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Improvement of polymer electrolyte membrane by radiation-induced grafting of styrene onto FEP film with subsequent sulfonation

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Abstract−Poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) film was homogeneously and highly grafted by styrene monomer under simultaneous irradiation with an electron beam, whereas preirradiation with an electron beam was insufficient to accomplish a high degree of grafting without activation of the styrene monomer. Following its subsequent sulfonation, the styrene-grafted FEP film exhibited considerably higher values of both the IEC and IC and less methanol crossover than the Nafion membrane. The grafting of styrene onto the FEP polymer is thought to be initiated by the abstraction of F atoms from the CF_3 groups in the polymeric structure. It was estimated that two sulfonic acid groups can be attached to the benzene ring of one styrene molecule. The profile of sulfur across the FEP film, which is related to the concentration profile of sulfonic acid groups inside the styrene-grafted FEP film, became more and more homogeneous over a period of several hours, due to the step by step diffusion of monomers into the film, eventually showing a high IC value of 0.25 S/cm in the case of the 125 μm thick FEP film, whereas Nafion 117 (125 μm thickness) exhibited an IC value of 0.12 S/cm.

Key words: Fuel Cell Membrane, FEP, Styrene, Electron Beam, Grafting, Sulfonation, IEC, IC, Sulfur Profile

INTRODUCTION

DMFCs (direct methanol fuel cells) or PEMFCs (proton electrolyte membrane fuel cells), which are types of PEFCs (polymer electrolyte fuel cells), can be used for the generation of electric power with methanol or hydrogen as a fuel, respectively. In recent years, it has been suggested that in the future PEFCs will become one of the most attractive sources of clean energy in automobile, distributed power, and portable power applications [1,2]. Several kinds of fluorinated polymers have been used as the basic polymers for manufacturing fuel cell membranes, of which DuPont's Nafion membrane is typically used as the polymer electrolyte membrane (FEM) in PEMFCs, because of its excellent chemical and mechanical stability, as well as its high proton conductivity [3]. However, Nafion membranes have some disadvantages [4] such as their high cost, low operating temperature and high methanol permeability when used in DMFCs [1,5-7]. The membranes used in PEFCs should exhibit good features in terms of several properties such as their ion conductivity, thermo-chemical stability, mechanical strength, and anti-permeability of fuel through the membrane [3]. Dupont Co. started developing Nafion membranes in 1968 and the most recent version, Nafion 120, has a lifetime of up to 60,000 hours at an operating temperature of 80 °C [1]. It has been found that the methanol crossover in a direct methanol fuel cell (DMFC) causes the poisoning of the novel metal catalysts at the cathode [8], resulting in the lowering of the performance of the fuel cell. In the near future, in order to successfully commercialize PEFCs, a low-cost manufacturing method needs to be developed. One possible method may involve the use of radiation technology with an accelerated electron beam for the grafting process in the manufacture of the membrane. Usually, fluorinated polymers have good resistance to chemical and thermal attack and are sensitive to radiation [9], which may allow the utilization of radiation energies, such as an electron beam and gamma rays, for the grafting of functional monomers onto the polymeric chains. Several kinds of fluorinated polymers such as FEP [10-12], PTFE [13,14], and ETFE [15] have been tested for the purpose of manufacturing fuel cell membranes. The grafted polymers should be sulfonated in order to introduce sulfonic acid groups into the polymeric structure, causing them to exhibit the hydrophilic polarity of SO_3^- in aqueous solution, which makes it possible to transfer protons from the anode to the cathode through such a membrane. The electron beam radiation process is known to be economical, due to its high production rate and high power efficiency. Moreover, this process allows the properties of polymers to be diversified through the grafting process with controlled dosages and the usage of functional monomers. Electron beam radiation makes it possible to homogeneously graft styrene monomer inside a film, initiating the grafting at the surface of film and propagating it inside the film.

Gamma rays or electron beams can be irradiated by two methods, preirradiation and simultaneous irradiation. Scherer et al. [11,12,16-18] used gamma radiation technology for the grafting of styrene onto FEP films by means of preirradiation or simultaneous irradiation under various experimental conditions. In their studies, the radicals generated on the FEP film could be preserved for about twenty hours with the preirradiation process and fifteen hours with the simultaneous one, and the grafting yield increased proportionally with the irradiated dosage. This paper studies the potential of FEP film, which is modified by the grafting of styrene monomer with two kinds of electron beam irradiations, i.e., preirradiation and simultaneous irradiation, to be used as a fuel cell membrane. The proper-

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ties of these two types of manufactured films are compared in order to determine which has the more homogeneous grafting. Also, this study examines the mechanisms of both grafting and sulfonation in detail using FT-IR analysis, and the effect of the sulfur profile across the FEP film on the values of the IC. This study allows us to estimate the effect of the methanol crossover on the degree of grafting, as compared with that of Nafion membranes.

EXPERIMENTAL SECTION

1. Materials

FEP films with thicknesses of 75 and 125 μm were purchased from Dupont Co. and were used as a base polymer for the manufacturing of PEM. Styrene monomer of reagent grade (Aldrich Co.) was used without further purification. Chlorosulfonic acid and dichloromethane used for sulfonation were of reagent grade (Kanto Chemical) and were also used without further purification. Methanol for the crossover test was of reagent grade (Aldrich Co.).

2. Grafting of Styrene Monomers onto FEP Film

The FEP film was cut into specimens with dimensions of 15×40 mm and cleaned with acetone for 24 hours and then dried at 80 °C for several hours. Two irradiation methods, preirradiation and simultaneous irradiation, were adopted for the grafting of styrene onto the FEP films. In the preirradiation method, the FEP film was placed inside a vinyl bag filled with nitrogen gas and irradiated by an accelerated electron beam, and then the irradiated film was immersed in styrene solution within one minute, thereby allowing the grafting to proceed under nitrogen degassing conditions and at a controlled temperature.

