

# Chemical and radiation crosslinked polymer electrolyte membranes prepared from radiation-grafted ETFE films for DMFC applications

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## Abstract

To develop a highly chemically stable polymer electrolyte membrane for application in a direct methanol fuel cell (DMFC), doubly crosslinked membranes were prepared by chemical crosslinking using bifunctional monomers, such as divinylbenzene (DVB) and bis(*p,p*-vinyl phenyl) ethane (BVPE), and by radiation crosslinking. The membranes were prepared by grafting of *m,p*-methylstyrene (MeSt) and *p-tert*-butylstyrene (*t*BuSt) into poly(ethylene-*co*-tetrafluoroethylene) (ETFE) films and subsequent sulfonation. The effects of the DVB and BVPE crosslinkers on the grafting kinetics and the properties of the prepared membranes, such as water uptake, proton conductivity and chemical stability were investigated. Radiation crosslinking was introduced by irradiation of the ETFE base film, the grafted film or the sulfonated membrane. The membrane crosslinked by DVB and BVPE crosslinkers and post-crosslinked by  $\gamma$ -ray irradiation of the corresponding grafted film possessed the highest chemical stability among the prepared membranes, a significantly lower methanol permeability compared to Nafion® membranes, and a better DMFC performance for high methanol feed concentration. Therefore, this doubly crosslinked membrane was promising for application in a DMFC where relatively high methanol concentration could be fed.

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**Keywords:** Polymer electrolyte membrane; Radiation grafting; Radiation crosslinking; Methanol permeability; Chemical stability; Direct methanol fuel cell

## 1. Introduction

Direct methanol fuel cells (DMFCs) have good potentialities for applications as power sources in portable and mobile devices due to their high power density and low emission. In essence, a DMFC consists of an anode to which methanol aqueous solution is directly supplied, a cathode to which oxygen is supplied, and a polymer electrolyte membrane that prevents mixing of the methanol and oxygen and permits the proton transportation from anode to cathode [1]. Today, commercially available DMFCs are based on Nafion® membranes or similar perfluorosulfonic membranes, which have excellent stability and high proton conduction. However, the use of methanol fuel with high concentration inevitably causes extensive degradation of performance because of drastic methanol crossover in those perfluorosulfonic membranes. This requires the extra auxiliary equipment

to dilute methanol with water more than 10 times, forcing the decrease in energy density of the system. Therefore, many efforts have been devoted to the modification of Nafion® membranes and to the development of new polymer electrolyte membranes. For instance, modifications of Nafion® membranes by introduction of inorganic particles or by coating organic layers on their surfaces can control the methanol crossover to a certain extent [2,3]. The new membranes under development include sulfonated hydrocarbon membranes [4], hybrid membranes [5] and radiation-grafted membranes [6,7]. In general, hydrocarbon or partially fluorinated membranes possess considerably lower methanol permeability, which allows the corresponding DMFC to be operated with a high methanol concentration. The high methanol concentration in fuel is more effective for reducing the mass and the volume of the cell and is possible for eliminating the need for a methanol dilution system in portable systems. However, the properties such as proton conductivity, mechanical strength and chemical stability of the hydrocarbon and partially fluorinated membranes have not yet reached a satisfactory level for commercial use in the market [7].

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The greater methanol crossover of Nafion<sup>®</sup> membranes may be due to its lack of a crosslinked structure. Efforts for introduction of a crosslinking structure into Nafion<sup>®</sup> membranes have been performed in our group. However, there are no satisfactory results yet that could be presented. On the other hand, the radiation-grafted membrane has a special chemical structure, composing of fluorinated main chains and sulfonated side chains. The former acts as a stable backbone that gives the necessary strength, dimensional stability and gas barrier while the latter gives the ability of proton transportation. A crosslinking structure can be readily introduced into the radiation-grafted membranes by graft copolymerization of bifunctional monomers, such as divinylbenzene (DVB). Styrene has been used to graft because the monomer units can be easily sulfonated to introduce sulfonic acid groups into the membranes. Introduction of a crosslinking structure into the membranes not only suppresses the methanol permeability but also improves membrane properties such as chemical stability [6,7]. The performance of a H<sub>2</sub>/O<sub>2</sub>-fed fuel cell containing such membranes compares favorably with that of cell containing Nafion<sup>®</sup> membranes, and the longest durability of the styrene/DVB-grafted membranes in the H<sub>2</sub>/O<sub>2</sub>-fed fuel cell has been reported to be 10,000 h [8,9]. On the other hand, Aricò et al. also reported that the performance degradation of a DMFC containing styrene/DVB-grafted poly(ethylene-co-tetrafluoroethylene) (ETFE) membranes operated for 1 month at 110 °C was significantly lower [10].

These results greatly encourage us to study the radiation-grafted membranes with the purpose of developing a long-term and high performance membrane. In our previous study [11], we prepared radiation-grafted membranes by graft copolymerization of *m,p*-methylstyrene (MeSt) and *p-tert*-butylstyrene (*t*BuSt) into ETFE films and subsequent sulfonation. The methyl and *tert*-butyl groups attached on the aromatic rings can modify the electronic structure of the aromatic ring and thus increase the stability of the  $\alpha$ -hydrogen of the graft chain [12,13]. Chemical crosslinking was introduced into the MeSt/*t*BuSt-grafted membranes by a DVB crosslinker for improvement of the chemical stability of the resulting membranes. The prepared membranes show a considerably higher chemical stability than the styrene/DVB-grafted membrane. However, the chemical crosslinking by a DVB crosslinker occurs only in the graft chains, and further introduction of the crosslinking structure leads to brittleness and lower proton conductivity of the membranes.

