Communication

1H nuclear magnetic resonance study of low-temperature water dynamics in a water-soaked perfluorosulfonic acid ionomer Nafion film

Jun Hee Han[a], Kyu Won Lee[b], Cheol Eui Lee[b,*]

[a] *Spin Engineering Physics Team, Korea Basic Science Institute (KBSI), Daejeon 305-806, Republic of Korea*
[b] *Department of Physics, Korea University, Seoul 02841, Republic of Korea*

ABSTRACT

We have employed proton nuclear magnetic resonance (NMR) spectroscopy in order to study the low-temperature water dynamics in a water-soaked perfluorosulfonic acid ionomer Nafion (NR-211) film. According to the recent models, Nafion may comprise water strongly bound to the sulfonic acid group, hydration water, and condensed water species. In this work, three separate NMR peaks from the water species revealing distinct behaviors were identified. A significant portion of the "bound" water remained unfrozen down to 200 K, whereas a slow-to-fast motional limit transition was observed at T_M=220 K from the relaxation measurements.

1. Introduction

Nafion is a perfluorosulfonated random copolymer with a tetra-fluoroethylene backbone and perfluoroalkyl ether side chains terminated by sulfonic acid groups. The Nafion ionomer has a selective permeability of cations that is valuable for fuel cells. The high proton conductivity and excellent chemical stability of Nafion are highly desirable for use as a proton-conducting membrane in a polymer electrolyte fuel cell [1,2]. Nafion's high proton conductivity is due to the presence of hydrophilic, sulfonate-rich domains within the membrane [3–6]. The presence of water in the proton exchange membranes (PEMs) is essential for achieving high proton conduction [7–10]. The water molecules in wide enough channels of Nafion may undergo diffusion, while water in the small-diameter pores may not freeze down to low temperatures. Below the ice phase transition temperature of water (273 K), some fraction of water molecules in the Nafion membrane may exist as liquid while others may form ice (solid) [11]. The unfreezing nature of water in PEMs may be vital for viable automotive applications as fuel cells must be able to operate in cold climates [12]. Water freezing and low-temperature properties of Nafion have received relatively little attention in the literature. However, processes occurring in the porous electrodes at sub-freezing temperatures need to be well understood for improved cold start-up reliability and performance of PEM fuel cells.

The nature of water in Nafion has been extensively studied by various means as high proton conduction is made possible by water in the membranes [7–10,4–6]. Recent studies have revealed the presence of water molecules strongly bound to the sulfonic acid group, and

hydrated water species and condensed water surrounding them [13,14]. Transportation of water in PEMs plays an essential role for optimal operation of fuel cells [15–19]. Hopping transportation of protons is facilitated by water molecules in the hydrophilic nanochannels [20,21,14,3]. In this work, proton nuclear magnetic resonance (NMR) was employed to study the low-temperature dynamics of the distinct water species in water-soaked Nafion [4,11,13]. It is quite noteworthy that the distinct water species have been separately detected in this work, allowing us a unique opportunity to study their interrelation.

2. Experimental

Nafion NR-211 films with a thickness of 25 μm were purchased from Dupont, and soaked in distilled water for two weeks. Proton NMR of the Nafion film sample was carried out at 400 MHz by using a Varian Unity Inova spectrometer with a magic-angle spinning (MAS) rate of 10 kHz between 200 K and room temperature. The laboratory-frame (T_1) and rotating-frame spin-lattice relaxation time ($T_{1\rho}$) measurements were also made in the same temperature range, the frequency of the rotating frame being $\omega_1/2\pi = 93$ kHz.

3. Results and discussion

Fig. 1 shows the temperature-evolution of the 1H NMR spectra of the Nafion sample. While only a broad peak which may be attributed to the "bound" water sites was observed at around 7 ppm at low temperatures, additional peaks emerged as the temperature was

