Preparation and Properties of Sulfonated ETFE-*g*-polyvinyltoluene Membranes for Application in Fuel Cells

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ABSTRACT: A new polymer electrolyte membrane prepared by radiation grafting of vinyltoluene into poly(ethylene-*co*-tetrafluoroethylene) (ETFE) film and subsequent sulfonation was developed for application in fuel cells. The effect of grafting condition on the degree of grafting was investigated in detail. Results indicated that the degree of grafting can be controlled over a wide range. The grafted films were sulfonated in a chlorosulfonic acid solution to obtain the polymer electrolyte membranes, which were characterized with respect to their use in fuel cells. It is concluded that the substituted methyl group on the vinyltoluene can improve the chemical stability of the resulting membranes, and the crosslinked ETFE-*g*-poly(vinyltoluene-*co*-divinylbenzene) membranes can be proposed for the future development of alternative low-cost and high-performance membranes for fuel cells. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2661–2667, 2006

Key words: polyelectrolyte; membrane; irradiation; graft copolymerization

INTRODUCTION

The polymer electrolyte membrane is one of the important components in the polymer electrolyte membrane fuel cell (PEMFC). The membrane acts as a separator to prevent mixing of the reactant gases and as an electrolyte for transporting protons from the anode to the cathode. The most generally acceptable and widely used membrane to date is the Nafion membrane, which has excellent chemical stability and high proton conduction. However, the high cost limits its use in the actual applications.[1–3] An alternative high performance membrane being less expensive is significantly required for the PEMFC. The new membranes under development include hydrocarbon membranes,[4,5] organic/inorganic hybrid membranes,[4,5] and the radiation-grafted membranes.[6–9]

The hydrocarbon membranes are general mechanically weak and are easily degraded in a working fuel cell.[10,11] It is recognized that the excellent chemical stability of the Nafion membrane is due to its perfluorinated structure. Recently, a significant number of partially-fluorinated membranes have been developed by grafting styrene/divinylbenzene (DVB) into the fluoropolymer films.[6–9] These radiation-grafted membranes have fluorinated main chains and sulfonated side chains. The former gives the necessary strength, chemical stability, and gas barrier, while the latter supplies the proton transport ability. Nevertheless, it is difficult to largely improve the chemical stability, although crosslinking has been introduced using the different crosslinkers.[12,13] Therefore, an alternative monomer is required for the preparation of the chemically stable membrane for fuel cells.[14–17]

In this study, vinyltoluene was chosen as the alternative monomer to graft into the poly(ethylene-*co*-tetrafluoroethylene) (ETFE) films. A comparative study was performed between the monomers of vinyltoluene and styrene, with and without the DVB crosslinker. The radiation-grafted membrane was prepared using the preirradiation grafting method. With respect to application in fuel cells, the ion exchange capacity, water uptake, proton conductivity, methanol permeability, thermal and chemical stability of the radiation-grafted membranes were characterized.

EXPERIMENTAL

The monomers of vinyltoluene (m,p-isomers), styrene, and divinylbenzene (DVB, 55% mixture of isomers, 45% of ethylvinylbenzene) were purchased from Aldrich Chemical, Japan, and were used without further treatment. The DVB acted as a crosslinker. The poly-(ethylene-*co*-tetrafluoroethylene) (ETFE) films, with a thickness of 50 μm, was obtained from Asahi Glass, Japan and was washed with acetone to remove any impurity on its surface before use.

The process for the preparation of the membranes is shown in Figure 1. The graft conditions that were

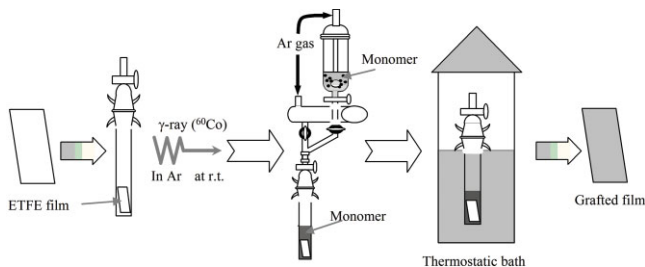*Correspondence to:* J. Chen (chen.jinhua@jaea.go.jp).

