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Relationship between ionic conductivity of perfluorinated ionomeric membranes and nonaqueous solvent properties

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Abstract

Ionic conductivity and swelling data are measured for Nafion® perfluorinated ionomeric membranes in nonaqueous solvents and solvent mixtures and correlated with solvent physical properties. The dependence of ionic conductivity on solvent uptake and cation type is examined for Nafion® 117 membranes with a nominal equivalent weight of 1100 g/eq. The most important factors determining ionic conductivity in membranes swollen with polar nonaqueous solvents are the solvent viscosity, molar volume, donor properties, and the solvent uptake by the membrane. Ionic conductivity is generally limited by dissociation of the cation from the fixed anion site indicating that the ionomer fixed anion site basicity is the critical membrane property. Means for increasing membrane ionic conductivity are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Batteries; Diffusion; Ion-exchange membranes; Nafion® membranes

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Abbreviations: ACE: acetone; ACN: acetonitrile; BG: *N*-butyl glycolate; DBA: *N*,*N*′-di-*n*-butylacetamide; DEE: diethoxyethane; DEC: diethyl carbonate; DIOX: 1,3-dioxolane; DMA: dimethylacetamide; DMB: *N*,*N*′-dimethyl butyramide; DMC: dimethyl carbonate; DMDA: *N*,*N*′-dimethyl decanamide; DME: dimethoxyethane; DMES: dimethyl ethane sulfonamide; DMF: *N*,*N*′-dimethyl formamide; DMPU: *N*,*N*′-dimethyl propyleneurea; DMSO: dimethyl sulfoxide; DMSU: dimethyl sulfite; DMTHF: 2,5-dimethoxytetrahydrofuran; EA: ethyl acetate; EAA: 2-ethoxyethyl acetate; EC: ethylene carbonate (1,3-dioxolan-2-one); EG: ethyl glycolate; FC1: $CH_3OC_4F_9$; FC2: $CF_3CF_2CF_2OCF(CF_3)CF_2OCHFCF_3$; GBL: γ-butyrolactone; MA: methyl acetate; MEED: 2-(2-(2-methoxyethoxy)ethoxy)-1,3-dioxolane; MeOH: methanol; MF: methyl formate; MG: methyl glycolate; MTBE: methyl *tert*-butyl ether; NBA: *N*-butyl amine; NMF: *N*-methyl formamide; NMP: *N*-methyl-2-pyrrolidone; PC: propylene carbonate; PEG: poly(ethylene glycol); PODO: 4-(1-propenyloxymethyl)-1,3-dioxolan-2-one; SULF: sulfolane; TBA: tetrabutylammonium; TEP: triethylphosphate; THF: tetrahydrofuran; TMS: 3-methyl sydnone

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1. Introduction

The excellent chemical stability and high cationic conductivity of water-swollen perfluorinated ionomeric polymers are well-known [1,2]. Perhaps the best-known of this class of ionomers is the Nafion® membrane, a copolymer of tetrafluoroethylene and a perfluoro vinyl ether, e.g. $–(CF_2CF_2)_m–(CF_2CF(OCF_2CF(CF_3)OCF_2\text{-}CF_2SO_3H))_n–$. Applications of water-saturated ionomer membranes in the presence of various organics have been explored for electro-organic synthesis, direct methanol fuel cells, batteries, and sensors [2]. However, there has been much less discussion of the use of Nafion® membranes in nonaqueous media [2].

Jorissen [3] demonstrated that acid-form perfluorosulfonic acid membranes can be used to carry out electroorganic synthesis reactions in nonaqueous media, such as *N*-methyl pyrrolidone without added salts. This approach allows electrolysis reactions to be accomplished at voltages where water or supporting electrolytes are not stable. In addition, the absence of mobile salts in these processes makes downstream product separations much easier. DeWulf and Bard [4] have demonstrated the use of Nafion®-solution-coated electrodes for voltammetric studies in nonaqueous media. Again, here the principal advantage is the elimination of side reactions with the background species. While these studies show that Nafion® membranes can conduct ionic current to a significant extent in nonaqueous solvent media, no measurements of ionic conductivity or studies of its dependence on choice of solvent were made.

For applications in nonaqueous batteries, Nafion® membranes were examined as possible separators in primary Li/SO_2 batteries and found to absorb and allow substantial rates of diffusion of both acetonitrile and sulfur dioxide in anhydrous environments [5]. Armand [6] measured the room-temperature lithium-ion conductivity of dry and propylene carbonate-swollen Nafion® membranes and found that the dry polymer conductivity is 10^{-7} S/cm and the PC-swollen N117 (Li^+) membrane is 2.05×10^{-5} S/cm.

Pineri et al. [7–9] examined the swelling behavior and ionic conductivity of Nafion® membranes and Nafion® solutions in Li^+ form in a handful of nonaqueous solvents including propylene carbonate (PC) and dimethoxyethane (DME). The conductivities were rather low for Nafion® membranes (6×10^{-5} S/cm for PC in N117 (Li^+)) but were significantly higher for gel-based liquid solutions. Yeo and coworkers [10,11] studied the swelling behavior of perfluorocarboxylic and perfluorosulfonic acid membranes in hydrogen bonding organic solvents, such as alcohols and amines. Pineri's swelling studies utilized the Li^+-form membrane rather than the acid form because of the lower reactivity of the former with nonaqueous solvents [9]. This same approach is followed here, although a wider range of nonaqueous solvents is examined.

Ionic conductivity data on conducting polymer films have had notorious difficulty with reproducibility and precision [12]. The present work utilizes a four-point-probe conductivity cell which eliminates many of the uncertainties of previous work. In addition to identifying highly conducting solvent-swollen membrane systems for use in industrial applications, it is important to understand the factors that lead to fast ionic transport in these solvent-swollen ionomeric polymers. As these phenomena are understood on a deeper level, it will be possible to design solvent-swollen ionomers to provide the desired transport and physical properties.

2. Experimental

All measurements were performed in a dry box (Vacuum Atmospheres) under a nitrogen environment due to 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 polytetrafluoroethylene (PTFE) base. Several studies [12,13] demonstrate that the ionic conductivity of Nafion® ionomeric membranes is constant and independent of frequency up to GHz frequencies when using four-point-probe cell designs to eliminate interfacial resistances and other artifacts.

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

$$\kappa\ (\text{S/cm}) = \frac{L}{R \times A} \tag{1}$$

where R is the value of the real component of the complex impedance (Ω), L the distance between the central leads (cm), and A 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 16,650 MHz). The sample impedance was calculated from the measured voltage induced by a small, imposed alternating current perturbation ($I_{\mathrm{rms}} = 0.2\,\mathrm{mA}$). The current flowed through the outer pair of parallel electrodes while the voltage difference was measured between the inner pair.

A very flat impedance response, with zero imaginary component and independent of frequency, was achieved in most cases because of the uniform current distribution and reduction of interfacial impedances in the four-point-probe geometry. The four-point-probe geometry greatly reduces artifacts due to interfacial impedance because the potential sensing electrodes do not support the current flow used to perturb the system. A picture of the four-point-probe cell is given in Fig. 1. The cell may be assembled into a mason jar lid for a relatively well-controlled environment allowing, for example, equilibration of the membrane sample with a given solution or removal from the glove-box environment for short periods of time. The size of the membrane sample was 1.0 cm wide × 1.5 cm long for conductivity measurement in these cells. Film thicknesses should not exceed approximately 0.4 mm to ensure that a uniform current distribution exists in the measuring region assuring that Eq. (1) holds.

