Water diffusion in fluoropolymer-based fuel-cell electrolyte membranes investigated by radioactivated-tracer permeation technique

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Summary. The self-diffusion coefficient of water, D, in proton exchange membranes (PEMs) based on crosslinked-polytetrafluoroethylene (cPTFE) films was measured by a radioactivated-tracer permeation technique using tritium labeled water (HTO). The D value was found to increase with the water volume fraction of the PEM, φ, probably because the water-filled regions were more effectively interconnected with each other at high φ, allowing water permeation to be faster through a PEM. Interestingly, the grafted PEMs showed the lower D compared to that of Nafion in spite of their high φ. This would be caused by tortuous structures of transport pathways and a strong coulombic interaction between water and the negatively-charged sulfonate (SO₃⁻) groups. Heavy-oxygen water (H₂¹⁸O) was also used in the similar permeation experiment to obtain the D. Since the HTO diffusion actually occurred not only by translational motion of water but also by intermolecular hydrogen-atom hopping, comparing the D of HTO with that of H₂¹⁸O was likely to give the information about the state of water in the PEMs.

1. Introduction

A polymer electrolyte membrane (PEM) fuel cell is an electrochemical device to generate electricity directly from hydrogen and oxygen gases. In the PEM fuel cell, protons dissociated from hydrogen at the anode conduct to the cathode through a PEM and react with oxygen to yield water. During the cell operation, water is not only produced at the cathode, but actively transported by electro-osmotic drag and concentration-gradient-driven back diffusion, which results in uneven water distribution in a PEM [1, 2]. This sometimes causes the deterioration of cell performance: more specifically, the anode side of the PEM tends to be dried to lose proton conductivity, and flooding of the cathode side could hamper the supply of oxygen gases. Accordingly, a water transport property of the PEM is an important issue toward stable fuel-cell operation over the short and long terms.

At present, the most widely used benchmark PEM is DuPont’s Nafion because of its excellent properties, but it is still too expensive for commercial use owing to its complicated production process. As one of the promising techniques for synthesizing Nafion-alternative low-cost PEMs, there has been much interest in a radiation-induced grafting method [3, 4]. We recently prepared a novel PEM by the γ-ray-induced post grafting of styrene into a crosslinked polytetrafluoroethylene (cPTFE) film and subsequent sulfonation [5, 6]. The two main characteristics of this PEM are (i) to possess the crosslinked fluoropolymer main chains that Nafion never has; and (ii) to exhibit the ion exchange capacity (IEC) up to 3.0 meq/g, which is far larger than that of Nafion (0.95 meq/g). Up to now, we have characterized it in terms of thermal stability [7], proton conductivity [8], and water diffusivity [9].

The self-diffusion coefficient of water molecules, D, which is a suitable parameter reflecting water transport properties, can be obtained by the following methods: (a) a ¹H pulsed-field-gradient nuclear-magnetic-resonance (PFG-NMR) technique [10–14]; (b) measurement of time-dependent weight change during the hydration or dehydration process [15–18]; and (c) water-tracer permeation technique [9, 19–22]. We measured the D of the cPTFE-based radiation-grafted PEMs by method (c) with tritium-labeled water (HTO) [9]. In this previous study, the D seemed to strongly depend on the λ, defined as the number of water molecules per sulfonic acid group; in other words, the D vs. λ was plotted on a single curve.

This work aims at more deeply investigating the water transport phenomena in our novel grafted PEMs by the same method. The D was plotted as a function of the water volume fraction, φ, which enabled us to discuss both tortuous structures of water transport pathways and an interaction between water and sulfonic acid groups as the determining factors. Moreover, heavy-oxygen water (H₂¹⁸O) was also used as tracer in the permeation experiment. We proposed an idea for the first time that comparing the D values between HTO
and H$_2^{18}$O could be effective for studying the state of water in PEMs.

