Proton Exchange Membranes for Fuel Cell Applications Prepared by Ion Track Technology

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Proton exchange membranes for use in fuel cells were prepared by our original ion-track technology, which involves (i) the swift heavy ion irradiation of polyvinylidene fluoride films and subsequent chemical etching to obtain cylindrical pores, and (ii) the filling of proton-conducting polymer chains into the etched pores by γ-ray-induced graft polymerization. We found that the membranes possessed one-dimensional straight proton conducting pathways parallel to the ion-beam incident axis. Such restricted structures probably led to less water uptake and lower methanol permeability compared to a commercially-available Nafion membrane.

Key Words : Ion Beam, Track-Etched Membrane, Proton Exchange Membrane, Fuel Cell Application

1 Introduction

The proton exchange membrane (PEM) is a key component in polymer electrolyte membrane fuel cells (PEMFCs) including direct methanol fuel cells (DMFCs). There can be no doubt that significant attention is being focused on the preparation of a variety of membranes as alternatives to Nafion. For the past several years, a group at the Japan Atomic Energy Agency (JAEA) has been independently developing PEM materials, which meet the characteristics required for PEMFC applications such as proton conductivity, mechanical strength, swelling properties, chemical stability, methanol permeability, etc., based on the techniques of polymer crosslinking and graft polymerization induced by ionizing radiation such as γ-rays or electron beam.

On the other hand, this study concerns the application of swift heavy ions, instead of the γ and electron radiations, for the preparation of PEMs. The bombardment of high-energy ions produces cylindrical damage along their trajectory in polymers. Our main focus is the use of such a localized damage area that is called a latent track. The approach using this ion track technology is being taken according to two techniques. One is the track etching and subsequent chemical modification inside the etched pores; and the other is ion-track grafting, i.e., direct grafting into the activated zone. In any case, we are the first to apply such a leading beam-engineering to the PEM preparation.

This communication reports, as the first step, the former attempt including the preparation methodology and properties of the resulting membranes. To be specific, as shown in Fig. 1, the latent track in a fluoropolymer film is preferentially dissolved in an alkaline etching solution to give uniform pores with a diameter of less than a few hundred nanometers, which were then filled with proton-conductive sulfonic acid (SO₃H) groups via the γ-ray-induced graft polymerization of styrene. It is well-known that the track etching technique allows very easy control over the size and shape of the pores compared to the other methods for preparing porous membranes: phase inversion, drawing and extraction processes. The samples were characterized in terms of their proton conductivity, water uptake, methanol permeability and microscopic morphology.

2 Experimental

The commercial fluoropolymer films were employed as a matrix for maintaining a reasonable mechanical and chemical stability. Twenty-five-μm thick poly(vinylidene fluoride) (PVDF) films were bombarded by a 129Xe ion beam with a total energy of 450 MeV[7] (eV = 1.6 × 10⁻¹⁹ J) from a cyclotron at the Takasaki Ion Accelerators for Advanced Radiation Application (TIARA) facility, JAEA. According to a previous study,[8] track etching was then performed in a 9 mol dm⁻³ KOH aqueous solution at 80 °C.

![Fig. 1 Scheme for our membrane preparation based on a heavy-ion irradiation technique: (1) the track etching, and (2) chemical modification for introduction of SO₃H groups into the etched pores.](image-url)
The pore density ranged between $3.0 \times 10^6$ and $3.0 \times 10^8$ cm$^{-2}$, which agreed with the number of actually irradiated ions per 1 cm$^2$.

The γ-ray-induced grafting of styrene onto the PVDF track-etched membranes was performed by our established procedure. The track-etched membranes were irradiated with $^{60}$Co γ-rays at a dose of 160 kGy (Gy = J kg$^{-1}$) in Ar at room temperature. The irradiated films were immediately immersed in neat styrene without exposure to air, and then stored for a certain period at 60 °C. The degree of grafting (%) was determined using the following equation: $100 \times (W_g - W_e)/W_e$, where $W_g$ and $W_e$ are the weights of the grafted and original track-etched films, respectively. For sulfonation, the styrene-grafted films were immersed in a 0.2 mol dm$^{-3}$ chlorosulfonic acid/1,2-dichloroethane mixture at 50 °C for 6 h.

The pore geometry of the track-etched PVDF membrane was confirmed by scanning electron microscope (SEM) observations. The ion exchange capacity (IEC) was determined by acid-base titration. The room-temperature proton conductivity of the fully hydrated membrane was measured in both the in-plane and thickness directions by an AC impedance technique. Water uptake (%) was defined as $100 \times (W_a - W_e)/W_e$, where $W_a$ and $W_e$ are the membrane weights in the wet and dry states, respectively. The methanol permeability was tested at room temperature in a two-compartment diffusion cell, which was filled with a 2 mol dm$^{-3}$ aqueous methanol solution and pure water in each compartment. A transmission electron microscope (TEM) was used to observe the morphology of the proton-conductive, hydrophilic domains in the membranes stained by ruthenium tetroxide (RuO$_4$) vapor.

