

Comparative Study on the Preparation and Properties of Radiation-Grafted Polymer Electrolyte Membranes Based on Fluoropolymer Films

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ABSTRACT: In this study the fluoropolymers, poly(ethylene-co-tetrafluoroethylene) (ETFE) and poly(vinylidene fluoride) (PVDF) films, together with the radiation-induced crosslinked polytetrafluoroethylene (cPTFE) film were compared on the basis of their preparation and properties of radiation-grafted polymer electrolyte membranes. The polymer electrolyte membranes were prepared by radiation grafting of styrene into the base films and subsequent sulfonation. The proton conductivity and chemical stability of the three types of membranes with a similar ion exchange capacity (IEC) near 1.0 mmol/g were investigated and are discussed in detail. Although the ETFE-based polymer electrolyte membrane was relatively more stable, its proton con-

ductivity was lower than those of the PVDF- and cPTFE-based membranes. On the other hand, the cPTFE-based membrane showed a significantly higher proton conductivity, but its chemical stability was shorter than that of the ETFE-based membrane. It is considered that the difference in the preparation and properties of the polymer electrolyte membranes was due to the difference in the degree of crystallinity as well as in the chemical structure of the fluoropolymer base films. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1966–1972, 2007

Key words: polymer electrolyte membrane; radiation grafting; proton conduction; stability

INTRODUCTION

Radiation grafting is an attractive means of modifying the physicochemical properties of polymer films, and is of particular interest for achieving specifically desired properties as well as excellent mechanical properties. The grafting can be initiated by high-energy irradiation, such as γ -rays and electron-beams, using the preirradiation method or simultaneous radiation grafting. For the preirradiation method, the grafted films are prepared by preirradiation of the base films to create polymer radicals, followed by graft polymerization in a monomer solution. The advantages of radiation grafting include the lack of need for chemical initiators, the easy preparation from the preformed films, and the easy control of the degree of grafting. The grafted materials possess the superimposition of properties related to the backbone and the grafted chains. Recently, a great deal of work has been dedicated to preparing low-cost polymer electrolyte membranes using the radiation grafting

method.^{1–5} This was prompted by their potential applications in fuel cells.

Many base films have been used for the preparation of polymer electrolyte membranes, which have been well reviewed by Nasef and Hegazy.² The base film in the membrane functions as a hydrophobic host that constrains the membrane swelling in water and provides the mechanical and chemical stability. Therefore, the nature of the base films to be used for membrane preparation is an important parameter that has to be carefully dealt with in order to address the material properties required for the target fuel cell membranes. Basically, the base films have to possess the ability to easily generate stable free radicals upon exposure to irradiation and high resistance towards radiation degradation. To ensure the long-term durability of the polymer electrolyte membranes, fluoropolymer films are often chosen as the base materials because of their outstanding thermal and chemical stabilities and their ability to produce highly stable radicals when exposed to high-energy radiation. It has recently been shown that fluoropolymer films can be structurally modified by radiation grafting with styrene and subsequent sulfonation for the preparation of fuel cell membranes.^{6–9}

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TABLE I
Fluoropolymer Base Films Used

Films	Structure	Producer	Melting point (°C)	Crystallinity (%)
ETFE	$-(CF_2CF_2)_m-(CH_2CH_2)_n-$	Asahi Glass	258	32
PVDF	$-(CF_2CH_2)_n-$	Kureha	176	48
cPTFE	$-(CF_2CF_2)_n-$	Nitto Denko	316	64

Poly(ethylene-*co*-tetrafluoroethylene) (ETFE) and poly(vinylidene fluoride) (PVDF) are partially fluorinated films, which generally undergo crosslinking when preirradiation is performed.^{10,11} These advantages have made them favorable substrates for radiation grafting. On the contrary, the polytetrafluoroethylene (PTFE) film is a perfluorinated material, which often undergoes chain scission upon preirradiation exposure. This behavior is unfavorable due to the drastic decrease in the mechanical properties after preirradiation.¹¹ Nevertheless, the interest in using the PTFE film for fuel cell membrane preparation has been renewed after the polymer was found to be crosslinked upon irradiation above its melting temperature. The crosslinked PTFE (cPTFE) film has an adequate resistance to radiation degradation so that it is favorable for radiation grafting.⁸ In addition, styrene is more easily grafted into the cPTFE film than the original PTFE film.^{12,13}