The validity of an ionic conductivity measurement based on alternating current impedance data can be judged based on the frequency dependence of the result. The ionic conductivity of Nafion® ionomeric membranes does not depend on signal frequency until frequencies in the GHz range are reached [14]. The systems studied in this work consist of only a single mobile ion, which eliminates concentration polarization effects (ignoring the possibility of preferential solvation of one portion of the membrane which could bring about low-frequency polarization). Hence, over

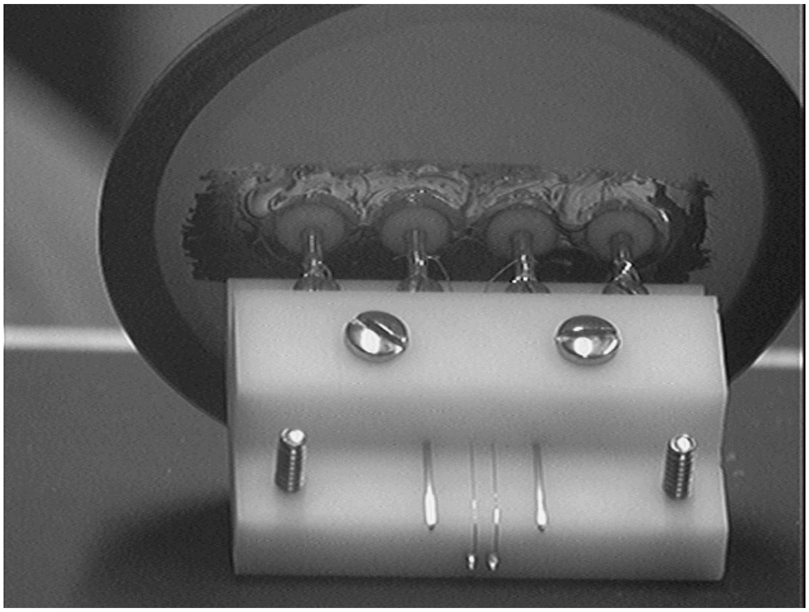

Fig. 1. Picture of the four-point-probe conductivity cell designed to give a uniform current distribution across the center two leads for accurate measurements of film resistance on thin polymer samples. The probe is shown with the cover removed. The shiny vertical strips at the bottom of the photo are the four conductors that contact the membrane. Current flows between the outer pair of electrodes and voltage is measured across the inner pair. A second PTFE piece slides down over the visible screws on top of the film sample to hold it in place during the measurement.

a very wide range of frequencies, the bulk sample resistance should be constant.

The capability of a given circuit to measure a constant resistance over a wide frequency range depends on the conductivity cell design and measuring circuitry and electronics. If a constant resistance (and hence conductivity) is measured over a wide range of frequencies, some confidence is obtained in the result. For practical purposes, a constant resistance over at least a decade of frequency space is sufficient. If the resistance depends on frequency over the whole range of frequencies (say from 1 to 100 kHz), then there is usually a problem with the measurement technique.

Several sets of raw data taken with the four-point-probe cell are presented in Fig. 2 in the form of the real component of the complex impedance (in Ω) versus frequency. The frequency dependence of the data depends on the magnitude of the sample resistance, with a more frequency-independent response over wider ranges of frequency achieved for lower resistance samples. The high-frequency roll-off expected from the measuring electronics occurs as the sample resistance increases. With the present cell and electronics, an accurate conductivity measurement is not possible for films with resistances in excess of 10 MΩ over the 0.2 cm length × 1.0 cm width measuring region. These high resistances correspond to conductivities of order 10^{-6} S/cm or lower.

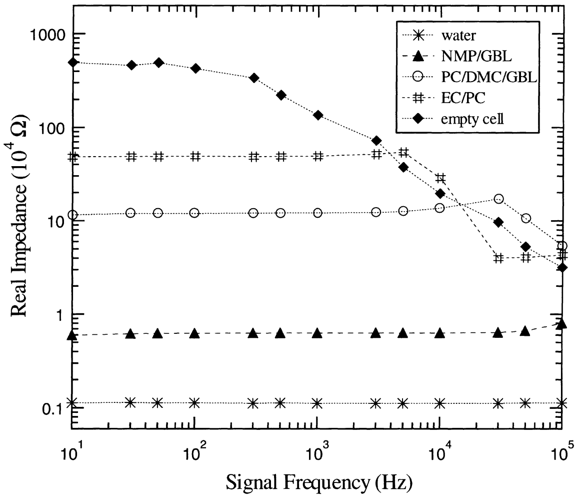

Fig. 2. Impedance data taken with the four-point-probe conductivity cell for films having various bulk resistances. The real component of the complex impedance is plotted vs. signal frequency over a range of frequencies. A frequency-independent impedance is desired for a more accurate measurement of bulk resistance or ionic conductivity. All films are Nafion® 117 membranes swollen with various solvents or solvent mixtures as indicated on the figure.

As the film resistance increases, the accuracy of the measurement decreases due to the frequency dependence of the impedance data. Thus, lower conductivity data are less accurate than data on highly-conducting films. The opposite is the case with two-electrode conductivity measurements where higher sample bulk resistances make elimination of interfacial effects easier. The present cell geometry measures the in-plane ionic conductivity for the membrane, whereas most applications depend upon through-plane conduction. However, only one study in the literature has claimed to see a directional dependence for the ionic conductivity of Nafion® membranes and the difference in the two directions was relatively minor [15,16].

Solvent uptake is measured by immersing a dry film sample into the solvent of interest, allowing the solvent to be imbibed into the film for a given amount of time at a given temperature, and measuring the initial and final weights and thicknesses of the film. The films are patted dry to remove surface solvent prior to all measurements. Solvent uptake and membrane swelling are calculated with respect to the initial dry weight and thickness of the films unless stated otherwise

$$\text{weight uptake } (\omega) = \frac{\omega_{\text{final}} - \omega_{\text{init}}}{\omega_{\text{init}}} \qquad (2)$$

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 mm.

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 <100 ppm water. Except for these latter solvents, the solvents were dried additionally by storing over lithium cation-exchanged 4 Å molecular sieves which typically was found to reduce water content into the 10–30 ppm range based on coulometric titration. A complete list of the nonaqueous solvents and their abbreviations used in this manuscript are given in the beginning.

All commercial Nafion® membrane products were obtained from the DuPont Company. These include the following products: N117 = Nafion® XR membrane with 1100 g/eq nominal EW and 7 mil thickness and N115 = Nafion® XR membrane with 1100 g/eq nominal EW and 5 mil thickness. Standardized membrane hydrolysis, cation exchange, and pretreatments are required to obtain high and reproducible ionic conductivities. For the most part, the ionomeric polymers examined were received in the sulfonyl fluoride form and hydrolyzed, lithium exchanged, and dried prior to the experimental work. The bulk of the data in this work was taken on Li^+-exchanged Nafion® 117 membranes.

For the membrane samples used in this work, a combined hydrolysis-lithium exchange procedure was carried out for 2 h at 60°C in a well-stirred vessel using a hydrolysis solution composed of 0.5 M LiOH in 1:1 H_2O:DMSO. After hydrolysis, membranes were rinsed and washed in deionized water for 2 h at 95–100°C to remove the remaining salt and organic solvent from the membrane. The membranes were dried for several days in a nitrogen-purged vacuum oven at 120°C prior to transfer directly into a glove box.

Nafion® 117 membranes in other cationic forms were obtained by immersing N117 (Li^+) in 0.1 M solutions of the metal chloride salt (or the metal nitrate for Ag^+) and waiting for equilibrium to occur based on ionic conductivity measurements made at one-day intervals. In some cases, such as tetrabutylammonium (TBA^+), this process took over 2 weeks to reach equilibrium. As an additional check on the extent of ion exchange, inductively coupled plasma analyses were done on cation-exchanged membrane samples and in all cases <0.5% of the fixed anion sites in the ionomers were occupied by residual foreign metal ions.

3. Results

3.1. Ionomer membrane hydrolysis and ion exchange processes

The ionic conductivity is a satisfactory indicator for both the extent of hydrolysis of the sulfonyl fluoride groups and the degree of ion exchange. Conductivity measurements were performed under ambient conditions with fully humidified films. Complete and rapid exchange of protons for lithium ions in a N117 membrane could be achieved in a period of 1 h using a 0.1 M LiOH solution in water. The ionic conductivity dropped from about 0.090 to 0.016 S/cm over the course of the procedure. The time constant for the cation exchange process, which can be written as

$$\begin{aligned}&\text{Nafion-SO}_3{}^-\text{H}^+ + \text{LiOH}\\&\quad\rightarrow \text{Nafion-SO}_3{}^-\text{Li}^+ + \text{H}_2\text{O}\end{aligned}$$

depends on the relative mobilities of both Li^+ and H^+ cations. This may be estimated from the two individual ionic diffusivities, each of which can be calculated from ionic conductivity data on N117 membranes using the Nernst–Einstein equation (sometimes referred to as the inter or mutual diffusion coefficient) [17].

