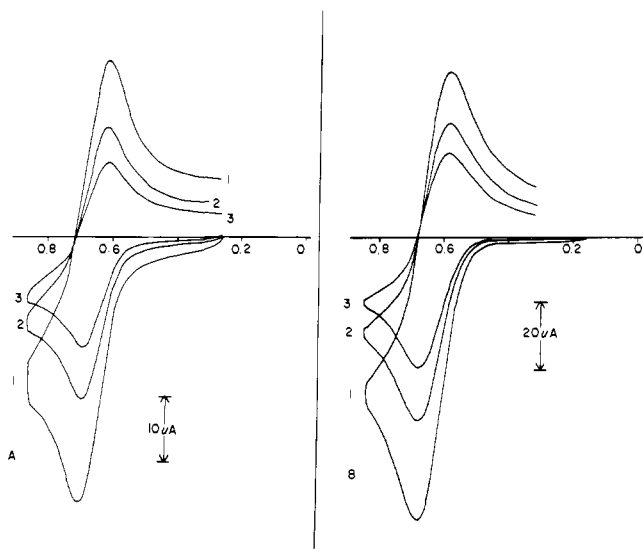

Figure 2. Cyclic voltammograms at 500 (1), 200 (2), and 100 (3) mV s⁻¹. (A) 1 mM $Ru(bpy)_3^{2+}$ in 0.1 M *p*-toluenesulfonic acid. Electrode area: 0.065 cm². (B) Electrode coated with an ~2-μm film containing 6.0×10^{-8} mol cm⁻² $Ru(bpy)_3^{2+}$. Supporting electrolyte: 0.1 M *p*-toluenesulfonic acid.

polymer are very close to those in an aqueous solution (Figure 2). This has been observed with other polymer electrodes[16] and suggests the absence of strong ion-pair formation[12,13] and an aqueous-like environment in the polymer. Note also that incorporation of the complex from a 10^{-3} M solution causes a greater than twofold increase in peak currents over those found for an uncoated electrode in the same solution.

Effect of Method of Electrode Preparation. Two methods were used to incorporate $Ru(bpy)_3^{2+}$ into the polymer: (a) incorporation after film formation as described above (two-step method) and (b) addition before film preparation (one-step method). In the one-step method, $Ru(bpy)_3Cl_2$ was mixed with the ethanol solution of the polymer prior to depositing the film. For PVP, which coordinates with metal complexes, films prepared by the one-step method had different electrochemical characteristics than equivalent films prepared by the two-step method;[5b] cyclic voltammograms showed apparent diffusion coefficients that were smaller for films prepared by the two-step method. This was attributed to an inhomogeneous distribution of the complex in the polymer film prepared by the two-step method (i.e., a higher local concentration at the film–solution interface than at the substrate–film interface). For Nafion, cyclic voltammograms of films prepared by both methods were essentially the same (Figure 3). Both electrodes had films containing about 3×10^{-8} mol cm⁻² $Ru(bpy)_3^{2+}$ (~30% loaded) and both films were 2 μm thick. Moreover, the apparent diffusion coefficients for the oxidation of $Ru(bpy)_3^{2+}$, D_{app}, were the same for both methods of preparation (see Table I). Note that the one-step procedure has the advantage of permitting an estimation of the fraction of incorporated material that is electroactive, provided that the equivalent weight of the polymer, the amount of the polymer, the amount of complex in the coating solution, and the amount of the solution applied to
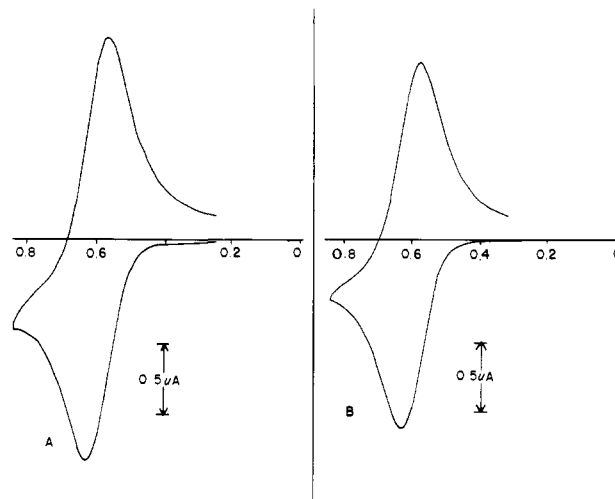

Figure 3. Cyclic voltammograms at 2 mV s⁻¹ in 0.1 M H_2SO_4 for two electrodes coated with ~2-μm-thick films. (A) One-step coating procedure; 2.8×10^{-8} mol cm⁻² $Ru(bpy)_3^{2+}$. (B) Two-step coating procedure; 2.7×10^{-8} mol cm⁻² $Ru(bpy)_3^{2+}$.

