

# NMR investigation of water and methanol transport in sulfonated polyarelenethioethersulfones for fuel cell applications

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Received 6 April 2005; accepted 17 May 2005

Available online 11 July 2005

## Abstract

We report an investigation of water and methanol transport in polymer electrolyte membranes based on highly sulfonated polyarelenethioethersulfones (SPTES) for direct methanol fuel cell (DMFC) applications. Measurements of both water and methanol self-diffusion coefficients of SPTES polymer as well as in a reference sample of Nafion-117 equilibrated in 2 M methanol solution have been carried out, using the pulsed gradient spin echo technique, over a temperature range of 20–140 °C. The selectivity of the membrane, defined as ( $D_{OH}/D_{CH_3}$ ), decreased from 6 to 2.4 as temperature increased from 20 to 140 °C in SPTES sample while in Nafion, the value decreased from 3.2 to 1.4 as temperature increased from 20 to 100 °C. These results indicate significantly lower fuel molecular permeability in SPTES compared to that of Nafion. All results suggest high-temperature stability in these materials, offering the possibility of fuel cell operation at temperatures >120 °C. High pressure NMR diffusion measurements were also carried out for three different water contents (between 20 and 55 wt.%) in a static field gradient in order to get supplemental information regarding water transport in SPTES materials. The calculated activation volume increased from 1.54 to 8.40 cm<sup>3</sup>/mol as the water content decreased from 55 to 20%. This behavior is qualitatively similar to previously reported results for Nafion-117.

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**Keywords:** Direct methanol fuel cells; Polymer electrolyte membranes; Water transport; Methanol transport; Pulse gradient spin-echo nuclear magnetic resonance diffusion

## 1. Introduction

The development of high-performance polymer electrolyte membrane fuel cells (PEMFC) is critically dependent upon the transport properties of the polymer electrolyte membrane available [1]. At present, Nafion, which is a perfluorosulfonated membrane with a hydrophobic fluorocarbon backbone and hydrophilic sulfonic pendent side chain, is the only commercially available and successfully used membrane in PEMFC applications [2]. However, since the performance of these membranes highly depends on their hydration levels, use of Nafion is limited to a temperature regime below

80 °C [3], yet significantly higher temperatures (~120 °C) are considered optimum for operation of the PEMFC [4].

Other disadvantages include the high cost of Nafion and its high permeability to methanol, which is used as a fuel in direct oxidation fuel cells (DOFC) [5,6].

Over the last decade, several new proton conducting polymer electrolyte membranes have been investigated [7–9]. Among these are high-performance sulfonated polyarylenether and polyaryleneether sulfone polymers, which have been described in the literature due to their exceptional thermal stability, good mechanical properties, and proton conductivity [10–12]. Advantages of DOFC include low cost, reduced weight and volume compared with indirect fuel cells in which the fuel is reformed into hydrogen before use. The most widely used fuel for DOFC is methanol. Methanol is of low cost and has easy storage capabilities. Nonetheless,

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it has a low boiling point ( $\sim 65^\circ\text{C}$ ) and permeates proton conduction membranes in fuel cells rather easily. This fuel permeability directly correlates with crossover, which refers to the transport of the intact fuel molecules to the cathode compartment, where the fuel molecules react with oxygen to produce water, carbon dioxide and heat. The result is the consumption of fuel without the production of electricity, thus, reducing the overall efficiency of the fuel cell. Methanol crossover is especially high in Nafion. Thus extensive effort has been made towards finding new low cost, solid polymer electrolytes with high ionic conductivity, high temperature operation capability (i.e. high temperature water retention), and low methanol permeability.

One potential solution is the synthesis of new high performance polymer electrolyte membrane materials using a wholly aromatic polymer backbone along with a high sulfonic acid content that enhances water retention and can consequently allow elevated temperature operation. Moreover, endcapping of these new highly sulfonated polymers takes advantage of a bulky aromatic end group to eliminate water solubility of these polymers without adversely affecting their proton conductivity. These materials offer the possibility of fuel cell operation at temperatures  $>120^\circ\text{C}$  [12].

In this paper, highly sulfonated polyarylenethioethersulfone (SPTES) polymer membrane were investigated, with particular emphasis on water and methanol transport. Self-diffusion coefficients were measured using nuclear magnetic resonance pulse gradient spin-echo (NMR-PGSE) [13]. In cases where the different nuclear (proton) environments can be resolved in the NMR spectrum, it is possible to measure distinct diffusion coefficients, for example those of water and methanol.

