Supporting Information

Nanometer-Scale Water Dynamics in Nafion Polymer Electrolyte Membranes: Influence of Molecular Hydrophobicity and Water Content Revisited

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1. Sample Preparation

Nafion117 membranes (Dupont, USA) were pretreated,[1] washed in distilled water, dried in air for more than two days at room temperature, and cut to sheets of 35 mm in length and 6 mm in width. The thickness and weight of each dry membrane sheet were 0.178 mm and 0.076 g, respectively. The membrane sheets were immersed in purified water (12.5 MΩ cm, μ-Pure water system, Pure Power, Korea) for at least 1 h. Then, each swollen Nafion membrane sheet was transferred to 5 mL of 2.5, 5, 7.5, 10, 12.5, 15, or 20 mM 4-amino-(2,2,6,6-tetramethylpiperidin-1-yl)oxyl (4-amino-TEMPO) solutions, which were denoted as A2.5, A5, A7.5, A10, A10, A12.5, A15, and A20, respectively. Since the water content in a water-swollen Nafion sheet was very small (~0.04 mL) compared to 5 mL, the water absorbed into the Nafion sheet had little effect on the 4-amino-TEMPO concentrations of the prepared solutions, even at the lowest concentration of 2.5 mM. After at least 1.5 days, the Nafion membrane sheets were removed from the solutions. The remaining solutions were retained for the calculation of the average number of 4-amino-TEMPO molecules per SO_3H (α) in each Nafion membrane. Each Nafion sheet was cut into circle-shaped pieces of 2 mm in diameter with a puncher, and 30 pieces were stacked in a quartz tube with an inner diameter of 2 mm and sealed with wax (CRITOSEAL, Leica Microsystems GmbH, Wetzlar, Germany).

Using the same procedure, another set of Nafion membrane samples was prepared by immersing Nafion sheets in solutions of 4-amino-TEMPO and 4-amino-(2,2,6,6-tetramethylpiperidine) (triacetonediamine, or TAD). The sum of the 4-amino-TEMPO

and TAD concentrations was 20 mM in each solution. The 4-amino-TEMPO/TAD concentration ratios were 0:20, 1:7, 2:6, 3:5, 5:3, and 6:2, corresponding to 4-amino-TEMPO concentrations of 0, 2.5, 5, 7.5, 12.5, and 15 mM. These solutions were denoted as M0, M2.5, M5, M7.5, M12.5, and M15, respectively.

Each solution-swollen Nafion membrane was packed into the capillary as quickly as possible to avoid evaporation of water from the membrane. With the knowledge that it took less than 4 min for a Nafion sheet to be removed from a solution and packed into a quartz tube, the water content in each Nafion sample was measured as described below. A fully water-swollen Nafion sheet was prepared and the Nafion sheet weight was measured as a function of drying time under ambient condition (20 °C, 10% relative humidity). For example, the weight of the fully water-swollen Nafion was 135 % of the dry Nafion sheet, which dropped to 131% after 4 min in air. The weight of a dry Nafion sheet (0.076 g) and of the remaining water in the Nafion sheet (0.024 g) after 4 min in air were used to calculate the ratio of the number of water molecules to the number of SO_3H groups (λ) to be 19. Likewise, each fully solution-swollen Nafion sheet was weighed as a function of drying time. The remaining water in a Nafion sheet when it was packed into a tube was measured as the weight difference between a Nafion sheet dried until there was no weight change and the Nafion sheet when it was packed into a tube.

2. Methods: EPR Spectroscopy

The 4-amino-TEMPO concentrations of the solutions were measured by comparing their electron paramagnetic resonance (EPR) peak areas of 4-amino-TEMPO with those of solutions with known concentrations, such as 5, 10, 15, and 20 mM, at room temperature. Double integration of EPR signals was carried out to obtain the peak area data because EPR spectra are typically displayed in a differential form. The resulting data was linearly proportional to the number of electron spins in the sample.[2] The EPR spectra of Nafion membrane samples that absorbed 4-amino-TEMPO were also obtained to evaluate the spatial distribution patterns of 4-amino-TEMPO in Nafion membranes. For the continuous wave (CW)-EPR experiments, a microwave frequency of 9.8 ± 0.003 GHz, microwave power of 0.632 mW, modulation frequency of 100 kHz, and modulation amplitude of 0.5 G were employed on an A200 EPR spectrometer (Bruker Biospin GmbH, Germany).