2. Experimental

2.1 PEM synthesis

The PEMs were prepared as already reported [5, 6]. We used, as a base material, a 42-$\mu$m thick film of PTFE crosslinked with electron beams at 100 kGy. The ePTFE film was irradiated with 15-kGy $\gamma$-rays in an Ar atmosphere at room temperature, and then immersed in a styrene monomer at 50 $^\circ$C for 4–48 h. After the grafting reaction, the film was extracted with toluene to remove any excess styrene. For sulfonation, the grafted film was immersed in a 0.2 M chlorosulfonic acid/1,2-dichloroethane mixture at 50 $^\circ$C for 6 h. Finally, the membrane was rinsed with pure water and then dried in a vacuum oven. The IEC (meq/g) of the resultant grafted PEM was measured by back titration with a standardized 0.1 M NaOH solution. The grafting under the various conditions gave us the PEMs with IECs ranging from 0.6 to 2.7 meq/g, and with a hydrated-membrane thickness ranging from 53 to 92 $\mu$m, respectively.

Nafion 112 and 1135 were pretreated by the following established procedure. They were boiled in a 3% hydrogen peroxide aqueous solution for 1 h, in pure water for 1 h, in a 1 M sulfonic acid aqueous solution for 1 h, and finally in pure water for 1 h. The thicknesses of Nafion 112 and 1135 in the hydrated state were 58 and 100 $\mu$m, respectively.

2.2 Water uptake

The dried PEM was equilibrated in pure water at 25 $^\circ$C for at least 24 h and then taken out for measurement. After the excess water was quickly wiped off from the surface, the PEM weight, $W_w$ (g), and volume, $V_w$ (cm$^3$), were measured. The $\phi$ was estimated by:

$$\phi = \frac{W_w - W_D}{V_w \rho_w},$$

where $W_D$ and $\rho_w$ denote the weight of a dried PEM (g) and density of water (g/cm$^3$), respectively.

2.3 Water-tracer permeation

The permeation experiment was performed as previously reported [9]. Fig. 1 shows a permeation glass cell having two 120-ml compartments separated by a PEM with an effective area of 3.1 cm$^2$. Pure and HTO-containing water (400 Bq/mL) kept at 25 $^\circ$C were poured into each compartment at the same time. Specimens of 1 ml were taken out from the receiving compartment at different time points, and then its HTO concentration, $C_R(t)$, was measured by $\beta$-scintillation counting using a liquid scintillation counter.

The H$_2^{18}$O permeation experiment was performed in a similar way. The initial H$_2^{18}$O concentration in the feeding compartment was about 2.5 wt%. The H$_2^{18}$O concentration in the receiving compartment was determined by the mass spectrometric method coupled with isotopic exchange [23].

2.4 Calculation of $D$

Fig. 2 exemplifies the time dependence of $C_R(t)$ for the grafted PEMs with different IECs of 0.84 and 1.8 meq/g. The $C_R(t)$ increased linearly with time, indicating a steady-state HTO flux from the feeding to receiving compartments through the PEM. Based on the Fick’s second law of diffusion, a HTO permeability, $P$, was estimated from the slope of the $C_R(t)$ vs. time straight line, $dC_R(t)/dt$, by the following equation:

$$P = \frac{V_R \cdot L \cdot A \cdot C_F}{C_F} \frac{dC_R(t)}{dt},$$

where $V_R$, $L$, $A$, and $C_F$ denote the volume of the receiving compartment (= 120 mL), the PEM thickness, the effective permeation area (= 3.1 cm$^2$) and the HTO concentration of the feeding compartment (= 400 Bq/mL), respectively. $C_F$ is considered constant because the permeation time was enough short. The $D$ was calculated by:

