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Citation: *Applied Physics Letters* **106**, 023104 (2015); doi: 10.1063/1.4905602

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# <sup>1</sup>H nuclear magnetic resonance study of hydrated water dynamics in perfluorosulfonic acid ionomer Nafion

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(Received 18 November 2014; accepted 26 December 2014; published online 12 January 2015)

We have studied the dynamics of hydrated water molecules in the proton exchange membrane of Nafion by means of high-resolution <sup>1</sup>H nuclear magnetic resonance (NMR) measurements. “Bound” and “free” states of hydrated water clusters as well as the exchange protons were identified from the NMR chemical shift measurements, and their activation energies were obtained from the temperature-dependent laboratory- and rotating-frame spin-lattice relaxation measurements. Besides, a peculiar motional transition in the ultralow frequency region was observed at 373 K for the “free” hydrated water from the rotating-frame NMR spin-lattice relaxation time measurements.

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Nafion is a most suitable material for proton exchange membrane fuel cells (PEMFC) and water electrolyzers—the effect of moisture in polymeric systems has been elucidated in previous works.<sup>1–3</sup> It is used as separator and solid electrolyte in electrochemical cells that require membranes transporting cations selectively.<sup>4</sup> The permeation of cations due to the energy difference between the sides of the membrane is very important for fuel cell applications. The selective cation permeability of Nafion has also been vital in the applications,<sup>5</sup> enabling it to be applied to logic circuits.<sup>6</sup> Proton exchange membranes such as Flemion, Aciplex, 3M polymer, Dow polymer, and Hyflon-Ion have also been developed, increasing the selective ion permeability being an important issue.<sup>1</sup>

Ionic hydration is one of the most interesting subjects in materials science.<sup>5</sup> There may be hydrated ions and neutral water molecules in Nafion with sulfonic acid as a counter anion, resulting in coexisting hydrophilic and hydrophobic groups.<sup>7</sup> Ion transport through perfluorosulfonic acid ionomers such as Nafion is controlled by both the microstructure and charge and water distribution. The negative electric environment permits cations to pass through the channels. Various transport models of Nafion have been suggested, such as Gierke’s cluster network model, Gebel’s structural inversion network model, Haubold’s sandwich-like model, Weber’s percolation network model, and Schmidt-Rohr’s parallel long channel model.<sup>8</sup> In the structure of Nafion, the sulfonic acid anion (SO<sub>3</sub><sup>−</sup>) at the end can be detached from the backbone or can be replaced with SO<sub>2</sub>F or SO<sub>3</sub>H. In Nafion, there are water channels comprising hydrogen ions and neutral water. The backbone composed of carbon and fluorine is very similar to that of teflon, being mechanically stable. Nafion has an entangled structure and the motion of the backbone is reptational.

Fast proton exchange takes place in water molecules, giving rise to a <sup>1</sup>H nuclear magnetic resonance (NMR) peak

around 4.5 ppm,<sup>9</sup> the chemical shift of water trapped in a pore being dictated by the size of water clusters and the pressure.<sup>9,10</sup> Water in Nafion can be in various forms, such as free water clusters and loosely or strongly bound water clusters.<sup>11,12</sup> Three distinct <sup>1</sup>H NMR peaks have previously been identified separately in samples treated differently.<sup>13</sup> However, our high-resolution NMR measurements enabled simultaneous observation of all the distinct NMR peaks in Nafion allowing us a unique opportunity to study the dynamics of the bound and free hydrated water, and proton exchange between them by means of the NMR spin-lattice relaxation measurements.<sup>14</sup>

Nafion films of 25-μm thickness, commercial model number NR-211, were purchased from E. I. DuPont de Nemour & Co., Inc.<sup>15</sup> NR-211 is currently a technological standard of non-reinforced membranes with resistant and durable chemical and mechanical properties, sensitively depending on the relative humidity or water content.<sup>15</sup> The perfluorosulfonic ionomer Nafion NR-211 can absorb water up to 10 times its volume.<sup>16</sup> No acid treatment was performed on our sample, and the water content in our Nafion sample was 2.5 wt. % according to the thermal gravimetric analysis (TGA). Water distribution in Nafion depends on the hydration level,<sup>17</sup> and the water content of 2.5 wt. % would indicate isolated tiny pores containing water clusters.<sup>8,18</sup>