3. Methods and Data Interpretation: ODNP-NMR Spectroscopy

For ODNP-NMR experiments, the signal enhancement factor (E), which is the ratio of the peak areas obtained after versus before the enhancement, is expressed by

$$1 - \lim_{p \to \infty} E(p) = \xi s f \ \frac{|\gamma_S|}{\gamma_I} \tag{1}$$

where $E(p)$ is the signal enhancement factor at a given microwave power (p); γ_s and γ_I are the gyromagnetic ratios of the electron spins of 4-amino-TEMPO and the proton nuclear spins producing NMR signals to detect, respectively; s is the saturation factor; and f is the filling factor. The saturated $E(p)$ at infinite microwave power ($\lim_{p \to \infty} E(p)$) can be obtained by extrapolating the $E(p)$ data measured at various p levels.[3] Since the 4-amino-TEMPO molecules in the Nafion membrane are bound to sulfonic acid groups and exist in very high concentrations (>>10 mM), the saturation factor can be regarded as 1 when the signal amplification is maximized by increasing the p level.[3] The filling factor is expressed as $1-(T_1/T_{10})$, where T_1 and T_{10} denote the spin-lattice relaxation times after and before 4-amino-TEMPO molecules are placed in the Nafion membrane sample, respectively. Thus, the experimental data fitting equation 1 yield the coupling factor (ξ) values.

From the ξ values, the diffusion correlation time (τ) values can be calculated using the relationship between ξ and τ according to the force-free hard-sphere (FFHS) model.[4] Then, using the following equation (2), the τ values can be converted to diffusion coefficients of water protons (D), assuming that in this case, D_w is equal to D

and the diffusion coefficient of the 4-amino-TEMPO molecules is much smaller than that of water due to the restricted translational motion of the 4-amino-TEMPO molecules. The conversion is

$$\tau = \frac{d^2}{D} \qquad\qquad (2)$$

where d is the distance between the 4-amino-TEMPO molecule and the nearest water molecule. The analysis used d = 3.8 nm, which was obtained from the previous study.[3,5]

The ODNP-NMR experiments were carried out using a system consisting of a commercial EPR spectrometer (SPINSCAN X, ADANI, Minsk, Belarus) and a homemade NMR console and coil. The NMR coil was located in the EPR cavity and tuned to 14.5 MHz, which is the Larmor frequency of proton at 0.34 T. Stacked Nafion membrane pieces (~10 mm long) in a capillary with an inner diameter of 2 mm were placed at the NMR coil center. Using an external source, a microwave frequency of 9.5 GHz was applied to the sample during NMR signal acquisition with an excitation pulse at 14.5 MHz. The microwave power was selected from the range of 0–8 W, and a series of the NMR spectra were taken at different microwave power levels for each sample. Representative ODNP-NMR spectra are shown in **Figure S2**. The typical number of acquisitions of 100, acquisition time of 2.5 or 6.25 ms, and delay time of 4 s were employed. To maintain the same sample temperature, cooling air was continuously supplied to the sample region at a flow rate of 5 L/min, and there was a 4 min waiting period after acquiring data at each microwave power level.

4. Methods: Proton Conductivity Measurements

An impedance measurement unit (Wonatech, Zive SP2, Korea) was used to measure the ionic conductivity of the prepared membrane. Membrane samples were assembled in Bekktech cells (BT-115, USA). The proton conductivity (σ) was determined by the following equation:

$$\sigma = L/(R \times W \times T) \tag{3}$$

where L is the distance between the anode and cathode electrodes in the Bekktech cell (0.425cm), R is the impedance of the membrane measured at a relative humidity of 100 % and 28 °C; W and T are the width and thickness of the membrane, respectively.

**Table S1.** 4-Amino-TEMPO Uptake Amount to Nafion Sheets and Related Data

Nafion Sample*	Concentration Difference of the Solution[†] (mM)	4-Amino-TEMPO Uptake (mmol)	α[‡]
Nafion-A20	13.3	0.067	0.97
Nafion-A15	12.7	0.064	0.92
Nafion-A12.5	11.6	0.058	0.84
Nafion-A10	9.3	0.047	0.67
Nafion-A7.5	7.1	0.036	0.51
Nafion-A5	5	0.025	0.36
Nafion-A2.5	2.5	0.013	0.18
Nafion-M15	5.8	0.029	0.42
Nafion-M12.5	2.5	0.013	0.18
Nafion-M7.5	0.6	0.003	0.043
Nafion-M5	0.2	0.001	0.014
Nafion-M2.5	0.5	0.0025	0.036

*Nafion-A*n* and Nafion-M*m* represent the Nafion membrane sheets prepared by immersing a 35 mm × 6 mm ×0.178 mm sheet in 5 ml of a *n* mM 4-amino-TEMPO solution or 5 ml of a solution of 4-amino-TEMPO and TAD with *m* mM 4-amino-TEMPO concentration, respectively. The sum of the concentrations of 4-amino-TEMPO and TAD was 20 mM for the mixture solutions.