$$D = \frac{P}{\phi}.$$
3. Results and discussion

During the permeation process, HTO molecules in the feeding compartment are introduced into a PEM, move through it by Fick’s law of diffusion, and finally are discharged to the receiving compartment. Here, one may consider that the water diffusion was impeded at the membrane/liquid water boundary. Indeed, in the previous study of the water vapor penetration through Nafion [24, 25], the water transport appeared so slow at the membrane interface that the overall penetration speed was lowered. One reason for this result was that the Nafion surface was originally hydrophobic and became the barrier against water vapor. In contrast, in our study, both sides of a PEM were in contact with liquid water so that the PEM could be kept hydrophilic. Therefore, water would be able to smoothly move through the membrane interfacing regions, as was reasonably predicted by the theoretical model for hydration of Nafion [26]. In order to verify the above argument experimentally, a comparison was made between the $P$ values of Nafion with the different $L$, i.e., Nafion 112 and 1135. If the interfacial transport is a rate-limiting step, the HTO flux across a PEM ($= dc/t/dt$) is constant. It follows that $P$ is proportional to $L$ in Eq. (2). In this case, however, the two Nafion membranes exhibited almost the same $P$ ($= 2.1–2.2 \times 10^{-10}$ m$^2$/s), demonstrating that the interfacial water transport resistance was negligible.

Fig. 3 shows the $P$ as a function of an $IEC$. For the grafted PEMs, the $P$ was found to increase with the $IECs$. This trend coincided with that of the $φ$, indicating the strong relationship between the volume of water-filled regions and water permeation. The PEM with a high $IEC$ would absorb much water to increase $φ$ so that water can easily permeate through the PEM. At the same $IEC$, the crosslinked PEMs showed the lower $D$ compared to the non-crosslinked ones. The crosslinking of the main chains probably made $φ$ low and decreased water permeation.

Fig. 4 shows the $D$ as a function of an $IEC$. This figure was reproduced by adding newly-obtained data points to that reported in our previous paper [9] in order to examine the $D$ change in the wider $IEC$ range. Nafion 112 exhibited the highest $D$ of $4.9 \times 10^{-10}$ m$^2$/s of all the measured samples, which is somewhat lower than the $D$ measured by a $^1$H PFG-NMR method ($7.1–7.3 \times 10^{-10}$ m$^2$/s) [10–12] (we discuss this discrepancy later). For the grafted PEMs, similarly to the $φ$, the $D$ increased with an $IEC$ and became lower by crosslinking structures of PTFE main chains (see Fig. 4). This indicates that the mobility of an individual water molecule ($D$) also would affect the $P$.

Then, let us consider the factors affecting the $D$ in more detail. In a PEM, water molecules are believed to aggregate around the negatively-charged sulfonate (SO$_3^-$) groups to form the hydrophilic regions. Naturally, they are randomly interconnected with each other to build the transport network throughout the PEM, and so in fact, the pathway is not perfectly straight but well curved and branched. As a consequence, the actual route length travelled by water from one side to the other of a PEM, $L$, is longer than the PEM thickness, $L$. The degree of complexity of water transport pathways is called tortuosity, $τ$, and is defined as:

$$τ = L_s/L.$$  \hspace{1cm} (4)

The $D$ can be re-expressed using the $τ$ as follows:

$$D = \frac{D_L}{τ^2}. \hspace{1cm} (5)$$

where $D_L$ denotes the self-diffusion coefficient in the local region of the pathway, in which we can ignore the effect of $τ$. Eq. (5) is widely used in the research of diffusive dynamics through various materials, e.g., fluid flow in rocks and gas permeation in polymers [27–30].

Based on the above discussion, we account for the difference between $D$ values for Nafion that was measured by the HTO tracer and $^1$H PFG-NMR methods. The point to notice is a distance for water molecules to reach within diffusion time. In the tracer method, an HTO molecule passes through the membrane, more exactly, moves along the tortuous hydrophilic pathways in the membrane. Thus, this $τ$ effect would reduce the $D$ as already described. On the other hand, the NMR method measures the water diffusion in a very small part of a PEM, since the time window is not more than
500 ms. Therefore, water molecules were presumably not so disturbed by tortuous transport pathways, thereby enhancing the measured \( D \).