For a N117 membrane, for example, a diffusional time constant of the order of 2 min is expected using the measured mobilities of Li^+ and H^+ based on the conductivity data. This agrees with the results of Yeager [18], who reported exchange times for H^+ and Na^+ of 2 min. For cations with lower mobilities in the membrane, the ion exchange process can become prohibitively slow, as for the TBA^+ cation. This might be due to the low hydration of TBA^+ salts leading to dehydration of the surface of the membrane.

An efficient procedure for the lithiation of Nafion® membranes is to carry out the Li^+ exchange directly during the membrane hydrolysis reaction. This process can be described as

$$\begin{aligned}&\text{Nafion-SO}_2\text{F} + 2\text{LiOH}\\&\quad\rightarrow \text{Nafion-SO}_3{}^-\text{Li}^+ + \text{LiF} + \text{H}_2\text{O}\end{aligned}$$

This reaction is frequently carried out using a KOH solution due to the increased solubility of KF compared with LiF. Lithium hydroxide concentrations from 0.1 to 1.0 M in H_2O:DMSO can bring about complete hydrolysis and lithium exchange of Nafion® membranes. This LiOH hydrolysis process was also attempted using either deionized water alone or water–methanol mixtures as solvents, but none of these baths were successful in bringing about complete lithium exchange within one day.

Previous experience within the industry has suggested that LiF precipitation within the membrane can lead to damage, such as voids in the membrane, which is one reason that KOH is the preferred base. To determine if this was a valid concern, SEM photographs were taken of N117 membranes hydrolyzed with either KOH or LiOH in a H_2O:DMSO hydrolysis bath. These photos did not show any damage to the membranes in either case, and it was concluded that the LiOH hydrolysis process is a satisfactory one.

The degree of hydrolysis and extent of lithium exchange may be measured in a number of ways. While the most accurate technique may be an FTIR-based approach [19], in the present study, we found the use of membrane conductivity to be straightforward. It is possible to quantify both the degree of lithium exchange and the degree of hydrolysis by using data on the conductivity of fully-hydrated N117 membranes in either Li^+ or acid-form. For example, to determine the extent of ion exchange from protons to Li^+, the conductivity can be assumed to vary linearly between the two values given earlier of 0.090 and 0.016 S/cm as the proton to Li^+ ratio changes. This same approach has recently been utilized in the literature for exchanges between protons and Ca^{2+} cations [20]. While approximate for the intermediate states of ion exchange, this approach works well for determining the point of completion of the ion-exchange reaction.

A successful hydrolysis-lithium exchange reaction for a Nafion® 117 membrane is exhibited by a room temperature ionic conductivity in the fully-hydrated state of about 0.016 S/cm. Fig. 3 demonstrates the diffusion-limited nature of the hydrolysis reaction by presenting ionic conductivity versus time of hydrolysis for two different solvents (1:1 DMSO:H_2O or 1:1 MeOH:H_2O at 60°C) with 1100 g/eq nominal EW Nafion® membranes. Small samples from a larger section of membrane were withdrawn, prepared, and ionic conductivity measured at 1 h intervals over the course of 9 h hydrolysis reactions. The diffusion processes dominating the hydrolysis reaction are reflected in the different degrees of hydrolysis for the N115 versus N117 membrane.

3.2. Dependence of ionic conductivity on cation type for N117

Various cation-exchanged N117 membranes were prepared as described and swollen with nonaqueous solvents. Conductivities of membrane samples equilibrated with liquid water were examined for comparison purposes. Table 1 gives conductivity data as they depend on cation type in a number of different solvents. These data for the solvents NMF and DMSO are plotted against Pauling cation radius and compared with the equivalent data for water in Fig. 4.

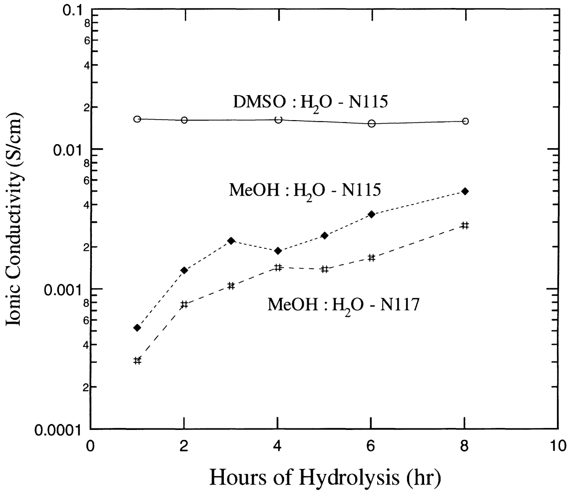

Fig. 3. Ionic conductivity of Nafion® membrane samples over the course of hydrolysis treatments at 60°C in 0.5 M LiOH solutions in either 1:1 H_2O:MeOH or 1:1 H_2O:DMSO solvents. During the hydrolysis, the sulfonyl fluoride sites in the polymer are converted to cationic sites, leading to the increase of ionic conductivity shown here. It is apparent that the DMSO bath fully hydrolyzes the membrane much more rapidly than the MeOH bath.

The dependence of conductivity on cation type is complicated and solvent dependent. No clear trends exist with cation radius for all three solvents. The data for NMF are remarkable for their independence on cation type, with all data grouped between 1 and 6 mS/cm. The lack of dependence on cation type of the swelling of Nafion® membranes by amide-based solvents, such as NMF and formamide was noted previously [9,10]. Similar to water, DMSO shows a marked dependence on cation valence (the conductivity of the trivalent ferric ion is too low to appear on Fig. 4), but little obvious correlation with cation radius. The highest conducting cations in both NMF and DMSO are H^+, Ag^+, and $NH_4{}^+$, followed by Li^+, K^+, Na^+, Cs^+, and Rb^+; however, the order of conductivities can change between different solvents. Weight gains for various cation-exchanged films correlate with conductivity, although the uptake depends more strongly on solvent than cation type.

As the cation changes from the ammonium and Ag^+ cations to the alkali metals, the conductivity

Table 1
Ionic conductivity data (in mS/cm) for Nafion® 117 membranes exchanged with various cations and equilibrated with specific dipolar solvents at $T = 23°C$

Cation type	Ionic conductivity in water	Ionic conductivity in TEP	Ionic conductivity in NMF	Ionic conductivity in GBL	Ionic conductivity in DMSO
H^+	90.20	0.487	5.56	0.827	3.62
$NH_4{}^+$	24.92	0.571	4.78	0.593	2.93
Ag^+	25.10	0.387	5.95	0.495	3.05
Li^+	16.10	0.345	4.60	0.475	1.60
Na^+	18.68	0.321	3.83	0.518	0.504
K^+	13.79	0.141	4.10	0.023	0.797
Rb^+	10.13	0.078	3.87	0.013	0.995
Cs^+	5.95	0.007	3.59	0.013	1.65
Mg^{2+}	8.87	$<1 \times 10^{-3}$	2.50	0.004	0.192
Ca^{2+}	9.09	$<1 \times 10^{-3}$	2.73	0.011	0.351
Sr^{2+}	8.03	$<1 \times 10^{-3}$	3.29	0.025	0.319
Ba^{2+}	7.34	$<1 \times 10^{-3}$	2.96	0.012	0.368
Fe^{2+}	8.21	$<1 \times 10^{-3}$	2.80	0.006	0.081
Ni^{2+}	9.43	$<1 \times 10^{-3}$	2.15	0.004	0.129
Cu^{2+}	9.08	0.001	2.86	0.012	0.258
Zn^{2+}	9.42	0.001	2.63	0.008	0.171
Fe^{3+}	2.96	$<1 \times 10^{-3}$	1.88	$<1 \times 10^{-3}$	$<1 \times 10^{-3}$

decreases for all solvents examined. These first two cations are the highest conducting in general, possibly because they are weakly bound by solvent molecules or interact less strongly with the fluorosulfonate ionic group. Among the alkali metal cations, the conductivity generally decreases with increasing cation radius, although more or less sharply for the different solvents. The difference between the smallest alkali metal cations (Li^+ and Na^+) is lower than expected due to the increased solvation of the smaller cations leading to larger effective radii. The variations in conductivity for the higher valence cations are more difficult to explain and could relate to specific solvation processes that vary from solvent to solvent.

