



Article

Electrochemical Characterization of Recast Nafion[®] Film-Modified Electrodes in Acetonitrile with Various Electrolytes

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Abstract: Nafion[®] is a cation exchange polymer that is commonly used in aqueous energy applications such as fuel cells due to its ability to exclude anions and neutral molecules and increase apparent diffusion of cationic redox molecules. However, this behavior is not well studied in nonaqueous solutions. The behavior of platinum electrodes modified with recast Nafion[®] films in nonaqueous solutions was observed to be different from its well-studied behavior in aqueous solutions. The reversible redox couple tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate was studied in the nonaqueous, aprotic solvent acetonitrile with different electrolytes (tetrabutylammonium tetrafluoroborate, tetrabutylammonium trifluoromethanesulfonate, tetrabutylammonium hexafluorophosphate, and ammonium trifluoromethanesulfonate) using cyclic voltammetry and rotating disk voltammetry. An unmodified platinum electrode in the nonaqueous systems and a recast Nafion[®]-modified platinum electrode equilibrated in an aqueous solution of tris(bipyridine)ruthenium(II)chloride hexahydrate were used as controls. Results indicate that the polymer structure in acetonitrile conditions does not allow apparent (Dahms–Ruff) diffusion but does allow significant physical diffusion that would make Nafion a great immobilization option for modifying electrodes with catalysts in nonaqueous systems.

Keywords: polymer-modified electrode; nonaqueous electrochemistry; acetonitrile voltammetry; recast Nafion film



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1. Introduction

Nafion is a co-polymer that consists of a polytetrafluoroethylene backbone with perfluorosulfonate pendant groups [1–8]. In aqueous systems, it is a cation exchange polymer often used in fuel cells as a separator between the anode and cathode compartments and in electrochemical reactions to promote the diffusion of an electrochemically active species to the electrode surface [1–3]. Electron transfer within aqueous Nafion films is acknowledged to occur by two main mechanisms: direct diffusion and apparent diffusion (Dahms–Ruff self-exchange through electron hopping) [1–4]. Unlike direct diffusion, electron hopping is a multistep process mediated by redox couple intermediates. The mechanism utilized by a film for electron transfer is dependent on its structure [1–4]. Nafion films establish a unique structure in aqueous solutions that promotes electron hopping; the perfluorosulfonate pendants form micellar structures that exchange protons for other cations. Cationic redox couples exchange into the hydrophilic, micellar pockets of the film and exchange electrons with each other, which leads to a faster apparent diffusion (observed via current) than physical diffusion to the electrode surface [1–4].

Nafion has been mostly studied in aqueous conditions, although there have been a few studies in nonaqueous conditions: The density and solubility of Nafion in a few solvents, including both water and acetonitrile, were studied [5]. The ionic conductivity and swelling of the polymer were studied in several solvents, including methanol, dimethylsulfoxide, N-methylformamide, triethyl phosphate, and γ -butyrolactone electrolytes; conductivity and swelling were also measured when the polymer was exchanged with several cations, including H^+ and NH_4^+ [9]. The ion exchange capacities of Nafion in propylene carbonate

and dimethoxyethane were studied to consider Nafion as a separator for lithium-ion batteries [9]. A recent study of lanthanide electrochemistry found that Nafion could be a useful polymer in applications with acetonitrile as the solvent [10]. However, there has been no in-depth electrochemical characterization of Nafion in acetonitrile until now. Acetonitrile is used as the solvent in some applications of organic redox flow batteries [11,12], electrosynthesis [13], and electrocatalysis [10,14]. A better understanding of Nafion in acetonitrile is necessary to consider its use in these applications as a separator or immobilization agent.

Here, the behavior of recast Nafion[®] films on platinum working electrodes is characterized by cyclic voltammetry and rotating disk voltammetry. Fundamental aspects of Nafion[®] membranes under nonaqueous media, especially the ion transport mechanism through the membrane, are unclear [7,10]. To bridge this gap, the behavior of Nafion[®] membranes was characterized in different nonaqueous environments. Platinum electrodes modified with recast Nafion[®] 117 films were analyzed in nonaqueous conditions (acetonitrile) with four nonaqueous electrolytes. Unmodified electrodes and Nafion-modified electrodes in aqueous (nitric acid electrolyte) conditions were analyzed as controls. Studies of each electrolyte variation involved both transient cyclic voltammetry and rotating disk voltammetry; the relationship between scan rate and peak current was explored for transient cyclic voltammograms and the relationship between rotation rate and limiting current was explored for rotating disk voltammetry.

From the results, mass transport in Nafion films in acetonitrile conditions is dominated by physical diffusion rather than apparent diffusion. This physical diffusion rate is much faster than physical diffusion in aqueous conditions. Thus, Nafion could have excellent applications in redox flow battery technologies or as an immobilization polymer for catalysts in nonaqueous electrosynthesis.

