

Cation Exchange Membranes by Radiation-Induced Graft Copolymerization of Styrene onto PFA Copolymer Films.

IV. Morphological Investigations Using X-Ray Photoelectron Spectroscopy

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ABSTRACT: Morphological investigations of poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA)-*g*-polystyrene sulfonic acid membranes prepared by radiation-induced graft copolymerization of styrene onto PFA films followed by sulfonation were performed by X-ray photoelectron spectroscopy. The analyzed materials included grafted film and sulfonated membrane samples having various degrees of grafting. Original PFA film was used as a reference material. The results of the X-ray photoelectron spectral analysis show that PFA film undergoes changes in terms of chemical compositions and binding energies of its basic elemental components under the influence of membrane preparation procedure, i.e., grafting and sulfonation. The chemical compositions of the surfaces of the membranes were found to be dependent on the degree of grafting unlike the binding energies of their elemental components (C, F, O, and S), which were found to be independent of the degree of grafting. The atomic ratio of F/C was found to decrease drastically with the increase in the degree of grafting and the membranes were found to have almost pure hydrocarbon structure at the layers close to their surfaces where degradation is suggested to be concentrated. The results of these investigations suggest that the morphology of the membranes plays an important role in the chemical degradation of the membranes. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2455–2463, 2000

Key words: cation exchange membranes; radiation-induced graft copolymerization; styrene; PFA films; XPS

INTRODUCTION

Recently, interest in the development of polymer electrolyte membrane (PEM) fuel cell for trans-

portation and stationary application has increased considerably. This is because of the improvements in the fuel cell technology and the environmental issues associated with the conventional power generation devices.^{1–3} However, the cost of the materials of the PEM fuel cell has to be reduced to enhance their widespread application. The polymer electrolyte represented by cation exchange membrane having sulfonic acid groups has a vital role in PEM fuel cell as it conducts

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protons from the anode to the cathode and prevents the bulk mixing of H_2 and O_2 . At present, Nafion® membranes are the most widely used polymer electrolyte membranes. However, the high cost of Nafion membranes has limited their use in large-scale applications and hindered the emergence of commercially competitive PEM fuel cells.^{4,5} Therefore, a large amount of work has been devoted to develop new proton exchange membranes having a combination of high conductivity, chemical stability, and low cost.^{6–10}

In the development of new membranes, modification of preformed polymers by grafting of chemical functionality is a versatile technique.¹¹ Among many available grafting methods, radiation-induced grafting is an advantageous technique, particularly in terms of membrane shaping and controlling composition.¹² Many studies have reported the preparation of sulfonic acid cation exchange membranes by radiation-induced grafting of styrene onto various fluorinated polymers. Because of the chemical stability requirements, the base polymers were only confined to fluorinated and partially fluorinated polymers.¹¹

Preparation of polystyrene sulfonic acid membranes based on poly(tetrafluoroethylene) (PTFE)^{13,14} poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)^{15,16} polyvinylidene fluoride (PVDF)^{17,18} and poly(ethylene-*co*-tetrafluoroethylene) (ETFE)¹⁹ has been reported in many occasions using simultaneous and preirradiation techniques. In our recent studies we reported the preparation of sulfonic acid cation exchange membranes radiation grafting of styrene onto poly(tetrafluoroethylene-*co*-perfluorovinyl ether) (PFA) films using simultaneous irradiation, followed by a sulfonation reaction.^{20,21} The degree of grafting of the membranes was found to be a function of the grafting conditions. The properties of PFA-*g*-polystyrene sulfonic acid membranes were found to be dependent heavily on the degree of grafting as degrees of sulfonation close to 100 % were achieved for all of the membranes at various degrees of grafting. The membranes were found to undergo substantial degradation upon treating with 3% H_2O_2 containing 4 ppm Fe^{++} at a temperature of 70°C for 5 h.²¹ Such results imply the need for conducting thorough investigations to determine the possible reason as well as the location of the degradation in these membranes to prevent it.

To address this problem, X-ray photoelectron spectroscopy (XPS) technique was applied to obtain a closer look at the changes that take place in

the morphology and the chemical composition of PFA-*g*-polystyrene sulfonic acid membranes under the influence of the two-step preparation procedure, i.e., grafting and sulfonation. Emphasis was given to the morphology of the surface of the membranes where the chemical attack is expected to occur upon applying these membranes as electrolytes in electrochemical applications such as PEM fuel cell.

In this article, we report on the results of the morphological investigations of PFA-*g*-polystyrene sulfonic acid membranes by means of XPS to monitor the structural changes that take place in the surfaces of the membranes as a result of styrene grafting and subsequent sulfonation as well as the variation of degree of grafting.

