Water and proton transport properties of hexafluorinated sulfonated poly(arylenethioethersulfone) copolymers for applications to proton exchange membrane fuel cells

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Abstract

In the present study, we examine the water and proton transport properties of hexafluorinated sulfonated poly(arylenethioethersulfone) (6F-SPTES) copolymer membranes for applications to proton exchange membrane fuel cells (PEMFCs). The 6F-SPTES copolymer membranes build upon the structures of previously studied sulfonated poly(arylenethioethersulfone) (SPTES) copolymer membranes to include CF_3 functional groups in efforts to strengthen water retention and extend membrane performance at elevated temperatures (above 120 °C). The 6F-SPTES copolymer membranes sustain higher water self-diffusion and greater proton conductivities than the commercial Nafion® membrane. Water diffusion studies of the 6F-SPTES copolymer membranes using the pulsed-field gradient spin-echo NMR technique reveal, however, the fluorinated membranes to be somewhat unfavorable over their non-fluorinated counterparts as high temperature membranes. In addition, proton conductivity measurements of the fluorinated membranes up to 85 °C show comparable results with the non-fluorinated SPTES membranes.
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1. Introduction

Fuel cells offer an alternative means of providing electrical energy to power homes and cars as well as portable devices such as notebook computers. Proton exchange membrane fuel cells (PEMFCs) operate at relatively low temperature and use reformed hydrogen or methanol as a fuel. This leads to, among other problems, CO poisoning of the anode catalyst [1].

High temperature (120–140 °C) fuel cell operation offers several advantages in addition to CO tolerance, including faster proton transport kinetics, better water management and heat rejection. Although Nafion exhibits high proton conductivity (e.g., around 80 mS cm^{-1} at room temperature and 100% RH), above 80 °C the conductivity drops due to water being driven out of the membrane [2]. Studies have shown that the proton transport mechanism in sulfonated polymer membranes is strongly correlated with water mobility [3]. Water retention is therefore an issue of main concern in synthesizing viable PEMs. At higher temperatures, degradation of the membrane may also occur due to condensing water vapor that acts to swell and shrink the membrane repeatedly [4]. Furthermore, at an operating temperature above the glass transition temperature of Nafion (between 100 °C and 110 °C), structural changes can arise and thus lower membrane stability and lifetime [5]. A great deal of research in PEM's today is concerned with searching for a membrane material, other than Nafion, which can withstand high temperature operation, and at the same time provide high proton conductivity.

Highly sulfonated polyarylenetheriosulfone (SPTES) copolymers with endcapping have been synthesized by the Air Force Research Lab as possible alternatives to Nafion. The SPTES copolymer incorporates highly sulfonated regions
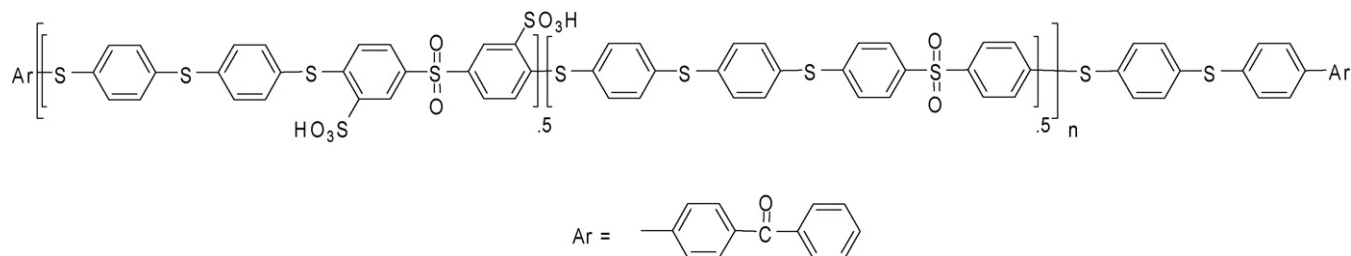
Fig. 1. Endcapped SPTES copolymer structure.

attached to an aromatic hydrocarbon polymer backbone as depicted in Fig. 1. The use of hydrocarbon groups is believed to offer greater structural and thermal stability than the fluorocarbons of Nafion. The SPTES copolymers are also cheaper to synthesize than Nafion. The high degree of sulfonation in these membranes serves to enhance water uptake and thereby increase proton conduction. Endcapping of the copolymers was carried out to minimize excessive swelling or even the potential for water solubility. Also, the aromatic polymers are characteristically high in molecular weight to ensure polymer chain entanglements that can produce durable membrane films when inserted into the fuel cell assembly [6].