In our previous study, the cPTFE and ETFE films were used as the base films in order to prepare the polymer electrolyte membranes and the performance of the fuel cells containing the ETFE-based membranes have been reported.^{8,9,14} Furthermore, the suitability of the commercially available fluoropolymer films have been studied as base films for preparation of polymer electrolyte fuel cell membranes, where preirradiation in air was performed before grafting.⁹ In this study we compared the preparation and properties of polymer electrolyte membranes from the most commercially available fluoropolymers, ETFE, PVDF, and PTFE films, which were preirradiated in argon to avoid the oxygen influence before grafting. The PTFE film was radiation-induced crosslinked prior to this study.⁸ The influence of the base films on the grafting process and the properties, such as ion exchange capacity (IEC), proton conductivity, water uptake, and chemical stability of the prepared membranes were compared and are discussed.

EXPERIMENTAL

The fluoropolymer films ETFE, PVDF, and cPTFE in the form of 50 μm thickness used in this study are shown in Table I. The cPTFE film was prepared by γ -ray irradiation of the original PTFE film with a dose of 100 kGy at 340°C under an argon gas atmosphere.⁸

The melting point and degree of crystallinity were measured using the differential scanning calorimetry (DSC) method, as described in our previous article.^{8,9}

The process for the preparation of the polymer electrolyte membranes involves three steps. As the first step, the glass tube with added base films at a size of 2 \times 3 cm was degassed for 12 h and argon gas was then filled in the tube for the γ -ray preirradiation at room temperature. A preirradiation dose of 10 kGy was performed for the samples within 1 h. After the preirradiation step, argon gas-bubbled 40 vol% styrene solution of toluene was quickly added to the tube. The grafting reaction was initiated by placing the tube in the thermostatic bath controlled at 60°C. 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_0 and W_g are the film weights before and after the grafting reaction, respectively.

As the third step, 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.

Ion exchange capacity (IEC) 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 0.1 M NaOH solution. Based on the titration results, the IEC was calculated as $0.1 V_{\text{NaOH}}/W_{\text{dry}}$, where V_{NaOH} (mL) is the volume of consumed NaOH solution at pH 7.0, and W_{dry} (g) is the dry weight of the membrane in the protonic form. The theoretical IEC was calculated as $1000d/(100M_1+dM_2)$, where d is the degree of grafting, M_1 and M_2 are 104 and 184, being the molecular weights of styrene and styrene sulfonic acid, respectively. The degree of sulfonation was defined as $IEC_d/IEC_t \times 100$, where IEC_d and IEC_t are the determined and theoretical IEC, respectively.

Water uptake was calculated from the weights in the wet and dry states of the polymer electrolyte membrane, as described previously.¹⁴

The proton conductivity of the membrane at 25°C was obtained by impedance spectroscopy measurement using a Solartron 1269 analyzer. The samples were hydrated in water overnight before measure-

TABLE II
Radiation-Grafted Polymer Electrolyte Membranes

Base films	Grafting time (h)	Grafting (%)	IEC (mmol/g)	Conductivity (S/cm)	Water uptake (%)	Durability time (h)
ETFE	1.0	14.3	1.01	0.011	19.9	60
ETFE	1.5	23.4	1.43	0.032	31.2	52
ETFE	2.0	27.8	1.62	0.060	36.4	36
ETFE	4.0	33.9	1.86	0.089	44.4	28
PVDF	1.0	7.4	0.66	0.013	8.2	36
PVDF	1.5	15.9	1.03	0.033	20.3	24
PVDF	2.0	19.4	1.22	0.055	25.6	18
PVDF	4.0	25.7	1.48	0.086	32.3	15
cPTFE	1.0	2.2	0.08	0.001	0.8	21
cPTFE	1.5	3.8	0.21	0.002	3.6	33
cPTFE	2.0	8.9	0.71	0.039	13.7	45
cPTFE	4.0	13.2	0.96	0.061	18.3	42

ment and clamped between two Pt electrodes for recording of the impedance spectroscopy. The real impedance taken at zero imaginary impedance was used to calculate the proton conductivity of the membrane.

The chemical stability was characterized by the weight loss of the membrane in an H₂O₂ aqueous solution. The membrane with a size of 2 × 2 cm² was immersed in the 3% H₂O₂ aqueous solution at 60°C. During the immersion the membrane was intermittently taken out of the solution and weighed after wiping off the excess surface water.

