

Synthesis of Poly((vinyl)oxy)ethanesulfonic acid)-Grafted ETFE Membrane via Radiation Grafting and Its Characterization

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ABSTRACT: We report the synthesis of a new fuel cell membrane, poly((vinyl)oxy)ethanesulfonic acid)-grafted poly(ethylene-co-tetrafluoroethylene) (ETFE) film by simultaneous radiation grafting of 2-chloroethyl vinyl ether onto ETFE film followed by sulfonation. The effects of various irradiation conditions such as the solvents, dose rate, and monomer concentration on the degree of grafting were investigated in detail. The sulfonation procedure of the grafted ETFE films used to replace the chlorine group with a sulfonic acid group includes the following steps. The first step is the formation of thiuronium salt with thiourea, the second step is the hydrolysis with NaOH to form thiol, and the final step is an oxidation of thiol using hydrogen peroxide to achieve the desired sulfonic acid group. Fourier transform infrared spectroscopy (FTIR),

x-ray photoelectron spectroscopy (XPS), and scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX) instruments were used to confirm the chemical reaction at every step of the process. In addition, the thermal degradation behaviors of the original ETFE film, grafted ETFE film, and sulfonated membrane were investigated by thermogravimetric analysis. To elucidate the possible applications of poly((vinyl)oxy)ethanesulfonic acid)-grafted ETFE membranes for direct methanol fuel cells, ion exchange capacity, water uptake, proton conductivity, and methanol permeability were investigated and compared with Nafion 212. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: fuel cell; sulfonation; IEC; MeOH crossover

INTRODUCTION

Fuel cells have been investigated as an alternative power source owing to their high-energy conversion efficiency and environmental friendliness. Among several types of fuel cells, such as Direct Methanol Fuel Cell (DMFC), Proton Exchange Membrane Fuel Cell (PEMFC), Solid Oxide Fuel Cell (SOFC), Molten Carbonate Fuel Cell (MCFC), and Alkaline Fuel Cell (AFC), the DMFC using the liquid methanol directly as fuel can provide advantages in terms of high hydrogen energy density and low operating temperature. These advantages of DMFC are quite suitable for portable power applications. Nafion[®] has been used as polymer electrolyte for DMFC; however, Nafion[®] is known to have disadvantages for DMFC application, as its high methanol uptake (MU) induces parasitic fuel loss (20%). Furthermore, the diffusion of methanol into the cathode can decrease the cell voltage.^{1–3} Therefore, it is necessary to develop

an alternative membrane that can overcome the problems associated with Nafion[®]. To enhance the cell performance, various methods have been introduced for preparing alternative membranes.

Among many methods, radiation graft polymerization is known to be an efficient and convenient method to prepare polymer electrolyte membranes from a commercial polymer film by grafting a new polymer chain with functionality for advantages such as (1) short grafting time, (2) unnecessary toxic radical initiator, (3) high penetration depth, (4) high grafting rate, and (5) convenient grafting conditions (low temperatures and low pressures). Also, the ion exchange capacity (IEC) of the membranes can be easily controlled by the proper selection of radiation grafting conditions such as irradiation doses, dose rates, and solvents.^{4–6} So far, various fluorinated polymers, either perfluorinated such as poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(tetrafluoroethylene-co-perfluoropropylvinyl ether), or partially fluorinated poly(ethylene-co-tetrafluoroethylene) (ETFE), and poly(vinylidene fluoride) have been utilized as grafting substrates owing to their excellent chemical and thermal stability. ETFE has been the most widely used partially fluorinated polymer owing to its higher radiation stability and superior mechanical properties compared to

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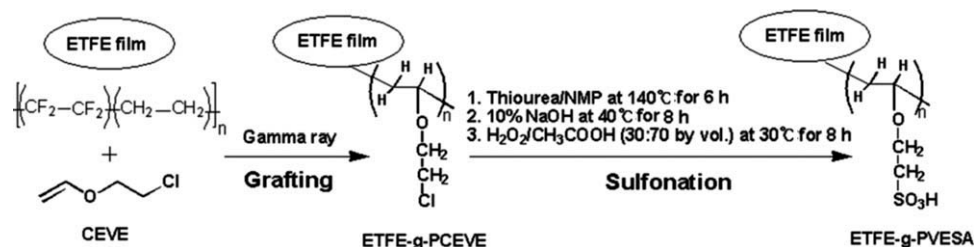


