

Preparation of Ion Exchange Membranes by Preirradiation Induced Grafting of Styrene/Divinylbenzene into Crosslinked PTFE Films and Successive Sulfonation

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Received 8 March 2005; accepted 15 July 2005

DOI 10.1002/app.22648

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Ion exchange membranes (IEMs) were prepared by preirradiation induced grafting of styrene with or without divinylbenzene (DVB) into crosslinked polytetrafluoroethylene (RX-PTFE) films and successively sulfonated by chlorosulfonic acid. The effects of the DVB concentration and solvent on the kinetic of the graft polymerization were studied. The ion exchange capacity (IEC) values of the prepared membranes ranging from 1.5 to 2.8 mequiv/g were obtained. The degree of swelling increased with the increase in the degree of grafting, while higher crosslinking density of both the RX-PTFE matrices and the grafts suppressed the degree of swelling. The chemical stabilities of the IEMs were tested by recording the weight of the membranes being soaked in hot H₂O₂ solutions. The weight-time curves of the

prepared membranes showed one-step quick decrease due to the decomposition of the poly(styrene-sulfonic acid) (PSSA) grafts. Higher crosslinking density in both the RX-PTFE matrices and the grafts improved the chemical stability of the IEMs. The ionic conductivity of the IEMs increases with the increase in the IEC values. The IEMs with IEC values higher than 2.2 mequiv/g hold the higher ionic conductivity than that of Nafion® 112 membrane. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3587–3599, 2006

Key words: ion exchange membrane; crosslinked polytetrafluoroethylene; pre-irradiation induced graft polymerization; styrene/divinylbenzene

INTRODUCTION

IEMs can be used for the desalination of sea water, softening of hard water, recovery of metal ions, purification of bio-products, and so on.^{1–3} Especially, the developing of the IEMs for polymer electrolyte fuel cell (PEFC) applications has gained much attention recently. Radiation induced grafting of styrene and comonomers into fluorinated polymer films and successive sulfonation was designed to obtain the relative low cost IEMs [Ref. 4,5 and the references cited therein] as compared with the perfluorinated sulfonic acid membranes, such as Nafion® membranes (DuPont de Nemours Ltd.). Almost all commercially available fluorinated polymers, such as PTFE,⁶ FEP,^{7,8} PFA,^{9–11} ETFE,¹² FVDF,^{13,14} and so on, were reported to be used for preparation the sulfonic acid membranes under radiation-induced grafting and sulfonation method.

Especially, Gubler et al. reported¹⁵ the single cell durability experiment using the membrane prepared from the styrene/DVB grafted and sulfonated FEP film at a cell temperature of 80–85°C having good performance over 7900 h. This result suggested that the radiation induced grafting method is a promising way to synthesize the new IEMs of considerably high performance and life-time, in fuel cell with relatively low cost.

Several years ago, it was reported that PTFE can be crosslinked by irradiation above its melting temperature under oxygen-free atmosphere.^{16–19} Crosslinked PTFE (RX-PTFE) showed remarkable improvements in several mechanical properties, radiation resistance, and optical properties and so on, compared with that of the noncrosslinked PTFE (V-PTFE).^{20–22}

RX-PTFE holds a radiation resistant and chemically stable network structure, and the network structure decreased the gases permeation rate.²³ For example, as compared with the 50 μm-thick V-PTFE film, the O₂ gas penetration coefficient was reduced to 69% for the RX-PTFE film with crosslinking doses of 45 kGy of the same thickness. For the RX-PTFE film with crosslinking doses of 300 kGy, the O₂ gas penetration coefficients were further reduced to 19%.²⁴ This suggested

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Contract grant sponsor: New Energy and Industrial Technology Development Organization (NEDO).

that the use of RX-PTFE films rather than V-PTFE films for the radiation induced grafting method to produce the functional membranes will increase the cell efficiency of the fuel cell by reducing the crossover of the fuel gases. Further, the crosslinking structure of the RX-PTFE should hold higher chemical stability than the crosslinking structure of the poly(styrene-co-DVB) (PS/DVB) grafts under same chemical circumstance due to the per-fluoride structure,^{25,26} which was also proved by the chemical stability test in this article. Using DVB together with styrene in the preirradiation induced graft polymerization into RX-PTFE membranes and then sulfonation is expected to obtain the sulfonic acid membranes with good performance and durability, which was executed in this work.

Our research group has developed the partially fluorinated sulfonic acid films for PEFC applications by the grafting of styrene into the RX-PTFE films using preirradiation induced graft polymerization method in gas and liquid phase. V-PTFE films were also used as a reference.²⁷⁻²⁹ However, the films used are thicker than the favorable thickness for the real PEFC applications. This is because the V-PTFE films are obtained by slicing of the sintered PTFE block.

Recently, our group has developed the thin V-PTFE films with thickness of 5–30 μm by coating the PTFE dispersion on the aluminum films. Then, the thin RX-PTFE films were obtained by radiation-induced crosslinking using electron beam above the melting temperature of PTFE under oxygen-free atmosphere. The RX-PTFE films, with different crosslinking doses, were used for preirradiation-induced grafting of styrene with or without DVB and then sulfonated, and the V-PTFE films were used as a reference. Therefore, the IEMs were obtained by sulfonating the grafted films. The using of the thin IEMs was believed will improve the cell performance, while the risk of increase in gas permeation should be taken into consideration.

Here, we will report the kinetic study of the graft polymerization, the sulfonation experiment, the swelling behavior, the chemical stability test, and the ionic conductivity of the sulfonated membranes.

EXPERIMENTAL

Materials

PTFE dispersion containing 60% solid component labeled as FLON XAD-911 was supplied from Asahi Glass Fluoropolymers Co. Ltd. (Japan). The molecular weight of the PTFE was about 1.0×10^7 from the determination by DSC analysis under Suwa's equation.³⁰ The V-PTFE films (abbreviated as V films) were obtained by coating the PTFE dispersion on the 50- μm aluminum sheets. The irradiations were performed with a Curetron EBC-200-AA2 electron beam acceler-

ator, Nissin-High Voltage Co., LTD. (Japan). The voltage was set at 200 kV and the current was set at 1 mA. The absorbed dose is 15 kGy per pass. The RX-PTFE films were made of the V films by electron beam irradiation around $(335 \pm 5)^\circ\text{C}$ under nitrogen gas atmosphere, as described in our previous papers.^{16,18} After the crosslinking, the aluminum sheets were removed from the RX-PTFE films by reacting with HCl solution. The RX-PTFE films used in this work were crosslinked by irradiating to doses of 150 and 450 kGy (abbreviated as RX150 and RX450 films, respectively). The thicknesses of the RX150 and RX450 films were 10 ± 1 and 8 ± 1 μm , respectively. The V films were used as a reference and the average thickness was 12 ± 1 μm .

Styrene monomer (99%, stabilized by 0.003% 4-*t*-butylpyrocatechol), carbon tetrachloride, cyclohexane, and 30% H_2O_2 aqueous solution were obtained from Wako Pure Chemical Industry, Ltd. (Japan) and used as received. DVB as a mixture of 55% *m*-, *p*-DVB in ethylvinylbenzene, and chlorosulfonic acid were supplied by Tokyo Kasei Kogyo Co. Ltd. (Japan), used as received. Nafion® 112 membranes were purchased from DuPont de Nemours Ltd. (USA), and were treated in concentrated HNO_3 at 80°C to activate all the ion exchange sites, and then washed with deionized water to make it acid free.

