An investigation of proton conduction in select PEM's and reaction layer interfaces-designed for elevated temperature operation

Chengsong Ma [a], Lei Zhang [a], Sanjeev Mukerjee [a,*], David Ofer [b], Bindu Nair [b]

[a] *Department of Chemistry, Northeastern University, 360 Huntington Avenue, Boston, MA 02115, USA*
[b] *Foster Miller Inc., 195 Bear Hill Road, Waltham, MA 02451, USA*

Abstract

The proton conductivity of several alternative proton exchange membranes, i.e. SPES-40 (a sulfonated polyarylene ether sulfone), SPSS-40 (sulfonated polysulfide sulfone) and SPES-PS (a polyether sulfone post-sulfonated) were studied using a four-probe ac-impedance method as a function of temperature. Further, proton conductivity was also investigated for the same ionomers in the form of micro-aggregates such as those typically encountered in the reaction layer (the interfacial layer of the electrode containing the catalyst). For this a new configuration of the conventional reaction layer in a membrane electrode assembly (MEA) was used, which enabled the isolation of proton conductivity to be the principle contributor to the ac-impedance. The results under 100% relative humidity, showed that SPES-40 has similar proton conductivity as Nafion® in the membrane within our experimental conditions. The values for the other membranes investigated were lower. Attempts to correlate these observed differences with parameters such as equivalent weight (EW), water uptake (λ), acidity (pK_a), etc. showed that the prime contributor was the difference in microstructure of the membranes. Conductivity of these polymeric ionomers when present as micro-aggregates in the reaction layer showed very different values as compared to the bulk membranes. There was a great divergence in conduction as a function of increase in temperature with Nafion® showed a far greater rate of increase of conductivity than SPES-50 and SPES-PS. Blends of these ionomers with Nafion® showed intermediate values, albeit lower with characteristics closer to Nafion®. Single cell PEM polarization curves were measured for both Nafion® 117 and SPES-40 membrane keeping the ionomer in the reaction layer same as the membrane. Comparison of the performance showed similar ohmic polarization characteristics. However, their performance in the low current density activation polarization region indicated poorer oxygen reduction reaction kinetics with SPES-40 material as compared to Nafion®.
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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are one of the most promising emerging power technologies in transportation and portable consumer applications. Central to this technology are the proton

* Corresponding author. Tel.: +1-617-373-2382;
fax: +1-617-373-8795.
E-mail address: smukerje@lynx.neu.edu (S. Mukerjee).

exchange polymer membrane, the current state of the art for which is based on perfluorinated sulfonic acid chemistry, such as those from Dupont (Nafion[®]), Asahi Chemicals (Aciplex[®]) and others. These membranes possess very desirable properties such as good mechanical strength, chemical stability, and high conductivity [1], which has revolutionized this technology and enabled very high energy densities. However, these membranes remain expensive and have several limiting factors such as low conductivity at low relative humidity [2], high methanol permeability [3,4] and a low T_g (glass transition temperature) [5] which restricts its application to below 100 °C.

Transitioning to temperatures above 100 °C does provide for several attractive options which include higher CO tolerance [6], better water and heat management. Recently, the use of non-volatile solvents as replacement for water have been attempted such as in the case of phosphoric acid, polybenzimidazole, butyl methyl imidazolium triflate, butyl methyl imidazolium tetrafluoroborate, etc. [7–11]. For proton conduction using hydrated membranes, there is an active interest in examining the role of additives to prevent the loss of water from ionic regions (pores) in the membrane, thereby maintaining an equivalent level of conductivity as those below the boiling point of water. In this context, several hydrophilic inorganic materials such as SiO_2, $Zr(HPO_4)_2$, heteropolyacids, etc. have been incorporated into conventional perfluorinated membranes such as Nafion[®] [12–14]. In all these systems, the strong hydrogen bonding to the ions and dipoles and additional acidity introduced by these moieties provide for effective proton conduction at elevated temperatures (100–130 °C). However, long term stability at elevated temperatures is still a concern based on the relatively low glass transition temperature of Nafion[®] (approximately 110–130 °C) [5]. Alternative hydrated membranes to the perfluorinated sulfonic acid based systems possessing high proton conductivity at lower relative humidity and stability at elevated temperatures are currently the focus of a lot of research and development. Most of these polymer systems are based on engineering polymers with high thermochemical stability [15], typically with a high degree of aromatic character, where the monomer consists of a variety of fused phenyl rings linked together with a number of bridging moieties (hereafter

referred to as membranes with aromatic backbone). Sulfonation of these materials involves either using sulfonated monomer in the polymer synthesis or a variety of methods for post-sulfonation. Several families of polymers have been developed in this context, these include polyether (ether) ketone (PEEK) [16], polyether sulfone (PES) [17], polysulfide sulfone (PSS) [18], polyphenyl quinoxaline (PPQ) [19], aryl oxyphosphazene (AOP) [20].

Proton conduction in polymer electrolyte membranes is an intimate function of equivalent weight (EW), water content (relative humidity (RH)), crystallinity (cluster structure involving hydrophilic and hydrophobic components). Proton conduction in perfluorinated and partially fluorinated membranes [21], with aliphatic chain backbone (hereafter referred to as aliphatic chain membranes) have been extensively studied in the context of all the above mentioned parameters. More recently, proton conduction has also been studied for the membranes based on a high degree of aromatic character [19]. This study [19] included sulfonated polyether (ether) ketone (SPEEK), a polyether sulfone (SPES) and polyphenyquinoxalene (SPPQ). It is well known that the transport of protons and associated water molecules is strongly dependent on the microstructure and acidity. A cluster network as proposed earlier by Gierke and Hsu [22] for Nafion[®] involves the formation of inverted micelles (∼50 Å) comprising of solvent and ion exchange sites separate from the polymer backbone and connected by narrow channels (∼10 Å). Prior report by Gavach and co-workers [23] have shown that the conductivity of Nafion[®], increases dramatically above a λ ([H_2O]/SO_3^-) value of 6. Six water molecules are considered to form the primary hydration shell of the SO_3H group. Lower water content leads to narrowing of the channels and hence a hindrance to proton conduction. In a comparison of fluorinated and partially fluorinated aliphatic polymer backbone membranes [21] the complexities of correlating conductivity with water content has been pointed out. The cross influence of acid concentration and different elasticity of the aliphatic polymer backbone provides for very different proton conductivity, when comparing within the same range of EW and λ. These differences are also evident from the comparison of conductivity of Nafion[®] membrane with some membranes with aromatic based backbone [19]. In this comparison