On the other hand, radiation crosslinking of a polymer has been well documented over the past 40 years [14]. For instance, radiation crosslinking has been used in the wire and cable industries, in which polyethylene (PE) and polyvinylchloride (PVC) are crosslinked to improve their thermal stability and mechanical strength [15]. In this study, the ETFE polymer used as the base film occupies a special position among fluoropolymers as it contains alternating structural units of PE and poly(tetrafluoroethylene) (PTFE) that confers it a unique combination of properties imparted from both fluoropolymer and hydrocarbon polymer. The ETFE film can be crosslinked by  $\gamma$ -ray or electron-beam irradiation at room temperature under oxygen-free atmosphere [16,17]. The use of a radiation crosslinking tech-

nique in the preparation of a highly crosslinked polymer electrolyte membrane is, therefore, taken into consideration in this study. By means of the radiation crosslinking, the thermal, chemical, mechanical barrier, and other properties of the radiation-crosslinked ETFE films can be improved [18].

In this study, a double crosslinking of the membranes was introduced by chemical and radiation crosslinking. Chemical crosslinking was introduced by graft copolymerization of monomers with DVB and bis(*p,p*-vinyl phenyl) ethane (BVPE) crosslinkers into the ETFE base film. Radiation crosslinking was introduced by  $\gamma$ -ray irradiation of the ETFE base film, the grafted film or the sulfonated membrane at room temperature under argon gas. In addition, the cell performance of a DMFC employing the doubly crosslinked membrane fed with 1 and 5 M methanol solutions was assessed.

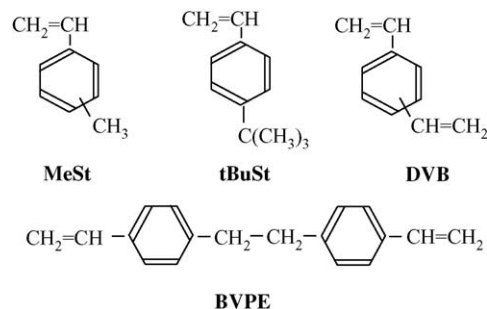
## 2. Experimental

### 2.1. Materials

The monomers of *m,p*-methylstyrene (MeSt, 99%, inhibited with 50 ppm *p-tert*-butylcatechol) and *p-tert*-butylstyrene (*t*BuSt, 93%, inhibited with 100 ppm *p-tert*-butylcatechol) were purchased from Aldrich. Divinylbenzene (DVB, 55% mixture of isomers, 45% of ethylvinylbenzene) and bis(*p,p*-vinyl phenyl) ethane (BVPE) were purchased from Wako Pure Chemical Ind., Ltd., Japan. The DVB and BVPE were used as crosslinkers. The monomers (containing crosslinkers) were used without further treatment. The chemical structures of the monomers are shown in Scheme 1. The ETFE film (25  $\mu$ m) was kindly provided by Asahi Glass Co., Japan and was washed with acetone to remove any impurity on its surface before use. The Nafion<sup>®</sup> 117 membrane (DuPont) was stored in distilled water at room temperature before use without any further treatment.

### 2.2. Preparation of the polymer electrolyte membranes

The preparation of the new polymer electrolyte membranes has been described in Ref. [11]. The ETFE films were  $\gamma$ -ray preirradiated under argon gas at room temperature, with an irradiation dose of 15 kGy. The preirradiated ETFE films were immersed into a monomer solution to initiate the grafting under argon gas at 50 °C. The compositions of the monomer solution are shown in Table 1. The degree of grafting was calcu-



Scheme 1. Monomers and crosslinkers used in this study.

Table 1  
Monomer solutions used in this study

Membrane	Crosslinking type	Monomer (g)		Crosslinker (g)		Toluene (g)
		MeSt	tBuSt	DVB	BVPE	
A	BVPE-crosslinked	40	40	–	20	150
B	DVB-crosslinked	47.5	47.5	5	–	150
C	DVB/BVPE-crosslinked	40	40	2.5	17.5	150
D	DVB/BVPE-crosslinked	40	40	5	15	150

lated as  $(W_g - W_0)/W_0 \times 100$ , where  $W_g$  and  $W_0$  are the film weights before and after the grafting, respectively. The grafted films were sulfonated in a 0.2 M chlorosulfonic acid solution of 1,2-dichloroethane at 60 °C for 8 h, hydrolyzed in distilled water at 80 °C for 12 h, washed and kept in distilled water at room temperature before use.

### 2.3. Ion exchange capacity, water uptake and proton conductivity

Ion exchange capacity was determined by acid–base titration. The dried membrane in the protonic form (about 80 mg) was immersed in 20 ml of NaCl saturated aqueous solution and equilibrated for 24 h. The solution was then titrated with 0.02 M NaOH solution. Based on the titration results, the ion exchange capacity was calculated. Water uptake was determined as follows. First, the membrane was immersed in distilled water at 25 °C for 24 h; then, the membrane was taken out and weighed after wiping off the excess surface water. The water uptake was calculated as  $(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100$ , where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the membrane weights in the wet and dry states, respectively. Proton conductivity was determined by impedance spectroscopy measurement using a Solartron 1269 analyzer with an AC perturbation of 10 mV. The samples were hydrated in water at 25 °C overnight before the measurement. The high frequency intercept on the real axis of the Nyquist plot was used to calculate the proton conductivity of the membrane.

