Free volume and gas permeation in ion-exchanged forms of the Nafion® membrane

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Abstract. Variations of free volume and gas permeability of the Nafion® membrane upon ion-exchange of H+ with Cs+ or Pt2+ was studied as a function of temperature. Free volume was quantified using the positron annihilation lifetime technique. Our results showed that the free volume (V_{FV,Ps}) of the dried membrane is enlarged by thermal expansion. It was found that the ion-exchange significantly expands the free volume and at the same time decreases the permeabilities of O2 and H2. Good linear correlations between the logarithm of permeabilities of O2 and H2 at different temperatures and 1/V_{FV,Ps} for the ion-exchanged forms of Nafion® in the dried state suggest an important role played by the free volume in gas permeation. Considerable downward deviation of the correlations for the ion-exchanged ionomers from the H+-form suggested the importance of polymer stiffening in gas permeation.

1. Introduction

The polymer electrolyte fuel cell (PEFC) has been considered as one of the most promising power sources for stationary and portable applications due to their high energy conversion efficiency and near-zero pollutant emission [1-4]. As a key component of PEFCs, the polymer electrolyte membrane (PEM) plays dual roles of ion conductor and gas separator [5]; the latter role is important because the crossover of H2 and O2 between the anode and cathode in PEFC decreases the efficiency of PEFC. DuPont’s Nafion® membranes with the chemical structure shown in Fig. 1 possesses high proton conductivity and excellent chemical stability and are considered as the state-of-the-art PEMs. According to the free volume model of gas permeation, free volume, present as sub-nanometer scale holes in the amorphous domain of the PEM, provides a pathway for diffusion of gases [6]. Hence the model states that the structure with less open volume is more amenable to lower permeability of small gas molecules such as O2 and H2.

Nanometer sized free volume holes in a polymer can be probed by the positron annihilation lifetime (PAL) spectroscopy, as long as a reasonable fraction of the positrons form positronium (Ps), the positron-electron bound state [7-10]. Ps is formed by a reaction between a positron and one of the electrons, ionized and liberated from the polymer molecules by the energetic positron itself, in the terminal positron spur [11]. The positrons that have formed Ps annihilate either from short-lived para-
positronium (p-Ps) or long-lived ortho-positronium (o-Ps). Thus the positron annihilation lifetime spectrum of a Ps-forming substance typically contains three components, which are due to p-Ps with lifetime $\tau_1 \sim 125$ ps and relative intensity $I_1$, free positrons with lifetime $\tau_2 \sim 500$ ps and intensity $I_2$, and o-Ps with lifetime $\tau_3 \sim 1-10$ ns and intensity $I_3$ [11, 12]. The annihilation of o-Ps in a polymer is governed by the “pick-off” process, in which the positron in o-Ps annihilates with one of the surrounding spin opposite electrons [12-14]. Approximating the free volume hole as a spherical potential well having infinitely high walls, Tao [15] and Eldrup et al. [16] derived the following relationship between the pick-off annihilation lifetime ($\tau_3$) and the radius ($R$) of the free volume hole as;

$$\tau_3 = 0.5 \left\{ \frac{1}{R_o} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_o} \right) \right\}^{-1} \text{(ns)},$$

where $R_o = R + \Delta R$ and $\Delta R = 0.166$ nm is the thickness of the homogenous electron layer in which the positron in o-Ps is postulated to annihilate [17]. The free volume size $V_{FV,Ps}$ in nm$^3$ is given as

$$V_{FV,Ps} = 4 \pi R^3/3.$$ 

The above equations have been successfully used for the study of the free volume in various polymers [18-20].

$\begin{align*}
\left[\text{CF}_2\text{CF}_2\right]_x \left[\text{CF}_2\text{OF}_2\text{CF}_2\right]_y & \text{n} \\
\text{O} & \text{CF}_2\text{CF}^{-}\text{O(CF}_2\text{CF}_2\text{)}\text{SO}_3\text{H} \\
\text{CF}_3 &
\end{align*}$

**Figure 1.** Chemical structure of Nafion®.

Previously, we investigated the free volume in Na$^+$- and K$^+$-forms of Nafion® [21,22]. The comparison of experimental data collected by different techniques revealed that not only free volume but also polymer stiffness plays an essential role in O$_2$ permeation. In this study, we extend our work on the mechanism of gas permeation to the Cs$^+$- and Pt$^{2+}$-forms of Nafion®. The study of the free volume in ion-exchanged Nafion® is of practical significance not only because an ion-exchanged form of Nafion® is sometimes used to fabricate PEFC [23,24] but also because contamination of such ions as Cs$^+$ and Pt$^{2+}$ is possible during fuel cell operation from humidified feed gases or catalyst layer [25-27]. Free volume was characterized by using the positron annihilation lifetime (PAL) technique and the permeabilities of O$_2$ and H$_2$ were measured as a function of temperature. The information on the crystallinity and mechanical properties was obtained by wide angle x-ray diffraction (WAXD), dynamic mechanical analysis (DMA).