Figure 1 Process of grafting of monomers into the ETFE films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

varied in this experiment included the preirradiation dose, graft temperature, and graft time. The monomer concentration in toluene was fixed at 40 vol %. In the case of preparation of crosslinked membranes, 5 vol % of DVB to the total monomers was used. As the first step, the glass tube with added ETFE films was degassed for 12 h, and argon gas was then filled in the tube for the γ-ray preirradiation at room temperature. After the preirradiation step, argon gas-bubbled monomer solution was quickly added to the tube. The grafting reaction was initiated by placing the tube in the thermostatic bath. After the desired grafting time, the grafted films were extracted with toluene to remove the ungrafted polymer and residual monomers. The degree of grafting was calculated as $(W_g - W_0)/W_0 \times 100$, where W_g and W_0 are the film weights before and after the grafting reaction, respectively.

The grafted ETFE film was sulfonated with a $0.2M$ chlorosulfonic acid ($ClSO_3H$) solution in 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.

The ion exchange capacity of the membrane was determined by acid-base titration. The proton conductivity was measured by impedance spectroscopy using a Solartron 1269 analyzer. The water uptake was calculated from the difference of the membrane weights in the wet and dry states. The thermal stability was determined in air by a thermogravimetric analysis. The measurements of ion exchange capacity, water uptake, proton conductivity, and thermal stability have been described in detail in our previous paper.[18] The chemical stability was measured in a 3% H_2O_2 aqueous solution at 60°C by determining the weight and conductivity of the membrane.[19]

The energy distribution X-ray spectroscopy (EDS) of sulfur as well as the scanning electron microscopy (SEM) image of the cross section of the membrane was measured using a JEOL JSM-5600 SEM, which has the added capability of conducting elemental analysis using the energy dispersive spectroscopy system.

The methanol permeability of the membrane was tested in a two-compartment diffusion cell. Prior to

testing, the membrane was equilibrated in distilled water at 80°C for 24 h. The initial concentration of the methanol solution was $10M$. The temperature was controlled at 80°C. The concentration of methanol in each compartment was detected as a function of time by a refractometer. Methanol permeability (P, $cm^2\ s^{-1}$) was calculated as

$$P = \frac{V \times d}{(M_{MeOH} - M_{H_2O})S} \times \frac{dM_{H_2O}}{dt}$$

where V (100 cm^3) is the water volume and d (cm) is the thickness of the membrane. M_{MeOH} and M_{H_2O} are the methanol concentrations at the time t (s). S (cm^2) is the area exposed to the two compartments. The dM_{H_2O}/dt is considered to equal M_{H_2O}/t when t is small enough.

RESULTS AND DISCUSSION

Radiation grafting of monomer into ETFE films

Figure 2 shows the effect of preirradiation dose on the grafting of vinyltolutene into the ETFE films. The graft temperature was 50°C. The preirradiation doses were 3, 5, 10, 15, and 60 kGy. For comparison, the grafting of styrene into the ETFE films with the preirradiation dose of 15 kGy was also plotted. Obviously, the graft polymerization appeared as an induction-period in the early stage, which is well known for general radical polymerization. After this period, the degree of
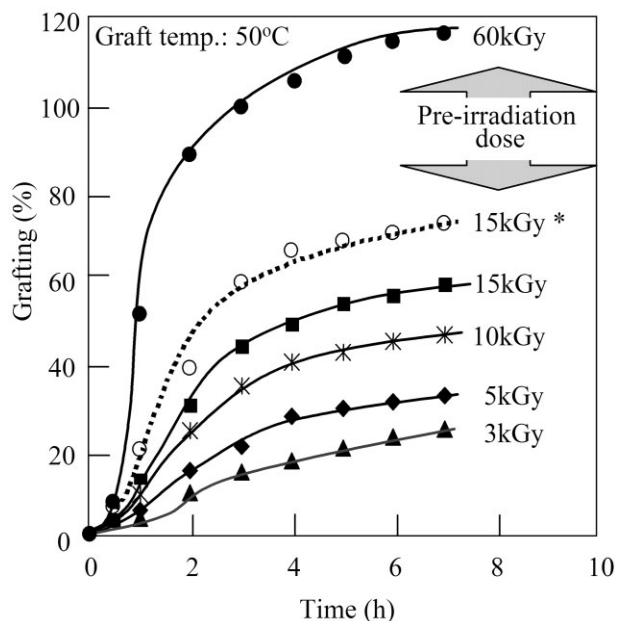