Graft polymerization

RX150, RX450, and V films were irradiated with the dose of 30 kGy under nitrogen atmosphere at room temperature by electron beam. Irradiated samples were stored in the refrigerator at -20°C under air for 4 days, to turn the trapped radicals into peroxide radicals. The irradiation under nitrogen atmosphere resulted mainly in alkyl radicals while the irradiation under air resulted mainly in end chain radicals.³¹ Then, the irradiated samples were cut into desired size and put into a reaction vessel made of stainless steel, and certain amount of the monomer mixture with or without cyclohexane, which acted as the solvent, was added to keep the films soaked in the liquid. Details of the composition of the monomers solution are provided in the discussion section. Thus, the reaction vessel was evacuated and then heated in oil bath set to 70°C . After desired reaction periods, the graft polymerizations were stopped and the films were taken out and washed with cyclohexane. The grafted films were soaked in cyclohexane in an ultrasonic washer labeled as USK-3 with power of 150 W (SND Co. Ltd., Japan) for 1 h, to remove the homopolymer stuck on the surfaces of the grafted films. Then, the grafted films were soaked in fresh cyclohexane for 24 h. After these procedures, the grafted films were washed again with fresh cyclohexane. Finally, the films were dried in vacuum until weights were constant.

The degrees of grafting (DOGs) were determined as the weight increase of the samples, according to the following equation:

$$\text{Degree of grafting (DOG)}(\%) = \frac{W_g - W_0}{W_0} \times 100\% \quad (1)$$

where, W_g and W_0 are the weights of the samples after and before grafting, respectively.

For the grafted films, the abbreviated labels are used in this article. For example, RX150-g-PS stands for the RX150 film grafted by styrene only and RX450-g-PS/DVB stands for the RX450 film grafted by styrene with DVB. To talk of the difference in the DVB concentration used, RX150-g-PS/4% DVB stands for the RX150 film grafted by 4% DVB with 96% styrene for example.

Sulfonation experiment

IEMs were obtained by sulfonating the grafted films using chlorosulfonic acid in carbon tetrachloride (1:9 v/v) at room temperature for 24 h. The sulfonated membranes were washed by deionized water for several times. Then, the membranes were soaked in 1M HCl solution for 24 h to turn the sulfonyl chloride groups to sulfonic acid groups. After that, the membranes were washed acid free using deionized water for several times until the pH values of the used water were exactly 7.0.

The abbreviated labels for the sulfonated membranes were adding -SA or -SNa in the end of the labels of the corresponding grafted films stand for the membranes in acid form or in salt form, respectively. For example, RX150-g-PS/4% DVB-SA means the membrane was prepared by the grafting of styrene with 4% DVB into RX150 film and successively sulfonated, and kept in acid form. While, RX450-g-PS/10%DVB-SNa means the membrane was prepared by the grafting of styrene with 10% DVB into RX450 film and successively sulfonated and neutralized by NaOH to salt form.

Swelling behavior of the sulfonated membranes

The sulfonated membranes in acid form were soaked in deionized water for 1 day at room temperature. The membranes were taken out, and the excess water on the surfaces was quickly removed by the blotter, and then weighed. The membranes were dried in vacuum at 80°C for 24 h. The dried membranes were also weighed. The degree of swelling was calculated according to the following equation:

$$\text{Degree of swelling (DOS)} (\%) = \frac{W_w - W_d}{W_d} \times 100\% \quad (2)$$

where, W_w and W_d are the weights of the wet and the dried membranes, respectively.

IEC value measurement

The IEC values of the sulfonated membranes were determined by titration. The dried membranes in acid form were soaked in 0.01M NaOH solution (NaCl was added to keep the concentration of Na^+ as 1M) at room temperature for 1 day. The basic solutions were then titrated with standard 0.01M HCl solution by a 716 DMS Titrimo automatic titrator (Metrohm Herisau Co., Switzerland) until pH 7 was reached. IEC values (mequiv/g) were calculated by dividing the amounts of NaOH neutralized with the dried weights of the membranes.

Chemical stability of the sulfonated membranes

The chemical stability of the sulfonated membranes was tested by recording the weight of the membranes being soaked in 6% H_2O_2 solution at 60°C. The membranes in acid form were firstly swelled in deionized water at 60°C for 1 day. Then the wet weights were taken as the initial weights of the membranes. After that, the membranes were soaked in 6% H_2O_2 solution at 60°C. After desired period, the membranes were taken out, and the wet weights of the membranes were recorded immediately. The membranes were soaked again in fresh 6% H_2O_2 solution at 60°C. The operations were repeated until the weight-time curves were obtained.

Ex situ ionic conductivity measurement

The membranes were soaked in deionized water at room temperature and cut into $1 \times 1 \text{ cm}^2$ before the measurements. The wetted membranes were gently placed between two pieces of $1 \times 1 \text{ cm}^2$ carbon paper (labeled as TGP-H-060 with thickness of 0.2 mm, purchased from Toray Co. Ltd., Japan). Then the carbon paper/membrane sets were clamped with two copper electrodes. The AC impedance was measured immediately with the frequency between 100 kHz and 0.1 Hz on a NF5080 Frequency Response Analyzer, NF Electronic Instruments Co. (Japan).

Measurements

Thicknesses of the films and membranes were measured by a MDC-25M μm , Mitutoyo Co. Ltd. (Japan).

The FT-IR spectroscopy analyses were performed in a step of 4 cm^{-1} by a JIR-700 FT-IR instrument, JEOL, Co., Ltd. (Japan).

High-performance liquid chromatography (HPLC) analyses were taken by an Agilent 1100 series system, Agilent Technologies, Inc. (USA). A SunFire® (Waters

Co. Ltd., USA) C18 ($4.6 \times 150 \text{ mm}^2$) column was used and the temperature was set at 40°C . The water and methanol were used as the solvent and the amount of the samples used was $10 \mu\text{L}$. The chemical components were detected by a UV detector with the wavelength of 220–400 nm.

RESULTS AND DISCUSSION

Influence of the concentration of DVB in graft polymerization

Figure 1(a) shows the dependence of the DOGs on the graft polymerization periods of the RX150 films grafted by styrene with different DVB concentrations. The initial grafting rates were calculated by linear fitting of the initial part of the kinetic curves and listed in Table I. The grafting rate increased with the increase in the DVB concentration used in the graft polymerization. Gulp et al. reported that the initial grafting rate was decelerated when the $50\text{-}\mu\text{m}$ -thick FEP films were grafted by styrene with 10% DVB at 60°C , compared with the initial grafting rate of the same films grafted by styrene only,³² which is different from our results. They attributed the deceleration to the lower diffusion rate of the monomers into the matrix of the FEP films to the formation of the crosslinking structure of the PS/DVB grafts. In the present work, the thickness of the RX150 films used was $10 \mu\text{m}$, which was about 20% of the thickness of the FEP films they used. The grafting temperature was 70°C in our work, which was higher than that in their work. These mean, it is easier for monomers to diffuse into the RX150 films; thus, the deceleration in the diffusion rate of the monomers did not play an important role in our work. On the other hand, the higher reactivity of DVB than that of styrene became the dominant factor, thus the initial grafting rate was accelerated with the increase in DVB concentration.