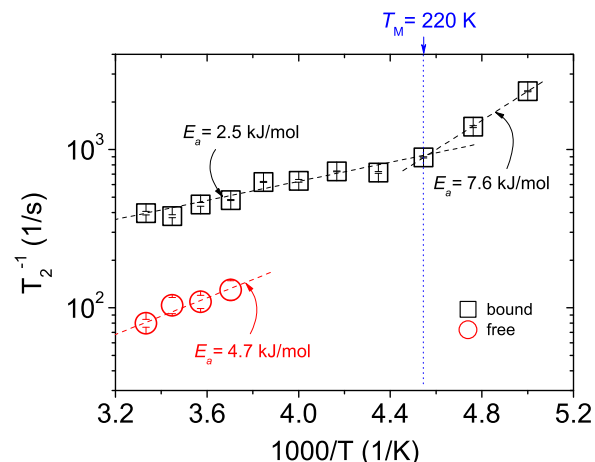* Corresponding author.
E-mail address: rscel@korea.ac.kr (C.E. Lee).
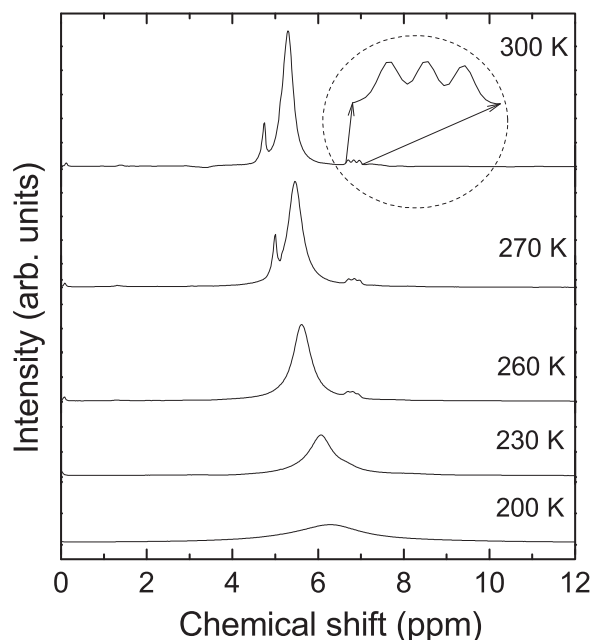
Fig. 1. ^{1}H NMR spectra of the water-soaked Nafion at various temperatures exhibiting distinct peaks of the water species.
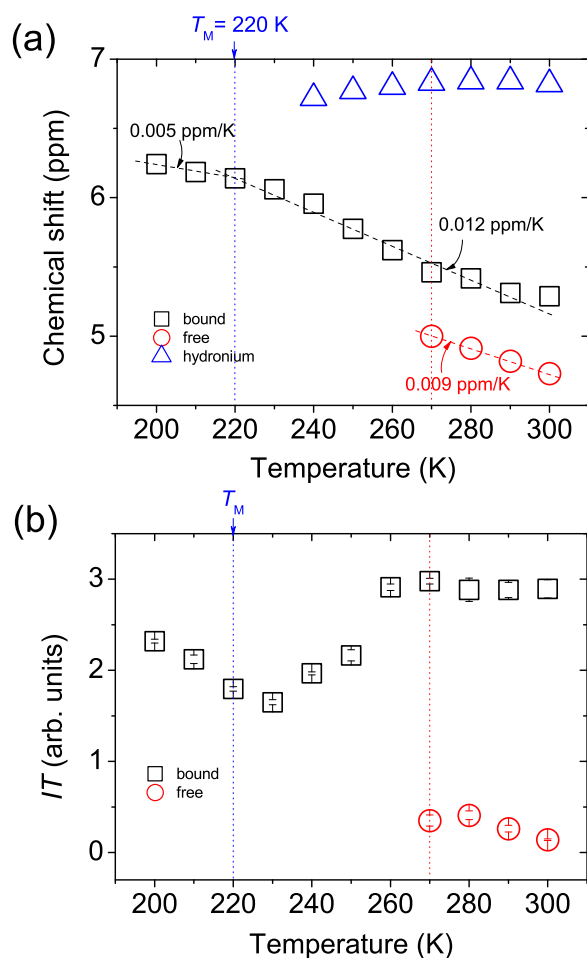
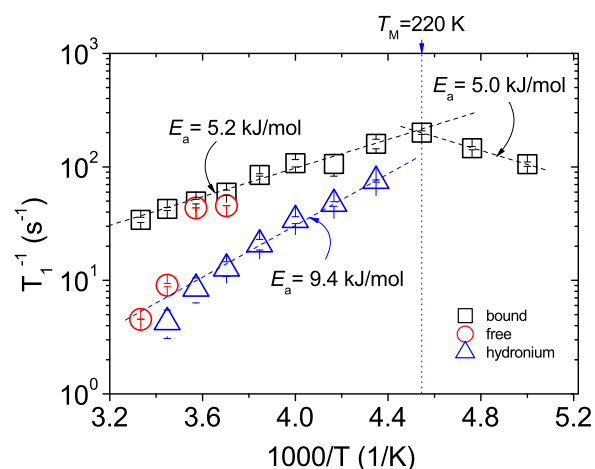**Fig. 2.** Temperature-dependent chemical shifts of the water species of the ^{1}H NMR spectra (a) and the proton density (IT) (b) of the water-soaked Nafion.
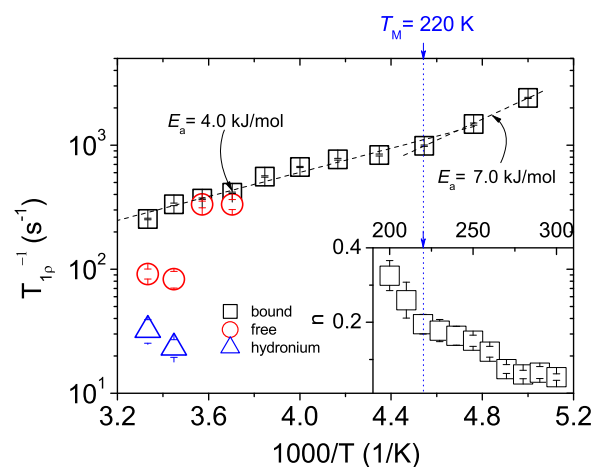