Figure 2 Effect of preirradiation dose on the grafting of vinyltoluene into the ETFE films (graft temperature, 50°C). The dotted line indicates the results from the grafting of styrene into the ETFE films.
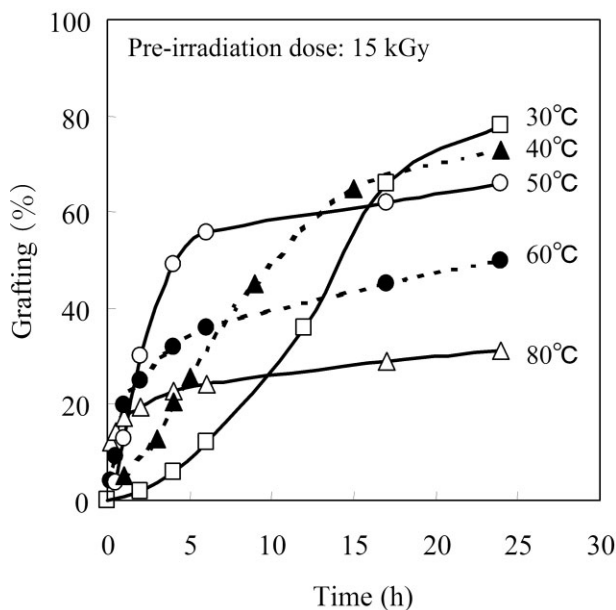
Figure 3 Effect of graft temperature on the grafting of vinyltoluene into the ETFE films (preirradiation dose, 15 kGy).

grafting quickly increased until it reached a steady state. In addition, the degree of grafting distinctly exhibited an increasing tendency with the preirradiation dose. This behavior can be easily ascribed to the fact that the radicals generated in the ETFE increased at the higher doses. After grafting, both the thickness and area of the film increased, indicating that the grafting was homogeneous throughout the film. It was considered that the grafting initially occurred at the film surface and then gradually proceeded inwards as the grafting zone was swollen by the monomer and the grafted chains.[7,8]

Compared with the styrene grafting at the preirradiation dose of 15 kGy, the grafting of vinyltoluene was relatively slow. Since the grafting was a diffusion-controlled process,[20] the methyl group influenced the vinyltoluene monomer to diffuse into the ETFE films, resulting in a relatively lower degree of grafting.

The graft temperature is also an important parameter for the graft reaction.[21,22] Figure 3 shows the effect of the graft temperature on the grafting. The preirradiation dose was fixed at 15 kGy. The initial graft rate increased with the graft temperature as expected. In the initial 2 h, the grafting at 80°C rapidly increased and reached 20%, while the grafting at 30°C was extremely slow. However, after 24 h, the grafting at 30°C was 78%, and the grafting at 80°C was only 31%. The degree of grafting at 24 h decreased with an increase in the graft temperature. This is due to the higher graft temperature that raised the initial graft rate but simultaneously terminated the free radical quickly.[9,23] Therefore, the final grafting at 80°C was lower, and the

graft chains were significantly shorter. On the other hand, the grafting at 30°C had a higher degree of grafting and relatively longer graft chains. In addition, at lower graft temperature, the growing chains became sufficiently immobilized, so that termination by combination was inhibited; while at higher graft temperature, the monomer swelled the matrix, increasing the polymer mobility and thus the termination was significantly enhanced, resulting in a lower degree of grafting.