2. Experimental
The H$^+$-form of Nafion® was supplied from Du Pont Japan as NR212 (formally NRE212) with an ionic exchange capacity (IEC) of 0.92 meq/g and a thickness of 50 μm. The Cs$^+$- and Pt$^{2+}$-forms were
prepared by exchanging H+ with Cs+ and Pt2+, respectively following the standard procedure [28]. Briefly as-received NR212 was soaked for 1 day in aqueous 1 mol/dm³ solutions of CsCl and Pt(NH3)4(OH)2(H2O)n. The soaked films were removed from the solutions, washed several times with deionized water and dehydrated in an oven at 70 °C for 3 h. All the chemicals used were of reagent grade (Wako Pure Chemical Industries).

The PAL measurements were performed using a fast-fast coincidence system with a time resolution of 280 ps (full width at half maximum, FWHM) [29]. A positron source (22Na), sealed between thin foils of Kapton, was mounted in a sample (stack of films with a total thickness of 1 mm)-source-sample sandwich. The channel width was 20.7 ps, and the data were recorded over 4096 channels. Before the measurements, the samples had been dried by evacuation for one day at room temperature (~25 °C) and then at 80 °C for 10 h under vacuum. Lifetime spectra were recorded as a function of temperature up to 100 °C. Each lifetime spectrum containing a total number of 2.5 x10⁶ counts was analyzed using the PALSfit program [30] into three lifetime components to deduce lifetime τ₃ and relative intensity I₃ of the longest-lived o-Ps component. No source correction was applied in the data analysis. The validity of our measurement and data analysis was confirmed with certified reference materials (NMIJ-CRM 5601-a, No.07 and NMIJ-CRM 5602-a, No.01) [31,32].

Gas permeability was measured by the equal pressure method with a GTR-Tech 30XFST apparatus equipped with a Yanaco G2700T gas chromatograph by monitoring the amounts of O₂ and H₂ that permeated across the membrane from one side to the other [21,22,33]. The temperature dependence of the permeation coefficient for O₂ and H₂ (P₀₂ & P₁₂) was measured up to 90 °C for dried samples using He and Ar as carrier gases of permeated O₂ and H₂, respectively, to the gas chromatograph. A 50 μm thick membrane was set in a cell with a gas inlet and outlet, where the temperature was controlled. Both O₂ and H₂ were supplied at a flow rate of 30 mL/min.

Dynamic mechanical analysis (DMA) was performed in the tensile mode on a Triton DMA analyzer (Tritec 2000 - Shimadzu) for the dehydrated samples. Loss tangent (tan δ) was measured at a fixed dynamic displacement of 0.5 % and a frequency of 1 Hz in air for a sample typically of 9.0 x 9.0 x 0.05 mm³. Elongation was measured with a static load of - 0.10 N. The samples were heated with a rate of 3 °C/min from 20 °C to 150 or 330 °C.

Wide angle x-ray diffraction (WAXD) was measured in the θ-2θ mode for the dehydrated samples by Ultima IV (Rigaku Corporation) with a 285 mm goniometer. A parallel monochromatic x-ray beam obtained by reflection of Cu Kα radiation (λ = 1.542 Å) from a fine focus x-ray tube operated at 40 kV and 40 mA by a parabolic multi-layer membrane mirror was used. Scattering profiles were recorded with a scintillation one-dimension position-sensitive detector over a range of 5° < 2θ < 65° with a step of 0.025° and at a rate of 0.5°/ min.