Figure 1 Chemical reaction scheme for the ETFE-g-PVESA membrane.

perfluorinated polymers, and it is also known to have better compatibility with the grafting components.^{7–10}

Vinyl-based monomers such as styrene, vinylbenzyl chloride (VBC), methacrylate, acrylate, and acrylonitrile have been mostly used during radiation grafting because radiation-induced grafting is known to occur as a radical polymerization mechanism.^{6,11–14} However, only a few examples of vinyl ether monomers have been used as radiation-induced grafting monomers, compared to the others mentioned above. Chen et al.¹⁵ reported the simultaneous radiation grafting of alkyl vinyl ether monomer onto a PTFE film and applied it to the preparation of a fuel cell membrane after treatment with chlorosulfonic acid. Abdel Aal et al.¹⁶ also reported on the radiation grafting of vinyl ether of monoethanolamine for the preparation of toxic metal absorbents.

In this article, we report the synthesis of a new polymer electrolyte membrane, poly((vinyl oxy)ethanesulfonic acid)-grafted ETFE membrane through the simultaneous radiation grafting of 2-chloroethyl vinyl ether (CEVE) onto ETFE film followed by a subsequent chemical conversion process for the introduction of a sulfonic acid group (Fig. 1). The CEVE is a relatively inexpensive monomer and has a vinyl ether double bond that can be involved in radiation grafting polymerization and the chloride leaving group where various functional groups can be introduced by substitution reaction. The effect of various irradiation conditions on the degree of grafting (DOG) of a CEVE monomer onto the ETFE films was studied and is reported herein. The physico-chemical properties of the prepared membrane for DMFC applications were measured and compared with those of Nafion 212.

EXPERIMENTAL

Materials

An ETFE film of 25 μm thickness was purchased from Asahi Glass, Japan. CEVE (Tokyo Chemical Industry, Japan) and thiourea (Acros Organics) were purchased and used as received. *N*-methyl-2-pyrrolidone (NMP) was purchased from Showa, Japan and used as received. All other chemicals including the

solvents are of reagent or higher grade and used without further purification.

Synthesis of poly((vinyl oxy)ethanesulfonic acid)-grafted ETFE membrane

CEVE-grafted ETFE film (ETFE-g-PCEVE)

ETFE-g-PCEVE was prepared through simultaneous radiation grafting of CEVE monomer onto an ETFE film. The ETFE film cut into 3 cm \times 4 cm was immersed in a vial containing a CEVE monomer and solvent. A series of mixture samples composed of the CEVE monomer and solvent were purged with nitrogen gas for 10 min to remove the oxygen, and then subjected to a γ -ray irradiation up to a total dose of 400 kGy at dose rates of 5 and 10 kGy/h for the grafting of VE monomers onto the ETFE films. After the designed absorbed dose, the films were washed with acetone for 24 h to remove the ungrafted homopolymer and residual monomers. After drying to a constant weight in a vacuum oven at 40°C, the DOG of the grafted films was calculated as follows

$$\text{DOG}(\%) = [(W_g - W_o)/W_o] \times 100$$

where W_g is the weight of the film after grafting and W_o is the weight of the film before grafting.

Poly((vinyl oxy)ethanesulfonic acid)-grafted ETFE membrane (ETFE-g-PVESA)

The prepared ETFE-g-PCEVE films were immersed in 0.13M thiourea NMP solution. The mixture was reacted at 140°C for 6 h to convert the chloride of the film to thiouranium salt. The prepared film was washed with NMP the first time, and then with ethanol several additional times. In the second step, the prepared poly((vinyl oxy)ethanethiouranium salt)-grafted ETFE (ETFE-g-PVETS) films were immersed in a 10% sodium hydroxide aqueous solution at 40°C for 8h. The film was washed three times with dilute hydrochloric acid and with distilled water until the pH of the washing solution was neutral. Finally, the prepared poly((vinyl oxy)ethanethiol)-grafted ETFE (ETFE-g-PVESH) films were added into a mixture of

30% hydrogen peroxide and acetic acid (volume ratio, 30/70). The mixture was then reacted at 30°C for 8 h. The prepared ETFE-*g*-PVESA membranes were washed several times with distilled water and then dried.

