



Surface analysis of the proton exchange membranes prepared by pre-irradiation induced grafting of styrene/divinylbenzene into crosslinked thin PTFE membranes

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Abstract

The proton exchange membranes were obtained by pre-irradiation induced grafting of styrene with or without divinylbenzene (DVB) into thin crosslinked polytetrafluoroethylene (RX-PTFE) membranes with the thickness around 10 μm and successive sulfonation. The surface chemical structure and morphology of the non-grafted, the grafted, and the grafted and sulfonated RX-PTFE membranes were studied by means of X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) analysis. From the F/C atom ratio result, it was known that there are mainly polystyrene grafts on the surfaces of the styrene grafted RX-PTFE membranes, while there are mainly PTFE chains on the surfaces of the RX-PTFE membranes grafted by styrene together with DVB. “Wave” shape morphology on the surfaces of the grafted RX-PTFE membranes was observed. The F/C atom ratios on the surfaces of the grafted and sulfonated membranes are little lower than the corresponding grafted membranes before sulfonation. On the surface of the sulfonated membranes, the “wave” shape morphology was also observed. The distributions of the polystyrene grafts in the RX-PTFE membranes matrixes were strongly affected by the concentration of the crosslinking co-monomer, DVB, used in the graft polymerization, and the sulfonation will not change the distribution of the grafts obviously.

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1. Introduction

Radiation induced grafting of styrene and its derivatives into fluoropolymer films or membranes and successive sulfonation was designed as an alternative way to synthesize the proton exchange membranes (PEMs) with low cost for the polymer electrolyte fuel cell (PEFC) applications [1]. Almost all market available fluoropolymer materials, such as PTFE [2–5], FEP [6–10], PFA [10–15], PVDF [16–20], ETFE [21,22], etc., were used as the base films or membranes for the grafting of styrene under simultaneous irradiation method or pre-irradiation method.

Among the fluoropolymer materials, PTFE is the most widely used in industrial fields due to its outstanding properties. But it was once thought to be difficult to apply for radiation induced grafting due to main chain scission by the ionizing irradiation [23,24]. However, several years ago, it was reported that PTFE can be crosslinked by irradiation above its melting temperature under oxygen-free atmosphere [25–28]. Crosslinked PTFE (RX-PTFE) showed remarkable improvements in several mechanical properties, radiation resistance, optical properties and so on, comparing with the non-crosslinked PTFE (V-PTFE) [29–31].

Our research group has developed the PEMs by grafting of styrene into RX-PTFE films by means of pre-irradiation method [32–34]. The most advantage of our research project is that RX-PTFE holds the network chemical structure. The formation of the network structure of RX-PTFE reduced the gases permeation rates [35]. As reported previously, in the PEMs prepared by styrene grafting and sulfonation, the resulted polystyrene sulfonic acid (PS-SA) grafts were easy to decompose in real fuel cell running and the reason is the diffusion of oxygen to anode side and then HO^\bullet radicals formed which may attack the tertiary hydrogen at the α -carbon of the PS structure [36]. This means that the use of RX-PTFE as the base polymer will increase the cell efficiency and will extend the lifetime of the fuel cell by reducing the crossover of the fuel gases. Further, in many works, divinylbenzene (DVB) and triallyl cyanurate (TAC) were used as the crosslinking co-monomers to obtain the PEMs with crosslinked graft structure [37–40]. The PEMs grafted by styrene together with DVB were

reported to give much long lifetime than those grafted by styrene only [41–43]. Due to the chemical stability of PTFE, the crosslinking structure of RX-PTFE should be more stable than the crosslinking structure of PS-SA grafts. Therefore, use of DVB together with styrene in the pre-irradiation induced graft polymerization into RX-PTFE membranes and successive sulfonation is expected to obtain much lower gas permeation rate and much longer lifetime of the PEMs.

Recently, we have developed RX-PTFE membranes with thickness around 10 μm by coating the PTFE dispersion on the aluminum sheets and then crosslinked by irradiation above its melting temperature under oxygen-free atmosphere using electron beam. The RX-PTFE membranes were used for pre-irradiation grafting of styrene/DVB, and the graft polymerization by styrene only was performed as a reference [44,45]. The membranes grafted by styrene without or with DVB are different in appearance. The membranes grafted by styrene only are white in color, but the membranes grafted with styrene/DVB are colorless which are the same as of the non-grafted RX-PTFE membranes. This phenomenon suggested the different distribution of the PS grafts in the membranes grafted by styrene without or with DVB. It was reported that the grafts chains in the PEMs grafted by styrene/DVB are uniformly distributed across the membranes while the grafts in the PEMs grafted by styrene only are more concentrated on the surface than in the matrix [46,47]. Also it was reported that there are mainly PS-SA grafts on the surfaces of the PTFE-g-PS-SA and PFA-g-PS-SA films by X-ray photoelectron spectroscopy (XPS) [48,49], and the PS-SA grafts on the surfaces will be decomposed within 50 h in real fuel cell running [50]. Thus, chemical compositions on the surfaces of the PEMs grafted by styrene without or with DVB should be different.

In this work, we have studied the surface chemical structure and morphology of the non-grafted, the grafted, and the grafted and sulfonated RX-PTFE membranes by means of XPS and scanning electron microscopy (SEM) analysis. The RX-PTFE membranes with different crosslinking doses, and the membranes grafted by styrene with 0%, 4% and 10% DVB (volume concentration to styrene used in the graft polymerization), and the corresponding

sulfonated membranes were used for the analysis. The PEMs prepared from V-PTFE membranes were not used in this work since the V-PTFE membranes were broken in the grafting of styrene with DVB due to its poor mechanical properties.

2. Experimental

2.1. Materials and graft polymerization

RX-PTFE membranes were obtained by coating the PTFE dispersion on the aluminum sheets and then crosslinked by electron beam irradiation above its melting temperature under oxygen-free atmosphere. The RX-PTFE membranes irradiated to 150 and 450 kGy were used, abbreviated as RX150 and RX450 membranes, respectively. The thicknesses of the RX150 and RX450 membranes are 10 ± 1 and $8 \pm 1 \mu\text{m}$, respectively. The aluminum sheets were removed by soaked in HCl solution after the cross-linking.