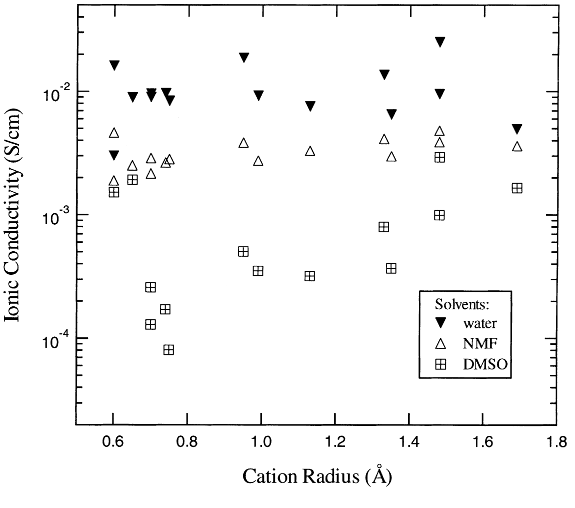

Fig. 4. Ionic conductivity data on various cation-exchanged forms of the N117 membrane in water, NMF, and DMSO at room temperature. Data are plotted for fifteen different univalent, divalent, and trivalent cations as a function of Pauling cation radius.

3.3. Dependence of ionic conductivity on solvent type for N117 (Li^+)

The ionic conductivity and swelling behavior of Li^+-form N117 membranes equilibrated with a number of nonaqueous solvents are given in Tables 2 and 3. The weight uptake and thickness increase are both based on the dry polymer. The solvents are split into the two tables based on their relative conductivities, with good solvents ($>10^{-4}$ S/cm) listed in Table 2 and poor ones ($<10^{-4}$ S/cm) in Table 3. The ionic conductivity varies over more than five orders of magnitude from the best conducting solvent to the poorest. Conductivities lower than approximately 10^{-6} S/cm, corresponding to film resistances of greater than about 10 MW, could not be measured with the present

Table 2
Ionic conductivities of Li^+-form N117 films at room temperature swollen in various solvents[a]

Solvent type	Weight uptake, ω (%)	Thickness increase (%)	Ionic conductivity (S/cm) at 23°C	Molar uptake, λ
H_2O	33	27	1.61×10^{-2}	20.2
NMF	284	90	5.43×10^{-3}	52.9
MeOH	161	66	4.95×10^{-3}	55.3
DMF	225	83	3.80×10^{-3}	33.9
DMA	167	45	3.08×10^{-3}	21.1
DMSO	136	38	1.60×10^{-3}	19.1
NMP	134	38	1.25×10^{-3}	14.9
ACE	40	13	7.09×10^{-4}	7.6
MG	88	26	7.05×10^{-4}	10.8
DMPU	230	61	5.77×10^{-4}	19.7
DMB	109	27	5.48×10^{-4}	10.4
EG	96	26	5.18×10^{-4}	10.2
GBL	88	27	5.03×10^{-4}	11.2
TEP	154	38	3.86×10^{-4}	9.3
TMS[b]	113	41	3.17×10^{-4}	12.4
BG	99	28	2.44×10^{-4}	8.3
DME	29	14	2.40×10^{-4}	3.5
EC[b]	71	16	1.43×10^{-4}	8.9
DBA	244	51	1.41×10^{-4}	15.7
NBA	44	28	1.01×10^{-4}	6.6
DMDA	213	39	9.05×10^{-5}	11.8

[a] Solvents listed provide conductivities in excess of 10^{-4} S/cm.

[b] Data taken at 40°C.

Table 3
Ionic conductivities of Li^+-form N117 films at room temperature swollen in various lithium battery solvents[a]

Solvent type	Weight uptake, ω (%)	Thickness increase (%)	Ionic conductivity (S/cm) at 23°C
PC	65	23	2.16×10^{-5}
MF	16	9	1.31×10^{-5}
THF	23	15	1.28×10^{-5}
PODO	16	4	8.95×10^{-6}
DMTHF	6	2	8.84×10^{-6}
PEG	132	36	7.66×10^{-6}
DMC	23	4	7.12×10^{-6}
ACN	19	11	5.36×10^{-6}
MA	21	10	5.0×10^{-6}
DEC	26	13	5.0×10^{-6}
DIOX	24	23	4.7×10^{-6}
DMES	26	13	3.4×10^{-6}
MTBE	−6	0	3.1×10^{-6}
DMSU	17	14	2.9×10^{-6}
DEE	10	10	2.4×10^{-6}
EA	31	8	2.1×10^{-6}
MEED	16	6	1.5×10^{-6}
EAA	29	15	1.4×10^{-6}
FC1	−1	5	$<1 \times 10^{-6}$
FC2	2	3	$<1 \times 10^{-6}$

[a] These solvents provide poor conductivities.

equipment. The ionic conductivity of dry Nafion® membranes, in either Li$^+$ or acid form, is significantly lower than 10^{-6} S/cm at room temperature. See abbreviation list for a key to solvent abbreviations.

Very high ionic conductivities are achieved by a number of nonaqueous solvents including alcohols, glycolates, dimethyl sulfoxide, amides, such as NMF, DMF, and NMP, triethyl phosphate, and the cyclic ester GBL. There is an obvious correlation between ionic conductivity and percent solvent uptake or thickness increase, with higher conductivities achieved for the solvents that induce more swelling.

However, there is not a one-to-one relationship between weight gain and conductivity as is apparent by the outlying solvents, such as water (low weight gain, high conductivity) and polyethylene glycol (high weight gain, lower conductivity). In addition, there is no direct correlation between conductivity and a single bulk solvent property, such as boiling point, dielectric constant, or viscosity. Trends do exist, such as conductivity increasing with decreasing solvent molecular weight and viscosity and increasing with dielectric constant and donor number. Some of these trends are illustrated in the figures to follow.

The conductivity data given in Tables 2 and 3 were taken after equilibration of a membrane sample with an excess of the solvent at room temperature. The effect of carrying out the equilibration process for longer times and at higher temperatures was also examined. Heat treatments have been shown in the literature to increase the uptake of organic solvents in Nafion® membranes [3,9,10]. However, in this work, only the more viscous solvents, such as PEG showed an appreciable and reproducible increase in uptake and conductivity after such heat treatments.

The effect of time in solvent and heat treatments (at 60°C in sealed containers) on the ionic conductivity for a number of solvents is illustrated in Fig. 5. Following the same symbol from left to right on the figure illustrates the changes in conductivity versus time in a given solvent; the vertical lines are only given to guide the eye. For the most part, the variations in conductivity between these experiments are minor although a slight increase in the values for some of the solvents might have occurred. The equilibrium solvent uptake is typically reached within 2 h and heat treatments to $T = 60^\circ$C do not increase uptake substantially further than the room-temperature soak. Higher temperature heat treatments would probably find a different result as has been discussed in the literature [3,9].