2. Materials and Methods

A three-electrode setup was utilized for all conditions: a platinum rotating disk working electrode (geometric area 0.196 cm²), a platinum mesh counter electrode, and the corresponding aqueous or nonaqueous reference electrode. A calomel reference electrode (SCE) was used for aqueous conditions, and a Ag/Ag⁺ quasi-reference electrode was used for nonaqueous conditions. The potential shift of the quasi-reference electrode was determined by analysis of the ferrocene/ferrocenium couple at the end of each trial; ferrocene was injected at the end of each set of measurements and the half potential ($E_{1/2}$) from a 100 mV/s cyclic voltammogram was used to normalize the data versus the Normal Hydrogen Electrode (NHE), where the standard reduction potential of ferrocene/ferrocenium is +0.64 V vs. NHE.

Before each measurement, the surface of the working electrode was polished successively with 0.3-, 0.1-, and 0.05-micron aluminum oxide polishing slurry, then rinsed with the corresponding solvent (either acetonitrile or 18 M Ω deionized water). The working electrode was modified with a recast Nafion[®] film by spin casting. Using a calibrated micropipette, 2 μ L of 5% Nafion[®] 117 dissolved in a mixture of lower aliphatic alcohols and water was pipetted onto the platinum surface of the electrode. The film was then spun at 700 RPM for 20 min and allowed to dry overnight.

All nonaqueous investigations used redox probe 1 mM tris(2,2'-bipyridine)ruthenium (II)hexafluorophosphate ([Ru(bpy)₃](PF₆)₂) and 0.1 M electrolyte dissolved in acetonitrile ($\geq 99.9\%$). To analyze the behavior of the polymer film in electrolyte, four different electrolytes were investigated: tetrabutylammonium tetrafluoroborate (TBABF₄), ammonium trifluoromethanesulfonate (NH₄CF₃SO₃), tetrabutylammonium trifluoromethanesulfonate (TBACF₃SO₃), and tetrabutylammonium hexafluorophosphate (TBAPF₆). All aqueous systems used redox probe 1 mM tris(bipyridine)ruthenium(II) chloride hexahydrate ([Ru(bpy)₃]Cl₂·6H₂O) and 0.1 M nitric acid. All reagents were obtained from Sigma Aldrich, St. Louis, MO, USA.

Following a 30 min sparging of a solution with N₂(g), the working electrode was equilibrated in the solution while maintaining a nitrogen blanket. During this time, cyclic

voltammograms were taken (Pine Research potentiostat 700E) every 30 min at 5 mV/s. Once equilibration (no change >1% in forward peak current) was achieved, 10 replicate cyclic voltammograms were taken at various scan rates (5, 10, 20, 50, and 100 mV/s) in random order. The cyclic voltammograms are plotted in polarographic convention, such that higher potentials are on the left and lower potentials are on the right; oxidative currents are negative and reductive currents are positive. Rotating disk voltammetry at 10 mV/s was conducted at various rotation rates (0, 2, 5, 10, 50, 200, 600, 1200, and 1800 RPM) in random order. All solutions were sparged with N₂(g) between scans to ensure an anaerobic environment.

3. Results

3.1. Equilibration Studies

Equilibration of the redox probe into the Nafion film was analyzed by measuring peak current (i_p) from a 5 mV/s cyclic voltammogram (taken every 30 min) for each system until i_p reached a steady value (<1% difference in peak current) for three consecutive cyclic voltammograms. Figure 1 shows an overlay of pre-equilibration and post-equilibration cyclic voltammograms for the well-studied aqueous system [6], while Figure 2 shows overlays of pre- and post-equilibration cyclic voltammograms for each nonaqueous system. It is well established that in aqueous systems, cationic molecules diffuse into the hydrophilic pockets of the Nafion film during the equilibration period; i_p will increase over time and eventually be larger than the current for an unmodified electrode. The concentration of redox molecules inside the film is often larger than the solution concentration, and electron hopping between molecules allows for Dahms–Ruff apparent diffusion, which is faster than physical diffusion in solution [2]. This behavior was confirmed here; i_p increased over the equilibration time for Nafion[®]-modified electrodes in 0.1 M nitric acid as the Ru(bpy)₃²⁺ exchanges into the Nafion[®] film until equilibrium was reached. The final i_p was significantly higher than that observed for an unmodified electrode in the same solution. It took an average of 10 h for each film to equilibrate in the aqueous solution.

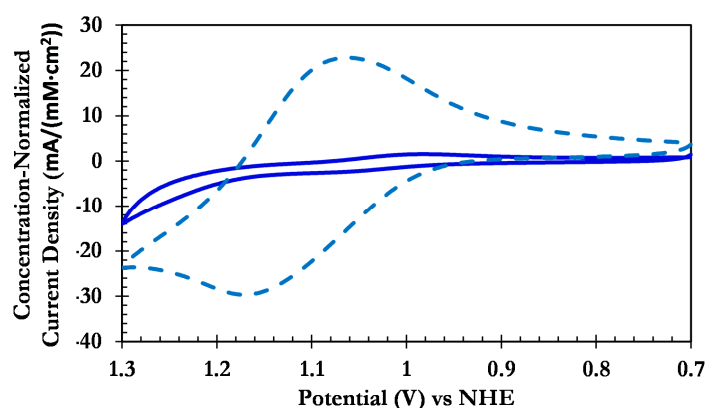


Figure 1. Overlaid 5 mV/s cyclic voltammograms for pre-equilibration (solid lines) and post-equilibration (dashed lines) for platinum working electrode modified with Nafion film, platinum mesh counter electrode, and saturated calomel reference electrode (converted to potentials vs. NHE) with 1 mM tris(bipyridine)ruthenium(II)chloride hexahydrate redox probe in aqueous 0.1 M nitric acid electrolyte. Data are normalized by redox molecule concentration (which varied between 0.993 and 1.03 mM) to eliminate effects of concentration on current.