### 2.4. Chemical stability

The chemical stability was characterized using a  $\text{H}_2\text{O}_2$  aqueous solution [19]. For this purpose, the membrane with a size of 2 cm  $\times$  2 cm was immersed in the 3%  $\text{H}_2\text{O}_2$  aqueous solution at 60 °C. During the immersion, the membranes were intermittently taken out of the solution and weighed after wiping off the excess surface water. The durability time, which was defined as the lasting time till the weight loss get started in the  $\text{H}_2\text{O}_2$

solution were used to characterize the chemical stability of the membrane.

### 2.5. Radiation crosslinking of the membrane

Preparation of the polymer electrolyte membranes involves two main processes, i.e. grafting and sulfonation. Radiation crosslinking of the membrane was performed by irradiation of the ETFE base film before grafting, the grafted film after grafting or the sulfonated film. The  $\gamma$ -ray irradiation was carried out at a dose rate of 25 kGy  $\text{h}^{-1}$  under argon gas at room temperature. After radiation crosslinking, the samples were heat-treated in a vacuum oven at 80 °C for 48 h to eliminate the residue radicals. Samples of the radiation crosslinking are shown in Tables 2 and 3.

The melting point and crystallinity of the radiation-crosslinked ETFE base film, the grafted film and the sulfonated membrane were determined by differential scanning calorimetry (DSC, type, Plus2/DSC 8230, Rigaku, Japan). The specimen (about 5 mg) was heated to 350 °C at a heating rate of 10 °C  $\text{min}^{-1}$ , with the nitrogen gas flow rate of 100 ml  $\text{min}^{-1}$ . For comparison, the crystallinity was calculated as the mass ratio of crystalline ETFE to the base ETFE film in the sample. The results are shown in Table 2.

### 2.6. Methanol permeability

The methanol permeability was tested in a two-compartment diffusion cell. In the two separate compartments, 100 ml of 5 M methanol solution and 100 ml of distilled water were added, respectively, and magnetically stirred to avoid concentration gradients in each compartment. The temperature was controlled at 80 °C. The concentration of methanol in the water-side compartment was detected as a function of time by a refractometer. The methanol permeability was calculated from the detected results and based on the Fick's law of diffusion.

Table 2  
Melting point and degree of crystallinity of the samples irradiated with different doses under argon gas at room temperature

	Melting point, °C (crystallinity, % <sup>a</sup> )	Irradiation dose (kGy)				
		0	200	500	1000	2000
1	ETFE base film	256 (34.0)	251 (36.0)	246 (34.2)	239 (29.9)	228 (21.7)
2	Grafted film	256 (30.4)	250 (31.7)	246 (30.5)	240 (26.8)	228 (14.3)
3	Sulfonated membrane	256 (27.2)	244 (20.3)	234 (15.4)	223 (11.3)	210 (8.9)

<sup>a</sup>For comparison, the ETFE crystallinity was calculated based on the mass of ETFE base film in the sample.

Table 3  
Properties of the membranes with and without radiation crosslinking

Sample	Radiation-induced crosslinking	Grafting (%)	IEC (mmol g <sup>-1</sup> )	Water uptake (%)	Conductivity (S cm <sup>-1</sup> )	Durability time (h)	Methanol permeability (10 <sup>-6</sup> cm <sup>2</sup> s <sup>-1</sup> )
#1	Without radiation-crosslinking	57	2.0	35	0.060	307	1.16
#2	Before grafting	57	2.0	32	0.059	350	0.09
#3	After grafting	57	2.0	28	0.056	452	0.65
#4	After sulfonation	57	1.7	37	0.061	180	1.69
#5	Nafion <sup>®</sup> 117	–	0.91	29	0.060	>1000	6.63

Water uptake and proton conductivity were determined at 25 °C under the water-saturated state, durability time was determined in a 3% H<sub>2</sub>O<sub>2</sub> solution at 60 °C, and methanol permeation was determined at 80 °C using the 5 M methanol aqueous solution.

## 2.7. DMFC measurements

The #3 membrane shown in Table 3 was selected for the DMFC testing. For this purpose, the membrane was sandwiched by anode and cathode electrodes, and hot-pressed at 130 °C under 10 MPa for 2 min, and then under 20 MPa for 1 min. The anode catalyst was a commercial Pt/Ru/C (20 wt.% Pt, 10 wt.% Ru), while the cathode catalyst was Pt/C (20 wt.% Pt). The loading of the Pt/Ru and Pt catalysts at the anode and cathode was 3.0 and 1.0 mg cm<sup>-2</sup>, respectively. The obtained membrane/electrodes assembly (MEA) was then set into a 5 cm<sup>2</sup> fuel cell for DMFC testing under atmospheric pressure at a cell temperature of 70 °C. 1 M (1 ml min<sup>-1</sup>) or 5 M (0.2 ml min<sup>-1</sup>) methanol aqueous solution as the fuel and the dry air (100 ml min<sup>-1</sup>) as the oxidant was fed into the anode and cathode, respectively. The current–voltage (*I*–*V*) performance of the cell was recorded at a current sweep rate of 100 mA min<sup>-1</sup> using an electronic loader. For comparison, Nafion<sup>®</sup> 117 was tested under the same conditions.

