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Tuning the Transport Properties of Poly(oxyethylene)bisamine−Nafion Polyelectrolyte Complexes by Dielectric Manipulation

Meera Parthasarathy, Bhalchandra A. Kakade, and Vijayamohanan K. Pillai*

Physical and Materials Chemistry Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411 008, India

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ABSTRACT: Polyelectrolyte complexes (PECs) of Nafion−H^+, a perfluorosulfonic acid ionomer, and Poly(oxyethylene)bisamine (Polyox) were synthesized, and the effect of electrostatic interactions on the physicochemical properties of the individual components was studied using a combination of spectroscopic and electrochemical techniques. More specifically, the pristine PECs were extensively characterized using viscosity, surface tension, and pH measurements and diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy and their transport properties were investigated using cyclic voltammetry and electrochemical impedance spectroscopy, by employing $[Fe(CN)_6]^{3-}$ as a redox probe. Acid–base interaction between Nafion and Polyox is evident from pH measurements of the blend solutions, which indicate salt formation at a 50:50 composition, supported further by the existence of a maximum in the plot of surface tension versus blend composition. DRIFT spectra of the PEC membranes indicate subtle changes in the ionic environment and a transition from a state of medium hydration to a partially dehydrated state of the parent ionomer, Nafion, after complexation with Polyox. Further evidence for polyelectrolyte−polyelectrolyte association is obtained from cyclic voltammetry, which shows that the interaction between the redox active chromophore, $[Fe(CN)_6]^{3-}$, and the pendent sulfonate groups of Nafion is minimized by complexation with the oppositely charged polyelectrolyte Polyox. The water-soluble nature of these PECs along with the tunable range of properties with blend composition could qualify them as suitable candidates for developing stimuli-responsive polymer systems for pharmaceutical and environmental applications.

1. Introduction

Polymer electrolytes are macromolecules or supramolecular entities containing a large number of ionizable groups either along the backbone or in pendent chains, which constitute the key components in a number of commercial applications including PEM fuel cells, solid-state supercapacitors, membrane-based separation systems, rheology modification, and targeted drug delivery.[1] In addition to their technological importance, increasing interest in polyelectrolyte research stems from their unique deviations both from the behavior of neutral polymers as well as that of the conventional electrolytes, which is collectively known as the "polyelectrolyte effect".[2] The distinctive properties of polyelectrolytes arise due to the long-range nature of the electrostatic interactions between the charged polymer chains and counterions, introducing new length and time scales, which most often precludes a satisfactory analytical description of the dynamical processes. Consequently, a deeper understanding of the static and dynamical properties of the electrically charged macromolecules is far from complete, in contrast to their neutral counterparts. Especially, polyelectrolyte solutions are to be treated at a higher level of complexity owing to the involvement of additional factors like chain conformation and solvation and are considered to be one of the least understood categories of condensed matter.[3]

Aqueous solutions of amphiphilic polyelectrolytes (containing hydrophobic as well as hydrophilic domains) exhibit interesting rheological properties and phase behavior, attributed to their characteristic self-assembling behavior governed by various noncovalent forces like electrostatic, hydrogen bonding, van der Waals, and hydrophobic interactions. The excellent sensitivity of polyelectrolyte solutions to changes in conditions like ionic strength of salt, pH, shear stress, and temperature qualifies them as potential candidates for the fabrication of stimuli-responsive polymer systems capable of capturing and delivering materials for pharmaceutical and environmental applications.[4] In addition to these factors, another method for tuning the transport properties of polyelectrolyte solution is to modify the local ionic environment by introducing an oppositely charged polyelectrolyte which results in the formation of a polyelectrolyte complex.