In the simultaneous irradiation method, the FEP film was put in a glass reactor filled with styrene solution to a depth of less than 2 mm, where a depth of styrene of 2 mm is nearly equal to the effective penetration depth for energy of 0.7 MeV. The electron beam was irradiated onto both the styrene and FEP film, and the FEP film was grafted by styrene in a dry oven at a controlled temperature. The electron beam accelerator used has a maximum beam energy of 0.7 MeV and maximum beam current of 35 mA (ELV-0.5, BINP in Russia).

To remove possible homopolymers, the grafted FEP film was boiled in toluene solution for two hours, followed by washing several times in cold toluene, and finally drying at 80 °C for around eight hours.

The degree of grafting was estimated by measuring the difference in weight before and after grafting with the following equation:

$$\text{The degree of grafting} = \frac{W_g - W_o}{W_o} \times 100$$

where, W_g and W_o are the weights of the grafted film and the virgin film, respectively.

3. Sulfonation of Grafted FEP Film

To impart conductivity of the protons, which were produced at the anode of the electrodes, to the FEP film grafted by styrene, the grafted film was sulfonated by boiling it with 0.2 M chlorosulfonic acid diluted by dichloromethane at 60 °C for 8 hours in a glass flask with a condenser. After sulfonation was accomplished, the film was hydrated by washing it several times with distilled water, and was then stored in deionized water.

The degree of sulfonation was estimated by measuring the difference in weight before and after sulfonation with the following equation.

$$\text{The degree of sulfonation} = \frac{W_s - W_g}{W_g} \times 100$$

where, W_g and W_s are the weights of the grafted film and the sulfonated film, respectively.

4. Structural and Thermal Analysis of Modified FEP Film

The structure of the grafted FEP film was analyzed by FT-IR (Jasco460+, Japan Spectroscopic Co., LTD), where each sample was scanned thirty two times and the values averaged.

The thermal degradation of the grafted and sulfonated FEP film was measured by TGA (TGA2050 Thermogravimetric, T.A. Instrument) at a rate of 10 °C/min from room temperature to 800 °C under N_2 gas.

5. Measurement of Ion Exchange Capacity (IEC) and Ion Conductivity (IC)

The ion exchange capacity (IEC) [3] was measured by using the following procedure. First, the sulfonated FEP membrane is immersed in a saturated NaCl solution and equilibrated for several hours to exchange the H^+ ions in the sulfonic acid groups with Na^+ ions. The equilibrated solution is titrated with 0.1 N NaOH solution with an acid-alkaline neutral titration, wherefrom the IEC of the FEP membrane can be estimated by the following equation.

$$\text{IEC (mmol/g)} = \frac{0.1 \times V_{NaOH}}{W_d}$$

where V_{NaOH} is the volume of NaOH solution consumed by titration and W_d is the dry weight of the sulfonated FEP membrane.

The hydrogen proton conductivity (IC) of the FEP membrane is estimated by measuring its impedance in a 100% humidity environment by using AC impedance spectroscopy (IM6, ZAHNER) with the following equation.

$$\text{IC} = \frac{L}{R \cdot A}$$

where L, R and A are the distance between the two electrodes, the resistance and the area of the FEP membrane, respectively.

6. Measurement of Sulfur Profiles Across the Sulfonated FEP Film

The sulfur profile across the sulfonated FEP film was determined by energy dispersive X-ray analysis (EDS) with a scanning electron microscope (SAM, S-4200, Hitachi). The film was cut transversely by a razor blade, and then the cut section was positioned with epoxy resin and coated by Pt-sputtering. The sulfur contents were measured at seven points across the cross-section of the film, including both the surfaces and center. The sulfur content in the film is the relative weight % on the basis of the F, C and S atoms

7. Measurement of Methanol Crossover

The methanol crossover in the sulfonated FEP membrane was evaluated by measuring the amounts of methanol transferred toward opposite side across the FEP film. Two glass bottles each with a volume of 200 ml were filled with 5 wt% methanol and distillated water, respectively, and the FEP film was positioned at the joint between the two bottles. The methanol concentration on the pure water side was measured by a gas chromatograph (GC-9A, Shimadzu

Co.) with an FID detector. The column material was Porapak Q (80-100 mesh, Waters Co.), operated at 120ºC under H_2 carrier gas.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Grafting of Styrene onto FEP Film with Preirradiation and Simultaneous Irradiation Methods

In this study, the ability of preirradiation with an electron beam to graft styrene onto the FEP film without degassing the monomer with nitrogen or argon was very poor, regardless of the irradiated dosage, reaction time, and solution temperature. On the other hand, the degassing of the styrene solution with argon gas enabled a slight degree of grafting of the styrene monomers onto the FEP film, as shown in Fig. 1. The degree of grafting at room temperature was very low, regardless of the irradiated dosage in the range of 5 to 50 kGy (A); however, it became much higher as the grafting temperature was increased (B). At a dosage of 100 kGy and 3 hours of grafting, the degrees of grafting were 0.1% at 30 ºC, 7.6% at 40 ºC and 18.2% at 60 ºC. The preirradiation method induces both a local and heterogeneous distribution of the styrene molecules grafted on the FEP film, as shown in Photo 1(A). This kind of FEP film is likely to be improper for fuel cell membranes, giving rise to low transportation of protons through the membrane.