EXPERIMENTAL

Membrane Preparation

The membranes were prepared by radiation-induced graft copolymerization of styrene onto PFA films using a simultaneous irradiation technique as reported previously.²⁰ The grafted PFA films were subsequently sulfonated using a chlorosulfonic acid/1,1,2,2-tetrachloroethane mixture. The degree of sulfonation of the membranes was found to be close to 100%. Details of sulfonation and the properties of the PFA-*g*-polystyrene sulfonic acid membranes were published elsewhere.²¹ Membranes having degrees of grafting in the range of 6–49% were used for the morphological investigations. The degree of grafting of the PFA graft copolymers was gravimetrically obtained using the following equation:

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

where, W_g and W_0 are the weights of grafted and original PFA films, respectively.

XPS Measurements

XPS measurements were conducted on dry samples (original, grafted, and sulfonated membranes in acid form) using Kratos XSAM-HS surface micro analyzer by Mg K_{α} X-ray source (1253.6 eV) in fixed analyzer transmission mode. Binding energies of the instrument were calibrated using pure silver plate and gives Ag $3d_{5/2}$ at 368.25 eV and

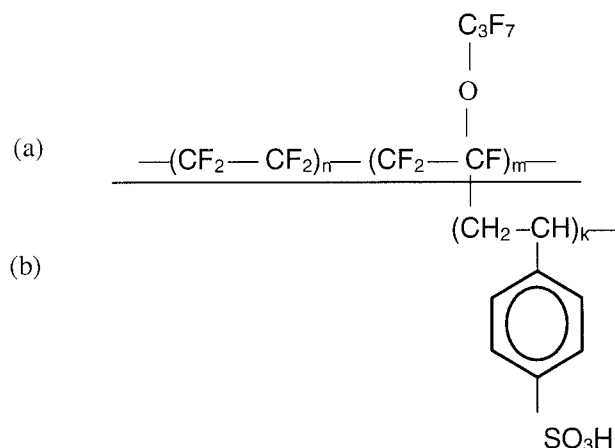


Figure 1 An idealized molecular structure of PFA-g-polystyrene sulfonic acid membrane. (a) PFA main chain, (b) sulfonated polystyrene side chain.

$\Delta Ag = 6.00$ eV. Low X-ray flux of the nonmonochromatized MgK_{α} line normally operated at 10 mA and 12 KV, while charge neutralizer was switched on to minimize the charging effect. The sample areas excited by the X-ray spot had a size of $240 \mu m^2$. The vacuum system was kept at 4.0×10^{-9} torr. Wide scans in the range of 50 to 1150 eV were recorded at pass energy of 160 eV with a step size of 1 eV and dwell time of a 0.1 s step. Narrow scans at higher resolution (at pass energy of 20 eV with a step size of 0.05 eV and dwell time of a 0.1 s step) were performed for the C1s, F1s, S2p, and O1s regions. Each element scanning is repeated 5 times to obtain reproducible results. Both surfaces of the samples were investigated to establish the symmetrical structure of each membrane. Binding energies of all photoelectron effects were corrected based on C1s at 284.5 eV for terminal hydrocarbon ($-C_{\alpha}-$). The Gaussian peak fitting parameter with straight baseline was applied for peak analysis using Vision software supplied by Kratos (UK).

RESULTS AND DISCUSSION

Radiation grafting of styrene onto PFA films and subsequent sulfonation of the grafted films resulted in PFA-g-polystyrene sulfonic acid membranes having degrees of grafting in the range of 6–49%. An idealized molecular structure of PFA-g-polystyrene sulfonic acid membrane is given in Figure 1.

Morphology of the Original PFA Film

Survey wide scan spectrum of original PFA film is shown in Figure 2. Three peaks can be clearly observed at 292.2, 689.1, and 529.1 eV (charging effect = 5.0 eV). These peaks are assigned for C1s of C—F, F1s, and O1s, respectively. The shift in the binding energy of C—F compared with the reported binding energy of C—H²² is due to the combined effect between the chemical shift owing to the electron attraction toward fluorine atom (7.7 eV) and the charging effect (5.0 eV). The F/C ratio calculated from XPS spectra is found to be 2.22 whereas that of O/C ratio is found to be 0.24. These values are higher than those theoretically obtained from the chemical structure of tetrafluoroethylene perfluorovinyl ether copolymer where F/C and O/C should be equal to 2.00 and 0.14, respectively. The high value of F/C ratio indicates that fluorine atoms are somewhat concentrated at the surface of the film. Moreover, the high value of O/C is mostly due to a contamination by oxygen that might have occurred during the film extrusion. These results confirm that PFA film is composed of fluorine, carbon, and oxygen as elemental components. From these results it can also be concluded that understanding of the morphology of the surface of PFA film requires the clear recognition of the overwhelming role of fluorine and carbon coming into play during grafting and sulfonation of PFA films.