[19] it is evident that besides the influence of EW, λ and the tertiary structure of the membrane (nature of cluster formation), there are additional effect due to pK_a. Nafion® type membranes are very strongly acidic, however, the simplest aromatic sulfonic acid such as benzene sulfonic acid has a pK_a of 0.7 [24], which implies that in a 1 M solution the acid is only 36% dissociated. Effect of various substituents on the phenyl rings therefore will effect the acidity of the ion exchange centers. In addition, most of the polymers with aromatic backbones have sulfonic acid groups directly on the phenyl rings, which is very different from the dangling sulfonic acid moieties in the aliphatic based fully or partially fluorinated membranes.

Besides the membrane, the membrane electrode assembly (MEA) forms an important determinant to fuel cell performance especially in avoiding high interfacial resistance and onset of mass transport limited behavior at lower current densities. The charge transfer interface with the membrane is called the 'reaction layer'. It is typically a thin layer of catalyst and ionomer (typically a solubilized form of the electrolyte membrane) with or without a binder such as Teflon, deposited on top of a teflonized carbon layer. This reaction layer therefore extends the charge transfer interface from the membrane surface deeper into the electrode structure in order to increase the interfacial area available to carry out the desired reactions. In the context of elevated temperature operation, it is therefore critical to maintain the mobility of ions in this reaction layer to retain activity of this increased interfacial area. Drying out this reaction layer would negate any advantage of choosing a better-elevated temperature proton conductor. The reaction layer typically has a different ionomer structure from that of the membrane. Ionomer in the reaction layer is deposited from aggregates in solution. The size and morphology of these aggregates therefore determine the nature of the tertiary cluster structure of the hydrophilic and hydrophobic domains. Examining proton conduction in reaction layers is therefore an important component of enabling alternative membranes for elevated temperature PEM operation.

This investigation forms the first of a series, examining a select group of alternative proton conducting membranes for elevated PEM fuel cell applications. The membranes used as part of this investigation are polyarylene ether sulfones (including polymers synthesized with sulfonated monomers and ones which were post-sulfonated), polyarylene sulfide sulfones and the control material, Nafion® (Dupont). The aim of this investigation was to compare the conductivity of these alternative membranes under fully hydrated conditions (akin to fuel cell operation) as a function of temperature in order to elucidate differences based on their acidity (pK_a), chemical structure, equivalent weight, etc. In addition, conductivity was investigated for these polymers in highly filled structures analogous to those they form in PEMFC electrode reaction layer interfaces.
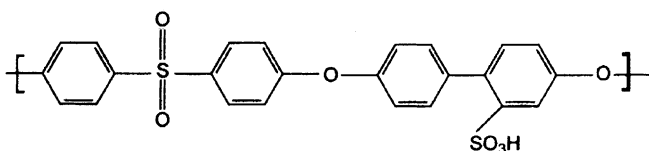
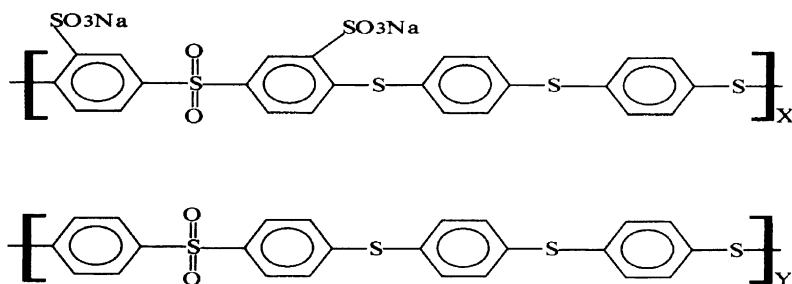## 2. Experimental

2.1. Membranes studied

Polyarylene ether sulfone membranes with structure A, containing two sulfonate groups per repeat unit were prepared at Virginia Polytechnic and State University (Professor James McGrath's group). This synthesis involved potassium carbonate mediated direct aromatic nucleophilic substitution polycondensation of disodium 3,3′-disulfonate-4,4′-dichlorodiphenyl sulfone (SDCDPS), 4,4′-dichlorodiphenylsulfone (DCDPS) and 4,4′-diphenol. Detailed preparation methodology, reaction conditions and membrane properties, such as t_g, hydrophilicity, viscosity, TGA, AFM (hydrophilic domain size, phase inversion) and proton conductivity are reported elsewhere [25]. The polymer used in this investigation was a 40:60 ratio in terms of SDCDPS/DCDPS ($100n/(n+m)$). This polymer, referred to as PBPSH-40 by the Virginia Tech. group, is referred to as SPES-40 in this paper in order to provide a common nomenclature for all polymers in this investigation. Polyarylene ether sulfone post sulfonated, structure B, prepared by post-sulfonation of RADEL-R (Solvay Polymers) by the Foster Miller group is referred to as SPES-PS in this investigation for the aforementioned reasons. Details of the preparation methods are given elsewhere [26]. Polyphenyl sulfide sulfones referred here as SPSS (structure C), were prepared according to methodology described in detail elsewhere [27]. The ratio of sulfonated to non-sulfonated sulfide sulfone components used was 4:6 referred to in this investigation as SPSS-40.
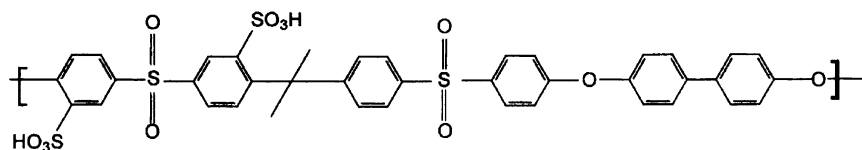
Structure **A**, polyarylene ether sulfone