The driving force for the formation of polyelectrolyte complexes (PECs) is the strong Coulombic interaction between oppositely charged polyelectrolytes, which leads to interpolymer ionic condensation. In addition, intermacromolecular interactions like hydrogen bonding, van der Waals forces, hydrophobic, and dipole interactions also play a role in PEC formation. Complexes between synthetic polyelectrolytes were first investigated by Michaels in 1961, who reported the association of poly(4-vinylbenzyltrimethylammonium chloride) with poly(sodium styrene sulfonate).[5] PECs are more attractive than simple polyelectrolytes, as they could yield synergistic properties different from those of the individual components.[6,7] For example, recently, Cayre et al. observed diode characteristics at the junction of two oppositely charged polyelectrolytes.[7] Similarly, PECs in the form of continuous thin films and membranes have been successfully applied for membrane separation processes[8] and dehydration of alcohols,[9] respectively. More recently, PEC membranes of chitosan and poly(acrylic acid) were synthesized for application as polymer electrolytes in direct methanol fuel cells.[10] Despite such considerable advances in the field of PECs, their potential utility in a wide range of applications has not gained much attention, probably due to the limited choice of effective combinations of the polyelectrolyte constituents. For instance, the microstructure and the size of the ionic domains of an amphiphilic polyelectrolyte could possibly be tuned by electrostatic interaction with a counter macroion. Such variations can have a significant impact on the transport properties of the individual components, as they manipulate the local dielectric distribution along the polymer chains.[11]

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* Corresponding author. E-mail: vk.pillai@ncl.res.in.

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Table 1

weight ratio (%) [Nafion/Polyox]	designation	percentage by weight of Nafion	percentage by weight of Polyox	ionic strength ($\times 10^{-2}$ M) (wrt ionic groups in the polyelectrolytes)
100:0	Nafion	3		9.0
90:10	N9010	2.8	0.3	8.8
80:20	N8020	2.7	0.68	8.9
70:30	N7030	2.5	1.27	9.2
60:40	N6040	2.5	1.5	9.1
50:50	N5050	2.2	2.2	8.9

In this connection, we investigate here the unique transport properties of novel PECs of Poly(oxyethylene)bisamine (will be designated hereafter as Polyox) and Nafion−H$^+$, electrochemically using $K_3[Fe(CN)_6]$ as a redox probe, which is known to have specific interactions with the pendent sulfonate groups of Nafion−H$^+$.[12] The anionic polyelectrolyte, Nafion−H$^+$, is a perfluorosulfonic acid ionomer with high charge density and chemical stability, whereas the cationic polyelectrolyte Polyox is basic in nature, possessing amino groups that can interact with the sulfonic acid groups of the former. More significantly, the chemical similarity between the side chains of Nafion−H$^+$ (with $-O-CF_2-$ repeat units) and the backbone of Polyox (with $-O-CH_2-CH_2-$ repeat units) together with the possible electrostatic interactions between the oppositely charged functional groups could offer excellent compliance between the polyelectrolyte partners. Further, since the average molecular weights of both of the polymers are of the same order of magnitude ($\sim 10^3$ g/mol), the relative orientation of the individual polymeric chains (especially at higher concentrations) could have interesting consequences on their transport properties.

2. Experimental Section

Materials. Nafion ion-exchange resin (5 wt % dispersion in water and lower alcohols; equivalent weight 1000), Poly(oxyethylene)bisamine (molecular weight 2000), and potassium ferricyanide were procured from Sigma Aldrich chemicals. Millipore deionized water (18 MΩ resistance) was used for preparing the solutions.

PEC Preparation. Salt-free aqueous solutions of Nafion−H$^+$ (2.5 wt % approx.) were ultrasonicated for 15 min followed by the addition of appropriate amounts of Polyox to obtain different proportions as explained in Table 1. The resulting mixture was ultrasonicated for a further 30 min to yield a clear solution. The blend designated as N8020 indicates that the resulting solution contains 80% Nafion and 20% Polyox.

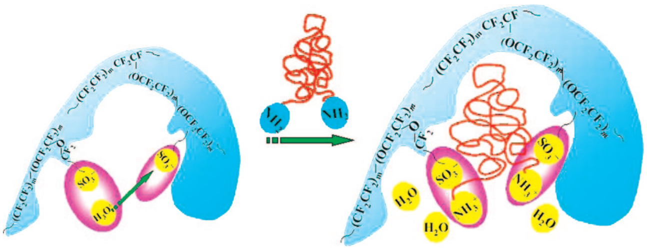
FTIR Studies. Fourier transform infrared (FTIR) spectra were recorded in a diffuse reflectance mode by casting the blends on clean Si wafers (cleaned thoroughly by treating with Piranha solution to form thin films and subsequently dried in air for 24 h). The response of blank Si wafer was subtracted from the resultant spectra before analysis.