The high-resolution proton NMR measurements were carried out in the temperature range 303 K to 403 K, with a magic-angle spinning (MAS) rate of 10 kHz by using a 400-MHz pulsed NMR spectrometer. The <sup>1</sup>H NMR spectra were referenced by using tetramethylsilane. The laboratory-frame spin lattice relaxation time (*T*<sub>1</sub>) measurements were carried out by the inversion-recovery method. The rotating-frame spin-lattice relaxation time (*T*<sub>1ρ</sub>) measurements were made by applying a 90° pulse, immediately followed by a long spin-locking pulse, phase shifted by 90° with respect to the 90° pulse. The 90° pulse width used for *T*<sub>1ρ</sub> was 2.7 μs, the frequency of the rotating frame being ω<sub>1</sub>/2π = 93 kHz.

Figure 1 shows the high-resolution proton NMR spectra measured at room temperature, exhibiting four distinct

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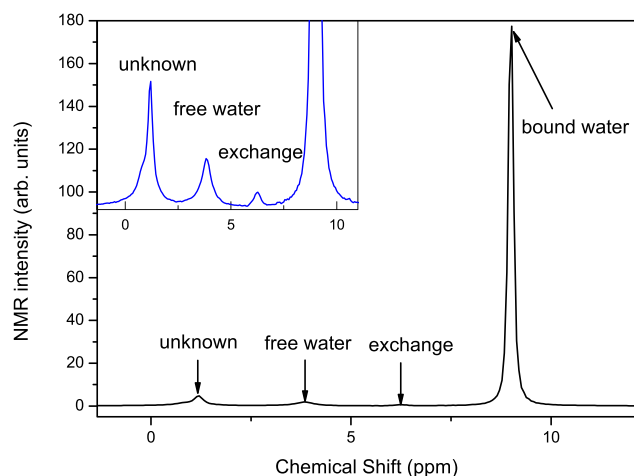
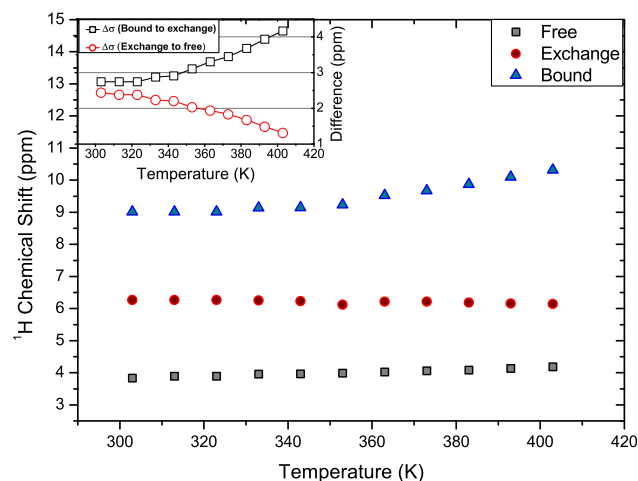


FIG. 1. Proton NMR spectrum of Nafion exhibiting the distinct peaks.