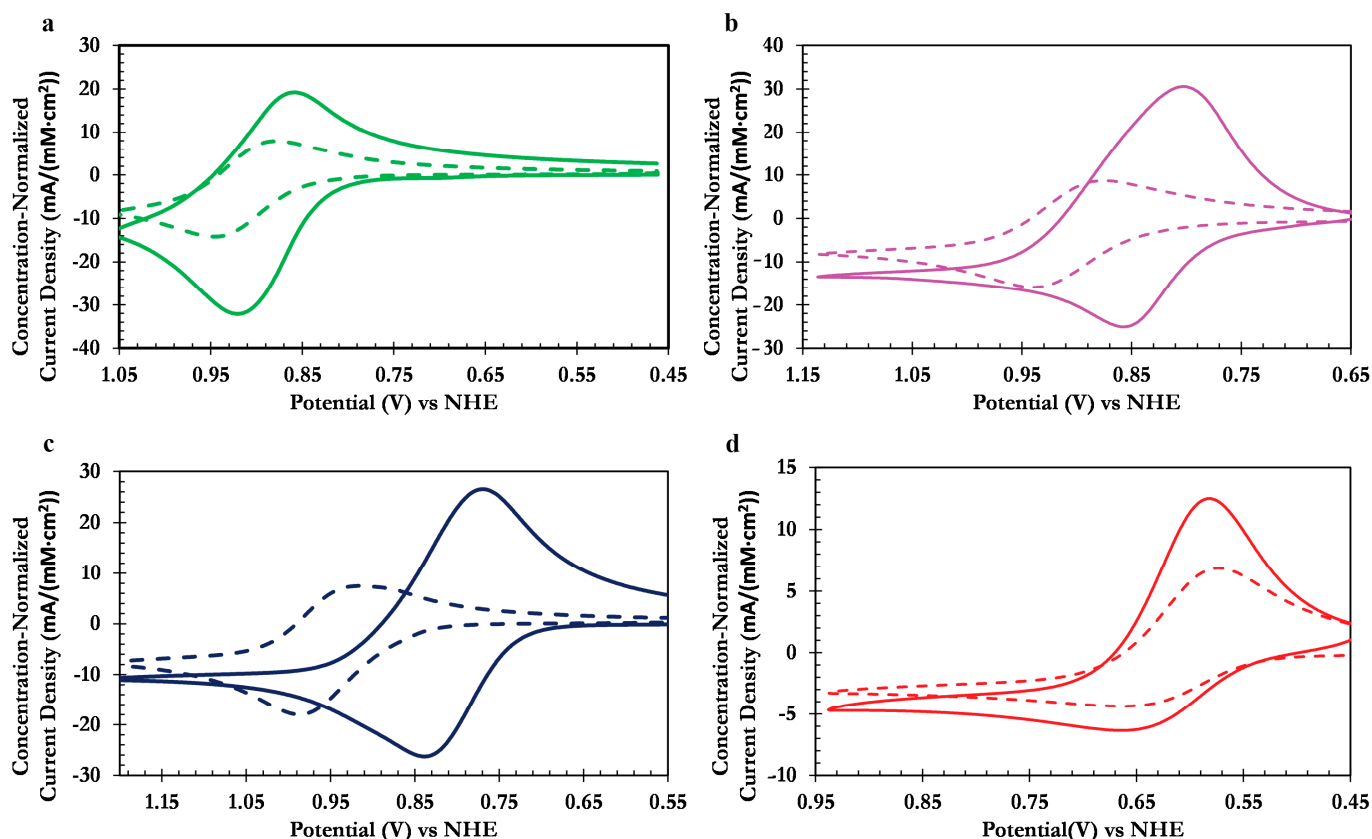


Figure 2. Overlaid 5 mV/s cyclic voltammograms pre-equilibration (solid lines) and post-equilibration (dashed lines) for platinum working electrode modified with Nafion film, platinum mesh counter electrode, Ag/Ag⁺ quasi-reference electrode calibrated to vs. NHE by Fc/Fc⁺ redox couple, 1 mM tris(2,2'-bipyridine)ruthenium(II)hexafluorophosphate redox probe, and 0.1 M electrolyte where the electrolyte is (a) TBA triflate, (b) TBABF₄, (c) TBAPF₆, and (d) NH₄ triflate. Data are normalized by redox molecule concentration (which varied between 0.9701 and 1.009 mM) to eliminate effects of concentration on current.