## 3. Results and discussion

### 3.1. Preparation of the polymer electrolyte membranes

The radiation-grafted membranes were prepared by radiation grafting of monomers into the ETFE films followed by sulfonation. As shown in Table 1, MeSt and *t*BuSt in a ratio of 1:1, together with the crosslinkers of (a) 20% BVPE, (b) 5% DVB, (c) 2.5% DVB + 17.5% BVPE and (d) 5% DVB + 15% BVPE in weight based on the total monomer amount were used to graft and crosslink the ETFE film simultaneously.

Fig. 1 shows the kinetics of grafting of the above-mentioned monomers into the ETFE films. The preirradiation dose was 15 kGy and the grafting temperature was 50 °C. Both the preirradiation and grafting processes were performed under argon gas. The radiation grafting occurs by a grafting front mechanism and is controlled by a diffusion process of the monomers into the base film [20]. Generally, higher crosslinking leads to a slower grafting rate. However, as shown in Fig. 1, with a total crosslinker of 20%, the grafting kinetics is not similar in each case. For instance, the 20% BVPE system shows the fastest grafting in the steeply increasing initial 10 h and finally reaches the highest degree of grafting of 86% at 24 h; for the 2.5% DVB + 17.5% BVPE system, the grafting is somewhat slower than that of the 20% BVPE system, and the degree of grafting at

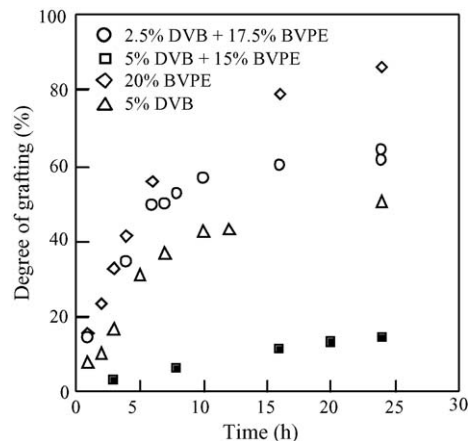


Fig. 1. Kinetics of the grafting of MeSt/*t*BuSt into ETFE films with different types and amounts of crosslinkers. Preirradiation dose, 15 kGy; grafting temperature, 50 °C; under argon gas.

24 h is 64%. On the other hand, for the 5% DVB + 15% BVPE system, the grafting is so slow that the degree of grafting at 24 h is only 14%, which is too low for preparation of the polymer electrolyte membrane. It is considered that the significant difference in the grafting kinetics is due to the different properties of the DVB and BVPE crosslinkers. The two vinyl groups in the DVB crosslinker are conjugated with respect to each other and their distance is relatively shorter; the reactivity is higher than that of MeSt and *t*BuSt. As a consequence, crosslinking with a higher DVB content results in a highly crosslinked and tight structure on the surface, which will hinder the monomers to diffuse into the film. Therefore, the increase in DVB content results in a decrease in grafting rate, and in turn, a lower final degree of grafting. As shown in Fig. 1, even if with only 5% DVB, the grafting was clearly slower than that of the 2.5% DVB + 17.5% BVPE system. On the contrary, BVPE has a flexible structure, and the two vinyl groups are non-conjugated and electronically isolated from each other, with a relatively longer distance [21]. The activity of the BVPE is similar to that of MeSt. Therefore, by graft copolymerization with the BVPE crosslinker, a crosslinking structure can be introduced into the grafted film homogeneously to a higher level.

The grafted film was sulfonated in a 0.2 M chlorosulfonic acid solution at 60 °C for 8 h and subsequent hydrolysis in distilled water at 80 °C for 12 h to obtain the polymer electrolyte membrane. Chlorosulfonic acid was chosen as a sulfonating agent as it is highly reactive in electrophilic substitutions of aromatic

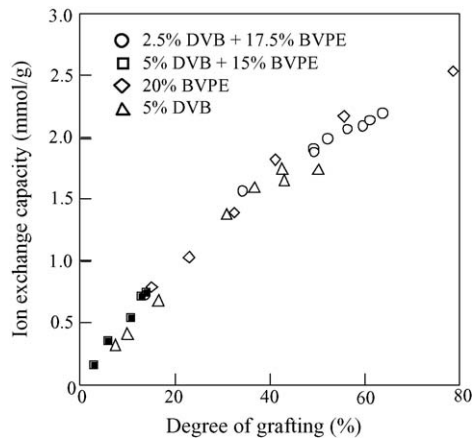


Fig. 2. Effect of degree of grafting on the ion exchange capacity of the radiation-grafted membrane.

rings and convenient for laboratory study [22]. All the grafted ETFE films shown in Fig. 1 were sulfonated into polymer electrolyte membranes. The introduction of sulfonic acid groups into the grafted films creates a pseudo two-phase, hydrophobic and hydrophilic. Ion exchange, water uptake and proton conductivity properties are all due to the hydrophilic phase in the membranes.