In a previous study, SPTES-50 ('50' referring to percentage of sulfonated polymer in a blend of sulfonated and unsulfonated polymer) copolymer saturated in 2 M methanol solution (in consideration of possible direct methanol fuel cell applications) was shown to retain water well as water diffusivity of the membrane remained high at higher temperatures (up to 160 °C) [7].

The proton and water transport properties of hexafluorinated SPTES copolymers, labeled 6F-SPTES-50 and 6F-SPTES-70, (structures shown in Fig. 2) are the subjects of this investigation. Modeled after the morphology of Nafion, the replacement of the central thioether group in the original SPTES copolymer structure by the addition of two hydrophobic CF_3 functional groups per repeat polymer unit had been hypothesized to enhance proton transfer by facilitating the formation of ionic clusters, which link together and provide a channel for transport [3]. Another reason for the inclusion of the CF_3 groups was to balance the hydrophilicity and hydrophobicity of the polymer backbone in an attempt to preserve the membrane structure as water is absorbed. Samples of 6F-SPTES-50 and 6F-SPTES-70 copolymers were studied as a function of only water (not methanol) content. The structural and dynamical measurements performed in this work include molecular weight measurements via gel permeation chromatography, ^{1}H NMR spin-relaxation and diffusion measurements, and proton conductivity measurements by means of AC Impedance Spectroscopy.

2. Experimental

2.1. Materials

4-Fluorophenylsulfone (99%, Sigma–Aldrich Co.), potassium carbonate (99%, ACS reagent, Sigma–Aldrich Co.), tetramethylene sulfone (sulfolane, 99%, Sigma–Aldrich Co.), 4-chlorophenylsulfone (98%, Sigma–Aldrich Co.), 4-fluorobenzophenone (97%, Sigma–Aldrich Co.), 4-chlorobenzophenone (99%, Sigma–Aldrich Co., and *N,N*-dimethylacetamide (DMAc, anhydrous, 99%, Sigma–Aldrich Co.), were used as received. Other chemicals were of a commercially available grade and used as received unless otherwise mentioned. 4,4-(hexafluoroisopropylidene)-diphenol (6F-BPA) was obtained from TCI America, 4,4′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene] bisbenzenethiol (hexafluorobisphenylthiol A) was prepared in AFRL/MLBP Laboratories following established procedures. The sulfonated monomer, 3,3′-disulfonate-4,4′-difluorodiphenylsulfone, was prepared following the procedures in the literature [6,8].

2.2. Synthesis and fabrication of 6F-SPTES copolymer with endcapping group

The 6F-SPTES-50 copolymer was prepared by the following procedure. 3,3′-Disulfonate-4,4′-difluorodiphenylsulfone (1.8333 g, 4.0 mmol), 4-fluorophenylsulfone, (1.0068 g, 3.96 mmol), hexafluorobisphenylthiol A (2.9468 g, 8.0 mmol), and potassium carbonate (2.8748 g, 20.8 mmol) were charged into a 100 ml round-bottom flask maintained under a back
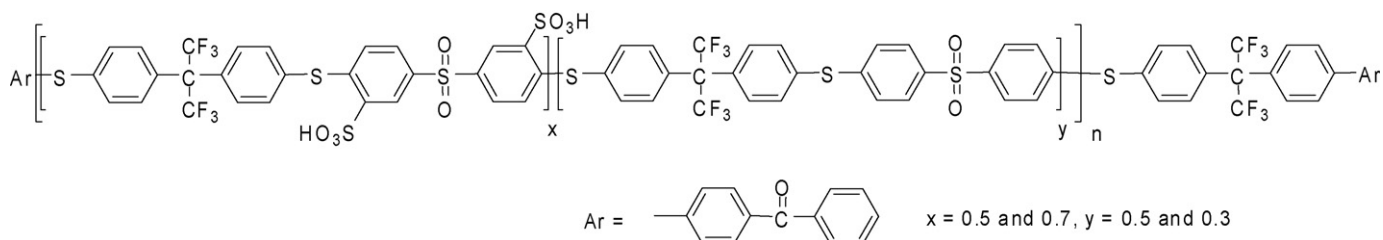

Fig. 2. The chemical structure of hexafluorinated sulfonated poly(arylenethioethersulfone) endcapped copolymers.

pressure of nitrogen and equipped with a magnetic stirrer and an oil bath on a hot plate. Fifty millilitres of sulfolane was added into the flask, stirred for 45 min at room temperature and at 100 °C overnight. This was followed by the addition of 4-fluorobenzophenone (0.008 g, 0.04 mmol) as an endcapping agent into the reaction solution. The reaction mixture was heated to 160–180 °C for 6 h, then cooled down to room temperature, quenched with acetic acid, and precipitated in methanol/acetone. The polymer was filtrated and air-dried, then, soxhlet-extracted with methanol for 48 h, and dried in vacuum at 80 °C overnight to afford a yield of 89%.