By contrast, currents generally decreased over the equilibration time for Nafion[®]-modified electrodes in acetonitrile systems, suggesting a change in the internal structure of the Nafion[®] film upon exposure to acetonitrile. The equilibration time was also significantly shorter, taking an average of two hours for each film. The mean oxidative peak current ($i_{p,ox}$) and reductive peak current ($i_{p,red}$) values $\pm$ standard deviation (triplicate electrodes measured three times at each scan rate) for pre- and post-equilibration cyclic voltammograms are listed for all systems for electrodes modified with Nafion and unmodified electrodes in Table 1. With tetrabutylammonium trifluoromethanesulfonate (TBA triflate) electrolyte, $i_{p,ox}$ decreased from $(-30.9 \pm 0.9) \mu\text{A}$ pre-equilibration to $(-13.6 \pm 0.5) \mu\text{A}$ post-equilibration. The reversibility of the reaction also changed. The pre-equilibration cyclic voltammogram had a peak current ratio $i_{p,ox}/i_{p,red}$ of 1.89, which is quasi-irreversible; post-equilibration, the ratio was 1.36. This is a 28% change in the ratios. With tetrabutylammonium tetrafluoroborate (TBABF₄) electrolyte, $i_{p,ox}$ decreased from $(-16 \pm 3) \mu\text{A}$ to $(-14.3 \pm 0.5) \mu\text{A}$. The pre-equilibration cyclic voltammogram had a peak current ratio of 0.80; post-equilibration, the ratio was 1.10. This is a 32% change in the ratios. With tetrabutylammonium hexafluorophosphate (TBAPF₆) electrolyte, $i_{p,ox}$ decreased from $(-25.7 \pm 0.9) \mu\text{A}$ to $(-17.3 \pm 0.6) \mu\text{A}$. The pre-equilibration cyclic voltammogram had a peak current ratio of 0.76; post-equilibration, the ratio was 1.43. This is an 88% change in the ratios. In systems with unmodified electrodes, pre- and post-equilibration $i_{p,ox}$ did not change significantly, nor did the $i_{p,ox}/i_{p,red}$ ratios; changes were at most 7%. With ammonium trifluoromethanesulfonate (NH₄ triflate) electrolyte, $i_{p,ox}$ decreased from

(-8.7 ± 0.5) μA to (-7.2 ± 0.4) μA . The pre-equilibration cyclic voltammogram had a peak current ratio of 2.09; post-equilibration, the ratio was 4.01. This is a 92% change in the ratios, but in the other direction from the other electrolytes; in the case of the NH_4 triflate electrolyte, the redox reaction becomes more irreversible after equilibration. With nitric acid electrolyte (aqueous), the forward peak current $i_{p,ox}$ increased from (-4.70 ± 0.06) μA to (-23.4 ± 0.8) μA . The pre-equilibration cyclic voltammogram had a peak current ratio of 1.48; post-equilibration, the ratio was essentially unchanged at 1.50 (a 1.3% change in the ratios).

Table 1. Peak oxidative ($i_{p,ox}$) and peak reductive ($i_{p,red}$) concentration-normalized current densities with units of $\text{mA}/(\text{mM}\cdot\text{cm}^2)$ for each electrolyte system with modified and unmodified electrodes before equilibration and after equilibration.

	Pre-Equilibration			Post-Equilibration			Change
	$i_{p,ox}$	$i_{p,red}$	$i_{p,ox}/i_{p,red}$	$i_{p,ox}$	$i_{p,red}$	$i_{p,ox}/i_{p,red}$	
NH_4 Triflate Nafion Film	-8.7 ± 0.5	4.2 ± 0.2	2.1	-7.2 ± 0.4	1.8 ± 0.5	4.0	92%
NH_4 Triflate Unmodified	-13.8 ± 0.6	13.3 ± 0.5	1.03	-13.9 ± 0.8	13.1 ± 0.7	1.06	2.0%
TBA Triflate Nafion Film	-30.9 ± 0.9	16.4 ± 0.5	1.89	-13.6 ± 0.5	9.9 ± 0.3	1.4	28%
TBA Triflate Unmodified	-13.8 ± 0.5	13.5 ± 0.4	1.03	-13.7 ± 0.5	13.6 ± 0.2	1.01	1.7%
TBAPF ₆ Nafion Film	-25.7 ± 0.9	34 ± 2	0.76	-17.3 ± 0.6	12.1 ± 0.3	1.43	88%
TBAPF ₆ Unmodified	-15.8 ± 0.6	14.8 ± 0.5	1.07	-13.8 ± 0.9	12.2 ± 0.7	1.13	6.0%
TBABF ₄ Nafion Film	-16 ± 3	23 ± 1	0.80	-14.3 ± 0.5	13.4 ± 0.2	1.10	32%
TBABF ₄ Unmodified	-14.9 ± 0.5	13 ± 1	1.1	-13.8 ± 0.2	13.3 ± 0.2	1.04	7.2%
Nitric Acid Unmodified	-10.85 ± 0.06	11.2 ± 0.2	0.97	-6.8 ± 0.2	7.1 ± 0.4	1.08	7.3%
Nitric Acid Nafion Film	-4.70 ± 0.06	4.93 ± 0.06	1.48	-23.4 ± 0.8	17.01 ± 0.05	1.50	1.3%

For the TBA cation electrolytes, there is a general shift from higher pre-equilibrium current density to lower post-equilibrium current density. This may indicate that the Nafion film initially retains some of its aqueous structure, with hydrophilic micellar pockets of sulfonate groups that attract the redox probe and prevent the oxidized species from diffusing out. But during the equilibration period, this structure collapses and diffusion is limited to physical diffusion. In TBABF₄ and TBAPF₆, the cyclic voltammograms become less reversible after equilibration, which may be because there is no longer interaction with the sulfonate pockets that leads to quasi-irreversible behavior. In TBA triflate, there is a more reversible redox reaction post-equilibration, likely because of the structural similarity between the sulfonate pendant groups and the triflate anion.

