Per-fluorinated sulfonic acid/PTFE copolymer studied by positron annihilation lifetime and gas permeation techniques

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Abstract. The mechanism of gas permeation in per-fluorinated sulfonic acid/PTFE copolymer Fumapem® membranes for polymer electrolyte fuel cells has been investigated from the viewpoint of free volume. Three different samples, Fumapem® F-950, F-1050 and F-14100 membranes with ion exchange capacity (IEC) = 1.05, 0.95 and 0.71 meq/g, respectively were used after drying. Free volume was quantified using the positron annihilation lifetime (PAL) technique and gas permeabilities were measured for O₂ and H₂ as function of temperature. Good linear correlation between the logarithm of the permeabilities at different temperatures and reciprocal free volume indicate that gas permeation in dry Fumapem® is governed by the free volume. Nevertheless permeabilities are much smaller than the corresponding flexible chain polymer with a similar free volume size due to stiff chains of the perfluoroethylene backbone.

1. Introduction
The polymer electrolyte fuel cell (PEFC) has been considered as one of the most promising power sources for stationary and portable applications [1] due to their high energy conversion efficiency and near-zero pollutant emission. The key element of PEFC is a proton conductive polymer electrolyte membrane (PEM). Currently, per fluorinated membranes and proton conductive polymer, Fumapem® is a commercially available per-fluorinated sulfonic acid/PTFE copolymer membrane used as the electrolyte in polymer electrolyte fuel cells. The proton conductivity must be affected by the electronic state near the ion exchange site, namely hydrophilic site, as well as the structure of nanoscale spaces (free volume). The free volume holes in polymers play a crucial role in determining its physical properties e.g., conductivity, permeability, thermal stability, etc [2]. The Positron Annihilation Lifetime (PAL) technique has been established as a powerful probe for microstructures of polymers; in particular, angstrom-sized free volume holes [3]. Positrons introduced from a radioactive source into a polymer annihilate either from the free state or positronium (Ps), the positron-electron bound state. Positronium can be formed in either a triplet state, ortho-positronium (o-Ps), or a singlet state, para-positronium (p-Ps), depending on the spin combination of the electron and the positron. A correlation between the radius R of a spherical free volume hole and the observed o-Ps lifetimes, τ₃, has been proposed by Tao [3] and Eldrup et al. [4] as follows;
\[
\tau_3 = 0.5 \left\{ 1 - \frac{R}{R_o} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_o} \right) \right\}^{-1} \text{ (ns),} \quad (1)
\]
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 annihilates [5]. The free volume size \(V_{FV,Ps}\) in nm\(^3\) is calculable as:

\[
V_{FV,Ps} = 4\pi R^3/3 \quad \text{(2)}
\]

The free volume hole size obtained by Equations (1) and (2) has been successfully applied to explain diffusion and permeation of various gases in polymers. Muramatsu \textit{et al.} [6] showed that \(V_{FV,Ps}\) can satisfactorily describe the variation of O\(_2\) permeability in both dry and hydrated ethylene vinyl alcohol copolymer. To date, no data regarding free volume and gas permeation is available, so the aim of this work is to study the free volume in dry per-fluorinated sulfonic acid/PTFE copolymer Fumapem® membranes by the PAL technique and relate it to O\(_2\) and H\(_2\) permeabilities. Further we discuss the mechanism of gas permeation based on the correlations between the permeabilities and \(V_{FV,Ps}\).

2. Experimental

P perfluorinated sulfonic acid/PTFE copolymers Fumapem® F-14100, Fumapem® F-1050 and Fumapem® F-950 with ion exchange capacity (IEC) = 0.71, 0.95 and 1.05 meq/g, respectively, were purchased from FuMA-Tech, St. Ingbert, Germany. The chemical structure of the membrane is shown in Figure 1.

\[
\begin{align*}
\text{CF}_2\text{CF}_2 \quad \text{CF} \quad \text{CF}_2\text{CF}_2 \quad \text{CF} \quad \text{CF}_2\text{CF}_2 \quad \text{SO}_3\text{H} \\
\text{CF}_3
\end{align*}
\]

\text{Figure 1.} Chemical structure of Fumapem® F-950, Fumapem® F-1050 and Fumapem® F-14100.

The positron annihilation lifetime (PAL) measurements were performed using a conventional fast-fast coincidence system with a time resolution of 280 ps. Positron lifetime spectra were recorded at different temperatures up to 140 °C with 10 degree steps. Before the measurements, the samples were dried by evacuation for one day at room temperature (~25 °C). The source correction was about 9% and contributed to the short lifetime components. Since we were interested in the long-lived component, this absorption was not separated in the analysis of the lifetime spectra. The PAL spectra, having about one million total counts, were analyzed into three lifetime components using the PALSfit program [7] without constraints or source correction.

