Electron Hopping of Tris (2,2′-bipyridyl) Transition Metal Complexes M(bpy)$_3^{2/3}$ in Nafion

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Voltammetric currents of transition metal complexes in films on electrodes increase with electron self exchange (hopping) rate k_{11}. In films, diffusion coefficients $D_f \propto k_{11}c_f^*$, where k_{11} sets frequency of electron hopping attempts and c_f^* film concentration sets distance between probes. Cyclic voltammetry of Nafion films on electrodes for six probes, tris(2,2′-bipyridyl) complexes, M(bpy)$_3^{z+}$ where M^{z+} is Ru^{2+}, Os^{2+}, Fe^{2+}, Cr^{3+}, Co^{3+}, and Co^{2+}, demonstrates D_f varies linearly with $k_{11}^{H_2O}$, literature k_{11} measured in water. From density of Ru(bpy)$_3^{2+}$ exchanged Nafion 1.95 g/cm^3 and nominal equivalent weight 1100, geometry establishes volume limited, z-independent c_f^* for all M(bpy)$_3^{z+}$. For concentrations of Ru(bpy)$_3^{2+}$ in HNO$_3$ where either Ru(bpy)$_3^{2+}$:HNO$_3$ ratio is fixed or Ru(bpy)$_3^{2+}$ is 1 mM and HNO$_3$ varies, c_f^* is statistically invariant. Based on aqueous titrations and dielectric constant sufficient to support ions, electron hopping is confined to hydrated domains of Nafion. From c_f^*, k_{11} in Nafion k_{11}^{Naf} is estimated as $k_{11}^{Naf} = 0.010k_{11}^{H_2O}$, consistent with higher ion concentration in Nafion. Measured D_f is 2×10^{-9} cm^2/s for Ru(bpy)$_3^{2+}$ and Os(bpy)$_3^{2+}$; 1×10^{-10} cm^2/s for Fe(bpy)$_3^{2+}$ and Cr(bpy)$_3^{3+}$; and 1.5×10^{-12} and 5×10^{-12} cm^2/s for Co(bpy)$_3^{2+}$ and Co(bpy)$_3^{3+}$. For physical diffusion $D_p \lesssim 10^{-12}$ cm^2/s. A self consistent view of M(bpy)$_3^{z+}$ self exchange in Nafion is outlined. For Os(bpy)$_3^{2/3}$, $k_{11}^{H_2O} \approx 4.5 \times 10^8$/Ms.

The perfluorosulfonate, cation exchange polymer Nafion finds wide use as a separator and sensor platform. Nafion is available as commercial membranes and as a suspension that is recast to modify electrodes. Tris (2,2′-bipyridyl) ruthenium cation Ru(bpy)$_3^{2+}$ and other M(bpy)$_3^{z+}$ complexes are used in Nafion as redox probes for sensors and fundamental interrogations of Nafion properties. The similarly sized and charged M(bpy)$_3^{z+}$ complexes extract into recast Nafion films at similar concentration. However, flux of M(bpy)$_3^{z+}$ complexes, measured as cyclic voltammetric current, varies widely. Self exchange (electron hopping) between the halves of the redox couple (M(bpy)$_3^{z/z\pm1}$) is known to increase the measured diffusion coefficient and thereby the flux;[1–4] this anticipates currents that correlate with the M(bpy)$_3^{z+}$ self exchange rate.[5–7] Electron hopping efficiency decreases with the distance between redox moieties, where concentration sets distance.

Considered here is the environment of M(bpy)$_3^{z+}$ in recast Nafion films and how the environment impacts M(bpy)$_3^{z+}$ flux in Nafion. Consideration of self exchange rates and M(bpy)$_3^{z+}$ concentration yields a self consistent view of M(bpy)$_3^{z+}$ self exchange in biphasic Nafion under voltammetric perturbation. Density of Ru(bpy)$_3^{2+}$ exchanged Nafion yields water fraction[8,9] and sets M(bpy)$_3^{z+}$ concentration and the distance between M(bpy)$_3^{z+}$ moieties.

Six M(bpy)$_3^{z+}$ complexes are evaluated for flux through recast Nafion films. From variation of cyclic voltammetric peak currents with scan rate, flux is reported proportional to $c_f^* D_f^{1/2}$ where c_f^* (moles/cm^3) is the M(bpy)$_3^{z+}$ concentration in Nafion and D_f (cm^2/s) is the measured M(bpy)$_3^{z+}$ diffusion coefficient in the film. From the data, $c_f^* D_f^{1/2}$ varied between 0.020 and 7.20 nmol cm^{-2}s$^{-1/2}$. Because all M(bpy)$_3^{z+}$ complexes have the same diameter and similar charges, c_f^* is anticipated similar for these complexes so that $c_f D_f^{1/2}$ correlates with self exchange rates. Several outcomes are reported. First, based on Nafion density and M(bpy)$_3^{z+}$ volume, c_f^* is insufficient to electroneutralize the negative charge of the sulfonates ($\sim RSO_3^-$).

Second, because c_f^* varies little with M(bpy)$_3^{z+}$, the range of observed $c_f^* D_f^{1/2}$ reflects variation in D_f with metal center M^{z+}, as predicted for diffusion augmented by self exchange. Third, from experiments for Ru(bpy)$_3^{2+}$ evaluated under various solution concentrations of probe and electrolyte, c_f^* is fixed for common voltammetric electrolyte concentrations. Finally, the impacts of the environment of M(bpy)$_3^{z+}$ in the hydrated domains of biphasic Nafion and the metal-dependent self exchange rate on flux are summarized.

Background

Nafion is a perfluorinated ion exchange polymer with a Teflon-like backbone and pendant perfluoroether side chains terminated with sulfonates. Sulfonate anions serve as cation exchange sites in the hydrated domains of Nafion. Because dielectric constants of water and fluorocarbon are disparate, Nafion forms a biphasic matrix.[10,11] Cationic metal tris-bipyridyl complexes bind strongly to sulfonates in the hydrated domains. Binding by z sulfonates is sufficiently strong that physical motion of M(bpy)$_3^{z+}$ is hindered and yet for some metals M^{z+}, cyclic voltammetric currents (flux) for M(bpy)$_3^{z+}$ in Nafion can equal or exceed flux of M(bpy)$_3^{z+}$ 1 mM in solution.[12] High M(bpy)$_3^{z+}$ concentration in hydrated domains narrows the gap between adjacent M(bpy)$_3^{z+}$ moieties sufficiently to allow efficient electron hopping (self exchange). Self exchange augments measured diffusion coefficient.

Dahms[1] and Ruff[2–4] proposed self exchange enhances transport in solutions that contain both oxidation states of a redox couple. For the couple M(bpy)$_3^{3+/2+}$ with moieties located at positions A and B, self exchange effects transposition with a self exchange rate k_{11}.

$$M(bpy)_3^{3+}|_A + M(bpy)_3^{2+}|_B \underset{}{\overset{k_{11}}{\rightleftharpoons}} M(bpy)_3^{2+}|_A + M(bpy)_3^{3+}|_B \quad [1]$$
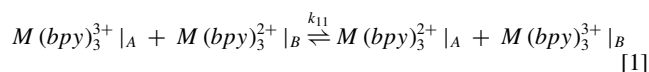
Self exchange transposition augments probe flux, so that measured diffusion coefficient D is set by physical diffusion D_p and self exchange diffusion D_{et}.

$$D = D_p + D_{et} \quad [2]$$

$$= D_p + \frac{k_{11}c^*\delta^2}{6} \quad [3]$$

c^* is probe concentration and δ is center to center contact distance for the couple. For a spherical probe, δ is the probe diameter. (A list of symbols is provided.) For $M(bpy)_3^{z+}$, $\delta = 1.36$ nm.[13] For fixed c^* and δ, the Dahms Ruff model (Equation 3) predicts D increases linearly with k_{11}. Effects on D of k_{11} depend on the relative values of D_p and D_{et}. In solution where c^* is low, $D_{et} \ll D_p$. In polymer layers and other viscous matrices where c^* is high and D_p is low, D_{et} can increase D substantially.

Several $M(bpy)_3^{z+}$ complexes are evaluated cyclic voltammetrically to investigate self exchange and flux in Nafion. Evaluations across several structurally identical and similarly charged complexes with different metal centers afford several insights into the Nafion environment. Because of strong binding to sulfonates, the fraction of $M(bpy)_3^{z+}$-bound sulfonates scales with z. Self exchange rates vary with M^{z+} where k_{11} varies over many orders of magnitude. Previously determined Nafion density[9] and equivalent weight[14] yield water content and the corresponding $M(bpy)_3^{z+}$ and sulfonate concentrations.

Several outcomes are detailed. (1) Based on Nafion density[8,9] and $M(bpy)_3^{z+}$ molecular volume, only a fraction of sulfonates are bound to $M(bpy)_3^{z+}$.[15] Electroneutrality requires electrolyte cations in the film. (2) The concentration of $M(bpy)_3^{z+}$-bound sulfonates is proportional to z of the complex initially present in the film. (3) The concentration of $Ru(bpy)_3^{z+}$ extracted into Nafion from solution is invariant for 0.05 M $\lesssim c^*_{electrolyte} \lesssim$ 0.5 M; c_f^* is better represented as constant than by the commonly used $c_f^* = \kappa c_s^*$, product of partition parameter κ and $M(bpy)_3^{z+}$ concentration in solution c_s^*. (4) Diffusion by self exchange is restricted to the hydrated domains because charge balance, extraction, and self exchange require dielectric constant sufficient to support ions. Only sulfonates in the hydrated domains exchange cations as determined by aqueous titration. (5) High $M(bpy)_3^{z+}$ concentration in the hydrated domains supports effective electron hopping. (6) Measured D_f scales linearly with $k_{11}^{H_2O}$, the self exchange rates for $M(bpy)_3^{z+}$ in water. (7) Strong electrostatic binding restricts physical diffusion and the measured D_p is correspondingly small. (8) For $M(bpy)_3^{z+}$, self exchange rates in water $k_{11}^{H_2O}$ and Nafion k_{11}^{Naf} are characterized as $k_{11}^{Naf} = 0.010 k_{11}^{H_2O}$. The ionic strength in the hydrated domains of Nafion is high as compared to k_{11} measurement conditions in water. (9) Strong linear correlation of measured $c_f^{*2} D_f$ with $k_{11}^{H_2O}$ for $M(bpy)_3^{z+}$ complexes in aqueous media further substantiates the role of electron hopping in sustaining flux (current) of transition metal complexes in Nafion. Experimental results and more details of the environment of $M(bpy)_3^{z+}$ in Nafion and its impact on flux follow.