Structure **B**, polyarylene ether sulfone-post sulfonated

Structure **C**,　　Sulfide sulfone 4:6, X = 40%, Y = 60%

2.2. Measurement of membrane properties

Accurate measurement of proton conductivity of polymer membrane is a significant experimental challenge, especially in the context of its use in understanding the performance of a PEMFC under actual operating conditions. Cahan [28] have demonstrated that in two electrode systems, interfacial impedance dominates the observed frequency response except at high frequencies (MHz). They compared two and four electrode configurations over a range of 1 Hz to 65 kHz, wherein the four electrode measurement essentially showed a constant impedance, thereby indicating that Nafion® 117 membrane was similar to conventional liquid electrolytes, i.e. it can be treated as a simple resistance. In present study proton conductivity was measured using a four-probe conductivity cell as shown in Fig. 1. The cell setup is based on a previously reported design [2]. Conceptually this measurement was similar to those published by others [29]. In our setup the four-probe home-made cell comprises of a smooth fritted disk on which the membrane is placed with current and potential probes on either end of the membrane. All conductivity measurement reported in this paper were conducted in plane. The distance between the potential probe were 1 cm with the current probes separated by 3 cm. Isotropic nature of proton conductivity in these membranes were tested by through plane measurements on all membranes reported in this study. In these measurements the potential and current probes were placed transverse to each other across the membrane. The incremental increase in the distance between the potential probes was
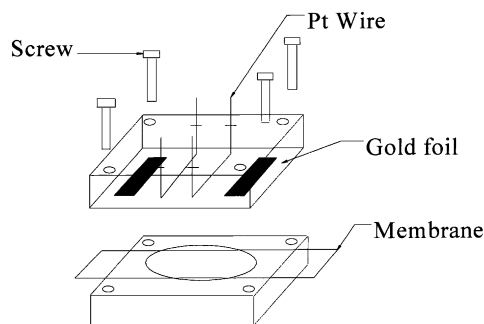
Fig. 1. Schematic of the conductivity cell, showing the four-probe arrangement for measurement of impedance. The Pt wires served as the potential probes, while the gold foil was the contact for current. The membrane was placed on a smooth glass frit with higher than 80% porosity. The bottom Teflon holder was connected to a humidified gas inlet with carrier gas input from a humidification system.

negligible in these measurements; no discernable difference in conductivity was measured using the two different modes (in- and transverse-plane). This cell was connected to humidification set up akin to a fuel cell humidification system with a conventional heated bubbler setup which included mass flow controlled wet and dry gas mixtures and the cell fixture in a constant temperature oven. By adjusting the carrier gas flow rates and bubbler temperature, humidification levels could be adjusted at any temperature *akin* to fuel cell operation. Humidity was measured using a sensor (series EE-305, E+E Electronik, Engerwitzdorf; Austria), placed close to the fritted disk. The conductivity was measured in the in-plane direction for all membranes and was calculated using the expression:

$$\sigma = \frac{l}{RS} \tag{1}$$

where σ, l, R and S are the ionic conductivity in S/cm, distance between the potential probes, membrane resistance at 1 kHz and the cross-sectional area of the membrane, respectively. Conductance measurements were performed using an Autolab potentiostat/galvanostat (model PGSTAT-30, Eco Chemie B.V., The Netherlands) with the frequency response analysis (FRA) system. The determination was carried out in galvanostatic mode with ac current amplitude of 0.01 mA (for membrane) and 0.001 mA (for reaction layer) in a frequency range from 1 Hz to 10 kHz. All measurements were conducted after an equilibra-

tion time in the range of 2–5 h (depending on the cell temperature). Measurements were made at different temperatures keeping the relative humidity constant at 100%.

Conductivity of several batches of the same membrane have been measured, the errors variation are within 5% of average value.

Ion exchange capacities (IEC (meq./g)) were measured using standard methods, which involved equilibrating known amount of H$^+$ form of the membrane in measured volume of a standard solution of 3 M Na$_2$SO$_4$ at 100 °C for 1 h to allow for the exchange with H$^+$ ions. This solution was then titrated to a phenolphthalein end-point with a standard NaOH solution.

Equivalent weight values (EW: mg/meq.) are calculated by equation EW = 1000/IEC. Membrane thickness were measured by a caliper (Mitutoyo, Japan).

Measurements of water uptake followed typical methods reported earlier [30]. Membranes were initially dried at 80 °C in a vacuum oven overnight (12 h). The membranes were then equilibrated by immersing them in an enclosed water container, which was placed in a constant temperature oven. Following equilibration for 4–6 h, the membrane was quickly weighed, taking care that excess water was removed prior to weighing. This allowed measurement of water uptake as a function of temperature. Number of water molecules per sulfonic acid group was then calculated (λ = # moles of H$_2$O/SO$_3^-$).

The pK_a values of the polymers were measured according to procedure described in detail elsewhere [31]. With the control sample, Nafion$^{\circledR}$ 117, the value of pK_a obtained was −3.09, which is in agreement with prior reports which put this value to be in between methane sulfonic acid (pK_a = −1.0) and triflic acid (pK_a = −5.1) [32].