Greater understanding of the mechanism of ion and molecular transport in polymers can be greatly assisted by employing pressure as the thermodynamic variable. Previous NMR and electrical conductivity investigations have been carried out in PEM materials as a function of applied pressure [8,9,14,15]. Variable pressure measurements can probe molecular motion and ionic diffusion processes associated with volume fluctuations. It is of interesting to compare new results taken from SPTES samples in this investigation with previous work reported for Nafion [8,9,14,15].

## 2. Experimental details

Synthesis of the SPTES polymers has been described in detail elsewhere [12]. The SPTES membranes were cut into thin ( $\sim 4\text{ mm} \times 10\text{ mm}$ ) rectangular strips, dried in a vacuum oven at  $50^\circ\text{C}$  for 24 h and then saturated in 2 M methanol/deionized water for 2 days. Nafion-117 membranes were purchased from DuPont, boiled in 5%  $\text{H}_2\text{O}_2$  solution and then 5%  $\text{H}_2\text{SO}_4$  solution, rinsed on deionized water, and then dried over  $\text{P}_2\text{O}_5$ . Total solution uptake was determined by using a microbalance and recorded as (weight of saturated film – weight of dry film)/weight of

dry film)  $\times 100\%$ . For NMR measurements, samples were packed into  $5\text{ mm (o.d.)} \times 20\text{ mm}$  NMR tubes and flame-sealed under ambient atmosphere. The temperature range investigated were  $20\text{--}140^\circ\text{C}$ , with equilibration times of  $20\text{--}25\text{ min}$  between each temperature change.

NMR measurements were performed on a Chemagnetics CMX-300 spectrometer with  $^1\text{H}$  operating frequency of 301.02 MHz. Spectra were obtained by transforming the resulting free-induction decay (FID) of single  $\pi/2$  ( $13\ \mu\text{s}$ ) pulse sequence. Self-diffusion coefficients ( $D$ ) were obtained by the NMR-pulse gradient spin-echo technique (NMR-PGSE). This technique involves the use of the Hahn spin-echo pulse sequence ( $\pi/2\text{--}\tau\text{--}\pi$ ) and the simultaneous application of square-shaped magnetic gradients of magnitude  $g$  and duration  $\delta$ . Diffusion results in attenuation of the echo amplitude  $A$  given by  $A(g) = \exp[-\gamma^2 g^2 D \delta^2 (\Delta - (\delta/3))]$  [16], where  $\gamma$ ,  $D$  and  $\Delta$  represents the nuclear gyromagnetic constant, self-diffusion coefficient, and interval between gradient pulses, respectively. Applied gradient strengths ranged from 0.2 to 2.2 T/m,  $\delta$  and  $\Delta$  ranged from 0.5 to 2.0 and 8–15 ms, respectively. The resulting echo profile versus gradient strengths is fitted to the above equation and  $D$  is extracted. Uncertainties in self-diffusion coefficient measurements are  $\sim 5\%$ .

For the high pressure NMR measurements samples were first dried in a vacuum oven at  $50^\circ\text{C}$  for 24 h and then saturated in water for another 2 days. Water uptake (without methanol) was determined in the same manner as described above. Variation of the water uptake in samples was achieved by slowly drying the saturated sample in a dry  $\text{N}_2$  atmosphere for a limited time until the desired water percentage was reached. Stack samples were made from five rectangular strips of film with dimensions  $6\text{ mm} \times 5\text{ mm} \times 1.5\text{ mm}$ . For NMR measurements, the samples were hermetically sealed in thin polyethylene bags, which were shown to produce a negligible proton NMR background signal compared to the signal from the sample. This was necessary in order to isolate the sample from the pressure transmitting fluid (hydrogen-free FLUORINERT electronic fluid, FC-77 manufactured by 3M Company).

The naturally existing field gradient of a conventional 7.3 T superconducting magnet was used for the measurements. The central field and gradient strength were varied continuously, within the limits of the magnet, by moving the NMR probe head within the bore of the magnet. The position of the NMR coil (which contains the sample) determines both the resonant frequency and the magnetic field gradient. A home-built computer controlled motorized stage, capable of moving the probe in precise steps of 0.25 mm, was used to center the coil at a field gradient strength ( $G = dB_z/dz$ ) of 0.26 T/cm. This value was determined experimentally using the standard self-diffusion coefficient of water [17]. Accurate variation of the pressure (0–2.5 kbar) was carried out using an ENERPAC 11–400 hydraulic system fitted to a sealed Cu–Be alloy high-pressure chamber (bomb) inside of which resides the NMR radiofrequency coil and sample.