On the other hand, the simultaneous irradiation method produced a high degree of grafting and highly uniform distribution of styrene (Photo 1(B)). Fig. 2 shows that the degree of grafting under simultaneous irradiation is dependent on the grafting temperature: with a dosage of 50 kGy and 5 hours of grafting, the degree of grafting reached 19.2% at 30 ºC, increasing slowly with grafting time, and reached 59.9% and 51.4% at 45 ºC and 60 ºC, respectively. The de-

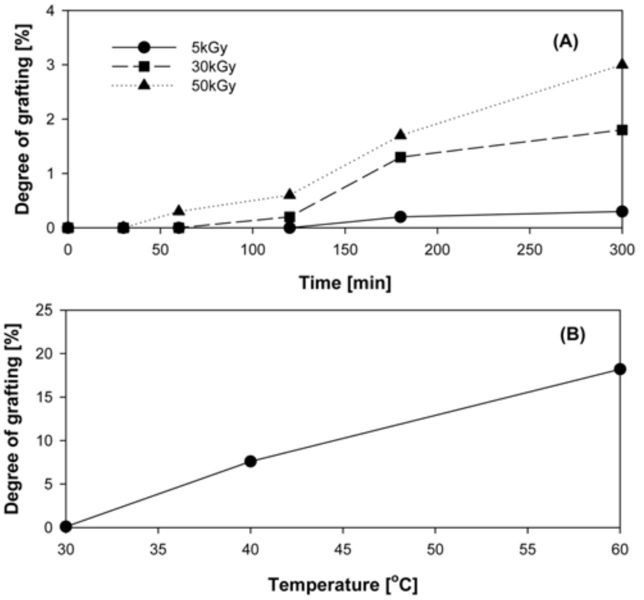

Fig. 1. Degree of grafting versus grafting time with several dosages (A) and versus grafting temperature (B) under preirradiation of electron beam (grafting temperature in (A): 26 ºC; irradiated dose in (B): 100 kGy).

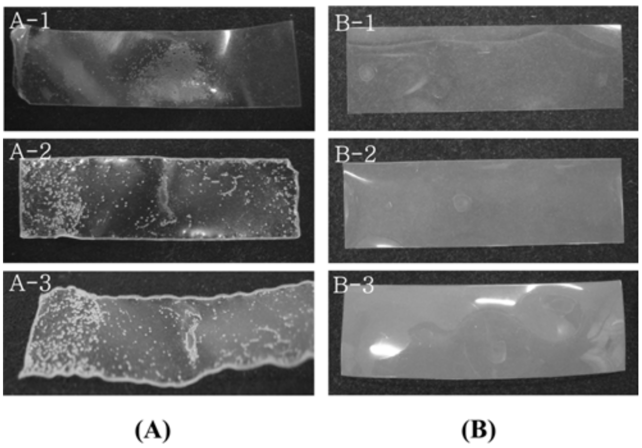

Photo 1. Surface images of the FEP films grafted by means of preirradiation (A) and simultaneous irradiation (B), where the degrees of grafting: A-1=3.2%; A-2=7.3%; A-3=14.3%; B-1=12.9%; B-2=30.3%; D=62.1%.

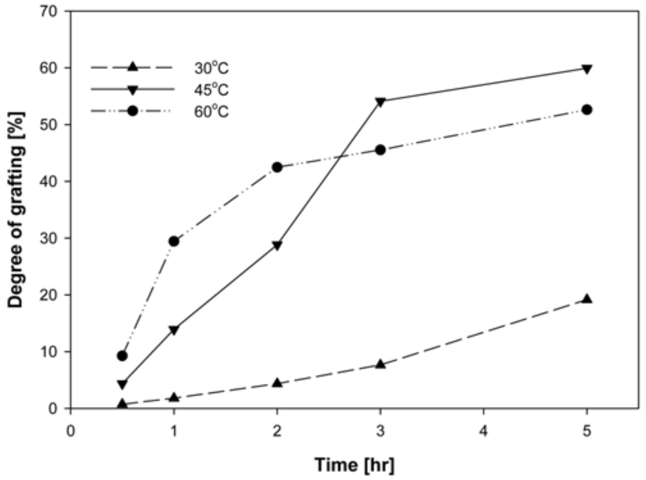

Fig. 2. Degree of grafting versus grafting time at several grafting temperatures and 50 kGy under simultaneous irradiation of electron beam.

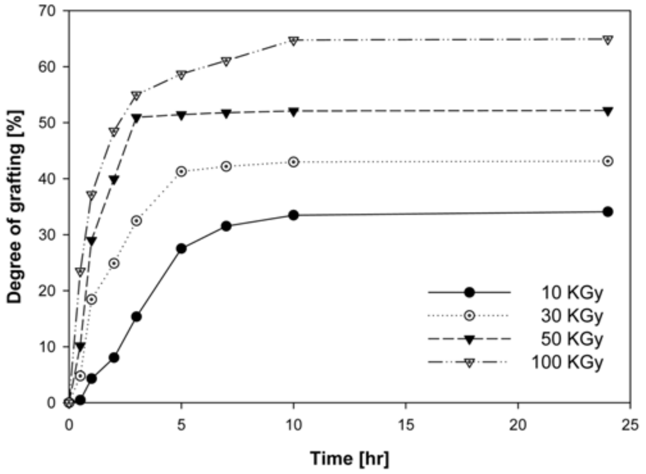

Fig. 3. Degree of grafting versus grafting time at several dosages under simultaneous irradiation of electron beam (grafting temperature: 60 ºC).

gree of grafting at 60 °C was lower than that at 45 °C after 3 hours of grafting, even though a higher temperature leads to a faster grafting rate in the early stage of grafting. This arises from the fact that although the amount of radicals formed by radiation is proportional to the irradiated dosage, the radicals formed disappear faster at a higher grafting temperature. Fig. 3 shows that increasing the irradiation dose considerably increases the grafting rate; for example, at a grafting temperature of 60 °C the final grafting values at the irradiated dosages of 10 kGy, 30 kGy, 50 kGy, and 100 kGy are 34.1%, 43.1%, 52.2% and 64.9% after several hours of grafting, respectively. In contrast to the preirradiation method, simultaneous irradiation allowed the FEP film to be homogeneously grafted by the styrene monomers, as shown in Photo 1(B).