For measurement of conductivity of reaction layers a special setup was used. A conventional reaction layer comprises of a mixture of electrocatalysts (carbon supported Pt or Pt alloy), solubilized ionomer (typically a 5% Nafion$^{\circledR}$ solution either in lower alcohol such as isopropyl alcohol or in 1-methyl 2-pyrrolidone (NMP) with or without a binder (Teflon dispersion such as TFE-30 from Dupont). Typical loading of Nafion$^{\circledR}$ (dry weight basis) in this reaction layer is 0.9 mg/cm^2. In order to enable the measurement of proton conductivity of the solubilized ionomer in this reaction layer,

the carbon supported Pt was replaced with α-alumina support material [Alfa Aesar] (1 μm particle size). This material was deposited on a hydrophilic Nylon film (Millipore filter, 0.22 μm pore size), using the same spraying method as used for the conventional carbon electrode substrates. The alumina to solubilized ionomer ratio was the same as the catalyzed carbon to ionomer ratio used for PEM electrodes (a ratio of 2:1 catalyst/alumina:ionomer). These films were then characterized in the same conductivity cell as those used for membranes, keeping the relative humidity constant at 100%. The arrangement for this modified reaction layer is depicted in Fig. 4. For the reaction layer studies the choice of SPES material was one with a slightly higher sulfonation level (1:1, higher IEC), this is referred to as SPES-50. Details of its IEC (EW) and conductivity as published [25] are given in Table 1.

Single cell PEM fuel cell test: This was conducted at a cell temperature of 70 °C under conditions of 413.68542 × 10^3/344.73785 × 10^3 Pa (60/50 psig) anode/cathode back pressure under conditions of O_2/H_2 (approximately 2 and 1.5 times stoichiometric flow, respectively). The humidification bottles temperature was controlled to ensure 100% relative humidity. A control experiment was run using Nafion® 117 MEA. The choice of Nafion® 117 was based on similarity of membrane thickness with the SPES-40 membrane (6.5–7 mils, dry membrane thickness). The thickness of the membranes after preparation of the MEA was also similar (5–5.5 mils, dry membrane thickness).

3. Results and discussion

3.1. Proton conduction in polymer membranes

Table 1 lists the values of proton conductivity for the various membranes measured at 100% relative humidity along with the data for EW (IEC), # of moles of water molecules/SO_3^- (λ), and pK_a. As evident from Table 1, all the polymer membranes samples have similar levels of λ when compared at 85 °C (within the levels of error ±5%, inherent in these measurements). The values for Nafion® 117 were in agreement with prior reports [21,30,33]. As pointed out before, the value of λ depends on the method used for drying the membranes. Our procedure involved drying under vacuum (12 h) at lower temperature (80 °C), instead of above 105 °C. This was done because it has been previously reported [33] that elevated temperature drying can leave the membrane incapable of complete rehydration and can cause possible irreversible phase changes within the membrane structure. Results for SPES-40 are also in agreement with previously reported values [25] when compared at room temperature (see Fig. 2). Normally water content of the membrane increases with decreasing equivalent weight, where the higher water content is consistent with the increased osmotic driving force for water sorption. However, water content does not necessarily correlate to proton conductivity for membranes, which have very different chemical structure. In that context, λ is a better measure, especially when comparing data under conditions of full hydration. Hence, when comparing

Table 1

Comparison of proton conductivity (@ 85 °C) under 100% relative humidity with water uptake (λ = [H_2O]/SO_3^-), ion exchange capacity (meq./g) or equivalent weight, thickness (fully hydrated state) and pK_a for select aromatic chain proton conducting membranes

Membrane	IEC (meq./g) (EW (mg/meq.))	Conductivity (85 °C)	Thickness (cm) (fully hydrated state) 85 °C	Activation energy (kJ/mol)	λ [H_2O]/SO_3^- (85 °C)	pK_a
SPSS-40	1.47 (680)	0.126	0.01	9.062	19.1	−1.25
Nafion® 117	0.91[a] (1100)	0.205	0.022	9.568	19.8	−3.09
SPES-40	1.59 (628)	0.203	0.016	9.352	20.8	−2.04
SPES-PS	2 (500)	0.139	0.009	8.635	21.5	−1.24
SPES-50	1.8[b]	0.284[c]	–		–	–

Data for Nafion® 117 is included as a control, all the data for which were experimentally determined under the same conditions used for the aromatic chain membranes.

[a] Based 1100 EW, as specified by Dupont.

[b] Data from [26].

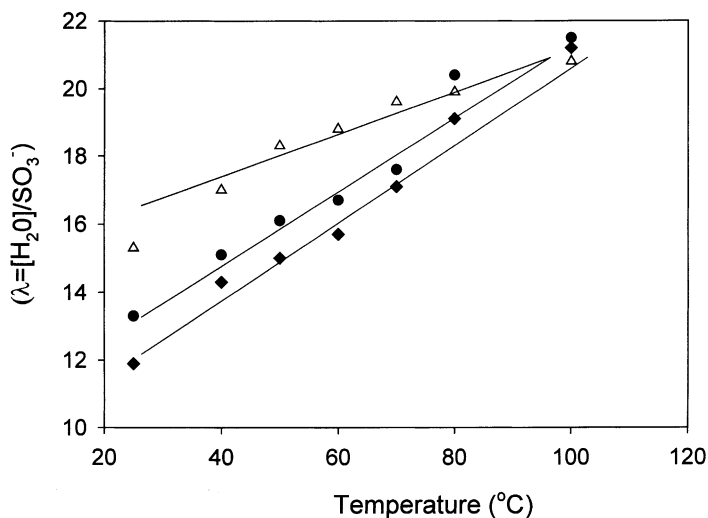[c] Data from [26] extrapolated to 85 °C based on the same slope of temperature variation as SPES-40.