Electronic connection between the coil (high pressure side) and external (ambient pressure side) matching and tuning capacitors was achieved by sealing the wire feedthroughs with an epoxy/ceramic composite. A homebuilt broadband NMR spectrometer operating at 69.35 MHz (the central field value corresponding to the position of the sample in the fringe-field) and utilizing a phase cycled spin-echo pulse sequence ( $\pi/2-\tau-\pi-\tau$ , *acquire*) was used to detect the proton echo signal from the sample. Pulse widths ( $\pi/2$ ) were typically of 2.5  $\mu$ s duration. This value was chosen on the basis of the maximum signal amplitude obtainable for a given pulse separation.

### 3. Results

A typical proton spectrum of an SPTES sample equilibrated in 2 M methanol is shown in Fig. 1. The sample chosen is denoted SP50 which is an endcapped 50/50 blend of sulfonated polyarylenethioethersulfone sulfite/polyarylenethioethersulfone sulfite. The two distinct proton environments namely that of water (OH) and (CH<sub>3</sub>) are clearly resolved, even in the membrane, allowing one to determine the equilibrium methanol concentration in the film and to measure self-diffusion coefficients separately for each component. Self-diffusion measurements were made as a function of temperature for SPTES and Nafion-117 samples, both equilibrated in 2 M MeOH aqueous solutions. Diffusive decay of the main peak (OH) of the spectrum represents the water self-diffusion because the water OH groups far outnumber the methanol OH groups for the present MeOH concentration.

The ratio of the integrated intensities of the CH<sub>3</sub> to OH proton NMR peaks is approximately proportional to the methanol concentration in the membrane (at low methanol concentration), and thus can provide a direct measure of selective methanol uptake (i.e. partitioning), if the equilib-

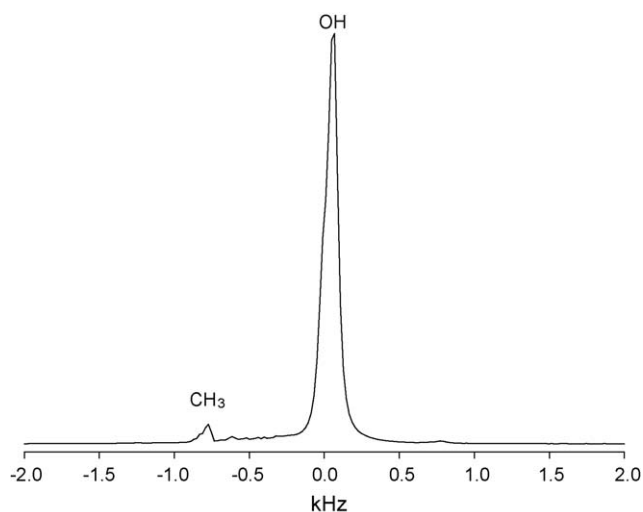


Fig. 1. <sup>1</sup>H NMR spectrum of SPTES equilibrated in 2 M MeOH at 313 K.

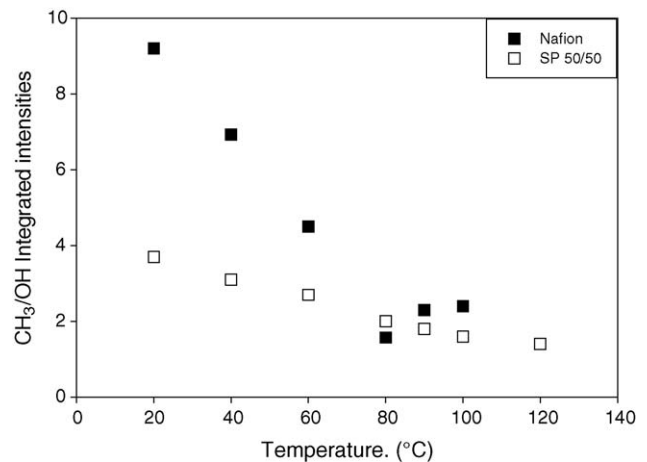


Fig. 2. Integrated proton NMR intensity as percentage of methanol to water peaks in SPTES and Nafion membranes equilibrated in 2 M MeOH.

rium concentration in the membrane is not equal to that of the solution. The CH<sub>3</sub>/OH percentage NMR intensity ratio is plotted in Fig. 2. The integrated CH<sub>3</sub>/OH intensity ratio in a 2 M solution was determined to be about 6%, in agreement with the calculated value. This is close to the values measured for Nafion below about 80 °C. From these results it is clear that the SPTES membrane takes up considerably less methanol from the 2 M starting solution than Nafion, especially at low temperature.

