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Investigation of Proton Conductivity of Cation-Exchanged, Sulfonated Poly(b-Styrene-b-Isobutylene-b-Styrene) Membranes

by Eugene Napadensky

ARL-TR-4940 **September 2009**

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14. ABSTRACT

In this study, membranes made with highly sulfonated (81%–97%) poly(styrene-b-isobutylene-b-styrene) polymer were exchanged with a variety of cations: Cu, Ba, Zn, Cs, Ag, Ca, and Mg. Absorption levels of the cation-exchanged materials was determined for water, methanol, and an equimolar water/methanol mixture, measured using a gravimetric technique. Proton conductivity of the membranes was measured in a dry state, as well as swollen in water, methanol, and the equimolar water /methanol mixture. Water-swollen membranes showed proton conductivity in the range of 2×10^{-3} to 1.2×10^{-2} S/cm, depending on the cation used for exchange. Conductivity increased proportionally to amount to the water molecules present in the membranes. Different cations promoted different levels of water absorption, with Cs and Ag having the highest amounts of water and conductivity, presumably because these two elements had only one valence electron compared to others used in this study.

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1. Introduction

Research in ionic polymers has been gaining popularity in the scientific community. Their potential use for novel fuel cell membranes, sensors, batteries, and ether electrochemical applications has promoted much work in the field. Most of the efforts are aimed at developing a less expensive version of Nafion* (a perflourosulfonate ionomer) for proton conductive, direct methanol fuel cells (DMFC).

Different types of ionic materials are being researched by various organizations throughout the world including poly(styrene-co-acrylonitrile) (*1*), poly(ethylenetetrafluoroethylene-graft-polystyrenesulfonic acid) (*2*), sulfonated trifluorostyrene (*2*), sulfonated poly(ether ketone ketone) (*3*), sulfonated poly[bis(3-methylphenoxy) phosphazene] (*4*), poly(vinylbenzyl phosphonic acid) (*5*). Most of the materials are comprised of polymeric backbones incorporating sulfonic acid (and, in some cases, phosphoric) groups that offer proper environment for conglomeration of water molecules around the ionic groups. As the amount of water clustered around the ionic groups exceeds a threshold level (percolation limit), the clusters create an interconnected network, allowing charge transfer through the membrane (*6*). This could include transfer of protons between anode and cathode for use as a fuel cell's membranes or transfer of various molecules/ions for various purification and sensing applications.

Sulfonated polystyrene-b-polyisobutylene-b-polystyrene (S-SIBS) is one example of such an ionic polymer. The sulfonic groups are attached to styrene molecules, creating polar polymer sections covalently bonded to aliphatic polyisbutylene. Thermodynamic incompatibility forces those two types of polymers to separate into different (hydrophobic – hydrophilic) domains. When the acidic groups in this (or similar) polymer are further modified with organic or inorganic cations, many properties undergo significant changes. It was shown that properties such as thermal stability, chemical agent resistance, and solvent resistance can be significantly altered by such modification (*7*, *8*).

In this work, the impact produced by exchanging acidic hydrogen of a sulfonic group in an S-SIBS polymer with various cations was examined. Specifically, proton conductivity was evaluated to gauge potential usefulness of these polymers for a DMFC membrane. In addition, membrane sorption of water and methanol was evaluated. An attempt was made to find patterns that allow predictions in how cation-substituted S-SIBS polymers will perform in membrane applications.

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*Nafion is a registered trademark of DuPont.

2. Experimental

2.1 Materials

Poly(styrene-b-isobutylene-b-styrene) block copolymer (SIBS) was provided by Kuraray Co., Ltd., Tsukuba Research Laboratories, with the reported properties: 30.84 weight-percent styrene, 0.95 specific gravity, Mw = 71,920 g/mol, Mn = 48,850 g/mol, and polydispersity index = 1.47. Other chemicals used in this study included magnesium perchlorate (Acros Organics), barium chloride (J. T. Baker), calcium chloride (EM Science, 90%), copper (II) chloride (Acros Organics, 99%), zinc chloride (EM Science, 98%), silver nitrate (Acros Organics), cesium chloride (Aldrich), water (J. T. Baker, HPLC grade), acetone (Warner-Graham Co., reagent grade), ethanol (VWR, reagent grade), toluene (EM Science, 99.5%), hexanol (J. T. Baker), and methanol (J. T. Baker, HPLC grade).

2.2 Membrane Preparation

Poly(styrene-b-isobutylene-b-styrene) block copolymer was sulfonated (figure 1) at the U.S. Army Research Laboratory with acetyl sulfate to the following various levels: 81%, 88% and 97%. The percent sulfonation refers to the percent of styrene groups in the polymer that were modified with the sulfonic acid group as verified by titration and elemental analysis. The sulfonation procedure is described in detail elsewhere (*9*).

