# Methanol Permeation Properties of Crosslinked-PTFE Electrolyte Membranes for DMFC Applications

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We prepared the polymer electrolyte membranes with a controlled ion exchange capacity (*IEC*) by the radiation-induced grafting of styrene into crosslinked polytetrafluoroethylene (PTFE) films and subsequent sulfonation, and then investigated their methanol permeation properties. The permeabilities of the electrolyte membranes based on radiation-crosslinked PTFE films increased with their *IEC* up to 3.0 meq $g^{-1}$, nevertheless, they were less permeable than Nafion, suggesting their high applicability to direct methanol fuel cells. Since the enhancement in permeation was accompanied by the uptake of an aqueous methanol solution into the membrane, expansion of hydrophilic regions as methanol transport pathways is considered to facilitate the permeation. It was found that the sulfonated polystyrene graft chains controlled the permeability and swelling of the membranes probably because of lower hydrophobicity of the hydrocarbon backbones. The permeability and solution uptake decreased as the crosslinking density of PTFE increased. This undoubtedly demonstrates the contribution of the crosslinks to the excellent barrier properties against methanol.
Key words: Direct Methanol Fuel Cell (DMFC), Crosslinked PTFE Electrolyte Membranes, Methanol Crossover

## 1. INTRODUCTION

In recent years, since the power consumption of mobile machineries such as note PCs and cellular phones has increased, enough operation time cannot be obtained by the conventional lithium-ion batteries. According to such limitations, direct methanol fuel cells (DMFCs), categorized as polymer electrolyte fuel cells (PEFCs), have been expected to have high power output per unit volume and superior portability. This is because an aqueous methanol solution is directly supplied to the anode as fuel [1].

The performance of the DMFCs strongly depends on the properties of a proton conducting polymer electrolyte membrane as a separator between the electrodes. In the case of Dupont's Nafion, the polymer electrolyte membrane most frequently used for PEFC applications, for example, methanol unexpectedly diffuses across it from the anode although it exhibits high chemical and thermal stability [2-4]. This so-called methanol crossover causes not only the waste of fuel but also the poisoning of the cathode catalyst. Thus concentrated methanol solutions cannot be used as they are for fuelling the anode of the DMFCs. At present, therefore, their dilution to concentrations as low as 1 mol $dm^{-3}$ is essential before use, hindering the high energy density as expected in the above.

The poor methanol-control capability of Nafion was explained by considering its molecular structure. Nafion has, in a macromolecule, both the hydrophobic part of the polytetrafluoroethylene (PTFE) backbone and the hydrophilic part containing the sulfonic acid groups. This underwent nano-phase separation between these two parts in contact with water or its alcohol mixtures. Such distinctive hydrophobic-hydrophilic interaction gave rise to excessive expansion of hydrophilic regions resulting in awfully large membrane swelling [5,6]. On the other hand, many researchers have reported lower methanol permeability of the electrolyte membranes based on hydrocarbon polymers such as sulfonated poly ether ketone [5] and aromatic polyimides [7]. These membranes seem to be promising for DMFCs and,

however, there remains a crucial problem related to the durability because they have no chemically-stable fluorocarbon structure [8].

We independently focused on the electrolyte membrane based on a PTFE film crosslinked with ionizing radiation [9-11]. The preparation of the membrane includes the radiation-induced grafting of styrene into the crosslinked PTFE films and subsequent sulfonation. In this method, the ion exchange capacity (*IEC*) was controlled up to about 3 meq $g^{-1}$ depending on the amount of graft components. It is expected that the membrane will exhibit lower methanol permeability because of the following two reasons. (i) The membrane is regarded as a hybrid system of the fluorocarbon (PTFE main chain) and sulfonated hydrocarbon polymer (polystyrene) grafts. These constituents can improve the durability, and reduce permeation and membrane swelling, respectively. The radiation grafting technique enables us to realize such hybridization, where each component is never compatible. (ii) In contrast to linear-chain Nafion, the membrane has a network structure due to the crosslinks in the PTFE substrate. This should provide high methanol barrier ability as well as defined swelling behavior in the water/methanol mixture. In this paper, we investigated the methanol permeation properties of the crosslinked-PTFE electrolyte membranes with various *IEC*s under the condition of high methanol concentrations (> 1 mol $dm^{-3}$). Also, the influence of the graft chains and the PTFE crosslinks was separately discussed.