Irradiation with an electron beam can form several kinds of radicals on polymer chains, in this case leading to a wide distribution of surface energies on the FEP film. In the preirradiation method, where a low and heterogeneous degree of irradiation is achieved, it is estimated that the electron beam may not cause FEP to be activated well, probably due to its radiation stability. On the other hand, simultaneous irradiation can activate both the polymer and monomer, even though the activation of the irradiated FEP may be low and heterogeneous. This can result in the more homogeneous and higher grafting of the FEP film with the activated monomers compared to the preirradiation method, regardless of the wide distribution of surface energies on the irradiated film. It is estimated that homogeneous grafting on the surface of FEP in the early stage of grafting is very important to achieve uniform grafting inside the film, eventually leading to the manufacture of a high performance fuel cell membrane.

2. FT-IR Spectra of Grafted FEP Films and Grafting Mechanism

The structural features of fluorine polymers grafted with styrene monomer have generally been examined by means of FT-IR spectroscopy [19], but many different grafting mechanisms have been proposed, including different radical species formed on the monomer and polymer and different bonding positions between the monomer and polymer molecules. Fig. 4 shows the FT-IR spectra of the virgin and grafted FEP films. The spectra of the grafted styrene are characterized by the appearance of new bands at around 3,200-3,000^{-1} and 1,492 cm^{-1} due to the stretching vibrations of =C-H and the skeletal C=C of the benzene ring, respectively. Also, absorption bands due to the aliphatic CH_2 (sp^3) group in styrene appeared at 2,924 cm^{-1} (-CH), 2,850 cm^{-1} ($-CH_2$) and 1,452 cm^{-1} ($-CH_2$), and all of these peaks for styrene tend to increase with increasing degree of grafting. It was found that the stretching vibration of C=C at 1,634 cm^{-1} corresponding to the aliphatic group of the styrene monomer disappeared during grafting, regardless of the degree of grafting. This means that the C=C bond formed on the aliphatic group of styrene combines with the polymer chain, resulting in the disappearance of the peak for the C=C bond.

Next, we examined what kinds of molecular structure on the polymer chain in FEP can combine with the styrene molecule. The spectra (a)-(i) in Fig. 4 show a sharp peak at 982 cm^{-1} due to the C-F stretching vibration of the CF_3 group on FEP and a broad band at 1,150-1,250 cm^{-1} due to the stretching vibration of the CF_2 groups in the original FEP polymer. Especially, the intensity of the peak at 982 cm^{-1} for the CF_3 group tends to decrease markedly with increasing degree of grafting till around 20% ((a)-(d)), whereas when the degree of grafting exceeds 40% the size of the peak remains fairly constant ((f)-(i)). This indicates that in the early stages of grafting the styrene molecules combine mainly with the $\cdot C\text{-}F_2$ radicals which are formed by abstracting F atoms from the CF_3 groups, and thereafter the $\cdot C\text{-}F_2$ radicals that are formed may be mostly used for grafting, resulting in the homo-polymerization of the styrene monomers.

Meanwhile, without the existence of the styrene monomer, the sharp peak at 982 cm^{-1} (C-F stretching vibration of the CF_3 group) does not change regardless of the irradiated dosage, as shown in Fig. 5. This means that, even though the F atoms in the CF_3 group

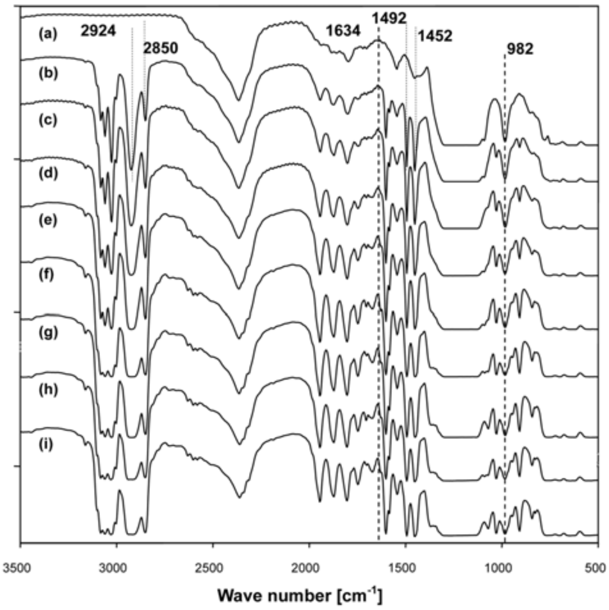

Fig. 4. Changing of FT-IR spectra in FEP films grafted at several dosages ((a): virgin film; (b)-(i): grafted FEP film with grafting degrees of 7.7%, 12.5%, 19.5%, 32.1%, 44.3%, 47.8%, 53.8% and 58.7%, respectively).

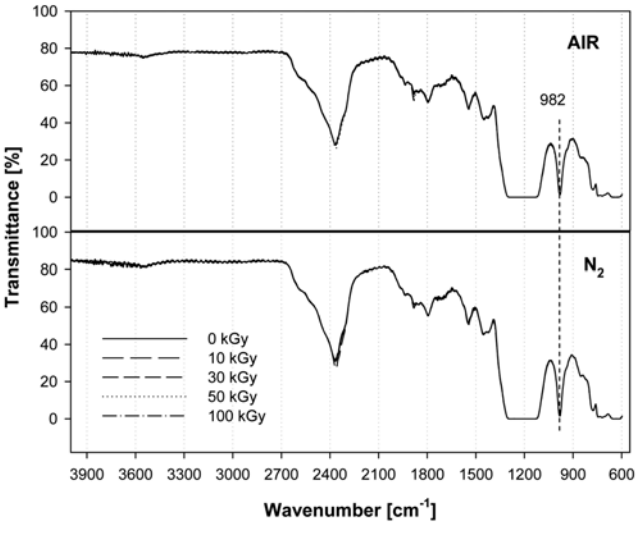

Fig. 5. FT-IR spectra of the virgin FEP films after being irradiated in air and N_2.