The fluorinated sulfonated poly(arylenethioethersulfone) copolymers (salt form) with the endcapping group were dissolved in the DMAc at 100 °C to a clear solution, and filtered at room temperature. The membranes were directly cast in a flat dish at 80 °C in vacuum for 24 h. The clear films were converted to the corresponding sulfonic acids in the presence of dilute sulfuric acid (4 M) at room temperature for 48 h. The films were dried at room temperature, then at 100 °C in vacuum for 24 h. Tough, clear and flexible films of the 6F-SPTES copolymers were fabricated.

2.3. Instrumentation

Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions, M_w and M_n, respectively, of synthesized polymer samples with respect to polystyrene standards. M_w measurement was performed on TriSEC Version 3.00 at 70 °C in NMP containing 0.5 wt.% LiBr. Intrinsic viscosity (IV) was measured at 30 °C in NMP, which contained 0.5 wt.% LiBr, by using an Ubbelohde Viscometer. Thermogravimetry (TGA) was conducted using an Auto TGA 2950HR V5.4A instrument in air at a heating rate of 10 °C min^{-1}.

The conductivity of 6F-SPTES copolymer membranes was measured using AC Impedance Spectroscopy and utilized a standard 4-electrode measurement setup to eliminate electrode and interfacial effects. The proton conductivity was calculated using $\sigma = l/Rdw$, where l is the distance between the electrodes, d and w are the thickness and width of the films, respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the abscissa axis.

A CMX-300 MHz spectrometer in conjunction with a JMT superconducting magnet of field strength $B_0 = 7.1$ T was used to characterize structural and dynamical properties of hydrated 6F-SPTES-50 copolymer. The same spectrometer but in operation with a different magnet (for availability purposes), of field strength $B_0 = 7.2$ T, was used to investigate hydrated 6F-SPTES-70 copolymer.

The spin-lattice relaxation times (T_1's) of the water protons as well as structural polymer protons were measured as a function of temperature by implementing the inversion recovery pulse sequence $(\pi - \tau - (\pi/2))$. T_1 gives crucial information regarding the local environment of a nuclear species on the timescale of 10^{-10} to 10^{-8} s [9]. Quoted values of T_1 are subject to ±3% uncertainty.

The self-diffusion coefficient, D, is useful in measuring long-range ion and molecular transport. Temperature dependent D values of water in the 6F-SPTES copolymers were measured using the pulsed gradient spin echo (PGSE) method. The method consists of enacting the Hahn spin-echo pulse sequence $(\pi/2 - \tau - \pi)$ with the inclusion of two square-shaped gradient pulses [10]. Eq. (1) was used to make a Gaussian fit of the echo amplitude and determine the self-diffusion coefficient D.

$$A(g) = \exp\left[-\gamma^2 D g^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right)\right] \qquad (1)$$

where A is the echo amplitude as a function of the gradient strength g, γ is the gyromagnetic ratio, δ is duration of each gradient pulse, and Δ is the time delay between gradients. For the diffusion experiments conducted on the 6F-SPTES-50 membranes, a Doty broadband diffusion probe was used with applied gradient values reaching 200 G cm^{-1} while δ and Δ values ranged from 0.8–2.5 ms and 10–13 ms, respectively. A Nalorac Z-Spec diffusion probe was used in performing D measurements on the 6F-SPTES-70 membranes with gradient strengths of up to 60 G cm^{-1}. δ and Δ values, using the Nalorac Probe, ranged from 3–4 ms and 8–10 ms, respectively. The uncertainty in measuring D is ±3 to 6% for either probe. For both T_1 and D measurements conducted at variable temperature, at least 20 min was allowed for equilibration after setting the temperature.

2.4. Water uptake measurements

Preceding ^{1}H NMR experimentation, the 6F-SPTES-50 copolymer was prepared with three different water contents. The water content in terms of percentage uptake by weight for the 6F-SPTES-50 samples were 11.5%, 18.3%, and 29.9%. The method of preparation involved first placing small, rectangular strips of the polymer material over P_2O_5 in a desiccator at room temperature. After allowing the strips to dry for 3–5 days, they were inserted into beakers placed over a reservoir of distilled water in a sealed larger vessel. The strips were left in the vessel to absorb water vapor for about 1–3 days. This procedure of hydration was, however, not undertaken for sample 6F-SPTES-50/29.9 wt.%, which stayed immersed in water for 1–3 days so as to reach a fully hydrated level. The other set of membranes, 6F-SPTES-70, were prepared with water contents of 17.4, 46.4, and 76.5 wt.%.