Fig. 2. Water uptake, expressed as λ ($[H_2O]/SO_3^-$) as a function of temperature for SPES-PS (●), and SPES-40 (△). Data for Nafion[®] 117 (◆) is also included as a control.

these membranes with very different chemical structures and EW, it is important to note that their primary hydration shell around the proton as far as each acidic center is concerned is approximately the same.

Fig. 2, shows the variation of water uptake expressed in terms of λ with temperature, for Nafion[®] 117, SPES-40 and SPES-PS membranes. The variation of λ for Nafion[®] 117 shows agreement with values reported earlier [34]. The variation of λ, exhibit very different slopes for the three membranes, however, they start to merge at elevated temperature (close to 100 °C). As evident from this figure, the trend in slope shown in descending order is Nafion[®] 117 > SPES-PS > SPES-40. Hence the importance of water uptake in the set of membranes used in this investigation will be more apparent at lower temperatures based on slopes of their variation with temperature and especially under lower relative humidity conditions.

Fig. 3 shows the variation of conductivity with temperature under fully hydrated conditions. Comparison of values at 85 °C (Table 1) for Nafion[®] 117 shows very good agreement with those published earlier [16,19]. The value for SPES-40 when compared at 20 °C also shows very good agreement with previously reported data [25].

Rationalizing proton conductivity with membrane parameters such as EW, λ, chemistry of the polymer backbone & sulfonation and acidity (pK_a) is

complex, especially when comparing such a diverse group of membranes. This is amply evident from previous reports [19,21]. Beattie et al. [21] compared the proton conductivity of several aliphatic chain membranes with different sulfonic acid end chains (both aliphatic and aromatic). Correlation of proton conductivity with parameters related to water uptake, i.e. EW, water content (%), λ, etc. showed very different relationships amongst the membranes investigated. Membrane with sulfonated styrene-(ethylene
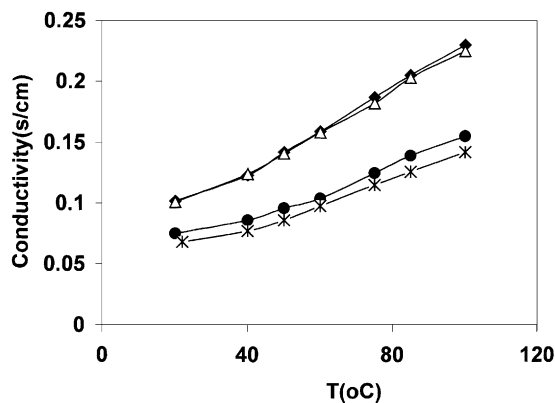

Fig. 3. Variation of proton conductivity measured under conditions of 100% relative humidity, as a function of temperature for SPES-40 (△), SPES-PS (●), SPSS-40 (✕). The data for Nafion[®] 117 (◆) is also reported as a control.

butylene)-styrene triblock copolymers (DAIS®) showed the smallest variation of conductivity for all the above mentioned parameters. However, a sulfonated $\alpha\beta\beta$-trifluorostyrene-$\alpha\beta\beta$ trifluorostyrene copolymer (BAM®, from Ballard) exhibited a Volcano type behavior, showing maximum conductivity in the intermediate range of EW. In contrast to these the ethylenetetrafluoroethylene-g-polystyrene sulfonic acid (ETFE-g-PSSA) membrane exhibited an almost exponential increase in conductivity with lowering of EW (increased water content). A study [19] comparing membranes of sulfonated polyether (ether) ketone (SPEEK), a polyether sulfone (SPES) and polyphenylquinoxalene (SPPQ) provided a similar perspective. All the membranes in this prior study exhibited relatively little variation of proton conductivity as a function of EW (in the mid range of percent sulfonation), which was in contrast to the earlier work reported by Beattie et al. [21] on aliphatic chain membranes.

Comparison of proton conductivity at 85 °C (Table 1) with values related to water uptake, EW and λ, shows that while SPES-40 and Nafion® 117 have similar conductivity in the entire temperature range investigated (Fig. 3), the EW for SPES-40 is half that of Nafion®, and therefore it has twice the water content. On the other hand SPES-PS has a lower conductivity as compared to SPES-40 even though it has a larger IEC (or smaller EW) and hence greater water content. This is particularly interesting in light of the two polymers having very similar polymer backbone structure. Likewise, despite having close equivalent weights (a difference of approximately 8%) and λ (and hence water content) the proton conductivity of SPSS-40 is 40% lower than SPES-40 within the studied temperature range. These comparisons show that there is no apparent correlation between the proton conductivity and water uptake. In this context it is important to note that the variation of proton conductivity with temperature had no correlation with variation of λ in the same temperature range.

As pointed out in a review by Kreuer [35], proton conduction of ionomers has to be viewed in the context of phase formation and clustering between hydrophilic and hydrophobic moieties. Further, when comparing membranes with aromatic polymer chains, the issue of acidity (pK_a) becomes important as pointed out recently by Kopitzke et al. [19]. The acidity of the

various proton conducting membranes are reported in Table 1. As expected, Nafion® 117 has a negative value of pK_a (-3.09), this is broadly in agreement with earlier report [36] that have put its value somewhere in between that of methane sulfonic acid ($pK_a = -1.0$) and tri-flouro methane sulfonic acid ($pK_a = -5.1$) [32]. As mentioned in the introduction section, compared to perflouro sulfonic acids, which fall in the category of super acids, the simplest aromatic sulfonic acid, benzene sulfonic acid, has a reported pK_a of 0.7 [24], which implies that a 1 M solution is only 36% dissociated. However, the polyaromatic ionomers in this study are considerably more acidic. The pK_a of SPSS-40 is measured at -1.25 and that of SPES-40 and SPES-PS are -2.04 and -1.24, respectively. These values, although different, indicate that all the polymer membranes are very strong acids and are completely dissociated in 100% relative humidity condition. Smaller variations in proton conduction may arise as a result of these different pK_a values when subject to very low humidification conditions.

