

ARTICLES

Ionic Conductivity of Nonaqueous Solvent-Swollen Ionomer Membranes Based on Fluorosulfonate, Fluorocarboxylate, and Sulfonate Fixed Ion Groups**Marc Doyle****DuPont Microcircuit Materials, 14 TW Alexander Drive, Research Triangle Park, North Carolina 27709-3999***Mark E. Lewittes† and Mark G. Roelofs‡***DuPont Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0357***Stephen A. Perusich§***Department of Chemical Engineering, Auburn University, Auburn, Alabama 36849-5127**Received: October 18, 2000; In Final Form: July 30, 2001*

High ionic conductivities of 10^{-4} to 10^{-2} S/cm are achieved with Li^+ -form perfluorosulfonate ionomers over a wide temperature range by swelling in nonaqueous organic solvents. The dependence of ionic conductivity on temperature, solvent absorption, and membrane equivalent weight is examined for Nafion perfluorinated ionomer membranes. These results are compared with other ionomer membranes, including those having hydrocarbon backbones and weaker acid groups, to correlate ionic conductivity with ionomer structure. The most important factors determining ionic conductivity in membranes swollen with polar nonaqueous solvents, beyond the solvent properties such as viscosity and molecular weight, are the basicity of the fixed anion group and the solvent uptake by the membrane. Ionic conductivity is generally limited by dissociation of the cation from the fixed anion site. Several means for increasing conductivity are demonstrated including the use of cation complexing agents to increase ionic dissociation.

Introduction and Background

Application of ionomer membranes in electrochemical systems, such as sensors, fuel cells, batteries, and electro-organic synthesis, requires an understanding of the factors determining membrane ionic conductivity.^{1,2} The best known of this class of ionomers is the Nafion membrane, a copolymer of tetrafluoroethylene and a perfluoro vinyl ether, e.g., $-(\text{CF}_2\text{CF}_2)_m-(\text{CF}_2\text{CF}(\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}))_n-$. The elimination of the supporting electrolyte is possible when using ionomers as the ion-conducting medium which has advantages including simplicity of the system, lack of corrosive anionic species, and high cation conductivity and unity transference number.

Although the use of ionomer membranes in proton-exchange-membrane (PEM) fuel cells has led to much study of the conductivity mechanism of water-swollen ionomers, few fundamental studies exist of the conductivity in nonaqueous media. Jorissen³ and DeWulf and Bard⁴ have demonstrated that ionomer membranes can be employed for electrochemical applications in media completely devoid of water. Yeo et al.^{5,6} and Pineri et al.^{7–9} examined the swelling and conductivity of Nafion membranes and solutions in certain nonaqueous media. Yeo and

co-workers studied the swelling behavior of perfluorocarboxylic and perfluorosulfonic acid membranes in hydrogen-bonding organic solvents, such as alcohols and amines. Pineri and co-workers focused on organic solvents used in lithium battery applications, such as propylene carbonate and dimethoxyethane. An earlier paper of ours examined the dependence of ionic conductivity on solvent physical properties for a wide range of nonaqueous solvents in perfluorosulfonate ionomeric membranes.¹⁰

Commercial development of the PEM fuel cell is motivating new studies into the conduction mechanism in ionomer membranes and means for improving their conductivity at elevated temperatures. Elevated temperature operation of the PEM fuel cell would reduce problems with catalyst poisoning by carbon monoxide and improve system thermal control and energy efficiency. However, the maximum use temperature of water-swollen ionomer membranes tends to be limited by the volatility of liquid water. A new approach proposed recently to avoid these problems is the use of nonvolatile solvents in the ionomer membrane system. For example, sulfonated polyether ketone membranes were imbibed with pyrazole or imidazole liquids under anhydrous conditions to give proton-conducting membranes with conductivities approaching 0.01 S/cm at 200 °C.¹¹

To understand the factors that lead to fast ionic transport in solvent-swollen ionomeric polymers, the relationship between

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polymer structure and ionic conductivity in nonaqueous solvents must be understood. Although these systems have much in common with low-molecular-weight electrolyte solutions, such as the importance of macroscopic solvent physical properties like viscosity and molecular weight, the structural features available to ionomeric polymer electrolytes give additional variables that can be controlled. Taking advantage of these features is necessary to achieve the high ionic conductivities required for electrochemical device applications. Additionally, microscopic modeling efforts examining the relationship between conductivity and structure in water-swollen ionomers would benefit from data on nonaqueous-solvent swollen ionomers.^{12–14}

Experimental Details

All measurements were performed in a drybox (Vacuum Atmospheres) under a nitrogen environment because of the presumed sensitivity of the membrane properties to water content. Ionic conductivity measurements on film samples were made using custom designed and fabricated four-point-probe conductivity cells having either platinum or stainless steel wire electrodes set into a PTFE base. Several studies demonstrate that the ionic conductivity of Nafion ionomeric membranes is constant and independent of frequency up to at least megahertz frequencies when using four-point-probe cell designs to eliminate interfacial resistances and other artifacts.^{15–17}

The ionic conductivity was calculated from the bulk sample impedance in the 10 Hz to 10 kHz range at zero phase angle using the formula for a uniform current distribution ($\kappa(\text{S/cm}) = R/[LA]$). In this formula, R is the value of the real component of the complex impedance (Ω), L is the distance between the central leads (cm), and A is the sample cross-sectional area (cm^2). Electrochemical impedance measurements were performed using either a transfer function analyzer (Voltech TF2000) or a lock-in amplifier (EG&G PAR model 5301) with a pulse/function generator (Wavetek model 166, 50 MHz). The sample impedance was calculated from the measured voltage induced by a small, imposed alternating current perturbation ($I_{\text{rms}} = 0.2 \text{ mA}$). The current flowed through the outer pair of parallel electrodes, whereas the voltage difference was measured between the inner pair. Accurate conductivity measurements down to 10^{-6} S/cm can be made using this system.