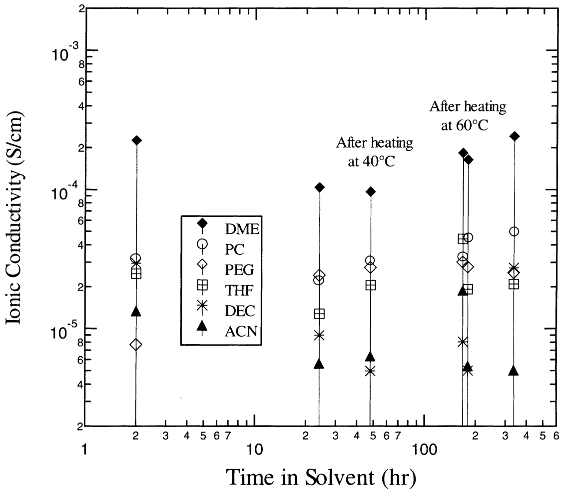

Fig. 5. Ionic conductivity data for a number of different solvents in N117 (Li$^+$) membranes over the course of several successive experiments taken at different times and after heat treatments. Following the same symbol from left to right on the figure illustrates the changes in conductivity over time and under different conditions. Much of the variation between the experiments is due to experimental error rather than any systematic influence of the time in solvent.

Examining the conductivity data in more detail, it becomes apparent that particular functional groups give highly conductive films, such as alcohols, amides, and sulfoxide. Hydrogen-bonding solvents fare especially well, such as water, alcohols, and glycolates. The high conductivity of GBL, a cyclic ester, is in contrast to the poor results with linear esters. Comparing this with the cycle carbonate (EC and PC) results demonstrates that the higher dielectric constant of the cyclic molecules provides an advantage over their linear analogues. Poor conductivities result from a number of other functional groups, such as nitriles, cyclic or linear ethers, linear esters, and carbonates.

The amide solvents tested all produce a high degree of swelling and a corresponding high ionic conductivity. The relative ranking of the amide swelling and conductivity from this work

$$\mathrm{NMF} > \mathrm{DMF} > \mathrm{DMA} > \mathrm{NMP} > \mathrm{DMPU} > \mathrm{DMB} > \mathrm{DMDA} > \mathrm{DBA}$$

largely follows the molecular weight or molar volume of the compounds. The first few amide solvents are extraordinary in their swelling and conductivity in Nafion® membranes, with both high conductivity and significant swelling. Given the much higher dielectric constant and donor number of NMF compared to amides without the amido hydrogen, such as DMF and DMA, it is surprising that their differences in conductivity are not greater. Rather, the lower molecular weight of NMF appears to be the only property needed to explain the difference. This also indicates that increasing the electron donating capabilities or dielectric properties of the solvent brings about an increase in conductivity only up to a point, after which diminishing returns are achieved as macroscopic solvent properties related to molecular motion become dominant, such as viscosity and molecular weight.

The high conductivity and swelling behavior of DMSO is contrasted with other sulfur-containing solvents, such as dimethyl sulfite, sulfolane, and various sulfamides which provided poor results. The marked difference between DMSO and DMSU is magnified compared to literature data on lithium trifluoromethane sulfonate (LiTf). The ionic conductivity of LiTf is approximately nine times higher in DMSO than in DMSU [21]. The poor results for sulfolane may simply be a viscosity effect, which is more severe in the environment of the membrane than in bulk solutions.

Poor results were found for most of the ether solvents. These solvents tend to have low dielectric constants and are expected to show poor ion solvating properties. This may be the cause of the low conductivity and uptake for even the cyclic ethers, such as THF and DIOX ($\varepsilon = 7.58$ and 7.13, respectively). Attempts to swell Nafion® membranes with MTBE resulted in negative weight gains, probably associated with the ether's ability to extract impurities, such as water from the membrane. Similar results were found for partially fluorinated alkyl ethers.

As expected, difunctional ether solvents, such as DME and diethoxyethane, were an exception. These solvents are known for their ability to complex alkali metal cations. DME was also exceptional in its ability to provide high conductivities in mixtures with other dipolar solvents, such as PC, a fact long recognized in the lithium battery industry and interpreted as resulting from the low viscosity of this solvent [22]. Solvent viscosity does not appear to be the key parameter because a number of other mixtures with low viscosity solvents did not show such an enhancement.

A variety of pure solvent physical properties were examined in attempting to correlate the swelling and conductivity behavior: dielectric constant, molar volume (calculated from molecular weight divided by solvent density), viscosity, molecular weight, melting and boiling points, dipole moment, index of refraction, air–liquid surface tension, Flory–Huggins solubility parameter, and donor number [23,24]. As mentioned earlier, no single property is able to explain the trends in ionic conductivity in N117 membranes but a rough correlation exists with several of the properties.

Fig. 6 demonstrates the relationship between conductivity and polymer swelling by plotting conductivity versus both percent weight uptake and percent thickness increase for a set of eighteen of the above solvents. There is a clear relationship between the conductivity and extent of swelling or thickness increase. The solid curve on the figure is a least squares fit to the conductivity versus weight uptake data (first having eliminated the data point for water from the fitting procedure). The only major discrepancy on

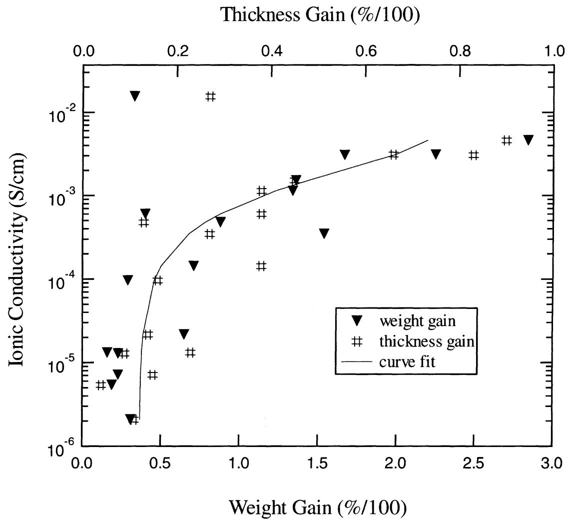

Fig. 6. Ionic conductivity data vs. weight gain and thickness increase for a number of different solvents in N117 (Li^+) membranes. A correlation exists between weight gain or thickness increase and ionic conductivity as demonstrated by the solid curve which is a least squares fit to the conductivity vs. weight gain data. The outlying data point in the upper left-hand corner of the plot is for water which was excluded from the curve fit.

this plot is the result for water. One might expect the conductivity to reach a very low value ($<10^{-7}$ S/cm) at zero weight uptake, corresponding to the conductivity of dry Nafion® membrane. However, as our equipment was not capable of measuring such a high resistance and this value is notoriously dependent on the measuring conditions and presence of trace water in the sample, we did not force the fit to accommodate such an end-point value.

The solvent's donor number, a measure of the Lewis base properties of the solvent, will often follow trends in conductivity data better than dielectric constant data. The donor number is given in units of kJ/mol and represents the heat of solvation of $SbCl_5$ by the solvent in question in dichloroethane [23,24]. Fig. 7 illustrates the dependence of conductivity on either property for a number of solvents. While both properties appear to correlate with conductivity, there is significant scatter in both data sets. The approximate correlation between ionic conductivity and solvent donor number highlights the importance of electron donation in solvation and ion conductivity [24]. The swelling study of Gebel et al. [9] concluded that solvent donor number was the most important parameter in predicting solvent uptake although these authors found a maximum in swelling with donor number.

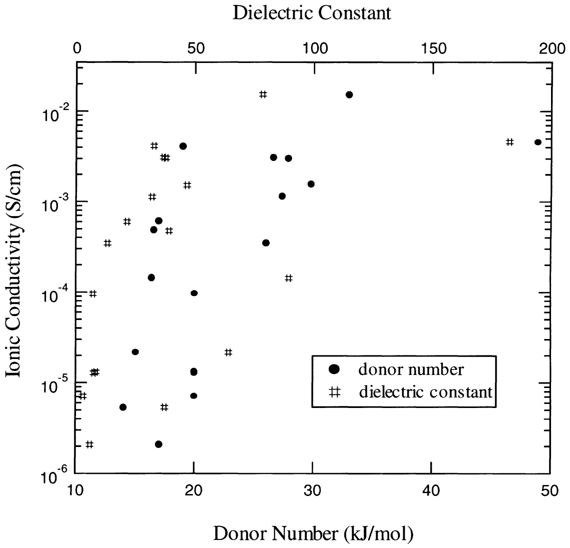

Fig. 7. Ionic conductivity data plotted against solvent donor number and dielectric constant for a number of different solvents in N117 (Li^+) membranes. Conductivity correlates reasonably well with both properties, although substantial scatter is apparent for both data sets.