The prime distinguishing parameter in comparing these membranes therefore is most likely their microstructure. This is a very important contributor to the overall proton conductivity value as explained in the introduction based in earlier work by Gierke [22]. This report was among the first to propose a cluster network formation with inverted micelles containing hydrophobic solvent and ion exchange sites as separate from the polymer backbone connected with narrow channels ($\sim$10 Å). As evident from the chemistry of these ionomeric polymer membranes, there are several important differences, (a) the polymer backbone (aliphatic fluorinated versus aromatic), (b) sulfonic acid groups bound directly to the aromatic polymer backbone versus being bound by relatively long dangling fluorinated aliphatic moieties. These differences appear to be the prime contributor to the observed differences in proton conductivity. A systematic study of these aromatic backbone membranes is expected to shed more light on their microstructure relative to Nafion® 117.

As expected, increase of temperature results in a concomitant increase in conductivity (Fig. 3) based on the simplified diffusion mechanism and thermal motion of protons in channels within the membranes. The variation of proton conductivity for the various membranes showed very similar slopes with the differences

in their respective conductivity remaining approximately the same in the range of temperatures studied. The order of decreasing conductivity was Nafion® 117 ≈ SPES-40 > SPES-PS > SPSS-40. It was interesting to note that the variation of proton conductivity of SPES-40 followed exactly that of Nafion® 117 in the entire temperature range of this investigation. This is interesting from the perspective of their very different expected microstructure environment. Standard Arrhenius relationship between the proton conductivity (σ), and temperature ($1/T$ (K)), can be expressed as:

$$\sigma = A e^{-E_a/RT} \tag{2}$$

where A is the frequency factor and R the universal gas constant. The values of the activation energies obtained are given in Table 1. The value for Nafion® 117 agrees well with those published earlier [37] by Yeo et al. (2.25 kcal/mol). Comparison with values obtained for the other polymer membranes show similar values in the range of 8.6–10 kJ/mol. All the ionomers studied have very similar activation energy for proton conduction. This is consistent with the fact that they all have similar values of λ and all have very high acid dissociation constants, and it indicates that they all conduct protons by a similar mechanism under the fully hydrated conditions used for this study. The prime reason for different values of proton conductivity in these membranes is due to different values of the pre-exponential factor (the term A in Eq. (2),

which is the intercept in the Arrhenius plots). This pre-exponential factor, to the simplest approximation, is comprised of orientation contribution and a frequency term, both of which ultimately depend on the microstructure.

3.2. Proton conduction in reaction layers

It is well recognized that it is not only important to ensure good proton conduction within the membrane structure, but also within the reaction layer in order to extend the reaction zone deeper into the electrode substrate. It is also well recognized that when using these alternative membranes in an MEA, a different ionomer in the reaction layer such as the often-used 5% solubilized Nafion® solution (Aldrich) can be deleterious. This could be due to (a) the possibility of a junction potential being set up at the electrode's interface with the membrane. (b) Lower thermal stability of Nafion® (the whole purpose of choosing a higher thermochemically stable polymer membrane being negated due to the use of Nafion® in the reaction layer). It is therefore imperative to attempt to measure the proton conduction of these solubilized ionomers in a reaction layer environment. Fig. 4 shows the design of reaction layer analogs that we have used to study their proton conduction. Both the conventional and the modified reaction layer schematics are shown. In the modified reaction layer 5% solubilized ionomer (pure or a blend) was mixed with α-Al_2O_3 and sprayed in

(a) **Reaction Layer of Electrode in Fuel Cell**
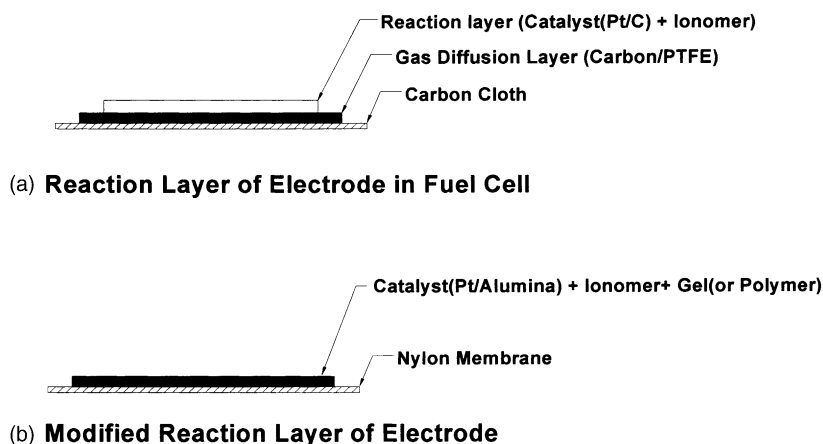

(b) **Modified Reaction Layer of Electrode**

Fig. 4. Schematic of the reaction layer showing (a) the arrangement in a conventional PEM fuel cell electrode and (b) the arrangement used to determine the proton conductivity of the solubilized ionomers.
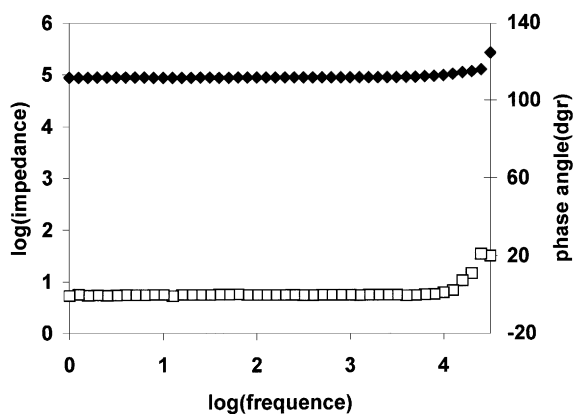
Fig. 5. Typical Bode plot of the impedance from the four-probe conductivity cell using the modified reaction layer containing solubilized Nafion® 117 ionomer as the sample, loading being 0.9 mg/cm². (◆) Log (impedance); (□) phase angle.

