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Time-dependent Diffusion Coefficient of Proton in Polymer Electrolyte Membrane

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Abstract

We investigated the time-dependent self-diffusion coefficients of water, $D(T_{eff})$, in polymer electrolyte membranes at 278 K. The $D(T_{eff})$ was measured from $T_{eff} = 0.7$ to 100 ms by field gradient NMR techniques. The results showed that the self-diffusion coefficients of water were dependent on T_{eff} less than 2 ms due to restricted diffusion, and were constant beyond 3 ms. The tortuosity and surface-to-volume ratio related to water diffusion were also estimated from $D(T_{eff})$. The obtained values revealed the existence of large-scale restricted geometry compared with well-known nanometer-sized domain in polymer electrolyte membranes.

Keywords

Polymer electrolyte membrane, Oscillating gradient, time-dependent diffusion

1. Introduction

Polymer electrolyte membranes (PEMs) are currently the object of intense interest due to their potential use in fuel cells. Many studies have been carried out to investigate electrical proton conductivity and its mechanism. Since a part of the proton conduction is caused by mass transport of water, the understanding of the water diffusion path is one of the subjects to clarify the proton transport mechanisms. Nano-scaled analyses of water path in PEMs have been achieved mainly by X-ray and neutron scattering techniques. However, little is known about long-range order (up to micrometer) structure in PEMs. In this study, we attempt to detect the micron-scale restricted structure from the observation of the restricted diffusion of water through field gradient NMR techniques.

2. Methods and Materials

Sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (SPPBP), whose preparation and characterization were found in the literature[1] as S-PPBP, and commercial perfluorinated

membrane, N112 and NRE212CS of DuPont (Wilmington, De), were used as PEMs. The membrane was cut into thin 2.5 mm × 5 mm rectangular strips. Pieces of the cut membrane were immersed in 1.0 M H_2SO_4 aqueous solution for 12 hours, and rinsed with deionized water at 353 K for 1 hour. After removing surface water by filtration paper, approximately 10 cut pieces of membrane are put into glass tube (4 mm od, 40 mm length). To control the water content of membrane, we employed humidity chamber (Tabai Espec Corp, Osaka, Japan). The atmosphere was controlled at 40 °C on 50 %RH. Equilibrium was achieved with glass tube for 5 days at least. After reaching equilibrium, the glass tube was sealed with silicone rubber plugs to avoid change of the water content during NMR measurements.

All measurements were carried out on a JEOL ECA-500 at 11.7 T, narrow-bore NMR spectrometer equipped with maximum gradient strength of 1330 G/cm. The 4 mm od glass tube including samples was sealed, inserted into 5 mm od NMR glass tube. Two pulse sequences as shown in Fig. 1, oscillating gradient spin echo (OGSE) and 13 interval bipolar pulse stimulated echo (13BPP), were employed to measure the ^1H self-diffusion coefficient. The observable NMR signal, $E(g)$, are expressed as a function of spin dephasing,

$$E(g) = E_0 \exp\left\{ -D(T_{\mathrm{eff}})\gamma^2 \int_0^t \left[\int_0^{t'} g(t'')\mathrm{d}t'' \right]^2 \mathrm{d}t' \right\} \equiv E_0 \exp\{-D(T_{\mathrm{eff}})b\} \qquad (1)$$

where $D(T_{\mathrm{eff}})$ is the self-diffusion coefficients, γ is the gyromagnetic ratio, E_0 is the NMR echo intensity without field gradient and $g(t'')$ is the applied effective field gradient. The b-value and T_{eff} of two pulse sequences are given in Table 1.
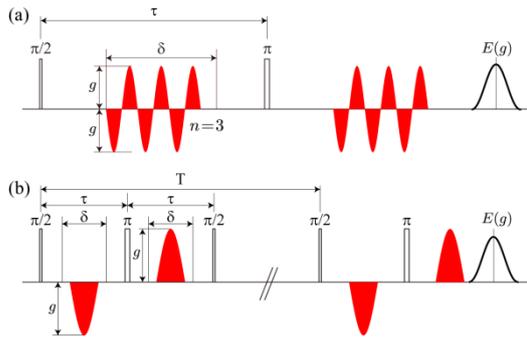
Fig. 1: Two pulse sequences were employed to measure $D(T_{\mathrm{eff}})$ on T_{eff} from 1 ms to 100 ms. (a)OGSE; the τ was fixed to 20 ms. The b is adjusted in changing n and δ. (b)13BPP; The b is adjusted in changing T.

	T_{eff}	b
OGSE	$\dfrac{3\delta}{8n}$	$\dfrac{3\gamma^2 g^2 \delta^3}{4\pi^2 n^2}$
13BPP	$T - \dfrac{\tau}{2} - \dfrac{\delta}{8}$	$4\gamma^2 g^2 \delta^2 \left(T - \dfrac{\tau}{2} - \dfrac{\delta}{8} \right) \dfrac{1}{\pi^2}$

Table. 1: b factor and T_{eff}, for OGSE and 13BPP. Each symbol corresponds to that of the sequences in Fig. 1.

