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PULSE FIELD GRADIENT NMR INVESTIGATION OF WATER DIFFUSION IN PROTON AND ANION EXCHANGE MEMBRANES

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Introduction

The environmental impact of fossil fuel energy production continues to drive the search and development of cleaner more efficient methods of generating energy. The emerging technology of fuel cells for use in vehicle applications and local power production is one example of ongoing efforts. Proton exchange membrane (also called "polymer electrolyte membranes") (PEM) fuel cells continue to be a promising candidate for such energy applications.[1] PEMs and the related anion exchange membranes (AEMs) are also used in water treatment and electrolysis and continue to see active development. Ultimately the conductivity and transport performance of these membranes is a function of both the polymer morphology and mobility of the water within the membrane. For example, it has been shown that the observed proton conductivity is directly proportional to the water self diffusion rate in many of the PEM membranes studies to date, supporting the argument that a vehicular conductivity mechanism is dominant.[2, 3]

The role of water within PEM and AEM systems has been probed by a variety of different techniques including X-ray, neutron scattering and NMR spectroscopy. NMR techniques including ^{1}H and ^{23}Na NMR, along with ^{1}H NMR microscopy have been used to characterize the structure, morphology, and transport properties of these membranes as well as the water distribution in active fuel cells.[4-7] Pulse field gradient (PFG) NMR has become one of the more useful tools for measuring the transport properties of water and other small molecules within polymer membranes, including a variety of different PEM systems.[2, 8]

As a larger research effort into the development of PEM and AEM systems we have used PFG ^{1}H NMR to measure the effective self diffusion rate (D_{eff}) of water for different systems. In this preprint, we report a recent observation of changes in the local water environment and diffusion properties with long term storage of membranes.

Experimental

NMR Spectroscopy. All NMR experiments were performed on a Bruker Avance600 operating at 600.1 MHz for ^{1}H with a water-cooled 5mm DIFF30 diffusion probe capable of gradient of up to 1250 G/cm at 25 °C. The diffusion of different proton environments was measured using the pulsed field gradient stimulated echo (PFG STE) sequence shown in **Figure 1**. For the STE diffusion experiment, the decay of the signal intensity, S(T+2τ), is given by:

$$S(T+2\tau)=\frac{S_0}{2}\exp\left(-2\tau/T_2-\mathrm{T}/T_1\right)\exp\left[-D_{\text{eff}}\gamma^2 g^2\delta^2\left(\Delta-\delta/3\right)\right] \quad (1)$$

where S_0 is the initial signal intensity, T and τ are inter-pulse spacings, T_1 is the spin-lattice relaxation time, T_2 is the spin-spin relaxation time, D_{eff} is the effective diffusion constant ($\text{m}^2\ \text{s}^{-1}$), γ is the gyromagnetic ratio of the observed nuclei, *g* is the gradient strength, δ is the length of the gradient pulse, and Δ is the diffusion time. The effective diffusion constant (D_{eff}) was obtained by fitting the experimental data to equation (1) for select chemical shift regions (see text) where a single exponential decay was observed. If the signal intensity for different spectral regions were combined during analysis then multi-exponential decay was observed. The gradient strength was varied in 16 step intervals, with the maximum strength chosen to produce an overall signal reduction of > 90%. For Δ = 7.5 ms, and δ = 1 ms, this corresponded to a maximum gradient strength of ~381 G/cm given the observed D_{eff}.

Membrane Preparation. The sulfonated Diels-Alder (DA) membranes were prepared as described.[9] Additional details about the membranes and water diffusion rates at different relative humidity (RH) levels have been previously reported.[3] The Nafion and DA membranes were soaked at room temperature in DI water for at least seven days before initial testing (100 %RH). The membrane samples describe in this preprint where equilibrated in a 98% RH humidity chamber for 6 weeks, then quickly placed in the bottom of a 5 mm NMR tube and flame sealed. A small cotton plug saturated with water was placed in top of the NMR tube (outside of the detection zone) prior to sealing to help prevent subsequent dehydration of the sample. PFG NMR studies of these sealed samples were performed (referred to as initial), and then the sealed NMR tubes were allowed to sit for 22 months at room temperature followed by additional PFG NMR analysis. The integrity of the seal following this aging was inspected and also confirmed by the continued presence of visible water in the upper saturated cotton plug.