For the diffusion kinetics in porous materials, the \( \tau \) was known to strongly depend on the volume fraction of the open space for the diffusive species to move. In our case, since water can diffuse only in the water-filled regions of the PEM, the \( \tau \) should be determined by the \( \phi \). Accordingly, we re-plotted the \( D \) as a function of the \( \phi \) in Fig. 5. In contrast to Fig. 4, the influence of PTFE crosslinks appeared to almost vanish; in other words, all the data points of the grafted PEMs were dispersed near a single curve. Such absolute \( \phi \) dependence of \( D \) can be explained by taking into account how the transport pathway network would grow. In our most recent study of dissipative particle dynamics (DPD) simulation on the same grafted PEMs [31], we found that the diameter of water-filled transport pathway was constant and independent of the \( \phi \). From this finding, it is reasonable to consider that the higher the \( \phi \), the larger the number of pathways. The resulting multiple pathways likely produced a well-interconnected network, making \( \tau \) lower and enabling water molecules to faster transverse a PEM.

The \( \tau \) makes it possible to rationalize the difference in \( D \) between the grafted PEMs and Nafion. In Nafion, water is said to gather to form clusters with a diameter of about 5 nm, thereby increasing the \( \tau \) beyond that of Nafion. Interestingly, compared with Nafion, the \( D \) of grafted PEMs was lower even at the largest \( \phi \). This result can be explained by considering that the smaller water clusters in the grafted PEMs were expected to contain many branches and dead-end pockets, leading to very complex structures, i.e., the high \( \tau \). Furthermore, the stronger attractive coulombic interaction between the SO3\(^-\) groups and water probably reduced the \( D \), thereby also lowering the \( D \). Finally, the diffusion behaviour of H\(_2\)\(^{18}\)O was compared with that of HTO. In Nafion, H\(_2\)\(^{18}\)O gave higher \( D \) than did HTO as seen in the bulk water, while in the grafted PEMs, HTO and H\(_2\)\(^{18}\)O exhibited almost the same \( D \) (see Fig. 4). We have to recall here that a hydrogen atom constantly hops between water molecules by the cleavage and formation of hydrogen bonds, and thus this molecular phenomenon as well as translational motion must be considered for the T atom diffusion. As discussed above, the translation of both HTO and H\(_2\)\(^{18}\)O should be retarded more seriously in the grafted PEMs, where the stronger interaction took place. In contrast, the hydrogen-atom hopping reaction was not thus impeded [33], and consequently remained rapid. It follows that the relative speed of T hopping to HTO translation would become higher in the grafted PEMs than in Nafion. As a result, the total \( D \) of HTO apparently increased until it reached that of H\(_2\)\(^{18}\)O in the grafted PEMs. We suggest that the \( D \) ratio of HTO to H\(_2\)\(^{18}\)O could provide us with the fundamental insight into the physico-chemical state of water in PEMs.

4. Conclusions

The water transport through the cPTFE-based radiation-grafted PEMs was investigated in terms of their \( D \) by the HTO-permeation experiment. The observed \( IEC \) or \( \phi \) dependence of \( D \) was discussed by the two factors representing water transport pathways, the \( \tau \) and \( D \). Interestingly, compared with Nafion, the \( D \) of grafted PEMs was lower even at the largest \( \phi \). This result can be explained by considering that the smaller water clusters in the grafted PEMs were expected to contain many branches and dead-end pockets, leading to very complex structures, i.e., the high \( \tau \). Furthermore, the stronger attractive coulombic interaction between the SO3\(^-\) groups and water probably reduced the \( D \), thereby also lowering the \( D \). Finally, the diffusion behaviour of H\(_2\)\(^{18}\)O was compared with that of HTO. In Nafion, H\(_2\)\(^{18}\)O gave higher \( D \) than did HTO as seen in the bulk water, while in the grafted PEMs, HTO and H\(_2\)\(^{18}\)O exhibited almost the same \( D \). We provide a possible explanation that the T transport by the hydrogen-atom hopping became more dominant over that by the translational motion of water in the grafted PEMs because only the latter was restrained by the strong coulombic interaction in the narrow water pathways as mentioned above. Consequently, taking the \( D \) ratio of HTO to H\(_2\)\(^{18}\)O could be one of the effective ways for analyzing the physico-chemical state of water in the PEMs.

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