CHARACTERIZATION

¹H-NMR study for the radiolytic polymerization of CEVE

¹H-NMR spectroscopy (JEOL, 500 MHz) was used to study the radiolytic polymerization of the CEVE monomer. The CEVE monomer was exposed to γ -ray irradiation for 20 h at a dose rate of 10 kGy/h. A small portion of the irradiated sample was diluted with CDCl₃ for the ¹H-NMR analysis.

XPS measurements

XPS measurements (AXIS-NOVA, Kratos) were used to monitor the reaction progress by measuring the binding energies of four nuclides (Cl, S, O, and N) in the prepared membrane and the intermediates. During XPS measurement, a charge neutralizer was utilized to prevent electron charging.

Fourier transform infrared spectroscopy analysis

Fourier transform infrared spectroscopy (FTIR) measurements were carried out using FTIR spectrometer Tensor-37 (Bruker, Germany) at transmittance mode, within the range of 400–4000 cm⁻¹.

SEM-EDX measurements

SEM-EDX measurements were carried out to investigate the relative distribution patterns of the graft polymers on the cross section of the prepared films. The prepared films were broken into liquid nitrogen and then coated with osmium for SEM-EDX analysis. The SEM-EDX operating conditions were set as follows: accelerating voltage with 10 kV, spot size of 4, and a working distance of 12.3 mm.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) studies of ETFE base film, grafted ETFE film (ETFE-*g*-PCEVE), and sulfonated graft polymer membrane (ETFE-*g*-PVESA) were carried out using a TA instrument (SDT Q600, Canada) in the range of 40–650°C at a rate of 10°C min⁻¹ under a dry nitrogen atmosphere.

IEC and degree of sulfonation

The IEC of the sulfonated graft polymer membranes (ETFE-*g*-PVESA) was measured using an acid-base

titration method. The membranes were immersed into 1M NaCl solution for 12 h at room temperature. The protons released into the medium during ion exchange process were titrated with 0.1M NaOH solution using an automatic titrator (DL22, Mettler Toledo, Greifensee, Switzerland). The IEC value was calculated using the following equation:

$$\text{IEC}(\text{meq/g}) = [0.1 \times V_{\text{NaOH}}]/W_{\text{dry}},$$

where V_{NaOH} and W_{dry} are the volume of 0.1M NaOH consumed and the dry weight of membranes, respectively. The degree of sulfonation (DOS) was defined as follows

$$\text{DOS}(\%) = (\text{IEC}_{\text{exp}}/\text{IEC}_{\text{theor}}) \times 100,$$

where $\text{IEC}_{\text{theor}}$ is the theoretical IEC calculated from the DOG and can be expressed by the following formula

$$\text{IEC}_{\text{theor}} = 1000 \text{DOG}/(100M_{\text{CEVE}} + \text{DOG} \times M_{\text{PVESA}})$$

where M_{CEVE} is the molar weight of the CEVE monomer, and M_{PVESA} is the molar weight of sulfonated CEVE monomer.

Proton conductivity

Proton conductivity of the ETFE-*g*-PVESA membranes was measured using AC impedance spectroscopy (SI 1260, Solartron, England) over a frequency range of 0.01–100 kHz. Each membrane sample was cut into sections of 4 cm × 1 cm. The membranes were hydrated in distilled water at room temperature overnight prior to the measurement. The membrane was clamped between two electrodes and measured in the horizontal direction at room temperature. The proton conductivity (σ , S/cm) was calculated using the following equation: $\sigma = L/(AR)$, where L is the distance between the two probes (cm), A is the cross-sectional area of the membrane (cm²), and R is the electrical resistance (Ω), respectively.