RX150 and RX450 membranes were then irradiated to 30 kGy under nitrogen atmosphere at room temperature by electron beam. After the irradiation, the RX150 and RX450 membranes were stored in the refrigerator at -20°C in air for 4 days to turn the trapped radicals completely into the peroxide radicals. Then the RX150 and RX450 membranes were grafted by styrene with 0%, 4% or 10% DVB (a mixture of 55% *m*-, *p*-divinylbenzene in ethylvinylbenzene) at 70°C in liquid phase. The reaction systems were evacuated to remove the oxygen. The graft polymerizations were performed either in monomers bulk or in 50% cyclohexane solutions. The labels of the grafted membranes are abbreviated as RX150-g-PS, RX150-g-PS/4% DVB, and RX150-g-PS/10% DVB for the RX150 membranes grafted by styrene, styrene with 4% DVB, and styrene with 10% DVB, respectively. The labels are similar for the grafted RX450 membranes.

The PS/DVB homopolymer was formed in the reaction system initiated by the decomposition of the peroxide radicals. And the homopolymer was removed by washing the grafted membranes in fresh cyclohexane, which is a good solvent for polystyrene, for several times and soaking in the fresh cyclohexane for at least 24 h.

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

$$\text{degree of grafting(DOG)}(\%) = \frac{W_g - W_o}{W_o} \times 100\%$$

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

The grafted membranes were then sulfonated by chlorosulfonic acid in carbon tetrachloride (1:9, v/v) at room temperature for 24 h. As an example, the label is RX150-g-PS/4% DVB-SA for the RX150 membrane grafted by styrene with 4% DVB and sulfonated (acid form). The details of the graft polymerization and the sulfonation experiments were reported in our papers on grafting and sulfonation experiments [44,45].

2.2. Measurement

XPS analyses were performed by a JPS-9010 Photoelectron Spectrometer, JEOL Co. Ltd. (Japan). An Mg K X-ray source was used in Constant Analyzer Energy mode. The non-monochromatized Mg K X-ray flux was used with the current set at 10 mA and the voltage set at 10 kV. Wide scans were carried out in the range of 1100 to 0 eV and were recorded with the pass energy of 50 eV at a step of 1 eV and the dwell time of 50 ms. Wide scans were repeated for three times to reduce the noise. Narrow scans were performed for C 1s, F 1s, O 1s and S 2p regions and were recorded with the pass energy of 10 eV at a step of 0.1 eV and the dwell time of 100 ms. Narrow scans for each element were repeated for 20 times to reduce the noise. The Gaussian peak fitting parameter with straight baseline was applied for peak analysis using a Microcal Origin[®] Version 6.0 software. The binding energies were corrected by assuming the binding energy as 284.5 eV for C– bond [51]. The analysis conditions used in the angle resolve method were the same as those in the narrow scans, and the electron take-off angles were set at 90° , 70° , 50° , 30° and 10° with respect to the membrane surface.

SEM images were taken by an S-2500CX, Hitachi Co. Ltd. (Japan). The voltage was set at 25 kV and the current was set at 10 mA. The images were amplified to $10,000\times$.

The membranes were dried at 60°C under vacuum for 24 h before XPS and SEM analyses.

3. Results and discussion

3.1. Surface analysis of the non-grafted RX-PTFE membranes

Fig. 1 shows the XPS wide scan spectra of the RX150 and RX450 membrane. In the spectra of the RX150 and RX450 membranes, strong peaks at around 693 eV standing for F 1s and weak peaks at around 296 eV standing for C 1s from CF₂ were observed, respectively. Also weak peaks at 533 eV standing for O 1s indicated the detection of a small amount of oxygen in the membranes. The containing of oxygen maybe due to the trace H₂O remained on the surface of the membranes.

The calculated F/C atom ratios are 1.83 and 1.78 for the RX150 and RX450 membranes, respectively. The F/C atom ratios of RX-PTFE membranes are lower than the theoretical value of PTFE, which should be 2. One reason for the lowering in the F/C atom ratios is the remaining non-ionic surfactant used in the PTFE dispersion. The surfactant was reacted with the PTFE during the crosslinking procedure therefore cannot be washed off. We soaked the membrane in the cyclohexane at 60 °C for 24 h and there is no change in the spectrum. A second possible reason is that there are Y type crosslinking structure and C=C bonds generated during the radiation induced

crosslinking of PTFE. It is reported that the relative intensity of the –C– peak to the CF₂ peak increases with the increase in the crosslinking doses in the XPS narrow scan spectra of the RX-PTFE [31]. In the spectrum of the RX-PTFE with crosslinking dose of 100 kGy, the relative intensity of the peak at 288 eV to the peak at 295 eV is about 0.25. And the RX-PTFE sheets used were made by sintering, which contains no surfactant. Unfortunately, the F/C atom ratios of the RX-PTFE sheets were not reported.

Fig. 2 shows the XPS narrow scan spectra of C 1s and curve fitting for the RX150 and RX450 membranes. As the curve fitting result for RX150 membrane, the main peak at 293.7 eV (charging effect 1.5 eV) attributed to the CF₂ units, while peak at 295.8 eV attributed to CF₃ units as the PTFE chain end groups and peak at 291.1 eV attributed to the CF units as the PTFE chain branch groups. The appearance of CF units indicated the crosslinking structure, while the appearance of CF₃ units was mainly due to the main-chain scission of PTFE by irradiation. And there are three weak peaks at 288.8, 286.7 and 284.5 eV should be attributed to –C–CF₃, –C– and C– units according to reference [31]. The curve fitting result of the RX450 membrane is similar to that of the RX150 membrane. The relative intensities of the –C– peak to the CF₂ peak are 0.15 for the RX150 membrane and 0.30 for the RX450 membrane. As carefully compared the