Figure 4 shows the effect of DVB crosslinker on the grafting of vinyltoluene and styrene into the ETFE films. The preirradiation dose and the graft temperature were 15 kGy and 50°C, respectively. The DVB content in the total monomers was 5 vol %. It was noted that the DVB clearly lowered the vinyltoluene grafting, but distinctly enhanced the styrene grafting. It is thought that the DVB crosslinker either enhanced or lowered the grafting, depending on the concentration in which they are used and the monomer properties.[7,24,25]

The DVB crosslinker also affected the microstructure of the grafted films. The ETFE films were colorless and transparent. After the styrene/DVB or vinyltoluene/DVB was grafted, the color of the films did not change. However, after only styrene or vinyltoluene was grafted, the film changed from colorless to white. This indicated that a different structure occurred between the crosslinked and noncrosslinked grafted ETFE films. The high branching and crosslinking structure of the former kept the grafted film transparent and colorless, and the long graft chains of the latter
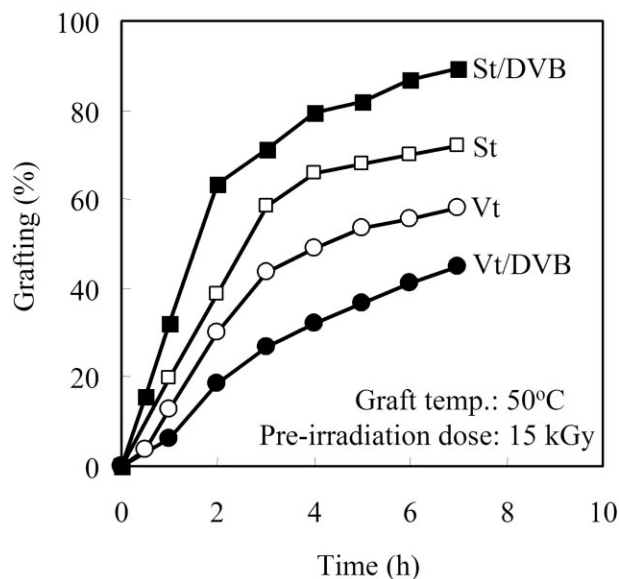

Figure 4 Effect of divinylbenzene (DVB) crosslinker on the grafting of vinyltoluene and styrene into the ETFE films (preirradiation dose, 15 kGy; graft temperature, 50°C; St, styrene; Vt, vinyltoluene).
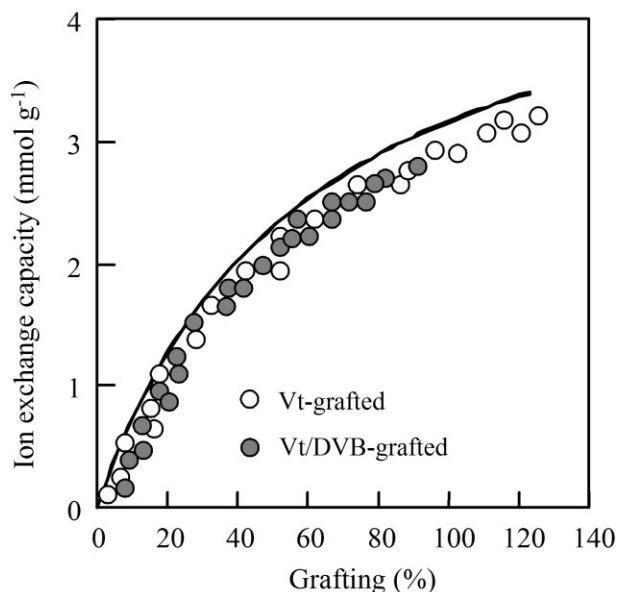
Figure 5 Relationship between the degree of grafting and ion exchange capacity of the radiation-grafted membranes.

were readily coiled and aggregated, resulting in a microphase separation in the grafted film.

Sulfonation of the grafted ETFE films

The grafted film was sulfonated by chlorosulfonic acid to obtain the polymer electrolyte membrane. The ion exchange capacity of the obtained membranes was determined and is plotted in Figure 5. The theoretical ion exchange capacity was calculated by assuming each aromatic ring substituted by one sulfonic group. The detected ion exchange capacity both from vinyltoluene and vinyltoluene/DVB-grafted ETFE films was in good agreement with the calculated data that showed about 90% sulfonation ratio under the experimental conditions. With the addition of DVB, the graft conditions and the degree of grafting did not affect the sulfonation. Therefore, the ion exchange capacity of the membrane could be controlled free by changing the degree of grafting. With a higher grafting such as 120%, the ion exchange capacity can reach a higher value of 3.0 mmol g^{-1}.

