Influence of Hot Pressing on the Pore Structure of Nafion Electrolyte Membrane Investigated by ^{1}H NMR

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The influence of hot pressing on the pore structures of Nafion membranes was investigated by observing the Nafion before and after hot pressing with ^{1}H nuclear magnetic resonance (NMR) spectroscopy. The freezing point depression and chemical shift data of water in the Nafion indicated the presence of two different pore size ranges in Nafion. Hot pressing mainly reduced the sizes and number of the big pores. The reduction of water uptake and proton conductivity after hot pressing was explained by this variation of pore size and number. We demonstrated the potential application of chemical shift data and NMR cryoporometry experiments to measure the relative pore sizes, on a nano scale, and numbers.

Key Words: NMR spectroscopy, Nafion, Hot pressing, Pore size, Cryoporometry

Introduction

Nafion, one of the best-known, proton-conducting, solid electrolytes for direct methanol fuel cells and polymer electrolyte membrane (PEM) fuel cells, consists of fluorinated polyethylene backbones and side chains ending with sulfonyl groups.[1] Hydrophilic sulfonyl groups form ionic pores while fluorinated backbones form hydrophobic phases.[1] The ionic pores are spheres of 1.5 nm size in the dry state but expand to bigger pores of ~ 4 nm size and become connected with ~ 1 nm-sized channels in the fully hydrated state.[1] The structure of Nafion has been reported to be a function of not only hydration amount but also treating temperature.[1] Typically, during fuel cell assembly, a cathode, PEM, and anode are hot pressed to increase the electric contact among them, although proton conductivities were reported to be reduced after hot pressing.[2] Although the molecular structure and/or porosity of the PEM can be affected by the hot pressing process, such effects have not yet been adequately studied.

Meanwhile the pore sizes in inorganic[3,4] and polymer materials[5,6] have been determined by nuclear magnetic resonance (NMR) crypoporometry in which the signals of unfrozen liquid samples used to fill the nano-size pores were measured at each temperature. Since liquid samples produce sharp peaks but solid materials much broader peaks in NMR spectra, liquid signals can be selectively measured. Liquid signals are reduced during the freezing, solidifying process. Therefore, a plot of the NMR signal versus temperature reveals the freezing points depressed from the bulk freezing point. The freezing points of the liquid in nano pores are depressed more for smaller pores obeying Gibbs-Thomson equation.[3] The pros and cons of many pore measurement methods have been discussed.[6] One of the big advantages of cryoporometry-type measurements is the detection of pore sizes in real operational conditions.

In this work, we report the influence of hot pressing on the pore structures of Nafion membranes by observing the Nafion before and after hot pressing with ^{1}H NMR. We interpreted the NMR spectra using both the peak area and the chemical shift of water in the Nafion, by taking the NMR spectra at a high magnetic field of 11.7 T which is higher than for a typical NMR cryoporometry.

Experimental

Pretreated Nafion (PTN) was prepared by boiling Nafion 117, purchased from Ion power Inc. (U. S. A.) which is the designated DuPont distributor, step by step for one hour in each of the following solutions: 3% H_2O_2, pure water, 0.5 M H_2SO_4, and pure water again. Water was purified with a μ-Pure water system at 12.5 MΩ (Pure Power, Korea) prior to use. Hot pressed Nafion (HPN-fresh) was prepared by pressing PTN at 135 ^oC for 3 minutes under a pressure of 100 kg/cm^2. HPN-Y was prepared by storing HPN-fresh in distilled water for Y days.

The proton NMR spectra of the Nafion samples in 5 mm NMR tubes were acquired with a UNITY INOVA 500 NMR spectrometer (Varian Co., U.S.A.). Nafion films were cut to dimensions of 25 mm × 25 mm after pretreatment and any bulk water on the Nafion surface was wiped off before placing the films in the NMR tubes. To place the Nafion films at the same position in the NMR tubes as quickly as possible, the films were wrapped with Teflon film prior to being pushed into the tube. The smooth Teflon film reduced the surface friction between the wet Nafion and the Pyrex inner surface of the NMR tubes. To acquire a spectrum, an excitation pulse of 5.5 μs (33° flip angle), spectral width of 100 kHz, pulse repetition delay of 10 s, and 8 scans were employed. Prior to signal acquisition, shimming was optimized with external D_2O and chemical shifts were calibrated externally with the methyl proton peak of a 0.1% solution of 2,2-dimethyl-2-silapentane-5-sulfonic acid in D_2O. The temperature was varied from 24 to -95 ^oC and a spectrum was obtained more than 20 minutes after each target temperature was reached to ensure temperature equilibrium. Since the NMR peak areas measured to determine the freezing points and melting points of water in our sample were confirmed to be the same without hysteresis, only the melting points were measured by ^{1}H NMR.