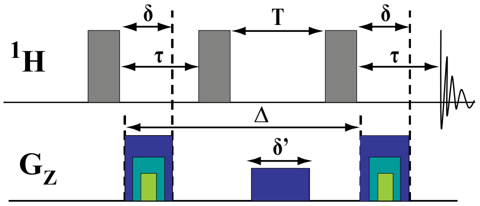

Figure 1: The ^{1}H STE PFG NMR pulse sequence.

Results and Discussion

Water Environments in Aged Nafion and Sulfonated DA PEMs. The ^{1}H NMR spectra of the Nafion and DA PEM membrane (ion exchange capacity = 2.2 mequiv/g) are shown in **Figure 2a** and **2b**, respectively. The NMR spectra for the membranes following initial equilibration at 98% RH are shown in black, while the NMR of the same membranes following 22 months of aging are shown in red. It should be that these ^{1}H NMR spectra are actually slices from the low gradient value (G_z = 5 G/cm) PFG diffusion experiment for a Δ = 50 ms diffusion time. Additional variations in the NMR spectra with Δ are discussed below.

For Nafion the ^{1}H NMR spectral changes over 22 months are relatively small. A single resonance at δ = 5.8 ppm (FWHM = 300 Hz) is observed following the initial 98% RH equilibration (~36 wt% H_2O). Following 22 months of aging this ^{1}H NMR resonance become slightly asymmetric and can be described by two ^{1}H environments of almost equal concentration at δ = 5.8 ppm (FWHM = 200 Hz) and a broader resonance at δ = 6.3 ppm (FWHM = 710 Hz). A minor resonance (2%) was also observed at δ = 7.2 ppm. These major ^{1}H resonances are assigned to water protons associated with the sulfonic acid groups in hydrogen bonded clusters. For dried Nafion membranes this proton environment is observed at even higher δ values due to increasing hydrogen bond strength.[4] The observation of a δ ranging from 5.8 to 6.3 ppm shows that at 98% RH the water concentration is higher within these hydrogen bonded cluster domains than in the dry state. Using ^{1}H PFG NMR experiments, the D_{eff} of the Nafion membrane-associated water were measured as a function of inter-pulse delay Δ. The small variation in D_{eff} with Δ is very small and indicates that there is almost no tortuosity in the Nafion diffusion pathway, consistent with previous results.[4] For the initial 98% RH equilibrated membrane $D_{\text{eff}} = 8.2 \times 10^{-10}$ m^2/s (Δ = 50 ms) decreasing to 7.0×10^{-10} m^2/s following 22 months of aging. The diffusion rates for the overlapping broad and narrow water environments in the 22 month Nafion sample were not resolved leading to the combined D_{eff} reported.

In contrast the ^{1}H NMR spectra for the sulfonated DA membrane in **Figure 2b** shows dramatic changes. For the initial 98% RH equilibrated sample (~137 wt% water) many different overlapping proton environments are observed, including a series of broad resonances between δ = 13 ppm and δ = 8.5 ppm (48 % of the total intensity) assigned to waters within the hydrogen bonded clusters around the sulfonic acid groups of the DA membrane. In addition narrower overlapping resonances between δ = 7.8 and 7.5 ppm (52 % total proton intensity) were assigned to waters in weaker hydrogen bonded cluster environments. The range of chemical shifts shows that a wide distribution of hydrogen bonded cluster domain sizes exist within the DA membrane. Following 22 months of aging these overlapping water environments become more distinct and can be grouped into 5 distinct regions as shown in **Figure 3**. **Region I** (δ = 15.5 to 8.5) and **region II** (δ = 8.5 to 6.5 ppm) again result from hydrogen bonded clusters around the sulfonic acid groups as described above. **Region III** (δ = 6.5 to 5.0 ppm) is assigned to bulk or interface water species that are in intermediate exchange within the membrane. The exchange rate of the **III** water species with environments **I** and **II** must be slow on the NMR time scale since a distinct non-average resonance was observed. The variation of intensity for these different spectral regions as a function of diffusion time Δ (**Figure 3**) also provides insight in the assignment of **III** revealing a very short T_1 relaxation (on the same order of the Δ = 50 ms delay) consistent with an intermediate exchange process. The water environment for **region IV** is assigned to adsorbed surface water and has a $D_{\mathrm{eff}} \sim 2.1 \times 10^{-10}$ m^2/s very similar to that expected for bulk water. The protons for **region V** show almost not decay during the PFG experiments arguing a $D_{\mathrm{eff}} \ll 10^{-12}$ m^2/s based on our maximum PFG gradient strength capabilities, and have not been assigned.