To confirm that the sulfonic acid was uniformly distributed in the entire membrane, the EDS of sulfur as well as SEM image of the cross section of the membrane was measured.[26,27] Figure 6 shows the distributions of sulfur across the ETFE-*g*-poly(vinyltoluene-*co*-DVB) membranes and their SEM images. Figure 6(a) shows the membrane with a lower grafting (12%) and Figure 6(b) shows the membrane with a higher grafting (48%). It was interesting that membranes with lower and higher grafting showed different sulfur distributions. In the case of lower grafting,

the sulfur concentration was not uniform. It was considerably higher on the membrane surface than in the membrane interior. This was due to the graft process that occurred from the surface to the inside. For the lower grafting, the inside of the ETFE film had not yet been grafted. On the other hand, in the case of higher grafting of 48%, the sulfur concentration was uniform because of the homogeneous graft in the ETFE films.[28] The uniform distribution of sulfonic acid groups is a very important issue for the proton transport through the membrane.

Water uptake and proton conductivity

Proton conductivity has a direct connection with the water uptake and ion exchange capacity. The higher ion exchange capacity of a membrane results in a higher water uptake, and consequently, a higher proton conductivity. High proton conductivity of the membrane is a basic requirement for the fuel cell, but a higher water uptake usually reduces the mechanical strength of the membrane. Figure 7 shows the relationships among the water uptake, ion exchange capacity, and proton conductivity of the radiation-grafted membranes.

In Figure 7(a), the water uptake of the membranes is presented as a function of ion exchange capacity. Different membranes, prepared from vinyltoluene, vinyltoluene/DVB, styrene, and styrene/DVB-grafted films, showed different relationships between the water uptake and ion exchange capacity. With the DVB crosslinker, the water uptake was largely constrained because of the crosslinking structure.[2,29] For instance, for both the membranes from the vinyltoluene and styrene-grafted films at the ion exchange capacity of 1.5 mmol g^{-1}, the water uptakes were around 25 and 45% with and without the DVB crosslinker, respectively. The water uptake of the vinyltoluene-grafted membranes was somewhat lower than that of the
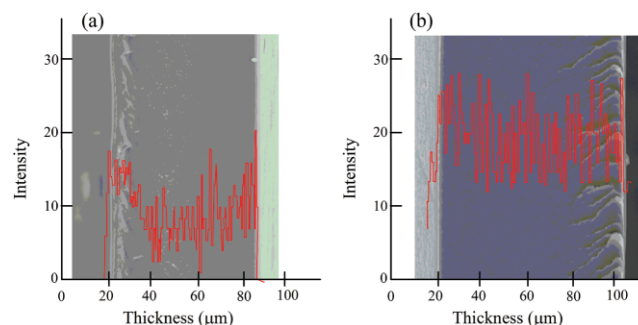

Figure 6 Sulfonic acid group distribution in the cross section of the ETFE-*g*-poly(vinyltoluene-*co*-DVB) membrane with a degree of grafting of 12% (a) and 48% (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
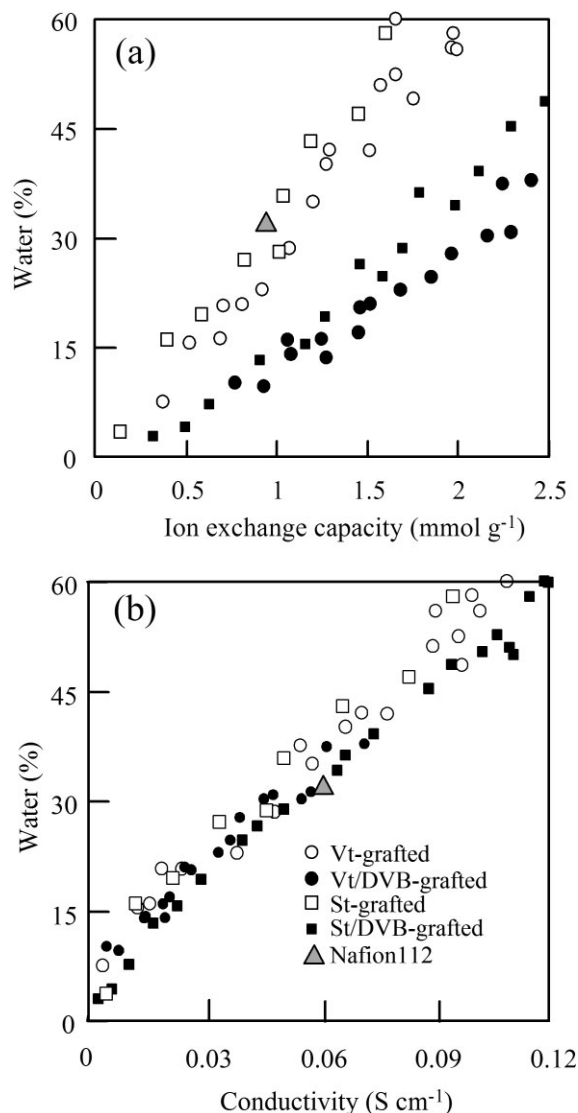
Figure 7 Relationships among the water uptake, ion exchange capacity, and proton conductivity of the radiation-grafted membranes and Nafion membrane. (a) Relationship between the ion exchange capacity and water uptake. (b) Relationship between the proton conductivity and water uptake. (Vt, vinyltoluene; St, styrene.)