Water uptake (WU) and Methanol uptake (MU)

Water uptake (WU) and Methanol uptake (MU) of the ETFE-*g*-PVESA membranes (3 cm × 3 cm) were measured after soaking the samples in distilled water and methanol solution overnight at room temperature. The weights of the wet membranes (W_w) were measured after the removal of the external water on the membrane surface with a paper towel, and the weights of dry membranes (W_d) were measured after vacuum drying the samples. The WUs/MUs of the membranes were calculated using the

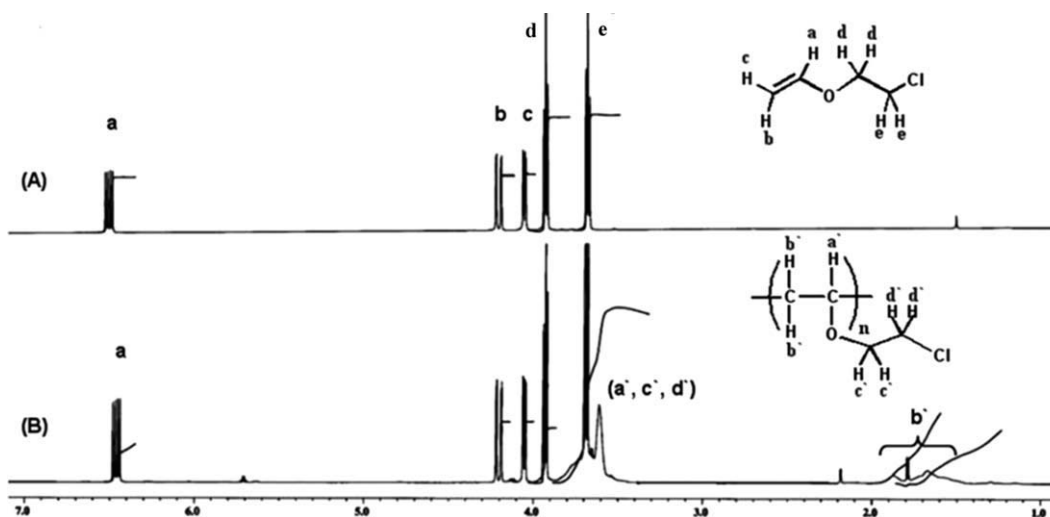


Figure 2 The ^1H -NMR spectra of pure CEVE (A) and the irradiated CEVE samples at a total dose of 200 kGy (B).

following equation: $\text{WU (or MU) (\%)} = [(W_w - W_d)/W_d] \times 100$.

Methanol permeability

Methanol permeability measurements were conducted at room temperature using a permeation cell composed of two chambers containing methanol solution in a solution chamber ($V = 120$ mL) and distilled water ($V = 120$ mL) in the other chamber, respectively. The amount of methanol that crossed through the membrane to the distilled water side was measured as a function of time. The concentration of methanol that passed through the membrane was analyzed using liquid chromatography equipped with Refractive Index (RI) detector, which was connected to water chamber. Detected refractive values were converted to RI signal data using the following equation

$$Y = 1.446 \times 10^{-6}X - 7.512 \times 10^{-4},$$

where X and Y are the RI signal data and concentration methanol (mol/kg), respectively. Finally, the methanol permeability (P , cm^2/s) was calculated as follows:

$$P = \frac{gV_B L}{C_A A},$$

where V_B , L , A , and C_A are the volume of water chamber (cm^3), the thickness of the membrane (cm), the size of the aperture (cm^2), and the methanol concentrations in methanol solution chamber (mol/kg), respectively. g (mol/kg s) is the slope that the increase of velocity of methanol concentration in the water chamber as a function of time, and is given as $C_B/(t - t_0)$, where C_B is the methanol concentrations

in distilled water chamber (mol/kg), t and t_0 are the experimental time (s) and the starting moment of the experimental time (s), respectively.