## 2. EXPERIMENTAL

### 2.1 Synthesis of electrolyte membranes

The membrane synthesis was carried out as already reported [9,10]. We used, as a base material, a 42-μm thick film of PTFE crosslinked with electron beams at total doses of 100-400 kGy. For the grafting, the crosslinked PTFE film was irradiated again with γ-rays at 60 kGy in a grass ampoule filled with Ar at room temperature. The irradiated films were immediately

immersed in a styrene monomer and its toluene solution (deaerated by Ar bubbling before use), where they were kept for 1-48 hours at 60°C. In this method, graft polymerization of monomers starts from the radicals generated on the PTFE backbones by the γ-ray irradiation and proceeds during the course of time. Thus the grafting time will vary the chain length of graft polystyrene.

After the grafting reaction, the films were taken out from the ampoule and washed with toluene to remove any excess styrene and homopolymer. The grafted films were then dried in a vacuum at 50°C to a constant weight. The degree of grafting (*DOG*) was defined as follows:

$$DOG\ (\%) = \frac{W_g - W_o}{W_o} \times 100$$

where $W_o$ and $W_g$ are the weights of the original and grafted films, respectively.

The grafted films were sulfonated using a mixture of 0.2 mol dm$^{-3}$ chlorosulfonic acid/1,2-dichloroethane at 50°C for 6 hours. Finally, the resulting membranes were rinsed with pure water and then dried in a vacuum oven.

## 2.2 Measurements
### 2.2.1 *IEC*

The membranes in an acid form were equilibrated in a 3 mol dm$^{-3}$ aqueous NaCl solution for 6 hours at 50 °C. The solution containing protons released from the membrane was titrated with a standardized 0.1 mol dm$^{-3}$ NaOH solution by an automatic titrator until pH 7 was reached. The amount of protons in the membrane was determined from the volume of the NaOH solution consumed in titration and so the *IEC* was evaluated by:

$$IEC\ (\text{meq g}^{-1}) = \frac{1000 \times N_s}{W_d},$$

where $N_s$ and $W_d$ are the number of the sulfonic acid (mol) and the weight of the dried membrane (g), respectively.

### 2.2.2 Uptake of aqueous methanol solutions

The dry membrane was equilibrated in the aqueous methanol solution at room temperature for 24 hours. After the swollen membrane was taken out, the solution-adhering surface was wiped with filter paper to weigh it as quickly as possible. The solution uptake, Q , was defined as the following equation:

$$Q\ (\%) = \frac{W_{swollen} - W_d}{W_d} = \times 100\,,$$

where $W_{swollen}$ is the weight of the swollen membrane (g).

### 2.2.3 Methanol permeability

Methanol permeability was measured at room temperature using an in-house diffusion cell shown in Fig. 1. The cell had two 100-ml compartments, into which we divided by the electrolyte membrane with a 4.9 cm$^2$ area. Compartment B was filled with pure water and, at the same time, an aqueous methanol solution at concentrations of 1-10 mol dm$^{-3}$ was poured into compartment A. The content in each compartment was kept being circulated slowly during the course of the experiment. The concentration of methanol was detected for 3 hours from the beginning using a methanol analyzer (INCOM Co.; FCD-100) [12]. The data on time variation of the methanol concentration showed a linear slope. The methanol permeability, P, is expressed as

[6,13]:

$$Slope = \left(\frac{dC_B}{dt}\right) = \frac{A}{V_B}\frac{P}{L}C_A$$

$$P\,(\text{cm}^2\ \text{s}^{-1}) = Slope \times \left(\frac{V_B L}{AC_A}\right)$$

where $C_A$ (mol dm$^{-3}$) and $C_B$ (mol dm$^{-3}$) are the methanol concentrations of compartments A and B, respectively. $C_A$ is assumed constant because the measuring time was enough short. A, L and $V_B$ are the effective area, the thickness of the swollen membrane and the volume of compartment B after the permeation, respectively
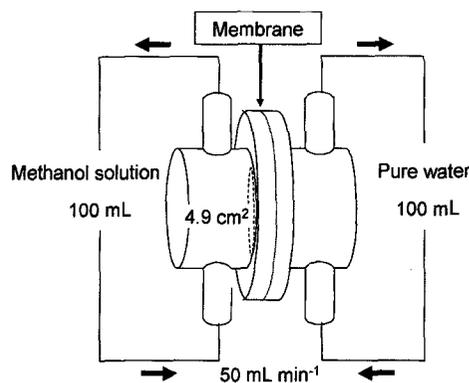


Fig. 1 Schematic picture of the diffusion cell for the methanol permeation measurements.