Table II. Effect of Quantity of $Ru(bpy)_3^{2+}$ Present in the Film on Percent of This Quantity That Is Electroactive^a

$Ru(bpy)_3^{2+}$ added, %^{b}	$Ru(bpy)_3^{2+}$ electroactive, %^{b}	fraction electroactive
5	1	0.20
11	4	0.36
50	31	0.62

^{a} ~2-μm films containing 1.9×10^{-7} mol cm⁻² sulfonate groups. ^{b} The quantities of $Ru(bpy)_3^{2+}$ are expressed as percent of the total stoichiometric amount.

the electrode surface are known. Thus the one-step procedure allows for study of how the fraction of the material that is electroactive varies with parameters such as film thickness and fractional loading. The results of such a study are shown in Table II. These data show that the fraction of material that is electroactive increases as the percent loading is increased. Identical results were obtained for PVP films[5b] and were explained by the electron-hopping mechanism and an increased film conductance as the total quantity of complex in the film increases.

Charge-Transport Rate in Polymer Film. A number of theoretical and experimental studies of charge and mass transport in polymer-coated electrodes have appeared.[1-3,5,7-9,19,20] In the

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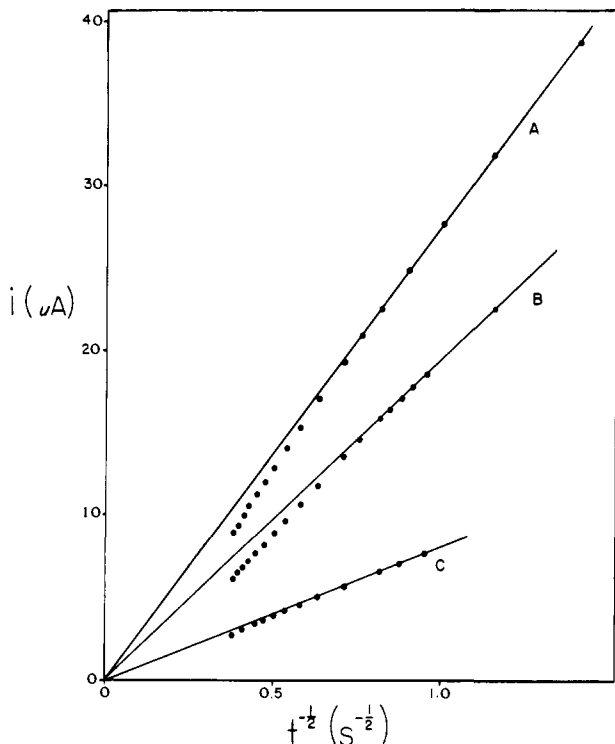
Figure 4. Cottrell plots for three electrodes coated with ~ 2-μm films. (A) 6.7×10^{-8} mol cm^{-2} Ru(bpy)$_3^{2+}$. (B) 4.8×10^{-8} mol cm^{-2} Ru(bpy)$_3^{2+}$. (C) 2.7×10^{-8} mol cm^{-2} Ru(bpy)$_3^{2+}$. Supporting electrolyte 0.1 M H$_2$SO$_4$.

absence of chemical kinetic complications (slow electron transfer at the solid–film interface or chemical reactions coupled to the redox process), the rate of the electrode reaction (and hence the current) is governed by charge transport through the film. The charge transport consists of mass transport (diffusion) of the electroactive species, electron hopping, and migration of counterions. The overall rate can be described in terms of an apparent diffusion coefficient, since the electron-hopping process has been shown to be equivalent to a diffusion process.[21-25]

Potential-Step Experiments. Diffusion coefficients can be obtained electrochemically by performing a potential step to a potential at which the heterogeneous electron-transfer rate is rapid and studying the current–time (i–t) behavior. Under these conditions, Cottrell plots, i. vs. $t^{-1/2}$, are linear and intersect the origin; D_{app} is determined from the slope of these plots. Typical data for electrodes with films containing three different amounts of Ru(bpy)$_3^{2+}$ are shown for relatively long times (0.75–7 s) in Figure 4. These plots show the effect of relative thickness of the diffusion layer to the electrode thickness. At longer times (>2 s), the diffusion-layer thickness approaches the film thickness and a transition to thin-layer behavior occurs. The deviations of the data points from the extrapolation of the i vs. $t^{-1/2}$ lines in Figure 4 show this transition. Similar effects have been reported previously.[5b,19]

Regardless of whether the bulk diffusion process is described in terms of electrons hopping through the polymer film from reduced to oxidized sites or in terms of true diffusion, migration of ions must occur if electroneutrality in the film is to be maintained. These films incorporate excess electrolyte from the con-

Table III. Effect of Supporting Electrolyte on Magnitude of the Apparent Diffusion Coefficient[a]

supporting electrolyte[b]	D_{app}, cm^2 s^{-1} [c]	D'_{app}, cm^2 s^{-1}
H$_2$SO$_4$	5.8×10^{-10}	6.8×10^{-10}
p-toluenesulfonic acid	5.8×10^{-10}	5.8×10^{-10}
K$_2$SO$_4$	5.8×10^{-10}	5.8×10^{-10}

[a] 2-μm-thick film containing 5.2×10^{-8} mol Ru(bpy)$_3^{2+}$. [b] 0.1 M in each case. [c] Apparent diffusion coefficient for Ru(bpy)$_3^{2+}$. [d] Apparent diffusion coefficient for Ru(bpy)$_3^{3+}$.