top of a hydrophilic Nylon film (see Section 2 for details). Blanks were run for this system without the presence of ionomer and values of conductivity were found to be below the measurable limits of our instrumentation. All conductivity values were measured in-plane. In order to ensure that we were not measuring erroneous effects due to a thin layer of ionomer on the top layer of this modified reaction layer, measurements were repeated with at least four different sets of samples for each case. All the measurements reported had variation in the range of 5–10%. The reported values are an average of these measured conductivity values. It is also important to note that the measured conductivity values were at least two orders of magnitude lower than those measured for polymer membranes. Fig. 5 shows the log-log plot of impedance versus frequency in the range of 1–10,000 Hz. This was for a reaction layer containing solubilized Nafion® (0.9 mg/cm²). The invariance of the impedance within this range of frequency and the fact that the phase angle was zero for most of this frequency range shows that the modified reaction layer was behaving as a pure resistor. The resistance could then be determined using the corresponding Cole plot.

Based on the discussion presented so far, it is evident that proton conduction in polymer ionomeric membranes is a complex phenomenon. For the materials studied here, differences between their conductivity are not related to parameters such as EW, λ, pK_a,

etc. This leaves the microstructure differences between these materials as the most likely source of their differing conductivity. The bulk membrane microstructure environments may or may not be preserved within the domains of polymer aggregates. Not only were solubilized forms of the pure ionomer used in this study, but blends were made with Nafion® in order to understand, albeit simplistically, the effect of close contact between these disparate polymer systems.

Fig. 6a shows the first set of comparisons between Nafion®, pure SPES-PS and blends of SPES-PS with Nafion® (8:2) and (1:1). The ionomers show relatively close proton conduction in the reaction layer analog at 20 °C. However, as temperature is raised the proton conduction values diverge significantly, with Nafion® conductivity showing far greater increases than that of the pure SPES-PS material. A blend of 8:2 (Nafion®: SPES-PS) has conductivity close to that of Nafion®, while a 1:1 (Nafion®: SPES-PS) blend has conductivity that is almost exactly intermediate between that of the two components. This system appears to behave in a straightforward rule of mixtures. Fig. 6b shows data for conductivity of SPES-50 material in reaction layer analogs. Here the pure SPES-50 has a higher value of proton conductivity at 20 °C than pure Nafion®. But the conductivity of Nafion® surpasses that of SPES-50 for temperature above approximately 70 °C. Due to this, blends of SPES-50 with Nafion® exhibited more complex behavior than the Nafion®/SPES-PS blends shown in Fig. 6a. While the 1:1 Nafion®: SPES-50 blend reaction layer analog has conductivity intermediate between that of the two constituent ionomers at 20 °C, at 70 °C the conductivity is closer to the Nafion® sample. The proton conductivity of pure SPES-50 reaction layer analogs was higher at all temperatures than that of SPES-PS, and the conductivity increase with temperature was greater. However, the 1:1 blend of the two polymers had conductivity that was not very different from that of the pure SPES-50. These plots suggest that mixing ionomers in reaction layers can have unexpected consequences for protonic conduction in those electrodes, and may offer a useful route to optimizing their performance under particular fuel cell operational regimes.

It is likely that incorporation of highly sulfonated ionomers in reaction layers greatly magnifies the role that their microstructure plays in determining conductivity. In bulk membranes, the tendency for highly
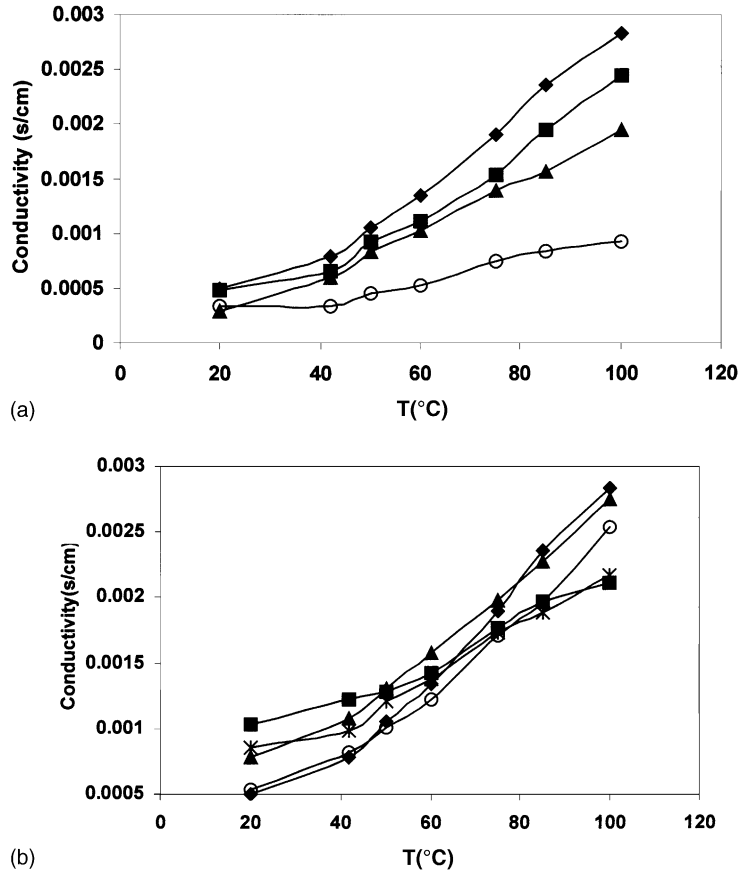
(a)