Figure 1(b) shows the dependence of the DOG on the graft polymerization period for the RX450 films grafted by styrene with different concentration of DVB. The RX450 films have high concentration of the active sites, which are available for graft polymerization than RX150 films, under the same preirradiation conditions, because of the higher $G(\text{R}\bullet)$,³¹ as listed in Table I. However, the RX450 films also hold a higher crosslinking density than that of RX150 films. Higher concentration of the active sites will accelerate the grafting rate, but higher crosslinking density resulted in deceleration in the monomers diffusion rate, thus decelerating the grafting rate. The combined effect results are that the initial grafting rate and final DOG of graft polymerization of the RX450 films are similar to those of the RX150 films under same reaction conditions.

Figure 1(c) shows the dependence of the DOG on the graft polymerization period for the V films grafted

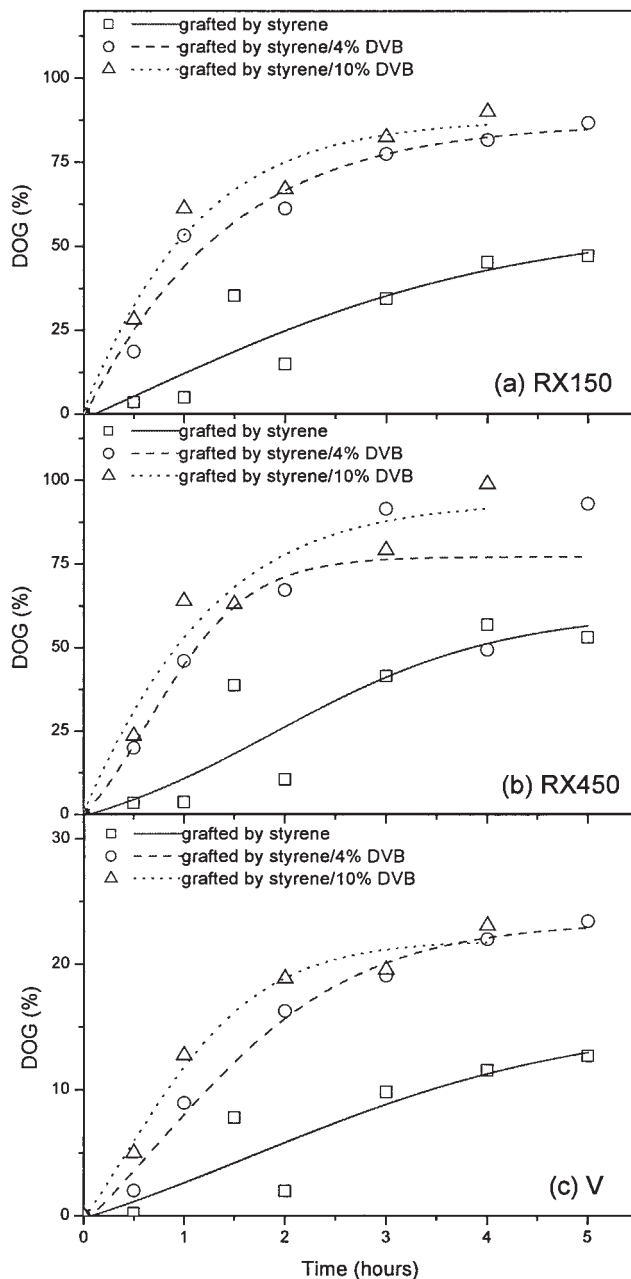


Figure 1 Variation of the degree of grafting in (a) RX150, (b) RX450, and (c) V films with the reaction time for grafting of styrene (solid line), styrene with 4% DVB (dash line), and styrene with 10% DVB (dot line), using preirradiation dose of 30 kGy at 70°C .

by styrene with different concentration of DVB. $G(\text{R}\bullet)$ of the V films was lower than those of the RX150 and RX450 films, thus the concentration of the active sites, which are available for the graft polymerization in the V films, is lower, and the initial grafting rate and the final DOG of the V films were lower than those of the RX150 and RX450 films under same graft polymerization conditions. The V films were broken into pieces when grafted by styrene with the existence of DVB, while they were not broken when grafted by styrene

TABLE I
The Radical G Values of the Films and the Initial Grafting Rate Under Different Monomer Compositions

Label	$G(R\bullet)$	Initial grafting rate (%/h)		
		0% DVB	4% DVB	10% DVB
RX150	1.2	10	51	64
RX450	2.0	12	46	67
V	0.15	3	9	13

only, even with similar DOG. This means that the formation of the crosslinking structure of the PS/DVB grafts destroyed the crystal structure of the V films without heat treatment.

Influence of dilution by the solvent in graft polymerization

In the existence of DVB, the gel was formed as the proceeding of the graft polymerization. For the RX150 films grafted by styrene/4% DVB, no gel appeared after reaction of 5 h, but there was about 40% (vol) gel that appeared after reaction of 16 h. When the concentration of DVB was increased to 10%, about 30% gel appeared in the grafting system after reaction of 5 h, and the system became completely gel after reaction of 16 h. Because of the gel sticking to the grafted films, the gel formation gave serious damage on the RX150 films. In such a way, all the films were broken into pieces in the grafting system. So, it should be avoided by adding suitable solvent to dilute the monomers concentration in the system. Therefore, cyclohexane, which is a nontoxic solvent and has good solubility for PS, was applied to dilute the monomers concentration. Typically, the volume ratio of the monomers to cyclohexane was 1:1, and the compositions of the monomers were the same as those corresponding graft polymerizations without solvent.

Figure 2 shows the dependence of the DOG on the graft polymerization period for the RX150, RX450, and V films in solution. Because of the dilution effect with the solvent, the concentration of the monomers decreased and resulted in the deceleration in the initial grafting rate. The final DOGs of the RX150 films grafted by styrene with DVB in the existence of solvent were decreased to around 50% from around 75% of those grafted in the absence of solvent. As reported by Huslage et al., among the sulfonic acid membranes made by grafting of styrene/DVB into 25- μm -thick FEP films, the membranes had poor mechanical properties that were broken during hot-press, when the DOGs were higher than 30%.³³ So, it is important to control the DOGs in the relatively low ranges from 20 to 30% considering the balance between the mechanical properties and the electrical properties of the IEMs. In our work, the controlling of the DOGs was

realized by dilution with cyclohexane. When cyclohexane was added, there was no gel formed in the graft polymerization system at our experiment periods.

The initial grafting rate and the final DOG of the grafting into the RX450 films were reduced by the dilution effect with cyclohexane. The similar phenomenon was found in the graft polymerization of the V films with cyclohexane.