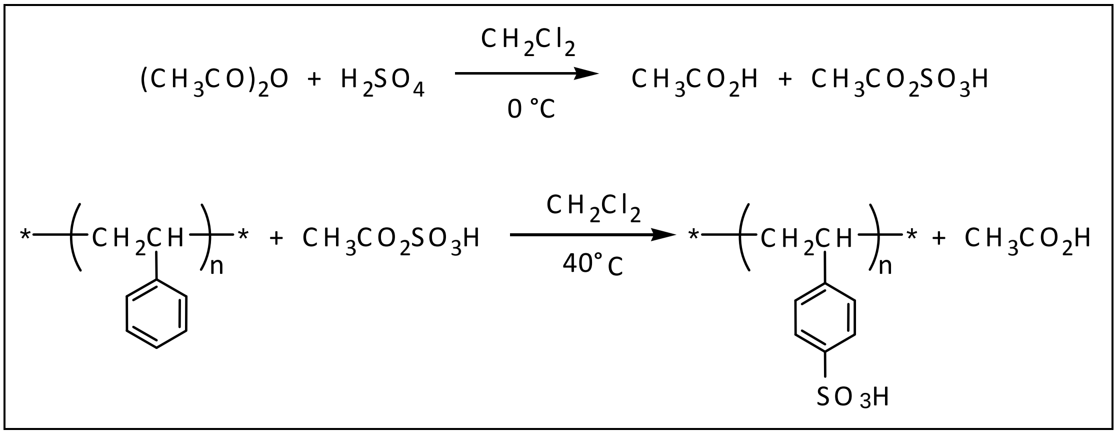

Figure 1. Sulfonation reaction scheme.

Membranes were prepared by solution casting of sulfonated SIBS using a mixed solvent of toluene/hexanol (85/15, w/w) at a polymer concentration of 2.5% (w/v). Solvent was allowed to evaporate at ambient conditions for ~1 week, and resulting films were dried/annealed in a vacuum oven at 50 °C for an additional 2 weeks to remove any residual hexanol. This resulted in flexible membranes roughly 100 μm thick.

Exchange of the acidic hydrogen with various cations was accomplished by immersing membranes into a 1 molar aqueous solution of an appropriate salt for at least 1 h. Subsequently, membranes were washed with copious amounts of deionized water, dehydrated using acetone or ethanol, and dried between cotton cloth under weight (1–2 lb) at ambient conditions. Table 1 lists sample name, percent sulfonation of each membrane, salt used for cation exchange, and valence of exchanging cation.

Table 1. Conterions used for S-SIBS exchange.

Sample	**Sulfonation (%)**	**Salt Used**	**Ion Type**
SIBS-97-H	97	NA	+1
SIBS-97-Cu	97	$CuCl_2$	+2
SIBS-97-Ba	97	$BaCl_2$	+2
SIBS-88-Zn	88	$ZnCl_2$	+2
SIBS-88-Cs	88	CsCl	+1
SIBS-88-Cu	88	$CuCl_2$	+2
SIBS-88-Ag	88	$AgNO_3$	+1
SIBS-88-Ba	88	$BaCl_2$	+2
SIBS-81-Ca	81	$CaCl_2$	+2
SIBS-81-Mg	81	$Mg(ClO_4)_2$	+2

2.3 Proton Conductivity

Proton conductivity values of the membranes were measured using Solartron Electrochemical Impedance Spectrometer "SI-1287" described elsewhere (*10*). Membrane resistance was measured at AC frequencies from 100 Hz to 1 MHz at room temperature. Proton conductivity was measured perpendicular to the plane of the membrane with two 1.22-cm^2 stainless steel electrodes encapsulated inside a sealable Teflon* drum to prevent solvent evaporation. Measurements were conducted at least three times to verify repeatability; reported values were the averages of those results. Conductivity of each membrane was measured in a dry state as well as swollen in water, methanol, and 50/50 molar water/methanol solution. Swollen membranes were allowed to equilibrate in the appropriate liquid for over 24 h at room temperature to ensure equilibrium levels of solvent absorption. Swollen membrane thickness (value required for calculation of conductivity) was measured prior to impedance measurements (*11*).

2.4 Solvent Sorption

Amount of solvent absorbed into membranes was determined using the commonly utilized gravimetric sorption method (*1*, *10*, *12*). Films were cut into circular samples, 15 mm in diameter, weighed (W_d), and placed into a vials containing selected solvent (water, methanol, or

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*Teflon is a registered trademark of E.I. DuPont de Nemours & Co.

equimolar water/methanol mixture) at room temperature. After 24 h, swollen polymer samples were removed from the vials, excess solvent was dabbed off the surface, and samples were weighed again (W_w). The difference in weight corresponded to the amount of solvent absorbed into the polymer during this time. Weight percent uptake can be calculated using the following equation:

$$Wt\% = \frac{(W_w - W_d)100}{W_d} . \tag{1}$$

In addition, in cases when pure water or methanol (MeOH) were used as the swelling solvent, a lambda (λ) value (defined here as mols of solvent per mol of sulfonic group) (*13*) can be easily calculated using the following equation:

$$\lambda = \frac{mols\_of\_solvent}{mols\_of\_SO_3} . \tag{2}$$

Mols of sulfonic groups are calculated based on sulfonation level, known weight ratio of polyisobutylene block to polystyrene block (6.9 to 3.1) and molecular weight and amount of cations incorporated into the polymer (with assumption of 100% exchange level with acidic hydrogens).

Lambda selectivity (relative ratio of water to methanol molecules per given number of ionic groups) was also calculated. It represented the extent of preference of absorption of water over the methanol by the ionic clusters in the polymer.

2.5 Spectroscopic Characterization

Vibration infrared (Fourier-transform infrared [FTIR]) spectra of dry and solvent-swollen polymeric films were collected using a Nicolet 6700 FTIR spectrometer equipped with a Golden Gate/Diamond crystal attachment. Spectra were collected from 4000 to 600 cm^{-1}, with a 4 cm^{-1} resolution, and 32 scans per sample. All spectra were corrected by background subtraction and collected immediately prior to the actual sample run.