### 3 Results and Discussion

Chemical etching of the latent tracks, a process of pore formation, depends on many factors such as the sensitivity of the material, the radiation dose, and, obviously, the etching solution and temperature. Since these were kept constant, the only factor that then determines the pore geometry should be the etching time. The evolution of the etched pores was therefore investigated during the course of the chemical etching although this was not our focus. As a result, the pore size was arbitrarily controlled by the etching time in the range of 50-450 nm in diameter. Figure 2 is a representative SEM micrograph of the surface and cross section of the track-etched PVDF films, clearly indicating the formation of cylindrical and open pores. This was consistent with the results by other researchers.

Yamaguchi et al. previously proposed a similar concept of membrane development. The pore-filling type membrane was prepared by anchoring the polyelectrolyte within the pores of a commercially-available porous polymer matrix for DMFC applications. However, our approach is different in that the porous substrate had an excellent uniformity of pore diameters (as also clarified in Fig. 2) in contrast to the three-dimensional random porous media used in a previous study. Another difference was the membrane porosity, which is widely controlled by a change in the experimental conditions. This was kept here as low as possible (up to 30% at most) in our expectation of improvement of the mechanical properties, while the usual porous substrate exhibited a 50% porosity or greater.

We now present the results of the styrene grafting onto the PVDF track-etched membranes with 100-nm diameter pores (area density: $3.0 \times 10^8$ cm$^{-2}$), which were obtained by a 50-h alkaline treatment. The prepared PEMs and their properties are listed in Table 1. Radiation-induced grafting has always been performed with γ-rays and electron beams. Nevertheless, it should be emphasized here that the grafting reactions were controlled with special consideration of their diffusion.

![Fig. 2 Representative SEM images of the PVDF track-etched membranes; (a) surface pores, and (b) cross section where the cylindrical pore appears to extend parallel to the transverse (i.e., thickness) direction.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degree of grafting (%)</th>
<th>IEC (mmol g$^{-1}$)</th>
<th>Conductivity (S cm$^{-1}$)</th>
<th>Methanol permeability ($\times 10^{-8}$ cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Thickness</td>
<td>In-plane</td>
</tr>
<tr>
<td>#1</td>
<td>6.9</td>
<td>0.40</td>
<td>0.003</td>
<td>N.D. ($^{a1}$)</td>
</tr>
<tr>
<td>#2</td>
<td>11</td>
<td>0.70</td>
<td>0.004</td>
<td>N.D.</td>
</tr>
<tr>
<td>#3</td>
<td>24</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>#4</td>
<td>23</td>
<td>1.6</td>
<td>0.024</td>
<td>N.D.</td>
</tr>
<tr>
<td>#5</td>
<td>53</td>
<td>2.6</td>
<td>0.054</td>
<td>0.043</td>
</tr>
<tr>
<td>Nafion117</td>
<td>–</td>
<td>0.91</td>
<td>0.08</td>
<td>0.08</td>
</tr>
</tbody>
</table>

$^{a1}$ This means “not detectable".
limiting properties. Irradiation with γ-rays or electrons induces a uniform distribution of radicals in the polymer films with a thickness up to millimeters, leading to a homogeneously grafted copolymer when the grafting reaction reaches a steady state. In this case, on the other hand, the graft chains must grow only on or near the internal walls of the pores, and also both sides of the membrane surface, without uniformly distributing them all over the film together with monomer diffusion. Thus the reaction was stopped in a very short time within 1 h from the beginning. The SEM images exhibited a smooth surface of the membranes, which confirms the filling of the poly styrene grafts into all the pores.

These grafted films were sulfonated under the above conditions to obtain the PEMs. On the basis of a simple calculation, we found that in the membranes, the number of SO₃H groups was almost identical to that of the aromatic rings of the styrene units. This suggests that the films at all degrees of grafting were fully sulfonated. Here again, note that the graft-chain distribution must be considered very crucial. As long as this requirement is fulfilled, it is possible to prepare membranes with the desired ionic content by the proper selection of the degree of grafting.

It becomes important to compare the σ values between that perpendicular to and along the surface direction. The latter in-plane measurement was carried out using two electrodes in an alternate configuration on either side as shown in Table 1. The σ in the thickness direction showed an increasing trend with the IEC. However, no in-plane value was surprisingly obtained at < 1.6 mmol g⁻¹ probably because it was too low to be detected (denoted by N.D. in the table). This anisotropic conductive property undoubtedly indicates the formation of one-dimensional straight proton conductive pathways parallel to the ion-beam incident axis. In contrast, the in-plane conductivity appeared in the membrane with a higher ionic content due to the progress of the grafting reaction to the innermost part with an increasing penetration depth.