Gas permeabilities were measured with a GTR-Tech 30XFST apparatus equipped with a Yanaco G2700T gas chromatograph by monitoring the amounts of O\(_2\) and H\(_2\) that permeated across the membrane from one side to the other. Temperature dependence of the permeation coefficients \(P\) of O\(_2\) and H\(_2\) was also measured from 40 to 120 °C. Ar and He were used as carrier gases of H\(_2\) and O\(_2\), respectively.

3. Results and Discussion

Figure 2 shows the temperature dependence of the o-Ps lifetime \(\tau_3\) and its relative intensity \(I_3\) for dry Fumapem® F-14100, F-1050 and F-950. The right hand ordinate of the left figure represents the free volume hole size quantified by Eqs. (1) and (2). It is seen that the free volume of all the samples is considerably enlarged by thermal expansion. Heating scans show an abrupt change of the thermal expansion coefficient of the free volume 75 - 110 °C which may be attributed to \(\alpha\)-transition caused by the glass transition of Fumapem®. This transition is associated with the onset of long-range mobility of both the main- and side-chains, which is facilitated by a profound weakening of the electrostatic interactions within the ionic aggregates. It is interesting to note that Fumapem® F-950 with higher IEC and little larger free volume than the other samples. The larger slope above the \(\alpha\)-transition
temperature for all the samples suggests that the backbone segmental motions significantly contribute to the free volume at high temperatures. 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. It is clear that sample with low IEC (Fumapem® F-14100) has high intensity compared with that in high IEC (Fumapem® F-950 and/or Fumapem® F-1050). 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.

Figures 3 and 4 show the temperature dependence of H$_2$ and O$_2$ permeabilities of dried Fumapem® F-950, Fumapem® F-1050 and Fumapem® F-14100. It is noticed that both H$_2$ and O$_2$ permeabilities increase by orders of magnitudes with increasing temperature and also they increase with increasing IEC at constant temperature. For example, at 80°C the O$_2$ permeability is $1.44 \times 10^{-13}$ and $3.57 \times 10^{-13}$ cm$^3$ cm$^{-2}$ s$^{-1}$ Pa$^{-1}$ in the Fumapem® F-14100 and Fumapem® F-950, respectively. At all the temperatures studied, H$_2$ is much more permeable than O$_2$. All the samples show similar tendency in H$_2$ and O$_2$ permeations with temperature. The IEC dependence of mass transport parameters can be simply interpreted on the basis of the water content of the fully hydrated membranes. The microstructure of perfluorosulfonate membranes such as Fumapem® is comprised of an amorphous hydrophilic phase containing the hydrated sulfonic acid sites, and partly crystalline hydrophobic Teflon backbone regions. Both of these hydrophobic and hydrophilic phases have been described in prior research similar to Nafion® as having a strong impact on the gases transport process [8]: the aqueous domain (hydrophilic phase) is predominately involved in the O$_2$ diffusion pathway, hence more water uptake enables a higher diffusion coefficient of oxygen in the membrane.

To correlate the hole volume $V_{FV,Ps}$ to gas permeability $P$, the following equation was used [9]:

$$ P = \frac{P_{H_2}}{1 + aT} $$

where $a$ is a constant for each membrane type.
\[ P = CT \exp (-b/V_{FV,Ps}) \]  

where \( b \) is a constant depending on the size of the permeant molecule, \( C \) is another constant depending on solubility and \( T \) is the absolute temperature. Figures 5 and 6 show the plots of \( \log P/T \) versus \( 1/V_{FV,Ps} \) for the permeation of \( \text{H}_2 \) and \( \text{O}_2 \), respectively, in dried three Fumapem® samples at different temperatures. A plot of \( \text{O}_2 \) permeability for relatively flexible chain polymers at different temperatures in vacuum and at different relative humidities at room temperature [6] is also included in Figure 6. The considerable downward deviation of the correlations for Fumapem® may be attributed to the stiff backbones of the ionomer in comparison with the other polymers. Reasonably good correlations in line with Eq. (3) are observed indicating the important role played by the free volume in \( \text{O}_2 \) permeation as shown in Figures 4 and 5. The considerable downward deviation of the correlations form Fumapem® F-950 to Fumapem® F-14100 is attributed to the stiff backbones of the ionomer by decreasing IEC (i.e., the concentration of the sulfonic groups). The stiffness of the ionomer is enhanced by decreasing IEC.

**Figure 5.** Correlation between the permeability of \( \text{H}_2 \) and reciprocal free volume hole size for dried Fumapem® F-950, Fumapem® F-1050 and Fumapem® F-14100 at different temperatures.

**Figure 6.** Correlation between the permeability of \( \text{O}_2 \) and reciprocal free volume hole size for dry ion-exchanged forms of Fumapem® F-950, Fumapem® F-1050 and Fumapem® F-14100 at different temperatures. The small dashed line shows the correlation for relatively flexible chain polymers [6].

4. Conclusion

For the development of a polymer electrolyte membrane with a supreme gas barrier property, molecular design optimizing not only free volume but also polymer stiffness is required.

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