Experimental

Experiments are undertaken for various $M(bpy)_3^{z+}$ complexes and for $Ru(bpy)_3^{2+}$ with varied concentrations of $Ru(bpy)_3^{2+}$ and nitric acid electrolyte.

Studies of $M(bpy)_3^{z+}$ for six different M^{z+}.—Cyclic voltammetric data were collected for $M(bpy)_3^{z+}$ complexes where neutral bipyridine ligands bind to M^{z+} of Ru^{2+}, Os^{2+}, Fe^{2+}, Cr^{2+}, Co^{2+}, and Co^{3+}.

Tris(2,2′-bipyridyl)dichlororuthenium (II) hexahydrate and tris(2,2′-bipyridyl)dichloroiron (II) hexahydrate were commercial available and used as received (Aldrich). Tris(2,2′-bipyridyl) osmium (II) perchlorate was prepared by modification of a literature procedure.[16,17] $Co(bpy)_3^{2+}$, $Co(bpy)_3^{3+}$, and $Cr(bpy)_3^{3+}$ were prepared in situ in 0.1 M Na_2SO_4 electrolyte by stoichiometric 1:3 mixture of the inorganic salt and 2,2′-bipyridine.

Measurements were made in 1.0 mM $M(bpy)_3^{3+}$ for all M^{z+} except 2 mM $Co(bpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$ and 1.42 mM $Co(bpy)_3^{3+}$. The electrolyte was 0.1 M HNO_3 for $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ and 0.1 M Na_2SO_4 for all other complexes.

Working electrodes were glassy carbon ($A = 0.458$ cm^2, Pine Instruments). Electrodes were cleaned by immersion in concentrated nitric acid for 2 minutes; sonication in excess 18.2 MΩ water (Millipore Model Milli-Q plus) for 2 minutes; polished by hand with successive grits (3, 1, 0.5, and 0.05 μm) of alumina oxide (Buehler); and rinsed and sonicated in 18.2 MΩ water for 2 minutes. Nafion 1100 suspension (Solution Technologies, 5 % wt/wt) was delivered to the electrode with an Eppendorf pipette so as to form a Nafion film of 3.6 μm thickness once casting solvents evaporated. Nafion density is taken as 1.95 g/cm^3.[9] Films were air dried for $\geq$30 minutes and placed in a vacuum desiccator for several hours to remove residual solvents. Films dried in the desiccator were more reproducibly formed and had lower relative standard deviations for voltammetrically determined values. Electrodes were placed in the measurement solution and allowed to equilibrate for 2 hours prior to measurement. The counter electrode, a high surface area platinum mesh (Aldrich, 6.5 cm^2 geometric area), was cleaned by immersion in concentrated nitric acid for 5 minutes followed by sonication in 18.2 MΩ water for 5 minutes. The calomel reference electrode (SCE) is 0.241 V vs NHE.

Voltammograms were recorded on a BAS 100B Electrochemical Analyzer at scan rates v of 25, 50, 100, 150, and 200 mV/s. Scan rates were recorded in a random order. Between scans, electrodes rested for 15 minutes so as to re-establish equilibrium film concentrations. For all $M(bpy)_3^{z+}$, three replicate films were each evaluated three times with v (9 replicates) except for three replicates of two films for $Co(bpy)_3^{2+}$ (6 replicates) and three films at one replicate for $Fe(bpy)_3^{2+}$ (3 replicates). For the data reported here, currents at a given scan rate for a given $M(bpy)_3^{z+}$ were averaged; i_p (v) versus $v^{1/2}$ was plotted with these averaged currents to determine the slopes and intercepts in Table I. Analysis of each individual replicate and then averaging slopes and intercepts yields statistically equivalent values.

Variation of $Ru(bpy)_3^{2+}$ and HNO_3 concentrations.—For two studies of $Ru(bpy)_3^{2+}$ in nitric acid, experimental conditions were as above except as noted. All measurements are single replicates.

In a study of fixed $c_s^*/c_{electrolyte}^*$, the concentration ratio of solution $M(bpy)_3^{z+}$ to electrolyte (HNO_3) was held constant, $c_s^*/c_{electrolyte}^* = 0.01$. A 3.0 μm thick Nafion film was equilibrated in a large volume (~70 mL) of 5 mM $Ru(bpy)^{2+}$ in 0.5 M HNO_3 for 24 hours. Voltammograms were recorded with resistive compensation at scan rates (2, 5, 10, 20, 50, 100, 200 mV/s) recorded in a random order. At least three minutes were allowed between measurements. After measurements,

Table I. Regression Statistics for Plots of i_p versus $\sqrt{v}$ for $M(bpy)_3^{n+}$ where M^{n+} is Ru^{2+}, Os^{2+}, Cr^{3+}, Fe^{2+}, Co^{2+}, and Co^{3+}. Slope and intercepts with uncertainties (standard errors) and correlation coefficient R^2 are reported for multiple replicates for each probe. Solution concentration of the probe is also shown.

Redox Probe	Slope (10^{-5} A$\sqrt{s/V}$)	Intercept (10^{-5} A)	R^2	c_s^* (mM)	z	$c_f^* D_f^{1/2}\|_{meas}$ (10^{-10} mol/cm^{2}s$^{1/2}$)	$c_f^{*2} D_f\|_{meas}$ (10^{-18} mol^2/cm^{4}s)	$k_{11}^{H_2O}$ literature values in water (/Ms)
$Ru(bpy)_3^{2+}$	85 ± 1	−1.3 ± 0.4	0.999	1.0	2	69 ± 1	48 ± 2	4.2×10^8[19]
$Os(bpy)_3^{2+}$	89 ± 2	−2.1 ± 0.7	0.998	1.0	2	72 ± 2	52 ± 3	4.2×10^8[20]
$Cr(bpy)_3^{3+}$	19 ± 1	2.2 ± 0.3	0.992	1.0	3	15.6 ± 0.8	2.4 ± 0.3	$(6 \pm 4) \times 10^7$[21]
$Fe(bpy)_3^{2+}$	19 ± 3	0.9 ± 0.8	0.960	2.0	2	16 ± 2	2.4 ± 0.7	1.3×10^7[22]
$Co(bpy)_3^{3+}$	4.3 ± 0.1	−0.04 ± 0.04	0.998	1.4	3	0.346 ± 0.009	0.120 ± 0.006	18[23,24]
$Co(bpy)_3^{2+}$	2.4 ± 0.1	−0.09 ± 0.03	0.994	2.0	2	0.197 ± 0.008	0.039 ± 0.003	18[23,24]

the electrode was removed from the electrolyte, rinsed, and patted dry. The electrode was then placed in a 0.02 mM $Ru(bpy)_3^{2+}$ in 0.02 M HNO_3 and equilibrated for 24 h. The scan rate study was repeated, the electrode rinsed and blotted, and placed in 1 mM $Ru(bpy)_3^{2+}$ in 0.1 M HNO_3 to equilibrate for 24 h. After the 1 mM $Ru(bpy)^{2+}$ measurements, the process was repeated for 0.1 mM $Ru(bpy)^{2+}$ in 0.01 M HNO_3. The different concentrations were formed by serial dilution of 4.97 mM $Ru(bpy)_3^{2+}$ in 0.5 M HNO_3 so that $c_s^*/c_{electrolyte}^*$ was fixed at 1/100. All measurements were made on a single film on a 0.458 cm² glassy carbon electrode with a CH Instruments model CHI 760B.

In a study of $Ru(bpy)_3^{2+}$ at fixed $c_s^* = 1.00$ mM, electrolyte concentration $c_{electrolyte}^*$ was varied as 10, 50, 100, 200, and 1000 mM, so that $c_s^*/c_{electrolyte}^*$ varied as 0.1, 0.02, 0.01, 0.005, and 0.001. For each $c_{electrolyte}^*$, a single fresh film of 5 μm thickness on 0.452 cm² glassy carbon electrode was equilibrated for 24 h. Cyclic voltammograms for seven scan rates between 10 and 150 mV/s were recorded in a random order, with 1 hour between scans; each scan rate was recorded three times. Measurements were made on a Pine Instruments Now potentiostat without resistive compensation.

Results

Three voltammetric studies were undertaken.

Variation of M^{z+} in $M(bpy)_3^{z+}$ for c_s^* of 1 to 2 mM and $c_{electrolyte}^* = 0.1$ M.—Representative cyclic voltammograms at 0.1 V/s are shown in Figure 1 for six $M(bpy)_3^{z+}$ complexes each recorded for 3.6 μm Nafion film cast on a glassy carbon electrode. For similar size and charge, similar c_f^* for $M(bpy)_3^{z+}$ in Nafion is expected. Despite similarity of concentration, size, and charge for the $M(bpy)^{z+}$ complexes, there are significant variations in peak currents. Peak currents reflect self exchange efficiency for the different metal centers.[5,7] From Equation 3, self exchange effects are characterized in $D_{et} = k_{11}c_f^*\delta^2/6$.

For cyclic voltammetry under conditions of rapid heterogeneous electron transfer, the Randles–Sevcik equation relates peak current on the initial, forward sweep i_p (A) to scan rate v (V/s). For film modified electrodes where the redox probe undergoes reversible electron transfer at the electrode surface ($O + ne \rightleftharpoons R$) and probe concentration and diffusion coefficient in the film are c_f^* (mol/cm³) and D_f (cm²/s), the Randles-Sevcik equation is

$$i_p(v) = 0.4463\sqrt{\frac{F^3}{RT}}n^{3/2}Ac_f^*D_f^{1/2}v^{1/2} \qquad [4]$$

where F, R, and T are Faraday constant, gas constant, and temperature (K) and A is the electrode area (cm²). At 25 °C, $0.4463\left[\frac{nF}{RT}\right]^{1/2}nF = 2.686 \times 10^5 n^{3/2}$ C/(mol V$^{1/2}$). A plot of i_p versus $v^{1/2}$ will yield slope proportional to $Ac_f^*D_f^{1/2}$ and intercept of zero. Equation 4 is appropriate for film modified electrodes provided the diffusion length ($\delta_0 \approx \sqrt{Dt}$ where t is roughly the time (s) since the onset of electrolysis) is less than the film thickness ℓ. When $\delta_0 \approx \ell$, a different analytical protocol is appropriate.[12]

From the data, Equation 4 yields $c_f^*D_f^{1/2}$ for each $M(bpy)_3^{z+}$ provided $\delta_0 < \ell$. The analysis is for reversible electron transfer. In Figure 2, plots of i_p versus $\sqrt{v}$ are linear, consistent with either reversible or irreversible heterogeneous electron transfer. (For an irreversible process, $i_p^{irrev} \approx i_p^{rev}/\sqrt{1.24\alpha}$ where α is the transfer coefficient [18]. Evaluation of an irreversible electron transfer by the reversible electron transfer model will underestimate $c_f^*D_f^{1/2}$ by ~20 % if $\alpha = 0.5$.) Irreversible, single electron transfer is marked by potential peak separations $\Delta E_p \geq 212$ mV;[18] here, $\Delta E_p < 212$ mV in all cases.