For electrolytes that have triflate anions, $E_{1/2}$ did not significantly shift from pre-equilibration to post-equilibration. However, for electrolytes with other anions, a shift was observed. All values are provided in Table 2 below. With TBABF₄, $E_{1/2}$ shifted from 0.894 V pre-equilibration to 0.972 V post-equilibration, a shift of 78 mV. With TBAPF₆, $E_{1/2}$ shifted from 1.279 V pre-equilibration to 1.426 V post-equilibration, a shift of 197 mV. No shift in $E_{1/2}$ is observed for unmodified electrodes, and their $E_{1/2}$ s reflect the $E_{1/2}$ s of the post-equilibration Nafion-modified cyclic voltammograms. The sulfonate pendant groups in Nafion have a very similar structure to the triflate anion; thus, there is no shift in ligand energies when the cations intercalate into the polymer. For other anions, there is expected to be a shift in ligand energies upon intercalation [10].

Table 2. Peak potentials, difference in peak potentials, and half potentials for each Nafion film-modified system pre-equilibration and post-equilibration, and the potential shift between pre- and post-equilibration. Mean potentials for triplicate measurements are reported; relative standard deviations are less than 1% for all.

	E_f (V)	Pre-Equilibration			E_f (V)	Post-Equilibration			Shift (V)
		E_r (V)	ΔE (V)	$E_{1/2}$ (V)		E_r (V)	ΔE (V)	$E_{1/2}$ (V)	
NH_4 triflate	0.661	0.593	0.068	0.627	0.662	0.535	0.091	0.599	-0.029
TBA triflate	0.926	0.864	0.062	0.895	0.942	0.883	0.069	0.913	+0.018

Table 2. Cont.

	E_f (V)	Pre-Equilibration		$E_{1/2}$ (V)	E_f (V)	Post-Equilibration		$E_{1/2}$ (V)	Shift (V)
		E_r (V)	ΔE (V)			E_r (V)	ΔE (V)		
TBAPF ₆	0.834	0.741	0.093	0.786	0.991	0.920	0.071	0.956	+0.168
TBABF ₄	0.855	0.786	0.069	0.821	0.941	0.875	0.066	0.908	+0.088
Nitric acid	1.083	0.989	0.094	1.036	1.171	1.063	0.108	1.117	+0.081

3.2. Scan Rate Studies

Figure 3 shows an overlay of post-equilibration cyclic voltammograms for Nafion-modified and unmodified electrodes in 0.1 M nitric acid while Figure 4 shows overlays of post-equilibration 50 mV/s cyclic voltammograms for Nafion-modified and unmodified electrodes in each electrolyte in acetonitrile. The current for aqueous Nafion-modified electrodes has significantly higher current density than the various nonaqueous conditions tested. The oxidative peak current for a Nafion electrode in aqueous conditions increased to $-104 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ from $-26.7 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ for an unmodified electrode. This observation is consistent with the behavior of Nafion[®] in aqueous environments outlined in previous studies; Dahms–Ruff apparent diffusion contributes to higher currents than the same concentration of redox molecule without a Nafion film [1,2].

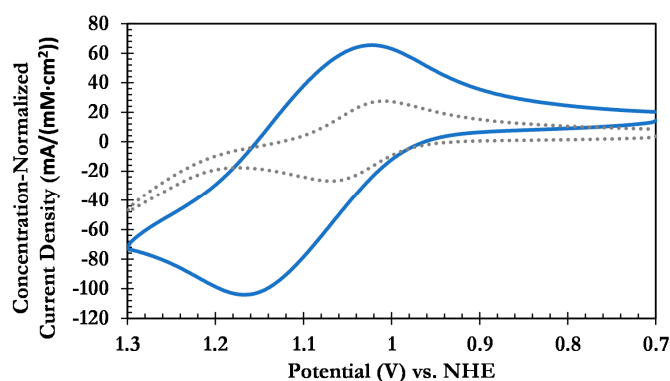


Figure 3. Overlaid 50 mV/s cyclic voltammograms for electrodes modified with Nafion film (solid line) and unmodified (dotted line), platinum mesh counter electrode, and saturated calomel reference electrode (converted to potentials vs. NHE) with 1 mM tris(bipyridine)ruthenium(II)chloride hexahydrate redox probe in aqueous 0.1 M nitric acid electrolyte. Data are normalized by redox molecule concentration (which varied between 0.993 and 1.03 mM) to eliminate the effects of concentration on current.