styrene-grafted membranes. This may be due to the hydrophobicity of the methyl groups. In addition, the water uptake of the Nafion membrane was similar to that of the noncrosslinked radiation-grafted membranes.

However, as shown in Figure 7(b), the effect of DVB crosslinker on the relationships between water uptake and conductivity was quite small. All of the membranes showed similar results. The crosslinking structure can constrain the water swelling, but simultaneously decrease the proton conductivity.[19,29] Even then, the trends in the slightly lower water uptake can be observed by introducing a crosslinking structure. On the other hand, the relatively lower water uptake

of the Nafion membrane to its proton conductivity may be due to its special microstructure, i.e., phase separation of the hydrophilic and hydrophobic region.

Thermal and chemical stability

The TG curves of the original ETFE film (1), crosslinked ETFE-*g*-poly(vinyltoluene-*co*-DVB) film (36% grafting) (2), polymer electrolyte membrane prepared by sulfonation of the grafted film of crosslinked ETFE-*g*-poly(vinyltoluene-*co*-DVB) (3), and Nafion 112 membrane (4) are shown in Figure 8. The ETFE-*g*-poly(vinyltoluene-*co*-DVB) film showed a two-step decomposition process, and the corresponding electrolyte membrane showed a three-step decomposition process. The isolated decomposition temperatures of about 280, 400, and 500°C originated from the decompositions of the sulfonic acid groups, graft chains, and ETFE substrate, respectively. The sulfonation and graft process did not influence the stability of the graft chains and the ETFE substrate. The first decomposition point of the sulfonic acid groups of about 290°C was considered as the stability temperature of the membrane. The four types of membranes, prepared from vinyltoluene, vinyltoluene/DVB, styrene, and styrene/DVB-grafted ETFE films, showed similar decomposition behaviors (not showed), indicating that the crosslinking structure in the membrane did not significantly influence the thermal properties.[20] In addition, the stability temperature of the ETFE-*g*-poly-
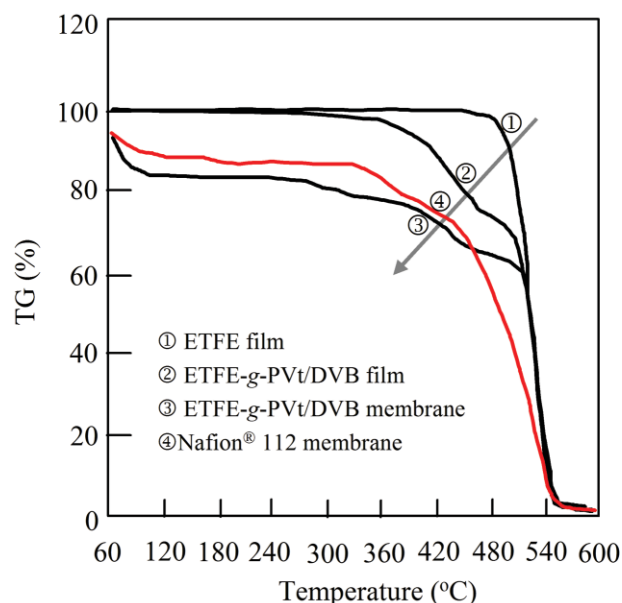