The wet membrane strips (swollen to some degree) were padded dry on the surface before being densely packed into 5 mm o.d. pyrex® tubes that were subsequently flame-sealed. Packing of the membrane material was done rather quickly to ensure minimal possible changes in the desired hydration level. Additionally, a teflon® plug was placed just above the sample to keep water from reaching the top portion of the tube since the loss of water remained a possibility in the high temperature experiments that were to follow. Similar methods of preparation were used for the 6F-SPTES-70 copolymer membranes, which tended to take up more water due to the presence of the higher content of sulfonic acid.

The following formula was used to compute water uptake in wt.%:

$$\text{Water uptake} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \qquad (2)$$

where m_{wet} and m_{dry} are the masses of the wet and dry membranes, respectively. An error of ± 0.0004 g was determined to be present in using the microbalance. The measured water uptake of 6F-SPTES was found to be somewhat higher than that of SPTES at a comparable level of sulfonation, compared to the non-fluorinated SPTES. This is expected of the polymer system in which the central thioether group was replaced by hexafluoroisopropylidene groups (6F), with the intent of enhancing backbone hydrophobicity. Our qualitative explanation for this observation is somewhat based on the 'cluster network model' description in the literature [11,12] of the microscopic structure of Nafion membrane in which the ion-exchange sites are separated from the perfluorocarbon backbone resulting in the formation of pores which are connected by short narrow channels. In the case of 6F-SPTES, the higher water uptake relative to SPTES is presumably due to the fact that the enhanced hydrophobicity of the backbone containing hexafluoroisopropylidene groups can cause more effective sequestration of the sulfonic acid-containing hydrophilic domains in the polymer microstructure. As will be discussed later, however, the high initial water uptake does not necessarily imply that this water is well retained at elevated temperature.

3. Results and discussion

3.1. ^1H NMR spectra of fluorinated SPTES copolymers

^{1}H NMR room temperature spectra, obtained after Fourier transformation of the free induction decay following a single $\pi/2$ pulse sequence, for the three different water contents of 6F-SPTES-50 copolymer are displayed in Fig. 3. Distilled water was used as the zero reference with a ^{1}H resonance frequency of 301.020 MHz. The relative intensities of the peaks for each sample are shown in Fig. 3. All spectra reveal a strong absorption peak shifted downfield, falling somewhere in the range of 330–410 Hz ($\sim$1–1.3 ppm) relative to the reference. The peak can be mainly attributed to water in the membrane since the largest concentration of protons can be found there. As for the observed shift, a plausible explanation is the effect of deshielding from the external field that the OH protons in water experience from the SO_3^- groups. The acid proton dissociated from the SO_3^- cannot be detected by itself as the total proton NMR signal is completely dominated by water protons.

In samples 6F-SPTES-50/11.5 wt.% and 6F-SPTES-50/18.3 wt.%, we clearly see a smaller and somewhat broad peak, which is upshifted about 2.4 ppm from the reference. The spectrum for sample 6F-SPTES-50/29.9 wt.% also seems to show such a peak, but it is nearly buried under a much larger water signal. The water resonance signal for 6F-SPTES-50/29.9 wt.% is, as expected, noticeably stronger (greater area under the spectral curve) than for the two 6F-SPTES-50 samples of lower water uptake, but it is also considerably broader. We may assign this secondary peak to the aromatic protons making up the backbone of the 6F-SPTES-50 membrane. In support of this claim, diffusion data reveals no observable attenuation of these secondary peaks with increasing gradient strength, i.e. these protons do not diffuse. The shift between water and aromatic ring protons is generally around 3 ppm, which also supports this assignment [13,14]. Lastly, the spectrum of 6F-SPTES-50/29.9 wt.% features a broad component shifted downfield ($\sim$6.7 ppm) and arises due to anisotropy of water in the membrane, i.e. the water is spread out in different parts of the sample. In fact, variable temperature T_1 data for this peak was separately found to resemble T_1 values measured for the main water peak and thus support this peak assignment. It may also be of interest to note that the linewidths of the main peaks shown in Fig. 4 span from approximately 100–150 Hz for the lower water contents while for 6F-50/29.9 wt.%, a linewidth of $\sim$410 Hz is found. The linewidths did not change widely with temperature except for sample 6F-SPTES-50/18 wt.%, which
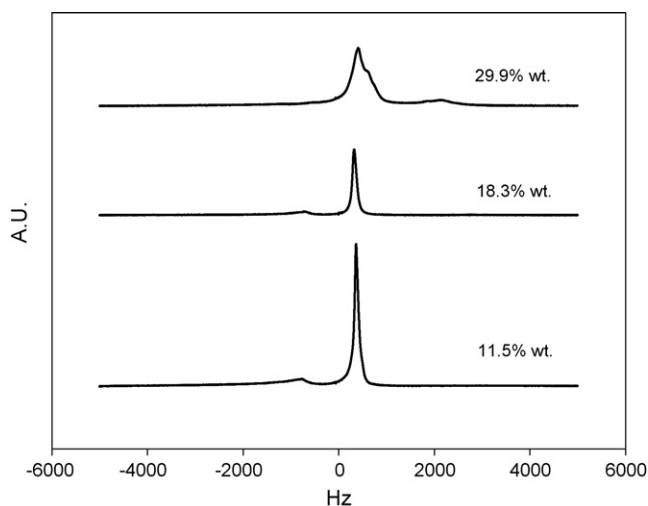