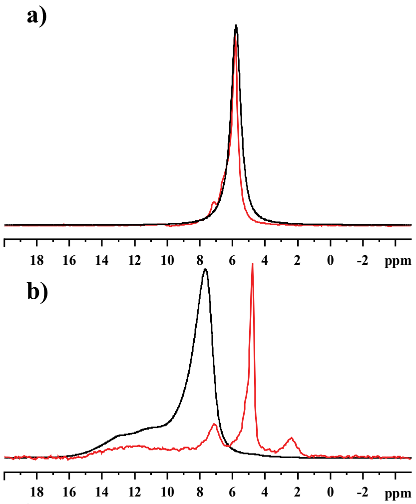

Figure 2: The ^{1}H NMR spectra for a) Nafion and b) DA (IEC = 2.2) membranes initially equilibrated at 98% RH (black) and following 22 months of aging (red).

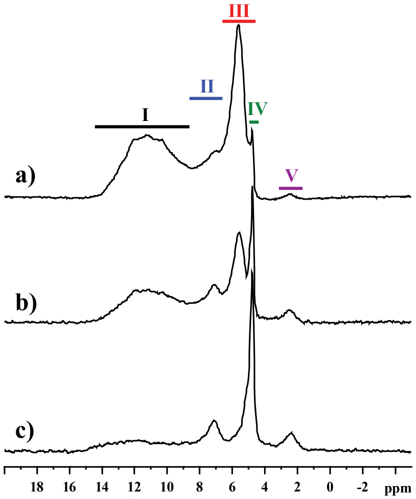

Figure 3: The variation of the ^{1}H PFG NMR spectra for the IEC = 2.2 DA membrane as a function of diffusion time a) Δ = 7.5 ms, b) Δ = 25 ms and c) Δ = 50 ms.

Figure 4 shows the changes in D_{eff} with Δ for spectral regions **I**, **II** and **III**. There is a ~2 fold decrease in D_{eff} between Δ = 5 ms and 50 ms, revealing a minor tortuosity for the diffusion process within these membranes. The similar slopes of the Δ dependence argue that the diffusion barriers are nearly equivalent for these three water environments. The rapid signal loss due to relaxation for **region III** produces a larger error D_{eff}, and did not allow for diffusion measurements beyond Δ = 50 ms.

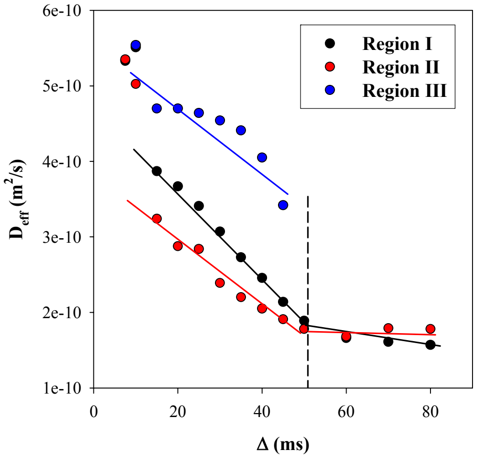

Figure 4: The variation of D_{eff} as a function of Δ for **regions I-III** in the 22 month aged DA (IEC = 2.2) membrane.

Of special interest in **Figure 4** is the change in the Δ dependence for **region I** and **II** at $\Delta \sim 50$ ms suggesting a change in the diffusion barrier length scale. The length probed by these diffusion measurements is given by

$$l_{Diff} = \sqrt{\left\langle z^2(\Delta)\right\rangle} = \sqrt{2D\Delta} \qquad (2)$$

such that for Δ = 50 ms and $D_{\mathrm{eff}} \sim 2 \times 10^{-10}$ m^2/s, the change in slope corresponds to a barrier length of 4.5 µm. It may also be possible that this Δ variation is related to the loss of exchange contributions from the **Region III** water magnetization as it vanishes due to relaxation on the same time scale.

Conclusions

This ^{1}H PFG NMR investigation demonstrates the wealth of information about water environments that can be obtained. In contrast to Nafion, aging of the sulfonated DA membranes has a very pronounced impact on the water environments. The different water environments within the aged DA membrane all show different diffusion rates, but have very levels of tortuosity.

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