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Results and Discussion

Representative ^{1}H NMR spectra of water in Nafion are presented in Figure 1. Not only the peak areas and widths, but also the chemical shifts were affected by the temperature. The peak areas of the same number of nuclei exhibited an inverse linear relationship with temperature according to Curie's law.[3] Hence, the proton peak areas of the Nafion samples were calibrated to be proportional to the number of water protons in the samples. The slope of Curie's law was taken from the proton peak area data of the HPN-fresh samples in the temperature range of 24 ~ -50 °C, where no water was frozen. After the calibration, the peak areas of the water proton signal were plotted versus temperature as shown in Figure 2. The PTN and all water swollen HPN (HPN-1, HPN-3, HPN-7) samples showed at least two different depressed freezing point regions as marked with arrows in Figure 2, indicating the presence of two different size groups of pores in the individual samples. In concept, the freezing points are the temperatures where the second derivatives of the temperature-(peak area) curves are zero, but in practice, the curves are fitted to the following equation to obtain the depressed freezing points.[3]

$$I(X) = \sum_{i=1}^{N} \frac{I_{oi}}{\sqrt{\pi}} \int_{-\infty}^{(X-X_{ci})/(\sqrt{2}\Delta i)} \exp(-u^2)$$

where I_{0i}, X_{ci}, Δ_i, and u represent the peak area, the inverse freezing temperature ($X_{ci} = 1000/T_{ci}$), the width of the temperature distribution curve of phase i, an integration variable, respectively.[3] The freezing points, obtained from the fitted curves, were -8.$_7$ °C and -90 °C for the PTN samples while -10.$_2$ °C and -90 °C for the water swollen HPN samples. The absolute size and size distribution of pores can be measured from the depressed freezing points by employing the equation of $\Delta T(R) = K/R$ where $\Delta T(R)$, K and R represent the difference of the freezing temperature of bulk liquid and that of liquid in the pores of radius R, a constant depending on the physical properties of liquid confined in the pores, and the radius of pores, respectively.[6] If the value of K is determined accurately, the absolute size of pores can be measured. However, generally the value of K has been known to be in a wide range. For example, if water is taken as liquid to measure the size of pores, K is in the range of 41 - 73 K·nm.[6] Since our primary interest was in detecting the size changes of the pores in Nafion by hot pressing rather than measuring the absolute sizes of pores, the absolute sizes of pores were not calculated.

Quick water evaporation during wrapping with Teflon resulted in irreproducibility of the peak areas at the high ends of the temperature range, but not at the low temperatures. The HPN-3 sample was used as an example of a sample with less water than required to fill the pores accurately. This water level effect was checked by examining samples with more water added than the accurate amount and then removing the water sequentially as demonstrated in Figure 3. A bulk water peak at 4.8 ppm that appeared separately from the water peak in Nafion and the latter peak was shifted to higher chemical shifts in the case of insufficient water to fill the pores.