All conductivity measurements were performed after equilibrating the membrane with pure liquid solvent or solvent mixtures. Thickness measurements were made using a digital micrometer (Ono Sokki EG-225) with an accuracy of $2.0 \mu\text{m}$.

Nonaqueous solvents were purchased commercially in high purity ($<0.1\%$ water). Battery grade carbonate and ester solvents were purchased from E. M. Industries (Selectipur) and contain less than 100 ppm water. Except for these latter solvents, the solvents were dried additionally by storing over lithium cation-exchanged 4 Å molecular sieves which was found to reduce water into the 10–30 ppm range based on coulometric titration.

All commercial and experimental Nafion membrane products were obtained from the DuPont company. These include the following products: N117 = Nafion XR membrane with 1100 g/equiv nominal equivalent weight (EW) and 7 mil thickness and N105 = Nafion XR membrane with 980 g/equiv nominal EW and 5 mil thickness. 1050 g/equiv nominal EW carboxylate-form Nafion CR pellets were melt pressed into clear and uniform films about 3–5 mils in thickness. Dais sulfonated Kraton membranes were purchased from the Dais Corporation and used as received.

Perfluorinated ionomer membrane samples were received in sulfonyl fluoride precursor form and hydrolyzed using proce-

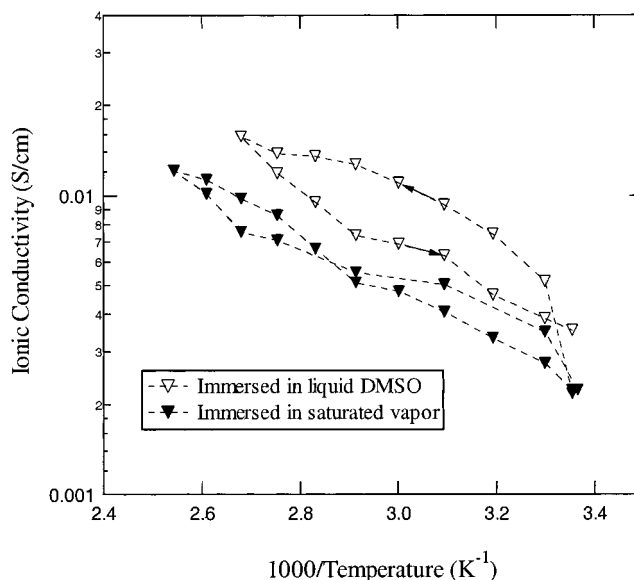


Figure 1. Temperature dependence of the ionic conductivity of N117 (Li^+) membranes equilibrated with either liquid DMSO or saturated vapor during the measurements. In the case of the liquid-equilibrated sample, arrows on the figure indicate the direction (heating or cooling) in which the data were taken.

dures described previously.¹⁰ Hydrolysis of the higher EW Nafion membranes employed 0.5 M LiOH in 1:3 H_2O :dimethyl sulfoxide (DMSO) solutions and temperatures of 80–90 °C for the hydrolysis bath, whereas lower EW membranes required lower DMSO contents in the hydrolysis bath. Membranes were dried at 120 °C in a nitrogen-purged vacuum oven for several days prior to use. By carrying out coulometric titrations of water released while flowing dry nitrogen gas over membrane samples held in an oven at 180 °C, we found that the membrane water content could be reduced to less than 1000 ppm by this drying procedure. Although these drying procedures leave some remaining water, the levels are too low to impact ionic conductivity in the organic solvents as will be demonstrated.

Discussion of Results

Dependence of Ionic Conductivity on Temperature for N117 (Li^+) in Nonaqueous Solvents. Temperature-dependent conductivity data allow comparisons between the conduction mechanism in solvent-swollen ionomer membranes with that of other gelled polymer electrolyte systems. Temperature-dependent conductivity data for Nafion membranes swollen with water often show very different behavior based on, among other factors, how the solvent content of the membrane is controlled.^{18–21} As the temperature is increased and the solvent evaporates, the conductivity decreases sharply. Holding the solvent content constant by equilibrating with vapor of known solvent activity is often difficult and time-consuming, especially for nonaqueous solvents where activity data may not be available.

The effect of the solvent equilibration procedure is examined in Figure 1. This figure illustrates conductivity data for N117 (Li^+) in DMSO where the membrane assembled into the conductivity cell is exposed to either excess liquid DMSO or a saturated DMSO vapor during the measurements. As the temperature is increased in the case of exposure to liquid DMSO, the uptake increases dramatically and the conductivity increases more so than in the case of DMSO vapor equilibration. There is also significantly more hysteresis in the case of liquid exposure during the measurement, probably resulting from exces-

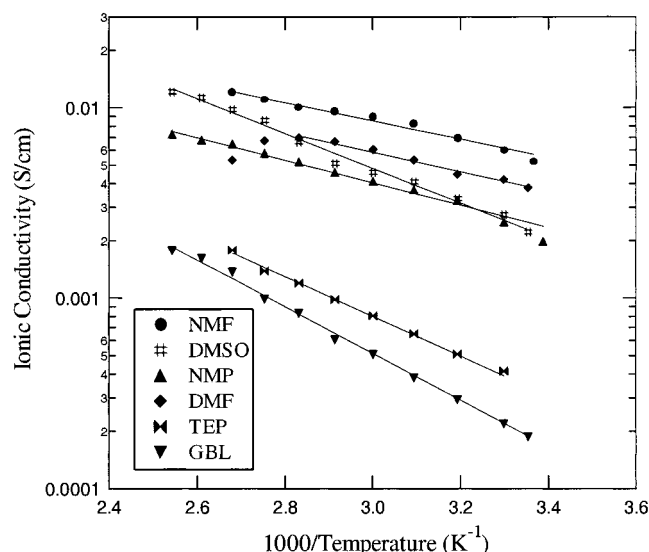


Figure 2. Dependence of ionic conductivity for N117 (Li^+) membranes on temperature for a number of different high boiling nonaqueous solvents. Solid lines represent least-squares fits to the data sets and are used to extract activation energies given in Table 1.