(b)

Fig. 6. Proton conduction in modified reaction layers for solubilized ionomers and ionomer blends as a function of temperature, comparing (a) Nafion® (◆), Nafion®–SPES-PS (8:2) (■), Nafion®–SPES-PS (1:1) (▲), and pure SPES-PS (○) and (b) Nafion® (◆), SPES-50 (■), Nafion®–SPES-50 (1:1) (▲), Nafion®–SPES-50 (2:8) (○) and SPES-50–SPES-PS (1:1) (✱).

sulfonated ionomers to form sulfonate-rich segregated microstructures may not be as critical for achieving a conductivity percolation threshold as it is in the reaction layer, where the ionomer is present as a diluted phase with limited continuity. Nafion® has clear and distinctive hydrophobic (the perfluorinated backbone) and hydrophilic ends (the pendant prefluorinated sulfonic acid groups), resulting in cluster formation. It is interesting to note that the SPES-PS is expected to have the least likelihood of a clear phase separation because it probably has the shortest average length of unsulfonated chain segment, and this may be why lower conductivity is observed at elevated temperature. It is clear however, that a lot more needs to be done to understand the effect of proton conduction in

the reaction layer. This is especially important when considering the use of these alternative polymers under conditions of lower relative humidity.

3.3. Fuel cell performance using alternate membrane electrode assembly

The use of these alternative membranes in a membrane electrode assembly was evaluated using SPES-40 as the membrane and a solubilized form of the ionomer (SPES-40) in the reaction layer (0.9 mg/cm^2). The results of the single cell PEM fuel cell test is reported in Fig. 7. The steady state polarization curve such as that shown in Fig. 7, is a combination of both the cathode and anode polarization.
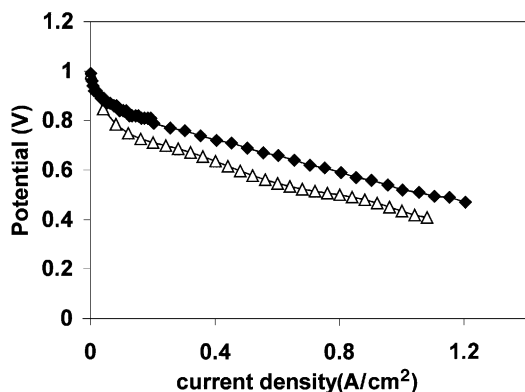
Fig. 7. Single cell polarization curves for MEA's containing Nafion® 117 (◆) and SPES-40 (△) membranes. SPES-40 membrane was combined with SPES-40-based electrodes (0.9 mg/cm² ionomer loading; same loading for Nafion® electrodes/MEA). The data corresponds to tests conducted with cell temperature at 70 °C, with 100% relative humidity using an anode/cathode back pressure of 413.68542 × 10³/344.73785 × 10³ Pa (60/50 psig), respectively.

Since the anode electrode kinetics with pure H_2 is very facile, the single cell polarization is largely a measure of the cathode electrode polarization behavior. A typical fuel cell polarization curve comprises of three zones based on the overpotential. At relatively low overpotentials, or low current density the dominant losses are due to electrode kinetics. In the mid range, ohmic contributions play a major role and, at the high current density regions, mass transport limitations become dominant. As evident from Fig. 7, Nafion® membrane performance was superior primarily in the low current density region. The performance in the mid current density range was very similar based on the similarity of slopes in the linear region. This indicates that kinetics of oxygen reduction in the SPES-50 reaction layers may be poorer than in perfluorinated sulfonic acid electrodes. A more detailed micro-electrode investigation is in progress for a systematic determination of reactant transport parameters and interfacial kinetics using these alternative membranes. Similarity of proton conduction between SPES-40 and Nafion® (Fig. 3) is borne out by the polarization curves showing performance in the ohmic region to be very similar. The primary contributor to the polarization in this region is proton conduction in the bulk of the membrane as well as in the reaction layer.

4. Conclusions

Several alternative membranes with potential for elevated temperature applications were investigated using Nafion® 117 as the control. These were based on engineering polymers with high thermochemical stability, with a high degree of aromatic character, where the monomer consists of a variety of fused phenyl rings linked together with a number of bridging moieties (hereby referred to as membranes with aromatic backbone). These were SPES-40 (a sulfonated polyarylene ether sulfone), SPSS-40 (sulfonated polyarylene sulfide sulfone) and SPES-PS (a sulfonated polyarylene ether sulfone post-sulfonated). The lack of a correlation of conductivity differences between ionomers with their EW (IEC), water content, λ and pK_a suggests that differences in microstructure may be the source of observed conductivity differences. All membranes exhibited similar activation energies for conduction, leaving the Arrhenius pre-exponential factor with its steric components as the main reason for observed conductivity differences. This could be expected to result from a combination of differences in the polymers' backbone flexibility and in their separation of hydrophobic and hydrophilic components.

Proton conductivity was also measured for micro-aggregates of the ionomers in reaction layer analog structures. The results diverged considerably from those measured in dense membranes of the pure ionomers, and may be due to the emphasized effects of microstructural differences between polymers in such reaction layers.

Comparison of single cell performance of SPES-40 and Nafion®-based MEAs indicate that they have very similar ohmic polarization behavior, but that electrodes based on the alternative polysulfone ionomer may have significantly poorer interfacial kinetics for oxygen reduction than Nafion®-based electrodes. A more detailed systematic study is required to resolve these differences.

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