The amounts of water in the HPN-7 sample at the high end of the temperature range in Figure 2, presented as $(3.4 \pm 0.1) \times 10^6$ in arbitrary unit of calibrated peak area, was observed to be the maximum amounts of water without bulk water peaks within an experimental error range. The similar peak areas of the HPN-1 and HPN-7 samples at the high end of the temperature range in Figure 2 indicated that 1-day water immersion of HPN-fresh was enough for saturation. Thus, the maximum water amount in the PTN samples without the bulk water peak, $(5.2 \pm 0.2) \times 10^6$, was about 150% of that in the swollen HPN, $(3.4 \pm 0.1) \times 10^6$. The unfrozen water amount of PTN higher than that of the swollen HPN at all the temperature range in Figure 2, seems to indicate that PTN had more water in both the small and big pores than the swollen HPN. However, the amount of water in the small pores, $(2.0 \pm 0.1) \times 10^6$ for PTN and $(2.4 \pm 0.1) \times 10^6$ for swollen HPN, was simply proportional to the film thickness: 230 ± 5 μm for PTN and 190 ± 3 μm for swollen HPN. In our NMR experiments, the NMR signal was proportional to the film thickness in the NMR tubes since the film length was slightly longer than the NMR coil length (here we assume that only the sample inside the coil is detected). However, the water amount in the big pores of swollen HPN, $[(3.4\text{-}2.0) \pm 0.2] \times 10^6$, was only ~ 50%

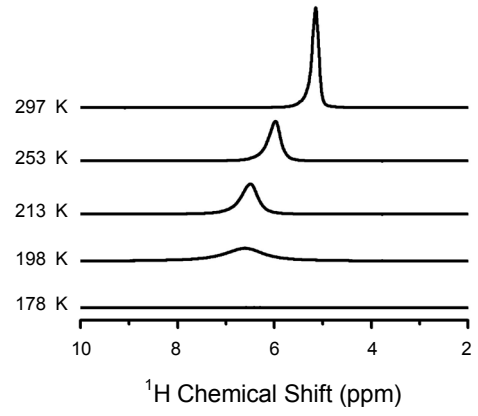


Figure 1. Representative ^{1}H NMR spectra of water in Nafion at various temperatures.

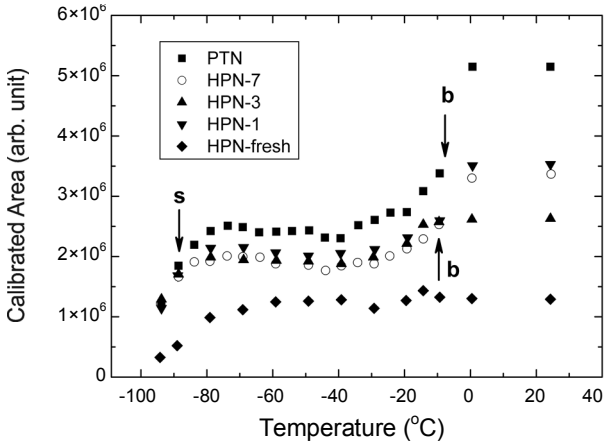


Figure 2. ^{1}H NMR peak areas of each Nafion sample at various temperatures after signal calibration due to Curie's law. Arrows indicate freezing points of water in the big (b) and small (s) pores.

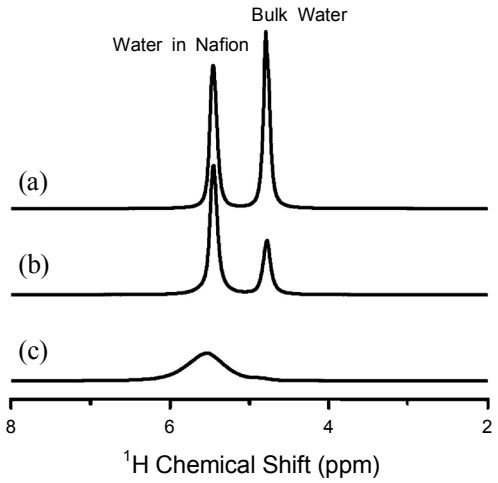


Figure 3. ^{1}H NMR spectra of the HPN-2 sample at room temperature according to the water amount: (a) as prepared following over-saturation with water, (b) after removing some of the bulk water, and (c) after removing all of the bulk water.