TABLE 1: Fitted Activation Energies for Ionic Conductivity of N117 (Li^+) Perfluorosulfonate Ionomer Membranes Swollen with Various Nonaqueous Solvents

solvent	activation energy (kJ/mol)	solvent	activation energy (kJ/mol)
<i>N</i> -methyl formamide	9.15	dimethyl sulfoxide	17.51
dimethyl formamide	9.81	triethyl phosphate	19.88
<i>N</i> -methyl-2-pyrrolidone	11.31	γ -butyrolactone	23.40

sive swelling of the membrane on the heating scan. These effects obscure the actual temperature dependence of the conductivity under conditions of constant solvent content. After these measurements, it was found that the liquid-exposed membrane had absorbed an additional 633 wt % solvent over the course of the temperature scan, whereas the vapor-exposed sample had lost 6% of its original solvent content. Clearly, the solvent content must be well controlled over the course of the temperature scan to obtain meaningful data for these solvent-swollen samples. This issue becomes even more challenging for noncrystalline ionomers such as lower equivalent weight perfluorosulfonate ionomer membranes.

Temperature-dependent conductivity data were taken on N117 (Li^+) membranes equilibrated with a number of different solvents. For these measurements, the membrane was initially equilibrated with liquid solvent at ambient temperature and then assembled into the cell without exposure to any additional solvent (in a dry nitrogen environment). Only high boiling solvents were employed, and the solvent content of the membrane before and after the conductivity measurements was checked to ensure that a significant loss of solvent did not occur over the temperature range studied.

Conductivity data versus temperature are plotted in Figure 2. If hysteresis was evident in the conductivity data between the heating and cooling scans, the data for the heating scan are given. However, in most cases, very little hysteresis was seen using these procedures. These data exhibit Arrhenius behavior over the range of temperatures examined. Activation energies calculated from the linear least-squares fits to the data (illustrated as solid lines in Figure 2) are given in Table 1. Data on propylene carbonate (PC) and ethylene carbonate (EC)/PC mixtures, not shown here, led to generalized Vogel law

temperature-dependent conductivity rather than Arrhenius behavior as might be expected for glass-forming liquids.²²

Activation energies vary from 9 to 24 kJ/mol in the same range reported for N117 (H^+) equilibrated with water.^{18–21} For reference, our measured activation energy for N117 (H^+) in deionized water is 17.2 kJ/mol over the range of 25–70 °C (data not shown in the figure). The solvents appear to fall into two groups based on their activation energies with the amide-based solvents having substantially lower values. Activation energies for the delta relaxation in Nafion membranes were reported to be between 12 and 23 kJ/mol.²³ Therefore, the rate-limiting step in conductivity in the nonamide based solvents might relate to motion of the ionic side chain coupled perhaps to dissociation of the cation.

Activation energies for the amide-based solvents are much lower than those of the other solvents and depend linearly on solvent molecular weight. This result, as well as the excellent degree of swelling and conductivity of amide-swollen perfluorinated ionomer membranes, suggests a different mechanism for ion transport in these systems involving as a rate-limiting step the motion of a solvated cation rather than dissociation from the fixed anion site. The conductivity of *N*-methyl formamide (NMF) swollen Nafion membranes was shown earlier to depend only weakly on cation type which also suggests less dependence on the dissociation process for amide-type solvents.¹⁰ For the dimethyl formamide (DMF) swollen membrane, solvent volatility at temperatures in excess of 90 °C led to a decrease in conductivity; only the data below this temperature were used to extract the activation energy given in Table 1.

Although these data are not given here, the activation energy for conductivity was found to depend very little on the equivalent weight of the ionomer. However, activation energies depended strongly on solvent content in the membrane. These results are consistent with the rate-limiting step being related to dissociation of the cation from the fixed anion site for most of the solvents examined.

Effect of Complexing Agents on Nonaqueous Conductivity. Addition of anion or cation complexing agents can promote much higher conductivities in electrolyte solutions by increasing salt dissociation and ion mobility. For Nafion membranes immersed into nonaqueous solvents, dissociation is a critical issue because of the poor solvating properties of many organic solvents. Hence, complexing agents that can bind to either the cation or the anion are expected to improve conductivity in these solvent-swollen ionomers, with larger improvements for poorer solvents. Anion complexing agents are preferred for practical purposes because these are expected to hinder cation mobility the least.

The addition of complexing agents to the swelling bath for Li^+ -form Nafion 117 membranes in 1:1 ethylene carbonate/dimethyl carbonate (EC/DMC) was examined. This solvent mixture is industrially relevant for lithium-ion battery applications and is a poor solvent by conductivity standards in the 1100 g/equiv nominal EW Nafion membrane.¹⁰ Figure 3 gives conductivity data as a function of the quantity of crown ether exposed to the membrane sample through the bathing solution. In each case, the solution was prepared by dissolving the appropriate quantity of crown ether (either in liquid or solid form) into 10 mL of 1:1 EC/DMC followed by immersing the membrane sample into the solution for a period of 24 h at room temperature. Data on the three compounds 12-crown-4, 15-crown-5, and 18-crown-6 ether are given in Figure 3.