In our measurement, Nafion117 exhibited the σ value of 0.08 S cm⁻¹ in both directions. On the other hand, the pore-filling membrane based on a porous PTFE substrate (see above) possessed a σ value of about 0.03 S cm⁻¹ under the same conditions, which was no greater than that shown in Table 1 (sample #4). Considering the lower porosity of the substrate matrix (24% in this case), we would say that the value obtained here was rather sufficient although it did not reach that of Nafion117.

Figure 3 is a TEM micrograph of a section of the PEMs with an anisotropic proton conductivity (sample #2). The micrograph revealed that the RuO₂-stained lines with about a 100 nm width were arranged almost perpendicular to the surface direction although all of them did not appear continuous due to a technical difficulty in producing very thin slices using the microtome. Thus it was confirmed that the membranes had a cylindrical electrolyte part with a diameter of about 100 nm, comparable to the size of the etched pore. This result demonstrates that grafting mainly occurred on the surface and inner pore wall of the track-etched membrane without extensive styrene diffusion into the internal bulk layer.

Figure 4 shows a plot of water uptake versus the IEC of our membrane prepared by ion-track technology. In all cases, the water uptake of the nano-structure controlled membranes was enhanced with an increase in the IEC. A notable result was apparent from the comparison with the properties of not only a Nafion membrane, but also the proton exchange membranes separately obtained by the usual γ-ray-induced homogeneous grafting (result not shown). The water uptake was found to be lower than the homogeneously-grafted membranes in spite of the same IEC; for example, it decreased from 36% to 23% (up to about two-thirds) at an IEC of 1.6 mmol g⁻¹. An inert fluoropolymer host was found to restrict the swelling of the entire membrane. However, as expected from the result of the proton conductivity, the swelling largely increased to converge to the same degree for both membranes at the higher IEC. Sample #5 was never the target material and should be excluded from

![Fig. 3 Cross-sectional TEM micrograph of the RuO₂-stained electrolyte membrane possessing an IEC of 0.70 mmol g⁻¹ (sample #2). The surface of the membrane is marked by the arrow outside the micrograph.](image)

![Fig. 4 A plot of water uptake versus the IEC of our membrane prepared by ion-track technology (samples #1 to #5; filled circle). For comparison, the result of Nafion117 is also plotted (open circle).](image)
our following investigation.

Accordingly, we expect that the membranes also show restricted swelling properties in methanol-water mixtures, which lead to the reduction of methanol transport through the membrane. In fact, the permeability of the PEMs with IECs of 0.70 and 1.3 mmol g\(^{-1}\) (samples #2 and #3) was determined to be $3.4 \times 10^4$ and $3.9 \times 10^7$ cm\(^2\) s\(^{-1}\), respectively. This is roughly 50 and 5 times lower than that of Nafion117, respectively. A metric for selecting a high performance PEM is its electrochemical selectivity, which is defined as a ratio of its proton conductivity to methanol permeability.\(^{10}\) Here, because both the values were obtained for sample #2 only, we tentatively try to combine the results of samples #3 (methanol permeability) and #4 (conductivity in the thickness direction) with the similar grafting yield or IEC and then compare them to that of Nafion117. This implies the higher selectivity of our membranes, although the possibility that such a comparison might be far from exact cannot be entirely excluded. It can be concluded, therefore, that the membranes are possibly applicable for use in a DMFC, thus extending the PEM performance beyond the limit of conventional ones.

Finally, our approach based on ion track technology is unique in the following two ways: (i) it is possible to easily control the size and area density as well as the total volume percentage of the electrolyte part by varying the conditions of the ion-beam irradiation and chemical etching. Therefore, this method probably assesses the higher degree of design freedom in performance control; (ii) The membrane has perfect one-dimensional proton-conductive pathways parallel to its thickness direction while the transport generally occurs in the three-dimensional random media. Such materials likely become interesting due to their specific structure, especially the microscopic domain of the proton conductive pathways. The research regarding these technical and scientific aspects is now in progress.

4 Conclusion

As a new technique for the PEM preparation, we demonstrated chemical track etching for obtaining uniform 100-nm cylindrical pores and then the subsequent chemical modification on the internal surfaces of the etched pores to be filled with proton-conductive electrolyte parts. The resulting membranes prepared based on this swift-heavy-ion technology characteristically possessed straight, proton-conductive pathways extending along the ion trajectory. They were found to exhibit a lower water uptake and reduced methanol permeability compared to the Nafion membrane.

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References

7) The energy per atomic mass unit corresponding to the incident-ion velocity was calculated to be 3.5 MeV/n.