### 3.2. Ion exchange capacity, water uptake and proton conductivity

Ion exchange capacity, which provides an indication of the content of acid groups in the membrane, is closely related to the proton conductivity. Fig. 2 shows the ion exchange capacity of the membranes plotted as a function of the degree of grafting. As expected, the ion exchange capacity increases with the increase in the degree of grafting. This tendency is due to the increased amounts of aromatic rings available for sulfonation in the more highly grafted ETFE films. Therefore, the ion exchange capacity of the membrane could be controlled freely by changing the degree of grafting. With a higher degree of grafting such as 80%, the ion exchange capacity can reach a high value of  $2.5 \text{ mmol g}^{-1}$ . This value far exceeds that of the Nafion<sup>®</sup> 117,  $0.91 \text{ mmol g}^{-1}$ . The relationship between the degree of grafting and the ion exchange capacity of the membranes crosslinked with different types and amounts of crosslinkers shows a similar tendency, indicating that the degree of crosslinking in the membrane does not influence the sulfonation reaction. In addition, by calculation, we found that the amount of sulfonic groups in the membrane is almost identical to that of the aromatic rings. Therefore, it can be concluded that each aromatic ring in the grafted film is substituted with one sulfonic group and that the sulfonation conditions in this study are sufficient for the introduction of sulfonic acid groups into the membrane.

After sulfonation, a hydrophilic phase is introduced into the resultant membrane, where water can be absorbed, and thus the sulfonic acid group can be ionized to form free protonic ions and fixed sulfonic ions in the membrane. Therefore, the proton conduction has a direct connection with the water uptake in the membrane. The higher ion exchange capacity of a mem-

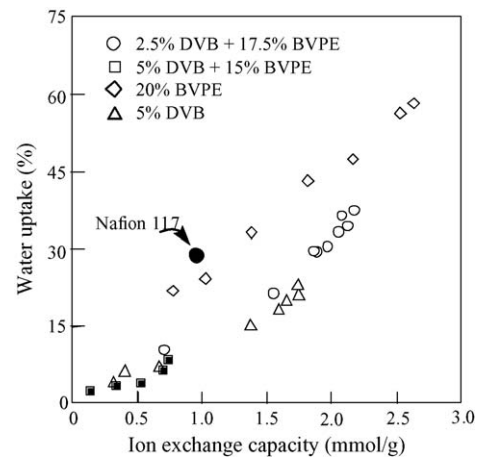


Fig. 3. Effect of ion exchange capacity on the water uptake of the radiation-grafted membrane.

brane results in a higher water uptake, consequently, a higher proton conduction. Fig. 3 shows the water uptake of the four types of the crosslinked membranes as a function of the ion exchange capacity. It can be seen that, in all cases, the water uptake increases with an increase in the ion exchange capacity. This is due to the increase in the hydrophilicity imparted to the membranes by the incorporation of sulfonic acid groups. In addition, in the case of the 20% BVPE-crosslinked membranes, the water uptake increases more rapidly with the ion exchange capacity than that of the DVB-crosslinked membranes. This is due to the loose crosslinking chain of the BVPE-crosslinked membranes that favors water absorption. On the other hand, the DVB and DVB/BVPE-crosslinked membranes show a similar tendency of the relationships between the ion exchange capacity and water uptake. It was also found that the water uptake at an ion exchange capacity of  $0.91 \text{ mmol g}^{-1}$  is clearly lower than that of the Nafion<sup>®</sup> 117 at a similar ion exchange capacity level. This is reasonably attributed to its special microstructure, i.e. the highly crosslinking structure and the highly hydrophobic *tert*-butyl groups of the grafted component.

Fig. 4 shows the proton conductivity of the membrane as a function of ion exchange capacity. The proton conductivity was

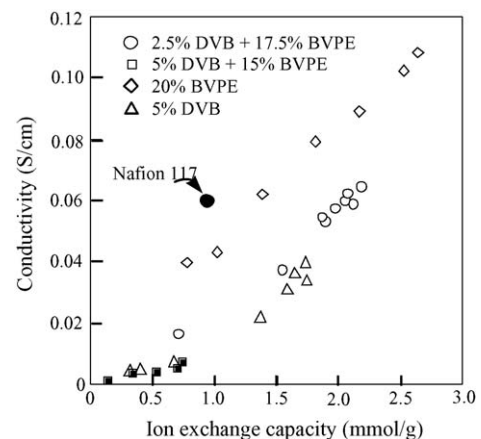


Fig. 4. Effect of ion exchange capacity on the proton conductivity of the radiation-grafted membrane.

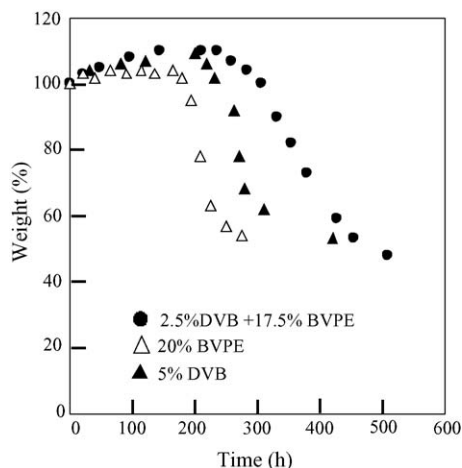


Fig. 5. Chemical stabilities of the MeSt/*t*BuSt-grafted membranes chemical crosslinked by 2.5% DVB + 17.5% BVPE; 20% BVPE and 5% DVB in the 3% H<sub>2</sub>O<sub>2</sub> solution at 60 °C.

determined in its water-saturated state at 25 °C. Similar to the water uptake, the proton conductivity increases with the ion exchange capacity. The 20% BVPE-crosslinked membranes show the highest proton conductivity. The higher proton conductivity is due to its greater ability for water uptake. Compared with the Nafion<sup>®</sup> 117, the 2.5% DVB + 17.5% BVPE-crosslinked membrane shows a doubled ion exchange capacity value of about 2.0 mmol g<sup>-1</sup> at the same conductivity of 0.06 S cm<sup>-1</sup>. Even then, the new membrane with a high ion exchange capacity of 2.0 mmol g<sup>-1</sup> and a thickness of about 43 μm shows a tensile strength of 29 MPa and an elongation at break of 48%, which are considerably better mechanical properties for fuel cells. Furthermore, the higher ion exchange capacity gives the membrane a higher ability for water retention, which is very important for a fuel cell operated under lower humidification.