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3. Results and Discussion

3.1 Solvent Sorption

Results of solvent absorption measurements (table 2) showed that in an ion-exchanged sulfonated SIBS, the amount of pure water absorbed was significantly higher than pure methanol. The amount of equimolar water/methanol solution absorbed by the membrane fell between those two extremes. The only exception was the acid form of the polymer. For SIBS-97-H, the amount of water/methanol mixture absorbed was higher than either of the two pure

Table 2. Solvent sorption results.

Solvent	**Weight Percent Uptake**			**Lamda (mols Solvent/mols SO_3)**		
	Water (%)	**Mix[a] (%)**	**Methanol (%)**	**Water**	**Methanol**	**Selectivity**
97-H	396	580	327	96.2	44.7	2.2
97-Cu	98	50	22	25.5	3.2	8.0
97-Ba	26	10	5	7.3	0.8	9.2
88-Zn	88	31	28	24.7	4.4	5.6
88-Cs	213	57	6	71.7	1.1	63.1
88-Cu	90	50	26	25.3	4.1	6.2
88-Ag	145	14	6	46.8	1.1	43.0
88-Ba	27	12	5	8.1	0.8	9.6
81-Ca	105	25	7	30.8	1.2	26.7
81-Mg	126	46	24	36.4	3.9	9.3

[a] Mix refers to equimolar blend of water and methanol.

solvents. Similar behavior was observed for Nafion-117 (also a polymer with ionic SO_3H clusters) by other researchers (*14*).

Results shown in this table suggested that interactions of a given solvent with ionic clusters were ion dependent. Observe Ba^{2+} and Cu^{2+} ions with different sulfonation levels. Lambdas of SIBS with different sulfonation levels exchanged with the same type of cation were almost identical for Cu^{2+} (25.3 and 25.5) and reasonably close for Ba^{2+} (8.1 and 7.3). The proximity of two ions on the periodic table did result, in certain cases, in a similarity of properties. Observe the Mg^{2+}, Ca^{2+}, Ba^{2+} set. All three were group 2 ions. A pattern of decreasing lambdas can be seen for both water (36.4, 30.8, and 8.1) and methanol (3.9, 1.2, and 0.8). The decrease, however, was not proportional when evaluating lambda's selectivity (ratio of lambdas commonly used to compare relative sorption properties in a normalized fashion). Selectivity for Ca^{2+} was actually much higher than for Ba^{2+} or Mg^{2+}.

Similarly, although Cu^{2+} and Zn^{2+} ions were located in different but adjacent groups of the same period, identical lambdas for water (25.3 and 24.7) and methanol (4.1 and 4.4) were shown. This, however, was not observed for the Cs^{+}-Ba^{2+} combination (71.3 and 8.1). The most obvious reason why it would not be similar to the Cu^{2+}-Zn^{2+} pair was the difference in valence. Cs is a +1 ion, and Ba is a +2 ion; this affected various properties.

Another example of different valence effects can be observed by examining Cu^{2+} (a +2 ion)- and Ag^{+} (a +1 ion)-exchanged SIBS. Even though they were in the same group, water lambda for Ag^{+} (46.8) ion was much higher than Cu^{2+} (8.1), contrary to the pattern observed for the group 2 elements Mg^{2+}, Ca^{2+}, and Ba^{2+} (all +2 ions), where lambdas decreased as elements proceeded farther down the periodic table. The significance of these observations was that ions with one-valence electron allowed larger clusters of water to aggregate (as much as twice or three times compared to ions with two-valence electrons). Single-charge cations presumably enabled low levels of crosslinking, which, in turn, allowed the polymer to swell to a higher degree. Interestingly, samples exchanged with one-valence electron ions, while exhibiting very high affinity for creating large water clusters as illustrated by large lambdas (46–71 molecules per sulfonic group), did not behave similarly when exposed to methanol. Methanol clusters for these cations were almost the smallest observed in this study—1.1 molecules per sulfonic group.

Plotting methanol lambda vs. water lambda (figure 2) showed no observable pattern other than the valence difference just mentioned. The values seemed to change independent of each other. This signified that there were two different mechanisms of interaction between ionic domains and these two solvents. This was important since it meant that we could potentially control these entities independently of each other and possibly find ions (or possibly a bend of two or more ions) that produced desired effects for a given application.

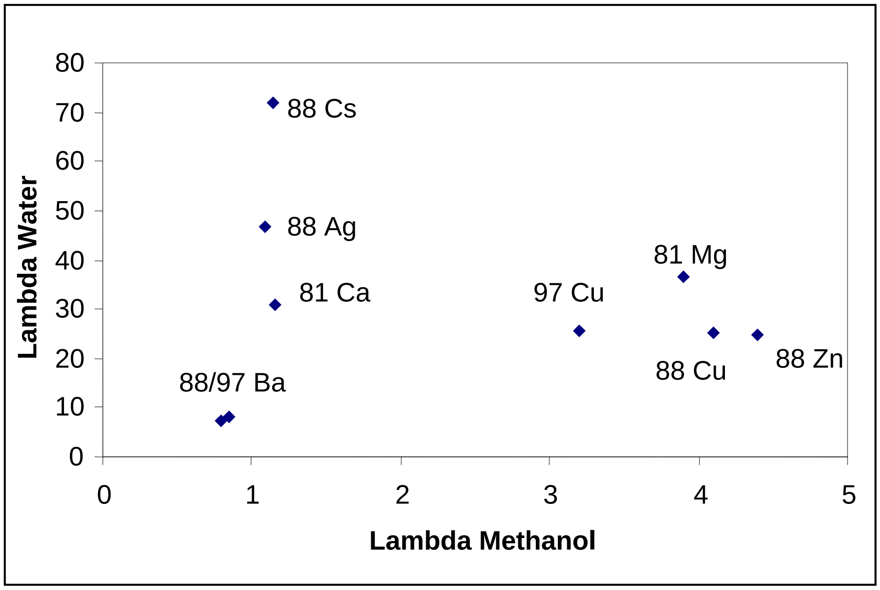

Figure 2. Lambda methanol vs. lambda water relationship for cation-exchanged S-SIBS.