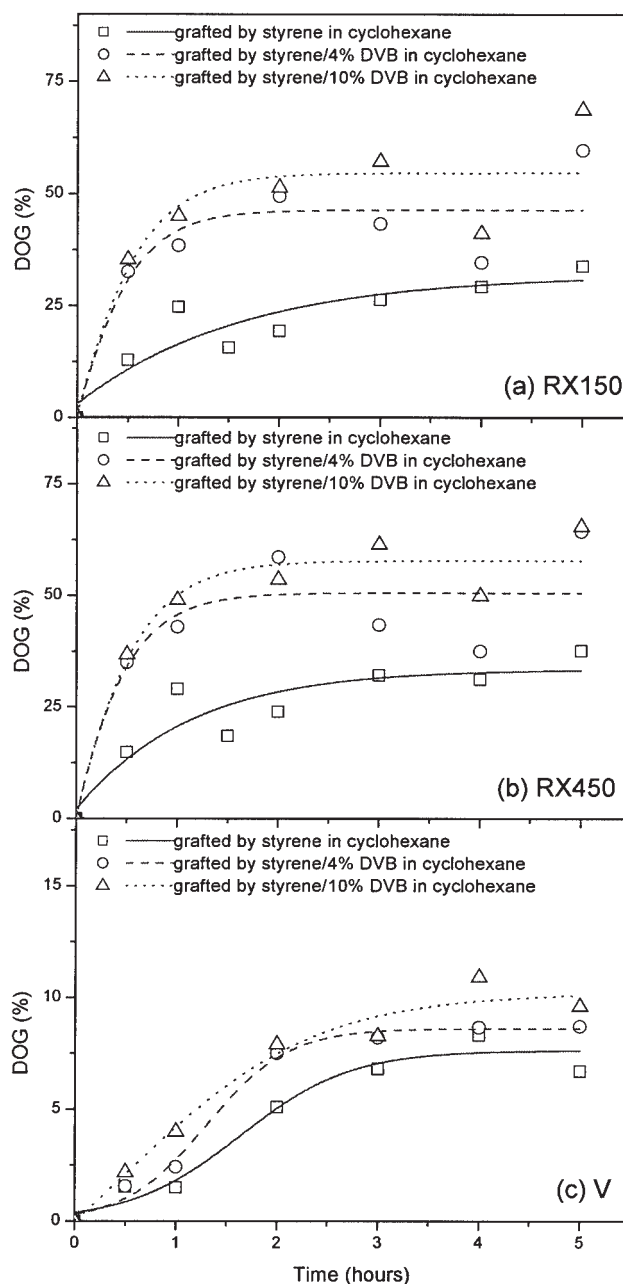


Figure 2 Variation of the degree of grafting in (a) RX150, (b) RX450, and (c) V films with the reaction time for grafting of styrene (solid line), styrene with 4% DVB (dash line), and styrene with 10% DVB (dot line) in 50% cyclohexane solution, respectively.

Sulfonation and IEC values test

IEMs were obtained by sulfonating the grafted RX150 and RX450 films using chlorosulfonic acid in carbon tetrachloride. The grafted V films were broken into pieces in the sulfonation reaction because of the poor mechanical strength.

The sulfonation using chlorosulfonic acid usually introduces the sulfynol chloride groups instead of sulfonic acid groups. In our case, the membranes were hydrolyzed with HCl catalyzed to turn the sulfynol chloride groups into sulfonic acid groups. The full hydrolyzation has been proved by three facts. The first fact is that the obtained IEC values of the sulfonated membranes are close to the calculated ones, as discussed in the following part. The second fact is that in X-ray photoelectron spectroscopy (XPS) analysis, there was no signal attributed to the Cl atom of the membranes, as reported in our previous work.³⁴ The third fact is that in the FT-IR spectra of the membranes, there is the band of O=S=O asymmetric stretching vibration of the sulfonic acid groups rather than the sulfynol chloride groups. The details will be discussed in the following FT-IR analysis section.

In the ideal case, when the grafted RX-PTFE films were sulfonated, one benzene ring of the monomer repeating units in the grafts should be substituted by one sulfonic acid group. Thus, the expected IEC values can be calculated from DOG as follows^{18,35}:

$$IEC_{\text{expected}} = \frac{1000 \times DOG / M_{\text{monomer}}}{100 + DOG + (DOG / M_{\text{monomer}}) \times M_{\text{sulfonate}}} \quad (\text{mequiv / g}) \quad (3)$$

When only styrene monomer was grafted, then the formula 3 can be rewritten as follows:

$$IEC_{\text{expected}} = \frac{9.62 \times DOG}{100 + 1.77 \times DOG} \quad (\text{mequiv / g}) \quad (4)$$

Figure 3 shows the experimental IEC values of the membranes made by grafting and sulfonating of the RX150 and RX450 films with the expected IEC values. Higher DOG resulted in higher IEC values. The reason is that there are more PS grafts available to bearing the sulfonic acid groups with the higher DOG. The experimental IEC values were close to those expected values since there was mainly styrene among the monomers used in the graft polymerization.

As mentioned in the previous part, if there are sulfynol chloride groups instead of sulfonic acid groups, in the reaction of the membranes with NaOH, there are two possibilities, one is the sulfynol chloride groups did not react with NaOH, therefore, the experimental IEC value would be zero. The other is that the

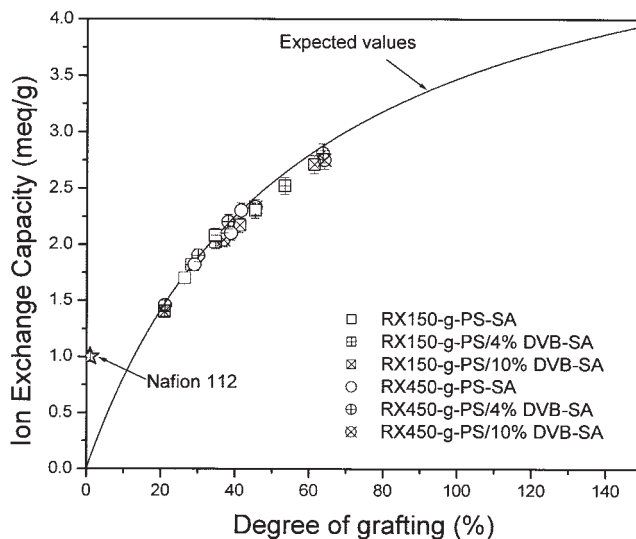


Figure 3 Variation of the calculated and the measured ion exchange capacity with the degree of grafting.

sulfynol chloride groups hydrolyzed in the NaOH solution, therefore, the experimental IEC value would be double of that of the calculated ones. In our case, the experimental IEC values are close to the calculated ones; this means the sulfynol chloride groups had been hydrolyzed to sulfonic acid groups in the HCl solution treatment.

The experimental IEC values of the sulfonated membranes are ranging from 1.5 to 2.8 mequiv/g, which are higher than that of Nafion® 112 (1.0 mequiv/g) membranes, as measured under the same way.

Swelling behavior analysis

Figure 4 shows the DOSs of the sulfonated membranes versus the DOGs. From the figure, it was obvious that the DOSs of the membranes range from 15 to 57% depending on the DOGs. Higher DOG resulted in higher DOS. As the DOG increase, there is higher concentration of the sulfonic acid groups in the membranes. Therefore, the membranes have higher hydrophilicity.

Higher crosslinking densities in both the RX-PTFE matrices and the PS/DVB grafts decreased the DOS of the membranes. The network structure formation restrained the mobility of the molecular chains, thus the DOS decreased with the increase in the crosslinking densities.