Ionic conductivity of the membrane increases then levels off with increasing quantities of crown ether added to the bathing

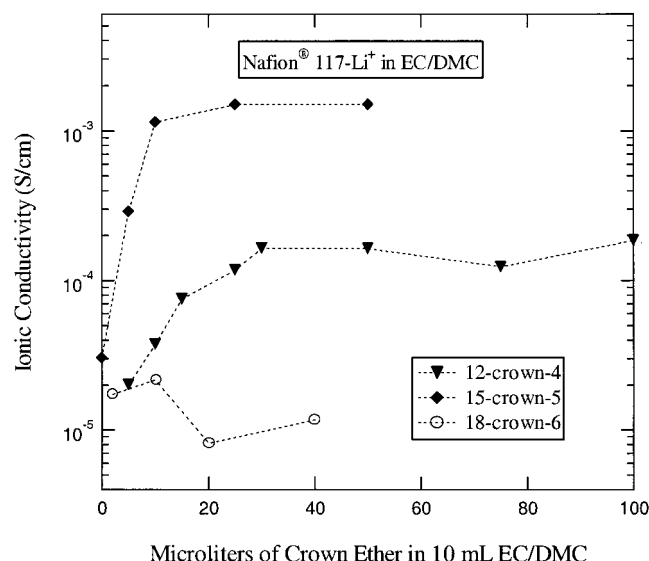


Figure 3. Ionic conductivity of N117 (Li^+) membranes plotted against the quantity of crown ether complexing agents added to the solvating bath containing 1:1 EC/DMC.

solution for the 12-crown-4 and 15-crown-5 ethers. This behavior results from saturation of the membrane with the complexing agent. The total number of equivalent cation sites in the membrane samples used in these experiments is approximately 6.2×10^{-5} moles (based on the 1100 g/equiv EW and the size of the membrane samples) which corresponds to 10 μL of 12-crown-4 ether. When the concentration was increased even further than shown in Figure 3, up to 100% of the bathing solution, the conductivity and solvent uptake rapidly decrease again to below 10^{-6} S/cm. This result is consistent with the earlier observations of the poor conductivity of 1100 g/equiv nominal EW Nafion membranes swollen with ether-based solvents.¹⁰

Perhaps surprisingly, the conductivity of the lithium-form ionomer increases much more rapidly and to a higher level when using the 15-crown-5 ether which is known to be sized appropriately for cations larger than Li^+ . However, the 18-crown-6 brings about no significant increase in conductivity, suggesting that it is too large to have an appreciable impact on dissociation. The improvements when using 15-crown-5 and 12-crown-4 suggest that both of the smaller crown ethers are able to disrupt ion association in these ionomers. The properly sized 12-crown-4 must reduce mobility of the dissociated and complexed cation to a greater extent than the 15-crown-5 ether.

A dramatic improvement in conductivity with 12-crown-4 or 15-crown-5 ether additives to ionomer membranes only occurred for the poorer solvents which initially exhibit room-temperature conductivities lower than 10^{-4} S/cm with N117 (Li^+). When attempting to increase the conductivity of N117 (Li^+) membranes swollen with either DMSO or PC/dimethoxyethane (DME), for example, no improvements were seen. This indicates that the better solvents bring about more complete dissociation within the ionomer as expected.

The effect of other additives on ionic conductivity is shown in Figures 4 and 5. The same procedures followed in Figure 3 were used. Several species were examined including the expected cation complexing agents 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTA), 1,4-dioxane, and 2,2'-dipyridyl (BPY; Figure 4), and additives chosen from good solvents such as water, DMF, DMSO, and poly(ethylene glycol) (PEG; Figure 5), as well as anion complexing agents BF_3 (as the etherate

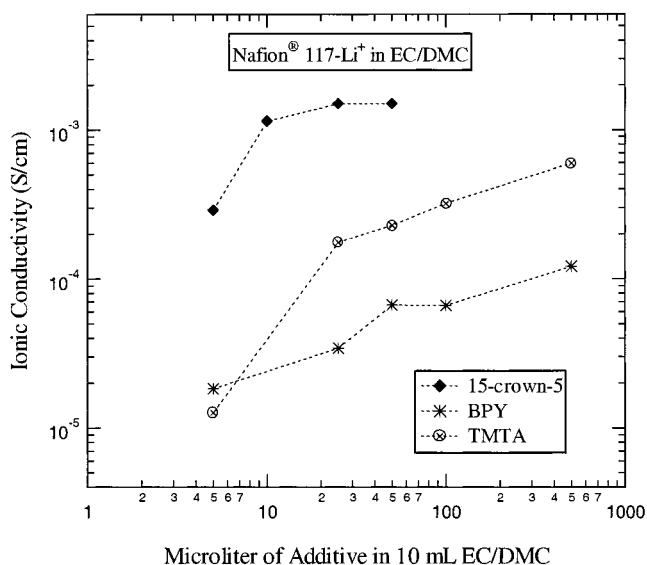


Figure 4. Ionic conductivity plotted against the quantity of species added to the solvating bath containing 1:1 EC/DMC.