The grafting time and degree of grafting, together with the IEC, water uptake, proton conductivity, and chemical stability of the prepared polymer electrolyte membranes are summarized in Table II.

RESULTS AND DISCUSSION

Radiation grafting of styrene into the different fluoropolymer films

The process for preparation of the polymer electrolyte membrane involves preirradiation, grafting, and the final sulfonation. Preirradiation in argon gas induces the scissions of the fluoropolymer films, leading to the formation of polymer radicals,^{10,15} which can act as active sites for initiating the graft polymerization. Therefore, on the addition of the styrene monomer the graft polymerization occurs. The radiation grafting initially occurs only on the surface that is in intimate contact with the monomer solution. The grafted region swells in the monomer and thus the monomer diffuses further into the film interior and reacts.¹⁶ The kinetics of the grafting of styrene into preirradiated ETFE, PVDF, and cPTFE films have been widely studied.^{13,17–19}

For the comparative study, radiation grafting of styrene into the three types of base films was carried out under the identical conditions: preirradiation under argon with a dose of 10 kGy and then reaction with styrene at 60°C in argon gas for different time dura-

tions. The degrees of grafting are summarized in Table II and the kinetic curves are plotted in Figure 1. For all the three types of base films the degree of grafting initially gradually increases with time over a period of about 2 h, then plateaus out into a gently sloping, fairly linear region extending to 4 h. However, the grafting rates are quite different. The initial grafting rates are 5%, 11%, and 16% per hour for the cPTFE, PVDF, and ETFE film, respectively. At the grafting time of 4 h the ETFE film shows the highest degree of grafting, while the cPTFE film shows the lowest degree of grafting. The low grafting ability of cPTFE film compared to the other two films is due to its perfluorinated chemical structure and high degree of crystallinity. On the other hand, grafting in partially fluorinated PVDF and ETFE films can be initiated by C-H and C-F bond splitting and this will boost the grafting compared to cPTFE films. However, although the PVDF and ETFE films have a similar chemical structure, the grafting rate of the PVDF film is slower than that of the ETFE film. This may be due to their different degree of crystallinity in the films. In general, styrene grafting occurs in the amorphous phase of the base films.² The ETFE film has a much lower degree of crystallinity, and thus a greater fraction of the amorphous region for grafting, resulting in the faster grafting rate.

Ion exchange capacity (IEC), proton conductivity, and water uptake

The grafted film was sulfonated to obtain the polymer electrolyte membrane. The sulfonation was performed in a 0.2 M chlorosulfonic acid solution of 1,2-dichloroethane at 60°C for 8 h followed by hydrolysis in distilled water at 80°C for 12 h. The introduction of the hydrophilic sulfonic acid groups into the strongly hydrophobic styrene-grafted films produces a two-phase structure, a hydrophobic and hydrophilic phase in the membrane.²⁰ The ion exchange, water uptake,

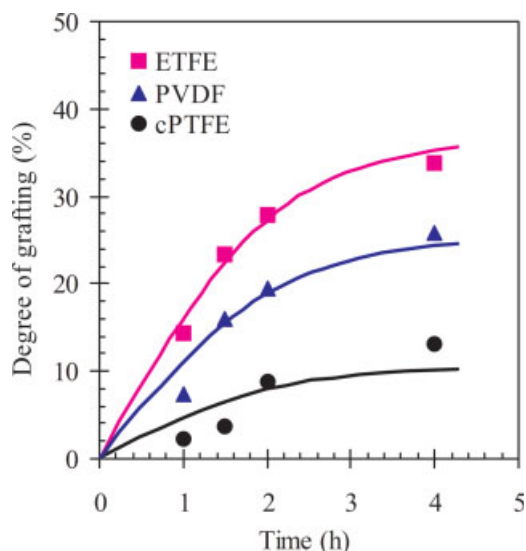


Figure 1 Grafting of styrene into the ETFE, PVDF, and cPTFE films. Preirradiation dose, 10 kGy; grafting temperature, 60°C; atmosphere, argon gas. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and proton conductivity properties are all due to the hydrophilic phase in the membrane.