Fig. 3. ^{1}H NMR spin–spin relaxation rates ($1/T_2$) derived from the water linewidths as a function of temperature.

Fig. 4. ^{1}H NMR laboratory-frame spin–lattice relaxation rates ($1/T_1$) of the distinct water species as a function of temperature.

Fig. 5. ^{1}H NMR rotating-frame spin-lattice relaxation rates ($1/T_{1\rho}$) of the distinct water species as a function of temperature. Inset: n value of the stretched-exponential fitting for the bound water as a function of temperature.

increased. A peculiar triplet peak emerged near 240 K, which may be related to the hydronium ions (H_3O^+) [5,22]. At a higher temperature of 270 K a narrow peak emerged from the broad peak, which may be ascribed to the "free" (condensed) water molecules melted to a liquid state [4].

Fig. 2(a) shows the temperature-dependent chemical shifts of the water species in the ^{1}H NMR spectra of the Nafion sample. The bound water underwent no change in the slope at the water-freezing temperature, but exhibited a change in the temperature-gradient at

T_M=220 K from 0.005 ppm/K to 0.012 ppm/K, indicating a change in the local environment of the water molecules. In comparison, the condensed water showed a temperature-gradient of 0.009 ppm/K. The triplet peak showed a slight change in the slope at the water-freezing temperature. Fig. 2(b) shows the NMR intensity multiplied by temperature (IT), which is proportional to the proton density [13], as a function of temperature. It is seen that emergence of the triplet and free water peaks is accompanied by changes in the proton density of the bound water.

Fig. 3 shows the temperature-dependent ^{1}H NMR spin–spin relaxation rates ($1/T_2$) obtained from the full-width at half-maximum linewidth $\Delta\nu$ of the bound water, which are related as $\Delta\nu = 1/(\pi T_2)$. A change in the slope of the $1/T_2$ of the bound water is noticed at T_M, and activation energies of 7.6 kJ/mol below T_M and 2.5 kJ/mol above T_M were obtained from the Arrhenius fits (Fig. 3) [12]. On the other hand, an activation energy of 4.7 kJ/mol was obtained for the condensed water.

The ^{1}H NMR laboratory-frame spin–lattice relaxation of the bound water peak showed a single-exponential decay pattern. The spin–lattice relaxation rate ($1/T_1$) of the bound water in Fig. 4 exhibits motional transition at T_M from a slow-motion limit to a fast-motion limit of the BPP (Bloembergen–Purcell–Pound)-type of relaxation. The activation energy E_a of 12 kJ/mol obtained from the Arrhenius fits is 5.0 kJ/mol below T_M and 5.2 kJ/mol above T_M (Fig. 4) [23]. The temperature-dependent spin–lattice relaxation rate of the triplet peak in Fig. 4 was also well fitted by an Arrhenius relation, giving an activation energy of 9.4 kJ/mol.