tacting solution phase, so that during oxidation of the complex, electroneutrality can be maintained by incorporating another anion from solution and/or by expelling a cation from the film. The rate of ionic migration through a polymer is related to the size of the diffusing ion. Therefore, if the rate is controlled by ionic migration, the D_{app} values obtained in the presence of large ions should be smaller than those obtained in the presence of smaller ions. Table III contains values of D_{app} obtained from i-$t^{-1/2}$ plots for electrodes with films about 2 μm thick containing about the same quantity of Ru(bpy)$_3^{2+}$. Note that D_{app} (for the 2+ species) and D'_{app} (for the 3+ species) are the same for these electrodes, in contrast with the results previously reported.[1b] The films used in this investigation were at most about one-tenth as thick as the films used in the previous study. The diffusion coefficients in the presence of the larger ions (H$^+$ and p-toluenesulfonate) are the same as those in the presence of smaller ions (K$^+$ and SO$_4^{2-}$). Therefore, at least over the range of ion sizes studied here, motion of the counterions or co-ions does not affect the rate of the bulk process.

A second study deals with the effect of the quantity of electroactive material present (as measured by the fraction of available sulfonic acid sites converted to the Ru(bpy)$_3^{2+}$ form, termed percent loading), on D_{app}. The electron-hopping model for charge transfer[3,21-23] predicts that D_{app} would vary with the concentration of homogeneously distributed electroactive sites in the film. Hence, a study of the dependence of D_{app} on concentration of Ru(bpy)$_3^{2+}$ in the film should test for the contribution of the electron-hopping model. In a recent similar study of Fe(CN)$_6^{3-}$ coordinately attached to PVP films,[5b] D_{app} values were found to be relatively insensitive to changes in concentration of the complex until this concentration dropped below about 1% of the total available coordinating sites. Below this level, an abrupt drop in D_{app} was observed. Values of D_{app} and D'_{app} for electrodes coated with films about 2 μm thick and containing various levels of incorporated complex are given in Table I. The fact that the D_{app} values are independent of the time window of the measurement suggests that they do not reflect the rate of some other time-dependent process that might occur in the film. While the values of D_{app} range from 8×10^{-10} to 3×10^{-10} cm^2 s^{-1}, no dependence of D_{app} on concentration is apparent. However, experiments comparing the rate of permeation of Ru(bpy)$_3^{2+}$ into the film, which is a measure of the actual rate of diffusion, with D_{app}[3] as well as comparison of D_{app} for different ions in Nafion films,[10] suggest an appreciable contribution of electron transfer for the Ru(bpy)$_3^{2+/3+}$ system. It is difficult to reconcile these results, which suggests that the simple Dahms–Ruff[22,23] model, which assumes a homogeneous polymer film, is not appropriate.

Cyclic Voltammetric Experiments. A second aspect of the electrochemical behavior of polymer films involves the shape and location of the cyclic voltammetric waves that reflect the kinetics of various processes contributing to the film redox reactions as well as the thermodynamic properties (formal potentials and interactions) of the film. In the simplest cases, where the heterogeneous electron-transfer kinetics are rapid and interactions between oxidized and reduced forms are absent or small, the i–v curves appear as a Nernstian thin-layer or semiinfinite linear diffusion-controlled waves. In such cases, ΔE_p (the separation between the anodic and cathodic peak potentials) would be zero at slow sweep rates (thin-layer behavior) and increase to $\sim 59/n$ mV, typical of a Nernstian solution process, at higher sweep rates. However, for many polymer films, the wave shapes are more complicated and must be interpreted in terms of slow heteroge-

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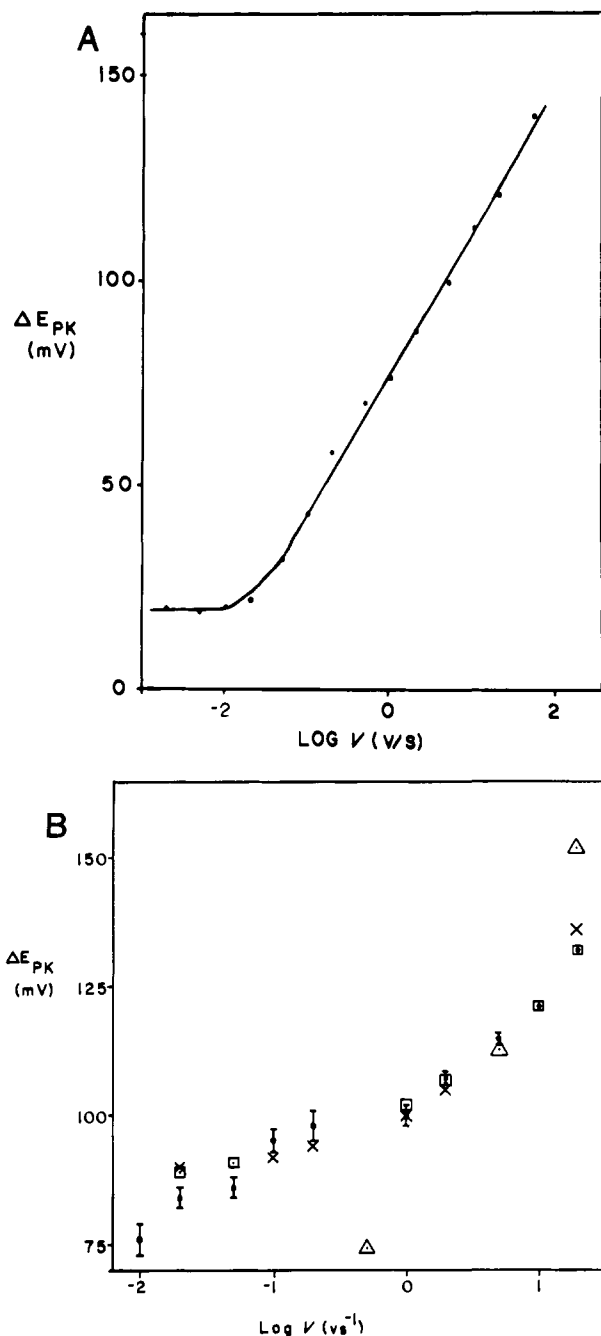
Polymer Films on Electrodes