The DOS for Nafion® 112 membrane was 21% as measured under the same way. The DOS for Nafion® 112 membrane is in the same range of the prepared membranes. But we think it is difficult to compare the DOS of the Nafion® 112 membrane with our membranes since the IEC values are different, which re-

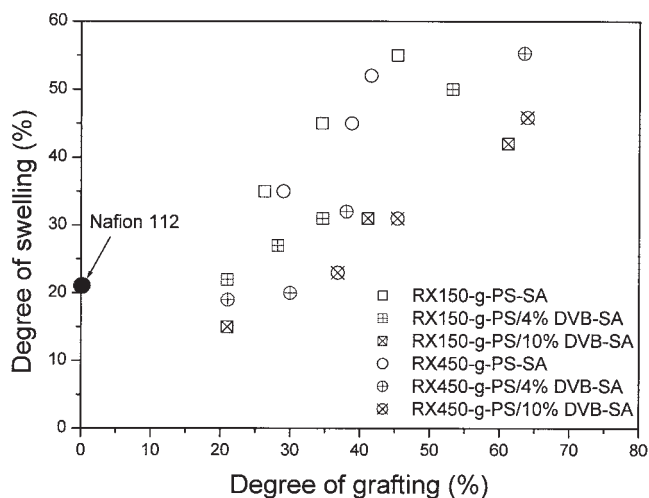


Figure 4 The degree of swelling of the ion exchange membranes versus the degree of grafting.

sulted in the different hydrophilicity. Therefore, λ values (the molar ratio of the absorbed water to the sulfonic acid groups) are meaningful for the membranes with different IEC values.

λ values of the IEMs can be calculated according to the following formula:

$$\lambda(n\text{H}_2\text{O} / \text{SO}_3\text{H}) = \frac{\text{AMOUNT}_{\text{H}_2\text{O}}}{\text{AMOUNT}_{\text{SO}_3\text{H}}} = \frac{(\text{DOS} / 100) \times W_d / M_{\text{H}_2\text{O}}}{\text{IEC} \times W_d / 1000} = 0.56 \times \frac{\text{DOS}}{\text{IEC}} \quad (5)$$

Figure 5 shows the λ values versus the DOG of the membranes. The λ values ranging from 5 to 14 were obtained. The λ values also increased with the increase in the DOG. This means, higher sulfonic acid groups' concentration resulted higher hydrophilicity of the membranes. However, the λ values decreased with the increase in the crosslinking densities of both the RX-PTFE matrices and the PS/DVB-SA grafts.

The calculated λ value for Nafion® 112 membrane was 12, which is much higher than those of our membranes prepared from styrene/DVB grafting. The formation of the crosslinking structure seems an effective way to depress the water uptake of the membranes.

FT-IR spectroscopy analysis

Figure 6 shows the FT-IR spectra of the nongrafted, the styrene grafted, and the styrene/10% DVB grafted RX150 films. In the RX150 films grafted by styrene only or with 10% DVB, the bands attributed to the PS or PS/DVB grafts and the RX-PTFE matrix were observed. The absorption bands are assigned according to the literature.^{22,36,37} The bands from 3100 to 3000 cm^{-1} are the $=\text{C}-\text{H}$ stretching vibration of the grafts.

The band at 2924 cm^{-1} is the asymmetric stretching of aliphatic CH_2 group of the grafts where the band at 2849 cm^{-1} is the symmetric stretching of aliphatic CH_2 group of the grafts. The bands at 1600 and 1583 cm^{-1} are skeletal $\text{C}=\text{C}$ stretching vibration of the grafts where the bands at 1492 and 1452 cm^{-1} are skeletal $\text{C}=\text{C}$ in-plane deformation of the grafts. The bands from 1140 to 1267 cm^{-1} are stretching vibration of CF_2 in the RX-PTFE matrix and the bands from 943 to 982 cm^{-1} are stretching vibration of CF_3 in the RX-PTFE matrix. The band at 842 cm^{-1} is due to the aromatic out-of-plane $\text{C}-\text{H}$ deformation of mono-substituted benzene ring. Since the chemical structure of DVB is similar to that of styrene, it is difficult to tell the difference in the FT-IR spectra. However, there is a band at 1508 cm^{-1} in the spectrum of the RX-150-g-PS/10%DVB film, while it is absent in the spectrum of the RX150-g-PS film as showed in the amplified spectra. This band was attributed to aromatic skeleton stretching vibration of DVB only.³⁸ Therefore, the existing of the crosslinker, DVB, in the styrene/DVB grafted films was proved.

Figure 7 shows the FT-IR spectra of sulfonated membranes in acid form and in salt form. The sulfonated membranes were dried at 80°C under vacuum for 24 h before the FT-IR analysis. As compared with the film before sulfonation, the FT-IR spectra of the sulfonated membrane showed several new absorbance bands besides the bands attributed to the RX-PTFE matrix and PS/DVB grafts. In the spectra of the sulfonated membranes in both acid form and salt form, there are sharp bands appearing at 1008 cm^{-1} due to the symmetric $\text{S}-\text{O}$ stretching vibration. There is also an $\text{O}=\text{S}=\text{O}$ asymmetric stretching vibration at 1352 cm^{-1} attributed to the sulfonic acid group. While in the sulfynol chloride groups, the $\text{O}=\text{S}=\text{O}$ asym-

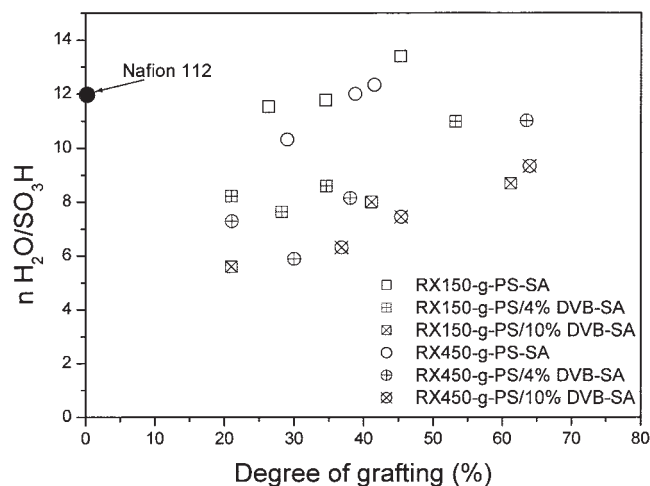


Figure 5 The molar ratio of the absorbed water to the sulfonic acid groups (λ values) of the ion exchange membranes versus the degree of grafting.

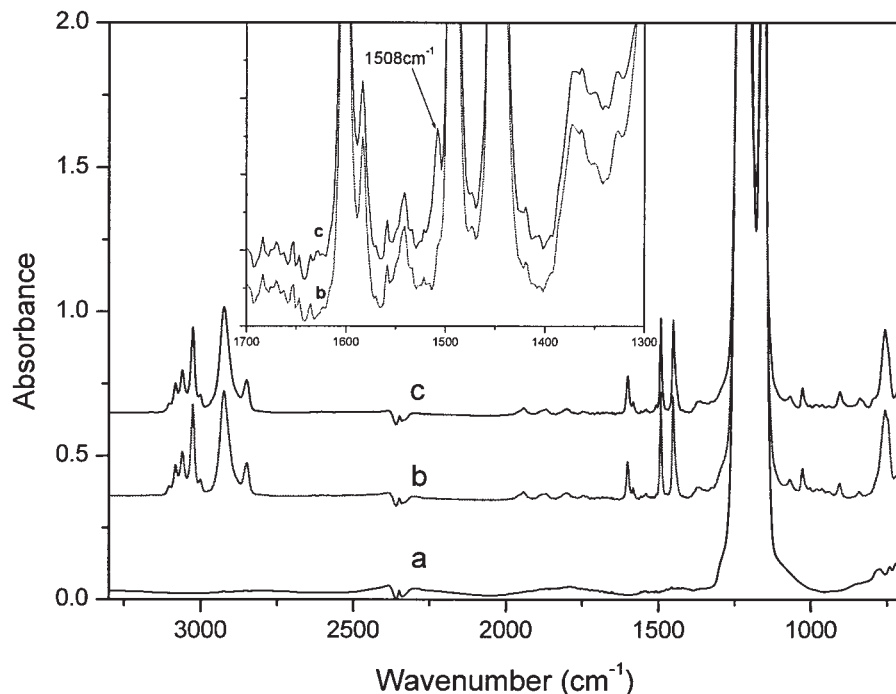


Figure 6 FT-IR spectra of (a) the non-grafted RX150 film, (b) the RX150-g-PS film (DOG = 35%), and (c) the RX150-g-PS/10% DVB film (DOG = 41%).