Viscosity Measurements. The blends were diluted 100 times with deionized water, and their relative viscosity (wrt water) was measured using a Schott AVS 350 viscometer with a Schott CK160-CT1650 temperature controller, at 303 K. The flow times were measured five times for each sample, averaged out, and then used for calculating the relative viscosity.

pH measurements were performed using a pH meter purchased from Eutech instruments.

pK_a Determination. The pK_a of protonated Polyox in water (in the absence of Nafion−H$^+$) was determined by pH-metric titrations. In brief, an aqueous solution of pristine Polyox (0.5 wt %; 5 mM $-NH_2$ groups) was protonated by titrating first with 10 mM HCl. The resulting solution containing protonated Polyox and excess acid was back-titrated with 5 mM NaOH. In this step, the excess HCl in the analyte solution gets neutralized first followed by the deprotonation of protonated Polyox. Assuming independent titration of the $-NH_2$ groups in each Polyox chain (a two-step protonation/deprotonation equilibria, corresponding to two $-NH_2$ groups per polyox chain, is not observed during the titrations probably because the individual pK_a values are too close to be detected within our experimental limits), the pK_a of protonated Polyox was found to be 7.7 (approx.) from three replicate titrations.

Scheme 1. Formation of a polyelectrolyte complex between Poly(oxyethylene)bisamine and Nafion−H$^+$ involving (i) the protonation of the amine groups of the former by the protons originally associated with the sulfonate groups of Nafion−H$^+$ followed by (ii) the association of the $-NH_3^+$ groups of Polyox with the sulfonate groups ($-SO_3^-$) of Nafion. Consequently, some of the hydronium ions present originally in the water clusters of Nafion−H$^+$ are expelled as water molecules, resulting in a secondary solvation shell



Contact Angle Measurements. The contact angle of the blend droplets on a clean, dry glass plate was measured by the sessile drop method using a Digidrop contact angle meter. For each sample, the measurement was repeated five times at different parts of the glass slide and the average value of the contact angle was noted.

Surface Tension Calculation. The surface tension of the blends at the liquid–air interface were calculated from contact angle-sessile drop measurements on plain glass substrates followed by independent capillary rise measurements using the expression

$$h = (2\gamma \cos \theta)/\rho g r$$

where h = height of the liquid lifted in the capillary, γ = liquid–air surface tension, ρ = density of the liquid, r = inner radius of the capillary, g = acceleration due to gravity, θ = contact angle.

Cyclic voltammetry was performed using a Solartron SI 1287 Electrochemical Interface instrument operated through Corrware software, and **electrochemical impedance** was performed using a Solartron 1255B instrument coupled to a frequency response analyzer, operated through Zplot software. A three-electrode cell consisting of a Pt working electrode, a Pt counter electrode, and a Ag wire quasi-reference electrode was used for the electrochemical measurements.

3. Results and Discussion

Scheme 1 depicts the electrostatic interactions between the two polyelectrolytes which involves (i) the protonation of the amine groups in Polyox by the protons originally associated with the pendent sulfonate groups of Nafion−H$^+$ followed by (ii) the association of protonated amine groups ($-NH_3^+$) of Polyox with the sulfonate groups ($-SO_3^-$) of Nafion.

Viscosity Measurements. Viscosity measurements have been frequently employed to understand polyion−counterion and polyion−polyion association. For a salt-free polyelectrolyte solution, the reduced viscosity (η_{sp}/C) increases markedly on dilution and passes through a maximum at low ionic strengths at zero shear rate.[13] Earlier, this was attributed to chain expansion at lower polyelectrolyte concentrations, but the concentration-dependent viscosity profiles of rigid and flexible ionic polyelectrolytes were later found to be similar, indicating that conformation effects are not of primary importance. On the contrary, it has been suggested that counterion-mediated attraction between polyions may play a crucial role.[14] The extent of electrostatic interactions and the consequent viscosity changes