Results are summarized in Table I, where $c_f^*D_f^{1/2}$ found from the slope of i_p versus $\sqrt{v}$ is squared to yield $c_f^{*2}D_f$. Measured $c_f^{*2}D_f$ decreases as $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$; $Cr(bpy)_3^{3+}$ and $Fe(bpy)_3^{2+}$; and $Co(bpy)_3^{3+}$ and $Co(bpy)_3^{2+}$.
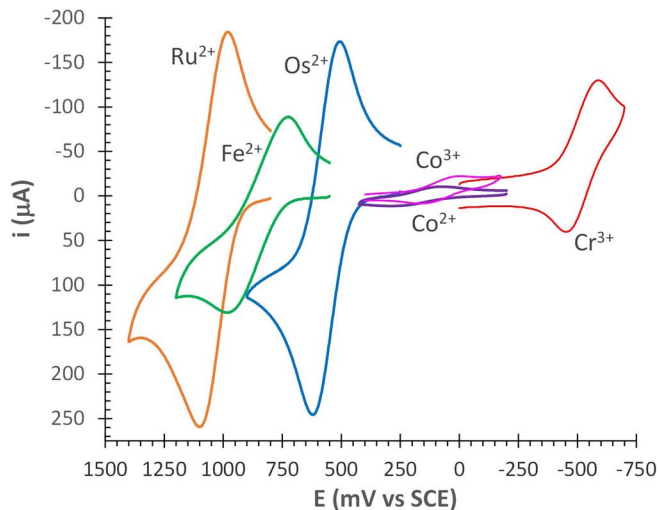

Figure 1. Cyclic voltammograms are shown for six different $M(bpy)_3^{z+}$ complexes at a Nafion modified glassy carbon electrode. All complexes have the same ligands and are of similar diameter (1.36 nm) and charges ($z = 2$ or 3), but vary in current response. The self exchange rate k_{11} for each complex maps the facility of electron hopping for each $M(bpy)_3^{z+}$. Peak currents correlate with k_{11}. Each $M(bpy)_3^{z+}$ is labeled as M^{z+} ($Ru(bpy)_3^{2+}$ orange, $Os(bpy)_3^{2+}$ blue, $Cr(bpy)_3^{3+}$ red, $Fe(bpy)_3^{2+}$ green, $Co(bpy)_3^{3+}$ pink, and $Co(bpy)_3^{2+}$ purple). Concentrations range 1 to 2 mM as listed in Table I. A = 0.458 cm², scan rate 0.1 V/s, 0.1 M electrolyte (HNO_3 for Ru and Os; otherwise Na_2SO_4). Potentials are reported vs SCE, which is 0.241 V vs NHE.

Values in Table I are ordered from high to low by $k_{11}^{H_2O}$, self exchange rate in water. All literature values of $k_{11}^{H_2O}$ are reported in aqueous solutions and are for the +2/+3 couple. As is common, $k_{11}^{H_2O}$ for $Os(bpy)_3^{2+}$ is approximated by $k_{11}^{H_2O}$ for $Ru(bpy)_3^{2+}$.[20] Literature values for $Cr(bpy)_3^{3+}$ range over several orders of magnitude with two reported values separated by an order of magnitude.[25,26] A more recent and detailed study[21] examined 18 chromium polypyridine complexes (bipyridine, phenanthroline, and derivatives) to find the average $k_{11}^{H_2O}$ reported in Table I. For $Fe(bpy)_3^{2+}$, as is typically done, $k_{11}^{H_2O}$ for iron phenanthroline is used.[22]
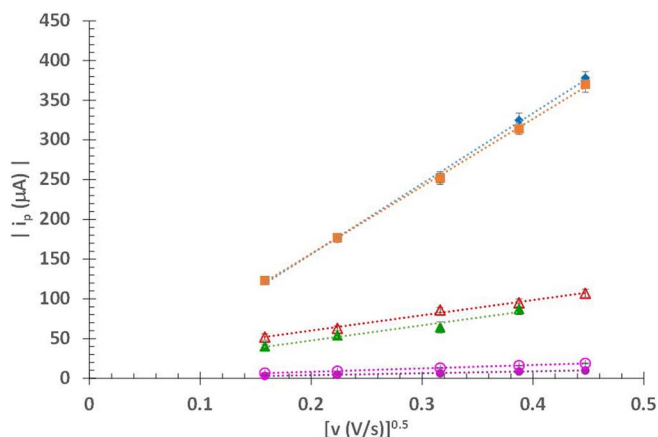
Figure 2. Plots of forward peak current i_p versus $\sqrt{v}$ for the six $M(bpy)_3^{n+}$ where M^{n+} is Ru^{2+} (orange filled square), Os^{2+} (blue filled diamond), Cr^{3+} (red open triangle), Fe^{2+} (green filled triangle), Co^{3+} (pink open circle), and Co^{2+} (purple filled circle). v is the scan rate (V/s). Error bars are shown for multiple replicates and are typically smaller than the marker. Regression lines are shown with statistics reported in Table I. The slope yields $c_f^*D_f^{1/2}$ and intercept of zero is anticipated.
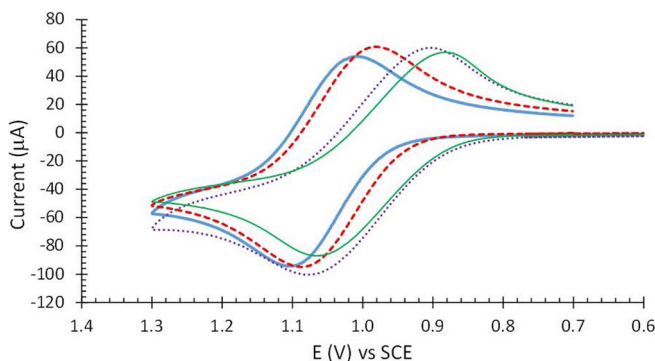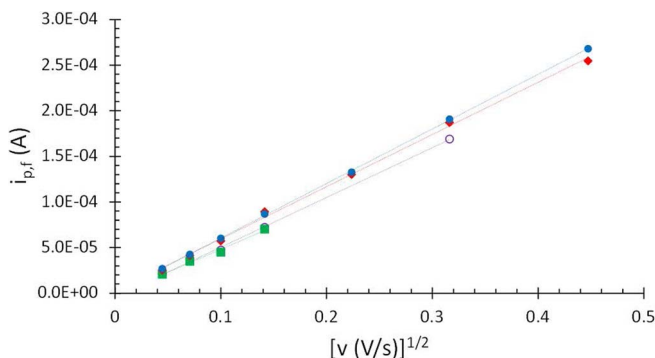
Figure 3. Cyclic voltammograms recorded at 20 mV/s for a 3 μm Nafion film first equilibrated in 5 mM $Ru(bpy)_3^{2+}$ in 0.5 M HNO_3 (blue thick solid line). The concentration ratio of $Ru(bpy)_3^{2+}$ to nitric acid is held constant at 1:100. The film is then re-equilibrated sequentially in 0.02 (green thin solid) mM, 1 mM (red dashed), and then 0.1 mM (purple dotted) $Ru(bpy)_3^{2+}$. Note the similar magnitude of the peak currents independent of the $Ru(bpy)_3^{2+}$ concentration in the solution, consistent with constant $Ru(bpy)_3^{2+}$ concentration in the film. At these concentrations, c_f^* is best modeled as a constant concentration of $Ru(bpy)_3^{2+}$ in the film, independent of concentration in solution.

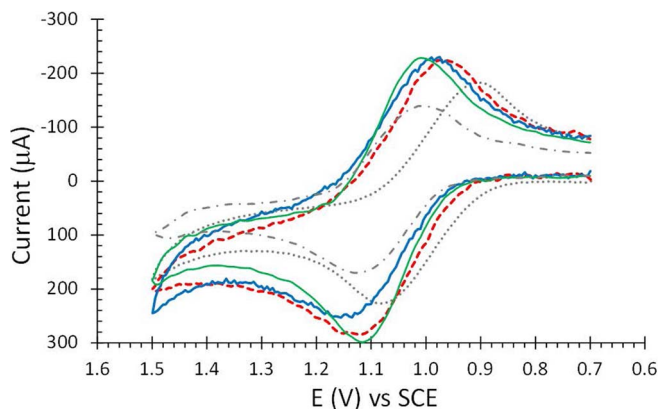**$Ru(bpy)_3^{2+}$ for $c_s^*/c_{electrolyte}^* = 0.01$ across four combinations of c_s^* and $c_{electrolyte}^*$.**—Cyclic voltammetric data were collected for $Ru(bpy)_3^{2+}$ in nitric acid for fixed ratio $c_s^*/c_{electrolyte}^* = 0.01$. The 3 μm Nafion film was first equilibrated in 5 mM $Ru(bpy)_3^{2+}$ and evaluated. The same film was then sequentially equilibrated and evaluated in solutions where c_s^* was 0.02, 1, and 0.1 mM, an order that alternates between higher and lower concentrations. Long equilibration time of 24 h allows redistribution of probe within the film by physical motion. For ℓ of 3 μm taken as δ_0, 24 h allows re-equilibration by physical diffusion $D_p \gtrsim \ell^2/5t \gtrsim 2 \times 10^{-13}$ cm²/s.

Voltammograms are shown in Figure 3 for v of 20 mV/s. Although morphologies for the lower $c_{electrolyte}^*$ (2 and 10 mM HNO_3) reflect greater solution resistance, peak currents are of similar magnitude independent of c_s^*, which ranged from 0.02 to 5 mM $Ru(bpy)_3^{2+}$. This suggests constant $Ru(bpy)_3^{2+}$ concentration in Nafion and c_f^* not set by equilibrium with the solution. If c_f^* were dominated by equilibrium with solution, c_f^* would decrease when the film is moved from higher c_s^* (e.g., 5 mM) to lower c_s^* (e.g., 0.02 mM).