3. Results and discussion

Figure 2A shows temperature dependence of the o-Ps lifetime τ₃ for dry Cs⁺- and Pt²⁺-forms of Nafion®. The right hand ordinate of the figure represents the free volume hole size quantified by Equations (1) and (2). It is seen that the free volume of all the samples is considerably enlarged by thermal expansion. Both Cs⁺- and Pt²⁺-forms of Nafion® have larger free volumes than the H⁺-form over the entire temperature range studied. Temperature dependence of the free volume for the H⁺-form shows an abrupt change of the thermal expansion coefficient around 20 °C due to β-transition caused by the glass transition of Nafion®. According to Osborn et al. [34], this glass transition of the H⁺-form of Nafion® is attributed to principally main-chain (backbone) motions within the framework of a static physically cross-linked (hydrogen-bonding) network. The absence of any abrupt change in the thermal expansion coefficient of the free volume for the Cs⁺- and Pt²⁺-forms suggests that their β-transition occurs above 80 °C. Figure 3 shows the tan δ measured by dynamic mechanical analysis (DMA) as a function of temperature for dehydrated Nafion® containing H⁺, Cs⁺ and Pt²⁺. A pronounced peak centered at 108 °C for the H⁺-form is due to α-relaxation, which may be associated with the onset of large-scale motions of the ionomer [35]. The peak is shifted to 230 and 295 °C for the Cs⁺- and Pt²⁺-forms, respectively, so that the relaxation temperature significantly rises upon ion-
exchange as reported by other authors [36,37]. The increase of the relaxation temperature by the exchange of H\(^+\) with Cs\(^+\) or Pt\(^{2+}\) is consistent with our result in Fig. 2A.

**Figure 2.** Lifetime \(\tau_3\) and its intensity \(I_3\) of o-Ps as a function of temperature for dried Nafion\(^\circledR\) of the H\(^+\), Cs\(^-\) and Pt\(^{2+}\)-forms. The scale of the right ordinate in (A) is the size of free volume hole \(V_{\text{FV}}\) deduced from Equations (1) and (2).

The o-Ps intensity \(I_3\) for all the samples varies only slightly with temperature, indicating that Ps formation does not significantly depend on temperature as shown in Fig. 2B. Regardless of temperature, exchange of H\(^+\) with Pt\(^{2+}\) substantially enhances \(I_3\) and that with Cs\(^-\) makes \(I_3\) even higher. Since free volumes favorable for Ps formation are in the amorphous region of a polymer, Ps formation is expected to be enhanced with decreasing crystallinity [38,39]. However, all the Nafion\(^\circledR\) samples have the o-Ps intensity \(I_3\) less than half the typical value of PTFE (\(\sim 19.4\%\)), in spite of their consistently lower crystallinity [29,40]. Moreover, Ps formation is significantly different between the Cs\(^-\) and Pt\(^{2+}\)-forms. Figure 4 displays WAXD patterns for dehydrated Nafion\(^\circledR\) in the H\(^+\)-, Cs\(^-\)- and Pt\(^{2+}\)-forms recorded at room temperature. A sharp peak around \(2\theta = 17^\circ\) is superimposed on an amorphous halo over a range of \(2\theta = 12 - 22^\circ\) in agreement with Laporta et al. [41]. The peak can be indexed as the (100) reflection of the hexagonal structure of polytetrafluoroethylene (PTFE)-like crystallites in Nafion\(^\circledR\) [42,43]. The crystalline reflection around \(17^\circ\) is weakened in the Cs\(^-\) and Pt\(^{2+}\)-forms in comparison with the H\(^+\)-form, suggesting that in ion-exchanged Nafion\(^\circledR\) large alkali ions make the regular arrangement of the molecular chains difficult and the crystallinity is decreased. Further the crystallinity of the Cs\(^-\) and Pt\(^{2+}\)-forms of Nafion\(^\circledR\) is similar to each other although there o-Ps intensities are significantly different. Therefore, the variations of Ps formation upon ion-exchange can not be fully accounted for in terms of crystallinity. Apart from crystallinity, a chemical structure or compound that captures an electron-positron pair, which would otherwise recombine with each other to Ps, can inhibit the formation of Ps [40,44,45]. Comparison of the chemical structure between Nafion\(^\circledR\) and PTFE suggests that the reduced Ps formation in the ionomer may be due to the inhibition effect of the electron-accepting SO\(_3\)X (X = H\(^+\), Pt\(^{2+}\), Cs\(^-\)). If this is the case, our results in Fig. 2B suggest that SO\(_3\)H and SO\(_3\)Cs are, respectively, strong and weak inhibitors of Ps formation. Figures 5 and 6 show O\(_2\) and H\(_2\) permeabilities in dried H\(^+\)-, Cs\(^-\)- and Pt\(^{2+}\)-forms of Nafion\(^\circledR\) at various temperatures, respectively. It is seen that both the permeabilities increase by orders of magnitudes with increasing temperature from 20 to 90 \(^\circ\)C. At all the temperatures studied, H\(_2\) is much more permeable than O\(_2\). Regardless of temperature both O\(_2\) and H\(_2\) are less permeable in the ion-exchanged ionomers than the H\(^+\)-form of Nafion\(^\circledR\).
Figure 3. Loss tangent (tan δ) as a function of temperature for Nafion® containing H⁺, Cs⁺ and Pt²⁺. The arrow indicates the peak due to α-relaxation.