metric stretching vibration should appear in higher wavenumber around $1390\text{--}1361\text{ cm}^{-1}$ due to the inductive effect of the chlorine atom. This means, the acid catalyzed hydrolyzation was complete. The spectrum of the membrane in acid form showed a broad band from $1550\text{ to }1920\text{ cm}^{-1}$ attributed to the in-plane skeleton stretching vibration of the substituted benzene ring, with strong participation from the sulfonic acid groups.³⁹ While in the spectrum of the membrane

in salt form, it showed a relatively narrowed band from $1550\text{ to }1740\text{ cm}^{-1}$ for the corresponding absorbance. In the spectrum of the membrane in acid form, there is very obvious increasing absorbance slope from $2500\text{ to }3330\text{ cm}^{-1}$ due to the hydrogen bonds between the neighboring sulfonic acid groups. While in the spectrum of the membrane in salt form, this slope nearly disappeared because the hydrogen bonds were dismissed in the absence of the hydrogen atoms in the sodium salt groups. From $3135\text{ to }3706\text{ cm}^{-1}$, there is the absorbance band due to the water molecules that remained, which combined strongly to the ionic groups.

Chemical stability test

The chemical stability of the sulfonated membranes was evaluated by recording the weights of the membranes being soaked in 6% H_2O_2 solutions at 60°C . The reason why we did not perform the chemical stability test under standard Fenton test by adding Fe^{2+} ions is that the addition of the Fe^{2+} ions accelerated the degradation of the sulfonated membranes, and therefore, the weight should be taken every 1 or 2 h. However, it was difficult to record the weight in such short time span in the mid-night. Therefore, it was impossible for us to perform the test under standard Fenton test in continuous a way. Thus, we performed the test under a relatively slow pattern in the absence of Fe^{2+} ions.

The weight-time curves of the sulfonated membranes made from RX150 films were shown in Figure

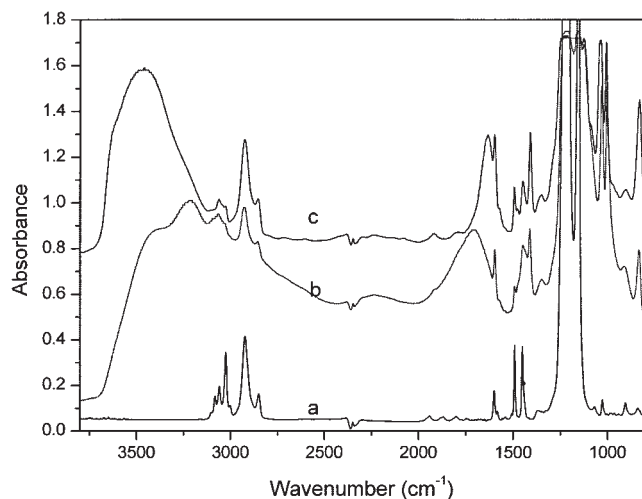


Figure 7 The FT-IR spectra of (a) the RX150-g-PS/10% DVB film (DOG = 41%), (b) the RX150-g-PS/10% DVB-SA membrane, and (c) the RX150-g-PS/10% DVB-SNa membrane.

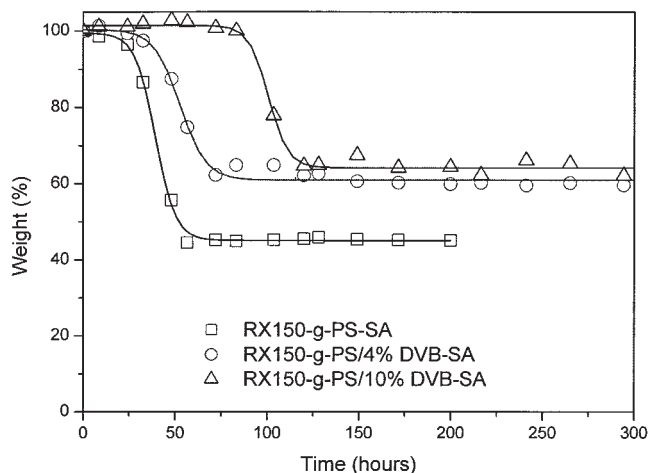


Figure 8 Weight recordings and Boltzmann fittings of (□) the RX150-g-PS-SA membrane, (○) the RX150-g-PS/4% DVB-SA membrane, and (△) the RX150-g-PS/10% DVB-SA membrane being soaked in 6% H_2O_2 solution at 60°C.

8. The curves underwent one quick weight decrease step pattern, and there were material remaining after the decomposition. The weight-time curves of the sulfonated membranes made from RX450 films are the similar.

The weight loss percents of the sulfonated membranes in the chemical stability test were calculated. The weight percents of the swelled grafts were also calculated by recording the weight increase of the nongrafted films after the grafting, sulfonation, and swelling. The data are listed in Table II. The comparison of the weight loss percents with the weight percents of the grafts indicated that all the sulfonated grafts decomposed in the oxidative circumstance and the remaining material was the RX-PTFE films. The membranes before and after the test were analyzed by the FT-IR spectroscopy to prove this fact. The FT-IR analyses of the RX150-g-PS/10% DVB-SA membrane were performed before the chemical stability test and after the weight-time curve was completed, which were shown in Figure 9. The bands attributed to the sulfonated grafts, which are presented in the FT-IR spectrum of the membrane, disappeared after the

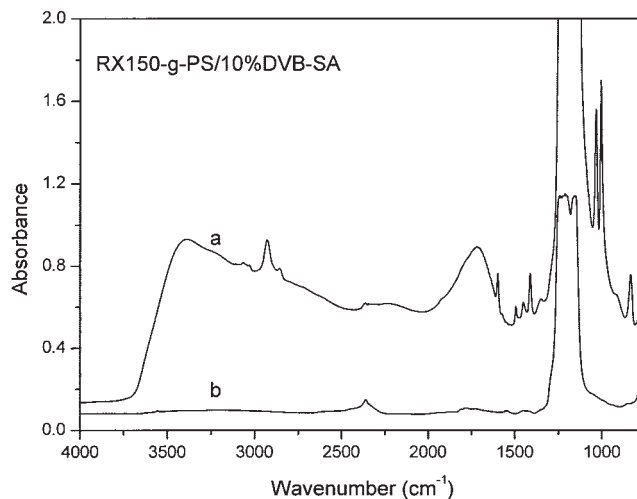


Figure 9 FT-IR spectra of the RX150-g-PS/10% DVB-SA membrane (a) before and (b) after the chemical stability test.

chemical stability test. While the bands attributed to the CF_2 groups in PTFE chains still exist after the test. This result again indicated that all the sulfonated grafts decomposed in the oxidative circumstance and the remaining material was the RX-PTFE films. The residual H_2O_2 solutions after the chemical stability tests were analyzed by HPLC, which were shown in the Figure 10. The HPLC analysis showed mainly one UV-absorb peak, which indicated there were mainly substituted benzene molecules in the residual solution. Also, the pH value of the residual solution was 4, which indicated the existing of the sulfonic acid groups in the residual solution.