Plots of forward peak current, $i_{p,f}$ versus $\sqrt{v}$ are shown in Figure 4 for $2 \leq v \leq 200$ mV/s. Intercepts are statistically zero. From the slope and Equation 4, $c_f^* D_f^{1/2}$ is found. Value of $c_f^* D_f^{1/2}(10^{-10}\text{mol/cm}^2\text{s}^{1/2}) \pm$ standard error and R^2 for each c_s^* are

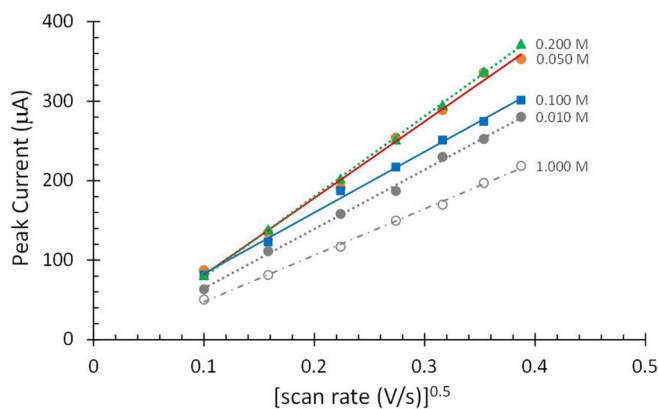**Figure 5.** Cyclic voltammograms are shown for 1.00 mM $Ru(bpy)_3^{2+}$ in nitric acid at concentrations of 0.010 (gray dots), 0.050 (red dash), 0.100 (blue heavy solid), 0.200 (green thin solid), and 1.00 (gray dot dash) M where $0.1 \geq c_s^*/c_{electrolyte}^* \geq 0.005$. Scan rate is 100 mV/s at a 0.452 cm² electrode modified with 5 μm thick Nafion films.

5 mM (48.6 ± 0.3, 0.9998), 1 mM (46.4 ± 0.9, 0.998), 0.1 mM (44.2 ± 0.9, 0.999), and 0.02 mM (41 ± 3, 0.99). In a pairwise comparison, $c_f^* D_f^{1/2}$ values do not differ to a confidence level of 99.8 % or greater with one exception, comparison of 0.1 and 0.02 mM data, where the confidence level is >96 %. The average $c_f^* D_f^{1/2}$ is (45 ± 3) × 10^{-10} mol/cm²s$^{1/2}$, which is outside the confidence interval for $c_f^* D_f^{1/2}$ measured in the experiments reported in Figures 1 and 5; data in Figure 3 were however collected on a single film.

$Ru(bpy)_3^{2+}$ for $c_s^* = 1.00$ mM and five $c_{electrolyte}^*$ values.—Data were collected for $Ru(bpy)_3^{2+}$ in nitric acid where $c_s^* = 1.00$ mM and $c_{electrolyte}^*$ varied, so that $c_s^*/c_{electrolyte}^*$ varied. A fresh film was evaluated at each electrolyte concentration with three replicates of each of seven scan rates. These studies were undertaken to determine if c_f^* is set by a strong competitive equilibrium of solution $Ru(bpy)_3^{2+}$ and H^+ for sulfonate sites in the film. Voltammograms at 100 mV/s are shown in Figure 5. Plots of i_p versus $v^{1/2}$ in Figure 6 exhibit similar slopes that do not vary systematically with c_s^*. For $0.1 \geq c_s^*/c_{electrolyte}^* \geq 0.005$, the responses are similar and independent of $c_s^*/c_{electrolyte}^*$. Again, results are consistent with c_f^* for $Ru(bpy)_3^{2+}$ invariant with $c_{electrolyte}^*$ in the range common to voltammetric experiments. At the highest concentration of nitric acid, 1 M where $c_s^*/c_{electrolyte}^* = 0.001$, currents are smaller.

Figure 4. Plot of $i_{p,f}$ versus $v^{1/2}$ for $Ru(bpy)_3^{2+}$ in HNO_3 where $c_s^*/c_{electrolyte}^* = 0.01$ and data were recorded for a single film in order as c_s^* of 5 (blue dots), 0.02 (green squares), 1 (red diamonds), and 0.1 (purple circles) mM. Note there is no systematic dependence of the slopes on $c_{electrolyte}^*$.

Figure 6. Plots of i_p versus $v^{1/2}$ for data in Figure 5 where 1.00 mM $Ru(bpy)_3^{2+}$ in the electrolyte is evaluated at different concentrations of HNO_3, 0.010 (gray circles), 0.050 (red solid circles), 0.100 (blue squares), 0.200 (green triangles), and 1.00 (gray open circles) M.

Table II. Regression Statistics for Plots of i_p versus $\sqrt{v}$ for 1.00 mM Ru(bpy)$_3^{2+}$ in HNO$_3$ where the nitric acid concentration varies from 10 to 1000 mM. Slope and intercepts with standard errors and correlation coefficient R^2 are reported for multiple replicates for each probe.

$c^*_{electrolyte}$ (mM)	Slope (10^{-5} A$\sqrt{s/V}$)	Intercept (10^{-5} A)	R^2	$c^*_f D_f^{1/2}$ (10^{-10} mol/cm^{2}s$^{1/2}$)	$c^{*2}_f D_f$ (10^{-18} mol^2/cm^{4}s)
10	75 ± 2	−1.0 ± 0.4	0.998	61 ± 1	38 ± 2
50	96 ± 3	−1.5 ± 0.8	0.995	79 ± 2	63 ± 4
100	77 ± 2	0.6 ± 0.6	0.997	63 ± 2	40 ± 2
200	101 ± 1	−2.2 ± 0.3	0.9995	83 ± 1	69 ± 1
1000	58 ± 1	−1.1 ± 0.3	0.998	48 ± 1	23 ± 1

Data analyses for Figure 6 are reported in Table II for a single film for each $c^*_{electrolyte}$. Values of $c^*_f D_f^{1/2}$ and $c^{*2}_f D_f$ do not vary systematically with $c^*_{electrolyte}$. For the highest (1 M) $c^*_{electrolyte}$, current is perhaps lower. Averaging over all concentrations, $c^*_f D_f^{1/2} = (67 \pm 14) \times 10^{-10}$ mol/cm^{2}s$^{1/2}$ and $c^{*2}_f D_f = (47 \pm 19) \times (10^{-18}$ mol^2/cm^{4}s). The average has a larger standard error but is statistically the same as found for Ru(bpy)$_3^{2+}$ in the series of M(bpy)$_3^{z+}$ experiments with >90 % confidence.

Discussion

From the Dahms Ruff model (Equation 3), electron hopping (D_{et}) is characterized by k_{11}, c^*_f, and δ. Typically, M(bpy)$_3^{z+}$ complexes undergo outer sphere electron transfer with negligible volume change. Diameter of M(bpy)$_3^{z+}$, δ = 1.36 nm.[13] For limited z and fixed δ, c^*_f should be similar for M(bpy)$_3^{z+}$ in Nafion. The wide variation with metal center M^{z+} of i_p and measured $c^{*2}_f D_{f|meas}$ correlates with k_{11}. In Table I, self exchange rates $k_{11}^{H_2O}$ are literature values measured in water at either low ionic strength or infinite dilution. Because the Nafion matrix differs from water (at least with respect to ionic strength), it is likely self exchange rates in Nafion k_{11}^{Naf} and water differ but that k_{11}^{Naf} and $k_{11}^{H_2O}$ are proportional.

c^*_f sets distance between redox centers, where self exchange rate decreases exponentially with distance. In the simplest view, for $k(x)$ an electron transfer rate across distance x where the rate at contact is $k(0)$, rate decreases as $k(x)/k(0) = \exp[-\beta x]$, where β is on the order of 10/nm (1/Å).[18] At $x \gtrsim 2$ nm, $k(2\,nm) \lesssim 10^{-9}k(0)$, which is negligible as compared to the rate at 1 nm, $k(1\,nm) > 10^4 k(2\,nm)$. For electrostatically bound probe, x is set by c^*_f and the flexibility of polymer side chains to move within the ion exchange matrix.[27] Based on M(bpy)$_3^{z+}$ molar volume and Nafion water content, zc^*_f is less than the sulfonate concentration.[15]

Density and equivalent weight estimate sulfonate concentration in the hydrated domains of Nafion. The limited volume of the hydrated domains precludes charge neutralization of sulfonate anions by M(bpy)$_3^{z+}$ alone. Sulfonates are also charge neutralized by smaller electrolyte cations drawn from solution. The environment inside biphasic Nafion is sketched based on known density d and equivalent weight (grams of Nafion/mole sulfonate) $EQWT$. This yields the concentration of M(bpy)$_3^{z+}$ in well hydrated Nafion as volume limited and fixed independent of z as well as the concentration of sulfonates and fraction of sulfonates charge neutralized by M(bpy)$_3^z$. Data in Table I are sussed based on these concentrations. Activity effects on self exchange rate are evaluated through the proportionality $k_{11}^{Naf} = a k_{11}^{H_2O}$ where a is a constant. For each M(bpy)$_3^{z+}$, D_{et} is considered and for all M(bpy)$_3^{z+}$, a single D_p is estimated.

A sketch of the Nafion environment based on density d, equivalent weight $EQWT$, and Electroneutrality.—Gierke and coworkers first proposed a cluster network model of Nafion nanostructure based on X-ray scattering measurements of silver,[10,28] where biphasic Nafion is modeled as a fluorocarbon phase that contains 4 to 5 nm water-filled inverted micelles interconnected by short 1 nm diameter channels. From 77 K cryo electron tomography of 100 nm thick,

water-hydrated, cast Nafion films, a nanostructure of 2.5 nm wide channels interconnect clusters separated center to center by 5.1 nm.[11] Similar measurements on cast but not hydrated films found 3.5 nm domains. Common to the models for hydrated Nafion is extensive interconnectivity of hydrated domains segregated from fluorocarbon, where the hydrated nanostructure has characteristic lengths of 1 to 3 nm channels and 5 nm clusters.

Macroscopic Nafion characterizations are consistent with the nanoscopic picture. Density (water content) and equivalent weight set concentration of sulfonates and M(bpy)$_3^{z+}$. M(bpy)$_3^{z+}$ concentrations are estimated by the maximum number of M(bpy)$_3^{z+}$ that will fit in the hydrated volume.[15] Estimates, reported as molar densities (M) and denoted N^*, are developed as summarized in Table III.

v_{aq} - hydrated volume fraction from density d.—Densities of as received Nafion membranes and cast Nafion films are reported.[8,9,29] In biphasic Nafion with aqueous and fluorocarbon phases, volume fractions of fluorocarbon v_{CF} and hydrated domains v_{aq} are calculated from density of fluorocarbon, estimated from Teflon $d_{CF} = 2.15$ g/cm^3, and density of water, $d_w = 0.9982$ g/cm^3 at 25 ^{o}C. Measured density $d = v_{aq}d_w + v_{CF}d_{CF}$, where $v_{aq} + v_{CF} = 1$. On substitution, $v_{aq} = (d - d_{CF})/(d_w - d_{CF})$. For Nafion films cast from as received suspension (no cation exchange after casting), densities of 1.65 ± 0.02[9] and 1.40 ± 0.15[8,29] g/cm^3 yield v_{aq} of 0.43 ± 0.01 and 0.65 ± 0.07.