Figure 4. Wide angle x-ray diffraction patterns for Nafion® in the H⁺-, Cs⁺- and Pt²⁺-forms.

Figure 5. O₂ permeability as a function of temperature for dried Nafion® in the H⁺-, Cs⁺- and Pt²⁺- forms. The straight lines are drawn just for guiding the eyes.

Figure 6. H₂ permeability as a function of temperature for dried Nafion® in the H⁺-, Cs⁺- and Pt²⁺- forms. The straight lines are drawn just for guiding the eyes.

According to the sorption-diffusion model, gas permeation coefficient $P$ is given as the product of permeant solubility $S$ and diffusion coefficient $D$ [6],

$$ P = S \ast D. $$

(3)

The permeant can diffuse when it finds large enough free volume around itself to make a jump to one of the neighbouring sites. Therefore, the diffusivity can be related to the fractional free volume $V_f$ by [46-48]

$$ D = A R_g T \exp (-B / V_f), $$

(4)
where $A$ and $B$ are constants depending on the permeant, $R_g$ is the gas constant and $T$ is the absolute temperature. Combination of Equation (3) with Equation (4) yields the following relationship between the permeability and free volume;

$$P = SAR_g T \exp (-B / V_f).$$  \hspace{2cm} (5)

To correlate the free volume obtained by the PAL technique to gas diffusivity and permeability, the following equations have been proposed by replacing $V_f$ in Equations (4) and (5) with $V_{FV,Ps}$

$$D = AR_g T \exp (-b / V_{FV,Ps}),$$  \hspace{2cm} (6)

$$P = SAR_g T \exp (-b / V_{FV,Ps}) = CT \exp (-b / V_{FV,Ps}),$$  \hspace{2cm} (7)

where $b$ is a constant depending on the permeant and $C$ is another constant depending on solubility and chain stiffness. Figures 7 and 8 show the plots of $\log P/T$ versus $1/V_{FV,Ps}$ for the permeation of $O_2$ and $H_2$, respectively, in dried Nafion® at different temperatures before and after ion exchange with $Cs^+$ and $Pt^{2+}$. Reasonably good correlations in line with Eq. (7) are observed, indicating the important role played by the free volume in gas permeation. However, the correlation for the $Cs^+$- and $Pt^{2+}$-forms of Nafion® is considerably shifted downward relative to the $H^+$-form. This shift is due to increase in $C$. The rise of transition temperatures upon ion-exchange in Fig. 3 indicates the increased chain stiffness, which is supposed to cause the increase of $C$ and the shift of the correlation between the permeabilities and free volume [21].

![Figure 7](image_url)  \hspace{2cm} ![Figure 8](image_url)

**Figure 7.** Correlation between the permeability of $O_2$ and reciprocal free volume hole size for dry ion-exchanged forms of Nafion® at different temperatures.

**Figure 8.** Correlation between the permeability of $H_2$ and reciprocal free volume hole size for dry ion-exchanged forms of Nafion® at different temperatures.

4. **Conclusions**

In the present work we studied free volume and gases permeation in Nafion® before and after ion exchange with $Cs^+$ and $Pt^{2+}$. The exchange of $H^+$ with $Cs^+$ or $Pt^{2+}$ enlarged the free volume but significantly reduced the gas permeabilities. As evidenced by good correlations between the
permeability and free volume, we confirmed the important role played by the free volume in gas permeation in dry Nafion® (H⁺-, Cs⁺- and Pt²⁺-forms). The smaller gas permeabilities in the Cs⁺- and Pt²⁺-forms of Nafion® than the H⁺-form may be attributed to chain stiffness enhanced by the ion exchange.

Acknowledgments
This work was financially supported by the Ministry of Economy, Trade and Industry (METI) and the New Energy and Industrial Technology Development Organization (NEDO).

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