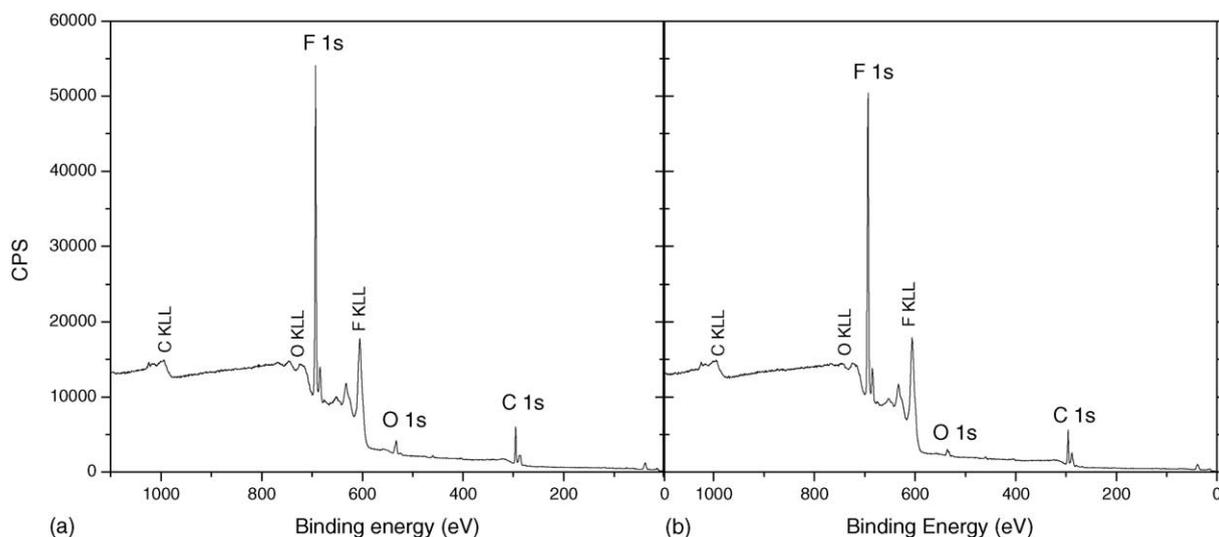


Fig. 1. The XPS wide scan spectra of the original (a) RX150 and (b) RX450 membranes.

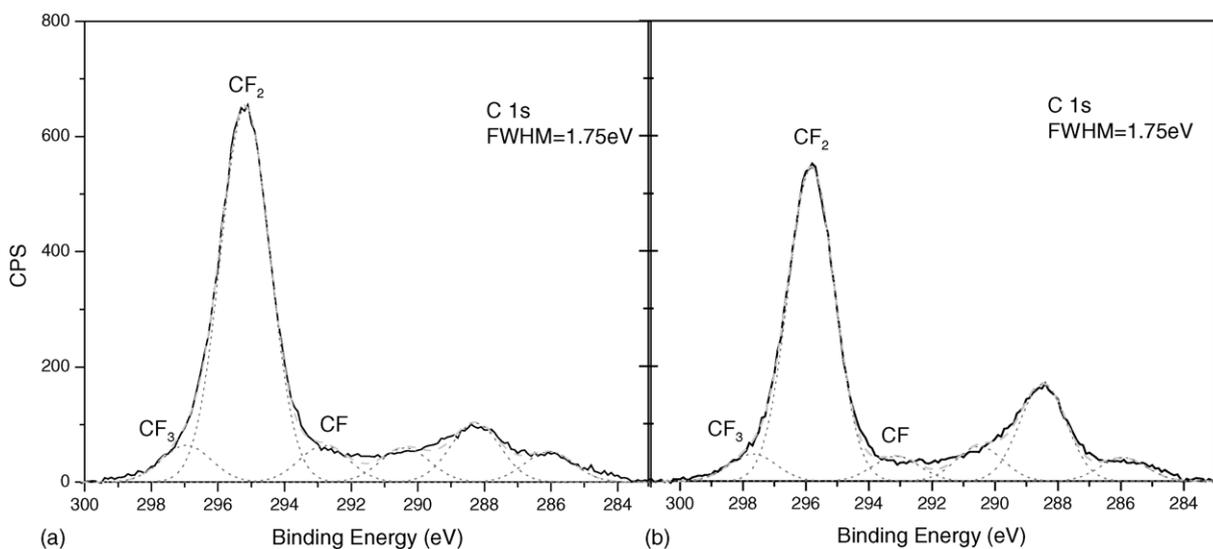


Fig. 2. The XPS narrow scan spectra of C 1s and curve fitting of the original (a) RX150 and (b) RX450 membranes.

XPS narrow scan of the RX-PTFE membranes in this work with those reported ones, we believe that the Y type structure together with the double bonds due to the irradiation induced crosslinking effect in the RX-PTFE membranes should be the main reason for the decrease in the F/C atom ratio rather than the remained surfactant. Fluorine gas treating the RX-PTFE membranes can saturate the double bonds,

but it also will substitute the hydrogen atoms in the surfactant molecules. Therefore, it is not a suitable way to tell the surfactant from the double bonds in the RX-PTFE membranes.

Fig. 3 shows the SEM images of the RX150 and RX450 membranes. The images were amplified to 10,000 \times . It is obvious that the surfaces of the RX150 and RX450 membranes are smooth.

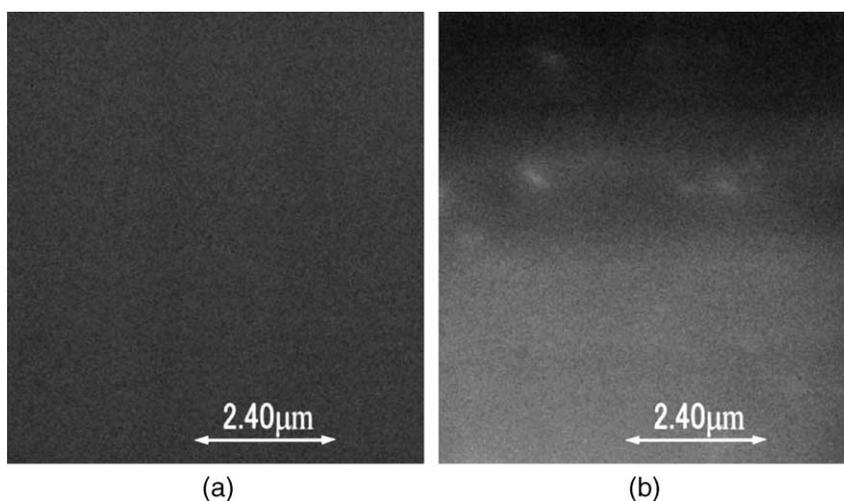


Fig. 3. The SEM images (10,000 \times) of the original (a) RX150 and (b) RX450 membranes.