Density of Ru(bpy)$_3^{2+}$ exchanged, recast Nafion films pretreated in either 18 MΩ water or concentrated nitric acid[9] are similar: 1.91 ± 0.12 g/cm^3 and 1.98 ± 0.21 g/cm^3. Similarly, average density of 1.95 ± 0.03 g/cm^3 is found for acid pretreated films exchanged with one of several cations (Ru(bpy)$_3^{2+}$, (CH$_3$)$_4$N$^+$, Fe^{2+}, and Ru(NH$_3$)$_6^{3+}$). In acid, the hydrated fraction contains water, proton, and M(bpy)$_3^{z+}$, all taken at density d_w. (Ion molar volume and molecular weight of Ru(bpy)$_3^{2+}$ yield 0.979 g/cm^3.[9]) On substituting densities, 1.95 = 2.15v_{CF} + 0.9982v_{aq} yields $v_{aq} = 0.17$ for Ru(bpy)$_3^{z+}$ exchanged Nafion.[9] For all M(bpy)$_3^{z+}$-exchange Nafion, v_{aq} is taken as 0.17.

$N^*_{SO_3,aq}$ - sulfonate concentration in the hydrated domain estimated from equivalent weight $EQWT$.—The nominal equivalent weight of cast Nafion films is 1100 g/mole of sulfonate. Titration of recast Nafion films is 996 ± 24 g/mol.[14] Sulfonate is determined by fully protonating weighed Nafion in strong acid; rinsing unbound proton; flushing all bound H$^+$ by exchange with excess Na$^+$; and titrating the H$^+$ with sodium hydroxide to a phenolphthalein end point. Because this is an aqueous acid base titration, measured sulfonate is specific to the aqueous (hydrated) domain.

For a nominal $EQWT = 1100$ g/mole of sulfonates and $d = 1.95$ ± 0.03 g/cm^3, sulfonate concentration is $d/EQWT = 1.77_3 \times 10^{-3}$ mol/cm^3. In the hydrated domain, sulfonate concentration is estimated as $N^*_{SO_3,aq} = d/(v_{aq} \times EQWT) = 1.04_3 \times 10^{-2}$ mol/cm^3, 10.4 M.

Notationally, distinction is made between total film volume and hydrated volume, denoted by subscript aq. For example, c^*_f is the probe concentration in the film; $c^*_{f,aq}$ is the probe concentration in the hydrated domains, so $c^*_{f,aq} = c^*_f/v_{aq}$. Voltammetry yields c^*_f but to conceptualize electron self exchange and impacts of distance, the hydrated domain and $c^*_{f,aq}$ are the critical parameters.

Table III. Concentrations (mmol/cm³) and Separation Distances (nm) as Estimated Based on Volume and Charge Balance Limitations for M(bpy)$_3^{z+}$ Exchanged Nafion.

Parameter	Symbol	Nafion		notes, references
density|$_{\text{M(bpy)}_3^+ \text{ in Nafion}}$	d (g/cm³)	1.95 ± 0.03		Ref. 9
vol. frac. |$_{\text{hydrated, M(bpy)}_3^+ \text{ in Nafion}}$	v_{aq}	0.17		$\frac{d-d_{CF}}{d_w-d_{CF}}$
Equiv. Wt. |$_{\text{nominal}}$	$EQWT$ (g/mol)	1100		[14]
concentration sulfonates |$_{aq}$	$N_{SO_3,aq}^*$ (M)	10.4$_3$		$d/\left(v_{aq} \times EQWT\right)$
		M(bpy)$_3^{2+}$	M(bpy)$_3^{3+}$	
diameter of M(bpy)$_3^{z+}$	δ	1.36	1.36	Ref. 13
charge	z	2	3	
In the hydrated domains |$_{aq \text{ in Nafion}}$				
Est. Max. Concentration M(bpy)$_3^{z+}$|$_{aq}$	$N_{f,aq}^*$ (M)	0.933	0.933	$\tilde{\delta} = \delta$ in Eq. 5
Est. Max. Conc. M(bpy)$_3^{z+}$-bound SO$_3^-$|$_{aq}$	$N_{SO_3M,aq}^*$ (M)	1.87	2.80	$zN_{f,aq}^*$
Est. Max. Frac. M(bpy)$_3^{z+}$-bound SO$_3^-$|$_{aq}$		0.18	0.27	$N_{SO_3M,aq}^*/N_{SO_3,aq}^*$
Est. Min. Conc. Coion-bound SO$_3^-$|$_{aq}$	$N_{coion,aq}^*$ (M)	8.56	7.63	$N_{SO_3,aq}^* - N_{SO_3M,aq}^*$
Est. Center to Center Distance for M(bpy)$_3^{z+}$	δ_{M-M}	1.36	1.36	$N_{f,aq}^* = \tilde{c}$ in Eq. 5
Est. Edge to Edge Distance for M(bpy)$_3^{z+}$	δ_{gap}	0	0	$\delta_{M-M} - \delta$
In the total Nafion volume				
Est. Max. Conc. M(bpy)$_3^{z+}$ across Nafion film	N_f^* (mmol/cm³)	0.159	0.159	$v_{aq} N_{f,aq}^*$
Est. Max. Conc. M(bpy)$_3^{z+}$-bound SO$_3^-$	$N_{SO_3M}^*$ (mmol/cm³)	0.318	0.476	$v_{aq} N_{SO_3M,aq}^*$

$N_{f,aq}^*$ *- estimated maximum concentrations of M(bpy)$_3^{z+}$ cations in the hydrated domains.*—Electrostatic interactions between sulfonates and M(bpy)$_3^{z+}$ are strong. Loading of M(bpy)$_3^{z+}$ into Nafion is slowed as M(bpy)$_3^{z+}$ binds and unbinds with successive sulfonates as M(bpy)$_3^{z+}$ "walks" into Nafion from solution toward the electrode. Charge balance for the sulfonate anions requires cations. High dielectric constant media such as water ($\varepsilon = 78$ for pure water) support formation of ions whereas low dielectric media such as fluorocarbons ($\varepsilon \approx 2$) do not. From the acid base titration, exchanged sulfonates are in the hydrated domain. For M(bpy)$_3^{z+}$ bound to sulfonate and able to engage in electron exchange, M(bpy)$_3^{z+}$ must also be either in or directly in contact with the hydrated domain to allow charge balance.

Extraction of M(bpy)$_3^{z+}$ is highly favored as demonstrated by high selectivity of M(bpy)$_3^{z+}$ over sodium and proton for electrolyte that contains very dilute M(bpy)$_3^{z+}$.[30] Because of strong electrostatic interactions and high selectivity for M(bpy)$_3^{z+}$, sulfonates are often approximated as fully M(bpy)$_3^{z+}$-exchanged. For $N_{SO_3,aq}^*$ of 10.4 M and sulfonates fully charge neutralized by M(bpy)$_3^{z+}$, M(bpy)$_3^{z+}$ concentration in the hydrated volume would be $N_{SO_3,aq}^*/z$; for M(bpy)$_3^{2+}$ and M(bpy)$_3^{3+}$, this would be 5.3 and 3.5 M.

For a concentration $\tilde{c}$ of spheres separated by distance $\tilde{\delta}$, the highest (close packed) density of sphere is $\pi/3\sqrt{2} = 0.7405$ where the volume of the sphere is $\frac{\pi}{6}\delta^3$. For N_0 Avogadro number,

$$\tilde{c} = \frac{\pi}{3\sqrt{2}} \frac{6}{\pi \tilde{\delta}^3 N_0} = \frac{\sqrt{2}}{\tilde{\delta}^3 N_0} \quad \text{or} \quad \tilde{\delta} = \frac{2^{1/6}}{[\tilde{c}N_0]^{1/3}} \quad [5]$$

If sulfonates are charge neutralized by only the transition metal complexes, either 5.3 M M(bpy)$_3^{2+}$ or 3.5 M M(bpy)$_3^{3+}$, then Equation 5 yields molecular diameters $\lesssim 2^{1/6}[c_{f,aq}N_0]^{-\frac{1}{3}}$ of $\lesssim 0.76$ nm for M(bpy)$_3^{2+}$ and $\lesssim 0.88$ nm for M(bpy)$_3^{3+}$. Because both values are well below the known diameter of M(bpy)$_3^{z+}$, $\delta = 1.36$ nm, volume restrictions prevent sulfonates from neutralization by M(bpy)$_3^{z+}$ alone. Smaller cationic electrolyte ions, coions, must enter the film to balance the anionic charge of the sulfonates.

An upper limit on the concentration of M(bpy)$_3^{z+}$ that will physically pack into the hydrated volume can be estimated. For δ of 1.36 nm, the volume of one M(bpy)$_3^{z+}$ is $1.31_7 \times 10^{-21}$ cm³. For dense packing, the upper limit of M(bpy)$_3^{z+}$ concentration that can physically accom-

modate in the hydrated volume of Nafion is estimated from Equation 5, $N_{f,aq}^* = 9.33 \times 10^{-4}$ mol of M(bpy)$_3^{z+}$ /cm³ $= 0.933$ M.

$N_{SO_3M,aq}^*$ *- estimated maximum concentrations of sulfonates bound to M(bpy)$_3^{z+}$ cations in the hydrated domain.*—From $N_{f,aq}^*$ and the strong electrostatic interaction that binds M(bpy)$_3^{z+}$ and sulfonates, the maximum concentration of sulfonates bound by M(bpy)$_3^{z+}$ in the hydrated domain is estimated as $N_{SO_3M,aq}^* = zN_{f,aq}^* = z\sqrt{2}\left[\delta^3 N_0\right]^{-1} = z9.33 \times 10^{-4}$ mol of sulfonates charge neutralized and bound to M(bpy)$_3^{z+}$ /cm³. For M(bpy)$_3^{2+}$ and M(bpy)$_3^{3+}$, $N_{SO_3M,aq}^*$ are 1.87×10^{-3} mol /cm³ and 2.80×10^{-3} mol/cm³. The estimated maximum fractions of sulfonates bound with M(bpy)$_3^{z+}$ are 0.18 and 0.27 for z of 2 and 3.