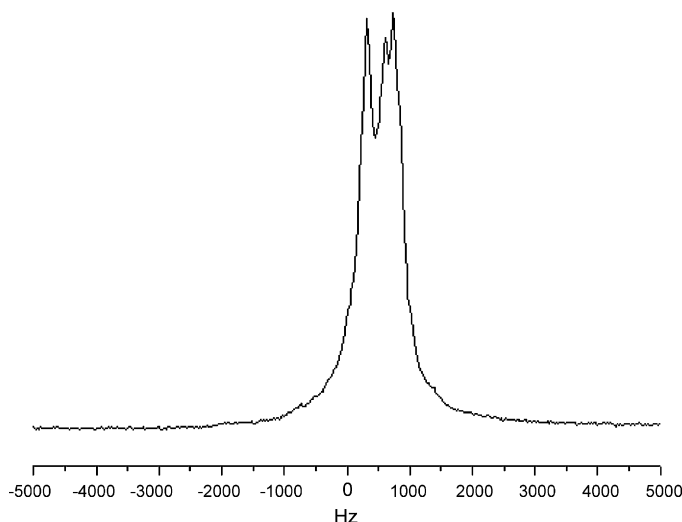Fig. 3. ^{1}H room temperature spectra of 6F-SPTES-50 copolymer membranes.

Fig. 4. ^{1}H room temperature spectrum of 6F-SPTES-70/45 wt.% membrane.

exhibited a linewidth of 107 Hz at room temperature and one of 63 Hz at ~80 °C.

With regard to ^{1}H NMR measurements carried out for hydrated 6F-SPTES-70 membranes, the experimental configuration included a different magnet with greater field inhomogeneity. Thus, the spectra arising from this set of samples tended to give somewhat broader peaks. A representative spectrum is shown in Fig. 4, which was referenced to distilled water but with a carrier frequency of 307.031 MHz. In this room temperature spectrum for 6F-SPTES-70/45 wt.%, we observe a water signal at about 1 ppm upfield and another closely spaced doublet at about 2.4 ppm, similar to the shifts in Fig. 3. Diffusion data reported for this sample were derived from decay of the 1 ppm peak. The hydrocarbon site cannot be distinguished because of the line broadening feature. The linewidths of the water peaks observed were several hundred Hz.

3.2. ^{1}H spin-lattice relaxation measurements of fluorinated SPTES copolymers

Fig. 5 displays Arrhenius plots of T_1 values of the water protons in hydrated 6F-SPTES-50 and 6F-SPTES-70 membranes. Focusing on the 6F-SPTES-50 membranes first, T_1 clearly increases with temperature throughout the temperature range investigated. The rising T_1 behavior suggests that the rates of tumbling and vibrational motions of the water molecules exceed the NMR (Larmor) angular frequency, characteristic of molecular motion in the high temperature regime [15]. Relatively short motional correlation times can therefore be ascribed to the water molecules. The 6F-SPTES-50 sample with the lowest water content exhibits a broad T_1 minimum around room temperature. Presumably, T_1 minima would be observed for the other samples at lower temperatures. As for 6F-SPTES-70 samples, we also observe an increasing trend in T_1 with temperature, however, the relaxation values drop above 70 °C for samples

6F-SPTES-70/17.4 wt.% and 6F-SPTES-70/46.4 wt.%, and above 90–95 °C for 6F-SPTES-70/76.5 wt.% The fall off in T_1 is associated with the loss of water in the membrane as higher temperatures are reached. This observation will be discussed later in the context of the water diffusion results. Sample 6F-SPTES-70/75 wt.% features the highest T_1 values, implying relatively fast molecular motion. This is not unexpected as the water molecules in the higher water content membranes begin to experience an environment approaching that of liquid water. T_1 measurements for water in the 6F-SPTES-70 membranes tended to be greater than that for the 6F-SPTES-50 membranes suggesting faster water mobility in 6F-SPTES-70 membranes, which is supported by higher water diffusion values measured for the 6F-SPTES-70 membranes discussed next. According to this reasoning, it would appear that the lower T_1 values of the 6F-SPTES-50 membrane with the highest water content are anomalous. However, this may be related to the significantly broader linewidth of this sample (Fig. 3), which suggests stronger local interactions between water molecules and their environment, leading to enhanced relaxation.