The time of the appearance of the weight loss depends on the crosslinking density in both RX-PTFE matrix and PS/DVB grafts. The later the appearance of the weight loss means the higher chemical stability of the sulfonated membranes under oxidative circumstance. Therefore, we use the middle points of the weight loss step in the fitting curves to index the chemical stability of the membranes. The weight loss middle points of the membranes were listed in Table III. From the Table it can be found that the weight loss middle points increased with the increase in the DVB

TABLE II
The Weight Loss Percent in the Chemical Stability Test Compared with the Weight Percent of the PSSA Grafts in the Sulfonated Membranes

Label	DOG (%)	IEC (mequiv/g)	Weight loss percent (%)	Weight percent of PSSA grafts (%)
RX150-g-PS-SA	35	2.1	54	57
RX150-g-PS/4%DVB-SA	21	1.5	39	40
RX150-g-PS/10%DVB-SA	21	1.5	37	37
RX450-g-PS-SA	42	2.4	59	62
RX450-g-PS/4%DVB-SA	30	1.9	42	45
RX450-g-PS/10% DVB-SA	45	2.3	60	58

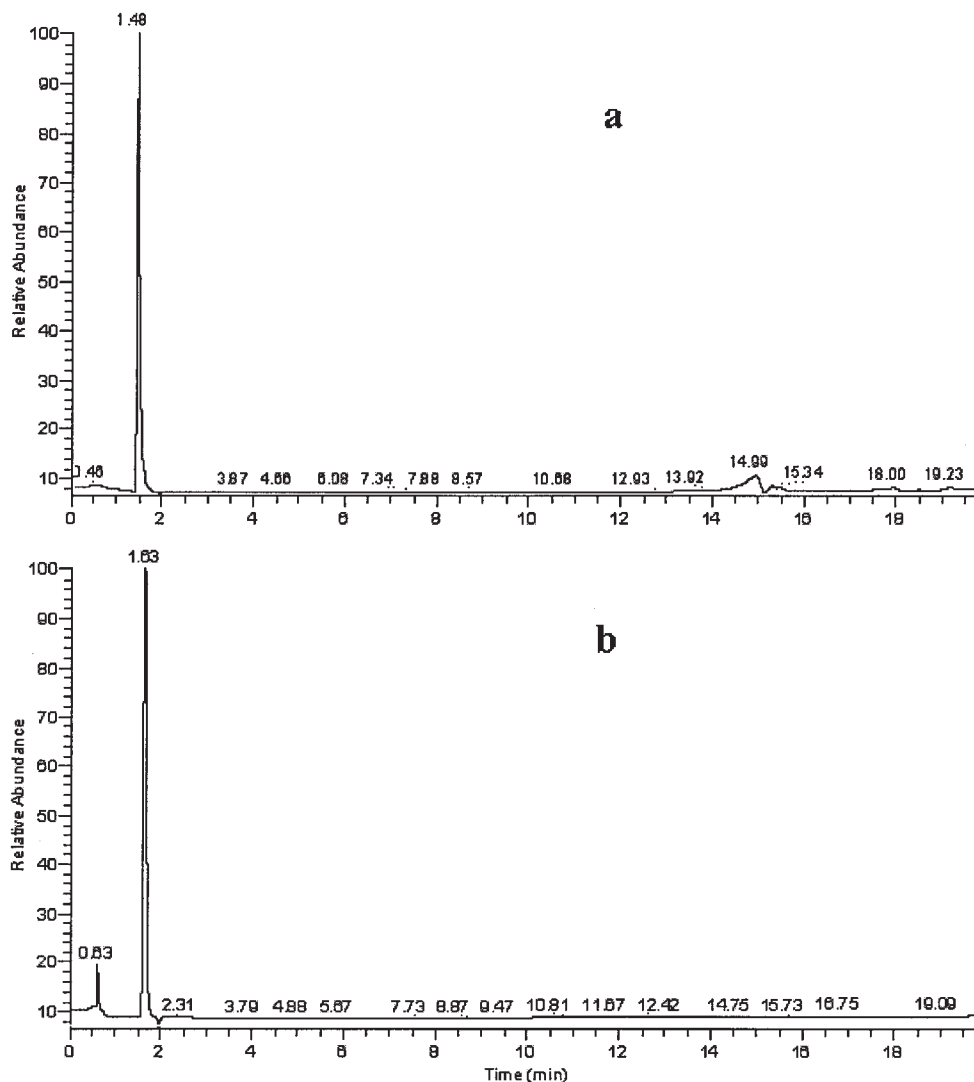


Figure 10 HPLC spectra of the residual H_2O_2 solution of the (a) RX150-g-PS-SA membrane and (b) RX150-g-PS/10% DVB-SA membrane after the chemical stability test.

concentration used in the graft polymerization. Also, the membranes made from RX450 films have higher chemical stability than the corresponding one made from RX150 films with same DVB concentration used in graft polymerization. This means, the increase in

the crosslinking density of both the RX-PTFE matrix and the PS/DVB grafts will effectively improve the chemical stability of the membranes under oxidative circumstance.

The decomposition of the sulfonated polystyrene chains is due to the attacking of the α -hydrogen atom in the repeating units by the oxidative agents.⁴⁰ Therefore, the increase in the crosslinking density of the RX-PTFE films can reduce the penetration rate of the oxidative agents, thus improving the chemical stability of the sulfonated membranes. As the structure of DVB is similar to that of styrene, and there is also the α -hydrogen atom in DVB, the copolymerization of DVB with styrene cannot improve the chemical stability of the polystyrene chains obviously. But as we studied, the surface structure of the sulfonated membranes by XPS analysis,³⁴ it was found that there are mainly PS-SA grafts on the surface of the membranes

TABLE III
The Weight Loss Middle Points of the Sulfonated Membrane in Chemical Stability Test Calculated by Boltzmann Curve Fitting

Label	DOG (%)	Weight loss middle point (h)
RX150-g-PS-SA	35	39
RX150-g-PS/4% DVB-SA	21	53
RX150-g-PS/10% DVB-SA	21	101
RX450-g-PS-SA	42	48
RX450-g-PS/4% DVB-SA	30	104
RX450-g-PS/10% DVB-SA	45	196