No significant statistical correlation between ionic conductivity and surface tension was seen in this work, while solubility parameter correlated with solvent uptake to a limited extent. Stokes' law considerations suggest conductivity should be inversely proportional to bulk viscosity because of the drag effects of the medium through which the ions move. A correlation between ionic conductivity and solvent viscosity was apparent only in the high conductivity range. The same can be said for solvent molecular weight, which appears to be important only when the conductivity is greater than about 10^{-4} S/cm.

Solvent properties, such as viscosity, only have a substantial influence when enough solvent molecules have been absorbed into the polymer structure. Prior to sufficient absorption of solvent, the local viscosity felt by the ions is dominated by the polymer structure and crystallinity. The solvent molar uptake is defined as the moles of solvent per mole of sulfonate ionic sites in the polymer under equilibrium conditions of unit solvent activity. Molar uptake is defined here as

$$\text{molar uptake}\ (\lambda) = \frac{\omega}{M_0}\text{EW} \qquad (3)$$

where M_0 is the solvent molecular weight and ω the solvent uptake. Molar uptakes of greater than about 6 to 8 appear necessary for high conductivity. Values of molar uptake for a number of solvents in N117 (Li^+) membranes were given in Table 2.

Once a sufficient number of solvent molecules exist to promote cation donation and solvation, bulk solvent physical properties, such as viscosity become important parameters for predicting ionic conductivity. The molar uptake parameter λ, calculated here using Eq. (3), is identical to the N parameter of Gebel et al. [9] which was calculated using volumetric expansion data. These authors reached a similar conclusion although their molar uptakes tended to be lower probably as a result of the different approaches used to calculate the values.

It is highly desirable to have a predictive capability for ionic conductivity in solvent-swollen ionomer membranes. The data of 23 different membrane-solvent combinations from Tables 2 and 3 spanning four orders of magnitude in conductivity were used as a basis set. The best empirical correlation found

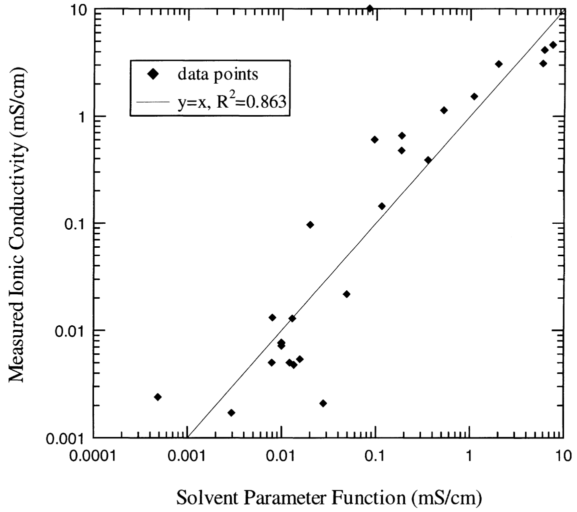

Fig. 8. Correlation between ionic conductivity of N117 (Li^+) membranes and solvent parameters. The functional form, referred to here as the solvent parameter function, used to generate the predicted values is given in the text.

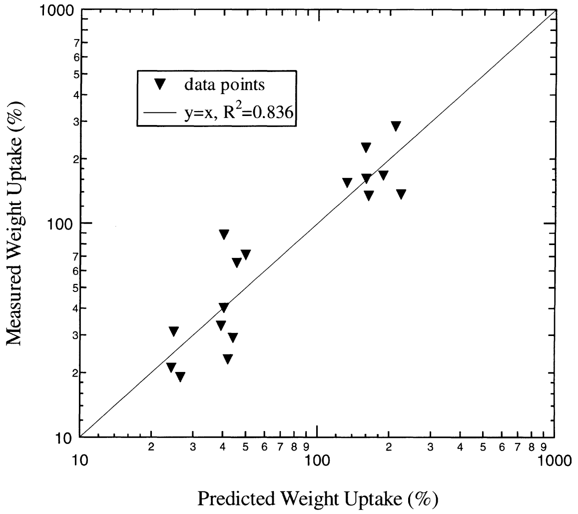

Fig. 9. Correlation between percent solvent weight uptake of N117 (Li^+) membranes and predicted or calculated value based on a correlation using various solvent parameter values. The correlation function used to generate the data in the figure is given in the text.

for the ionic conductivity of N117 (Li^+) membranes swollen with various solvent parameters is illustrated in Fig. 8. This figure plots the measured conductivity of the film against the calculated or predicted value. The plot is on log–log axes so that the large span of conductivity values can be displayed. The line $y = x$ is also shown on the figure to guide the eye. The relation between the measurements and the calculated conductivities has a Chi-squared correlation of 0.863. The empirical equation used to calculate the values of the conductivity in Fig. 8 is

$$\kappa\,(\mathrm{mS/cm}) = 4.902 \times 10^{-5}\left[\frac{\omega^3\rho}{\eta\,\mathrm{MW}}\right]^{0.965} \qquad (4)$$

where ω (%) is 100 times the weight uptake from Eq. (2).

The correlation of Eq. (4) uses the experimental solvent weight uptake of the N117 membranes. It would be desirable to be able to predict this weight uptake. This has been accomplished and the correlation is shown in Fig. 9. The Chi-squared correlation value for this empirical expression is 0.836. The equation for the calculated percent weight uptake of the solvent is

$$\omega\,(\%) = 0.05341 \times \left\{\frac{(\mathrm{DN})^3\varepsilon^{1/2}}{\delta}\right\}^{0.9452} \qquad (5)$$

where DN is the donor number and δ the solubility parameter.

The function for calculating the percent weight uptake of the solvent by the membrane includes only three solvent properties. There is no fundamental basis for the functional form chosen; the parameters used are those that showed the best capability to fit the data. The functional form was assumed to be a power function of the parameters and the powers of each of the parameters were varied to obtain the best fit to the data. A preference was given to positive or negative integer values, or in the case of the dielectric constant, the square root was allowed. Note that the ratios of the powers of the different parameters are actually the important factor in the correlation. The entire function can be raised to any arbitrary power and combined with a multiplicative constant in order to force the function to give the “correct numerical value” of the calculated percent weight uptake.

In determining the functional relationship between the solvent parameters and the swelling of the Nafion® membrane by the solvents, the following physical considerations were considered. There is a certain amount of free volume initially within the polymer that the solvent can occupy. Once a small amount of solvent is in the film, the solvent will dissociate some of the lithium ions from the anionic sites. The initial number density of the lithium ions in solution will depend on the solvent. Properties, such as the basicity (measured by the donor number), the dielectric constant, and solubility parameter were considered to be likely candidates for affecting the solvent's capability to solvate the lithium cations. Once there is an initial concentration of ions within the swollen polymer membrane, then osmotic pressure forces will try to reduce this concentration. As more solvent enters the film, it will solvate more of the ions. However, the mechanical properties of the polymer (such as elasticity) will provide a force to oppose the swelling pressure. Given a particular technique for the swelling procedure that allows equilibrium to be established, a predictable amount of solvent uptake will occur.

3.4. Characterization of mixed solvent systems with N117 (Li^+)

It is known that mixtures of two nonaqueous solvents, such as PC/DME or EC/DMC, can have advantages over either pure solvent for nonaqueous battery applications. The explanation usually given for the enhancement in ionic conductivity in these mixtures is related to the more rapid decrease in viscosity than dielectric constant as the low viscosity additive is mixed with the higher viscosity solvent [22]. It is generally believed that both viscosity and dielectric properties are essential to achieve high ionic conduction, because ionic solvation and mobility are both necessary for conductivity according to the classical dilute-solution theory description of conductivity [25].