3.3. Water self-diffusion measurements and proton conductivity data of 6F-SPTES copolymers

Shown in Fig. 6 are the Arrhenius diffusion curves for the hydrated 6F-SPTES-50 and 6F-SPTES-70 membranes. We readily observe a common trend through each sample tested, namely, that the water diffusivity rises with temperature yet undergoes a gradual drop as the sample is heated to a temperature lying in the range of 70–110 °C. The membrane sample begins to dehydrate in the specified range of temperatures. We recall that Nafion experiences water loss at a comparable temperature, approximately 80 °C, and special measures must be taken to keep the membrane hydrated when operating in the fuel cell assembly at or above this temperature. It is thus believed that
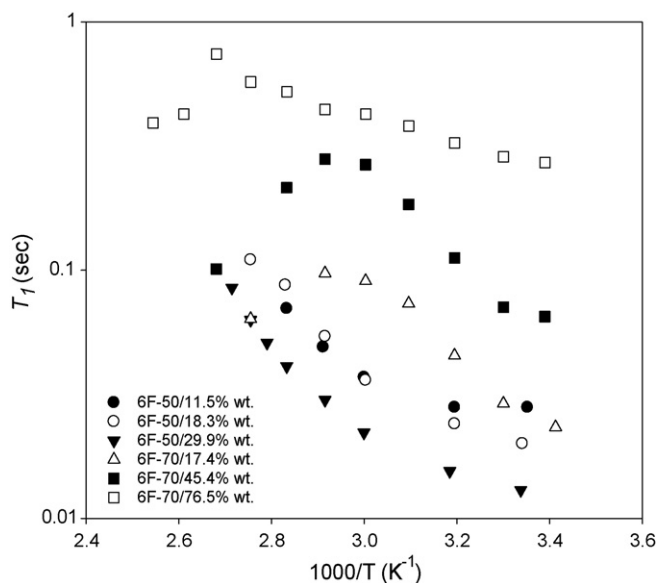

Fig. 5. Semilog plot of ^{1}H spin-relaxation times of water molecules in 6F-SPTES copolymer membranes.
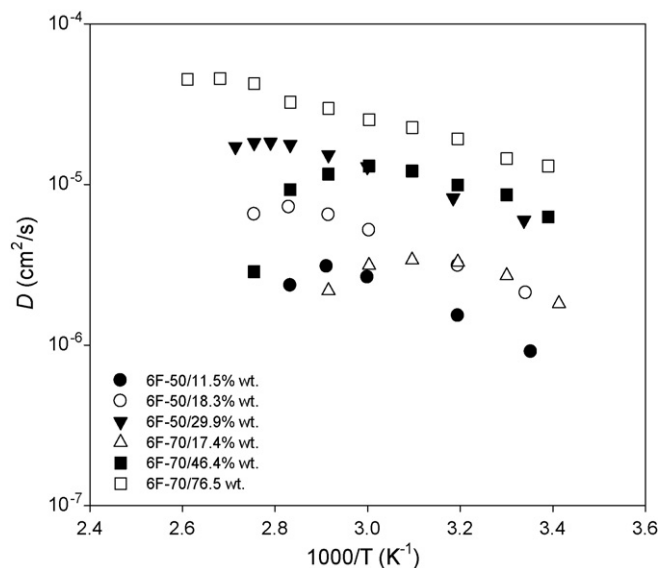

Fig. 6. Water diffusion in 6F-SPTES copolymer membranes as a function of temperature.