The Nafion-modified cyclic voltammogram for NH₄ triflate has a smaller current density for the oxidative and reductive peaks than the unmodified electrode. The oxidative peak decreased to $-20.2 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ from $-42.1 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ and the reductive peak decreased to $11.9 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ from $30.4 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$. For TBA electrolyte acetonitrile systems, the peak currents are very similar with or without Nafion films. For TBA triflate, the current density of the oxidative peak was found to be $-40.9 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ for Nafion-modified and $-42.5 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ for unmodified. For TBAPF₆, the current density of the oxidative peak was found to be $-43.4 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ for Nafion-modified and $-41.4 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ for unmodified. For TBABF₄, the current density of the oxidative peak was found to be $-47.1 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ for Nafion-modified and $-48.7 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ for unmodified. The current density of the reductive peak was found to be $31.8 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ for coated and $28.7 \text{ mA}/(\text{mM}\cdot\text{cm}^2)$ for unmodified. This similarity indicates that the higher pre-equilibration currents observed must be due to the Nafion briefly retaining its micellar structure before expelling any exchanged redox probes and changing structure.

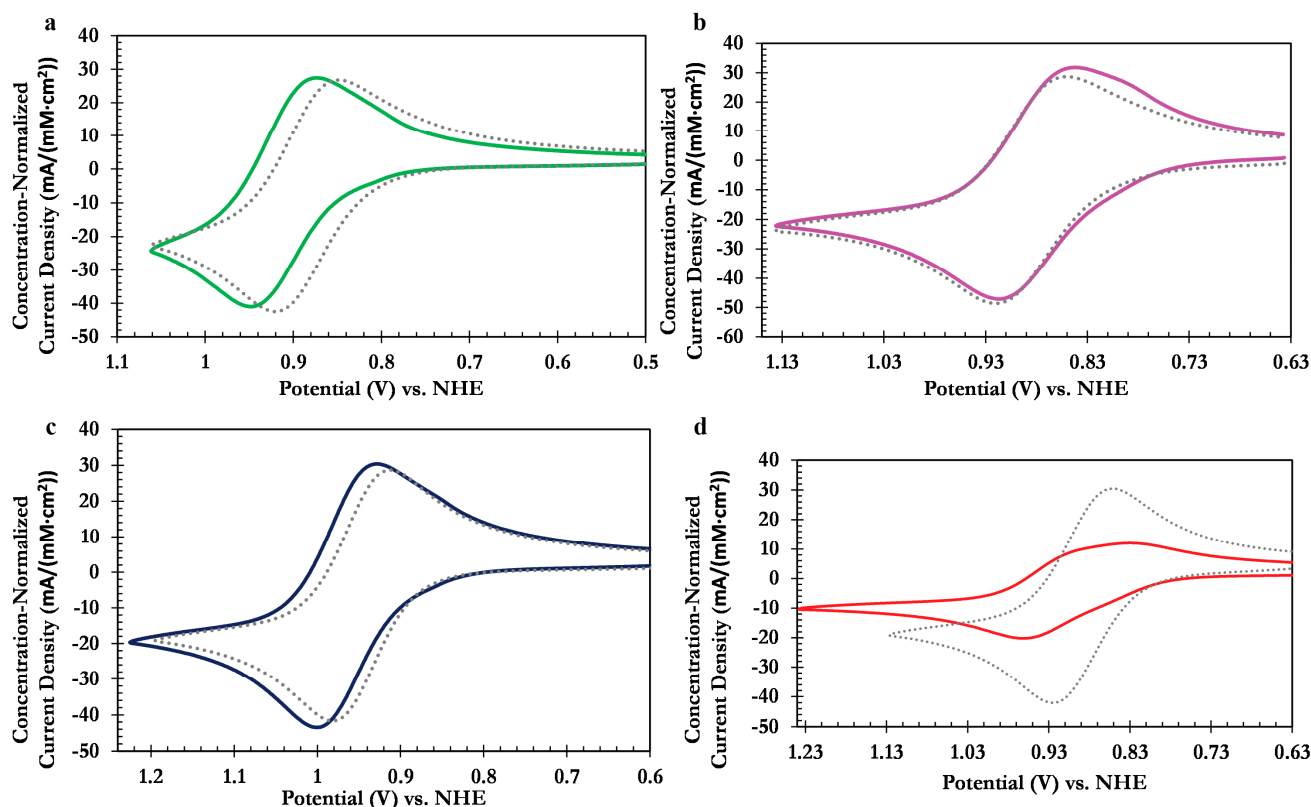


Figure 4. Overlaid 50 mV/s cyclic voltammograms for platinum working electrodes modified with Nafion film (solid line) and unmodified (dotted line), platinum mesh counter electrode, Ag/Ag⁺ quasi-reference electrode calibrated to vs. NHE by Fc/Fc⁺ redox couple, 1 mM tris(2,2'-bipyridine)ruthenium(II)hexafluorophosphate redox probe, and 0.1 M electrolyte where the electrolyte is (a) TBA triflate, (b) TBABF₄, (c) TBAPF₆, and (d) NH₄ triflate. Data are normalized by redox molecule concentration (which varied between 0.982 and 0.992 mM) to eliminate the effects of concentration on current.