## 3. RESULTS AND DISCUSSION
### 3.1 Membranes

Fig. 2 shows the *DOG* vs. time curves for the styrene grafting into the PTFE films crosslinked at a dose of 100 kGy. The results of the non-crosslinked film are also presented for comparison. In this case, the *DOG*s gradually increased during the first 3 hours and then leveled off at a saturated value of about 35%. On the contrary, the crosslinked films exhibited a much higher *DOG* at all the grafting times, and it reached almost 100%. These observations, similar to that of our previous reports [8,9], indicate that the use of the crosslinked films enabled us to obtain a wide range of *DOG*s depending on reaction time. But then, the only technical drawback of the present method was the difficulty in controlling *DOG*s at lower level because of their too high increase rate. This is why the styrene monomer diluted by 40vol% in toluene was used as the grafting solution. As also shown in Fig. 2, the films at the *DOG*s of < 40% were obtained in a reproducible fashion within ten hours of reaction time and consequently, the *DOG* determining the *IEC* of the membrane ranged from 20 to 100%.

The grafted films were then sulfonated under the above conditions to obtain proton exchange membranes. The ratio of the sulfonic acid group to the styrene unit was found to be close to unity, suggesting that the films at all *DOG*s were fully sulfonated. The membranes showed the *IEC*s of 1.0-3.0 meq g$^{-1}$ depending on the *DOG*. Since the grafting reaction in the pre-irradiation method proceeds from the surface of the film into the interior, it is regarded as a diffusion-controlled system. It was confirmed that the reaction for over 3 hours afforded ion exchange membranes with an even concentration profile of sulfonic acid groups over the range of thickness. Such homogeneous membranes can establish uniform properties in relation to their methanol permeability and swelling behavior.
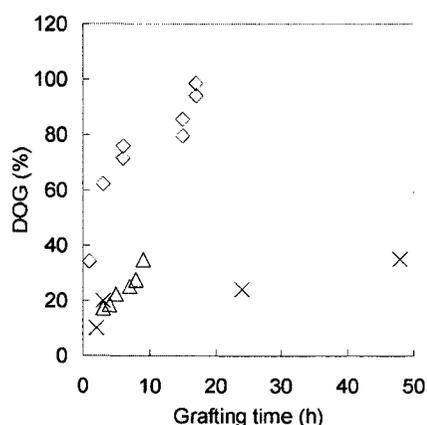
Fig. 2 The *DOG* vs. time curves for the styrene grafting; substrate: a 100-kGy crosslinked PTFE film, the pre-irradiation dose: 60 kGy, the grafting solution: neat (◇) or 40vol% (△) styrene. The results of the grafting into the non-crosslinked PTFE films ( × ) are also compared.

### 3.2 Methanol permeability

Fig. 3 shows the methanol permeability at $C_A = 2$ mol dm$^{-3}$ of 100-kGy crosslinked-PTFE electrolyte membranes as a function of *IEC*. The values of P increased with the *IEC*s and reached $1.8 \times 10^{-6}$ cm$^2$ s$^{-1}$ at an *IEC* of 2.7 meq g$^{-1}$. This was lower than that of Nafion ($1.9 \times 10^{-6}$ cm$^2$ s$^{-1}$) in spite of the three times higher *IEC* of the membrane. When compared at the same *IEC* as Nafion, i.e., around 1.0 meq g$^{-1}$, the membrane was almost five times less permeable. Such a fair comparison reveals the great ability of our membranes to inhibit the permeation of methanol in water.
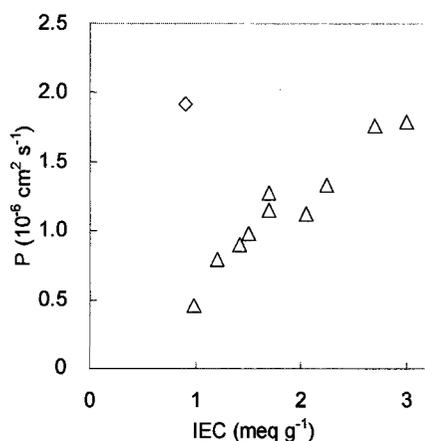


Fig. 3 Plots of P vs. *IEC* for 100-kGy crosslinked-PTFE electrolyte membranes at $C_A = 2$ mol dm$^{-3}$. The result of Nafion (◇) is also compared in this figure.