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Table IV. Apparent Heterogeneous Rate Constant (k°_{app}) for $Ru(bpy)_3^{3+/2+}$ in the Nafion Film

v, V s^{-1}	ΔE_p, mV	Ψ^a	$k^\circ_{app} \times 10^{4\ b}$
0.2	98	0.62	0.61
0.5	105	0.50	0.79
1	100	0.58	1.3
2	107	0.47	1.5
5	114	0.40	2.0
10	121	0.35	2.5
20	132	0.28	2.8
50	155	0.22	3.5

^{a} See ref 26. ^{b} cm sec^{-1}.

Scheme I
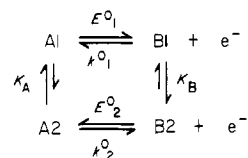
conditions prevail at all scan rates employed. Since uncompensated resistance in the film can cause increases in ΔE_p with increasing v (because i_{pa} increases with v), positive feedback techniques, as described in the Experimental Section, were employed to minimize such effects. Further evidence that the shift of E_{pa} with v is not dominated by resistance effects is the large deviation from linearity of a plot of E_{pa} vs. i_{pa}.

Heterogeneous electron-transfer kinetics can give rise to such a variation of ΔE_p with v. To test this possibility we calculated an apparent heterogeneous rate constant (k_{app}) using Nicholson's method[26] on the data in Figure 5B (Table IV). Note that k$^\circ_{app}$ calculated from the ΔE_p values is not constant and increases with v. This trend was observed for all cyclic voltammetric data obtained for the polymer-bound complex. Moreover, the magnitude of k$^\circ_{app}$ found is much lower than the value of 0.07 cm/s obtained when this method is used on data obtained for this complex in aqueous solution.[6] While the smaller heterogeneous rate constant could result from the effect of the polymer matrix on the rate of the electron-transfer reaction, the lack of constancy of k$^\circ_{app}$, as shown clearly by the results of a digital simulation[7] using the experimental film thickness and diffusion coefficient and a k^0 of 1×10^{-4} cm/s (triangles in Figure 5B), makes us reject slow heterogeneous electron transfer as the prime source for peak separation, especially at the lower scan rates. A similar problem was encountered in this laboratory for treating the cyclic voltammetry of poly(vinylferrocene) (PVF) modified electrodes, and digital simulation techniques were used to obtain a suitable model.[7] For the PVF modified electrode, good agreement between experimental and simulated behavior was obtained by assuming that there were interactions between electroactive sites, that there were different classes of electroactive sites, and that interconversion between these classes of sites was possible. This latter process was accounted for by assuming a square redox scheme (of the type shown here for an oxidation, Scheme I) where A1 and B1 are the reduced and oxidized forms, respectively, of the first type of electroactive species and A2 and B2 are the reduced and oxidized forms, respectively, of the second class. The K's are equilibrium constants and the k^0's are heterogeneous rate constants. The E° values are related by the equation[7]

$$E^\circ_2 = E^\circ_1 - 0.059 \log (K_A K_B)$$

The digital simulation technique was applied to the Nafion, $Ru(bpy)_3^{2+/3+}$ system with a modified verision of the program described earlier.[7] The known parameters are the thickness of the film, the number of coulombs required to oxidize or reduce completely the Ru species present in the film, and the diffusion coefficients. The adjustable parameters are the k° values, the

Figure 5. ΔE_p vs. log v for (A) $\sim$0.1-μm film containing 2.2×10^{-9} mol cm^{-2} Ru(bpy)$_3^{2+}$. Supporting electrolyte 0.1 M H$_2$SO$_4$. (B) $\sim$2.0-μm film containing 2.2×10^{-8} mol cm^{-2} Ru(bpy)$_3^{2+}$. Supporting electrolyte 0.1 M H$_2$SO$_4$. (●) Experimental data. (△) Simulated data assuming only slow kinetics ($k^\circ = 4 \times 10^{-4}$ cm s^{-1}. (X) Simulated data assuming interactions between redox sites (see text). (□) Simulated data assuming both interactions and the square scheme (see text).

neous electron transfer, kinetics of film reorganization, and interactions within the film (see ref 7 and references therein). Such complicating effects are apparent with the Nafion films.