[†]The 4-amino-TEMPO concentration difference before and after a Nafion sheet was immersed in a solution A*n* or M*m*.

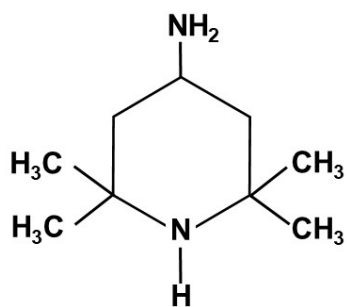[‡]Average number of 4-amino-TEMPO per SO_3H group
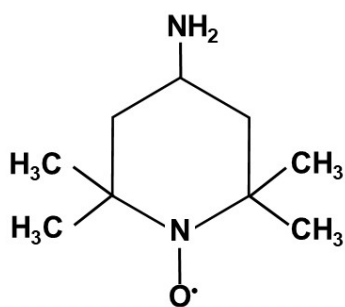
Figure S1. Molecular structures of (a) 4-amino-(2,2,6,6-tetramethylpiperidin-1-yl)oxyl (4-amino-TEMPO) and (b) 4-amino-(2,2,6,6-tetramethylpiperidine) (triacetonediamine, or TAD)
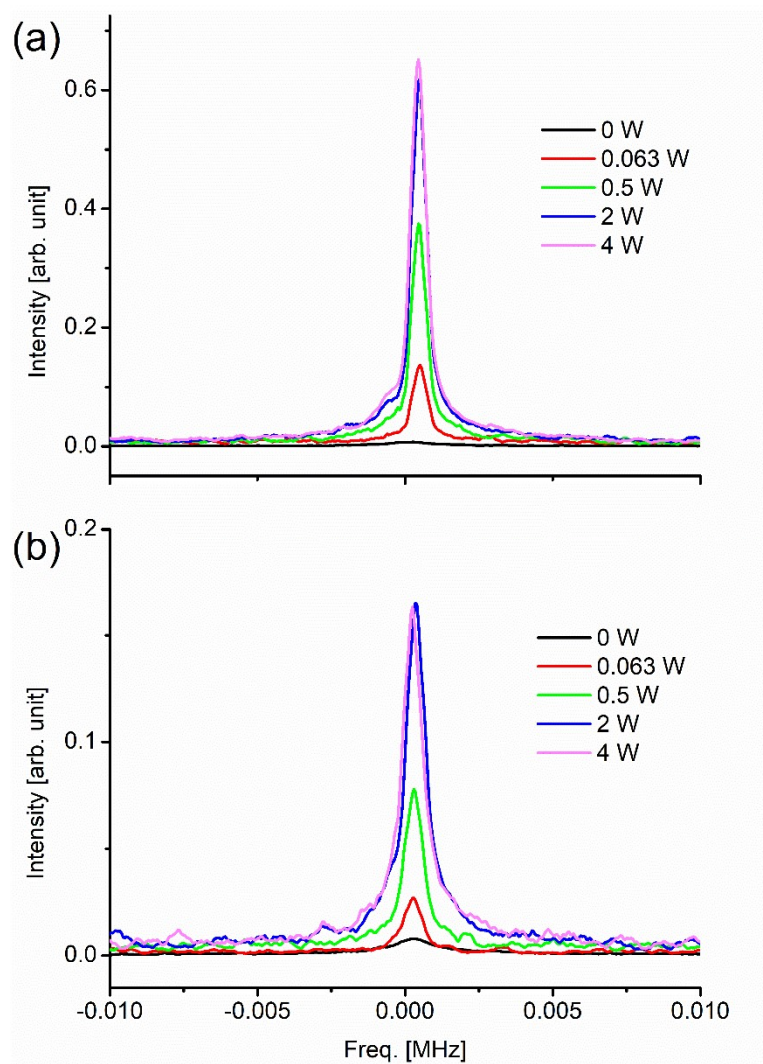
Figure S2. ^{1}H ODNP-NMR spectra of the Nafion membrane samples prepared with (a) 12.5 mM 4-amino-TEMPO solution and (b) the solution of 4-amino-TEMPO (7.5 mM) and TAD (12.5 mM) at various microwave power levels

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