To identify the individual components contributing to the film structure, the narrow spectrum of C1s is obtained. With the help of the curve fitting, the core level spectrum of C1s is deconvoluted into

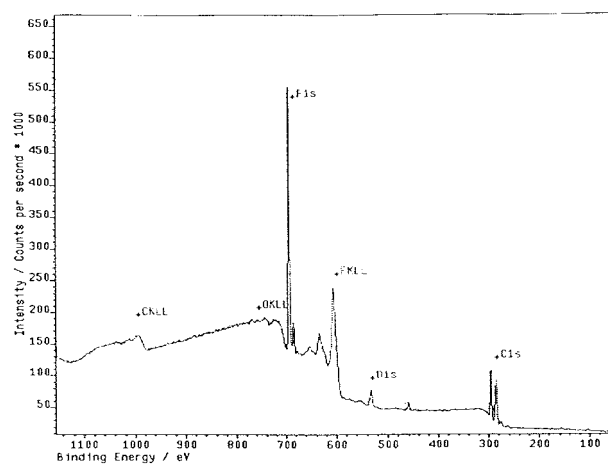


Figure 2 XPS survey wide scan spectrum of original PFA film.

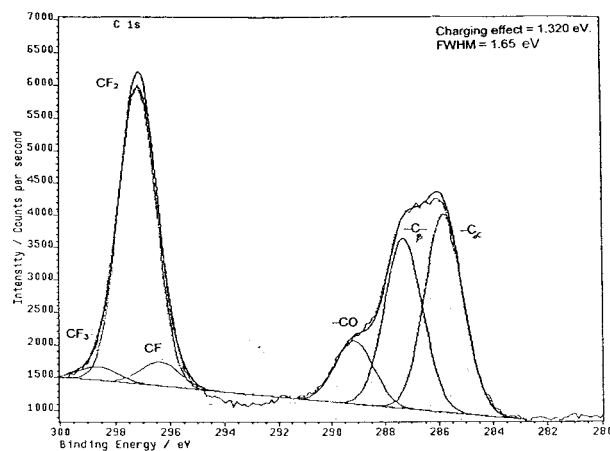


Figure 3 Narrow scan of C1s spectrum of original PFA film.

six component peaks as depicted in Figure 3. These peaks have corrected binding energies of 297.3, 295.7, 295.1, 287.9, 286.0, and 284.5 eV (charging effect = 1.32 eV), which can be assigned to CF_3 ; CF_2 ; CF ; CO ; or $\text{C}-\text{CF}$; $-\text{C}_\beta-$ and $\text{C}_\alpha-$, respectively. The shifts in the binding energies of CF_3 , CF_2 , and CF peaks from the values reported in literature^{23,24} are probably due to the presence of some $-\text{CF}_2\text{O}$ in $-\text{CF}_3$ peak, some $-\text{CFO}$ in $-\text{CF}_2$ peak, some $>\text{C}=\text{O}$ in $-\text{CF}$ peak, and some $-\text{CO}$ in $-\text{C}_\beta-$. Such results are in good agreement with those reported by Wang et al. (1993)²⁵ for the same fluorine-containing groups. Comparing the intensities of the peaks representing fluorine-containing components show that $-\text{CF}_2$ apparently dominates the surface of PFA film. Therefore, it is evident that $-\text{CF}_2$ groups belong to the main chain of the PFA structure and $-\text{CF}$, $-\text{CF}_3$, and $-\text{CO}$ belong to the perfluorovinyl ether side chain attached to the main chain. The CF_2 related to the perfluorovinyl ether side chain could not be differentiated from that belonging to the main chain.

The concentration of oxygen is found to be 7.5% of the fluorinated structure of PFA film. The most expected source for this oxygen is the ether group ($-\text{O}-$) present in the PFA structure. However, some other oxygen contamination forms such as $\text{C}=\text{O}$ and $\text{O}-\text{H}$ of water might be associated. The O1s spectrum is deconvoluted into three peaks as illustrated in Figure 4. These peaks, which are located at 535.4, 533.2, and 531.60 eV are assigned $-\text{OH}$ for water, $-\text{O}-$ for the ether group, and $>\text{C}=\text{O}$, respectively. From the peak intensity of deconvoluted spectrum, it is evident that the oxygen is mainly present in the ether form ($-\text{O}-$).