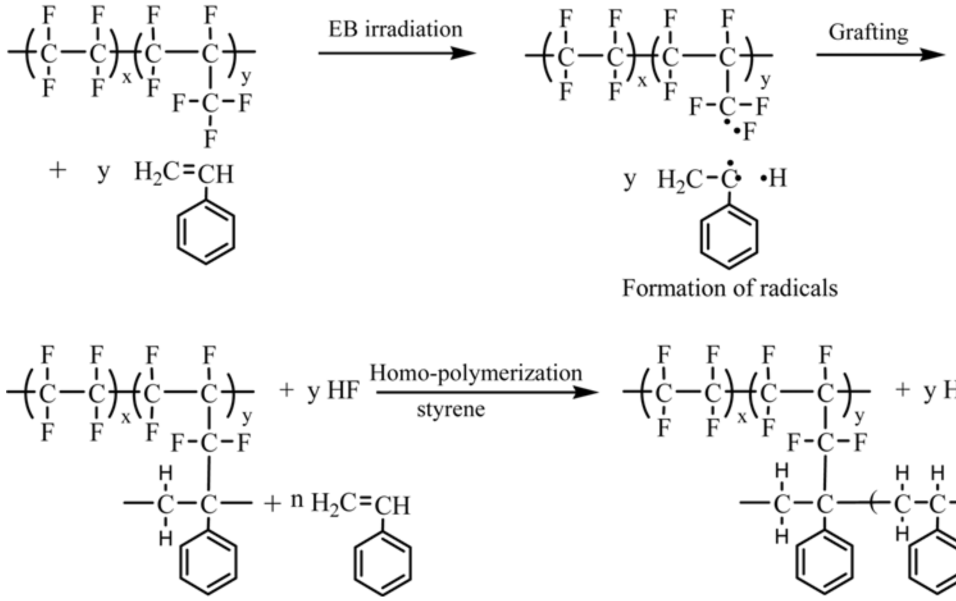

Fig. 6. Schematic mechanism during grafting of styrene onto FEP polymer.

can be abstracted by electron beam irradiation, the F radicals formed cannot be consumed, since there is no monomer available for grafting. In the presence of the styrene molecules, the H radicals abstracted from the aliphatic group (CH_2=CH-) in styrene combine with the F radicals abstracted from the CF_3 group, probably forming hydrogen fluoride.

This study shows that the styrene molecules grafted on the FEP film are hardly removed by boiling in toluene for 48 hours, showing only 1.6% weight loss. This means that the styrene monomers grafted onto the FEP film can be homo-polymerized to a small extent even in the simultaneous irradiation process. This study also found that a pure styrene solution is able to be home-polymerized only by electron beam irradiation. However, the amount of polymerized styrene was less than 1 wt% at 50 °C after three hours, with the degree of polymerization increasing with increasing dosage and the average molecular weight negligibly varying around the average value of 30,000.

From the above considerations, the possible mechanism for the grafting of the styrene molecules onto the FEP polymeric chains is shown in Fig. 6. In the first stage, the electron beam irradiation on both the styrene and FEP film produces radicals, with $\cdot$C-F_2 radicals being formed by the abstraction of F atoms from the CF_3 groups and C radicals being formed by the abstraction of H atoms from the C-$\dot{C}$=H moiety in the aliphatic group of styrene; these two radicals eventually combine to graft onto the FEP polymeric chains with HF gas being produced from the abstracted H and F atoms. As mentioned above, in the first stage, the grafting process may be dominant and then homo-polymerization follows.

3. Sulfonation of Styrene-grafted FEP Film

In order to use it as a fuel cell membrane, the styrene-grafted FEP film should be sulfonated by chlorosulfonic acid to form SO_3H groups on the grafted styrene. As mentioned in another research paper [20], Fig. 7 shows that the degree of sulfonation is proportional to the degree of grafting.

The number of sulfonic acid groups attached to one molecule of styrene, which is referred to as the ‘R factor’, can be estimated from the degree of grafting (G) and the degree of sulfonation (S) by using the following equation:

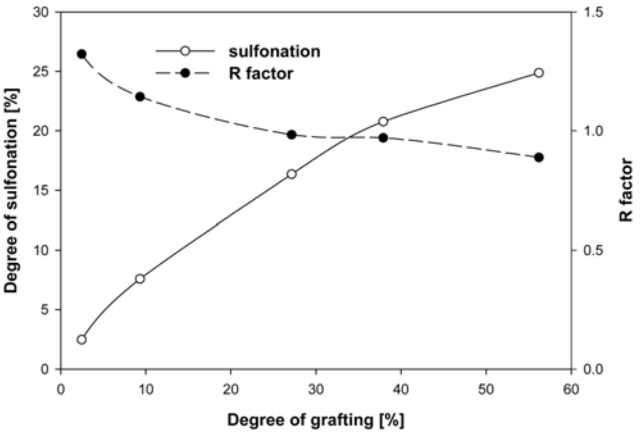

Fig. 7. Degree of sulfonation and R factor versus degree of grafting, where the grafting temperature and irradiated dose under simultaneous irradiation are 45 °C and 50 kGy, respectively.

$$R=\frac{104.06\cdot S(1+0.01G)}{81.0622\cdot G}$$

As shown in Fig. 7, the R values decrease with increasing degree of grafting, ranging from 1.32 at 2.5% grafting to 0.89 at 56.2% grafting, with a value of less than 1.0 being observed at around 25% grafting. This indicates that, at a low degree of grafting, more than one sulfonic acid group can attach to one styrene molecule; however, at a high degree of grafting all of the grafted styrene molecules may not be substituted by sulfonic acid groups, probably due to steric hindrance between the sulfonic acid groups attached to the highly-crowded styrene molecules [20]. At this point, it is believed

