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

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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_{CH3}), 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^3/mol as the water content decreased from 55 to 20%. This behavior is qualitatively similar to previously reported results for Nafion-117.

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 perflurosulfornated 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 (~65 °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 °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 (~4 mm × 10 mm) rectangular strips, dried in a vacuum oven at 50 °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% H_2O_2 solution and then 5% H_2SO_4 solution, rinsed on deionized wtrer, and then dried over P_2O_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) × 100%. For NMR measurements, samples were packed into 5 mm(o.d.) × 20 mm NMR tubes and flame-sealed under ambient atmosphere. The temperature range investigated were 20–140 °C, with equilibration times of 20–25 min between each temperature change.

NMR measurements were performed on a Chemagnetics CMX-300 spectrometer with ^{1}H operating frequency of 301.02 MHz. Spectra were obtained by transforming the resulting free-induction decay (FID) of single $\pi/2$ (13 μs) 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 ($\pi/2$–τ–π) and the simultaneous application of square-shaped magnetic gradients of magnitude g and duration δ. 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 γ, D and Δ 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, δ and Δ 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 ~5%.

For the high pressure NMR measurements samples were first dried in a vacuum oven at 50 °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 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 mm × 5 mm × 1.5 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.