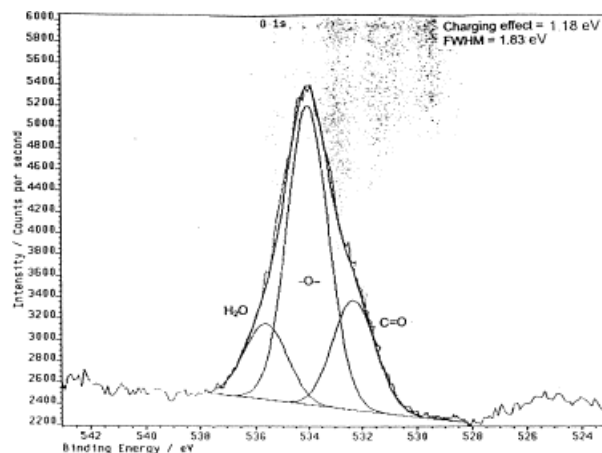


Figure 4 Narrow scan of O1s spectrum of original PFA film.

Morphology of the PFA-g-polystyrene

Figure 5 shows survey wide scan spectrum of PFA-g-polystyrene film having a degree of grafting of 49%. As can be seen, the intensity of C1s peak increases whereas that for C1F decreases as compared with the spectrum of the original PFA film. The incorporation of polystyrene side chain grafts enhances the rupture of $-\text{CF}-$ bonds near the surface and introduces hydrocarbon components in the form of aliphatic ($-\text{CH}_2-\text{CH}=\text{}$) and aromatic ($-\text{C}_6\text{H}_5$) into the fluorinated structure of PFA film. Consequently, considerable increase in the intensity of C1s followed by a decrease in the intensity of F1s peak takes place and as a result the F/C ratio falls to 0.22. In the meantime, a considerable amount of oxygen (16.3 atomic

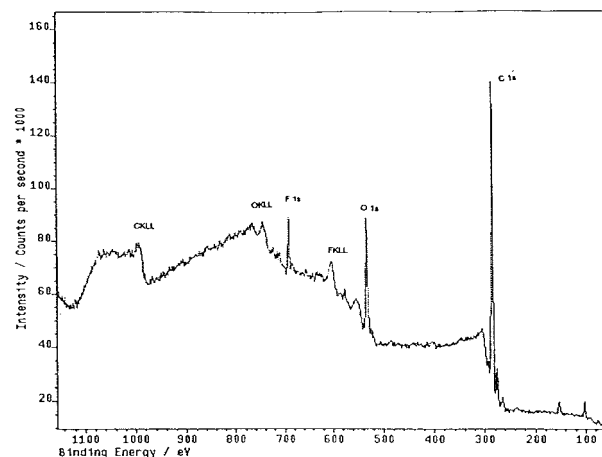


Figure 5 XPS survey wide scan spectrum of PFA-g-polystyrene film having a degree of grafting of 49%.

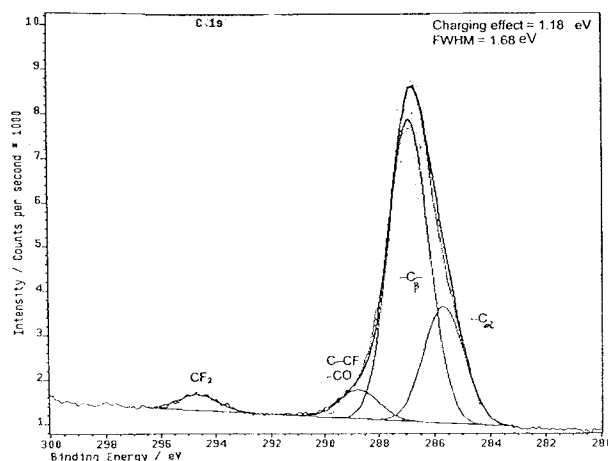


Figure 6 Narrow scan of C1s spectrum of PFA-g-polystyrene film having a degree of grafting of 49%.

conc %) is detected in the grafted film as can be seen from the increase in the intensity of O1s peak compared with that of the original PFA film. The increase in the amount of oxygen is probably due to the reaction with the oxygen that might remain in the grafting mixture during the grafting reaction. Moreover, there is a possibility for oxygen contamination as a result of the reaction with the atmospheric oxygen when the grafted film is exposed to air, leading to the formation of more —CO and >C=O groups.