### 3.3. Chemical stability

During the fuel cell operation, the H<sub>2</sub>O<sub>2</sub> is originated from oxygen diffusion through the membrane and incomplete reduction at the fuel cell anode, bringing about a severe degradation of the membrane. Testing polymer electrolyte membrane lifetimes in an actual fuel cell is both time-consuming and expensive. Thus, it is desirable to develop rapid and simple methods for evaluating the new candidate membranes. In this study, the chemical stabilities of the 5% DVB, 20% BVPE and 2.5% DVB + 17.5% BVPE-crosslinked membranes were tested in a 3% H<sub>2</sub>O<sub>2</sub> aqueous solution at 60 °C. The degrees of grafting of the three membranes were 50, 33 and 57%, and their proton conductivities were 0.040, 0.062 and 0.059 S cm<sup>-1</sup>, respectively. The weight changes in these chemically crosslinked membranes are shown in Fig. 5. It was found that the crosslinked membranes continuously swelled and then decomposed. The initial swelling is due to the partial scission of the crosslinking structure of the membrane. The durability times are 160 and 200 h for the 20% BVPE and 5% DVB-crosslinked membranes, respectively, and are 307 h for the 2.5% DVB + 17.5% BVPE-crosslinked membrane. Thus, the latter membrane was considerably stabler than

the former two membranes. It is interesting that the durability times of the MeSt/*t*BuSt-grafted membranes crosslinked by DVB and BVPE crosslinkers are far longer than that of the traditional styrene/DVB radiation-grafted membrane, which is about 72 h determined under the same conditions [11].

The high crosslinker content in the membrane is an important reason for the high chemical stability of these polymer electrolyte membranes. In our preliminary experiments, the MeSt/*t*BuSt-grafted membrane without DVB or BVPE crosslinking shows a durability time of only 84 h, which is far lower than those of the crosslinked membranes reported here. The membrane crosslinked by 5% DVB shows a longer durability time than that of the 20% BVPE-crosslinked one, reflecting that the DVB is more efficient for crosslinking the membrane. However, a further increase in the DVB content leads to brittleness and lower proton conductivity of the membrane. Therefore, DVB and BVPE were used together to obtain a higher crosslinked and flexible polymer electrolyte membrane with high chemical stability. In this study, the 2.5% DVB + 17.5% BVPE-crosslinked membrane shows the longest durability time in the 3% H<sub>2</sub>O<sub>2</sub> solution at 60 °C.

### 3.4. Radiation crosslinking of the polymer electrolyte membranes

As in the case of many other polymer materials, irradiation of fluoropolymer films causes the crosslinking and chain scission simultaneously [16]. The final result depends on the nature of the material and the irradiation conditions. We tried to introduce radiation crosslinking into the ETFE-based polymer electrolyte membranes by the γ-ray irradiation. The radiation crosslinking can be introduced into the base film before grafting, the grafted film after grafting or the final sulfonated membrane. The effect of irradiation on the melting point and crystallinity of the ETFE base film, grafted film and sulfonated membrane is summarized in Table 2. The irradiation doses are in the range of 0–2000 kGy. For comparison, crystallinity is calculated based on the mass of ETFE base film in the corresponding sample. As a tendency, increasing the irradiation dose decreases the melting point. The graft chain in the grafted film has little effect on the melting point but slightly decreases the crystallinity of the base film. The crystallinity in both the ETFE base film and the grafted film increases initially and then decreases, which is similar to the radiation crosslinking of PTFE films at 340 °C under oxygen-free atmosphere [23]. Sulfonation of the grafted film further decreases the crystallinity. Even then, considerable crystalline ETFE remains in the final sulfonated membrane. It is noted that both the melting point and crystallinity of the irradiated sulfonated membrane decreased drastically with the increase in irradiation dose, suggesting that chain scission is the predominant reaction in the irradiated sulfonated membrane.

Due to the significantly higher chemical stability, the above-mentioned DVB/BVPE-crosslinked membrane was chosen for induced radiation crosslinking to further explore its feasibility as a high performance membrane. A dose of 500 kGy was used for irradiation of the base film, the grafted film and the sulfonated membrane to introduce the radiation crosslinking. Identical de-