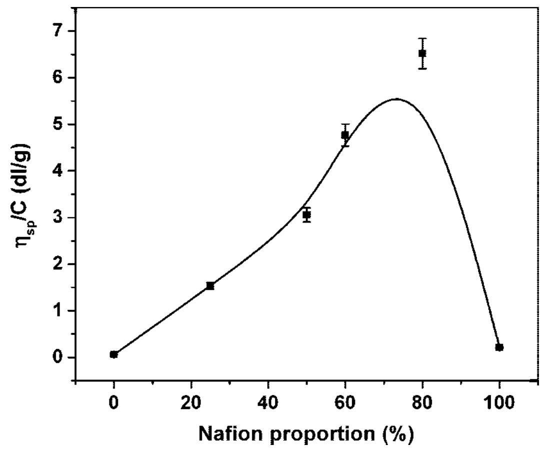


Figure 1. Variation of reduced viscosity (η_{sp}/C) with the composition of Nafion−Polyox blends at 303 K.

have been found to depend on a parameter, called the electrostatic persistence length of the polyelectrolyte, defined as,[15]

$$l_e = l_B/4\kappa^2 b^2$$

where l_e is the electrostatic persistence length, l_B is the Bjerrum length, κ^{-1} is the Debye–Huckel screening length, and b is the average charge separation on the contour of the polyelectrolyte chain.

Accordingly, Figure 1 shows the variation of viscosity with the composition of Nafion−Polyox blend solutions. However, in the present case, the concentrations of the individual polyelectrolytes in the blend solutions are high enough to show their characteristic polyelectrolyte effects[16] corresponding to their respective electrostatic persistence lengths as discussed above. Hence, the maximum observed in Figure 1 could be attributed to the electrostatic association of Nafion−H^+ and Polyox probably resulting in the formation of polyelectrolyte complexes.

Surface Tension and pH Measurements. Surface tension measurement at varying concentrations of polyelectrolyte solutions is a classical method for the determination of critical micellar concentrations. Figure 2A shows the variation of surface tension (calculated by independent capillary rise measurements and the sessile drop method) of the polyelectrolyte blends with composition, whose values are found to be of the same order as that reported for pristine Nafion dispersions.[17] A clear maximum is observed in the plot of surface tension (polyelectrolyte−air interface) with blend composition, probably indicating that the electrostatic interactions between the polyelectrolyte components is maximum at a composition of 50:50. A more convincing evidence for the acid–base interaction between Nafion and Polyox is the variation in the pH of the blend solutions with composition, as shown in Figure 2B. The pH of the blend solutions is found to vary from 8.0 (approx.) for an aqueous solution of pristine polyox to pH 2 (approx.) for an aqueous dispersion of Nafion similar to an acid–base potentiometric titration with the neutralization point approximately at a composition of 50:50 in accordance with the surface tension measurements, indicating salt formation. In addition, the excess Polyox added after the neutralization point does not disrupt the stability of the PECs by deprotonation of Polyox−NH_3^+ in the range of blend composition under investigation, as the pH of the blend solutions is considerably below the pK_a of protonated Polyox determined independently (described in the experimental section). For pendent-type polyions with charges residing in their side chains like Nafion, it is found that an equilibrium salt structure is easily formed due to interactions of adjacent reactive sites that follows immediately after at least one ionic bond is formed.[16] In the present case, the salt formation could occur in two steps, namely, (i) the initial protonation of the amine groups of Polyox by the protons originally associated with the sulfonate groups of Nafion−H^+ followed by (ii) the electrostatic interactions between the $-NH_3^+$ and $-SO_3^-$ groups of Polyox and Nafion, respectively. This could also be compared with the acid–base interactions observed between 2-amino benzimidazole (a basic polymer) and sulfonated poly(ether ether ketone) (an acidic polymer).[18] Although there could be concomitant changes in the respective conformations of both of the polyelectrolytes, we could make a fair assumption that the contribution of conformational changes may be negligible compared to that of the electrostatic forces. For example, Wei and Hudson have studied the binding of sodium dodecyl sulfate (SDS) to chitosan of various degrees of acetylation to demonstrate that the initial binding constant is unchanged, indicating that the contribution of charge-density-induced conformational changes of the individual polyelectrolytes may not be high enough to influence the effective potential at the polymer electrolyte interface.[19] Hence, we consider here mainly the changes in the solution structure of the polyelectrolytes occurring after the second step of salt formation, namely, Coulombic interaction between the charged functional groups, and attribute the changes in the properties of the blend solutions to the same.