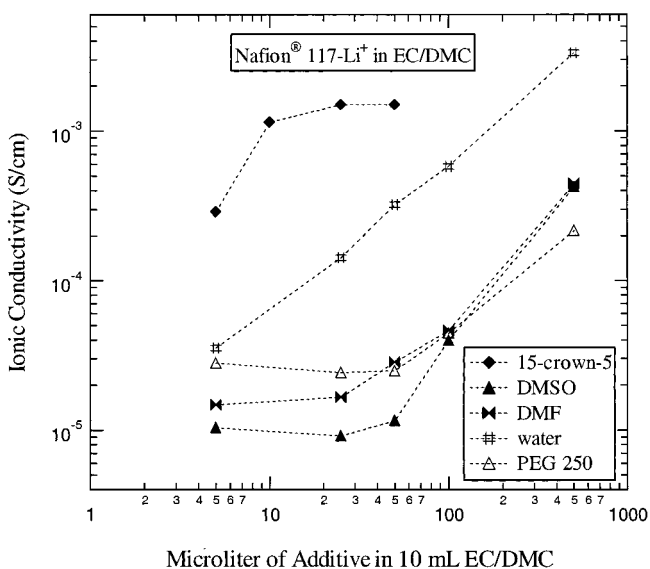


Figure 5. Ionic conductivity versus membrane equivalent weight for Li^+ -form Nafion membranes in a number of different solvents.

complex) and $\text{B}(\text{C}_6\text{F}_5)_3$. The results for 1,4-dioxane and the boron-based anion complexing agents are not shown on the figures because these had no impact on the ionic conductivity of N117 (Li^+) in 1:1 EC/DMC.

On the basis of the results in Figures 4 and 5, three different types of behavior are realized. Many of the additives tested showed little to no impact on conductivity or even decreased conductivity such as the weak cation binding agent 1,4-dioxane and the anion complexing agents. Other additives increased conductivity only when present in quantities in excess of 1.0% of the external bathing solution at which point significant absorption of the additive into the membrane must occur. Additives in this category include solvents such as DMF, DMSO, and PEG. Finally, the third category includes species which improve conductivity dramatically at low levels such as the crown ethers and TMTA.

It is rather surprising that the boron-based anion complexing agents do not show any improvement in conductivity. This family of anion receptors have recently been shown to allow dissolution of LiF leading to appreciable conductivity in

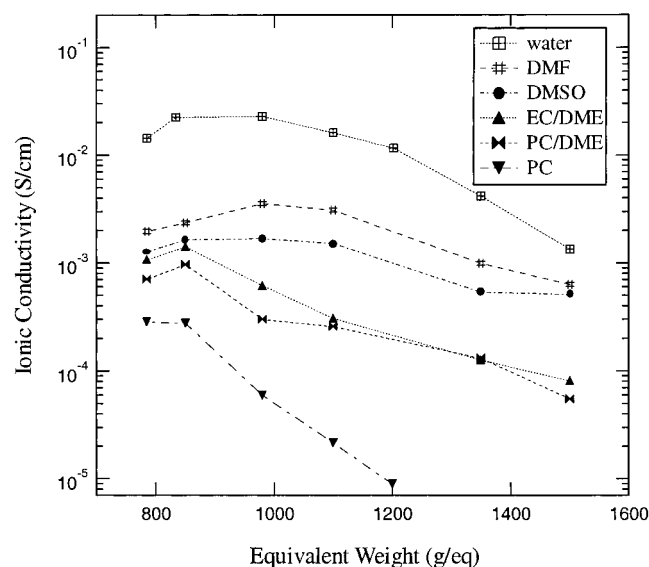


Figure 6. Solvent uptake versus membrane equivalent weight for Li⁺-form Nafion membranes in a number of different solvents.

carbonate mixed solvents.²⁴ They should show a similar effect on the weakly dissociated triflate anion site in the Nafion membrane in the presence of a poor solvent system like EC/DMC. It is possible that B(C₆F₅)₃ has solubility problems in EC/DMC although this was not apparent at the levels used during the experiments.

Dependence of Ionic Conductivity on Equivalent Weight.

One critical variable for optimization of ionomers is the equivalent weight of the polymer. EW impacts a number of different final properties including polymer crystallinity and structure and swelling and transport properties. In some cases, there is significant motivation to use the highest possible EW in a given application because of the costs associated with ionomeric monomers containing weakly basic groups such as the fluorosulfonate anion.

Figure 6 compares the dependence of conductivity on membrane equivalent weight for solvents such as water, DMF, DMSO, EC/DME, PC/DME, and PC for perfluorosulfonate ionomers. In all cases, the conductivity goes through a maximum in the EW range of 900–1000 g/eq. This result appears to be a general feature of these polymers and can be explained based on the degree of swelling of the polymer. Reduction of ionomer EW impacts conductivity in two ways: it causes an increase in the concentration of ions present in the dry polymer and a reduction in crystallinity of the copolymer. However, because of increases in solvent swelling in the lower EW polymers, the effective ionic concentration may actually be lower for low EW ionomers depending on the specific composition in use.

The dependence of conductivity on EW is much stronger for less conductive solvents. This implies that the conductivity of membranes swollen in poor solvents such as carbonates or ethers can be improved much more significantly by using lower EW membranes, whereas the conductivity of water or amide-swollen membranes can be improved to a lesser extent. As a general rule, the membrane conductivity can be increased into the 10⁻³ S/cm range for the nonaqueous solvents tested in this work, but further improvements in conductivity are difficult to obtain. In other words, ionic conductivities for the optimum EW membranes are less dependent on choice of solvent, as all conductivity values have the same order of magnitude for the perfluorosulfonate ionomer.