Electrostatics requires that the sulfonate charges be electroneutralized with cations. Because the number of M(bpy)$_3^{z+}$ extracted into the hydrated domains is volume limited, cations are provided by the electrolyte coions, here Na$^+$ and H$^+$. Because these coions are monocations, the lower limit on coion concentration in Nafion $N_{coion,aq}^*$ is estimated as $N_{coion,aq}^* = N_{SO_3,aq}^* - N_{SO_3M,aq}^*$. From $N_{SO_3,aq}^*$ and $N_{f,aq}^*$ summarized in Table III, minimum $N_{coion,aq}^*$ are estimated as 8.56×10^{-3} mol /cm³ and 7.63×10^{-3} mol/cm³ or a minimum of 9.1 to 8.2 monocationic coions per M(bpy)$_3^{z+}$. With fewer coions, the distance between moieties for films loaded with M(bpy)$_3^{3+}$ is less than M(bpy)$_3^{2+}$. In Table I, D_f for films initially loaded with Co(bpy)$_3^{3+}$ is about three fold larger than for Co(bpy)$_3^{2+}$. This suggests that electron hopping contributes to measured D_f for the cobalt complexes despite the common, small $k_{11}^{H_2O}$ value of 20 /Ms.

These estimates of $N_{f,aq}^*$ and $N_{SO_3M,aq}^*$ do not vary with either the concentration of M(bpy)$_3^{z+}$ in solution (Figure 3) or the ratio of concentration of M(bpy)$_3^{z+}$ to electrolyte cation (Figure 5). Where selectivity dominates loading of M(bpy)$_3^{z+}$ into Nafion, as at very dilute concentrations of M(bpy)$_3^{z+}$ and very high concentrations of electrolyte, selectivity should be considered. The data in Figure 3 were taken over a wide range of solution electrolyte $c_{electrolyte}^*$ and solution Ru(bpy)$_3^{z+}$ c_s^* concentrations where $c_{electrolyte}^*/c_s^*$ is held constant at 100, and except for solution resistance effects at low electrolyte, the voltammetric responses are similar. In Figure 5, where c_s^* is 1 mM Ru(bpy)$_3^{z+}$ and nitric acid concentration is varied as $0.1 \geq c_s^*/c_{electrolyte}^* \geq 0.005$,

responses are again not systematic with $c_s^*/c_{electrolyte}^*$, except perhaps at the highest electrolyte concentration. From these outcomes, selectivity of Nafion for $M(bpy)_3^{z+}$ relative to the electrolyte coion has minor impact on c_f^* under common electrochemical conditions where at least $c_{electrolyte}^* \lesssim 0.5$ M. Thus, for common voltammetric conditions, c_f^* is well-modeled as fixed.

The water content in the hydrated domains is roughly estimated by approximating the density of the hydrated domain and all the species in the hydrated domain as equal to water (1.0 g/cm³). For each species, the product of its concentration and molecular weight yields a value $\rho_{i,aq}$ (g/cm³). The sum of $\rho_{i,aq}$ values is taken as equal to 1.0 g/cm³. The hydrated domain includes $M(bpy)_3^{z+}$ at $N_{f,aq}^*$, coion of either H^+ or Na^+ at $N_{coion,aq}^*$, and water at $N_{w,aq}^*$. For $Ru(bpy)_3^{2+}$, 1000 g/L = (574.4 g/mol) $\times N_{f,aq}^*$ + atomic weight$_{coion}$ $\times$ $N_{coion,aq}^*$ + (18.0 g/mol)$N_{w,aq}^*$. For H^+, $N_{w,aq}^*$ = 23.2 M or 2.2 waters per sulfonate; for Na^+, $N_{w,aq}^*$ = 12.8 M or 1.2 waters per sulfonate. The sulfonate is assumed at the fluorocarbon | hydrated domain interface and accounted in the fluorocarbon phase. Perfluorobutane sulfonic acid, structurally similar to the Nafion pendant chains, has density of 1.811 g/cm³ and low solubility in water, <1.8 mM. High density and low solubility are consistent with the perfluorosulfonates in the fluorocarbon phase with the sulfonate at the interface of the fluorocarbon and hydrated domain.

δ_{M-M} *separation distance between* $M(bpy)_3^{z+}$ *centers in the hydrated domains and* δ_{gap} *their edge to edge separation.*—The Dahms Ruff model was developed from freely diffusing species at high concentration in solution where the electron transfer occurs on collision of two moieties of different charge. In a polymer, such as Nafion, the redox probes are not freely diffusing as $M(bpy)_3^{z+}$ is held strongly by z sulfonates, where sulfonates pendant on Nafion side chains have limited motions.[27] For effective electron exchange in a rigid matrix, the separation between redox moieties must be small enough to allow electron exchange.

The distance center to center δ_{M-M} between $M(bpy)_3^{z+}$ complexes for close packed spheres can be estimated on substitution of $N_{f,aq}^*$ into Equation 5, where δ_{M-M} is the shortest center to center distance between close packed spheres. The edge to edge distance between complexes or the gap between complexes $\delta_{gap} = \delta_{M-M} - \delta$. For $N_{f,aq}^* = 9.33 \times 10^{-4}$ mol/cm³, $\delta_{M-M} = 1.36$ nm, which equals molecular diameter δ for $M(bpy)_3^{z+}$, as appropriate for the assumed close packed sphere. Because the model assumes $\delta_{M-M} = \delta$, $\delta_{gap} = 0$. The values in Table III serve as idealized representations of the physical system, which may vary from the approximations.

N_f^* *and* $N_{SO_3M}^*$ - *estimated maximum concentrations of* $M(bpy)_3^{z+}$ *cations and* $M(bpy)_3^{z+}$-*bound sulfonates in the total Nafion volume.*— The maximum estimated $M(bpy)_3^{z+}$ concentration normalized to the total film volume, $N_f^* = v_{aq} N_{f,aq}^* = 1.59 \times 10^{-4}$ mol/cm³. The corresponding estimated maximum concentrations of $M(bpy)_3^{z+}$-bound sulfonates in the total film volume $N_{SO_3M,aq}^* = zN_f^*$ or 0.32 and 0.48 M for z of 2 and 3.

The concentration of $Ru(bpy)_3^{2+}$ extracted into a Nafion film formed by drop casting 10 μL of 2.5 wt/vol % of Nafion suspension on a 1 cm² surface was measured by UV-vis spectroscopy as 2.1×10^{-8} mol/cm².[31] For the casting conditions and a density of 1.95 g/cm³, the $Ru(bpy)_3^{2+}$ in the total volume of Nafion is 1.6×10^{-4} mol/cm³, which is in excellent agreement with the value estimated here for N_f^* of 1.59×10^{-4} mol/cm³.

Self exchange of $M(bpy)_3^{z+}$ ***complexes in Nafion.***—The sketch of the environment in Nafion drives the interpretation of the diffusion coefficients and self exchange rates in Nafion. Concentration sets δ_{M-M} and so the efficiency of electron hopping that impacts D_{et} and D_f.

In Figure 1, representative cyclic voltammograms for six different redox reactions and five different metals map current that varies with the metal center. Data plotted according to Equation 4, (Figure 2) are

linear with intercepts near zero and slopes proportional to $c_f^* D_f^{1/2}$, as reported in Table I. From the slopes, diffusion length does not exceed film thickness ($\delta_0 \leq \ell$). In Table I, $c_f^{*2} D_f$ varies with metal center and in proportion to $k_{11}^{H_2O}$.

From Equation 3 and fixed δ, $c_f^{*2} D_f$ varies linearly with $k_{11}^{H_2O}$. From Table I, regression of the experimentally determined $c_f^{*2} D_f$ values against $k_{11}^{H_2O} \delta^2 / 6$ yields $c_f^{*2} D_f = (3.9 \pm 0.2) \times 10^{-14} [k_{11}^{H_2O} \delta^2 / 6] - (0.8 \pm 1.4) \times 10^{-18}$ with $R^2 = 0.99$. The regression is of good linearity. For c_f^* fixed, D_f is then linearly correlated with self exchange rate in water ($k_{11}^{H_2O}$), so D_{et} contributes to D_f (Equation 3).

Relationship between k_{11}^{Naf} *and* $k_{11}^{H_2O}$: $k_{11}^{Naf} = a k_{11}^{H_2O}$.—Because the regression of $c_f^{*2} D_f$ with $k_{11}^{H_2O} \delta^2 / 6$ is linear and fixed δ and z of +2/+3, $k_{11}^{H_2O}$ is proportional to k_{11}^{Naf}, but not necessarily equal. Self exchange rates vary with the matrix through activity effects. For water, $k_{11}^{H_2O}$ is measured at infinite dilution and high dielectric constant; in Nafion, k_{11}^{Naf} may differ from $k_{11}^{H_2O}$[32] because of high ion concentrations and lower dielectric constant[33] of 20 in well hydrated Nafion. Allow a proportionality, $k_{11}^{Naf} = a k_{11}^{H_2O}$, where $0 < a < 1$ if $k_{11}^{H_2O}$ overestimates k_{11}^{Naf}. On multiplication by c_f^{*2} and substitution of $k_{11}^{Naf} = a k_{11}^{H_2O}$, Equation 3 yields

$$c_f^{*2} D_f|_{measured} = c_f^{*2} \left[D_p + \frac{a k_{11}^{H_2O} c_f^* \delta^2}{6} \right] \qquad [6]$$

A plot of $c_f^{*2} D_f|_{measured}$ versus $k_{11}^{H_2O} \delta^2 / 6$ yields slope $a c_f^{*3}$ and intercept $c_f^{*2} D_p$.

To estimate the smallest value of the proportionality constant a, let $c_f^* = N_f^* = 1.59 \times 10^{-4}$ mol/cm³, the z-independent, hydrated volume-limited concentration . The regression slope is then $a N_f^{*3} = (3.9 \pm 0.2) \times 10^{-14}$ mol³/cm⁹, and the estimated lower limit of $a = 0.0097 \pm 0.0005$. This approximates that $k_{11}^{Naf} = 0.010 k_{11}^{H_2O}$ or the rate of self exchange in water is no more than a hundred fold higher than in Nafion. Suppression of k_{11}^{Naf} as compared to $k_{11}^{H_2O}$ arises from activity effects of ionic strength and to a lesser extent dielectric constant in Nafion that differ from dilute aqueous systems. The Nafion matrix rather than the individual $M(bpy)_3^{z+}$ complexes suppresses the rate of self exchange.