DRIFT Analysis. Diffuse reflectance FTIR (DRIFT) spectra of the polyelectrolyte complex membranes prepared by blending Nafion−H^+ and Polyox in different proportions are presented in Figure 3. In the case of perfluorosulfonic acid ionomers, whenever the sulfonate groups of the ionic clusters interact electrostatically with counterions, water molecules bound to them are expected to be expelled away.[1] For example, Lowry and Mauritz have observed a similar decrease in water content of Nafion as a consequence of its electrostatic interactions with alkali metal ions.[20] Accordingly, Figure 3A shows a transition from a state of medium hydration (3452, 1566 cm^{-1}) in the case of pristine Nafion to a partially dehydrated state (3202, 2881, and 1715 cm^{-1}) with increasing Polyox content.[21] This could have interesting consequences for PEM fuel cells, as one could envision polymer electrolyte membranes which could sustain lower humidity conditions. However, the poor mechanical stability of the Nafion−Polyox blend membranes in the present work has precluded the verification of their solid-state proton conductivity, which is an important requirement for fuel cell applications. Additionally, the peak at 1058 cm^{-1} corresponding to the symmetric stretching mode of the sulfonate groups gets broadened and becomes almost undetectable with increasing Polyox content in the films. More interestingly, there is a gradual change in the 1100–1400 cm^{-1} region with increasing Polyox proportion (Figure 3B). Although the asymmetric stretching vibration of the sulfonate groups is expected to absorb in this region, the peak assignment often becomes uncertain due to interference from the C−F vibrational modes of Nafion.[10] Nevertheless, in the present case, despite the invariance in the shape and position of other peaks in this region (1170, 1290 cm^{-1}), the relative intensity of the peaks at 1267 and 1303 cm^{-1} shows an interesting variation with polyox proportion. Hence, the latter peaks could probably be due to the asymmetric stretching vibrations of the sulfonate groups, which are known to split into a doublet depending on the environment and water structure in the ionic clusters.[21]

Transport Properties. Having analyzed the interactions between Nafion and Polyox, the electrochemical transport properties of the blend solutions are investigated using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry using $K_3[Fe(CN)_6]$ as a redox probe, which is known to have specific interactions with the pendent sulfonate groups of

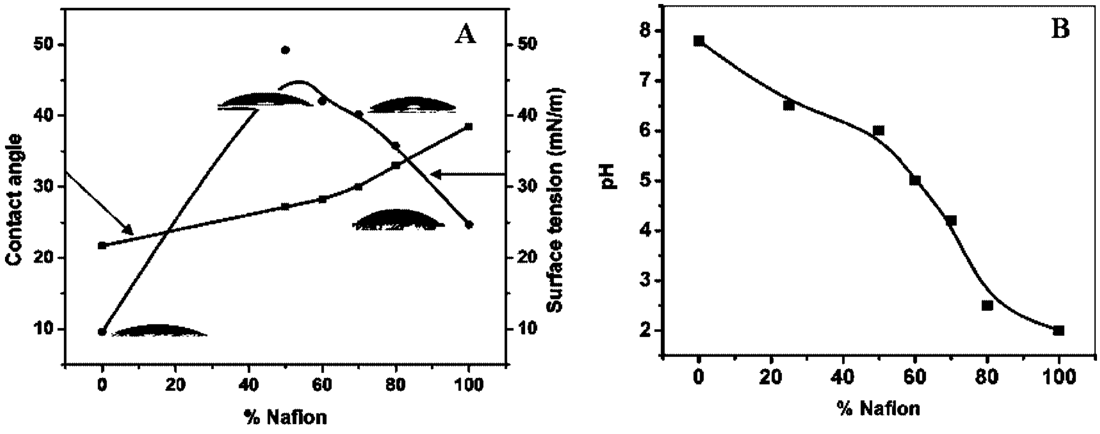


Figure 2. Variation of (A) contact angle, surface tension, and (B) pH of the blend solutions with composition (0% Nafion in the *x*-axis indicates 100% Polyox), indicating electrostatic association between Nafion−H$^+$ and Poly(oxyethylene)bisamine.