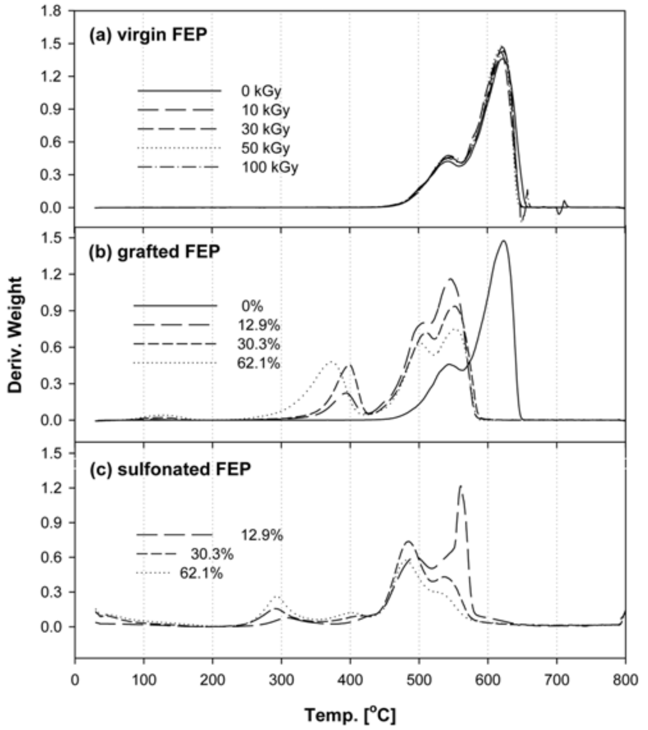

Fig. 8. TG-DTA spectra of the virgin FEP films irradiated (a), grafted (b), and sulfonated (c), where irradiated dose in (b) and (c) is 50 kGy.

that two sulfonic acid groups can attach to one benzene ring of styrene, for example, the ortho- and para-positions, at a low degree of grafting.

4. Thermal Properties of Grafted/Sulfonated FEP Film

As shown in Fig. 8(A), the TGA spectra of the irradiated virgin FEP film are almost the same, regardless of the irradiated dosage, indicating the complete decomposition of FEP at around 600 °C. This means that the FEP polymer has high radiation stability without undergoing any change of its structure, likely in the FT-IR spectra of the radiated virgin FEP film as shown in Fig. 5. On the other hand, as shown in other studies [8,20-22], the decomposition of the styrene-grafted FEP film (Fig. 8(B)) tends to shift to a lower temperature, and an additional decomposition peak appears at around 400 °C due to the decomposition of the grafted styrene. The lowering of the decomposition temperature related to the virgin FEP may arise from the irreversible change of its FEP, where an F atom is subtracted from the CF_3 group in FEP, eventually forming HF during grafting, as indicated by the FT-IR spectra. In the sulfonated FEP film (Fig. 8(C)), a large decrease of the size of the decomposition peak at around 400 °C was caused by decreasing the amount of the grafted styrene due to the sulfonation of the grafted styrene molecules. On the other hand, another decomposition peak appears largely at around 250 °C. It is estimated that the peak cannot arise from the removal of only the sulfonic acid groups as mentioned by other papers [20-22], because the size of the decomposition peak at around 400 °C could not be largely decreased if the sulfonic acid groups were removed from the grafted styrene molecules at 250 °C. Therefore, this indicates that styrene combined with the sulfonic acid group was separated from the FEP chain rather than the sulfonic acid group separating from styrene, probably due to the weakening of the chemical bonding between the styrene molecules and FEP chains through the sulfonation process.

This study shows that the grafting of styrene onto FEP chains can decrease the thermal stability of FEP, and that sulfonation cannot further change the thermal stability of FEP, but that it does have an effect on the thermal stability of the grafted styrene. Even though the thermal stability of the sulfonated FEP is much lower than that of the virgin FEP, the manufactured FEP membrane can be used because it is thermally stable at around 100 °C, which is the normal temperature for the operation of both proton exchange membranes (PEMs) and direct methanol fuel cells (DMFCs).

5. Methanol Crossover of FEP Membrane

The hydrophobic property of FEP can be changed to hydrophilic through the sulfonation of the styrene-grafted FEP film, thereby increasing its water-uptake [11,20]. The sulfonic acid group (SO_3H) in the sulfonated FEP film can be easily dissociated to SO_3^- and H^+ ions in aqueous solution. Such a sulfonated FEP film can be largely swelled in aqueous solution, resulting in methanol crossover through the membrane in a DMFC. Also, the methanol crossover can depend on such factors as the membrane thickness, methanol concentration, and operating temperature. Thinner membranes give rise to lower electrical resistances in the cell, but tend to have a higher methanol crossover. A higher concentration of methanol as well as a higher temperature in the cell increases the permeability of methanol through the membrane [23,24]. At the cathode, methanol causes a mixed potential due to the interference of methanol oxidation with the oxygen reduction reaction, resulting in a decrease in the cell performance [25].

Fig. 9 shows that the methanol crossover in the FEP membrane is much more highly suppressed than in Nafion 125 (film thickness of 125 μm). The methanol crossover in Nafion 125 starts after about one hour with 5 wt% methanol in water. On the other hand, even though the crossover in the FEP membranes is significantly dependent on the degree of grafting, the crossover in the FEP membranes with degrees of grafting of 52.6%, 29.4% and 19.2% starts after about 4, 18 and 22 hours, respectively. Since a higher degree

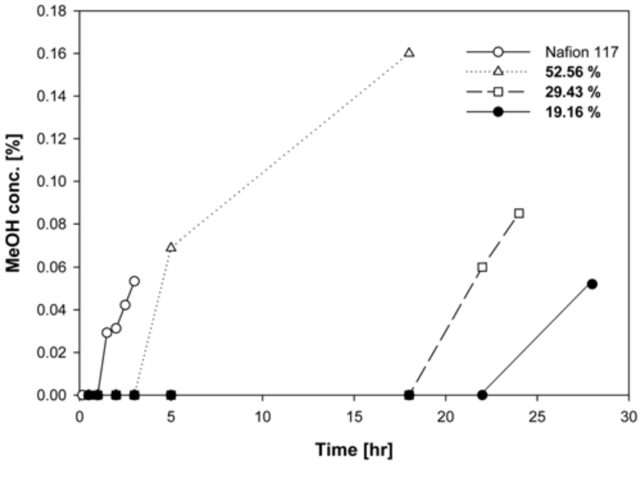

Fig. 9. Effects of the degree of grafting on the methanol crossover across the sulfonated FEP film, where initial concentration of MeOH is 5 wt%.