The direct comparison of self-diffusion coefficients as a function of temperature between SPTES and Nafion is shown in Fig. 3. The water diffusion coefficients in both membranes are quite comparable up to 80 °C, as are previously reported conductivity measurements [12]. However above 80 °C, the water diffusion coefficient in Nafion is reduced whereas it is increased in SPTES all the way up to the highest measurement temperature, 140 °C. This result provides indirect but

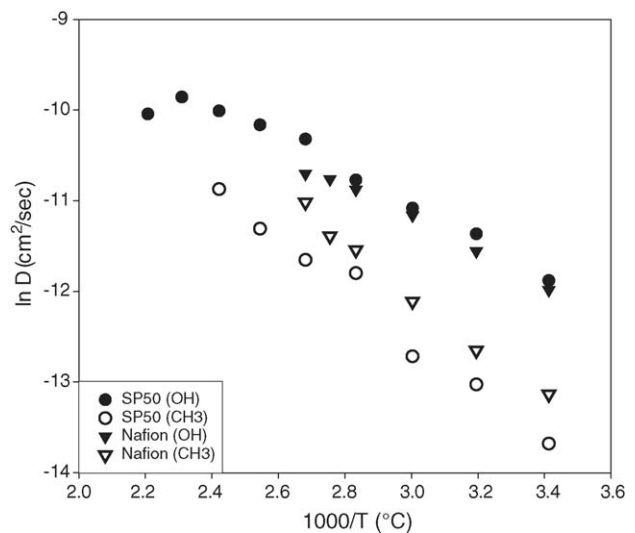


Fig. 3. <sup>1</sup>H self-diffusion coefficients of 2 M MeOH saturated SPTES and Nafion membranes.

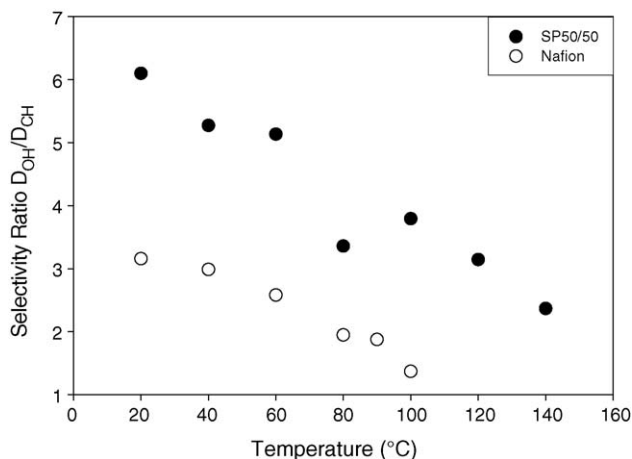


Fig. 4.  $^1\text{H}$  selectivity ratio of 2 M MeOH saturated SPTE and Nafion membranes.

nevertheless compelling evidence that water is well retained in SPTEs at temperatures up to 140 °C. The drop in water diffusion in Nafion above 80 °C has been previously attributed to membrane dehydration [2].

Results of the diffusion coefficient of  $\text{CH}_3$  in both samples are also included in Fig. 3. Methanol diffusion is clearly lower in SPTEs than in Nafion, but in order to obtain more meaningful results with respect to operation in a DMFC, we define the membrane selectivity as the ratio  $D(\text{OH})/D(\text{CH}_3)$ . The rationale for this definition is that  $D(\text{OH})$  is correlated with proton conductivity and  $D(\text{CH}_3)$  is correlated with methanol permeability and hence crossover. It is thus desirable to have a proton conduction membrane with high selectivity. Variable temperature selectivity results for the two membranes are plotted in Fig. 4. The selectivity ratio of SPTEs is about a factor of two higher than that of Nafion, although both membranes exhibit a decrease in selectivity with increasing temperature.

For high-pressure NMR measurements we used SPTEs60 (SPTEs 60/40) and SPTEs50 (the latter being the same material discussed above) membranes for three different water contents. Because of the large magnetic field inhomogeneity, characteristic of the high pressure diffusion apparatus, it is impossible to resolve water and methanol peaks. Therefore, membranes equilibrated in only water were investigated. Proton spin echo intensities  $M(\tau)$  were measured as a function of the pulse separation,  $\tau$ , and self-diffusion coefficients  $D$  were extracted from the data using Eq. (1) [13].

$$M(\tau) = M_0 \exp \left\{ \frac{-2}{3} \left[ \frac{3\tau}{T_2} + \gamma^2 g^2 D \tau^3 \right] \right\} \quad (1)$$

In this expression,  $M_0$  is the maximum magnetization (extrapolated to  $\tau=0$ ). To assist in the analysis, proton transverse relaxation times  $T_2$  were measured independently and the data were fit to a linearized version of Eq. (1) with slope,  $2(\gamma g)^2 D/3$  and intercept,  $2/T_2$ . In this way, the diffusion coefficients were gathered with respect to applied pressure. The self-diffusion coefficients were extracted from the above