We have measured $E(g)$ for eight linearly spaced values of g for a maximum value corresponding to the maximum signal attenuation of about 20 %. It is assured that $E(g)$ is still in the Gaussian regime, and the self-diffusion coefficients can be obtained from eq. (1) for 13BPP and OGSE sequences, respectively. This procedure was performed by a linear regression analysis on $\ln(E(g)/E_0)$ versus b.

3. Results and Discussions

Figure 2 indicates $D(T_{\mathrm{eff}})$ of N112, NRE212CS, SPPBP membranes and 5 mM $CuSO_4$ aqueous solution at 278 K. On the calculation of the self-diffusion coefficients, the signal attenuation with applied field gradient can be expressed by eq. (1) as a single diffusion component. It is well-known that there are several kinds of proton species in PEMs such as $SO_3^-H^+$, H_3O^+ and H_2O. However, since the exchange process among these species occurs rapidly compared with the time scale of the NMR diffusion measurement, the obtained self-diffusion coefficients cannot be identified these species individually. We thus should regard

the measured values as weight-average of these species. The self-diffusion coefficients in 5 mM $CuSO_4$ were 1.31×10^{-9} m^2/s on all over the diffusion time. This value is appropriate as compared with the result of water[2]. On the other hand, The ^1H self-diffusion coefficients in all membranes clearly depended on T_{eff} less than 2 ms at least. These results demonstrated that there is restricted structure for these membranes on the length scale probed by this experiment. The self-diffusion coefficients for T_{eff}>3 ms were nearly independent on T_{eff} and seem to be approaching a constant. The tortuosity, α, related to tortuous diffusion path can be determined in this time scale of T_{eff}=100 ms.

$$\alpha = \frac{D_{bulk}}{D(T_{eff} = 100 \text{ ms})} \qquad (2)$$

where, D_{bulk} is bulk diffusion coefficients of water (D_{bulk}=1.3$\times10^{-9}$ m^2/s). In addition, to extract surface-to-volume ratio, S/V, Mitra equation[3] was applied to the $D(T_{eff})$ for the short diffusion time region less than 2 ms,

$$D(T_{eff}) = D_0 \left(1 - \frac{4}{9\sqrt{\pi}}\frac{S}{V}\sqrt{D_0 T_{eff}}\right) \qquad (3)$$

where D_0 is the bulk diffusion coefficient. The $D(T_{eff})$ are plotted as a function of square root of T_{eff}, are fitted by Mitra equation with the straight lines. The S/V and D_0 are provided from the slope and the intercept of the straight lines as shown Fig. 2. These values are summarized together with α in Table 2. The values of D_0 obtained from Mitra equation are quite lower than the bulk diffusion coefficients of water. It is thought that the values of D_0 reflect the diffusion within the homogeneous network of cavities and so contains the transfer effect through the tortuous water path. In our results, the pore size (=$6V/S$ for spherical pore) is micrometer order, and is quite large compared with well-known hydrophilic domain size[4] (nanometer size in Gierke model). A feasible interpretation for the obtained S/V is the density fractionation of cavities resulting from heterogeneous distribution of cavity. The existence of heterogeneous cavity distribution may produce restricted wall for water diffusion.
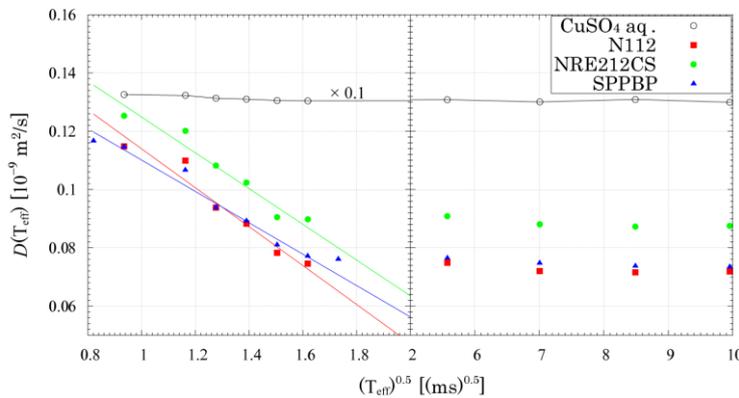
Fig. 2: Measured $D(T_{eff})$ versus the square root of T_{eff}. The data for N112, NRE212CS and SPPBP were fitted by eq. (3) at the range of T_{eff} < 2 ms. The straight lines show fitted results.

	S/V μm^{-1}	D_0 10^{-9} m^2/s	α a.u.
N112	3.5±0.2	0.18±0.01	18
NRE212CS	3.0±0.2	0.19±0.01	15
SPPBP	3.2±0.1	0.16±0.01	18

Table. 2: Estimated values of S/V, D_0 and α in membranes. Errors reported here are the standard error of the fitting lines to experimental data.

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