Figure 6 shows the narrow scan spectrum and the curve fitting of C1s of PFA-g-polystyrene film having a degree of grafting of 49%. The spectrum is deconvoluted into four component peaks having corrected binding energy of 293.5, 287.6, 285.7, and 284.5 eV and representing CF_2 , CO , $\text{—C}_\beta\text{—}$, and $\text{C}_\alpha\text{—}$, respectively. Grafting of styrene onto PFA film induced considerable changes in its structure in terms of the concentration of fluorine as well as carbon. It is found that the two peaks representing CF_3 and CF disappear from the surface spectrum as a result of incorporation of hydrocarbon polystyrene grafts. Moreover, the intensity of the remaining fluorine-containing peak (CF_2) was drastically reduced due to the consumption of the C—F bond in radical formation. Simultaneously, the intensity of $\text{—C}_\beta\text{—}$ is remarkably increased. The difficulty in the specific determination of $\text{—C}_\beta\text{—}$ and $\text{—C}_\alpha\text{—}$ of aliphatic ($\text{—CH}_2\text{—CH=}$) and aromatic ($\text{—C}_6\text{H}_5$) of the polystyrene incorporated in the grafted film is due to the minor chemical shifts in these carbon atoms.^{26,27} It can also be seen that the contribution of $\text{—C}_\beta\text{—}$ is higher than that of $\text{—C}_\alpha\text{—}$, whereas

the contribution of —CO groups is lower compared with both of them. These features indicate that PFA film surface is predominated by hydrocarbon structure as a result of styrene grafting.

The deconvolution of O1s spectrum shows the same features as the original film in terms of the number and types of peaks. Figure 7 shows the curve fitting of O1s spectrum of PFA-g-polystyrene film having a degree of grafting of 49%. Three peaks having corrected binding energies of 534.4, 532.8, and 531.1 eV are assigned for oxygen O—H of water, —O— of the ether group, and C=O , respectively. From the peak intensity of deconvoluted spectrum, it is evident that the oxygen is mainly present in the form of ether group (—O—).

Morphology of PFA-g-Polystyrene Sulfonic Acid Membrane

Figure 8 shows survey wide scan spectrum of PFA-g-polystyrene sulfonic acid membrane having a degree of grafting of 49%. It can be seen that one additional peak appears at 168.5 eV (corrected) compared with the spectrum of the PFA-g-polystyrene film. This peak can be assigned to S2p of sulfur. Moreover, the peak intensity of O1s at 531.9 eV (corrected) increases whereas that of F1s at 688.8 eV (corrected) remarkably decreases and F/C ratio further decreases to a value as low as 0.034. This is ascribed to the introduction of sulfonic acid groups (SO_3^-) in the surface of the grafted PFA film via sulfonation of the polystyrene side chains. Consequently, more disappearance of the main-chain components (CF_2 groups)

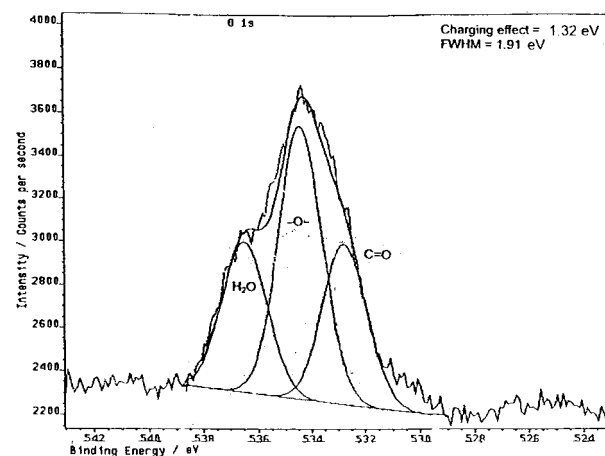


Figure 7 Narrow scan of O1s spectrum of PFA-g-polystyrene film having a degree of grafting of 49%.

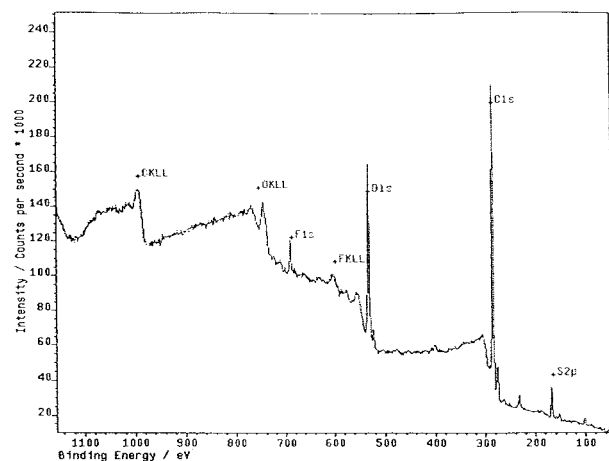


Figure 8 XPS survey wide scan spectrum of PFA-g-polystyrene sulfonic acid membrane having a degree of grafting of 49%.

available near the surface of the film takes place, leading to an increase in the peak intensity of O1s accompanied by the emergence of a new S2p peak.