The IEC indicates the content of sulfonic acid groups in the membrane. The detected IECs of the prepared membranes are summarized in Table II and are plotted in Figure 2. For comparison, the calculated theoretical curve is also plotted in Figure 2. The detected IEC is somewhat lower than that of the calculated value. This may be due to a deviation from the assumption that each styrene unit was attached with

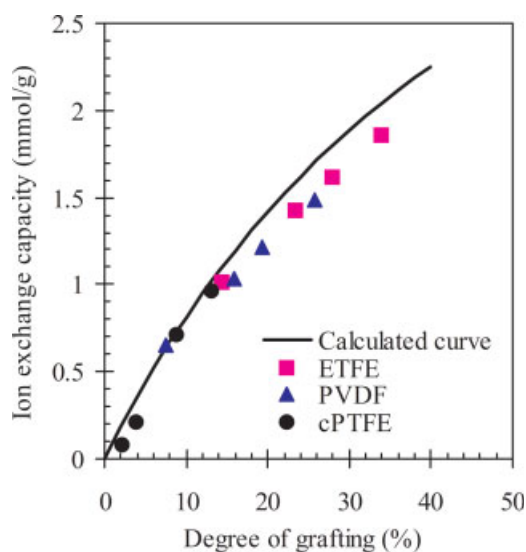


Figure 2 IEC of the ETFE-, PVDF-, and cPTFE-based membranes as a function of degree of grafting. For comparison, the calculated curve was also plotted. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

one sulfonic acid group, and the sulfone formation between the two sulfonic acid groups at high temperature.²¹ Even then, the degree of sulfonation under the experimental conditions is considered to be about 90% and is independent of the base films. The IEC 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 films. Therefore, the IEC of the membrane can be freely controlled by changing the degree of grafting. With a higher degree of grafting, such as 34%, the IEC can reach a higher value of 1.8 mmol/g.

The proton conductivity and water uptake of the membranes prepared from different films are summarized in Table II. The proton conductivity was determined in its water-saturated state at 25°C. As expected, both the proton conductivity and water uptake of each type of membrane increases with the increasing degree of grafting, due to the increased IEC. However, the proton conductivity is not only in close relation to the IEC, but is also quite affected by the properties of the base film. Figure 3 shows the proton conductivity and water uptake of the radiation-grafting polymer electrolyte membranes and the commercial Nafion membrane with a similar IEC near 1.0 mmol/g. The proton conductivities of the membranes prepared from the ETFE, PVDF, and cPTFE films were quite different, being 0.011, 0.033, and 0.061 S/cm, respectively, while their water uptakes are very similar, locating in the narrow region of 18.3–20.3%. The water uptake is considerably lower than that of the Nafion membrane (30%). Even then, the cPTFE-based electrolyte membrane shows the same proton conductivity as the Nafion. The quite different proton conductivity of the three radiation grafting membranes with the similar IEC

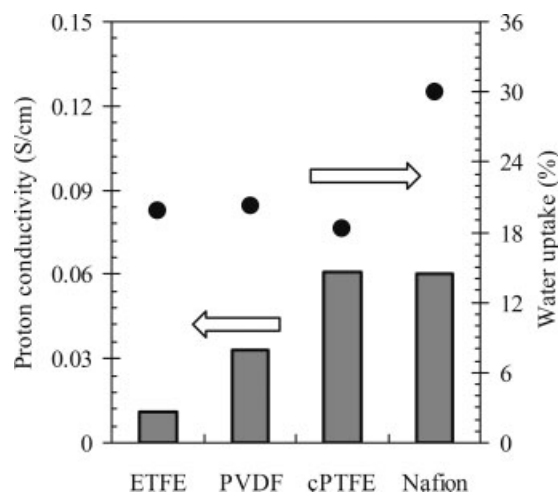


Figure 3 Proton conductivity and water uptake of the ETFE-, PVDF-, and cPTFE-based membranes with an IEC near 1.0 mmol/g. For comparison, the Nafion 112 membrane is also given in the figure.

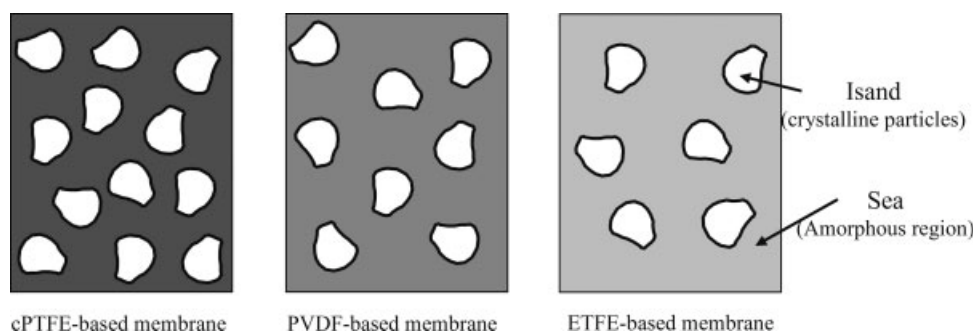


Figure 4 Hypothesized "sea-island" structure for the ETFE-, PVDF-, and cPTFE-based membranes.

and water uptake is in close relation to the properties of their base films.