Consider the plot of ΔE_p vs. log v (Figure 5A) for an electrode with an $\sim$0.1-μm film containing 2.2×10^{-9} mol cm^{-2} Ru(bpy)$_3^{2+}$. At $v < 30$ mV/s, ΔE_p was small and independent of v, suggesting thin-film behavior for these scan rates. This is confirmed by the finding that the anodic peak current (i_{pa}) varied directly with v (Figure 6A). An increase in ΔE_p occurred at $v > \sim$0.05 V/s. This probably reflects the occurrence of kinetic effects for both bulk and surface processes. For thicker ($\sim$2 μm) films containing 2.2×10^{-8} mol cm^{-2} of Ru(bpy)$_3^{2+}$, no region of monolayer behavior was observed (Figure 5B). For such films a plot of i_{pa} vs. $v^{1/2}$ is linear (Figure 6B), indicating that semiinfinite diffusion

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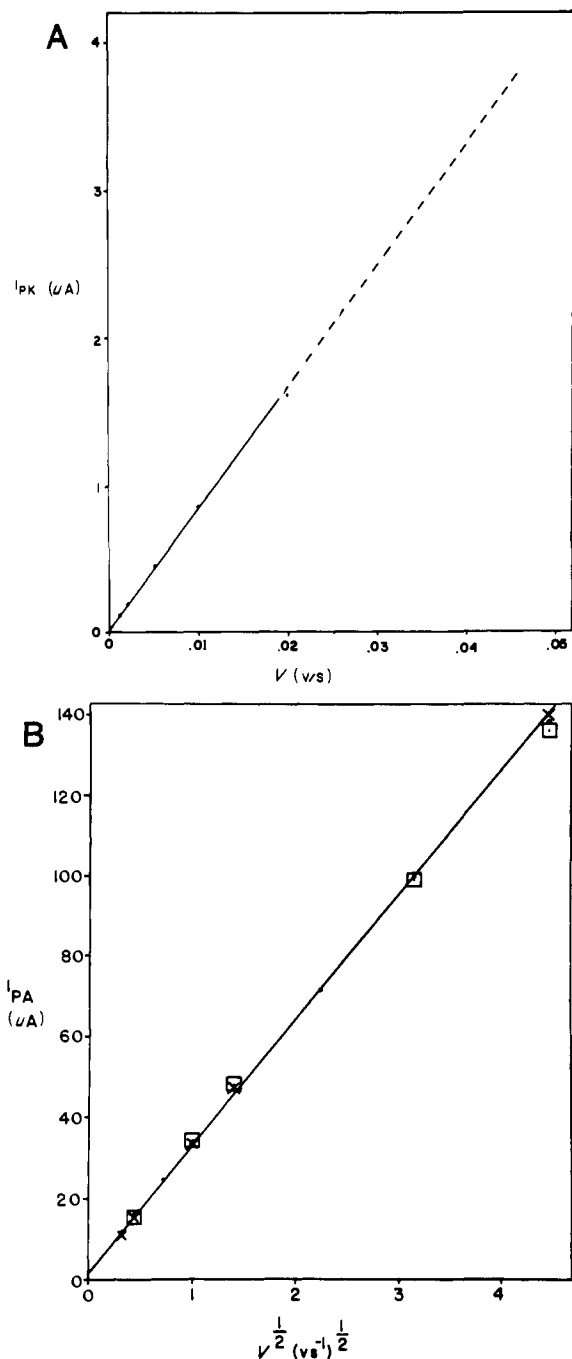(27) Laviron, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *52*, 395.

Figure 7. Cyclic voltammogram at 10 mV s^{-1} for electrode described in Figure 5A.

Figure 6. i_p vs. v for (A) electrode described in Figure 5A; (B) electrode described in Figure 5B. (Symbols explained in Figure 5.)

values of the interaction parameters, the $E°$ values, and one equilibrium constant. The existence of repulsive interactions between redox sites in the film is indicated by cyclic voltammograms for very thin ($\sim$0.07 μm) films, which show peak-width-at-half-height values at low scan rates of about 150 mV (Figure 7). This is significantly larger than the ΔE_p for a thin-layer Nernstian system of 90.6/n mV,[27] and broadening is known to result from repulsive interactions.[7,21] The effect of repulsive interactions on the simulated cyclic voltammogram in a plot of ΔE_p vs. log v for l = 2.0 μm, D_{app} = 4 × 10^{-10} cm^2 s^{-1}, and 178 μC to oxidize all of the Ru(bpy)$_3{}^{2+}$ present in the film is shown in Figure 8. Note that for these conditions and for rapid heterogeneous electron transfer ($k°$ = 0.1 cm s^{-1}) $\Delta E_{1/2}$ is independent of v. For a smaller $k°$ (5 × 10^{-4} cm s^{-1}), $\Delta E_{1/2}$ increases with increasing scan rate.