Plots of peak current i_p vs. the square root of the scan rate v are useful in the characterization of mass transport. The relationship between peak current and scan rate is outlined in the Randles–Sevcik equation (Equation (1)) [15–18]. For a reversible electron transfer reaction where there is solution-based mass transport (the redox molecule is not surface-bound), the peak current i_p will increase in magnitude linearly as a function of the square root of the scan rate v . The magnitude is affected by the number of electrons n , the electrode area A , the redox molecule concentration C , and the diffusion coefficient D . Deviations from linearity are indicative of complications in the kinetics of the observed electron transfer.

$$i_p = 2.69 \times 10^5 n^{2/3} A D^{1/2} C v^{1/2} \quad (1)$$

The linearity of peak current versus square root of the scan rate observed for all conditions, unmodified and Nafion[®]-modified electrodes in both aqueous and nonaqueous solutions, suggests that a diffusion-controlled process is occurring, not a surface adsorbed process. The linear regression calculated for each condition can be found in Table 3. The larger slope for Nafion[®]-modified electrodes in aqueous conditions is expected given previous work establishing Dahms–Ruff apparent diffusion by electron hopping [1,2]. Voltametric currents of transition metal complexes, such as Ru(bpy)₃, in films on electrodes are known to increase with electron self-exchange. This form of long-distance electron transfer is aided by the hydrophilic pockets formed in aqueous solutions as previously identified. Alternately, the very small (but statistically significant) differences between the peak currents recorded for unmodified electrode conditions and Nafion[®]-modified electrodes in

nonaqueous solutions indicate that electron hopping does not occur in nonaqueous Nafion[®] films. Instead, the likely mode of action in these films is the direct, physical diffusion of electrons across the film, where the film is much less viscous than it is in aqueous conditions due to swelling.

Table 3. Linear regression data (using the least-squares method) for peak currents versus square root of scan rate. u_m is the standard uncertainty of the slope and u_b is the standard uncertainty of the y-intercept.

	Slope ($\mu\text{A}/\sqrt{\text{V/s}}$)	u_m	Intercept (μA)	u_b	R^2
NH ₄ Triflate Nafion Film	−2.48	0.05	−1.9	0.3	0.9990
NH ₄ Triflate Unmodified	−5.96	0.05	0.9	0.3	0.9998
TBA Triflate Nafion Film	−5.20	0.05	−2.5	0.3	0.9997
TBA Triflate Unmodified	−5.83	0.01	−0.42	0.06	1.0000
TBAPF ₆ Nafion Film	−5.64	0.05	−1.7	0.3	0.9998
TBAPF ₆ Unmodified	−5.51	0.01	−1.97	0.03	1.0000
TBABF ₄ Nafion Film	−6.26	0.06	0.5	0.4	0.9997
TBABF ₄ Unmodified	−6.08	0.07	−0.8	0.4	0.9996
Nitric Acid Nafion Film	−13.54	0.06	−2.6	0.5	0.9999
Nitric Acid Unmodified	−4.13	0.04	−0.13	0.2	0.9999

Cyclic voltammograms for the NH₄ triflate electrolyte had lower peak currents and less steep slopes than cyclic voltammograms with the electrolytes containing TBA ion. This suggests that in the presence of the large TBA cation Nafion[®] preferentially forms structures conducive to mass transport of the redox molecule. Due to this higher current capacity, TBA⁺ salts are commonly used in acetonitrile solutions [7,19]. For TBABF₄ and TBAPF₆, the slope is slightly (statistically significant at a 95% confidence level using *t*-tests) higher for Nafion-modified electrodes than for unmodified electrodes. For NH₄ triflate, the slope is larger for the unmodified electrode. Interestingly, the TBA triflate also shows a larger slope for the unmodified electrode over the Nafion-modified electrode. The triflate anion may interact with the polymer's sulfonate pendant groups to keep more of the dense, micellar structure of the aqueous Nafion than when there is no triflate anion present. The linearity of the peak current versus square root of scan rate plots indicates that there is no surface-bound diffusion, so physical diffusion through the polymer is occurring at a rate not limited by the time scale of the scan rate. Given that Nafion films are less dense in acetonitrile [5], it is logical that a faster physical diffusion rate can be achieved. The peak currents for the acetonitrile systems are much higher post-equilibration than those in the pre-equilibration aqueous system (during pre-equilibration in an aqueous system, there will only be physical diffusion and no electron hopping), also confirming that a higher physical diffusion rate is achieved.