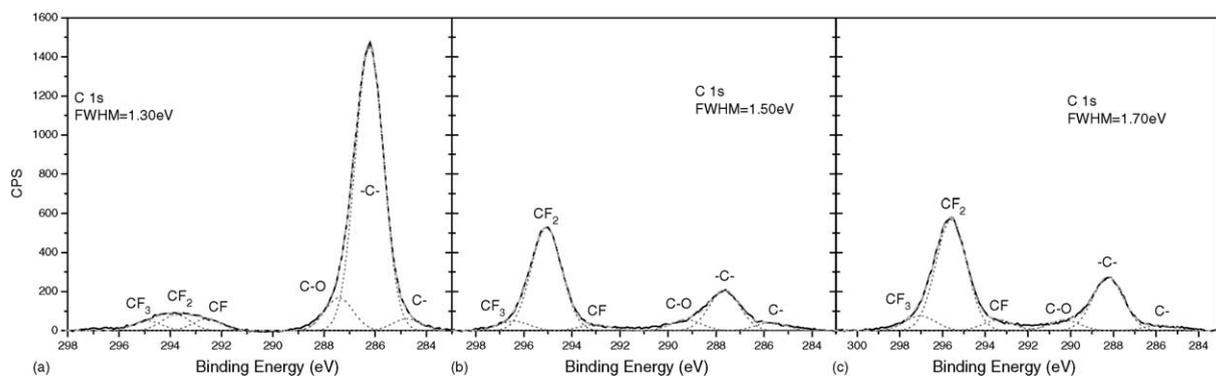


Fig. 4. The XPS narrow scan spectra of C 1s and curve fitting of the (a) RX150-g-PS (DOG = 35%), (b) RX150-g-PS/4% DVB (DOG = 33%) and (c) RX150-g-PS/10% DVB (DOG = 41%) membranes.

3.2. Surface analysis of the grafted membranes

The XPS wide scan spectra of the styrene or styrene/DVB grafted RX150 and RX450 membranes are similar to those of the non-grafted RX-PTFE membranes, where the peaks attributed to F 1s, O 1s and C 1s appeared.

Fig. 4 shows the XPS narrow scan spectra of C 1s and curve fitting of the styrene or styrene/DVB grafted RX150 membranes. The curve fitting parameters and corrected binding energy for every bond of the grafted RX150 and RX450 membranes are listed in Table 1. As the curve fitting results, there are peaks attributed to CF₃, CF₂, and CF bonds at 295, 294, and 292 eV in the spectra [51]. Also the peaks should be attributed to C–O, –C– and C– bonds at 287, 286, and 284.5 eV. The concentration of DVB used in the graft polymerization did not affect the binding energy of the bonds obviously. The existing of the double bonds in the RX-PTFE is the weak point in the membranes.

In this work, the membranes were pre-irradiated and then grafted. Therefore most of the double bonds should be turned into radicals to initiate the graft polymerization. The signal of the surfactant was further diluted with the PS/DVB grafts introduced. Thus the contribution of the surfactant can be omitted.

The F/C atom ratios of the styrene or styrene/DVB grafted RX150 and RX450 membranes are also listed in Table 1. The F/C atom ratios are 0.05 and 0.06 for the RX150-g-PS and RX450-g-PS membranes. These facts mean that there are mainly PS grafts on the surfaces of the styrene grafted membranes. The F/C atom ratios of 0.26 for the PTFE-g-PS film and of 0.22 for PFA-g-PS film were reported [48,49]. The low atom ratios mean that the high incompatibility between the crosslinking structure of the RX-PTFE matrix and the PS grafts.

However, the F/C atom ratios are high for the styrene/DVB grafted RX150 and RX450 membranes, which are close to those of the non-grafted RX150 and

Table 1

The DOGs, the thickness, the atom ratios, the curve fitting parameters for C 1s spectra and the corrected binding energy for every bond of the styrene or styrene/DVB grafted RX150 and RX450 membranes

Label	DOG (%)	Atom ratio		Curve fitting parameters		Binding energies by curve fitting (eV)					
		F/C	O/C	FWHM (eV)	Charging effect (eV)	CF ₃	CF ₂	CF	C–O	–C–	C–
RX150-g-PS	35	0.05	0.02	1.30	0.3	294.6	293.5	292.3	287.1	285.9	284.5
RX150-g-PS/4% DVB	33	1.68	0.07	1.50	1.2	295.2	293.9	291.8	288.0	286.4	284.5
RX150-g-PS/10% DVB	41	1.78	0.03	1.70	1.3	295.8	294.3	292.1	289.0	286.9	284.5
RX450-g-PS	42	0.06	0.02	1.25	0.4	294.4	293.3	292.2	286.9	285.8	284.5
RX450-g-PS/4% DVB	38	1.77	0.03	1.70	1.2	295.5	293.9	291.6	288.7	286.6	284.5
RX450-g-PS/10% DVB	45	1.78	0.04	1.75	1.1	294.4	293.1	290.3	288.0	286.2	281.5