Attempts to match the experimental data for the electrode of Figure 5B by adjusting AOX, ARED, and $k°$ were undertaken. As shown in Figures 5B and 6B, good agreement between ex-
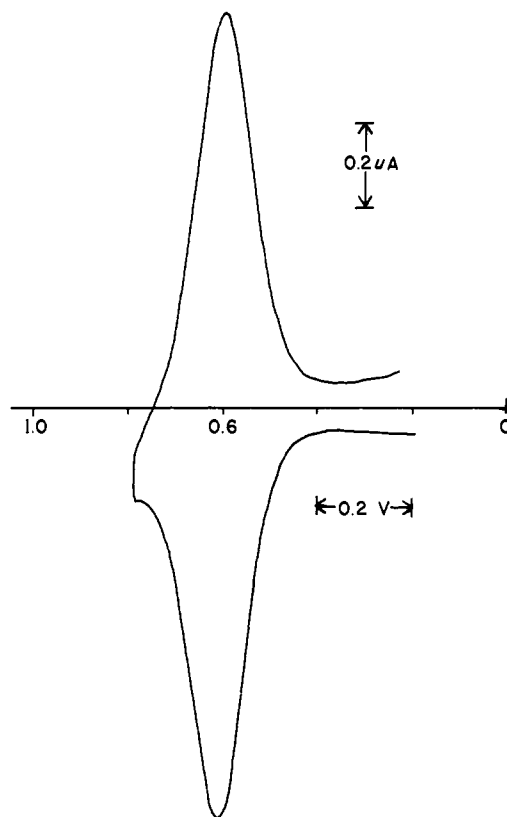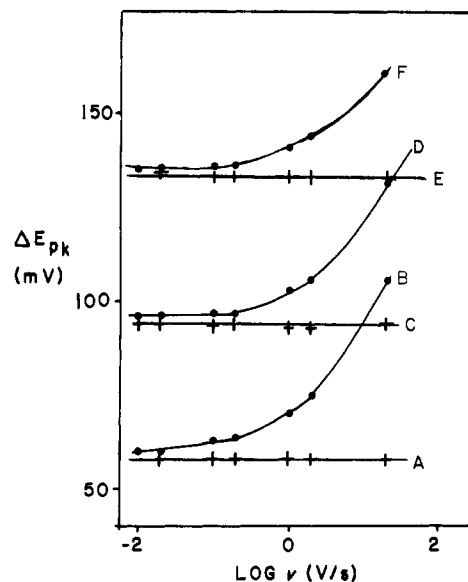

Figure 8. Simulated plots of ΔE_p vs. log v for the electrode described in Figure 5B: (A) $k°$ = 0.1 cm s^{-1}, AOX = ARED = 0; (B) $k°$ = 5.0 × 10^{-4} cm s^{-1}, AOX = ARED = 0; (C) $k°$ = 0.1 cm s^{-1}, AOX = -2.0, ARED = 0 or ARED = -2.0, AOX = 0; (D) $k°$ = 5.0 × 10^{-4} cm s^{-1}, AOX = -2.0, ARED = 0 or ARED = -2.0, AOX = 0; (E) $k°$ = 0.1 cm s^{-1}, AOX = ARED = -2.0; (F) $k°$ = 5.0 × 10^{-4} cm s^{-1}, AOX = ARED = -2.0. AOX and ARED are interaction parameters.[7]

perimental and simulated ΔE_p and i_p data could be obtained over 3 orders of magnitude in v with $k°$ = 4 × 10^{-4} cm s^{-1} and AOX = ARED = -1. A comparison of the experimental and simulated voltammograms with these values of k^0, AOX, and ARED is shown in Figure 9.

While a good match between experimental and simulated data was obtained for the thick-film (2.0 μm) electrodes by assuming only interactions between sites, other simulation conditions could
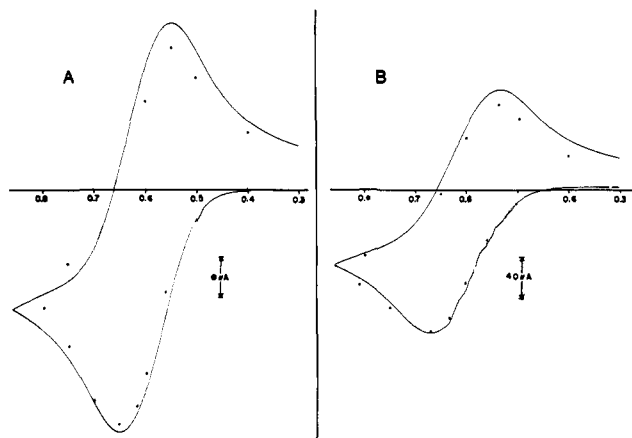
Polymer Films on Electrodes

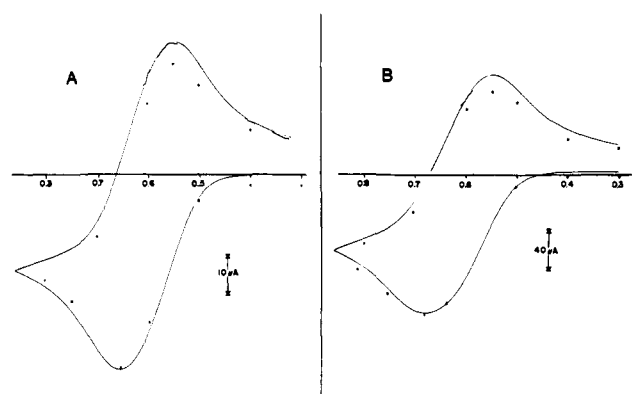*J. Am. Chem. Soc., Vol. 104, No. 18, 1982* 4823

Figure 9. Comparison of simulated and experimental voltammograms at (A) 2 V s^{-1} and (B) 20 V s^{-1} for electrode described in Figure 5B, assuming $k^0 = 4 \times 10^{-4}$ cm s^{-1}, AOX = ARED = -1.0. (—) Simulation. (●) Experimental.