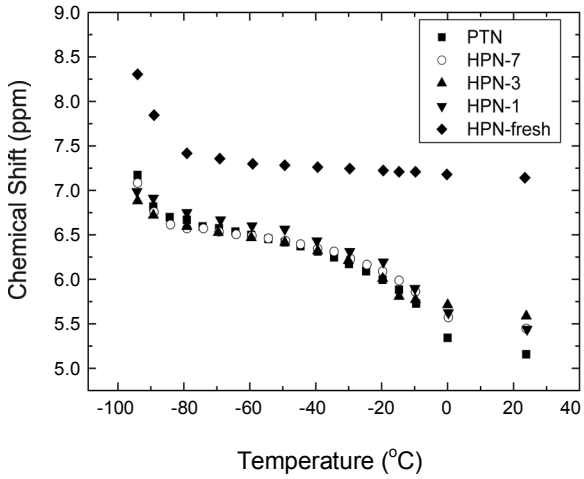


Figure 4. ^{1}H NMR chemical shifts of each Nafion sample at various temperatures.

of that of PTN, $[(5.2\text{-}2.4) \pm 0.2] \times 10^6$, indicating real water reduction of 33 % in swollen HPN compared to PTN even after consideration for the film thickness reduction. Where did this 33 % reduction come from? The pore size reduction of the big pores accounted ~ 10% since the freezing point depression difference was ~ 1 °C corresponding to 10% difference. Then the rest of the reduction should be explained by the reduction of the number of big pores.

In HPN-fresh, where the pores were not saturated with water, the calibrated peak area started to decrease slowly below ~ -60 °C but not sharply. This indicates that the water started to freeze at various temperatures below ~ -60 °C. When the pores were not filled up with water, the water was expected to freeze as in the pores of the same size with the effective thickness or volume of water. Therefore, the data indicated that the water in HPN-fresh was covering the inner surfaces and the majority of the water was in a similar thickness or volume on the surfaces but not necessarily filling up the pores, especially the relatively big ones. Alternatively, it is possible that the pores, especially the big ones, in HPN-fresh were shrunken during the hot pressing.

Figure 4 shows the chemical shift data of water in Nafion pores at various temperatures. The proton chemical shifts of water in Nafion are related with the number of waters per sulfonyl proton, λ.[7] As λ is increased, the chemical shift is reduced. Thus, as observed in Figure 4, increased chemical shifts were expected with increased frozen water amount in each pore, due to the reduced number of water protons able to exchange with the sulfonyl protons. Consequently, the chemical shifts of water in Nafion pores were correlated with pore size, although not linearly, as long as the Nafion sample was water-saturated.

Our data demonstrated that measurements of the chemical shift and peak area of water in pores of Nafion can be used to determine pore sizes when Nafion is saturated with water. Chemical shift measurements take less time than taking peak areas, but cannot provide the absolute pore sizes. In addition, for pores unsaturated with water, the chemical shifts and peak areas would generate inaccurate pore sizes, as shown in HPN-3. Below ~ -35 °C, the chemical shifts of swollen HPN and PTN were the same, indicating the equivalent size of their small pores. On the other hand, at 0 °C and higher temperatures, the chemical shift of PTN was smaller than that of swollen HPN indicating that the big pores of PTN were bigger than those of swollen HPN, which was consistent with the peak area data.

Conclusion

Our data indicated that (1) HPN held less water than PTN, which was attributed to the smaller sizes and number of the big pores, (2) the small pore sizes were similar for PTN and swollen HPN, (3) both the proton peak areas of the unfrozen water and the chemical shifts versus temperature can be used to determine the pore sizes, and (4) the chemical shifts and peak areas can be used complimentarily since the chemical shifts reflected only the pore sizes while the peak areas provided the total amount of water in the pores as well as the pore sizes. We demonstrated that measuring the peak areas and chemical shifts of unfrozen water in Nafion at a high magnetic field can reveal different pore size groups and determine their relative populations in Nafion. High magnetic fields are preferable due to the greater precision of the chemical shift measurements. One drawback of our method is the impossibility of characterizing the pores of Nafion unsaturated with water and comparing the results with water-saturated samples. Hence, we could not determine the extent to which the pore sizes were changed during the swelling of HPN-fresh to make the swollen HPN. Nevertheless, we confirmed that the HPN pore structure did not return to that before hot pressing, even after swelling for 7 days. Our data indicated that hot pressing mainly reduced the sizes and number of the big pores and did not markedly influence the small pores in Nafion. Thus, the reduced water uptake of HPN was attributed to the reduced size and number of the big pores, which

depleted the proton conductivity. The method presented here to measure pore sizes and total pore volumes can easily be extended to other PEMs.

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