Figure 9 shows the curve fitting of C1s of the spectrum of the 49% PFA-g-polystyrene sulfonic acid membrane. It is found that the deconvolution of the spectrum shows the emergence of a new peak at 288.2 eV (corrected) and disappearance of two of the three fluorine-containing peaks found early in the grafted PFA film. The newly emerged peak is assigned to the C—S group introduced by sulfonation of benzene ring of the polystyrene grafts. The disappeared peaks were assigned to CF_3 and CF groups that were found in the grafted PFA film and the remaining small peak at 292.6

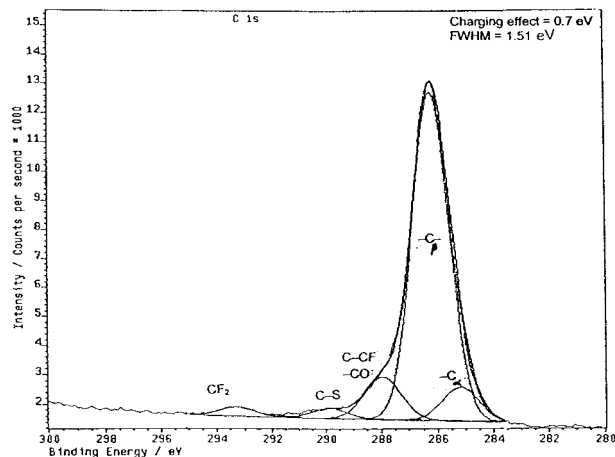


Figure 9 Narrow scan of C1s spectrum of PFA-g-polystyrene sulfonic acid membrane having a degree of grafting of 49%.

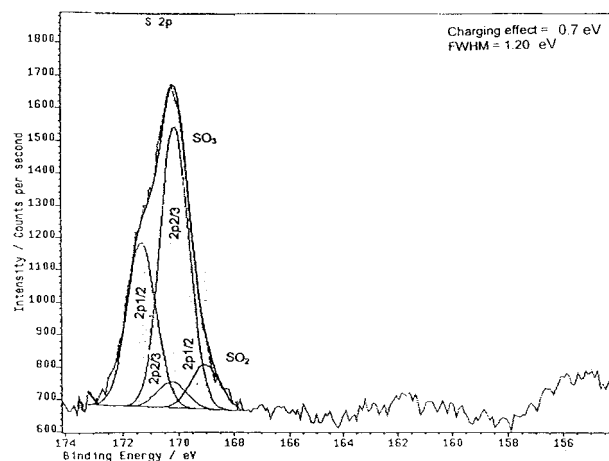


Figure 10 Narrow scan of S2p spectrum of PFA-g-polystyrene sulfonic acid membrane having a degree of grafting of 49%.

eV is characteristic for CF_2 . In addition, the intensities of CO , C—CF , $\text{—C}_\beta\text{—}$, and $\text{C}_\alpha\text{—}$ peaks found at 287.3, 285.5, and 284.5 eV are shown to be decreased. This indicates that the addition of (SO_3^-) groups induces more changes in the surface of the grafted film and such changes are most likely to occur at the expense of fluorine-containing components, which further disappear at the surface. It can also be concluded that the surface of PFA-g-polystyrene sulfonic acid membrane is nearly pure hydrocarbon.

Figure 10 shows the curve fitting of S2p spectrum of 49% PFA-g-polystyrene sulfonic acid membrane. The spectrum is deconvoluted into four peaks at 170.14, 171.4, 169.3, and 170.3 eV (charging effect = 1.26). The major two peaks at 170.1 and 171.4 eV are assigned to 2p3/2 and 2p1/2 of sulfur having a higher oxidation-state (SO_3^-). Whereas, the minor peaks at 169.1 and 170.3 eV, assigned to 2p3/2 and 2p1/2 of sulfur having a lower oxidation-state (SO_2^-) might be associated with the sulfonic acid groups. The percentage of (SO_3^-) calculated from the deconvoluted spectrum is found to be equal to 87%.