Figure 10. Comparison of simulated and experimental voltammograms at (A) 2 V s^{-1} and (B) 20 V s^{-1} for electrode described in Figure 5B, assuming $k^0 = 1.5 \times 10^{-3}$ cm s^{-1}, AOX = -1.6, ARED = -2.6, and square scheme (see text). (—) Simulation. (●) Experimental.

also produce reasonable agreement, with a larger k° value. Because oxidation of the complex from the 2+ to the 3+ form clearly changes both the ionic content and water content of the film, the square scheme might also be appropriate. No good match between experimental and simulated data could be obtained by using only the square scheme; over 150 simulations with different rate and equilibrium constants were attempted. If, however, the square scheme is used in conjuncation with negative interaction parameters, a good fit is obtained. This is shown in Figures 5B and 6B, where the data shown as squares assume a square scheme in which $E^\circ_1 = 0.62$ V, $E^\circ_2 = 0.57$ V ($K_A K_B = 2.65$), the forward rate constants for the chemical steps are 40 s^{-1}, $k^\circ_1 = k^\circ_2 = 1.5 \times 10^{-3}$ cm s^{-1}, AOX = -1.6, and ARED = -2.6. As shown in Figure 10, a good match between experimental and simulated voltammograms is also obtained under these conditions.

Conclusions

The results allow for some generalizations to be made about chemically modified electrodes based on polymers like Nafion, which take up electroactive counterions. First, as has also been observed for PVP$^+$ polymer layers,[5b] not all of the material in the film is electroactive, and the fraction of material that is electroactive increases with loading. Second, as is frequently the case of polymer-modified electrodes, coincidence of the aqueous and polymer E° values is observed here. This probably indicates that ion-pair formation[10] in the film is small. Third, the concentration of the electroactive material in the film can be much greater than the solution concentration used to load the film; hence, larger currents may be obtained at the coated electrode than at a bare electrode under similar conditions. The relative currents at the Nafion-coated electrode compared to those in solution depend on

the relative magnitudes of the diffusion coefficients. This indicates that electrodes of this type might be useful in electroanalytical determinations of low concentrations.[5a] Fourth, film-thickness measurement is a major problem in obtaining quantitative data from polymer electrodes. Although the profilometer is useful in obtaining film thickness, problems remain because of changes attributable to solvent swelling and takeup of ions. Moreover, depending upon the method of preparation, the film thickness may not be uniform.[28] The uncertainties in thickness generate even greater uncertainties in diffusion and extraction coefficients measured electrochemically. Fifth, electrochemical measurements on these films, as well as with other polymer electrodes, show the transition from thin layer to bulk behavior depending upon the time scale of the experiment. The value of D_{app} for Ru(bpy)$_3^{2+}$ was shown to be independent of loading. However, there is evidence that the electron-transfer contribution to charge transport in the film is significant.[3,10] This suggests that the homogeneous model of the film is not appropriate. Indeed, the currently accepted model for Nafion[11,14,15] is based on the existence of two phases within the material, a bulk polymer phase (mainly fluorocarbon) and an ionic cluster phase. The ionic cluster phase is randomly distributed throughout the bulk polymer phase and forms because of the repulsive interactions between the charged groups and the low dielectric constant chain material.[29] The cluster contains the covalently attached ions, their counterions, water, and significant amounts of the polymer chain material.[11] According to the most recent model,[15a] the clusters in 1200 equiv wt Nafion are roughly spherical ($\sim$40 Å in diameter) and are interconnected through a system of narrow channels. Conduction processes within Nafion membranes have been treated by a percolation model,[30] and such a model may be more appropriate for the processes in the films as well. Another factor of importance is the possible nonuniformity of the polymer structure as a function of distance normal to the polymer surface, with the zones near the solution and near the substrate interfaces being somewhat different than the bulk polymer.

Some results with Nafion are different from those obtained for both other ionic polymer and coordinating polymer based electrodes. First, the Nafion-based electrode has a greater lifetime; the film stays on the electrode and retains the electroactive molecule for longer times than other electrodes of this type.[5,16,18] This extended lifetime will be useful in possible applications (e.g., incorporation of electrocatalysts). Second, the mechanism of retention of the electroactive ion is apparently different in Nafion than in other electrostatically binding polymers.[5] There is much evidence that indicates that hydrophobic interactions dominate retention in Nafion polymers whereas electrostatic forces seem to be important in, for example, PVP$^+$.[5] This is probably due to the fundamental differences between the polymers, which include differences in the dielectric constant of the chain material (Nafion, very low; PVP, unprotonated, rather high) and differences in the charge density (Nafion, rather low; PVP$^+$, rather high). Third, while differences in electrochemical properties between films prepared by the one-step coating procedure and films prepared by the two-step procedure are observed for a coordinating polymer,[5b] no differences are observed for Nafion. This can probably be attributed to the presence of only relatively weak electrostatic interactions in the Nafion polymer and to the ionic cluster morphology, which allows for easier diffusion.

The digital simulation of cyclic voltammograms for polymer electrodes[7] has proved useful in probing the nature of the processes occurring in the films. However, the variety of possible processes and the number of adjustable parameters do not allow unambiguous determination of rate constants and thermodynamic parameters. The results suggest, however, that interactions exist between active sites that contribute to the observed ΔE_p at slow

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scan rates, and that the rate constant for heterogeneous electron transfer for $Ru(bpy)_3^{2+}$ incorporated in the polymer is somewhat smaller than that at a bare electrode.