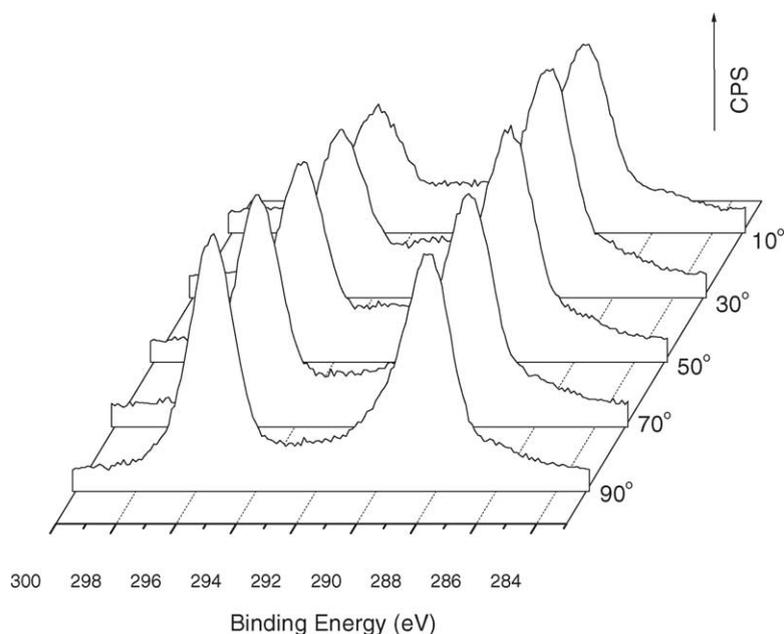


Fig. 5. The XPS angle resolve C 1s spectra of the RX150-g-PS/10% DVB (DOG = 41%). The angles are the electron take-off angles with respect to the membrane surface.

RX450 membranes. It means that on the surfaces of the styrene/DVB grafted RX150 and RX450 membranes there are mainly PTFE matrix. The F/C atom ratios are even higher than the calculated values by DOGs assuming the average distribution of the PS/DVB grafts on the surfaces of the grafted membranes. This means that the amount of the grafts on the surfaces is lower than that in the inner region of the grafted membranes. The possible reason is that the decay of the radicals on the surfaces of the membranes when the irradiated membranes were stored in the refrigerator in air before graft polymerization to turn the trapped radicals into peroxide radicals. As the existing of the PS/DVB grafts was confirmed by FT-IR analysis [44], the grafts should be contained in the inner region of the membranes. The maximum escape depths of the photoelectrons are 4.8 and 7.3 nm for F atom and for C atom, respectively, using Mg K X-ray in the XPS analysis [52], which are much smaller than the thickness of the membranes. Thus it is impossible to obtain the distribution of the PS/DVB grafts in the inner of the membranes.

From the atom ratio data, it is also obvious that the increase in the crosslinking density of both PTFE

matrix and PS grafts will increase the F/C ratio. The O/C ratios for the styrene/DVB grafted RX150 and RX450 membranes are in the same order of those of the styrene grafted RX150 and RX450 membranes.

The reason for the difference in the distribution of the grafts in the styrene/DVB grafting membranes with that of the styrene grafted ones is the formation of the network in the grafts. The grafted PS chains are incompatible with the PTFE chains. So on the styrene grafted membranes, the phase separation should take place and the PS grafts accumulated on the surfaces of the membranes. In the styrene/DVB grafted membranes, the network structure of the PS grafts formed which suppressed the phase separation, thus the distribution of the grafts came uniform. As the result, the grafts were better distributed across the matrix in the case of the styrene/DVB grafted membranes.

An XPS angle resolve analysis was performed for the RX150-g-PS/10% DVB membrane to study the incompatibility between the RX-PTFE matrix and the grafts. Fig. 5 shows the angle resolve spectra of C 1s, and the F/C atom ratios versus the take-off angles are listed in Table 2. With the decreased electron take-off angle with respect to the membrane surface, in other

Table 2

The atom ratios of the RX150-g-PS/10% DVB (DOG = 41%) membranes vs. the angles of the XPS angle resolve spectra of C 1s

	90°	70°	50°	30°	10°
F/C	1.74	1.66	1.42	1.22	1.10
O/C	0.13	0.13	0.12	0.10	0.10

The angles are the electron take-off angles with respect to the membrane surface.

word, the decreased analyzed thickness of the membrane [52], the intensity of the peak attributed to CF_x became weaker and the F/C atom ratio is also decreased. In the styrene/DVB grafted membranes, the grafts also tend to accumulate due to the incompatibility between the RX-PTFE matrix and the grafts. Thus the uniform distribution of the PS/DVB grafts in the RX-PTFE membranes is due to the network structure formation.

The fewer grafts on the surfaces of the PEMs produced by styrene/DVB grafted membranes, the less chance for the attacking by the oxidative chemicals produced during fuel cell running, thus the lifetime of the PEMs should be increased. The better distribution of the grafts in the styrene/DVB grafted membranes than that of the styrene grafted membranes should be an important reason for the improvement of the lifetime of the PEMs produced by styrene/DVB grafted membranes.

Fig. 6 shows the SEM images (10,000×) of the grafted RX150 and RX450 membranes. On the

surfaces of grafted membranes, the wave shape morphology was observed which should be the accumulation of the PS chains due to the incompatibility between PS grafts and PTFE matrix. This is similar to the PVDF-g-PS films as previously reported [53,54]. From the SEM images it is obvious that there are much smooth surfaces of the styrene/DVB grafted RX150 and RX450 membranes than those of the styrene grafted ones, and the wave shape morphology on the surfaces of the styrene/DVB grafted membranes seems in higher order. Also, the increase in the crosslinking density of both PS grafts and PTFE matrix increased the amount of “waves” on the surfaces of the styrene/DVB grafted RX150 and RX450 membranes. The possible reason is the higher crosslinking density resulted in the higher inner forces in the grafted membranes.