Figure 8 TG curves of the original ETFE film (1), ETFE-*g*-poly(vinyltoluene-*co*-DVB) film (36% grafting) (2), polymer electrolyte membrane prepared by sulfonation of the ETFE-*g*-poly(vinyltoluene-*co*-DVB) grafted film (3), and Nafion 112 membrane (4). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
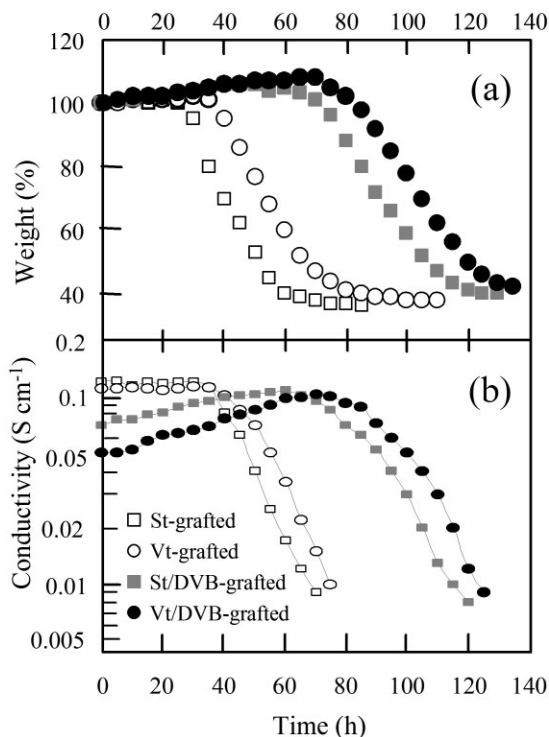
Figure 9 Chemical stability of the radiation-grafted membranes in 3% H_2O_2 at 60°C. (a) Weight changes; (b) proton conductivity changes; degrees of grafting, 35–38%.

(vinyltoluene-*co*-DVB) electrolyte membrane (290°C) is close to that of the Nafion membrane (320°C).

However, in a working fuel cell, the membrane faces stringent conditions, such as high temperature, oxidation, and reduction reactions, and the by-product of hydroxyl radicals.[26] Therefore, the high chemical stability of a membrane is significantly required for a long-term fuel cell. The chemical stability of the radiation-grafted membranes was characterized at 60°C, using a 3% H_2O_2 aqueous solution. Figure 9 shows the results of the weight [Fig. 9(a)] and the conductivity change [Fig. 9(b)] in the membranes prepared from the vinyltoluene, vinyltoluene/DVB, styrene, and styrene/DVB-grafted ETFE films. The degrees of grafting of the corresponding grafted films were in the range of 35–38%.

From the weight changes shown in Figure 9(a), it was found that the radiation-grafted membranes continuously swelled and then quickly decomposed. The stability times of the membranes defined as their initial weight loss were 25, 36, 72, and 83 h for the membranes prepared from the styrene, vinyltoluene, styrene/DVB, and vinyltoluene/DVB-grafted ETFE films, respectively. The crosslinking structure by DVB improved the chemical stability of the membrane several times. The substituted methyl on the aromatic ring made the vinyltoluene-grafted membrane more stable than the styrene-grafted membrane. The weight

and dimension of the final membranes returned to the values of the original ETFE films. Therefore, the weight loss was due to the graft chains, together with the sulfonic acid groups leaving the ETFE substrate. Similar chemical stability results were also obtained from the conductivity change in the membranes. As shown in Figure 9(b), the conductivities of the above four membranes quickly decreased near the stability times, and finally the membranes became proton insulators.