To understand why different proton conductivities occurred in the membranes for similar IEC, the structure of the polymer electrolyte membranes should be clarified. The radiation-grafted polymer electrolyte membrane is very complex, having the "sea-islands" special structure (Fig. 4). The ungrafted crystalline particles appear as the "islands" and the sulfonated grafted amorphous region appears as the "sea." The latter still has a two-phase microstructure, i.e., hydrophilic and hydrophobic. The aggregated sulfonic acid groups in the "sea" form the ionic clusters that play a role in proton transport. For the membranes with similar IEC, the higher degree of crystallinity results in a lower fraction of the amorphous region and, consequently, a higher ionic cluster concentration in the "sea" of the membrane. In other words, the ionic cluster concentration in the "sea" is in proportion to the volume of the "islands" (degree of crystallinity) of the base film. The cPTFE, PVDF, and ETFE base films have the degrees of crystallinity of 64, 48, and 32%, respectively (Table I). Therefore, the ionic cluster concentrations in the "sea" of the membranes with similar IEC are in the following sequence: cPTFE- > PVDF- > ETFE-based membranes, resulting in the same sequence for the proton conductivity (Fig. 3).

The distribution of the graft chains in the base films is another important parameter that strongly affects the proton transport in the target membranes. It was concluded that the higher the degree of crystallinity, the more uniform the distribution of the graft chains in the grafted fluoropolymer films with the same degree of grafting.⁹ Furthermore, the other intrinsic properties of the base fluoropolymer films, such as molecular weight, crystallinity size, and orientation, are also important parameters that influence the graft chain distribution. Therefore, the graft penetration limit, where the graft chains penetrate into the entire base films, is considerably different for the PVDF, ETFE, and cPTFE films. In Figure 5 the thresholds of IEC for the available proton transport are about 0.3, 0.8, and 1.2 mmol/g for the cPTFE, PVDF, and ETFE-based electrolyte membranes, corresponding of the

degree of grafting (graft penetration limit) near 4%, 12%, and 18%, respectively. Therefore, the 1.0 mmol/g is above, near, and below of the IEC threshold for the cPTFE-, PVDF-, and ETFE-based electrolyte membranes, respectively, resulting in a proton conductivity in the series: cPTFE- > PVDF- > ETFE-based electrolyte membrane.

Chemical stability of the polymer electrolyte membrane

Chemical stability is one of the most important requirements for fuel cell membranes. During a fuel cell operation, the H_2O_2 originates from oxygen diffusion through the membrane and incomplete reduction at the fuel cell anode, bringing about a severe degradation of the membrane.^{22,23} In this study the chemical stability of the polymer electrolyte membrane was tested in a 3% H_2O_2 aqueous solution at 60°C. The weight of the membrane was determined as a function of time. Figure 6 shows the weight changes of the

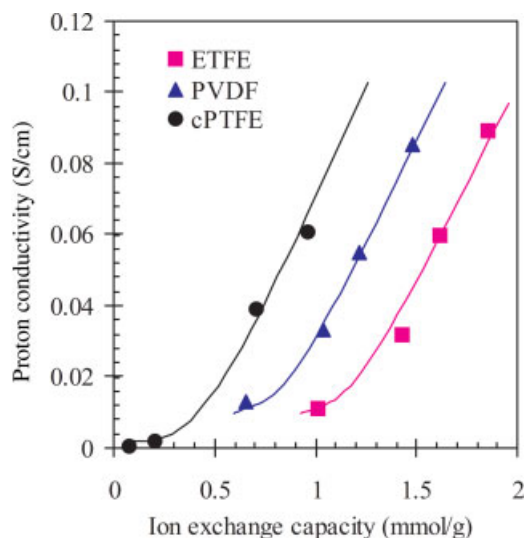


Figure 5 Relationship between the IEC and proton conductivity of the radiation-grafted polymer electrolyte membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