3.3. Surface analysis of the sulfonated membranes

Fig. 7 shows the XPS wide scan spectra of the sulfonated RX150 membranes as the PEMs. In the spectra of the PEMs, beside the peaks attributed to F 1s, O 1s and C 1s, there are new weak peaks at 236 eV attributed to S 2s and at 171 eV attributed to S 2p, which indicate the membranes contain sulfonic acid groups. Considering there are possible dangling double bonds on DVB in the grafts, therefore there was a possible side reaction when the membranes were sulfonated by chlorosulfonic acid. The side reaction is the addition reaction of the chlorosulfonic

Table 3

The DOGs, the IEC values, the thickness, the atom ratios, the curve fitting parameters for C 1s spectra and the corrected binding energy for every bond of the styrene or styrene/DVB grafted and sulfonated RX150 and RX450 membranes

Label	DOG (%)	IEC (meq/g)	Atom ratio				Curve fitting parameters		Binding energies by curve fitting (eV)						
			F/C	O/C	S/C	O/S	FWHM (eV)	Charging effect (eV)	CF ₃	CF ₂	CF	C–S	C–O	–C–	C–
RX150-g-PS-SA	35	2.1	0.03	0.15	0.07	2.28	1.35	0.6		292.9		288.5	287.3	286.0	284.5
RX150-g-PS/4% DVB-SA	33	2.0	1.21	0.18	0.07	2.77	1.30	1.1	294.3	293.2	291.9	288.5	287.1	285.9	284.5
RX150-g-PS/10% DVB-SA	41	2.2	1.45	0.18	0.05	3.58	1.35	1.3	294.6	293.0	290.8	288.8	287.3	286.0	284.5
RX450-g-PS-SA	42	2.4	0.04	0.18	0.07	2.69	1.30	0.4		292.9		287.9	286.8	285.8	284.5
RX450-g-PS/4% DVB-SA	38	2.2	1.65	0.10	0.03	3.19	1.45	1.2	295.0	293.3	291.6	288.5	287.7	286.2	284.5
RX450-g-PS/10% DVB-SA	45	2.3	1.61	0.08	0.03	2.89	1.30	1.2	294.4	293.4	291.9	288.6	287.0	285.9	284.5

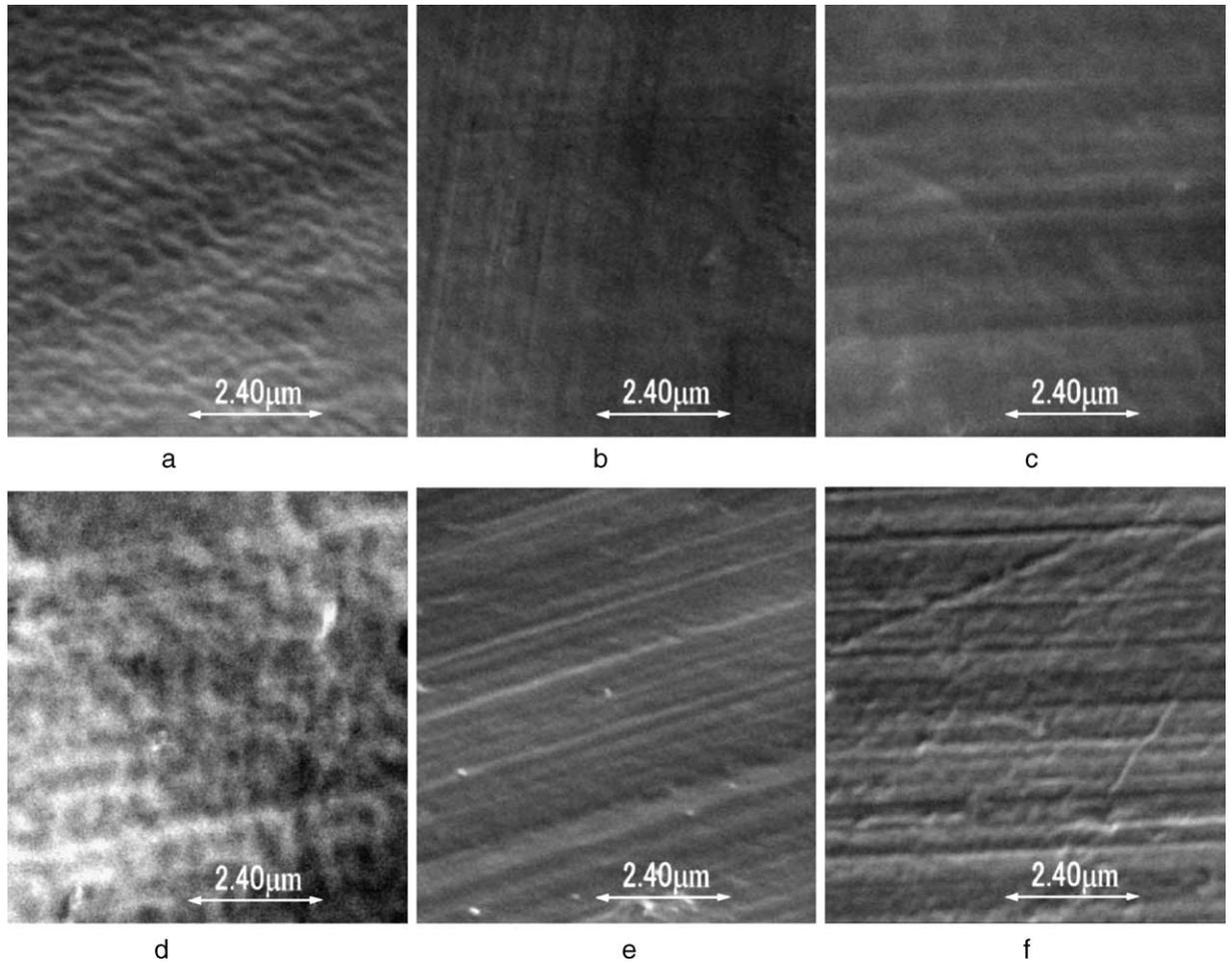


Fig. 6. The SEM images (10,000 \times) of the (a) RX150-g-PS (DOG = 35%), (b) RX150-g-PS/4% DVB (DOG = 33%), (c) RX150-g-PS/10% DVB (DOG = 41%) membranes and the (d) RX450-g-PS (DOG = 42%), (e) RX450-g-PS/4% DVB (DOG = 38%), (f) RX450-g-PS/10% DVB (DOG = 45%) membranes.