The ionic conductivities of N117 (Li^+) membranes were measured while swollen in a number of mixtures of two or three solvents. The solutions with which the membranes were equilibrated were prepared by mixing equal volumes of the constituent solvents. Only the total weight of solvent mixture absorbed by the membrane was measured; the relative amount of each solvent component (i.e. the composition) absorbed within the membrane was not measured. The emphasis was on solvent mixtures involving the cyclic carbonate solvents EC and PC. These results are summarized in Tables 4–6.

Table 4 illustrates data on binary mixtures where either propylene carbonate or ethylene carbonate is one component of the mixture. The conductivities of N117 (Li^+) in these mixtures vary significantly but tend to follow the order seen for the single solvents. EC mixtures are generally better conducting than PC mixtures. Preferred mixtures for lithium-ion batteries, such as PC/DEC and EC/DMC provide only poor conductivity values in the 1×10^{-5} S/cm range.

Table 4
Ionic conductivities of Li^+-form N117 membranes swollen in various PC- and EC-based binary solvent mixtures (1:1 by volume)

Solvent mixture	Weight uptake, ω (%)	Thickness increase (%)	Ionic conductivity (S/cm) at 23°C
PC/DME	68	20	2.57×10^{-4}
PC/EC	85	17	1.00×10^{-4}
PC/DEE	44	19	6.37×10^{-5}
PC/DMC	28	19	1.32×10^{-5}
PC/DEC	30	5	1.49×10^{-5}
PC/PEG	172	41	6.72×10^{-5}
PC/NMF	278	78	3.44×10^{-3}
PC/GBL	78	30	2.99×10^{-4}
PC/ACN	30	20	1.19×10^{-4}
PC/MA	33	17	6.56×10^{-5}
PC/MEED	58	31	5.53×10^{-5}
PC/DIOX	30	19	1.39×10^{-5}
PC/THF	45	22	4.86×10^{-5}
EC/DME	85	19	3.06×10^{-4}
EC/DMC	36	1	7.00×10^{-6}
EC/DEC	44	4	1.49×10^{-5}
EC/GBL	81	29	3.11×10^{-4}
EC/DMSO	122	33	1.48×10^{-3}

Table 5
Ionic conductivities of Li^+-form N117 membranes swollen in various binary solvent mixtures (1:1 by volume)

Solvent mixture	Weight uptake, ω (%)	Thickness increase (%)	Ionic conductivity (S/cm) at 23°C
DME/PEG	60	33	1.15×10^{-4}
DME/GBL	56	20	5.02×10^{-4}
DME/DMSO	186	53	1.97×10^{-3}
DME/SULF	38	17	1.17×10^{-4}
DME/NMP	108	36	1.20×10^{-3}
PEG/DEE	64	23	3.21×10^{-5}
PEG/DMC	71	24	4.82×10^{-5}
NMP/DMSO	141	45	1.39×10^{-3}
NMP/DMF	169	41	1.81×10^{-3}
NMP/GBL	153	44	1.16×10^{-3}
GBL/ACE	50	15	5.55×10^{-4}
GBL/ACN	51	15	3.37×10^{-4}
GBL/MA	40	14	1.23×10^{-4}
GBL/DEE	48	21	1.21×10^{-4}

Weight uptake and conductivity data on other binary solvent mixtures in N117 (Li^+) are given in Table 5. Of primary interest was the identification of conditions under which a positive “synergy” between the two solvents would occur, leading to an increase in conductivity over the value with either solvent alone. This phenomenon is known to occur with certain combinations of solvents, such as PC/DME. The same result was found here, with the conductivity of N117 (Li^+) swollen with PC/DME and EC/DME exceeding the individual values for the solvents by a substantial margin. The linear carbonate solvents DEC and DMC, on the other hand, more often brought about a decrease in solvent uptake and conductivity from the single solvent values when used in mixtures.

Data for a handful of ternary solvent mixtures are given in Table 6. The strong negative influence of the linear carbonates DMC and DEC is again apparent, as the comparison of EC/PC mixtures with DMC, DME, and DEE shows. PEG, on the other hand, is a favorable additive when present in mixtures with lower viscosity solvents. This is consistent with the relationship between the PEG and DME structures. None of the present ternary mixtures exceeds 10^{-3} S/cm, although several exceed 10^{-4} S/cm.

3.5. *Dependence of ionic conductivity on solvent weight uptake*

The results presented above, using a standard swelling procedure consisting of complete immersion of the membrane into an excess of solvent, demonstrate the critical relationship between swelling and conductivity. This swelling procedure may not be

Table 6
Ionic conductivities of Li^+-form N117 membranes swollen in various EC- or PC-based ternary solvent mixtures (1:1:1 by volume)

Solvent mixture	Weight uptake, ω (%)	Thickness increase (%)	Ionic conductivity (S/cm) at 23°C
PC/DME/PEG	169	47	3.33×10^{-4}
PC/DMC/GBL	58	8	7.92×10^{-5}
PC/DEC/DME	33	8	6.49×10^{-5}
PC/PEG/GBL	168	45	3.51×10^{-4}
PC/DME/DMC	38	12	7.65×10^{-5}
PC/EC/DMC	36	3	1.66×10^{-5}
PC/EC/DME	75	21	3.85×10^{-4}
PC/EC/DEE	71	24	1.47×10^{-4}
EC/DME/PEG	141	39	3.34×10^{-4}
EC/DEC/DME	39	22	1.39×10^{-4}

favored in some cases, because an excess of solvent is used and excessive swelling of the polymer can occur (for example, with lower EW membranes). In some cases, it is desirable if possible to increase the uptake of solvent for poorly conducting solvents to attain higher conductivities. In other cases, it may be preferred to reduce swelling from its fully-immersed equilibrium value. Alternative approaches to control uptake for solvent-swollen ionomer membranes are explored here.

Based on the aqueous membrane literature, it is known that starving the membrane of solvent brings about a reduction in conductivity [2]. Ionic conductivity versus solvent activity for PEM–FC membranes is often measured by exposing a membrane to different vapor-phase water partial pressures [26]. Rather than take that approach here, membranes were exposed to a controlled quantity of solvent corresponding to less than the equilibrium uptake. This is accomplished by applying a given quantity of solvent uniformly to the surface of the membrane using a pipette then measuring conductivity over time until equilibrium occurs. Additional quantities of solvent can be applied in subsequent doses until such a time that the maximum solvent level is reached. The procedure is only reproducible with high boiling solvents where solvent losses due to volatility under ambient nitrogen-purged glove-box conditions are reduced.

The ionic conductivity of N117 (Li^+) as a function of the weight uptake of DMF is presented in Fig. 10. While the equilibrium uptake and conductivity are expected to be 225% and 3.80×10^{-3} S/cm, following the above procedure led to the conductivity maximizing at a value of 2.98×10^{-3} S/cm at an uptake of about 105%. Higher uptakes could not be achieved without substantial liquid pooling around the membrane sample. This suggests a difference between solvent uptake for liquid-immersed and vapor-equilibrated membrane samples similar to what is seen with water. Conductivity rises sharply with increasing uptake to about 60%, then levels off at greater uptakes.

For poorly conducting solvents, it is preferable to have a method of increasing uptake substantially to improve conductivity. For example, heat treatments were mentioned earlier to increase uptake for some solvents. While not done here, it is suggested that even higher temperature heat treatments, in pressurized vessels if necessary, could increase uptake further and lead to improved conductivities.