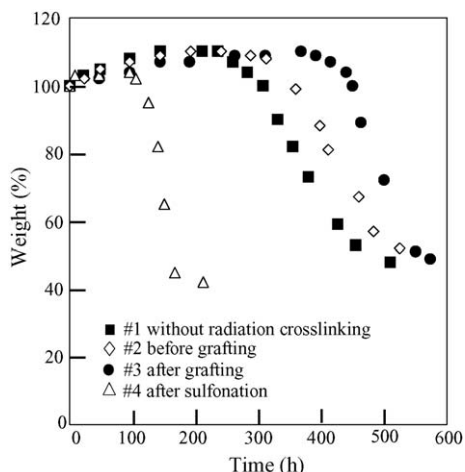


Fig. 6. Effect of radiation crosslinking on the chemical stabilities of the 2.5% DVB + 17.5% BVPE-crosslinked MeSt/*t*BuSt-grafted membranes in the 3% H<sub>2</sub>O<sub>2</sub> solution at 60 °C.

degrees of grafting of 57% of the grafted films with and without radiation crosslinking were used for this study. The chemical stabilities of the three radiation-crosslinked membranes, prepared by irradiation of the base film before grafting, the grafted film after grafting, and the sulfonated membrane, and the membrane without radiation crosslinking are shown in Fig. 6. The membrane that was radiation-crosslinked before grafting shows somewhat longer durability time (about 350 h) than that of the DVB/BVPE-crosslinked membrane without radiation crosslinking (307 h), and the membrane radiation-crosslinked after grafting shows the longest durability time (450 h). However, we also found that the durability time of the membrane irradiated after sulfonation decreased drastically to 120 h. The drastic decrease in durability time of the irradiated-sulfonated membrane supports the conclusion that the chain scission occurs in the membrane. The different effect of radiation crosslinking on the chemical stability reflects the different crosslinking efficiency. For the membranes radiation-crosslinked by irradiation of the base film or the grafted film, two types of crosslinking, chemical and radiation crosslinkings are introduced into the membranes. Especially for the radiation-crosslinked membrane by irradiation of the grafted film, the crosslinking bonds can be introduced into the whole membrane, i.e. among the base film and the graft chains, and between them. Therefore, the high chemical stability of these doubly crosslinked membranes can be expected.

The other properties of the radiation-crosslinked membranes, such as ion exchange capacity, water uptake and proton conductivity, were determined and are summarized in Table 3. For comparison, the properties of the radiation-grafted membrane without radiation crosslinking and the Nafion<sup>®</sup> 117 are also given in Table 3. The ion exchange capacities of the radiation-crosslinked membranes by irradiation before and after the grafting are essentially unchanged, showing a value of 2.0 mmol g<sup>-1</sup>. However, the irradiated sulfonated membrane (#4) shows a relatively lower ion exchange capacity of 1.7 mmol g<sup>-1</sup>. This may be due to the high irradiation dose that decomposes the sulfonic acid

groups and initiates the chain scission in the membrane. Water uptake and proton conductivity show similar tendencies. For instance, due to the radiation-crosslinking of #2 and #3 membranes, both the water uptake and proton conductivity decrease to a certain extent; and due to the chain scission occurring in the irradiated sulfonated membrane (#4), both the water uptake and proton conductivity increase in spite of their lower ion exchange capacity.

### 3.5. Methanol permeability

The membrane for DMFC is required not only to have a high proton conductivity but also to provide an effective separation of the methanol and oxygen. Diffusion or leakage of the methanol or oxygen across the membrane leads to a power loss and other undesirable consequences. Membranes with lower methanol permeability may allow for higher methanol feed concentration, thereby increasing the effective energy density of the fuel cell system.

The methanol permeability of the DVB/BVPE-crosslinked membranes with and without the radiation crosslinking and the Nafion<sup>®</sup> 117 was determined using a two-compartment cell, under the condition of 5 M methanol concentration and at 80 °C. As shown in Table 3 and Fig. 7, the diffusion coefficients calculated from a dynamic model of the system based on Fick's law of diffusion are  $0.63 \times 10^{-6}$ ,  $1.12 \times 10^{-6}$  and  $6.63 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for the membranes with (#3) and without (#1) radiation crosslinking, and the Nafion<sup>®</sup> 117, respectively. It is clear that the methanol diffusion in Nafion<sup>®</sup> 117 is considerably faster than that in the DVB/BVPE-crosslinked membranes and that the radiation-crosslinked membrane shows the lowest methanol diffusion coefficient. The DVB/BVPE-crosslinked membranes without and with radiation-crosslinking show 6 and 10 times lower methanol diffusion coefficient, respectively, compared to the Nafion<sup>®</sup> 117. Therefore, the lower methanol permeability is mainly attributed to the crosslinking structure introduced in the membrane and the intrinsic properties of the ETFE base film and graft chains.

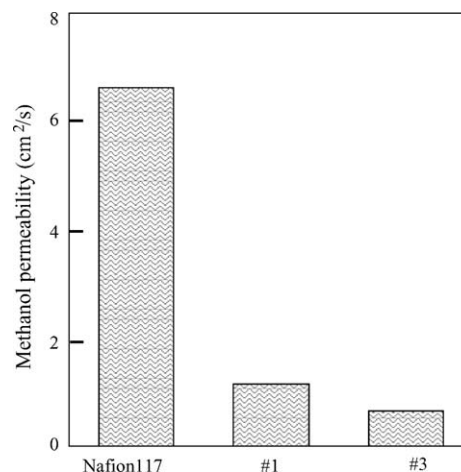


Fig. 7. Methanol permeabilities of the Nafion<sup>®</sup> 117; #1, only chemical crosslinked membrane and #3, doubly crosslinked membrane.