3.2 Conductivity

The real impedance was determined from the x-intercept of imaginary vs. real impedance data (Z’ vs. Z”). Depending on the shape produced by the plot, a linear or circular fit was used to determine the x-intercept (R). For linear fits, an attempt was made to use a frequency range that produced a linear region on the Z-vs.-Hz curve, usually corresponding to a frequency from 10^4 to 10^6 Hz. Table 3 lists conductivity K in siemens per centimeter (S/cm) values as calculated based on sample thickness L (cm), sample area A (1.22 cm^2), and resistance R (ohms).

Table 3. Conductivity in various swelling solvents.

Solvent	Conductivity (S/cm)				Lamda (mols Solvent/mols SO_3)	
	Dry	**Water**	**Mix**	**Methanol**	**Water**	**Methanol**
97-H	0.0053	0.042	0.021	0.0420	96.2	44.7
97-Cu	0.0000	0.009	0.002	0.0002	25.5	3.2
97-Ba	0.0001	0.002	0.000	0.0000	7.3	0.8
88-Zn	0.0000	0.008	0.002	0.0000	24.7	4.4
88-Cs	0.0000	0.013	0.008	0.0000	71.7	1.1
88-Cu	0.0000	0.007	0.002	0.0000	25.3	4.1
88-Ag	0.0000	0.012	0.001	0.0000	46.8	1.1
88-Ba	–0.0001	0.001	0.000	–0.0006	8.1	0.8
81-Ca	0.0000	0.007	0.002	0.0000	30.8	1.2
81-Mg	0.0000	0.010	0.002	0.0000	36.4	3.9
Nafion[a]	—	0.025	—	—	22	—

[a] Nafion (registered trademark of E.I. DuPont de Nemours & Co.) data is taken from DeLuca and Elabd (*10*).

$$K = \frac{L}{R \cdot A}. \tag{3}$$

In cases of methanol-swollen and dry membranes (except for SIBS-97-H), membranes were practically unconductive. This was judged based on very small (and, in some cases, negative) values for calculated conductivity as well as the general shape and position of the impedance data curves.

3.2.1 Effect of Solvent Composition

Examining the effect of swelling solvent on the conductivity of the different ion-exchanged membranes (figure 3), in most cases, there was a dramatic drop in conductivity when equimolar mixture of water/methanol (stociometricly proper mixture for electrochemical reaction in DMFC) was used as a swelling solvent. One notable exception was the Cs^+-exchanged membrane. While conductivity was smaller for a pure water-swollen membrane, the drop in conductivity was less than for other cations tested in this study. This deviation from the behaviors of all other cations has been verified by repeated experiments and may warrant a more detailed investigation into its causes.

Overall, inclusion of tested ions had a detrimental effect on the conductivity of water-swollen membranes. Conductivity of cation-containing membranes is roughly 25% of the value obtained for the nonexchanged acid form of SIBS, or 50% of the value reported for Nafion-117 (*10*). However, lower methanol cross-over (not yet evaluated) might provide overweighing benefits that will produce an overall more efficient DMFC system.

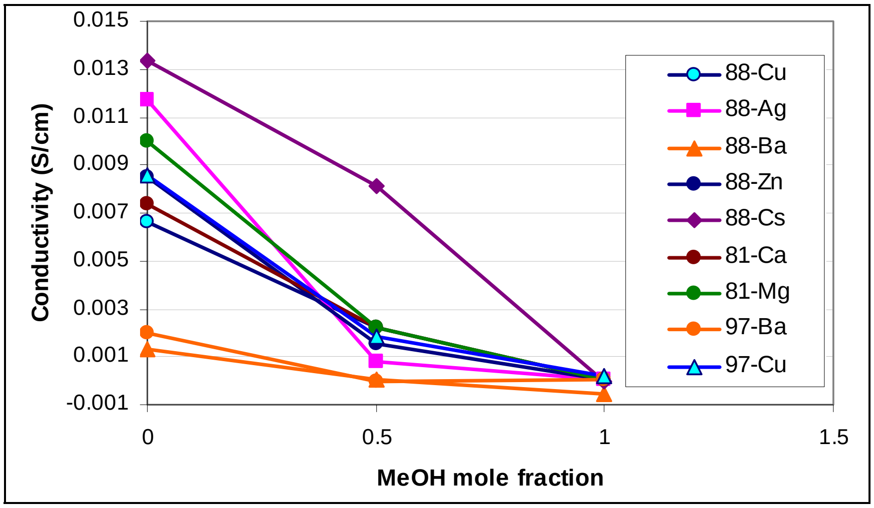

Figure 3. Conductivity as function of methanol content.

3.2.2 Lambda Effects

It was well documented that conductivity in ionic-polymeric membranes was heavily dependent on levels of water absorbed into the membrane (*2*, *12*). In order to examine the effects different cations in exchanged ionic membranes have on conductivity, we need to determine if changes in conductivity followed changes in lambda or if there were some additional factors affecting it. As shown in the plot of water lambda vs. conductivity (figure 4), conductivity was directly proportional to the log of lambda. This result implied that the effect various cations had on proton conductivity was limited to the amount of water molecules allowed to aggregate into the ionic clusters. Lambda and proton conductivity of the membrane increased as more water molecules were attracted to the clusters.