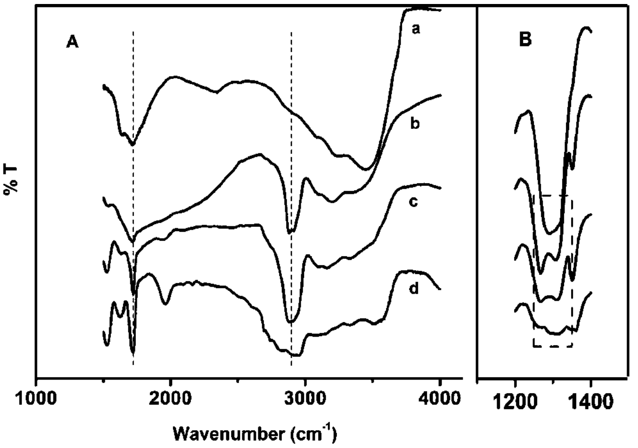


Figure 3. Diffuse reflectance FTIR spectra of (a) pristine Nafion, (b) N8020, (c) N6040, and (d) N5050 films (cast on a clean Si wafer) at 303 K.

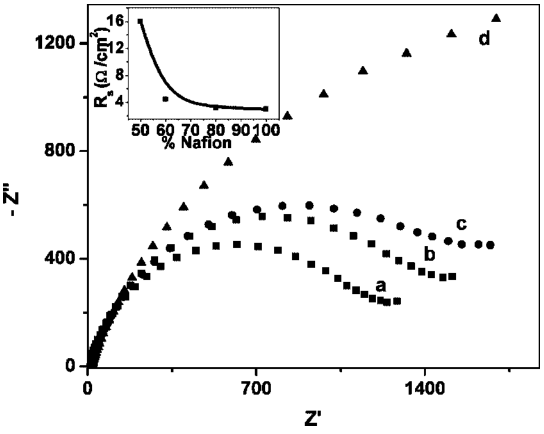


Figure 4. Electrochemical impedance of [Fe(CN)$_6$]$^{3-}$ solutions of (a) pristine Nafion (2.5 wt %), (b) N8020, (c) N6040, and (d) N5050 blends, under open circuit conditions. The inset shows variation in the solution resistance (R_s) values.

Nafion−H$^+$.[12] Figure 4 shows an interesting trend in the complex plane impedance plots [Z(Im) versus Z(Re)] of ferricyanide-dissolved solutions with varying compositions of the polyelectrolyte blends. Usually, when the mass transport of a dissolved redox species is very fast compared to the rate of interfacial electron transfer, a semicircle appears in the high frequency part, the diameter of which is proportional to the rate of electron transfer to the redox couple. Here, the semicircle spans the whole frequency range (10 mHz to 100 kHz), indicating that the electron transfer rate is considerably high compared to the mass transport rate, as is also obvious from the shape of the cyclic voltammograms [Figure 5 (left)]. When each of the plots is fitted into a semicircle, a gradual increase in its diameter with increasing Polyox content could be observed. This indicates important differences in the dielectric constant distribution in the light of the Hubbard−Onsager model[11] for solvation in macroion systems that could probably arise from changes in the solution structure of Nafion due to electrostatic interactions with Polyox, as depicted in Scheme 1. Thus, the dielectric constant distribution in an ionomer could be manipulated by deliberately introducing an oppositely charged polyelectrolyte. Accordingly, the proton conductivity of the PEC solutions decreases exponentially with increasing content of Polyox, as understood from the inset of Figure 4. This could be compared with the ion cluster-channel model, according to which, even in solid polymer electrolyte membranes, minor changes in the cluster sizes could lead to significant changes in proton conductivity.[22] Further, the right-hand side of Figure 5 shows a remarkable variation of ferricyanide diffusion coefficients (calculated from the peak current variation with square root of scan rate from cyclic voltammograms) with increasing Polyox content in the blends. However, compared to that expected on the basis of viscosity changes shown in Figure 1, the variations in the diffusion coefficients are somewhat subtle, indicating that the effect of interpolymer interactions is more pronounced than that of the viscosity changes with composition. Another possibility is the involvement of polymer conformation effects in addition to electrostatic effects analogous to polyion−counterion condensation explained by the dynamical scaling theory of polyelectrolyte conductivity.[23]