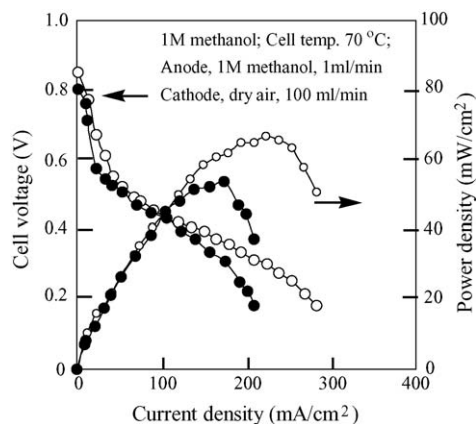


Fig. 8. Cell performance of the DMFC employing the doubly crosslinked membrane and the Nafion® 117.

### 3.6. DMFC performance

Due to the highest chemical stability and lower methanol permeability, together with its satisfactory proton conductivity, water uptake and mechanical strength, the #3 membrane (thickness, 43  $\mu\text{m}$ ) in Table 3 was used for evaluation of the DMFC performance. The single cell employing the #3 membrane was fed with 1 or 5 M methanol aqueous solution and dry air to the anode and cathode, respectively, and was operated at 70 °C under atmospheric pressure. After the cell reached stable conditions, the current–voltage ( $I$ – $V$ ) performance of the cell was recorded and is shown in Figs. 8 and 9. For comparison, Nafion® 117 (thickness, 178  $\mu\text{m}$ ) was also tested under the same conduction.

Fig. 8 shows the  $I$ – $V$  performances and the power density curves for the #3 membrane and Nafion® 117. The methanol feed concentration was 1 M. The maximum power density of Nafion® 117, about 53  $\text{mW cm}^{-2}$ , is seen to be somewhat lower than that of the commercial MEA containing Nafion® 117, about 75  $\text{mW cm}^{-2}$ . This may be due to the MEA prepared in the laboratory. Although the MEAs prepared here are somewhat less active, they were prepared identically for comparison studies of

our membranes and Nafion® 117. As shown in Fig. 8, the performance of the #3 membrane is observed to be better than that of the Nafion® 117. In spite of the thinner #3 membrane, the open circuit voltage (OCV) is still slightly higher than that of the Nafion® 117, indicating that the methanol crossover is lower than that of Nafion® 117 [24]. At higher current densities, a significant voltage and power performance improvement with the #3 membrane is seen. As a consequence, the maximum power density (about 67  $\text{mW cm}^{-2}$ ) is, therefore, higher than that with Nafion® 117.

Due to the lower methanol crossover, the #3 membrane is expected for use in a DMFC with higher methanol feed concentration. Nafion® membranes are not recommended for use in a DMFC with a methanol feed concentration higher than 2 M due to its serious methanol crossover [24]. In attempt to assess the #3 membrane operated at a high methanol concentration, we used a 5 M methanol solution. The results are shown in Fig. 9. In this case, large reductions in OCV,  $I$ – $V$  performance and maximum power density are seen for Nafion® 117, as anticipated from an increase in methanol crossover due to the increased methanol concentration of the feed solution. However, the DMFC employing #3 membrane fed with 5 M methanol solution shows almost identical  $I$ – $V$  performance to that with 1 M methanol solution, indicating that the effect of methanol concentration on the cell performance with the #3 membrane is considerably lower. In this case, the maximum power density with the #3 membrane reaches 70  $\text{mW cm}^{-2}$ , which is more than double that with Nafion® 117 under the same conditions. In addition, the performance of this doubly crosslinked membrane could be further improved by optimizing the interface between the catalyst and the electrolyte membrane, where the Nafion® solution was used as the binder in the catalyst layer of this study.

## 4. Conclusions

Graft copolymerization of MeSt and *t*BuSt into ETFE films by the preirradiation grafting method and subsequent sulfonation appears to produce promising membranes for DMFCs. Chemical crosslinking of the radiation-grafted membranes by 2.5% DVB + 17.5% BVPE results in the highest chemical stability, together with satisfactory water uptake, proton conductivity and mechanical strength of the membrane.

Radiation crosslinking of the DVB/BVPE-crosslinked membrane can be carried out by irradiation of the ETFE base film before grafting and of the grafted film after grafting. The DVB/BVPE-crosslinked membrane with radiation crosslinking introduced after grafting shows a considerably higher chemical stability and significantly lower methanol permeability and has a better DMFC performance than that with Nafion® 117. Especially at the higher methanol feed concentration of 5 M, the maximum power density of the doubly crosslinked membrane has improved by more than double that of Nafion® 117 under the same conditions, suggesting that the new membrane is promising for use in a DMFC in which a relatively higher methanol concentration can be fed.

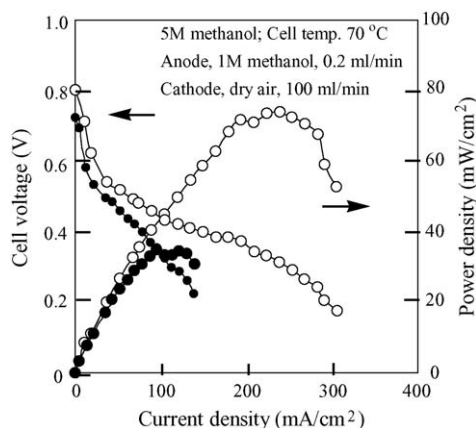


Fig. 9. Cell performance of the DMFC employing the doubly crosslinked membrane and the Nafion® 117.



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