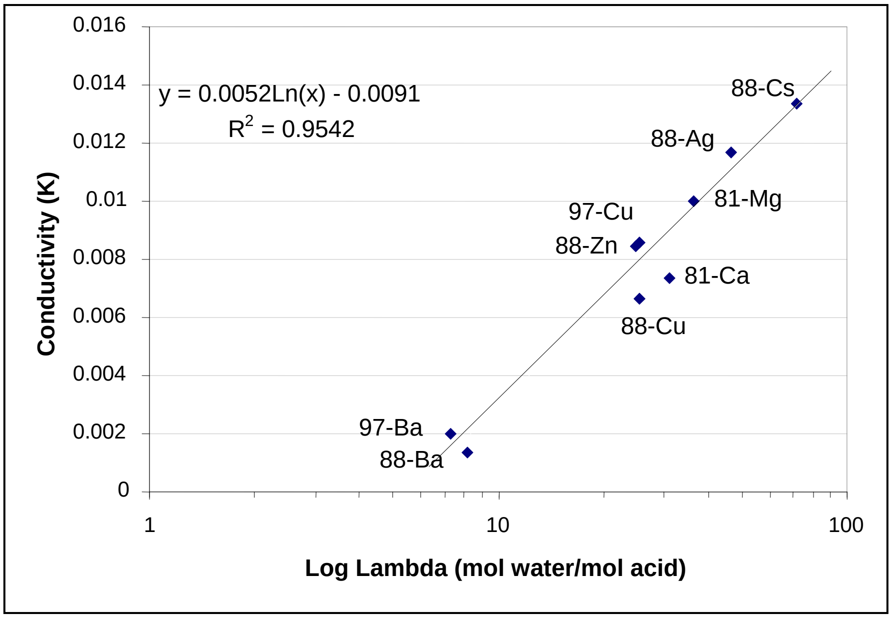

Figure 4. Dependence of conductivity on lambda for water-swollen membranes.

However, this pattern was only valid for ionic S-SIBS membranes exchanged with cations; neither acid form of SIBS-97-H nor Nafion-117 fell on this line. In order to better illustrate the cation data, those two data points were not shown but were located at 112 × 0.042 and 22 × 0.025, respectively (off scale).

In order to evaluate the relationship of water content to proton conductivity for membranes swollen in an equimolar methanol-water mixture, it was necessary to determine relative quantities of water and methanol sorbed into the membranes. This was attempted by FTIR analysis. Spectra of dry samples and those swollen in water, methanol, and mixed solvent were collected using conditions just described. The following peaks were selected as representative entities of interest: 1020 cm^{-1}-methanol, 1366 cm^{-1}-isobutylene, and 3396 cm^{-1}-water. Some of these bands were indicated with arrows in a representative FTIR spectrum shown in figure 5.

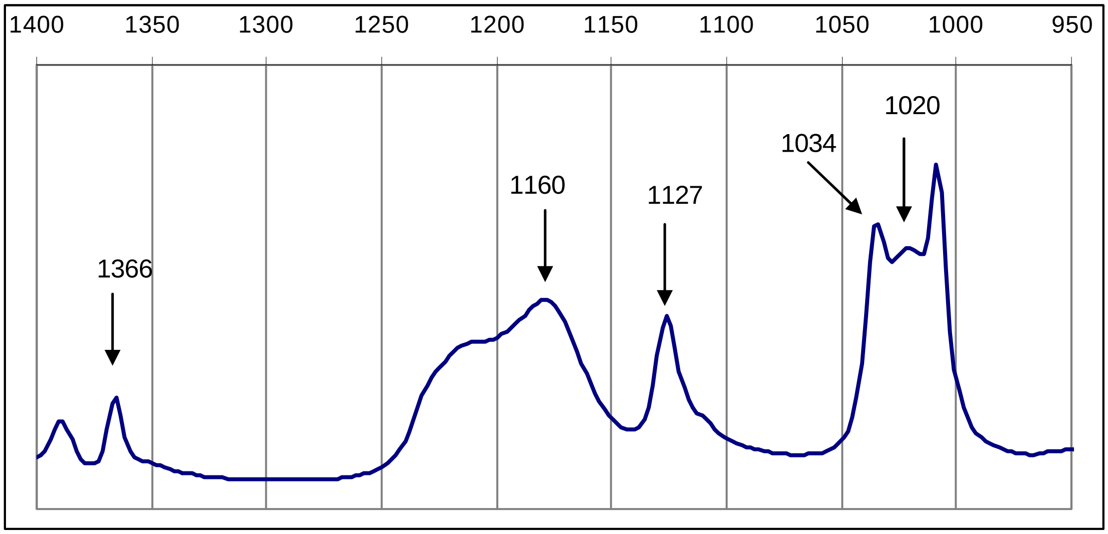

Figure 5. Representative FTIR spectra of water/methanol-swollen SIBS-88-Cs.

Unfortunately, the methanol peak was flanked by sulfonic group peaks on both sides, making it impossible to estimate the areas. As a result, it was decided to use a somewhat less-accurate peak height as an indicator of relative concentrations of the corresponding molecule. The isobutylene peak was chosen as an internal standard since it was relatively unobscured in the spectra. The O-H stretching signal at 3396 cm^{-1} was chosen to represent water quantity in the sample. While, technically, methanol also produced vibrations in that part of spectra, no significant difference in intensity of the peak between dry and methanol-swollen samples was found from the raw data. Thus, it will not be a significant source of error.