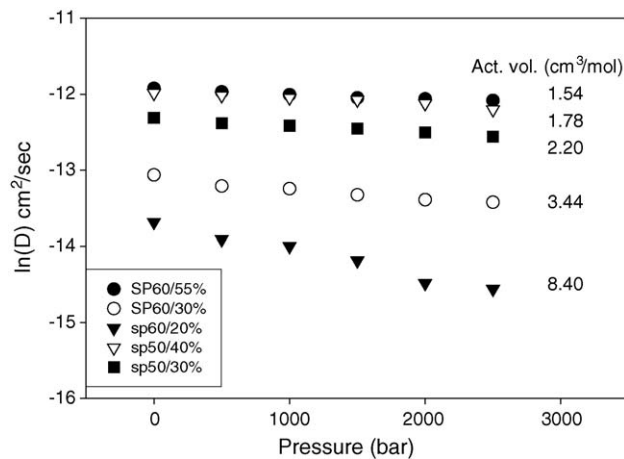


Fig. 5.  $^1\text{H}$  diffusion coefficients of SPTEs50 and SPTEs60 membranes as a function of pressure for different water concentrations.

graphs as a function of pressure for four different water contents in SPTEs 60 are plotted in Fig. 5.

The data in Fig. 5 can be further analyzed to yield the activation volume  $\Delta v$  associated with the diffusing water molecules according to Eq. (2).

$$\Delta v = -kT \left( \frac{\partial \ln D}{\partial P} \right)_T \quad (2)$$

The activation volumes for four different water contents in SPTEs 60 are listed on the same plot. The self-diffusion coefficient generally decreases with decreasing water content and also with increasing pressure as this reflects greater restrictions for water molecular motions. In addition, the membranes with higher water content have smaller  $\Delta v$  than those with lower water content. A relatively large  $\Delta v$  of 8.4 cm³/mol is observed for 30% water content in SPTEs60 membrane. Similar behavior has been observed from diffusion and electrical conductivity measurements of hydrated Nafion-117 films with lower water content [8,9,14,15,18]. The observation that high activation volumes are often associated with solvent-free polymer electrolytes suggests that ion transport in these cases is controlled by polymeric segmental motion [8,17]. The highest activation volume we have seen here is lower than the values usually associated exclusively with segmental motion. It is surmised that significantly higher values of  $\Delta v$  would be observed for nearly dry membranes (<10% water), but the proton NMR signal strength is insufficient to verify this. At high water contents,  $\Delta v$  is relatively small in both membranes and does not vary much with increasing water content. In a previous paper [14], it was suggested that the diffusion in this region is controlled by bulk water more than by the polymer. Zawodzinski et al. has also pointed out that the conductivity mechanism at high water content is expected to approach that of bulk water due to the large number of pores within the polymer that are filled with water [2].

#### 4. Conclusions

Water and methanol mobility in Nafion and SPTES membranes equilibrated in 2 M MeOH were studied by PGSE–NMR diffusion techniques. The new membranes exhibit significantly higher water diffusion than Nafion, especially for temperatures above 80 °C. Diffusivity remains high even beyond 140 °C, providing evidence of water being well-retained at higher temperatures. We have also defined a selectivity criterion  $D(\text{OH})/D(\text{CH}_3)$  and SPTES exhibits a higher one than Nafion.

High-pressure NMR measurements of the water self-diffusion coefficient in SPTES60 and SPTES50 were conducted in the non-uniform region (fringe) of a superconducting magnet. Activation volumes associated with water mobility have been obtained at several different water contents. The largest activation volume (8.4 cm<sup>3</sup>/mol) is found at the lower water content (20%) of SPTES60 membrane. As the water content increases,  $\Delta v$  decreases rapidly and only gradually thereafter. This indicates that the transport mechanism in low-water content films is controlled to an extent by segmental motions of the polymer. At higher water content, the  $\Delta v$  values are comparatively small, suggesting that the transport mechanism in high-water content membranes is dominated by bulk water. These results, which are in good agreement with the previous studies of spin-lattice relaxation, diffusion and electrical conductivity of Nafion, illustrate how the pressure dependence of self-diffusion coefficients can be a useful tool in characterizing molecular motion for new fuel cell membranes.

#### Acknowledgments

This work was supported by the US Air Force Office of Scientific Research, and Wright Patterson Air Force Base,

and an RCMI Infrastructure grant from the National Institutes of Health.

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