the 6F-SPTES copolymer membranes therefore do not offer a significant advantage over Nafion in terms of membrane performance at elevated temperature, as water is seen not to be retained well in the 6F-SPTES copolymer membranes for temperatures even below the boiling point of water. An exception may be made for sample 6F-SPTES-70/76.5 wt.%, in which water diffusivity was observed to be fairly high up to 110 °C. At room temperature, D was measured to be $1.30 \times 10^{-5} \mathrm{\,cm^2\,s^{-1}}$, which is about a factor of two lower than the diffusion value of free water at room temperature (i.e., $D \sim 2.29 \times 10^{-5} \mathrm{\,cm^2\,s^{-1}}$). At 100 °C, D reached a value of $4.57 \times 10^{-5} \mathrm{\,cm^2\,s^{-1}}$ and then decreased at higher temperature. By observing the highest water diffusivity in this particular highly sulfonated 6F-SPTES-70 copolymer, affirmed is the claim that water mobility is a function of the degree of initial water uptake, which in turn is related to the degree of sulfonation. With such a high level of water uptake in 6F-SPTES-70/76.5 wt.%, however, issues regarding membrane integrity may still need to be considered when the membrane is finally put into the cell assembly. The high rate of water diffusion in 6F-SPTES-70/76.5 wt.% is consistent with T_1 data for this sample, as short correlation times for the water molecules in the membranes could be inferred from the data in Fig. 5. T_1 of water was also shown to decrease at ~100 °C, about the same temperature at which water diffusion begins to diminish, thus indicating a reduced molecular mobility over a broad range of time scales.

In comparing the 6F-SPTES copolymer membranes, including 6F-SPTES-70/76.5 wt.%, to SPTES copolymer membranes, we conclude that water retention decreases as a result of inserting the fluorine functionalities in the backbone structure of SPTES copolymers. We can cite, as evidence, prior diffusion studies performed on SPTES-50 copolymer membranes [7], in which these membrane demonstrated good water retention up to 160 °C, where the water self-diffusion coefficient rose to a value of approximately $4.50 \times 10^{-5} \mathrm{\,cm^2\,s^{-1}}$. It may be the case that the addition of fluorine groups lowers the glass transition temperature T_g of the polymer matrix, which affects the retention properties of the membrane in a way opposite to what was sought. High degrees of sulfonation in SPTES copolymer membranes can raise T_g of the polymer matrix, which may be an additional factor (besides increased hydrophilicity) for somewhat better water retention in 6F-SPTES-70/76.5 wt.% [16].

We can gain more understanding into the mechanism of water retention by drawing a comparison between samples 6F-SPTES-50/18.3 wt.% and 6F-SPTES-70/17.4 wt.%, which both possess comparable water contents. As seen in Fig. 6, the samples exhibit similar diffusive behavior for the first few temperatures. However, for 6F-SPTES-70/17.4 wt.%, water diffusion drops at about 70 °C, while for 6F-SPTES-50/18.3 wt.%, diffusion keeps rising to almost 90 °C. Thus, higher initial water uptake dictated by a higher degree of sulfonation does not necessarily correlate with water retention capability at elevated temperature, at lower water content. This finding has obvious relevance to fuel cells operating under relatively low relative humidity (RH) conditions. The effect of lower initial water content also produces a similar trend in the 6F-SPTES-50 membranes, where fall-off in the diffusion is observed at lower temperature than for the more hydrated sample.
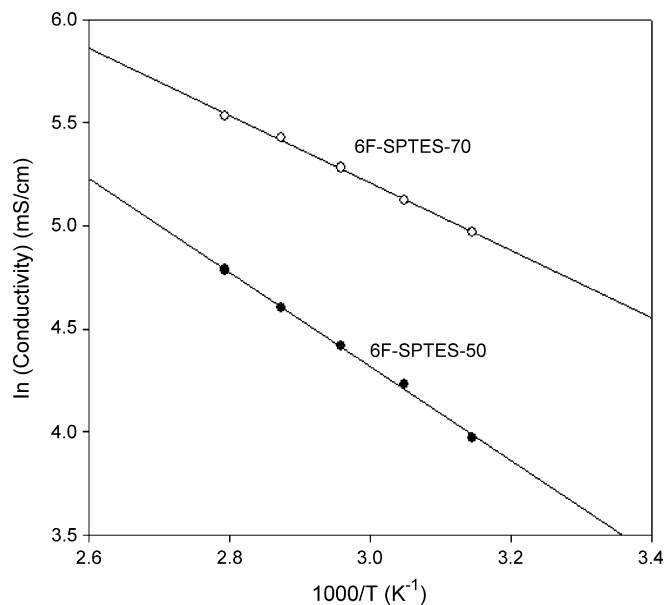

Fig. 7. Proton conductivity of 6F-SPTES copolymer membranes at 85% RH.

Table 1
Properties of 6F-SPTES copolymers

Polymer	IV (dL g^{-1})	GPC (M_w/M_n)	TGA (T_{sd}/T_d, °C)	σ (mS cm^{-1})
6F-SPTES-70	1.35	63.8/29.2	308/552	195
6F-SPTES-50	0.92	61.2/25.8	322/565	83

Notes: Proton conductivity (σ) was tested at 65 °C, 85% relative humidity. T_{sd} refers to the temperature at which the sulfonate group detaches; T_d refers to polymer decomposition. Both values determined by TGA in air.