3.3. Rotating Disk Studies

When an electrode is rotated in solution, fluid (redox probe, electrolyte, and solvent) immediately near the electrode surface is carried with the electrode such that a stagnant layer is established at the electrode surface in which steady-state diffusion occurs [3,15–18,20]. The Levich equation (Equation (2)) describes the relationship between the limiting current i_L and the square root of the rotation rate, where n is the number of electrons, F is the Faraday constant, A is the area of the electrode, D is the diffusion coefficient, ω is the rotation rate, ν is the kinematic viscosity, and c is the concentration of redox probe.

$$i_L = 0.620nFAD^{2/3}\omega^{1/2}\nu^{-1/6}c \quad (2)$$

Levich plots of limiting current (i_L) versus the square root of the rotation rate (ω) and Koutecky–Levich plots of inverse limiting current versus the inverse square root of the rotation rate were used to examine the rotating disk data, and the method for determining

the thickness of uniform films reported by Knoche et al. was used to compare the relative thicknesses of Nafion in the acetonitrile versus aqueous systems [16,20]. The Levich slopes and calculated film thicknesses are reported in Table 4. As expected, Koutecky–Levich plot slopes were statistically similar for modified and unmodified electrodes in each system [20], confirming that the measurement parameters were appropriate for the analysis.

Table 4. Linear regression data (using the least-squares method) for Levich plots of rotating disk data (limiting currents versus square root of rotation rate) and calculated film thicknesses. u_m is the standard uncertainty of the slope and u_b is the standard uncertainty of the y-intercept.

	Levich Slope ($\mu\text{A}/\sqrt{\text{rad/s}}$)	u_m	Intercept (μA)	u_b	R^2	Film Thickness (μm)
NH ₄ Triflate Nafion Film	6.87	0.04	1	2	0.9989	3.1 ± 0.4
NH ₄ Triflate Unmodified	14.06	0.05	−0.8	2	0.9998	----
TBA Triflate Nafion Film	12.92	0.05	0.6	1	0.9965	4.9 ± 0.6
TBA Triflate Unmodified	12.68	0.03	1	2	0.9997	----
TBAPF ₆ Nafion Film	13.64	0.05	−1	5	0.9896	4.9 ± 0.5
TBAPF ₆ Unmodified	13.57	0.02	0.5	1	0.9999	----
TBABF ₄ Nafion Film	16.34	0.01	4	3	0.9978	5.9 ± 0.7
TBABF ₄ Unmodified	15.97	0.01	−2	3	0.9986	----
Nitric Acid Nafion Film	1.06	0.03	2	1	0.9998	0.77 ± 0.09
Nitric Acid Unmodified	6.79	0.02	0.03	0.09	0.9999	----

The difference in Levich slopes between Nafion[®]-modified and unmodified electrodes in aqueous conditions is expected given that electron hopping is known to occur in Nafion[®] in aqueous conditions and, thus, there is an additional effect beyond steady-state mass transport. The slopes for Nafion[®]-modified and unmodified electrodes in acetonitrile with TBA salts have small (but still statistically significant at a 95% confidence level using *t*-tests) differences between each other, which can be accounted for by the viscosity difference between the film and solution. Calculated film thicknesses confirm that Nafion swells significantly more in acetonitrile than in aqueous solutions [5]. Film thicknesses in acetonitrile with TBA electrolytes ranged between 4.9 and 5.9 μm , whereas the calculated film thickness for the film in water with nitric acid was 0.77 μm . The films swelled to almost six times the thickness in acetonitrile compared to aqueous solution, which is consistent with previous studies of Nafion swelling in acetonitrile [5,9]. The decrease in density (and thus viscosity) explains the significant increase in physical diffusion rates through the films in acetonitrile.

4. Discussion

The behavior of Nafion-modified electrodes has been observed to differ between aqueous (nitric acid electrolyte) and nonaqueous (acetonitrile) solutions. The results of the equilibration study suggest that Nafion[®] does not exchange redox molecules in the same manner in nonaqueous solutions and likely has a different structure in acetonitrile systems; this structure may be heavily influenced by the cations and anions of the electrolyte choice [2,10]. Currents generally decreased from pre-equilibration to post-equilibration for Nafion[®]-modified electrodes in acetonitrile systems, suggesting a change in the internal structure of the Nafion[®] film upon exposure to acetonitrile. The equilibration time was also significantly shorter, taking an average of two hours for each film. The peak currents for the acetonitrile systems are much higher post-equilibration than those in the pre-equilibration aqueous system (during pre-equilibration in an aqueous system, there will only be physical diffusion and no electron hopping), also confirming that a higher physical diffusion rate is achieved.

The similarity between unmodified and Nafion-modified electrodes in acetonitrile systems post-equilibration indicates that the higher pre-equilibration currents observed must be due to the Nafion briefly retaining its micellar structure before expelling any exchanged redox probes and changing structure. Scan rate studies suggest that mass transport across the films is still solution-based. Film thicknesses calculated from rotating disk experiments indicated that Nafion films swell to almost six times greater thickness

in acetonitrile versus water, which aligns with previous studies [5]. This means the films are less dense and less viscous, explaining the significantly higher physical diffusion rates observed.

5. Conclusions

In conclusion, mass transport in Nafion films in acetonitrile conditions is dominated by physical diffusion rather than apparent diffusion. This physical diffusion rate is much faster than physical diffusion in aqueous conditions. The altered behavior of Nafion® in nonaqueous solutions could be an advantage when immobilizing a species of interest onto the electrode surface. As an immobilizing agent, Nafion® would enable the study of another electrically active species without producing a significant background signal. Thus, Nafion could have excellent applications in redox flow battery technologies or as an immobilization polymer for catalysts in nonaqueous electrosynthesis [11,14].

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