As mentioned in the introduction, it is accepted that methanol permeability concerns with membrane swelling in the aqueous methanol solution: the methanol barrier property deteriorates as the solution uptake becomes high. Fig. 4 shows Q values at a methanol concentration of 2 mol dm$^{-3}$ as a function of *IEC*. The value of Q appeared to increase linearly with *IEC*s; in other words, it exhibited a similar trend to P shown in Fig. 3. This result suggests that as in the case of Nafion, expansion of hydrophilic regions allowed methanol to permeate easily through the membrane. Anyway, it should be emphasized here that the radiation grafting of

styrene into the crosslinked PTFE films provided the membranes with a superior barrier property to the methanol solution as well as higher *IEC*s compared to commercially-available perfluorosulfonic acid membranes such as Nafion.
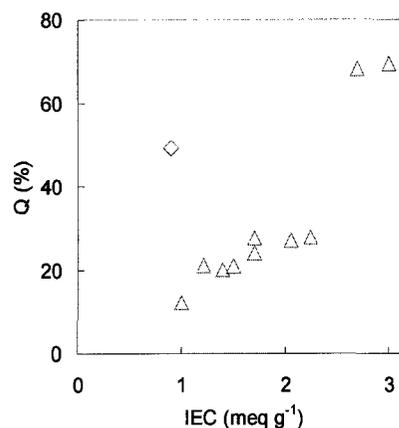


Fig. 4 Plots of Q at a concentration of 2 mol dm$^{-3}$ vs. *IEC* for 100-kGy crosslinked-PTFE electrolyte membranes. The result of Nafion (◇) is also compared in this figure.

In order to rationalize the high performance being up to our expectations, we consider two factors, i.e., a sulfonated hydrocarbon polymer as graft component and crosslinking structure of PTFE as a base polymer, both of which are likely to influence the methanol permeability of the membrane, of course, although the possibility that the permeation process might involve some complexities cannot be entirely excluded. Fig. 5 presents the P values at $C_A = 2$ mol dm$^{-3}$ for electrolyte membranes based on non-crosslinked, 100- and 400-kGy crosslinked PTFE fillms, together with their Q at the same concentration. All the three membranes compared here possessed an *IEC* of 1.2 meq g$^{-1}$, which is about equal to Nafion's. Based on this figure, the reasonable explanation is given in the following.

At first, the result of the non-crosslinked PTFE-based electrolyte membrane is compared to that of Nafion. There is no crosslink in the fluoropolymer part of both these membranes. Accordingly, this comparison could make it possible to discuss the effect of the hydrocarbon graft component on the methanol permeation and swelling property to the exclusion of everything else affecting them. It was found that the P and Q values were reduced by about half from Nafion. This observation provides absolute evidence that a hybridization of the hydrocarbon graft component with the PTFE part, not a perfluoro molecular structure like Nafion, is one of the origins of methanol-control capability of the membrane. Less hydrophilic polystyrene sulfonic acid can lead to indistinctive phase separation due to its interaction with the other hydrophobic part.

Next, how the crosslinking of PTFE influenced the P and Q values? Compared among the membranes based on non-crosslinked, 100-, 400-kGy crosslinked PTFE films, they apparently decreased in this order. For example, the 400-kGy crosslinked electrolyte membrane exhibited P = $0.3 \times 10^{-6}$ cm$^2$ s$^{-1}$, which was roughly one-quarter that of the non-crosslinked one ($1.1 \times 10^{-6}$ cm$^2$ s$^{-1}$). In addition, Q also appeared to decrease considerably in parallel with P. The network structure due to the crosslinks in the PTFE main chain probably restricts membrane swelling, more microscopically expansion of hydrophilic regions as methanol transport pathways, thereby improving the methanol barrier property.
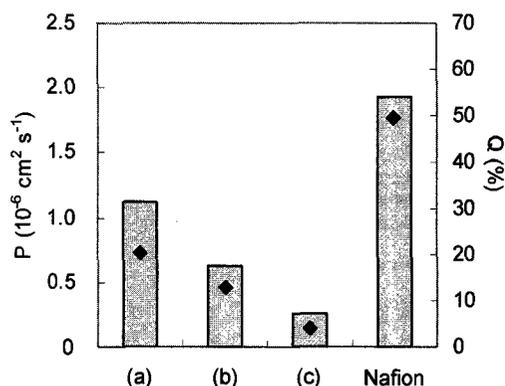
Fig. 5 The P values (bar) at $C_A$ = 2 mol dm$^{-3}$ for electrolyte membranes based on (a) non-crosslinked, (b) 100- and (c) 400-kGy crosslinked PTFE films, together with their Q (◆) at the same concentration. All the three membranes compared here possessed the *IEC* of 1.2 meq g$^{-1}$. The figure also contains the results of Nafion.