peaks, corresponding to various hydrated water clusters. In contrast to the previous results, all these peaks were simultaneously observed in our sample.<sup>13</sup> A low-field peak and a high-field peak have been attributed to the “bulk” water and the immobile H<sub>2</sub>O molecules attached to sulfonic acid, respectively. Besides, a peak in between has been assigned to the protons undergoing fast proton exchange between the two water species.<sup>13</sup> Accordingly, the major peak at 8.9 ppm in Fig. 1 can be attributed to the water molecules attached at the sulfonic acid (bound water), and a minor peak at 4.1 ppm can be assigned to the “free” hydrated water clusters in the pore. Furthermore, the peak in between at 7 ppm may be assigned to the protons undergoing exchange between the two hydrated water species (“exchange”). An additional peak located at 1 ppm is of an unknown origin. In order to check for the validity of our assignments of the hydrated water species, the temperature dependencies of the chemical shifts of the “bound” and “free” water and “exchange” peaks identified in Fig. 1 are shown in Fig. 2. The inset of Fig. 2 indicates that with the increase in temperature, the environment of the “exchange” site becomes closer to that of the “free” sites as opposed to the case of the “bound” sites, thus

FIG. 2. Temperature-dependent <sup>1</sup>H NMR chemical shifts of the different water species identified in Fig. 1. Inset: temperature-dependent chemical shift differences between the water species.

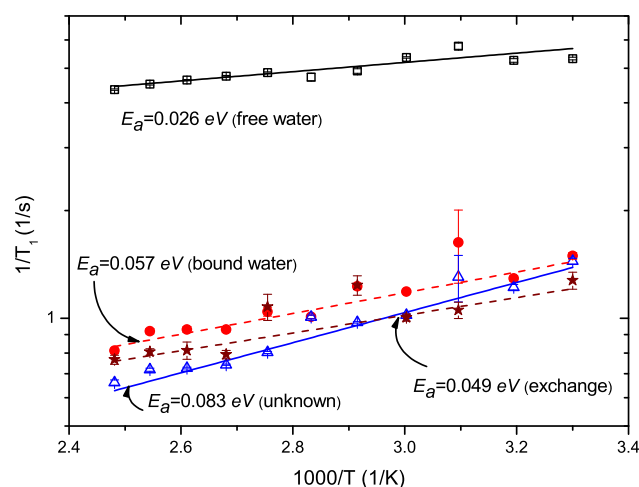
providing evidence that the “small bump” in Fig. 1 is due to exchange.

NMR relaxation method can be very useful for examining the motion of the molecules. Water molecules in Nafion may undergo rotational (reorientation) and translational (hopping, vehicle, and diffusion) motions. While the water molecules at the hydrophilic end of the sulfonic acid will undergo anisotropic rotational motion, different from that in free water, the anisotropy will not be reflected in our NMR spectra obtained with magic angle spinning. The rotational motion of trapped water molecules is quite intriguing.<sup>19</sup> Water clusters in Nafion in this work are trapped in pores and will undergo rotational motions, as in the case of those trapped in a buckyball (C<sub>60</sub>).<sup>20</sup> Figure 3 shows the temperature-dependent laboratory-frame NMR spin-lattice relaxation rates ( $1/T_1$ ) of our Nafion sample, which are expected to be well described by the BPP (Bloembergen-Purcell-Pound)-type relaxation taking into account the effect of tumbling motion of molecules on the local magnetic field disturbance<sup>21,22</sup>

$$T_1^{-1} = \frac{2}{3} \gamma^2 M_2 \left[ \frac{\tau_c}{1 + (\omega\tau_c)^2} + \frac{4\tau_c}{1 + (2\omega\tau_c)^2} \right], \quad (1)$$

$$\tau_c = \tau_0 e^{E_a/kT}, \quad (2)$$

where  $\gamma$ ,  $M_2$ ,  $\omega$ , and  $E_a$  are the proton gyromagnetic ratio, the second moment, the Larmor frequency, and the activation energy, respectively. The data shown in Fig. 3 in fact were well fitted by the Arrhenius law,  $T_1^{-1} \propto e^{E_a/kT}$ , which can be regarded as a fast-motion limit of the BPP-type of relaxation.<sup>21–23</sup> The spin-lattice relaxation rate of the free water peak is much greater than those of the other peaks. The activation energy  $E_a$  obtained from the fitting of the data for the “free” and “bound” hydrated water was 0.026 eV and 0.057 eV, respectively. On the other hand, that for the exchange protons was 0.049 eV, in between the two values. Water molecules in Nafion may be in the forms of neutral water, hydronium (H<sub>3</sub>O<sup>+</sup>), and hydroxyl (OH<sup>−</sup>) clusters. They are trapped in tiny pores of a few nm,<sup>24</sup> and the protons can be exchanged among them. In comparison, the proton

FIG. 3. Laboratory-frame NMR spin-lattice relaxation rates ( $1/T_1$ ) of the distinct water species and exchange protons as a function of temperature.