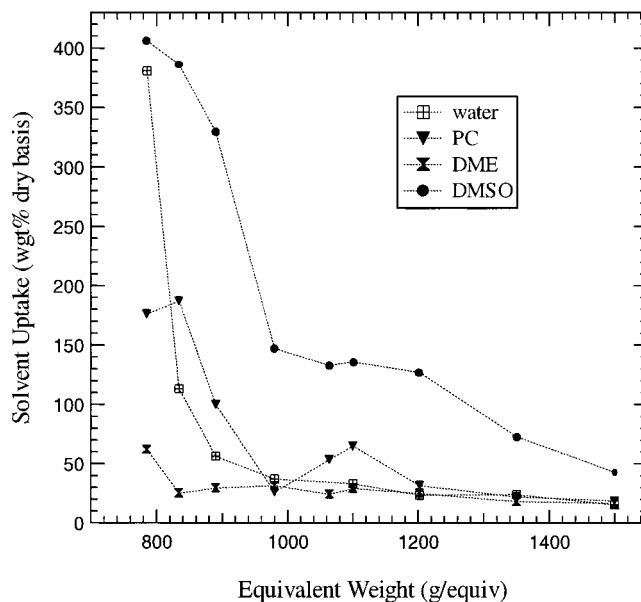


Figure 7. Solvent uptake versus membrane equivalent weight for Li⁺-form Nafion perfluorosulfonate membranes in a number of different solvents.

The use of lower EW Nafion membranes with the more poorly conductive solvents such as PC improves substantially the conductivity relative to that of the N117 membrane. For example, the conductivity of EC/DMC can be raised by an order of magnitude by using an 800–900 g/eq EW membrane, up to about 1.80×10^{-4} S/cm. Solvent uptakes for EC/DMC in these lower EW membranes are also substantially increased into the 100–125% range. The strong relationship between conductivity and uptake appears to be the only factor needed to explain these results.¹⁰

Figure 7 plots solvent uptake against EW for various solvents in Nafion membranes having equivalent weights ranging from 1500 to 785 g/eq. The swelling increases with decreasing EW as expected, although there is more scatter in swelling data than in conductivity data because of the nature of the measurement. A substantial increase in conductivity is expected when uptake increases to 100% and greater as described in previous work because of the formation of a minimum number of solvent molecules per anion site needed for good dissociation of the cation (this result should truly be expressed in terms of a molar uptake criteria rather than a weight uptake due to the latter's association with solvent molecular weight).¹⁰ For better solvents such as DMSO, this point is reached at a higher EW than for poorer solvents such as PC. Some solvents are not capable of swelling the polymer significantly enough to obtain high conductivities at any EW.

At very low EW, the swelling starts to become a hindrance to conductivity as the extent of solvent uptake by the polymer increases dramatically at low EWs. The increase in swelling tracks the reduction in polymer crystallinity. The swelling causes the effective ionic concentration in the polymer to be diluted making the conductivity decrease at lower EW as seen in Figure 6. In fact, by plotting the conductivity data versus effective ionic concentration (by dividing the density of the solvent swollen membrane by the equivalent weight) rather than EW, a linear relationship between conductivity and ionic concentration is realized. This is illustrated in Figure 8, where ionic conductivity of H⁺-form ionomers in liquid water is plotted for a series of Nafion membranes having EWs ranging from 785 to 1500. Thus, means for increasing ionic concentration even further by

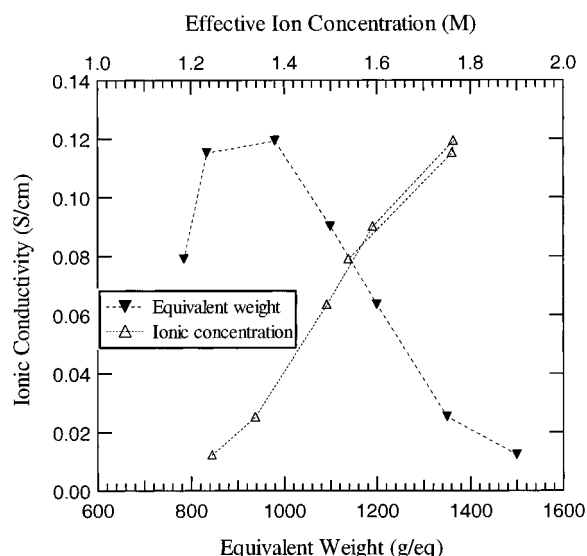


Figure 8. Ionic conductivity for various acid-form Nafion membranes having different equivalent weights plotted against both equivalent weight (top axis) and effective ionic concentration (bottom axis). Ionic concentration is calculated using the degree of swelling as a function of equivalent weight.

preventing complete loss of crystallinity should be advantageous. This has long been recognized in the aqueous ionomer membrane literature but may be even more important in nonaqueous solvent media.

Ionic Conductivity of Non-Perfluorosulfonate Li⁺-Form Ionomeric Membranes. The ionic conductivity and solvent uptake were measured for several different ionomeric polymers in nonaqueous solvents to compare with results given previously for perfluorosulfonate ionomer membranes. The polymers include perfluorinated ionomers such as the CR-form (carboxylate) membranes, hydrocarbon-based carboxylate-form ionomers, and the Dais Corporation's sulfonated Kraton ionomer. Understanding the structural factors that influence ionic conductivity provides guidance for future ionomer synthesis work.

In choosing the different ionomers to examine, two properties believed to be the most important structural features were varied: the type of fixed anion group and the degree of fluorination of the polymer backbone. Considerations of cation dissociation discussed earlier suggest that different ionic side chains should have a tremendous impact on ionic conductivity. Hence, several different side groups were chosen for study including perfluorocarboxylate, styrene sulfonate, and carboxylate.