of grafting can give rise to a higher degree of sulfonation, those membranes with a higher degree of grafting are likely to swell more in aqueous solution. Actually, a low concentration of methanol can be preserved at the anode with the proper concentration of methanol, because the methanol is catalytically dissociated into CO_2 and H^+ ions at the anode in the case of a fuel cell electrode with a platinum catalyst, thereby limiting the methanol crossover.

6. Ion Exchange Capacity (IEC) and Proton Conductivity (IC)

Since the sulfonic acid group (SO_3H) attached to the styrene molecules is dissociated into SO_3^- and H^+ in aqueous solution, the IEC has a direct relation to the degree of sulfonation. Assuming that one styrene molecule grafted on the chains of FEP will affix one sulfonic acid group and that the number of moles of H^+ ions is equivalent to the number of moles of grafted styrene, which means that all of the grafted styrene molecules are sulfonated, the theoretical value of the IEC can be expressed as the number of moles of H^+ ions per dry weight of sulfonated FEP [26].

$$\text{IEC (mmol/g)} = \frac{9.62G}{100+1.77G}$$

Fig. 10 shows that the IEC value increases with increasing degree of grafting, since the degree of sulfonation increases with increasing degree of grafting, as shown in Fig. 7. All of the measured values of the IEC are lower than the theoretical ones, due to insufficient sulfonation. The IEC value of the commercialized Nafion 117 is 0.9 mmol/g, which is much lower than that of the FEP membrane manufactured in this study. The IEC of the FEP membrane with a degree of grafting of around 15% is equal to that of Nafion 117 and the FEP membrane with a degree of grafting of 66.8% exhibits a high IEC value of 2.55 mmol/g.

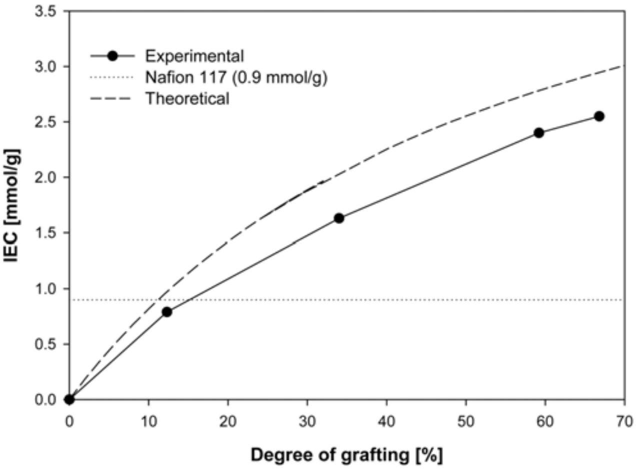

Fig. 10. Effect of grafting degree on the ion exchange capacity of the sulfonated FEP film.

Compared to the IEC, the ion conductivity (IC) is a more direct barometer to estimate the performance of FEP membranes in fuel cells, because the IC value is directly determined by the amount of protons transported through the membrane, whereas the IEC value is only related to the total amount of sulfonic groups existing in the bulk FEP film, regardless of their distribution across the membrane. The IC values may be dependent on the distribution of sulfonic groups across the FEP film, as will be considered in more detail later. This can be confirmed from the difference in the values of IEC and IC for two membranes with different thicknesses, 75 μm and 125 μm, as shown in Table 1. Their IEC values are likely to be dependent merely on the degree of grafting, regardless of the film thickness, whereas the IC values are strongly dependent on the film thickness as well as the degree of grafting. The thinner film tends to have a higher IC value when comparing two films with an equal degree of grafting. For example, the IC value of the film with a thickness of 75 μm and degree of grafting of 23.5% is 0.21 S/cm, whereas that with a thickness of 125 μm and degree of grafting of 34.0% is 0.18 S/cm, which is less than that of the former in spite of its higher degree of grafting. The IC values of films with a thickness of 75 μm at a degree of grafting of 56.1% and a thickness of 125 μm at a degree of grafting of 59.2% are 0.27 S/cm and 0.25 S/cm, respectively. In the case of the Nafion membranes with film thicknesses of 25 μm (111), 50 μm (112) and 125 μm (117) in Table 1, the IC values also decrease with increasing film thickness. One of the reasons why the IC is dependent on the film thickness is that the film resistance on the ion conductivity is proportional to the film thickness.

7. Sulfur Profile Across the Sulfonated FEP Film

The sulfur profiles in the sulfonic acid group across the sulfonated membrane may play an important role in the performance of the fuel cell. Some studies [11,14,27] show the sulfur profiles

Table 1. Degree of grafting, IC, and IEC for Nafion and FEP membranes

Samples	Thickness (μm)	Degree of grafting (%)	Monomer	IC (Scm^{-1})	IEC (mmol/g)
Nafion 111	25	-	-	0.27	-
Nafion 112	50	-	-	0.15	-
Nafion 117	125	-	-	0.12	0.9
FEP-1	75	23.5	Styrene	0.21	1.52
FEP-2	75	54.7	Styrene	0.25	2.30
FEP-3	75	55.1	Styrene	0.26	2.29
FEP-4	75	56.2	Styrene	0.27	2.40
FEP-5	75	58.1	Styrene	0.27	2.42
FEP-6	125	12.3	Styrene	0.15	0.79
FEP-7	125	34.0	Styrene	0.18	1.63
FEP-8	125	59.2	Styrene	0.25	2.40
FEP-9	125	66.8	Styrene	0.25	2.55