For practical applications to DMFCs with high energy density, the concentrated methanol aqueous solution needs to be directly supplied to the anode. Fig. 6 plots the P values of the 100-kGy crosslinked PTFE electrolyte membranes with *IEC*s of 1.0, 2.0, and 3.0 meq g$^{-1}$ under various $C_A$ conditions. Strikingly in the crosslinked-PTFE electrolyte membrane, P was found to become lower at higher $C_A$. This decreasing trend, being especially true at higher *IEC*s, is in contrast to a continuous increase observed for Nafion as has been reported in a number of papers [5,6,13]. Generally, sulfonic acid membranes never show such behavior and so the result cannot be explained at present. There might be correlation with not only the above two factors, the fluorocarbon-hydrocarbon hybridized structures and PTFE crosslinks, but also the unique nature of the hydrophilic regions themselves given by the very fine balance between the base and graft polymers. If so, it is assumed as a range of possibilities that the difference in the interaction involved in the membrane-constituent polymers is prominent in contact with the aqueous methanol solution at higher concentrations.
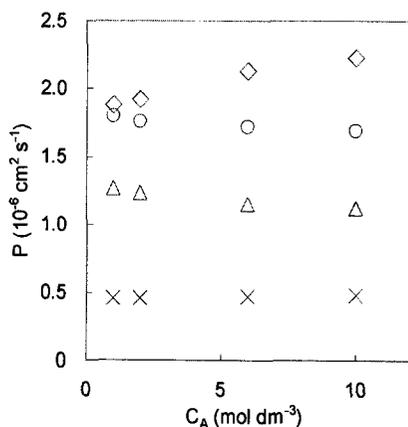


Fig. 6 Plots of P for 100-kGy crosslinked-PTFE electrolyte membranes with *IEC*s of 1.0 (×), 2.0 (△) and 3.0 meq g$^{-1}$ (○) under various $C_A$ conditions. The figure also contains the results of Nafion (◇).

It is necessary to investigate the microscopic interactions among methanol, water, the PTFE backbone and polystyrene sulfonic acid groups. This will provide an insight into the mechanism of methanol permeation through the membrane. Actually, our radiation-grafted sulfonated electrolyte membranes contain a large amount of PTFE microcrystallites originating from the

base film. To be exact, therefore, crystallinity should also be taken into consideration especially when their methanol permeability is discussed for such a scientific purpose. The study in this regard is now in progress. From the standpoint of development of high-performance membranes, the most important result of this paper was that our membranes showed restricted swelling properties in methanol/water mixtures and a greater barrier to methanol permeation even in the high concentration range. Our future expectation is that the membranes hardly suffer from severe mechanical limitations at larger *IEC*. These should encourage the application of the obtained membrane to the construction material in DMFCs, thus extending the performance beyond the limit of conventional ones.

## 4. CONCLUSIONS

The electron-beam-crosslinked PTFE-based electrolyte membranes with different *IEC*s were investigated in terms of their methanol permeability, related to the effects of the polystyrene sulfonic acid graft chains and PTFE crosslinks. The P value at $C_A$ = 2 mol dm$^{-3}$ became large as the *IEC* was varied from 1.0 to 3.0 meq g$^{-1}$. According to a similar *IEC* dependence of Q, we thus consider the expanded methanol transport route, in other words the large aggregation of the sulfonic acid groups and water, to be origin of the accelerated permeation. However, despite higher ionic content compared to Nafion, all of the membranes were less permeable and more dimensionally stable than it. Such a high tolerance to the aqueous methanol solution was found to come from the polystyrene sulfonic acid component introduced by the radiation-induced grafting. As reported by many research groups, the distinctive nano-phase separation between the hydrophobic and hydrophilic parts could not occur in the membranes containing the hydrocarbon polymer-based sulfonic acid groups. This result indicates the effectiveness of fluorocarbon-hydrocarbon hybridization characteristic of our membranes. Moreover, the PTFE crosslinks Nafion never has also restricted the membrane swelling, and thereby enhancing the barrier to methanol permeation. From these two structural properties, we can expect practical applications to electrolyte membranes in DMFCs.

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