Solvent uptake and conductivity data for a variety of solvents in Nafion CR membranes are given in Table 2. These films were prepared by melt pressing 1050 nominal EW carboxylate-form ionomer pellets. The hydrolysis and lithium exchange were performed using 0.5 M LiOH in a 9:1 H₂O:DMSO bath at 60 °C for 2 h followed by extensive rinsing and drying. Very few nonaqueous solvents provided measurable conductivities with the carboxylate-form Nafion membranes tested. The only solvents exceeding the 10⁻⁶ S/cm lower measurement limit were DMF, DMSO, and methyl glycolate (MG). These three solvents gave room-temperature ionic conductivities of greater than 10⁻³ S/cm with fluorosulfonate-type membranes, whereas here they barely achieved over 10⁻⁵ S/cm. Even with relatively high solvent absorption in cases such as DME, the ionic conductivities of these films were immeasurable. In other cases, such as

TABLE 2: Ionic Conductivities of 1050 g/eq EW Li⁺-Form Nafion CR Perfluorocarboxylate Ionomer Membranes Swollen in Various Solvents

solvent type	weight uptake	thickness increase	ionic conductivity (S/cm) at 23 °C
propylene carbonate	8%	2%	<1 × 10 ⁻⁶
γ-butyrolactone	22%	4%	<1 × 10 ⁻⁶
dimethyl formamide	55%	16%	3.61 × 10 ⁻⁵
dimethyl carbonate	33%	8%	<1 × 10 ⁻⁶
diethyl carbonate	36%	15%	<1 × 10 ⁻⁶
methyl glycolate	38%	14%	4.83 × 10 ⁻⁵
acetonitrile	12%	2%	<1 × 10 ⁻⁶
1,3-dioxolane	11%	8%	<1 × 10 ⁻⁶
dimethyl sulfoxide	56%	32%	5.23 × 10 ⁻⁵
tetrahydrofuran	43%	6%	<1 × 10 ⁻⁶
methyl acetate	33%	4%	<1 × 10 ⁻⁶
poly(ethylene glycol) (250 MW)	58%	40%	<1 × 10 ⁻⁶
dimethoxyethane	75%	21%	<1 × 10 ⁻⁶

TABLE 3: Ionic Conductivity and Solvent Uptake Data on Li⁺-Form Ionomers of Ethylene and Methacrylic Acid (19%) Swollen in Various Solvents

solvent type	weight uptake	ionic conductivity (S/cm) at 23 °C
25% neutralized with LiOH (0.4% Li)		
H ₂ O	1.5	<8 × 10 ⁻⁷
PC	0.0	<1 × 10 ⁻⁶
DMSO	31	<1 × 10 ⁻⁶
50% neutralized with LiOH (0.7% Li)		
H ₂ O	3.3	1.5 × 10 ⁻⁶
PC	0.0	<1 × 10 ⁻⁶
DMSO	2.6	<1 × 10 ⁻⁶
75% neutralized with LiOH (1.0% Li)		
H ₂ O	19	6.8 × 10 ⁻⁶
PC	0.0	<1 × 10 ⁻⁶
DMSO	6.3	<1 × 10 ⁻⁶
100% neutralized with LiOH (1.3% Li)		
H ₂ O	13	2.3 × 10 ⁻⁴
PC	9.0	<1 × 10 ⁻⁶
DMSO	8.1	<1 × 10 ⁻⁶

with PC or γ-butyrolactone (GBL), both uptake and conductivity were very poor for the perfluorocarboxylate-type membrane.

These poor results with the carboxylate-form membrane are attributed to poor dissociation of the lithium cation from the anion fixed site. Although the fluorocarboxylate group is considered a moderately weak base, it is a relatively strong one in many nonaqueous solvent environments. Lack of ionic dissociation causes conductivity to suffer because of an absence of mobile charge carriers.

Further support is found by examining uptake and conductivity data for other carboxylate-form ionomers. Copolymers of ethylene and methacrylic acid were tested in their lithium-cation-exchanged form. A variety of methacrylic acid-based ionomeric copolymers are available commercially for different applications. Methacrylic acid copolymers were neutralized to varying extents with LiOH. Different loadings of methacrylic acid were examined, but the results did not depend on the molar concentration of acid sites.

Table 3 presents data on ethylene-methacrylic acid ionomeric copolymers in either water or different nonaqueous solvents. The same polymer having 19% methacrylic acid was lithium-exchanged to varying extents using LiOH. Although the increasing extent of lithium exchange caused the aqueous conductivities to increase (still at low levels compared to N117), the nonaqueous conductivity values were immeasurable even in the best of the nonaqueous solvents, such as DMSO. Aqueous

TABLE 4: Ionic Conductivity and Solvent Uptake for the Dais Corporation 60% Sulfonated Kraton G1650 in Li⁺-Form Swollen in Various Nonaqueous Solvents

solvent type	weight uptake	Ionic conductivity (S/cm) at 23 °C
PC	~0	$<4 \times 10^{-5}$
DME	~0	$<4 \times 10^{-5}$
EC/DMC	~0	$<8 \times 10^{-5}$
DMSO	100	5.52×10^{-4}
GBL	100	$<5 \times 10^{-5}$
NMF	367	3.12×10^{-3}
DMF	50	1.78×10^{-3}
NMP	33	6.12×10^{-4}

TABLE 5: Comparison of Room Temperature Conductivity Data for N117 (Li⁺), Li⁺-Form Dais Corporation Sulfonated Kraton Polymer, and Perfluorocarboxylate-Type Nafion CR Ionomer Membrane in Various Nonaqueous Solvents^a

solvent type	N117 (Li ⁺)	Li ⁺ -form Dais ionomer	Nafion CR ionomer
EC/DMC	1.83×10^{-5}	nm	nm
PC	2.16×10^{-5}	nm	nm
DME	9.16×10^{-5}	nm	nm
GBL	0.000475	nm	nm
NMP	0.00113	0.000612	n/a
DMSO	0.00152	0.000552	5.23×10^{-5}
DMF	0.00319	0.00178	3.61×10^{-5}
NMF	0.00460	0.00312	n/a

^a nm = below measurement threshold. n/a = no measurements made.

conductivities are poor without any lithium exchange because this acid group is nearly completely undissociated in water. The lithium-cation exchange achieves some conductivity but still lower than that of either the Nafion CR or XR membranes.