FTIR peak heights obtained from dry spectra of cation-exchanged membranes were subtracted from FTIR peak heights for the same swollen membrane and pure water and pure methanol (3396 and 1020 cm^{-1}). The resulting values were normalized by dividing them by the height of internal standard peak at 1366 cm^{-1} (isobutylene). This provided an FTIR signal ratio of "moles of solvent per moles of isobutylene." Real values for moles of solvent per moles of isobutylene can be calculated from experimental data collected by the gravimetric sorption method. When compared to corresponding FTIR signal ratios, a calibration between signal level and solvent absorbed can be archived. By evaluating FTIR spectra of the swollen membrane in mixed solvent, normalizing water (3396 cm^{-1}) and methanol (1020 cm^{-1}) peaks to "isobutylene" levels (1366 cm^{-1}), and comparing peak heights to the calibration obtained earlier, the quantity of individual solvents present in a given membrane was estimated.

When the amount of water and methanol estimated to be present from the FTIR spectra was converted to total weight and compared to experimental data obtained by the gravimetric uptake method, FTIR results provided values that, in most cases, were 20%–100% larger. Presumably, this discrepancy is caused by the use of peak height instead of peak area in the calculations. In order to improve accuracy of estimation, data obtained by FTIR will be used to calculate mass ratios of methanol to water. These ratios, coupled with experimentally gained weight uptake of the solvent mixture, will then be used to estimate actual amounts of water and methanol in swollen membranes shown in table 4.

Table 4. Deconvoluted lambdas for water/methanol-swollen samples.

Solvent	**K (S/cm)**	**Water (λ)**	**MeOH (λ)**
97-H	0.021	112.1	16.2
97-Cu	0.002	10.9	1.2
97-Ba	0.000	1.7	0.6
88-Zn	0.002	6.6	1.2
88-Cs	0.009	16.9	1.3
88-Cu	0.003	13.1	0.6
88-Ag	0.001	4.0	0.3
88-Ba	0.000	2.8	0.4
81-Ca	0.003	6.1	0.7
81-Mg	0.003	10.2	1.7

While certainly not as accurate as direct measurements, the estimated lambdas followed the trend found in the pure water-conductivity relationship, as can be seen in figure 6. The plot incorporated lambda-vs.-conductivity data for membranes swollen in pure water (blue) and in the equimolar water/methanol mixture (red). For the water/methanol mixture, values plotted represented only the water contribution of absorbed solvent.

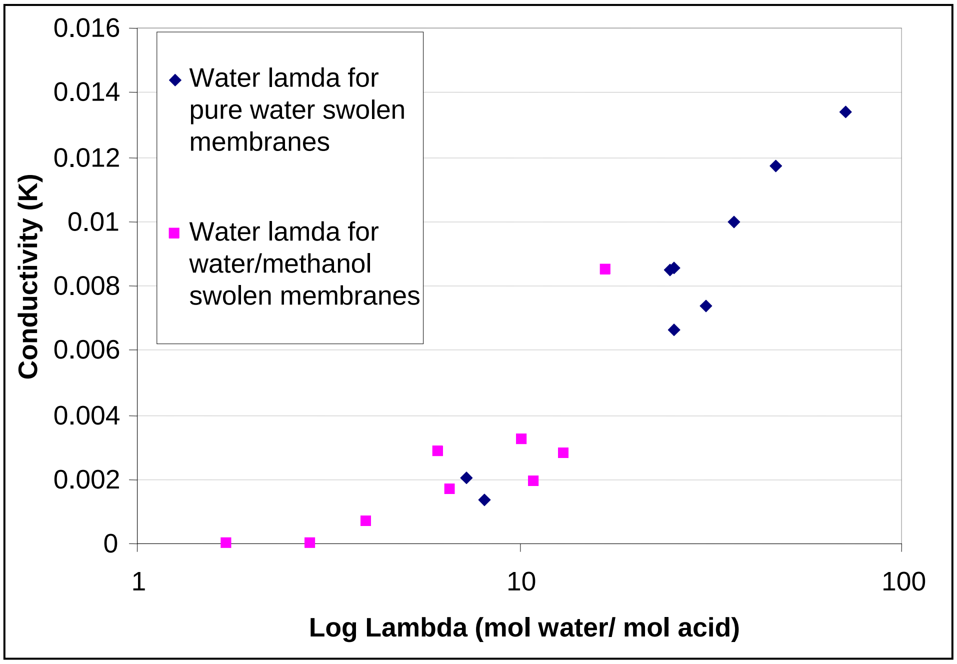

Figure 6. Dependence of conductivity on lambda values for water- and water/methanol-swollen membranes.

All data fell on the straight line again, confirming that conductivity was largely governed by the quantity of water in the membrane. The trend line intercepted the x-axis at ~3, indicating that, in this system, any sort of conductivity will require water molecule levels of more than three per each sulfonic group in order to participate in proton conductivity.

3.2.3 FTIR Band Shifts

Figure 7 shows the effect various solvents and cations impose on the shift of the asymmetric stretching vibrations band of the sulfonate group located around 1160 cm^{-1} (*9*). The plot shows four different points for each cation representing different conditions of the sample: dry, swollen in methanol, swollen in water/methanol mix, and swollen in pure water. It was apparent that the band shifted to a higher and higher position as the sample's state changed from dry, to methanol-swollen, to swollen in the water/methanol mixture, and finally (a highest value), swollen in water. This shift in IR band position generally indicated more restricted movement of the bands, which, in turn, implied a higher level of interaction between solvent and sulfonic groups. It did not, however, have any apparent correlation to affinity for a particular solvent or proton conductivity.