Electrochemical Control of the Luminescent Lifetime of Ru(bpy)₃²⁺* Incorporated in Nafion Films on Graphite Electrodes

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Abstract: The formal potential of the $Ru(bpy)_3^{3+/2+}$ redox couple incorporated in a Nafion film was measured spectroelectrochemically. An electrochemical (Stern–Volmer) method is presented that can be used to determine the rate of quenching of the luminescence of one half of a redox couple by the other half. The method is also shown to give qualitative information about cases in which the quenching is by an independent redox couple. The kinetics of the quenching process yield information on the Nafion film structure. The magnitude of the rate constant for quenching of the $Ru(bpy)_3^{2+}$ excited state by $Ru(bpy)_3^{3+}$ is used to elucidate the mechanism of production of this excited state in the electrochemiluminescent reaction of $Ru(bpy)_3^{3+}$ with oxalate.

The increasing popularity of polyelectrolyte coatings as matrices for binding redox complexes to the surfaces of electrodes[1–8] has enhanced the need for studies of the effects of the polyelectrolyte environment on the thermodynamic properties and kinetic behavior of the incorporated redox reagents. Rubinstein and Bard[5,6] recently described the use of polyanion films of Nafion[9] to bind $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) to the surface of pyrolytic graphite, glassy carbon, and Pt electrodes to study the chemiluminescence of $Ru(bpy)_3^{2+*}$ that was electrogenerated by oxidizing $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ in the presence of oxalate ions. The time and potential dependence of the luminescence could be accounted for by either of two alternative mechanisms that were difficult to choose between on the basis of the data obtained.[6] We have also been investigating the properties of cationic redox complexes electrostatically bound in Nafion films.[4] By measuring the lifetime of photogenerated $Ru(bpy)_3^{2+*}$ ions in Nafion coatings on graphite electrodes as a function of the electrode potential it has been possible to measure the rate at which $Ru(bpy)_3^{3+}$ quenches $Ru(bpy)_3^{2+*}$ within the polyelectrolyte film. The results point to the likely mechanisms by which $Ru(bpy)_3^{2+*}$ was generated in the experiments of Rubinstein and Bard[6] as well as provide information on the internal structure of Nafion films cast on graphite electrodes.

Experimental Section

Materials. A 5.2 wt % solution of relatively low molecular weight Nafion (in the sulfonic acid form) in a 5/1 mixture of 2-propanol/water was available from a sample supplied by Du Pont a number of years ago. Commercially available $Ru(bpy)_3Cl_2$ and $Ru(NH_3)_6Cl_3$ were recrystallized from water prior to use. Basal plane pyrolytic graphite (BPG) electrodes (Union Carbide Co., Chicago, IL) were cut and mounted as

previously described.[10] The antimony-doped tin oxide optically transparent electrodes (OTE) were available in these laboratories. The electrochemical cell used in the emission experiments with the BPG electrodes was a standard 1-cm emission cell joined at the top to a reference compartment. The cell used in the spectroelectrochemical and lifetime measurements, shown in Figure 1, was fabricated from a block of Kel-F. A hole was cut through the center of the block, and a glass microscope slide was glued to one side of the block and the OTE to the other to form a watertight compartment. The glue was type S-804 epoxy (Saunders Corp., Los Angeles, CA). The reference and auxiliary electrodes were introduced into the cell through two holes drilled through the top. The connection to the OTE was made by clamping an electrical connector directly to the electrode. The reference electrode was Ag/AgCl(KCl, sat), with respect to which all potentials are quoted. The supporting electrolyte was 0.1 M CF_3COOH–0.1 M CF_3COONa.

Procedures and Instrumentation. Nafion films on graphite electrodes were prepared by carefully syringing microliter amounts of the 5.2 wt % stock solution onto a freshly cleaved electrode, making sure that the polymer solution completely covered the surface. The solvent was allowed to evaporate at room temperature until the films were dry (approximately 5 min). Incorporation of $Ru(bpy)_3^{2+}$ into the films was accomplished by exposing the coated electrodes to 1 mM aqueous solutions of $Ru(bpy)_3Cl_2$ for times determined by the extent of incorporation desired. The electrodes were then washed and soaked for at least 30 min in pure water. The soaking step helped to provide a more uniform distribution of the complex within the coating and enhanced the reproducibility of the results. The quantity of electroactive complex present in the coatings was determined either by integration of cyclic voltammograms recorded at low scan rates (2 mV s⁻¹) or by absorbance measurements with the optically transparent electrode. Nafion films on OTE's were prepared prior to cell assembly by evaporating aliquots of the solution applied to the electrode surface. The resulting film does not have a uniform thickness. The outer quarter of the film is about 3–5 times thicker than its central portion.[11,12] Much of the $Ru(bpy)_3^{2+}$ that enters this thicker portion of the film is not in electronic contact with the underlying electrode and is thus electroinactive. This becomes clearly evident if the electrode potential is adjusted to 1.3 V, where all of the electroactive complexes in the film are oxidized to $Ru(bpy)_3^{3+}$, which shows no luminescence under irradiation. Illumination of such oxidized films with

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