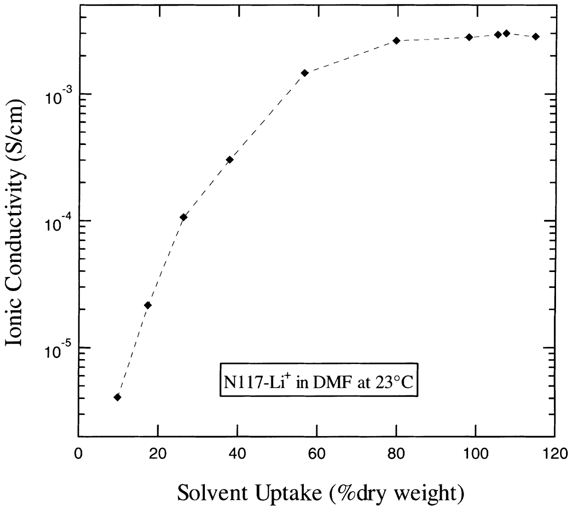

Fig. 10. Dependence of room-temperature ionic conductivity of N117 (Li^+) membranes on solvent content for dimethyl formamide. Various quantities of DMF are added to the surface of the membrane and allowed to equilibrate prior to taking the data shown in the figure.

Solvent uptake was also increased by carrying out solvent exchanges where a “good” solvent is imbibed by the membrane followed by immersing the membrane into an excess of a “poor” solvent. For example, a N117 (Li^+) membrane was equilibrated with DMSO followed by immersion directly into a THF bath. This procedure gives a higher total weight uptake than would be obtained by the standard procedure, and hence leads to a higher conductivity.

However, this effect is eliminated if the first solvent is removed completely from the membrane, such as through extensive drying. Hence, the good solvent is bound by the membrane even in the presence of an excess of the poor solvent and is actually the solvent species responsible for the higher conductivity. That the membrane returns to its original state after complete removal of the DMSO is consistent with the interpretation that swelling by DMSO under these conditions induces only a reversible elastic expansion of the perfluorocarbon backbone of the ionomer. This improvement in conductivity can only be utilized in applications where the presence of small amounts of the better solvent can be tolerated.

Considering the strong dependence of ionic conductivity on solvent swelling, other means for increasing swelling can be accomplished by changing the ionomer structure. The equivalent weight of the ionomer is expected to figure prominently in ionic conductivity due to the change in ionic concentration as well as the change in polymer crystallinity and hence elastic force resisting the swelling process. Solution-cast ionomer membranes, as opposed to melt extruded membranes, are also expected to give higher ionic conductivity because these can have reduced crystallinity and absorb larger quantities of solvent.

4. Conclusions

Ionic conductivity for lithiated 1100 g/eq nominal EW Nafion® perfluorinated ionomeric membranes are strongly dependent on the properties of the swelling solvent. The cationic form of the membrane influences conductivity to a varied extent depending on the choice of solvent with the relative order of conductivities being similar to those in water: $H^+ > Ag^+, NH_4{}^+ > Na^+ > Li^+ > K^+ > Rb^+ \gg$ divalent cations $> Cs^+ \gg$ trivalent cations $\gg$ tetrabutylammonium$^+$. Ionic conductivities for the N117 (Li^+) membrane exceed 10^{-3} S/cm at room temperature for a number of solvents showing that appreciable current densities can be sustained in environments other than aqueous solutions.

The most important factors influencing the ionic conductivity are the weight uptake of solvent by the polymer and solvent physical properties including molar volume, donor number, and viscosity. 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. Reasonably accurate correlations for predicting membrane conductivity and swelling for N117 (Li^+) as a function of solvent physical properties were given.

While membrane solvent properties are important in determining ionic conductivity, polymer structural properties are also critical. As cation dissociation can be the rate-limiting step in ionic conductivity in poorly solvating media, the basicity of the fixed anion group is expected to be a strong factor influencing conductivity. Membrane properties that dictate solvent swelling, such as equivalent weight and polymer crystallinity should also be important. These structural factors will be examined in future work.

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References

[1] A. Eisenberg, H.L. Yeager (Eds.), Perfluorinated Ionomer Membranes, American Chemical Society Symposium Series No. 180, Washington, DC, 1982.
[2] C. Heitner-Wirguin, Recent advances in perfluorinated ionomer membranes: structure, properties and applications, J. Membr. Sci. 120 (1996) 1.
[3] J. Jorissen, Ion exchange membranes as solid polymer electrolytes (SPE) in electro-organic synthesis without supporting electrolytes, Electrochim. Acta 41 (1996) 553.
[4] D.W. DeWulf, A.J. Bard, Application of nafion/platinum electrodes (solid polymer electrolyte structures) to voltammetric investigations of highly resistive solutions, J. Electrochem. Soc. 135 (1988) 1977.
[5] F.M. Kimmerle, R. Breault, SO_2 diffusion through acetonitrile-saturated perfluorosulfonic acid membranes, Can. J. Chem. 58 (1980) 2225.
[6] M.B. Armand, Ionically conductive polymers, in: C.A.C. Sequeira, A. Hooper (Eds.), Solid State Batteries, Martinus Nijhoff, Boston, 1985.
[7] M. Guglielmi, P. Alderbert, M. Pineri, Ionic conductivity of perfluorinated ionomer solutions and gels, J. Appl. Electrochem. 19 (1989) 167.
[8] P. Aldebert, M. Guglielmi, M. Pineri, Ionic conductivity of bulk, gels, and solutions of perfluorinated ionomer membranes, Polym. J. 23 (1991) 399.
[9] G. Gebel, P. Aldebert, M. Pineri, Swelling study of perfluorinated ionomer membranes, Polymer 34 (2) (1993) 333.
[10] R.S. Yeo, C.-H. Cheng, Swelling studies of perfluorinated ionomer membranes, J. Appl. Polym. Sci. 32 (1986) 5733.
[11] R.S. Yeo, Dual cohesive energy densities of perfluorosulphonic acid (Nafion) membrane, Polymer 21 (1980) 432.
[12] B.D. Cahan, J.S. Wainright, AC impedance investigations of proton conduction in Nafion®, J. Electrochem. Soc. 140 (1993) L185.
[13] Y. Sone, P. Ekdunge, D. Simonsson, Proton conductivity of Nafion® 117 as measured by a four-electrode AC impedance method, J. Electrochem. Soc. 143 (1996) 1254.
[14] S.J. Paddison, D.W. Reagor, T.A. Zawodzinski, High frequency dielectric studies of hydrated Nafion®, J. Electroanal. Chem. 459 (1998) 91.

[15] C.L. Gardner, A.V. Anantaraman, Measurement of membrane conductivities using an open-ended coaxial probe, J. Electroanal. Chem. 395 (1995) 67.

[16] C.L. Gardner, A.V. Anantaraman, Studies on ion-exchange membranes. II. Measurement of the anisotropic conductance of Nafion®, J. Electroanal. Chem. 449 (1998) 209.

[17] F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962, p. 269.

[18] R.S. Yeo, H.L. Yeager, Structural and transport properties of perfluorinated ion-exchange membranes, in: R.E. White, J.O'M. Bockris (Eds.), Modern Aspects of Electrochemistry, Vol. 16, Plenum Press, New York, 1985, p. 437.

[19] S.A. Perusich, Fourier transform infrared spectroscopy of perfluorocarboxylate polymers, Macromolecules 33 (2000) 3437.

[20] T. Okada, N. Nakamura, M. Yuasa, I. Sekine, Ion and water transport characteristics in membranes for polymer electrolyte fuel cells containing H^+ and Ca^{2+} cations, J. Electrochem. Soc. 144 (1997) 2744.

[21] N.-P. Yao, D.N. Bennion, Transport behavior in dimethyl sulfoxide. I. Conductance studies, J. Electrochem. Soc. 118 (1971) 1098.

[22] H.-J. Gores, J. Barthel, Conductance of salts at moderate and high concentrations in propylene carbonate-dimethoxyethane mixtures at temperatures from -45°C to 25°C, J. Solution Chem. 9 (12) (1980) 939.

[23] V. Gutman, The Donor–Acceptor Approach to Molecular Interactions, Plenum Press, New York, 1978.

[24] Y. Marcus, Ion Solvation, Wiley, Chichester, 1985 (Chapter 6).

[25] J. Newman, Electrochemical Systems, Prentice-Hall, Englewood Cliffs, NJ, 1991.

[26] T.A. Zawodzinski Jr., T.E. Springer, F. Uribe, S. Gottesfeld, Characterization of polymer electrolytes for fuel cell applications, Solid State Ionics 60 (1993) 199.