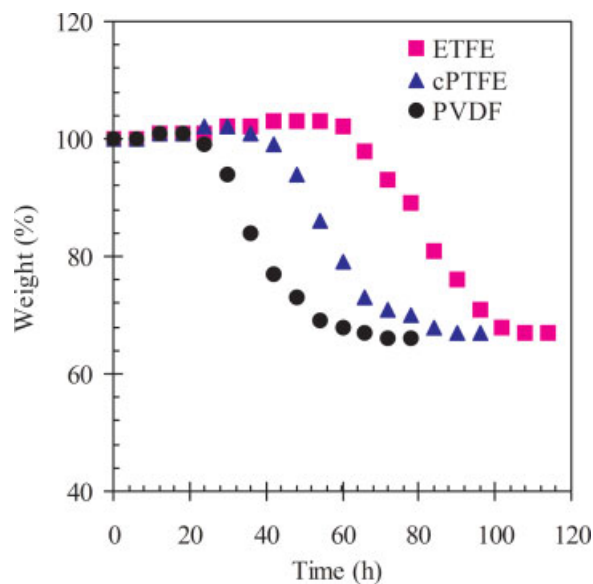


Figure 6 Durability of the ETFE-, PVDF-, and cPTFE-based membranes with an IEC of about 1.0 mmol/g in a 3% H₂O₂ aqueous solution at 60°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

membranes based on the ETFE, PVDF, and cPTFE films, with a similar IEC near 1.0 mmol/g. During testing, it was found that the outset of degradation (determined as a weight loss) occurred after 24 h with the PVDF-based membrane, after 42 h with the cPTFE-based membrane, and after 60 h with the ETFE membrane. In this study, the time at the outset of degradation is defined as the durability time. The degradation is caused by the reaction between H₂O₂ and the α -hydrogen on the graft chain.²⁴ In Figure 6 the cPTFE-based membrane shows a longer durability time than the PVDF-based membrane, but a shorter durability time than the ETFE-based membrane.

Since the degradation is caused by the reaction between H₂O₂ and the α -hydrogen on the graft chains, the H₂O₂ diffusion in the membrane is an important parameter that affects the durability time. In Figure 6 the IECs and water uptakes have very close values in the three types of membranes. However, the H₂O₂ diffusion through the membrane is considerably different. It is believed that the H₂O₂ diffusion has the same sequence as proton transport, being cPTFE- > PVDF- > ETFE-based membranes. However, the cPTFE-based membrane shows a longer durability time than that of the PVDF-based one. This can be due to the high chemical stability of its perfluorinated backbone and the crosslinking structure, which can protect graft chains (ion cluster) from degradation. In other words, there is a competition in the cPTFE-based membrane between the two effects: the positive effect from the crosslinked perfluoropolymer PTFE base film and negative effect from the high ionic cluster concentra-

tion in the amorphous region ("sea region" in Fig. 4). On the other hand, for membranes with a similar proton conductivity near 0.06 S/cm, as shown in Table II, the durability time of the perfluoropolymer cPTFE-based membrane (durability time, 42 h) is clearly longer than those of the partially fluorinated ETFE- and PVDF-based membranes (durability times, 36 and 18 h, respectively). This can be explained by the quite different water uptake of the electrolyte membrane, the chemical stability, and degree of crystallinity of the base films.⁹

CONCLUSIONS

The introduction of the styrene monomer into ETFE, PVDF, and cPTFE films using the preirradiation grafting method and subsequent sulfonation appears to produce promising polymer electrolyte membranes for fuel cells. The cPTFE film was modified by radiation-induced crosslinking at high temperature in an argon gas atmosphere prior to the study. The grafting rate of the PVDF film is faster than that of the cPTFE film, but is slower than that of the ETFE film under the same grafting conditions. Sulfonation of the grafted films reaches a high sulfonation ratio of about 90%, which is independent of the base film.

For the membranes with a similar IEC near 1.0 mmol/g, the proton conductivity is in the following sequence: cPTFE- > PVDF- > ETFE-based membranes, and the durability time is in the following sequence: ETFE- > cPTFE- > PVDF-based membranes. However, the water uptakes of these membranes are quite similar to each other. It is concluded that the intrinsic properties, such as the chemical structure (PTFE, ETFE, or PVDF) and degree of crystallinity, are the key parameters that affect the styrene grafting and the properties of the corresponding membrane, such as proton conductivity and durability time.

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