More interesting evidence for the Coulombic interactions between Nafion−H$^+$ and Polyox is obtained by a comparison of the first cyclic voltammeric scan of ferricyanide-containing pristine Nafion dispersions with that of the N6040 blend solution (Figure 6). The sulfonate-containing pendent chains of the perfluorosulfonic acid ionomer, Nafion, are known to interact chemically with [Fe(CN)$_6$]$^{3-}$ and Fe^{3+} species, resulting in a release of sulfonate radicals from our earlier studies and independent reports from other groups, respectively.[12] However, here Polyox is found to minimize such degradation reactions, as is evident from the cyclic voltammograms shown in Figure 6. When the potential is swept in the positive direction starting from the open circuit potential, an anodic peak is noticed in the ferricyanide-dissolved pristine Nafion dispersion, which does not appear in the case of similar dispersions with Nafion−Polyox blends. The appearance of such an anodic peak indicates that some amount of ferricyanide added initially into the polyelec-

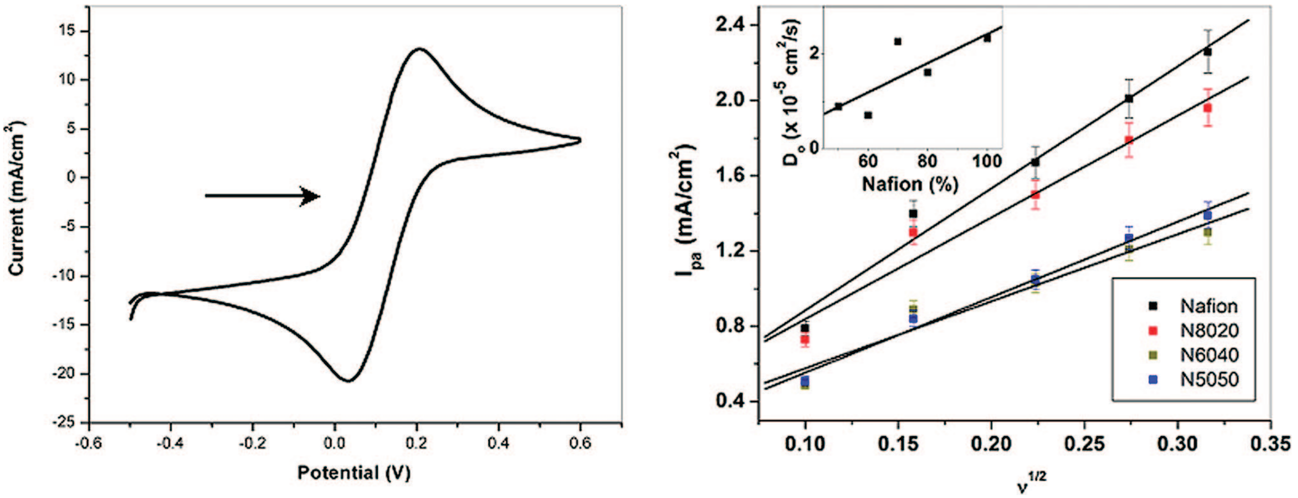


Figure 5. (left) Cyclic voltammogram of a N8020 blend solution containing $K_3[Fe(CN)_6]$ as a redox probe at a scan rate of 25 mV/s and (right) anodic peak current versus square root of scan rate from cyclic voltammograms of $[Fe(CN)_6]^{3-}$-dissolved blend solutions ($C_{[Fe(CN)_6]^{3-}} = 5$ mM; the ionic strength of the pristine blends was maintained constant at 90 ± 0.5 mM) at 303 K. The iset shows the variation in $[Fe(CN)_6]^{3-}$ diffusion coefficient with blend composition.