Proton conductivity data of hydrated 6F-SPTES-50 and 6F-SPTES-70 membranes carried out at 85% RH, are displayed in Fig. 7 with molecular weights, inherent viscosities, and conductivity values recorded in Table 1. As expected, proton conductivity measurements were higher for the 6F-SPTES-70 membrane in the temperature range investigated (45–85 °C). Proton conductivity is thus shown to be directly related to the water content of the membrane.

A previous study on SPTES-50 copolymer with 41% water uptake at 65 °C and 85% RH, had been reported to generate a proton conductivity of 100 mS cm^{-1}, a 25% greater value than that found for hydrated Nafion-117 under similar conditions [6]. With regard to the study contained herein, 6F-SPTES-50 membrane yielded a conductivity of 83 mS cm^{-1}, a 17% decrease from the SPTES-50 conductivity measurement. A SPTES-70 copolymer, also at 65 °C and 85% RH but with 73% water uptake, had been reported to produce a conductivity measurement of 175 mS cm^{-1} [6]. 6F-SPTES-70 copolymer provided a modest 11% increase in proton conductivity at the same temperature and relative humidity (see Table 1). It should be noted that replacement of the thioether spacers with the 6F functionalities results in a modest decrease in ion exchange capacity, although this does not appreciably change the interpretation of the results herein.

4. Conclusions

The proton and water transport properties of 6F-SPTES copolymers (6F-SPTES-50 and 6F-SPTES-70) were investigated in this study. The conductivities measured for the 6F-SPTES copolymer membranes were significantly higher than those of commercial Nafion membranes. Although initial water uptake of the 6F-SPTES copolymer membranes was fairly high, they exhibited decidedly inferior water retention capabilities at elevated temperature, compared to their non-fluorinated counterparts.

Acknowledgments

References

[1] O.J. Murphy, G.D. Hitchens, D.J. Manko, Space Electrochem. Res. Technol. 11 (1993) 149–166.

[2] P. Dimitrova, K.A. Fridrich, U. Stimming, B. Vogt, Solid State Ionics 160 (2002) 115–122.

[3] T.A. Zawodzinski, T.E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio, S. Gottesfeld, J. Electrochem. Soc. 140 (1993) 1981–1985.

[4] X. Liu, C. Suo, Y. Zhang, X. Wang, C. Sun, L. Li, L. Zhang, J. Micromech. Microeng. 16 (2006) S226–S232.

[5] C. Yang, S. Srinivasan, A.B. Bocarsly, S. Tulyani, J.B. Benziger, J. Membr. Sci. 237 (2004) 145–161.

[6] Z. Bai, T.D. Dang, M.F. Durstock, J. Membr. Sci. 281 (2006) 508–516.

[7] J.R.P. Jayakody, A. Khalfan, E.S. Mananga, S.G. Greenbaum, T.D. Dang, R. Mantz, J. Power Sources 156 (2006) 195–199.

[8] Z. Bai, T.D. Dang, Macromol. Rapid Commun. 27 (2006) 1271–1277.

[9] M.H. Levitt, Spin Dynamics: Basics of Nuclear Magnetic Resonance, 1st ed., John Wiley and Sons, New York, 2001, pp. 315–320.

[10] E.O. Stejskal, J.E. Tanner, J. Chem. Phys. 42 (1965) 288–292.

[11] T.D. Gierke, W.Y. Hsu, in: A. Eisenberg, H.L. Yeager (Eds.), Perfluorinated Ionomer Membranes, ACS Symposium Series No. 180, American Chemical Society, Washington, DC, 1982, p. 283.

[12] B. Smitha, S. Sridhar, A.A. Khan, J. Membr. Sci. 259 (2005) 10.

[13] J. Kawamura, K. Hattori, T. Hongo, R. Asayama, N. Kuwata, T. Hattori, J. Mizusaki, Solid State Ionics 176 (2005) 2451–2456.

[14] R.S. Macomber, A Complete Introduction to Modern NMR Spectroscopy, 1st ed., John Wiley and Sons, New York, 1998, pp. 78–81.

[15] E. Fukushima, S.B. Roeder, Experimental Pulse NMR: A Nuts and Bolts Approach, Addison-Wesley, Massachusetts, 1981, pp. 125–135.

[16] J. Rozière, D.J. Jones, Ann. Rev. Mater. Res. 33 (2003) 503–555.