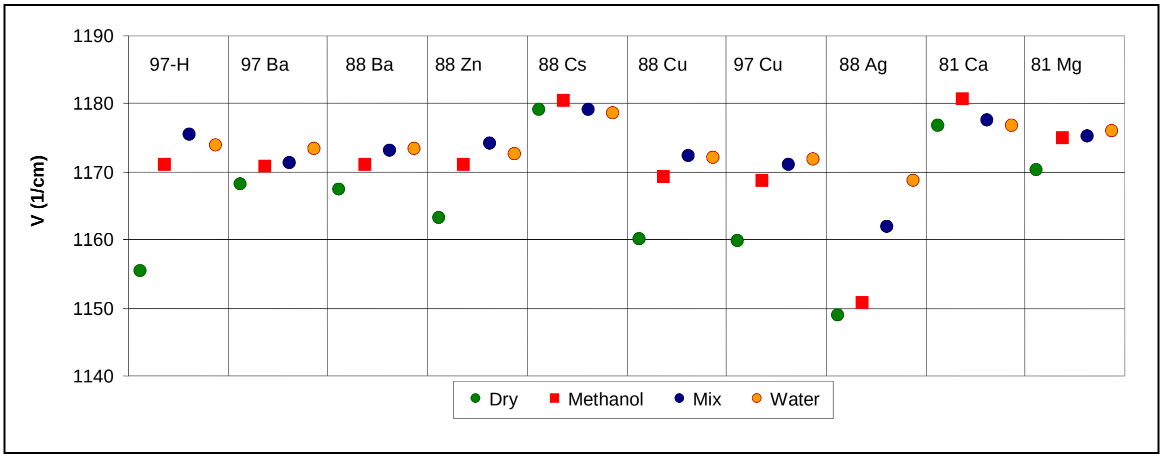

Figure 7. FTIR band shifts as induced by various solvents.

Band position in cation-exchanged samples showed an interesting shift from acid form (SIBS-97-H), the magnitude which can be correlated to electronegativity of the incorporated cation (figure 8). To demonstrate this, exact position of 1160 cm^{-1} peak for the acid form of the polymer was subtracted from positions of the same peak obtained from FTIR spectra of cation-exchanged samples, normalizing them. Dry samples were normalized to dry samples of the acid form, methanol-swollen samples were normalized to methanol-swollen acid form, polymer spectra, etc., to minimize solvent effects from consideration. The band-shifting effect was more pronounced in dry polymers and increased linearly as elecronegativity of the cation decreased (except for Ag).

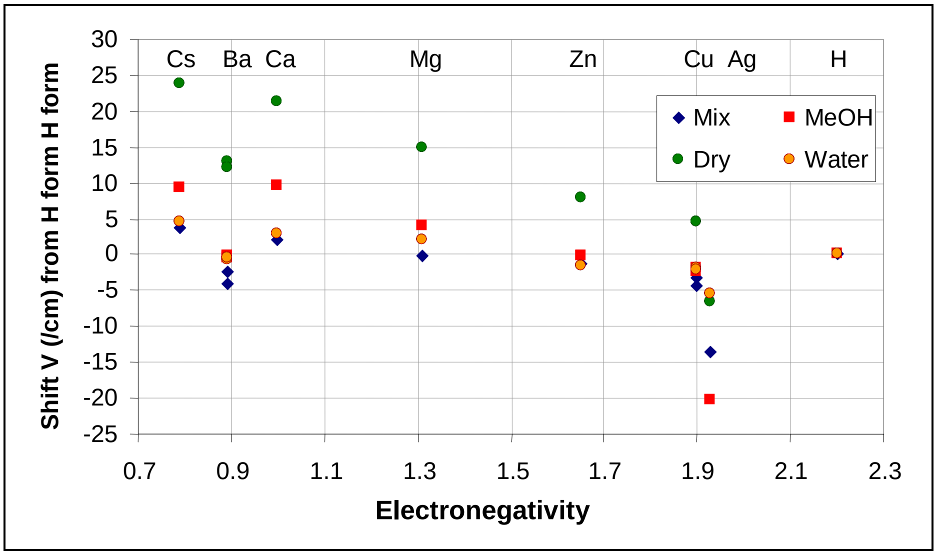

Figure 8. Shift in asymmetric stretching vibration band of the sulfonate group is related to electronegativity of cation.

Introduction of solvents into the membranes also had an effect on the asymmetric stretching vibration of the sulfonate group. As sample state changed from dry to swollen, the band at 1160 cm^{-1} shifted to a higher field compared to spectra of the dry sample. The magnitude of the shift was linearly proportional to the electronegativity of the cation attached to the sulfonic group (figure 9). Since the shift was related to the strength of interactions between sulfonic group cation and the surrounding solvent, electronegativity having a strong effect on interactions with polar solvents like water and methanol was not surprising. This did not correlate with lambdas obtained during gravimetric portion of the experiments because swelling levels were limited by a crosslinking effect that constrained the membrane and was observed even in +1 cations.