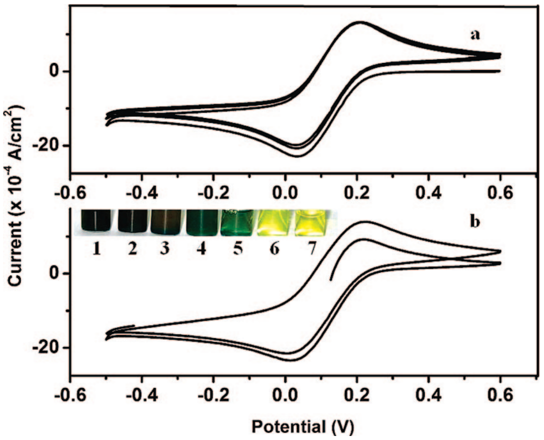


Figure 6. Cyclic voltammograms of (a) N6040 blend and (b) pristine Nafion containing dissolved $K_3[Fe(CN)_6]$, at a scan rate of 25 mV/s. The inset shows the gradation in color of the ferricyanide solutions of (1) pristine Nafion (2.5 wt %), (2) N9010, (3) N8020, (4) N6040, (5) N5050, (6) pristine Polyox (1 wt %), and (7) aqueous solution of potassium ferricyanide after 2 days.

trolyte dispersion is converted chemically to the ferrocyanide form. Also, there is a gradation in the color of the blends containing $K_3[Fe(CN)_6]$, ranging from a turbid dark blue color of pristine Nafion dispersion to an apparently clear green color of Nafion−Polyox blend (50:50) approaching the yellow color of ferricyanide solution in water and pristine polyox (Figure 6, inset). This is further supported by the open circuit potential (OCP)−time profiles, which show a larger decrease in OCP for pristine Nafion solutions compared to the N6040 blend solution (Figure 7). In many circumstances, employing a charged chromophore that interacts specifically (or more selectively) with one of the polyelectrolytes has been an efficient method for confirming the formation of PECs.[16] By a similar argument, the formation of PEC between Nafion and Polyox by Coulombic attraction possibly minimizes the interaction of the former with the ferricyanide species, improving the oxidative stability of Nafion. Many of the properties investigated in the present work, arising due to specific interactions between the polyelectrolyte components, could be reflected in the respective membranes, as the conformations of Nafion molecules in the casting solutions are known to have a significant effect on the morphology of membranes prepared by casting them.[24] However, the oxidative stability and proton conductivity of the blend solutions may not necessarily be observed in the case of solid membranes, in which case it would have a significant impact for different applications utilizing solid polymer electrolytes like PEM fuel cells, supercapacitors, and membrane-based separation systems.

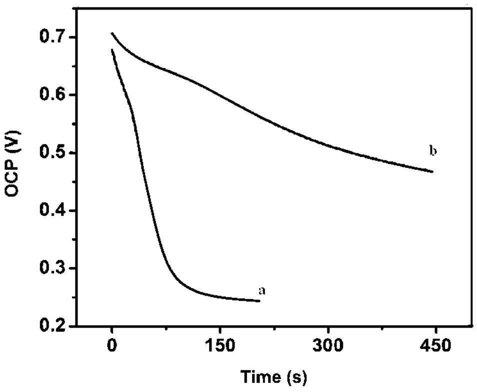


Figure 7. Evolution of the open circuit potential (OCP) with time for $K_3[Fe(CN)_6]$ solutions of (a) pristine Nafion (2.5 wt %) and (b) N6040 blend indicating the better oxidative stability of the latter towards $[Fe(CN)_6]^{3-}$ species.

4. Summary and Conclusion. Polyelectrolyte complexes of Nafion−H^+ and Poly(oxyethylene)bisamine were synthesized and characterized using a combination of spectroscopic and electrochemical techniques. The formation of PECs was confirmed by FTIR and pH measurements and cyclic voltammetry using a $[Fe(CN)_6]^{3-}$ species, a redox active chromophore, as an internal probe. More specifically, considerable changes in the diffusion coefficient of the $[Fe(CN)_6]^{3-}$ as a function of blend composition, indicating the effect of PEC formation on the transport properties, is noticed in the EIS as well as the CV results. Interestingly, the $[Fe(CN)_6]^{3-}$ species is found to have minimum interaction with the sulfonate groups of Nafion after blending with Polyox, signifying polyelectrolyte−polyelectrolyte association. In addition, plots of viscosity and surface tension versus blend composition pass through a maximum, indicating specific interactions between the polyelectrolytes. These results demonstrate that a wide range of properties of a polymer electrolyte could be tuned by complexation with an oppositely charged polyelectrolyte, which could be utilized in developing stimuli-responsive polymer systems for targeted drug delivery, rheology modifiers, and environmental applications.

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