Methanol permeability

In the case of application in direct methanol fuel cells (DMFCs), the methanol permeability of the membrane must be taken into account. The high methanol permeability of the Nafion membrane as well as its high cost presents a major obstacle for application in DMFCs.[2] The methanol permeability of the crosslinked ETFE-*g*-poly(vinyltoluene-*co*-DVB) membrane at 80°C is plotted in Figure 10. As expected, the methanol permeability of the membrane increased with an increase in its proton conductivity. This relationship was similar to that between the water uptake and conductivity. It is interesting that the methanol permeability was significantly lower than that of the Nafion membrane. For instance, at a similar conductivity of 0.06 S cm^{-1}, the conductivity of the crosslinked ETFE-*g*-poly(vinyltoluene-*co*-DVB) membrane was 1.8×10^{-6} $cm^2 s^{-1}$ and the conductivity of the Nafion membrane
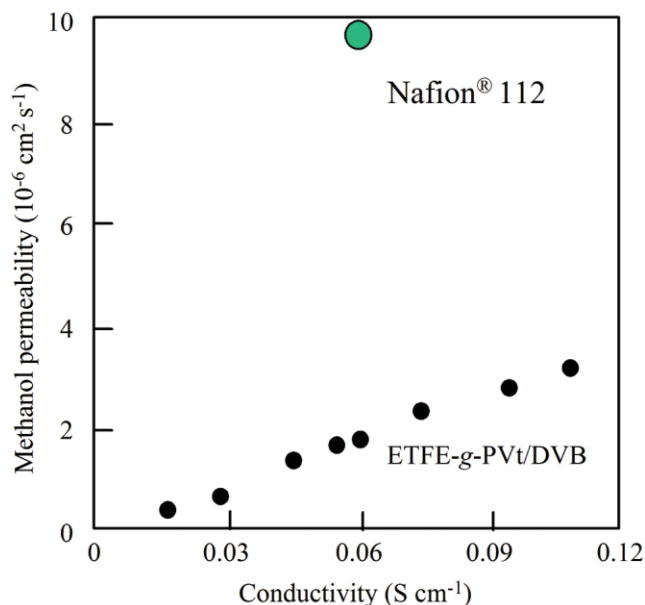

Figure 10 Methanol permeability of the ETFE-*g*-poly(vinyltoluene-*co*-DVB) membranes at 80°C. For comparison, the value of Nafion 112 membrane is also plotted. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was 9.7×10^{-6} cm^2 s^{-1}; the crosslinked ETFE-*g*-poly-(vinyltoluene-*co*-DVB) membrane showed a five times lower methanol permeability than the Nafion membrane. The difference in the methanol permeability between the crosslinked ETFE-*g*-poly(vinyltoluene-*co*-DVB) membrane and the Nafion membrane was due to the fact that the Nafion membrane preferred the adsorption of methanol, while the crosslinked ETFE-*g*-poly(vinyltoluene-*co*-DVB) membrane preferred the adsorption of water. Therefore, the crosslinked ETFE-*g*-poly(vinyltoluene-*co*-DVB) membrane is a more promising material for the DMFC.

CONCLUSIONS

The monomers of vinyltoluene and vinyltoluene/DVB, as well as the traditional monomers of styrene and styrene/DVB were successfully grafted into the ETFE films, using the preirradiation method. The grafting was influenced by the preirradiation dose, graft temperature, and the DVB crosslinker. In the presence of 5 vol % DVB, the graft reaction of vinyltoluene/DVB into the ETFE films was lowered, while that of styrene/DVB was enhanced. The degree of grafting can be controlled over a wide range by the preirradiation dose and the graft time.

Polymer electrolyte membranes were successfully prepared by sulfonation of the grafted films and subsequent hydrolysis. The sulfonation reached a high ratio of about 90%. The DVB-crosslinking structure in the membrane distinctly constrained the water uptake but simultaneously lowered the proton conductivity. Even then, the crosslinking structure was highly advantageous for improving the chemical stability of the membrane. The methyl substitution further improved the membrane stability.

Results of the methanol permeability indicated that the crosslinked ETFE-*g*-poly(vinyltoluene-*co*-DVB) membrane was an efficient barrier to deter the methanol crossover to the cathode in a DMFC. Together with the high proton conductivity, appropriate thermal and chemical stabilities, the crosslinked ETFE-*g*-poly(vinyltoluene-*co*-DVB) membrane could be expected to be an attractive material for the fuel cells.

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