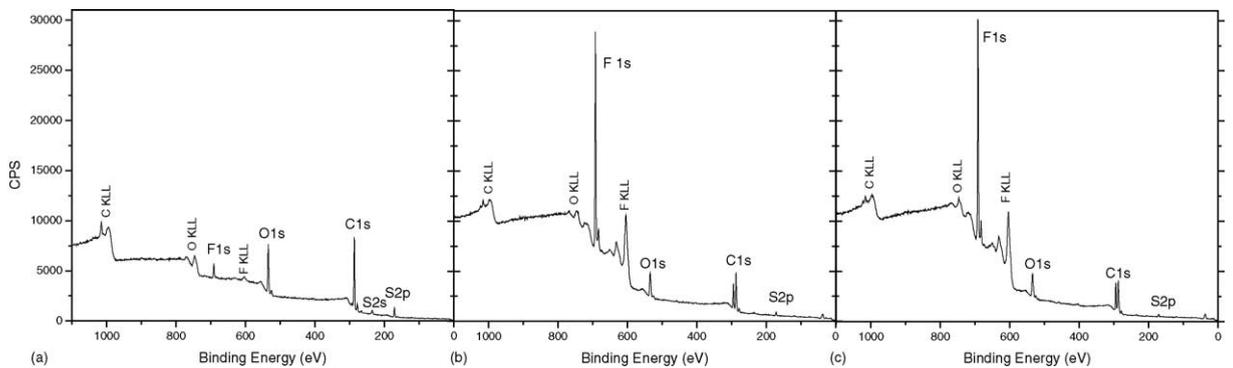


Fig. 7. The XPS wide scan spectra of the (a) RX150-g-PS-SA (DOG = 35%, IEC = 2.1), (b) RX150-g-PS/4% DVB-SA (DOG = 33%, IEC = 2.0) and (c) RX150-g-PS/10% DVB-SA (DOG = 41%, IEC = 2.2) membranes.

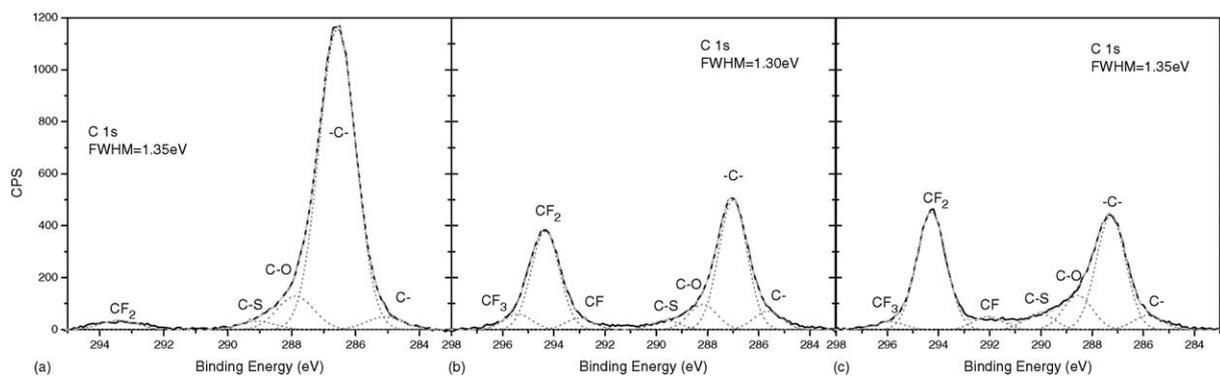


Fig. 8. The XPS narrow scan spectra of C 1s and curve fitting of the (a) RX150-g-PS-SA (DOG = 35%, IEC = 2.1), (b) RX150-g-PS/4% DVB-SA (DOG = 33%, IEC = 2.0) and (c) RX150-g-PS/10% DVB-SA (DOG = 41%, IEC = 2.2) membranes.