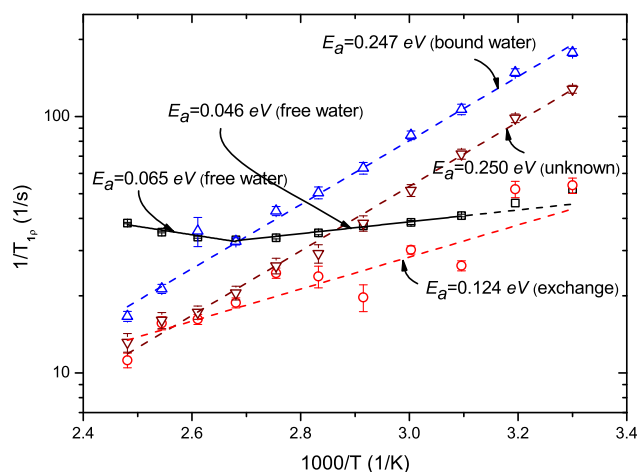


FIG. 4. Rotating-frame NMR spin-lattice relaxation rates ( $1/T_{1\rho}$ ) of the distinct water species and exchange protons as a function of temperature.

hopping activation energy in water was reported to be 0.1 eV,<sup>25</sup> and the activation energy of the rotational motion was experimentally determined to be 0.555 eV in the case of ice.<sup>26</sup> The larger activation energy of the bound hydrated water in our Nafion sample would reflect the isolated (supposedly rotational) motion, and smaller activation energies would reflect the motions of the free hydrated water and exchange protons.

Figure 4 shows the temperature dependencies of the rotating-frame NMR spin-lattice relaxation rates ( $1/T_{1\rho}$ ) of our Nafion sample. A distinct behavior of the free water is noticed, i.e., an apparent transition in the motional limits (fast motion to slow motion) in the vicinity 373 K, indicating distinct motions taking place. The activation energies obtained from fitting of the data were 0.046 eV at low temperatures and 0.065 eV at high temperatures for the free water, and 0.25 eV for the bound water. Again, the exchange protons showed a value in between the two, i.e., 0.12 eV. The different activation energies appear to reflect different motions (different axis rotation or vehicle motion). The activation energies of the proton transport in Nafion have previously been reported to be 0.114 eV (hydrated) and 0.170 eV (dried) by the NMR spin-spin relaxation time ( $T_2$ ) measurements,<sup>13</sup> compatible with our results from the  $T_{1\rho}$  measurements. In particular, the activation energy of the exchange protons (0.12 eV) is in good agreement with that of  $\sim 0.1$  eV from the macroscopic conductivity measurements.<sup>27</sup> Again, the bound water attached to sulfonic acid has the larger activation energy in comparison to those of the other proton motions.

In summary, we have carried out proton nuclear magnetic resonance spectroscopy measurements on the proton

exchange membrane Nafion. In particular, simultaneous observation of the NMR peaks from the “bound” and “free” hydrated water clusters as well as the exchange protons provided us with a rare opportunity to elucidate the hydrated water and exchange proton dynamics in the tiny Nafion pores. Besides, the activation energies of the reorientational and translational or hopping motions of the hydrated water species and exchange protons were obtained from the laboratory- and rotating-frame relaxation measurements.

This work was supported by the National Research Foundation of Korea (Project Nos. 2013057555, NRF-2010-0027963, and 2014028954). The measurements at the Korean Basic Science Institute (KBSI) are acknowledged.

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