One additional ionomeric polymer examined was a styrene-ethylene/butylene-styrene triblock copolymer in which the aromatic groups were approximately 60% sulfonated (Dais Corporation's sulfonated Shell Kraton G1650). The polymer was provided with a PTFE-based matrix for improved mechanical strength in the swollen state. The acid form of this polymer gave high aqueous ionic conductivities approaching one-half that for N117-H⁺ and much higher water uptake compared to 1100 g/equiv nominal EW Nafion membranes. The acid strength and extent of dissociation of this styrene sulfonate ionomer should fall between that of the alkyl carboxylate and fluoro-sulfonate-form ionomers.

Ionic conductivity data for the lithiated ionomer are given in Table 4. The film samples were less than 1 mil in thickness, and measurement errors were increased as a result. The consequence is an increase in the lower limit on conductivity as seen in the results in Table 4 for the poorer solvents such as PC as well as significantly poorer precision in the solvent weight uptake data. Although the lower limit on conductivity is approximately 4×10^{-5} S/cm for these films, true values are probably much lower based on the low swelling by the organic solvents. The conductivities for the better solvents, on the other hand, are excellent and nearly reach values in the Nafion perfluorosulfonate membrane.

Table 5 compares the conductivity for the Li⁺-form Dais membrane with that for N117 (Li⁺) and Nafion CR carboxylate-type membranes in the same solvents. This table demonstrates the importance of anion Lewis basicity in the conductivity behavior in different solvents. Where the conductivities for some solvents, such as NMF, DMF, and DMSO, are similar for the two polymers, the conductivities for others are much lower when using the weaker acid group ionomers. The capability of various

solvents to distinguish between these ionomeric groups is a function of the solvent donor properties. For more weakly donating solvents such as acetonitrile, ethers, and the linear carbonate solvents, very weakly Lewis basic anion groups are required to bring about sufficient dissociation to give high ionic conductivity under ambient conditions.¹⁰ Other polymer structural considerations such as crystallinity and hydrophobicity or polarity of the polymer backbone have a secondary influence through their effect on solvent swelling.

Ionomers based on fluorocarboxylate, carboxylate, and styrene sulfonate anion groups are ineffective for promoting high ionic conductivity in poorly donating organic solvents. Thus, the very high ionic conductivities needed for certain applications such as nonaqueous batteries require the use of good solvents or ionomeric polymers with very weakly basic anions such as the perfluorosulfonate group. Anion groups that are even weaker than perfluorosulfonate, such as perfluorosulfonimide or perfluorosulfonyl methide, should be expected to increase ionic conductivity even further in these environments.

Conclusions

Ionic conductivities of solvent-swollen ionomer membranes vary widely depending on polymer structural factors such as equivalent weight, fixed anion group, and solvent choice. Most of the data taken in the present study utilized the Li⁺ form of perfluorosulfonate ionomers. Ionic conductivities for the N117 (Li⁺) membrane exceed 10^{-3} S/cm at room temperature for a number of solvents. The temperature dependence of the conductivity exhibits an Arrhenius behavior over the temperature range of 25–120°C with activation energies falling between 9 and 24 kJ/mol for the different solvents tested. The activation energy depends strongly on solvent weight uptake for low solvent contents and weakly on polymer equivalent weight.

The most important factors influencing the ionic conductivity are the Lewis basicity of the anionic group on the polymer, the weight uptake of solvent by the polymer, and solvent physical properties including molar volume, donor number, and viscosity. Higher solvent uptakes are achieved with lower equivalent weight polymers as might be expected based on reductions in polymer crystallinity. The weight uptake of the solvent is directly related to ionic conductivity, with higher weight uptakes leading to higher ionic conductivity. At high levels of swelling, the conductivity depends only weakly on solvent uptake and can decrease in some cases as ionic concentration begins to be reduced because of the excessive swelling.

For most of the organic dipolar solvents examined, the rate-limiting step in the conduction process is the dissociation of the cation from the fixed anion group. This conclusion is reached based on the strong dependence of conductivity on cation type and degree of swelling, the range of activation energies measured, and the strong effect of complexing agents on the conductivity. The amide-based solvents tested appear to show a different behavior with conductivity potentially limited by motion of the solvated cationic species in a vehicular transport process.

The addition of a number of anion and cation complexing agents was attempted as a means for improving ionic conductivity. Specific crown ethers and other cation complexing agents markedly improved conductivity of poor dipolar solvents such as the mixture of ethylene carbonate and dimethyl carbonate. These same additives had little impact on ionic conductivity for the better dipolar solvents.

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Appendix A. List of Abbreviations Used for Nonaqueous Solvents

Throughout the text, the following abbreviations have been used to refer to particular solvents:

BPY = 2,2'-dipyridyl.
 DMC = dimethyl carbonate.
 DME = dimethoxyethane.
 DMF = N,N'-dimethyl formamide.
 DMSO = dimethyl sulfoxide.
 EC = ethylene carbonate (1,3-dioxolan-2-one).
 GBL = γ -butyrolactone.
 NMF = N-methyl formamide.
 NMP = N-methyl-2-pyrrolidone.
 PC = propylene carbonate.
 PEG = poly(ethylene glycol).
 TEP = triethyl phosphate.
 TMTA = 1,4,7-trimethyl-1,4,7-triazocyclononane.

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