

## Nmr Investigation Of Highly Sulfonated Polyarylenethioethersulfones For Fuel Cell Applications

J.R.P. Jayakody<sup>1</sup>, Ameesh. Khalfan<sup>1</sup>,  
Steve G. Greenbaum<sup>1</sup>, Thuy D. Dang<sup>2</sup>, Robert Mantz<sup>2</sup>,  
Zongwu Bai<sup>3</sup>

<sup>1</sup>Hunter College of CUNY, New York, NY 10021 USA

<sup>2</sup>AFRL/MLB, 2941 Hobson Way, Wright-Patterson Air Force Base, OH 45433 USA

<sup>3</sup>University of Dayton Research Institute, 300 College Park, Dayton, OH 45469 USA

High performance sulfonated polyaryleneether, polyaryleneether sulfone, and polyarylenethioether polymers have been described in the literature from the viewpoint of their exceptional thermal stability, good mechanical properties, and proton conductivity[1, 2, 3]. The development of new high performance polymer electrolyte membranes has also been necessitated by the fact that commercial Nafion membranes do not meet all of the requirements in fuel cell applications. Our approach to the development of new high performance polymer electrolyte membrane materials is to utilize an all-aromatic polymer backbone along with a high sulfonic acid content that enhances water retention and can consequently allow elevated temperature operation. Furthermore, 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. High molecular weight sulfonated polyarylenethioethersulfone polymers and copolymers have substantial mechanical, thermal and chemical stabilities, form tough films, and exhibit high proton conductivities. A typical polymer structure is shown on the right. The endcapped sulfonated polyarylenethioether sulfone polymers and copolymers maintained a high conductivity, and exhibited enhanced water retention. This presentation describes the characterization of proton and water transport in films of sulfonated polyarylenethioethersulfone polymers and copolymers with and without an endcapping group.

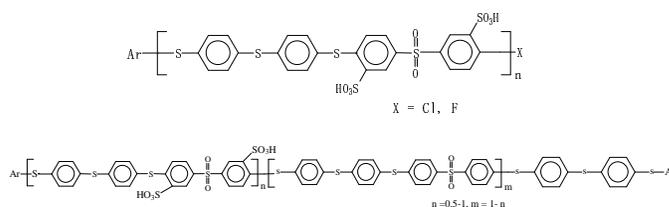
Because proton conductivity is strongly correlated with water mobility in sulfonated polymers, we have determined proton self-diffusion coefficients in these materials by using the pulsed field gradient nuclear magnetic resonance (PFGNMR) technique over a range of temperatures. Several compositions have been studied as a function of water uptake. The data shown here refer to a sulfonated polyarylenethioethersulfone copolymer (SP50/50). The films were dried over P<sub>2</sub>O<sub>5</sub> and then exposed to water vapor at 100% relative humidity for variable times, and water uptake was calculated by weighing the samples before and after water exposure. Proton NMR measurements were conducted at 300 MHz, and self-diffusion coefficients were determined by the PFGNMR technique. The <sup>1</sup>H NMR signal is overwhelmingly dominated by water protons in these materials.

Several <sup>1</sup>H NMR spectra for films with different water contents and their corresponding proton self-diffusion coefficients are displayed in Fig. 1, and a clear (and expected) correlation between water diffusion and water content is observed. Figure 2 shows the temperature

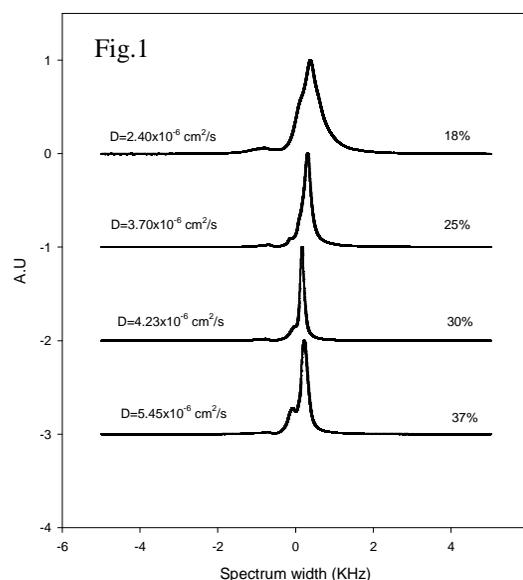
dependence of the <sup>1</sup>H self-diffusion for several different water contents. The significant increase in diffusion of the highest water-content film (30%) suggests that water is reasonably well retained at elevated temperature. These results will be correlated with proton conductivity measurements.

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<sup>1</sup>H NMR spectra of PEM (SP50/50) Vs water contents at RT



<sup>1</sup>H diffusion of PEM (SP50/50) + different water contents Vs temperature