Figure 11 shows the curve fitting of spectrum of O1s of PFA-g-polystyrene sulfonic acid membrane having 49% degree of grafting. The spectrum is deconvoluted into four peaks at 534.3, 533.0, 532.0, and 530.1 eV (charging effect = 0.70 eV). The new peak emerged at a 530.8 eV is assigned to the oxygen present in the sulfonic acid group whereas the three peaks that have corrected binding energies of 535.0, 533.7, 532.7 eV are assigned to oxygen O—H of water, —O— of

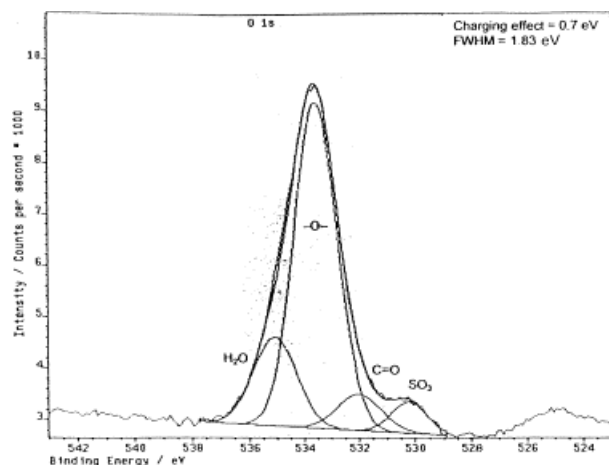


Figure 11 Narrow scan of S2p spectrum of PFA-g-polystyrene sulfonic acid membrane having a degree of grafting of 49%.

ether group, and $>C=O$, respectively. It can be concluded that sulfonation of the grafted polystyrene film brings more changes into the layer closed to the surface of PFA film in terms of chemical composition as well as binding energy.

Morphology of PFA-g-Polystyrene Sulfonic Acid Membranes Having Various Degrees of Grafting

Figure 12 show the wide scan spectra of PFA-g-polystyrene sulfonic acid membranes having various degrees of grafting. It can be clearly seen that the intensities of C1s, F1s, O1s, and S2p peaks depend on the degree of grafting. The intensities of C 1s, O1s, and S2p peaks increase as the degree of grafting increases while the intensity of F1s decreases. Such behavior can be attributed to the increase in the content of sulfonated polystyrene side chains, at the expense of fluorine content of the main chain of the membrane.

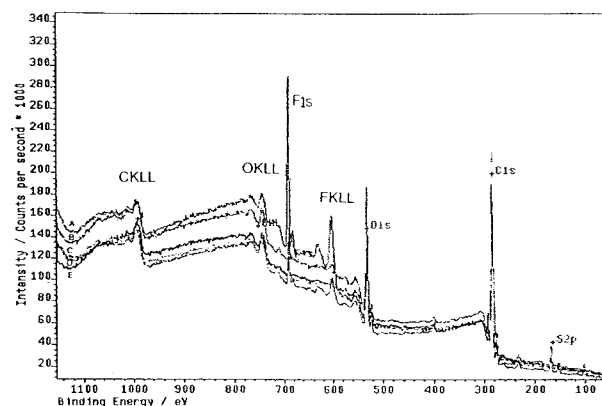


Figure 12 XPS survey wide scan spectra of PFA-g-polystyrene sulfonic acid membranes having various degrees of grafting: (A) 6%, (B) 16%, (C) 26%, (D) 38%, and (E) 49%.

To obtain better understanding of the structural changes that took place in the surfaces of PFA-g-polystyrene sulfonic acid membranes with the increase in the degree of grafting, the changes in binding energies of C1s, F1s, O1s, and S2p were investigated. Moreover, the atomic ratios F/C, O/C, S/C, and O/S were also calculated from the XPS spectra. Table I shows the corrected binding energies of C1s, F1s, O1s, and S2p of PFA-g-polystyrene sulfonic acid membranes having various degrees of grafting. It can be seen that the binding energies of C1s, F1s, O1s, and S2p peaks almost have no significant shift despite the increase in the degree of grafting within the membrane. This indicates that there are no changes in chemical structures or the oxidation states of the elemental components of the membrane and therefore, it can be concluded that the binding energies of the elemental components of the membranes are independent of the degree of grafting. These results are similar to those reported for

Table I Corrected Binding Energy of C1s, F1s, O1s, and S2p of PFA-g-Polystyrene Sulfonic Acid Membranes Having Various Degrees of Grafting