The ^{1}H NMR rotating-frame spin–lattice relaxation of the water species was well fitted by a stretched-exponential form (see inset of Fig. 5),

$$M(t) = M(0)\exp[-(t/T_{1\rho})^{1-n}], \tag{1}$$

where $M(t)$ is the time-dependent magnetization, and the exponent n reflects the degree of random distribution of the correlation times. The rotating-frame spin–lattice relaxation rate ($1/T_{1\rho}$) of the bound water in Fig. 5 shows a slow-motion limit at all temperatures, displaying a change in the slope at T_M. Activation energies of 7.0 kJ/mol below T_M and 4.0 kJ/mol above T_M were obtained for the bound water from the Arrhenius fits. The n-value decreased with increasing temperature representing more homogeneous environments.

In summary, dynamics of the distinct water species in the proton exchange membrane Nafion NR-211 soaked in distilled water has been studied by means of high-resolution proton nuclear magnetic reso-

nance measurements. The "bound" water mostly remained unfrozen down to 200 K, undergoing a motional transition from a slow-motion limit to a fast-motion limit. Activation energies of the rotational motion for the water species were also obtained from the relaxation measurements both at 400 MHz and at 93 kHz. Besides, a triplet peak apparently representing the hydronium ion (H_3O^+) emerged near 240 K, and the condensed water showed freezing near 270 K.

References

[1] K.A. Mauritz, R.B. Moore, Chem. Rev. 104 (2004) 4535.
[2] D.K. Lee, T. Saito, A.J. Benesi, M.A. Hickner, H.R. Allcock, J. Phys. Chem. B 115 (2011) 776.
[3] K.D. Kreuer, Chem. Mater. 8 (1996) 610.
[4] J.H. Han, K.W. Lee, G.W. Jeon, C.E. Lee, W.K. Park, E.H. Choi, Appl. Phys. Lett. 106 (2015) 023104.
[5] R. Iwamoto, K. Oguro, M. Sato, Y. Iseki, J. Phys. Chem. 106 (2002) 6973.
[6] M. Laporta, M. Pegoraroa, L. Zanderighi, Phys. Chem. Chem. Phys. 1 (1999) 4619.
[7] Q. Zhao, P. Majsztrik, J. Benziger, J. Phys. Chem. B 11 (2011) 2717.
[8] S. Ge, X. Li, B. Yi, I. Hsing, J. Electrochem. Soc. 152 (2005) A1149.
[9] P.W. Majsztrik, M.B. Satterfield, A.B. Bocarsly, J.B. Benziger, J. Membr. Sci. 301 (2007) 93.
[10] T.A. Zawodzinski, C. Derouin, S. Radzinski, R.J. Sherman, V.T. Smith, T.E. Springer, S. Gottesfeld, J. Electrochem. Soc. 140 (1993) 1041.
[11] K. Schmidt-Rohr, Q. Chen, Nat. Mater. 7 (2008) 75.
[12] Y.S. Kim, L. Dong, M.A. Hicker, T.E. Glass, V. Webb, J.E. McGrath, Macromolecules 36 (2003) 6281.
[13] C. Wakai, T. Shimoaka, T. Hasegawa, Phys. Chem. B 8 (2015) 8048.
[14] T. Shimoaka, C. Wakai, T. Sakabe, S. Yamazaki, T. Hasegawa, Phys.Chem.Chem.Phys. 17 (2015) 8843.
[15] D. Rivin, C.E. Kendrick, P.W. Gibson, N.S. Schneider, Polymer 42 (2001) 623.
[16] T. Takamatsu, M. Hashiyama, A. Eisenberg, J. Appl. Polym. Sci. 24 (1979) 2199.
[17] D.R. Morris, X.D. Sun, J. Appl. Polym. Sci. 50 (1993) 1445.
[18] P. Krtil, A. Trojanek, Z. Samec, J. Phys. Chem. B 105 (2001) 7979.
[19] D.J. Burnett, A.R. Garcia, F. Thielmann, J. Power Sources 160 (2006) 426.
[20] W.Y. Hsu, T.D. Gierke, J. Membr. Sci. 13 (1983) 307.
[21] G. Gebel, Polymer 41 (2000) 5829.
[22] J.I. Musher, J. Chem. Phys. 35 (1961) 1989.
[23] R.J. Wittebort, M.G. Usha, D.J. Ruben, D.E. Wemmer, A. Pines, J. Am. Chem. Soc. 110 (1988) 5668.