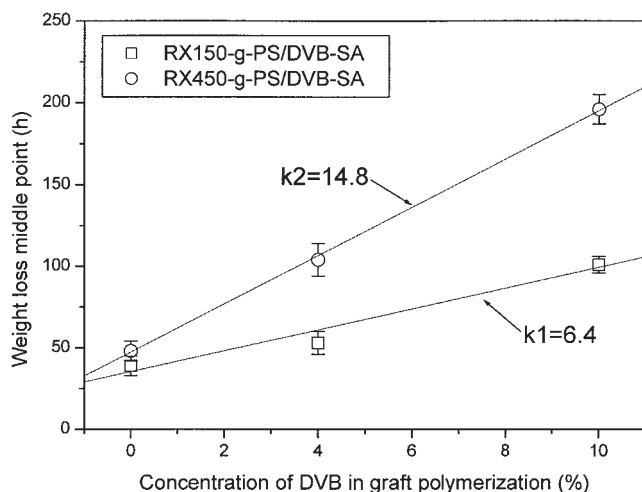


Figure 11 The weight loss middle points of the sulfonated membranes being soaked in 6% H_2O_2 solution at 60°C versus the concentration of DVB used in graft polymerization.

grafted by styrene only, while there are mainly PTFE chains on the surfaces of the membranes grafted by styrene with DVB. This means, the existing of the DVB units resulted in the crosslinking in the PS/DVB-SA grafts, and therefore, the tendency of the accumulation of the grafts on the surfaces of the sulfonated membranes was suppressed. The fewer grafts on the surfaces of the membranes make it more difficult for the grafts to be attacked by the oxidative agents. Also, the crosslinking in the grafts reduced the penetration rate of the oxidative agents further. Therefore, the increased DVB concentration used in the graft polymerization will increase the chemical stability of the sulfonated membranes obviously.

The operation condition of the chemical stability test here is different with that in real fuel cell running. Therefore, it is difficult to directly calculate the lifetime of the membranes in real fuel cell running from the chemical stability test. However, the higher chemical stability means the potentially longer lifetime in real fuel cell running among the membranes under same operation conditions.

Assuming the chemical stability of the sulfonated membranes has a simple dependence on the crosslink-

ing density, we connected the weight loss middle points with the concentration of DVB used in the graft polymerization using linear fitting, which was shown in Figure 11. The k value indicated the different dependence of the chemical stability of the membranes on the DVB concentration used. It can be found that the k value for the membranes made from RX150 films is 6.4, while the k value for the sulfonated membranes made from RX450 films is 14.8. This means, the increase of the DVB concentration used in the graft polymerization improved the chemical stability of the sulfonated membranes made from highly crosslinked RX-PTFE films more effectively.

Ex situ ionic conductivity

Previously, we measured the ionic conductivity of the sulfonated membranes by directly clamping the wetted membranes within Pt electrodes. However, it seemed the contact between the electrodes and membranes was bad because the membranes are very thin, with the thickness ranges from 14 to $18\ \mu\text{m}$, as shown in Table IV. Therefore, we improved the measuring method by using the pliable carbon paper instead of Pt electrodes clamping the membrane to improve the contact. In the Nyquist representation of the AC impedance spectra of the membranes, the resulted data were fitted into a semicircle, therefore, the ohmic resistance was obtained at the crossing site of the fitted circle with the real axis in the high frequency region. The ionic conductivities were calculated from the ohmic resistances and the thickness of the membranes. The ionic conductivities of the membranes together with that of Nafion® 112 membrane, which was used as a reference, were listed in Table IV. The *ex situ* ionic conductivity of Nafion® 112 membrane is lower than the value reported by Gubler et al.,¹⁵ which should be attributed to the relatively low humidity state of the membrane in our measuring system. The ionic conductivity increases with the increase in the IEC values of the prepared membranes. When the IEC value of the prepared membranes is lower than 2.2 mequiv/g, the ionic conductivity is lower than that of Nafion® 112 membrane. However, the ionic conductivity of the

TABLE IV
The *Ex Situ* Ion Conductivity of the Sulfonated Membranes at 25°C

Label	DOG (%)	IEC (mequiv/g)	Thickness in wet form (μm)	Ion conductivity (mS cm^{-1})
Nafion 112		1.0	60	16
RXI50-g-PS-SA	35	2.1	18	14
RXI50-g-PS/4% DVB-SA	21	1.5	15	7
RXI50-g-PS/10% DVB-SA	21	1.5	14	8
RX450-g-PS-SA	42	2.4	17	20
RX450-g-PS/4% DVB-SA	30	1.9	16	12
RX450-g-PS/10% DVB-SA	45	2.3	17	19

membranes with IEC higher than 2.2 mequiv/g is higher than that of Nafion® 112 membrane.

The membrane-electrode assemblies (MEA) of the grafted and sulfonated RX-PTFE were prepared by hot-pressing. The real fuel cell running of the IEMs are now undergoing. According the fuel cell running of the membranes, we will adjust the preparing conditions such as the thickness and crosslinking dose of the RX-PTFE films, the concentration of DVB used, the DOGs and so on, to gain the best performance.

CONCLUSIONS

V-PTFE films were prepared by coating the PTFE dispersion on the aluminum films. RX-PTFE films were obtained by means of electron beam irradiation above the melting temperature of PTFE under oxygen-free atmosphere. The RX-PTFE films, which were irradiated to 150 and 450 kGy, and the V-PTFE films were used for the preirradiation induced grafting of styrene with DVB in liquid phase. The films were preirradiated to 30 kGy and grafted by styrene with 0, 4, and 10% DVB at 70°C. The increase in the DVB concentration accelerated the initial grafting rate.

The existing of DVB caused the gel formation in the graft polymerization system as reaction progress. Cyclohexane was added in the graft polymerization system as a solvent to dilute the concentration of the monomers; thus, the reduced initial grafting rate and the delayed gel formation were realized.

Ion exchange membranes were obtained by sulfonating the grafted membranes using chlorosulfonic acid and then hydrolyzed. The IEC values of the sulfonated membranes are ranging from 1.5 to 2.8 mequiv/g, and are proportional to the DOG. The degree of swelling and the λ values also increased with the increase in the DOG. However, the increase in the crosslinking density in both RX-PTFE matrix and PS/DVB grafts suppressed the degree of swelling and the λ values. The membranes with higher IEC values and lower degree of swelling than those of Nafion® 112 membrane were obtained by using high DVB concentration used in the graft polymerization and DOG around 30–40%.

FT-IR spectra proved the existence of the PS/DVB grafts and the PTFE matrix in the grafted films. And in the spectra of the sulfonated membranes, there are absorbent bands attributed to the existing of the sulfonic acid groups and proved the hydrolyzation was complete.

The chemical stability of the sulfonated membranes was tested by being soaked in hot H₂O₂ solutions. The sulfonated grafts decomposed in the oxidative circumstance, while the PTFE main-chains remained after the test. The increase in the crosslinking density of both the RX-PTFE matrix and the PS/DVB grafts improved the chemical stability of the sulfonated membranes.

The reason for the increase in the chemical stability of the membranes is that the higher crosslinking density reduced the diffusion rate of the oxidative radicals. Also, the increase in the DVB concentration used in the graft polymerization reduced the amount of the grafts on the surfaces of the membranes, and therefore, the grafts were better protected by the high stable PTFE chains.

The *ex situ* ionic conductivity of the sulfonated membranes were measured using AC impedance method. Higher IEC value resulted in higher ionic conductivity. The ionic conductivity of the membranes with IEC higher than 2.2 mequiv/g is higher than that of Nafion® 112 membrane.

The authors acknowledge Prof. Y. Katsumura and Dr. C. Matsuura for various discussions. One of the authors (Dr. J.Y. Li) acknowledges the Japan Society for the Promotion of Science (JSPS) for the fellowship.

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