Although N_f^* may overestimate c_f^*, the hydrated volume-limited estimate of $N_f^* = c_f^* = 1.59 \times 10^{-4}$ mol/cm³ is a better estimate than $k_{11}^{H_2O} = k_{11}^{Naf}$. When $a = 1$, activities in water and Nafion are set equal. Activity effects in the high ionic strength, hydrated domains of Nafion differ substantially from the negligible activity effects in water at infinite dilution, consistent with $a \neq 1$. The $Ru(bpy)_3^{2+}$ concentration in cast Nafion films measured spectroscopically[31] is the same as N_f^*, 1.6×10^{-4} mol/cm³. For $a = 1$, the experimental slope yields c_f^* of about $N_f^*/5$, and similarly $N_{f,aq}^*/5$, where Equation 5 yields $\delta_{M-M} = 2.3$ nm with $\delta_{gap} = 0.9$ nm. The hopping distance $\delta_{gap} = 0.9$ nm substantially reduced hopping efficiency, $k (0.9$ nm$) = 10^{-4} k (0)$. The selectivity of Nafion for $M(bpy)_3^{z+}$ over electrolyte coions is very high as shown by dilute $M(bpy)_3^{z+}$ measurements.[30] Here, $Ru(bpy)_3^{2+}$ concentration in the film is invariant across a range of HNO_3 concentrations for 1 mM $Ru(bpy)_3^{2+}$ (Figure 5) and across a range of $Ru(bpy)_3^{2+}$ concentrations at fixed ratio of 100:1 HNO_3 to $Ru(bpy)_3^{2+}$ (Figure 3). These observations are consistent with an estimated loading of $M(bpy)_3^{z+}$ as high as can be physically accommodated in the hydrated domains. Based on these observations, the estimate of $a = 0.010$ better characterizes the Nafion matrix than an assumption of a as 1.

Diffusion coefficients D_f, D_p, *and* D_{et} *where* $c_f^* = N_f^* = 1.59 \times 10^{-4}$ *mol/cm³.*—The intercept of the regression $c_f^{*2} D_p$ is nominally

Table IV. Determination of D_f from the measured $c_f^{*2}D_f$ and c_f^*. D_{et} estimated from D_f - D_p. These values are based on the hydrated volume-limited film concentration $c_f^* = N_f^* = 1.59 \times 10^{-4}$ mol/cm^3. These are lower estimates on D_f and D_{et}. D_p is estimated as $\leq 5 \times 10^{-12}$ cm^2/s.

Redox Probe	$c_f^{*2}D_f|_{meas}$ $(10^{-18}$ mol^2/cm^{4}s)	D_f $(10^{-10}$ cm^2/s)	D_{et} $(10^{-10}$ cm^2/s)
Ru(bpy)$_3^{2+}$	48 ± 2	19.0 ± 0.8	19.0 ± 0.8
Os(bpy)$_3^{2+}$	52 ± 3	21 ± 1	21 ± 1
Cr(bpy)$_3^{3+}$	2.4 ± 0.3	0.9 ± 0.1	0.9 ± 0.1
Fe(bpy)$_3^{2+}$	2.4 ± 0.7	0.9 ± 0.3	0.9 ± 0.3
Co(bpy)$_3^{3+}$	0.120 ± 0.006	0.047 ± 0.002	≈ 0.04
Co(bpy)$_3^{2+}$	0.039 ± 0.003	0.015 ± 0.001	≈ 0.005

negative ($-(0.8 \pm 1.4) \times 10^{-18}$ mol^{2}cm^{-4}) but of high uncertainty. The results are consistent with physical diffusion, D_p small.

Values of $c_f^{*2}D_f|_{measured}$ are reported in Table I. For c_f^* taken as the hydrated volume-limited $N_f^* = 1.59 \times 10^{-4}$ mol/cm^3, D_f is estimated in Table IV. D_f ranges from 1.9×10^{-9} to 1.5×10^{-12} cm^2/s. The lowest values provide an estimate of D_p of no greater than $\sim 10^{-12}$ cm^2/s. For all the complexes except Co(bpy)$_3^{3+}$ and Co(bpy)$_3^{2+}$, $D_f \gtrsim 10^{-10}$ cm^2/s so that self exchange dominates the flux and $D_{et} = ak_{11}^{H_2O}N_f^*\delta^2/6 \longrightarrow D_f$.

For Co(bpy)$_3^{3+}$ and Co(bpy)$_3^{2+}$, D_f is substantially smaller than for the other complexes; consistent with small $k_{11}^{Naf}(Co(bpy)_3^{3/2})$, estimated as 0.2/Ms from $k_{11}^{Naf} = 0.0097 k_{11}^{H_2O}$. The values of D_f are however, not the same where D_f is higher for Co(bpy)$_3^{3+}$ than Co(bpy)$_3^{2+}$ by a factor of 3. The diffusion coefficient in Nafion for Co(tpy)$_2^{3+}$ is similarly three fold higher than Co(tpy)$_2^{2+}$ (tpy = terpyridine).[34] There are more electrolyte cations in the film when the film is initially loaded with M(bpy)$_3^{2+}$ than M(bpy)$_3^{3+}$. The electrolyte cations may introduce incremental separation between adjacent M(bpy)$_3^{z+}$. For $k(x) = k(0)\exp[-\beta x]$, the ratio of self exchange rates for z of 3 and 2 yields $k_3(x)/k_2(x) = 3 = \exp[-\beta\Delta x]$ where Δx would be the increased distance for electron transfer for z of 2 relative to 3. For β of 10/nm, a factor of 3 arises from Δx of 0.11 nm, which is a small distance equal to the diameter of a Bohr model hydrogen atom and comparable to the 0.96 Å H-O bond in water. Because minimal electron hopping between Co(bpy)$_3^{2+}$ and Co(bpy)$_3^{3+}$ cannot be excluded, D_f for the cobalt species provides an upper estimate on D_p. From Co(bpy)$_3^{3+}$ and Co(bpy)$_3^{2+}$, the upper estimate of D_p is of the order of $\lesssim 10^{-12}$ cm^2/s.

For an upper limit $c_f^* = N_f^* = 1.59 \times 10^{-4}$ mol/cm^3, a lower estimate of D_f and D_{et} results, as shown in Table IV. To calculate diffusion by electron hopping, $D_{et} = D_f - D_p$, where D_p is estimated as 1×10^{-12} cm^2/s. For D_p of 1 to 5×10^{-12} cm^2/s, D_p is comparable to the uncertainty in the measured D_f for all but the cobalt complexes so that the flux (current) is dominated by electron self exchange. For the cobalt complexes, flux due to electron hopping is small to negligible, but at $D_p = 1 \times 10^{-12}$ cm^2/s, electron hopping nominally carries half the flux when Co(bpy)$_3^{3+}$ is initially loaded into the film and a third for Co(bpy)$_3^{2+}$.

To better characterize z-dependence: analysis based on $c_{SO_3M}^*$.— From the data for Co(bpy)$_3^{z+}$ complexes, z impacts measured D_f. The concentration of M(bpy)$_3^{z+}$ bound sulfonates $c_{SO_3M}^*$ is z dependent ($c_{SO_3M}^* = zc_f^*$). On substitution into Equation 6, the experimentally determined $c_f^{*2}D_f|_{measured}$ is expressed in terms of $k_{11}^{H_2O}\delta^2$ and z, where z is the charge on the probe initially equilibrated into the Nafion film from solution.

$$z^2 c_f^{*2}D_f|_{measured} = c_{SO_3M}^{*2}\left[D_p + c_{SO_3M}^*\frac{ak_{11}^{H_2O}\delta^2}{6z}\right] \quad [7]$$
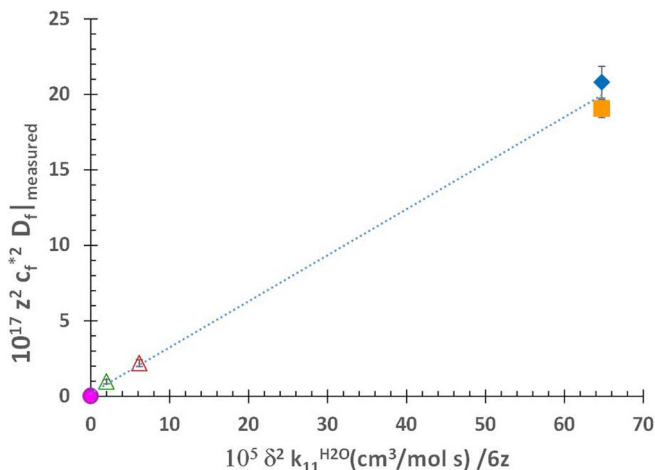
Figure 7. Analysis of the experimental data in Table I for six M(bpy)$_2^{z+}$ complexes in Nafion where z of the complex initially extracted from solution is characterized by $c_{SO_3M}^* = zc_f^*$ in Equation 7. The intercept is consistent with small to negligible D_p. The slope characterizes $ac_{SO_3M}^{*3}$. Regression yields $z^2 c_f^{*2}D_f|_{measured} = (3.05_0 \pm 0.08_7) \times 10^{-13}$ mol^3/cm^9 $\delta^2 k_{11}^{H_2O}/6z + (2._0 \pm 3._3) \times 10^{-18}$ mol^2/cm^{4}s with $R^2 = 0.997$. Each M(bpy)$_3^{3+}$ is labeled as Ru(bpy)$_3^{2+}$ orange square, Os(bpy)$_3^{2+}$ blue diamond, Cr(bpy)$_3^{3+}$ red triangle, Fe(bpy)$_3^{2+}$ green triangle, Co(bpy)$_3^{3+}$ pink solid circle, and Co(bpy)$_3^{2+}$ purple open circle.

A plot of the experimentally determined values $z^2 c_f^{*2}D_f|_{measured}$ versus the known parameters $k_{11}^{H_2O}\delta^2/6z$ yields a slope $ac_{SO_3M}^{*3}$ and an intercept $c_{SO_3M}^{*2}D_p$.

Data in Table I plotted as $z^2 c_f^{*2}D_f|_{measured}$ versus $k_{11}^{H_2O}\delta^2/6z$ are shown in Figure 7 for the six M(bpy)$_3^{z+}$ complexes. Linear regression yields slope of $(3.05_0 \pm 0.08_7) \times 10^{-13}$ mol^3/cm^9 and an intercept of $(2._0 \pm 3._3) \times 10^{-18}$ mol^2/cm^{4}s with a correlation coefficient $R^2 = 0.997$. The strong linear correlation between $z^2 c_f^{*2}D_f|_{measured}$ and $k_{11}^{H_2O}\delta^2/6z$ again denotes D_f dependent on self exchange rate. The intercept is nominally positive but of large uncertainty. The analysis is based on 225 voltammograms with $k_{11}^{H_2O}$ literature self exchange rates in water. Introduction of the z dependence through $c_{SO_3M}^*$ improves the regression statistics over those of $c_f^{*2}D_f|_{measured}$ with $k_{11}^{H_2O}\delta^2/6$ as expressed by R^2, number of statistically significant figures, and the nominally positive intercept. The better regression statistics highlight the importance of z and likely activity effects in the Nafion matrix.