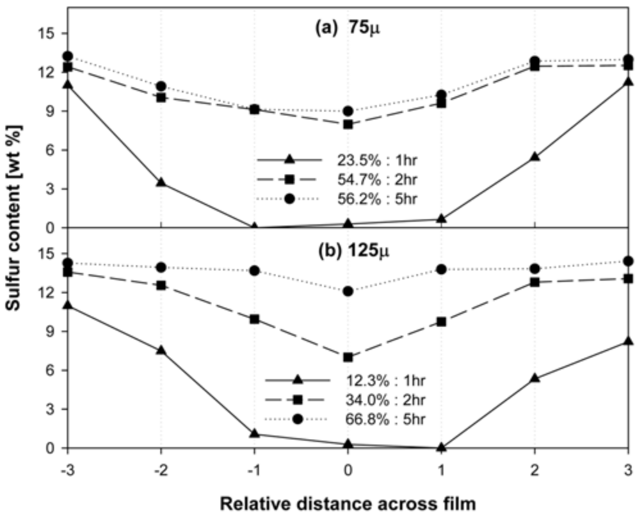

Fig. 11. Concentration gradient of sulfur (S) in the sulfonated FEP film at film thicknesses of 75 μm (a) and 125 μm (b).

across the sulfonated membranes; however, little attention has been devoted to the effect of the sulfur profiles on the IC values. The sulfur profile across the film was measured by energy dispersive X-ray analysis (EDS) with a scanning electron microscope. Fig. 11 indicates that the grafting is initiated at both surfaces of the film and then propagates toward the inside of the film. In the case of the FEP film with a thickness of 75 μm (Fig. 11a), the degree of grafting reaches 23.5%, 54.7%, and 56.2% after one hour, two hours, and five hours, respectively. The sulfur profile at a degree of grafting of 23.5% is concentrated around the surface and tends to penetrate toward the center of the film as the grafting time increases, leading to an almost homogeneous profile after two hours of grafting.

It took more time for the styrene grafted in the thicker film to propagate into the center of the film. After one hour of grafting, the 125 μm thick FEP film has a degree of grafting of only 12.3%, because small amounts of styrene are grafted over the entire film (Fig. 11b), showing a similar sulfur profile to the 75 μm thick FEP film with a degree of grafting of 23.5%. After two hours of grafting, the degree of grafting of the 125 μm thick FEP film reaches 34.0%, showing much lower grafting than the 75 μm thick FEP film (54.7%) at an equal grafting time. Both the 75 μm and 125 μm thick films are likely to reach their ultimate values of grafting within five hours.

A comparison of Fig. 11 and Table 1 indicates that the sulfur profile can have a more direct effect on the IC value than the degree of grafting, with a high IC value being observed in the case of a homogeneous distribution of sulfur inside the film. The dependence of the sulfur profiles across the film on the grafting time shows that the grafting of styrene onto the FEP chains begins at the surfaces of the film under electron beam irradiation, and subsequently the grafting is propagated step by step towards the inside of the film, with a long time being required to achieve a homogeneous profile of sulfur with a high concentration of sulfur at the center of the film. On the other hand, this study found that the styrene monomer is unable to penetrate into the FEP film even after seven days. This means that the grafting of styrene as well as the possible homo-polymerization of the styrene monomers are capable of swelling the polymeric structures inside the film, so that the styrene molecules can easily penetrate inside the film, allowing them to subsequently graft onto the polymeric chains of FEP.

From this study, it can be inferred that the simultaneous irradiation with an electron beam can generate sufficient radicals on both the styrene monomer and polymer chains, and this can initiate grafting at the surface of the FEP film and propagate grafting inside the FEP film under the continuous supply of radical type styrene monomers through the diffusion layer of swelled polymeric structures [12]. After the irradiation of the electron beam, the polymeric chains already contain many radicals, which may cause the radicals and electrons to be trapped in the polymeric chains for a long time, because the grafting procedure could last for several hours. Therefore, the styrene molecules that diffuse into the polymeric chains can be grafted with the trapped radicals.

CONCLUSIONS

We used the simultaneous irradiation method with an electron beam to manufacture PEM with a comparably high IC value for use in fuel cells, and the experimental results can be summarized as follows:

1. In the initial stage of grafting, the simultaneous irradiation of the electron beam could distribute uniform spots for grafting over the entire FEP film, whereas the preirradiation of the electron beam gave only locally distributed spots for grafting. In this way, the simultaneous irradiation method gave rise to a high degree of homogeneous grafting inside as well as at the surface of the film.
2. With simultaneous irradiation, the grafting of styrene onto the FEP film is likely to be initiated by abstracting F atoms from the CF_3 moieties in FEP and H atoms from the aliphatic groups in styrene, leading to the step by step propagation of the grafting inside the film through the swelled polymeric structures that allow the styrene molecules to penetrate easily, while suppressing the homopolymerization of styrene.
3. In contrast to other studies which usually suggested the attachment of one sulfonic group to a single styrene molecule, it was found that two sulfonic acid groups can attach to each styrene molecule.
4. The TGA analysis shows that the decomposition of the sulfonated FEP with simultaneous irradiation occurs in three temperature ranges corresponding to the degradation of FEP, the grafted styrene, and sulfonated styrene, respectively. On the other hand, in the case of electron beam radiation no change of the decomposition temperature was observed in the case of the virgin FEP.
5. The methanol crossover across the FEP membrane increased with increasing degree of grafting, due to the swelling of the polymeric structure in aqueous solution.
6. The IEC and IC values reach their ultimate values at a degree of grafting of around 50%; therefore, the FEP film with this degree of grafting is recommended for use in fuel cell membranes suppressing the methanol crossover problem.
7. A uniform profile of sulfur with a high degree of sulfonation around the center of the film is essential for manufacturing high performance fuel cell membranes with a high IC value.

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