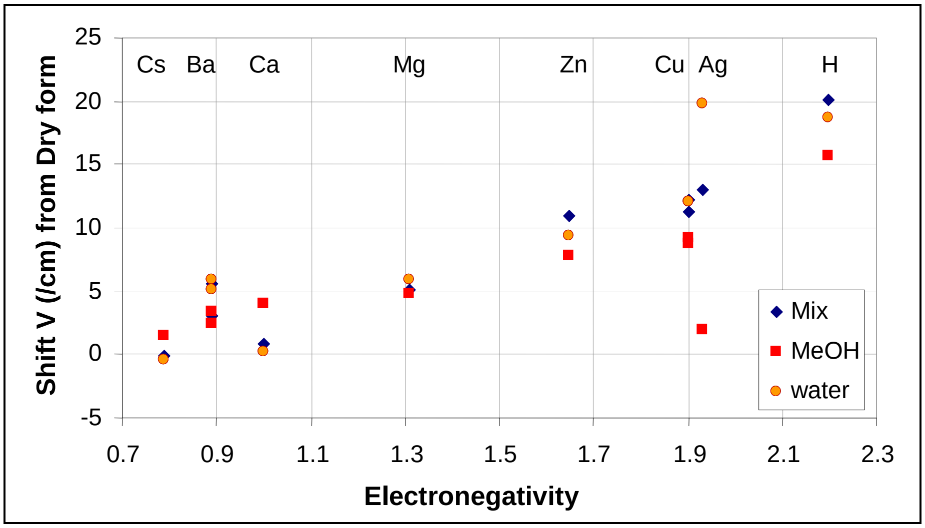

Figure 9. Solvent induced shift in 1160 cm^{-1} FTIR band from dry state.

There was a correlation that could estimate the level of proton conductivity K of the membranes based on very small shifts in FTIR spectrum of water-swollen, cation-exchanged samples. Two affected FTIR bands were in plane bending vibrations of the sulfonate anion attached to the aromatic ring 1127 cm^{-1} and symmetric stretching vibrations of the sulfonate group at 1034 cm^{-1} (*9*).

In response to levels of solvent absorbed into the membrane, the peak shifted (shown in figure 10 for the 1127-cm^{-1} band). This corresponded to an observed increase in proton conductivity and could be used as an indicator of a highly swollen state of the membrane. Since the level of water was proportional to proton conductivity in the system, this observation may be utilized as a prescreening tool for the prediction of proton conductivity. Note that this correlation existed only for polymers swollen in pure water. Methanol and water/methanol-swollen polymers produced band shifts disproportionally large for observed levels of exhibited conductivity. Also, the acid form of the polymer did not follow the same trend line and was not even shown on the plot as being dramatically off the scale (SIBS-97-H FTIR peak was 1126.36 cm^{-1}, and conductivity was 0.042 S/cm).

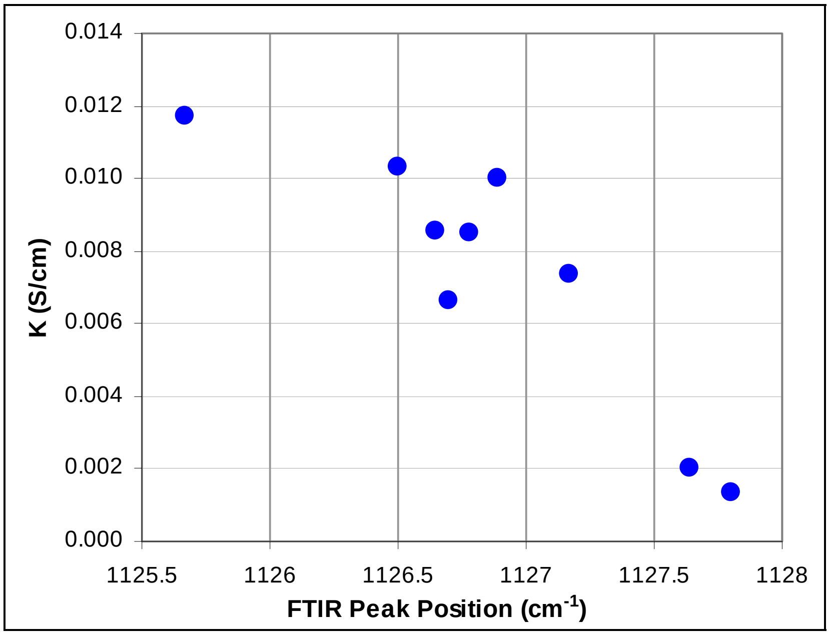

Figure 10. Relationship between proton conductivity and position of 1127 cm^{-1} FTIR band.

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4. Conclusion

Novel, cation-exchanged ionic polymer membranes were synthesized. Their interactions with water and methanol were evaluated using the gravimetric method. It was observed that levels of solvent absorbed into the membranes varied depending on the cation used, with a valence difference resulting in the most dramatic changes. While the amount of water absorbed by cation-containing membranes decreased by 50%–95% (as compared to acid form), decreases in the amount of methanol absorbed by the same membranes were significantly higher (90%–98%, an order of magnitude). This might significantly reduce methanol crossover in DMFCs, thus reducing catalyst poisoning on the cathode side and increasing life of the cell (*15*). Proton conductivity of water-swollen membranes was measured and varied from 2×10^{-3} to 1.2×10^{-2} S/cm, depending on the cation. Conductivity for those materials correlated to water content in the membranes and, in all other ways, was independent of specific ions used. Proton conductivity in water/methanol-swollen membranes was also dependent on water content in the membrane and followed the same trend.

While exchanging acidic hydrogens in sulfonated SIBS membranes with cations did make the membranes stronger due to crosslinking effects, swollen membranes still exhibited weakness detrimental to the performance as DMFC. Further work is needed to address these issues, such as physical encapsulations into a strong but porous substrate, stronger crosslinking, or a plasma treatment to create surface-level crosslinks (*16*).

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