Degree of Grafting (%)	C1s						O1s				S2p			
	CF ₂	C—S	—CO/ C—CF	—C—	—C	F1s	H ₂ O	—O—	SO ₃	SO ₂	(SO ₃) 2p1/2	(SO ₃) 2p2/3	(SO ₂) 2p1/2	(SO ₂) 2p2/3
6	292.5	289.3	287.3	285.4	284.5	688.9	534.7	533.3	531.7	529.7	170.4	168.9	169.4	168.0
16	292.5	289.1	287.4	285.6	284.5	688.8	534.6	533.1	531.6	529.6	170.3	168.9	169.4	168.0
26	292.3	289.2	287.4	285.4	284.5	688.7	534.4	533.0	531.5	529.7	170.3	168.7	169.2	167.9
38	292.5	289.1	286.9	285.7	284.5	688.7	534.5	533.0	531.4	529.6	170.1	168.8	169.2	167.7
49	292.6	289.3	287.3	285.5	284.5	688.7	534.4	532.9	531.4	529.6	170.1	168.9	169.1	167.9

Table II Variation in the Ratios of F/C, S/C, O/C, and O/S Calculated from XPS Spectra as a Function of Degree of Grafting

Degree of Grafting (%)	F/C	S/C	O/C	O/S
0	2.22	—	0.24	—
6	0.34	0.040	0.26	8.0
16	0.10	0.040	0.26	7.2
26	0.05	0.045	0.30	7.9
38	0.04	0.040	0.30	7.7
49	0.03	0.047	0.30	7.2

PTFE-g-polystyrene sulfonic acid and FEP-g-polystyrene sulfonic acid membranes.^{28,29}

Table II shows the variation in the atomic ratios of the elemental components of PFA-g-polystyrene sulfonic acid membranes as a function of the degree of grafting. Elemental ratio of the original film is included as a reference. The F/C ratio presented in the first column is shown to be drastically decreased by the introduction of sulfonated polystyrene side chains as compared with that of original PFA film. Moreover, it continues to decrease with the increase in the degree of grafting, i.e., the content of sulfonated polystyrene grafts. The sharp decrease in F/C ratio upon the introduction of sulfonated polystyrene grafts is due to the consumption of C—F bonds available at the film surface in the formation of the radicals required to initiate the grafting in the presence of styrene molecules upon exposure to γ -radiation. Whereas, the continuous decrease in the F/C ratio with the increase in the degree of grafting is attributed to the increase in the consumption of C—F bonds, which results in the formation of more radicals in the film. Consequently, the degree of grafting is enhanced and the content of polystyrene grafts increases while that of fluorine is reduced.

The S/C as well as O/C ratios are shown to have no significant shifts despite the increase in the degree of grafting in the membranes. It is well known that the increase in the polystyrene content provides more chain grafts for sulfonation. As a result, the sulfur and oxygen comprising the content of sulfonic acid group ($-\text{SO}_3^-$) increase with the increase in the degree of grafting. However, all membranes were found to have a degree of sulfonation close to 100% regardless the degree of grafting. Therefore, there is no significant change in the S/C and O/C ratio with the increase

in the degree of grafting as the fraction of the sulfonated phenyl groups in polystyrene grafts is equal to 1.

The O/S ratios presented in the fourth column also show no significant change with the increase in the degree of grafting. However, it is higher than the theoretical ratio, which equals 3 referring to the chemical structure of ($-\text{SO}_3^-$) group. This is due to the increase in the oxygen content in the membranes as a result of the presence of ether group in the structure of the PFA film, the contamination of the sample by moisture, and the oxygen early found in the original and grafted PFA films.

From the previous results, it can be concluded that there is a qualitative as well as quantitative correlation between the structural changes that take place in the surface of the membranes and the degree of grafting. The depletion in the fluorine content and the increase in the hydrocarbon content are strongly dependent on the degree of grafting. Furthermore, the membrane surface is shown to be nearly pure hydrocarbons. These results suggest that the chemical degradation that took place in the membranes upon treatment with 3% H_2O_2 containing 4 ppm Fe^{++} at a temperature of 70°C for 5 h²¹ is due the chemical attack on the hydrocarbon fraction in the membrane concentrating at the surface by HO^\cdot radicals generated in the solution. The high value of weight loss due to the chemical degradation is suggested to be owing to the dissolution and leaching of some of the sulfonated polystyrene chains, which is not chemically bound to fluorinated backbone and is probably formed together with binded ones upon using simultaneous radiation grafting for membrane preparation. These results are in a complete agreement with those reported by Scherer (1990)³⁰ upon evaluation of the stability of similar commercial radiation grafted membranes that were proposed for PEM fuel cell application.

Finally, the results of XPS morphological investigation obtained in this study can be utilized in predicting the stability of PFA-g-polystyrene sulfonic acid membranes upon their use as electrolytes in PEM fuel cell and their possible degradation mechanism. Such information is very important to take certain precaution to enhance the membrane stability and to prevent degradation. Moreover, it can be suggested that membrane behavior in the PEM fuel cell not only de-

depends on its bulk properties but also on the surface properties.

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