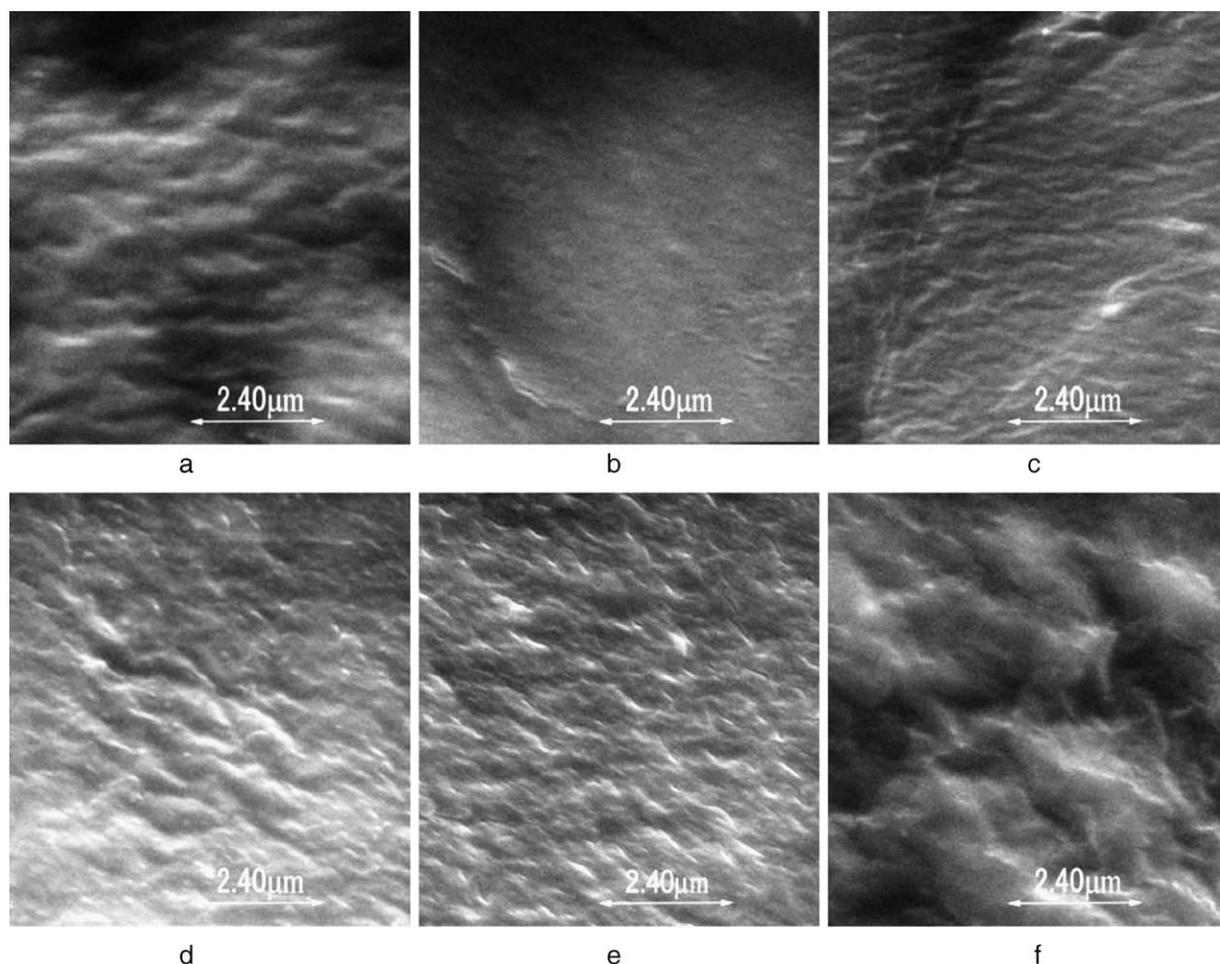


Fig. 9. The SEM images (10,000 \times) of the (a) RX150-g-PS-SA (DOG = 35%, IEC = 2.1), (b) RX150-g-PS/4% DVB-SA (DOG = 33%, IEC = 2.0), (c) RX150-g-PS/10% DVB-SA (DOG = 41%, IEC = 2.2) membranes and the (d) RX450-g-PS-SA (DOG = 42%, IEC = 2.4), (e) RX450-g-PS/4% DVB-SA (DOG = 38%, IEC = 2.2), (f) RX450-g-PS/10% DVB-SA (DOG = 45%, IEC = 2.3) membranes.

acid with the dangling double bonds on DVB in the grafts. The result of the side reactions is that there will be Cl atoms in the sulfonated membranes. However there is no signal attributed to Cl atom in the wide scan spectra. Hence, if there are dangling double bonds on DVB units which will react during sulfonation, the amount of such dangling double bonds are too low to be considered.

Fig. 8 shows the XPS narrow scan spectra and curve fitting of the grafted and sulfonated RX150 membranes as the PEMs. As compared with the curve fitting result of the grafted membranes before sulfonation, there is one new peak at around 288.5 eV (corrected) which is attributed to the C–S bond of the sulfonated benzene rings on the PS-SA side chains. The curve fitting parameters for C 1s spectra and the corrected binding energy for every bond of the grafted and sulfonated RX150 and RX450 membranes are listed in Table 3. From the table, it is obvious that the concentration of DVB used in grafting does not affect the binding energy of the bonds.

The atom ratios of the PEMs made from both RX150 and RX450 membranes were also listed in Table 3. The results are similar to those of the grafted RX150 and RX450 membranes before sulfonation. On the surfaces of the styrene grafted membranes there are mainly PS-SA chains while on the surfaces of the styrene/DVB grafted membranes there are fewer PS-SA chains. The F/C atom ratios of the PEMs are lower than that of the corresponding grafted membranes before sulfonation. The lowering in the F/C atom ratios are the result of the further phase separation between the hydrophilic PS-SA grafts with the hydrophobic PTFE matrix. The O/S ratios of all PEMs are close to 3, which is in accordance with the stoichiometry of the sulfonic acid group.

Fig. 9 shows the SEM images (10,000 \times) of the grafted and sulfonated RX150 and RX450 membranes as PEMs. Similar to those grafted RX150 and RX450 membranes before sulfonation, there are fewer “waves” on the surface of the styrene/DVB grafted membranes than those of the styrene grafted membranes. The sizes of the “waves” on the surfaces of the sulfonated membranes are larger than those of the corresponding grafted membranes before sulfonation. The reason should be the sulfonation introduces

the hydrophilic sulfonic acid groups. The groups are incompatible with the hydrophobic PTFE matrix.

4. Conclusion

RX-PTFE membranes with thickness around 10 μm were obtained by coating the PTFE dispersion on the aluminum sheets and then irradiated above its melting temperature under oxygen-free atmosphere using electron beam. The PEMs were prepared by pre-irradiation induced grafting of styrene with DVB of different concentrations into RX-PTFE membranes and successive sulfonation. The surface chemical structure and morphology of the non-grafted, the grafted, and the grafted and sulfonated RX-PTFE membranes were analyzed by XPS and SEM. The F/C atom ratios on the surfaces of the RX-PTFE membranes are lower than 2 due to the crosslinking, and the surfaces are smooth. The F/C atom ratios on the surfaces of the styrene grafted RX-PTFE membranes are close to 0 which means there are mainly polystyrene grafts accumulated on the surfaces. But there are mainly PTFE chains on the surfaces of the membranes grafted by styrene together with DVB. Angle resolve analysis showed that the existing of DVB did not improve the compatibility between the RX-PTFE matrix and the grafts. The uniform distribution of the grafts in the styrene/DVB grafted membranes was due to the crosslinking structure formation in the PS/DVB grafts. The “wave” shape morphology was observed on the surfaces of the grafted RX-PTFE membranes, and the amount and size of the “waves” were strongly affected by the DVB concentration used in graft polymerization. The F/C atom ratios on the surfaces of the grafted and sulfonated membranes are little lower than the corresponding grafted membranes before sulfonation. On the surface of the sulfonated membranes, there are “waves” with larger size than those of the corresponding grafted membranes before sulfonation. The analysis showed that the distribution of the polystyrene grafts in the RX-PTFE matrix were strongly affected by the concentration of the crosslinking co-monomer, DVB, used in the graft polymerization and the sulfonation will not change the distribution of the grafts obviously.

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