From Equation 7, D_p is estimated as intercept divided by (slope/$a)^{2/3}$, which estimates small D_p (10^{-11} cm^2/s) but with uncertainty greater than the estimate. Because the uncertainty is high and this D_p is greater than D_f for the cobalt complexes, the estimate of the physical diffusion coefficient overstresses the data. It remains that D_p is small. The slope ($ac_{SO_3M}^{*3}$) has better statistical significance (± 2.6 %). For $a = 0.0097$, the slope yields $c_{SO_3M}^* = 3.16 \times 10^{-4}$ mol/cm^3, which estimates $c_{SO_3M}^*/c_f^* = 2.0$ or two sulfonates per M(bpy)$_3^{z+}$. This value of $c_{SO_3M}^*$ found from Figure 7 invokes only differences in the activity in Nafion as compared to dilute solution as $a = 0.0097$. Alternatively, for $c_f^* = N_f^*$ and $c_{SO_3M}^* = zN_f^*$ where z is 2, a similar a of 0.009 is found.

The plot based on Equation 7 fits the data well and yields information consistent with the regression of $c_f^{*2}D_f|_{measured}$ with $k_{11}^{H_2O}\delta^2/6$. The results suggest that the high ionic strength in Nafion leads to $k_{11}^{Naf} < k_{11}^{H_2O}$ and that redox probes are at concentrations near the closed packed limit within the hydrated volumes, $N_{f,aq}^*$. Electron self exchange dominates D_f and the current (flux) of all the M(bpy)$_3^{z+}$ complexes where M^{z+} is Ru^{2+}, Os^{2+}, Cr^{3+}, and Fe^{2+}. Based on

differences in D_f for Co(bpy)$_3^{z+}$, self exchange contributes to D_f for the cobalt complexes as well. Physical diffusion D_p will be the same for all M(bpy)$_3^{z+}$ and is $\lesssim 10^{-12}$ cm^2/s.

It is noted from Figure 7, that taking $k_{11}^{H_2O}$ for Os(bpy)$_3^{2+}$ as equal to $k_{11}^{H_2O}$ for Ru(bpy)$_3^{2+}$ may slightly underestimate $k_{11}^{H_2O}$ for Os(bpy)$_3^{2+}$. For $D_p \ll D_{et}$, $k_{11}^{H_2O}$ for Os(bpy)$_3^{2/3+}$ may be about 8% higher than for Ru(bpy)$_3^{2+}$ or 4.5×10^8/Ms. It is also noted that often Nafion is characterized by an extraction parameter such that $\kappa c_s^* = c_f^* = c_{SO_3M}^*/z$. Substitution of κc_s^* for c_f^* into either Equation 6 or 7 yields an equivalent expression. However, successful analysis similar to the above requires either that κ is known for each complex or that κ is invariant for all complexes.

Summary Depiction of M(bpy)$_3^{z+}$ Environment in Nafion

The above depicts the environment of M(bpy)$_3^{z+}$ inside Nafion. Nafion is biphasic and when exchanged with M(bpy)$_3^{z+}$, contains segregated domains of water and fluorocarbon where the hydrated domain fraction is 17%, calculated from a density of 1.95 g/cm^3 and a nominal equivalent weight of 1100. Effective ion exchange occurs in the water domains where the anionic sulfonic acid sites are at concentration $N_{SO_3,aq}^*$ of 10.4 M, based on aqueous acid base titration. The diameter of M(bpy)$_3^{z+}$ is largely invariant at $\delta = 1.36$ nm, which yields the M(bpy)$_3^{z+}$ volume. Ions are only supported in the higher dielectric constant aqueous domain; the dielectric constant of fluorocarbon of ~ 2 is insufficient to support ions. To maintain electroneutrality in hydrated domains of Nafion, the 10.4 M negative charge of the sulfonates must be charge neutralized by cations. Because the available hydrated volume of Nafion is insufficient to 10.4 M/z M(bpy)$_3^{z+}$, cations of the solution electrolyte extract into the film to complete charge balance for the sulfonates. Based on close packing of spherical M(bpy)$_3^{z+}$, the approximate maximum M(bpy)$_3^{z+}$ concentration in the hydrated domains $N_{f,aq}^*$ is 0.933 M. Because the concentration is volume limited, $N_{f,aq}^*$ is independent of z. Cations of the electrolyte will be at concentration determined by z of M(bpy)$_3^{z+}$. The corresponding concentration of M(bpy)$_3^{z+}$ for the Nafion film, $N_f^* = 0.17 N_{f,aq}^*$. This is sketched in Figure 8.

Cyclic voltammetric data for six different M(bpy)$_3^{z+}$ couples for five different M^{z+} are analyzed to find $c_f^{*2} D_f$. Self exchange is known to enhance measured diffusion coefficient D_f, where $D_f = D_p + D_{et}$. Equation 2 specifies D_{et} as proportional to the self exchange rate k_{11}. Literature values of self exchange rates for M(bpy)$_3^{z+}$ in water $k_{11}^{H_2O}$, M(bpy)$_3^{z+}$ diameter δ, and experimentally determined $c_f^{*2} D_f$ yield an estimate of $D_p \lesssim 10^{-12}$ cm^2/s, which is $\lesssim D_f$ for the cobalt complexes, which have the lowest $k_{11}^{H_2O}$.

The self exchange rates in water are measured at either low ionic strength or at infinite dilution. Because the hydrated domains in Nafion are at high ionic strength (roughly 10 M), it is anticipated that the self exchange rate in Nafion k_{11}^{Naf} is linearly proportional but not equal to $k_{11}^{H_2O}$. For $k_{11}^{H_2O} = a k_{11}^{Naf}$ and the highest allowed M(bpy)$_3^{z+}$ concentration in the film $c_f^* = N_f^*$, $a = 0.010$ is found so that the k_{11}^{Naf} is a hundred fold smaller than $k_{11}^{H_2O}$ and likely reflects activity effects of the Nafion matrix rather than properties of the individual M(bpy)$_3^{z+}$ complexes. The values of D_{et} are proportional to $k_{11}^{H_2O}$ where for Ru(bpy)$_3^{2+}$ and Os(bpy)$_3^{2+}$ $D_f = D_{et} = 2 \times 10^{-9}$ cm^2/s; for Fe(bpy)$_3^{2+}$ and Cr(bpy)$_3^{3+}$ $D_f = D_{et} = 1 \times 10^{-10}$ cm^2/s; and for Co(bpy)$_3^{2+}$ and Co(bpy)$_3^{3+}$ D_f is 1.5×10^{-12} and 5×10^{-12} cm^2/s, statistically distinct and slightly larger than D_p. The magnitude of D_f tracks $k_{11}^{H_2O}$ linearly. Thus, flux (current) of M(bpy)$_3^{z+}$ is augmented by self exchange of the highly concentrated M(bpy)$_3^{z+}$ in the hydrated domains of Nafion.

List of Symbols

| Symbol	Description
A (cm^2)	electrode cross section area
a	proportionality constant, $k_{11}^{Naf} = a k_{11}^{H_2O}$
c^* (moles/cm^3)	concentration
$c_{electrolyte}^*$ (moles/cm^3)	electrolyte concentration in solution
c_f^* (moles/cm^3)	probe concentration in film
c_s^* (moles/cm^3)	probe concentration in solution
D (cm^2/s)	diffusion coefficient
D_{et} (cm^2/s)	electron hopping diffusion coefficient
D_f (cm^2/s)	measured probe diffusion coefficient in film
D_p (cm^2/s)	physical diffusion coefficient of probe in film
d (g/cm^3)	density of Nafion film
i_p (A)	cyclic voltammetric forward peak current
$EQWT$ (g/mol)	equivalent weight of ion exchange polymer
k_{11} (M^{-1}s^{-1})	Self exchange rate
$k_{11}^{H_2O}$ (M^{-1}s^{-1})	Self exchange rate in H$_2$O
k_{11}^{Naf} (M^{-1}s^{-1})	Self exchange rate in Nafion
ℓ (cm)	film thickness
N_f^* (M)	maximum concentration M(bpy)$_3^{z+}$ in Nafion film
$N_{f,aq}^*$ (M)	maximum concentration M(bpy)$_3^{z+}$ in hydrated domain
$N_{SO_3,aq}^*$ (M = mmol/cm^3)	sulfonate concentration in hydrated domain
$N_{SO_3M}^*$ (M)	maximum concentration M(bpy)$_3^{z+}$ bound SO$_3^-$ in Nafion film
$N_{SO_3M,aq}^*$ (M)	maximum concentration M(bpy)$_3^{z+}$ bound SO$_3^-$ in hydrated domain
v (V/s)	cyclic voltammetric potential scan rate
$v_{aq}; v_{CF_2}$	volume fractions of hydrated and fluorocarbon; $1 = v_{aq} + v_{CF_2}$
z	probe charge
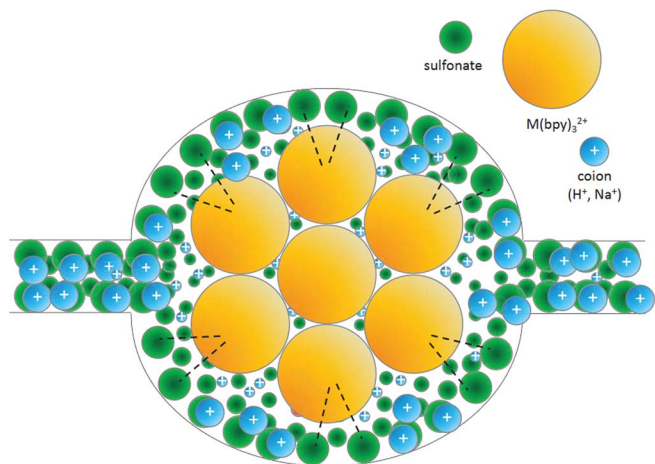
Figure 8. A sketch of the environment in M(bpy)$_3^2$ inside a 5 nm hydrated domain of Nafion.

Greek

δ (nm)	diameter of probe; for $M(bpy)_3^{z+}$, 1.36 nm
δ_{M-M}	center to center distance for $M(bpy)_3^{z+}$
δ_{gap}	edge to edge gap between $M(bpy)_3^{z+}$
δ_0 (cm)	diffusion length proportional to $\sqrt{Dt}$
κ	ratio initial concentrations, $\kappa = c_f^*/c_s^*$

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