RESULTS AND DISCUSSION

CEVE-grafted ETFE film

Radiation-induced graft polymerization is a more efficient method for the enhancement of the antecedent properties of polymer substrate and is of particular interest for achieving specifically desired physicochemical properties.^{17,18} To explore the possibility of using a radiation grafting monomer under simultaneous irradiation conditions, a sample of the CEVE monomer was irradiated at a total dose of 200 kGy with a dose rate of 10 kGy/h.⁶ Small amounts of the CEVE sample before and after irradiation were diluted with CDCl_3 prior to the ^1H -NMR analysis. The ^1H -NMR spectra show that the radiation-induced polymerization was found to take place in the CEVE sample. The ^1H -NMR spectra of the pure CEVE and irradiated CEVE samples are shown in Figure 2. As shown in Figure 2(A), the two triplets at 3.71 and 3.94 ppm correspond to two methylene protons (H^d and H^e) and the two doublets at 4.07 and 4.24 ppm correspond to terminal hydrogens (H^b and H^c) on the double bond. The multiplet (doublet of doublet) observed at 6.47 ppm can be assigned for proton (H^a) on the double bond adjacent to ether oxygen. New broad peaks at around 1.7, 1.9, and 3.7–3.9 shown in Figure 2(B) can be assigned for the protons ($\text{H}^{b'}$ and $\text{H}^{a'}$, $\text{H}^{c'}$, $\text{H}^{d'}$) of the polymerized CEVE, respectively. The peak at 3.6 can be assigned to the protons ($\text{H}^{d'}$) adjacent to the chloride functional group of the polymer, indicating that the functional group is fairly stable at the given irradiation condition. These results indicate that the CEVE

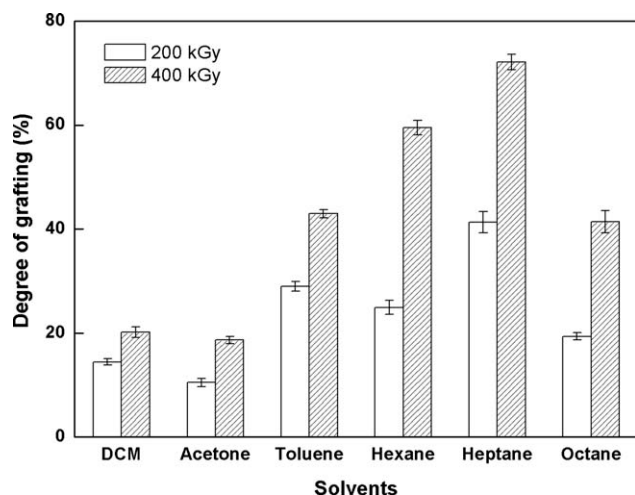


Figure 3 The DOG of the CEVE-grafted ETFE films prepared in various solvents: DCM, acetone, toluene, hexane, heptane, and octane. Each sample containing an ETFE film and CEVE/solvent (1 : 1 v/v) mixture was irradiated at total doses of 200 and 400 kGy with a dose rate of 10 kGy/h.

monomer could be applied to a simultaneous radiation grafting. The process for the synthesis of the polymer electrolyte membrane is shown in Figure 1 in which the first monomer is applied to the simultaneous radiation grafting onto the ETFE film using the γ rays from the ^{60}Co source and then sulfonated to achieve the desired sulfonic acid group.

Grafting solvent is known to affect the DOG and the property of the film. It is often used to enhance the graft yield or to minimize the use of an expensive monomer. Therefore, selecting the proper grafting solvent during radiation grafting is very crucial in obtaining the desirable grafted film. To find a suitable solvent that can lead to high grafting efficiency with less homopolymer formation during the grafting of CEVE monomer onto an ETFE film, several solvents including aliphatic, aromatic, and halogenated hydrocarbon solvents were used as the grafting solvent. The ETFE film was immersed in mixtures containing CEVE at a solvent ratio of 1 : 1 (v/v), and then irradiated at total doses of 200 and 400 kGy with a dose rate of 10 kGy/h. The DOG of the samples irradiated in various solvents is calculated and shown in Figure 3. Interestingly, among the solvents used, a higher grafting efficiency was observed from the aliphatic hydrocarbon solvents such as hexane, heptane, and octane. We found that similar results were also observed in the previous literature when ethyl vinyl ether monomer was grafted onto the polyethylene film using simultaneous radiation grafting.¹⁹ In the case of the simultaneous radiation grafting of styrene and VBC onto a fluorinated film, halogenated solvents such as dichloromethane and chloroform are known to be

more efficient than aliphatic hydrocarbon solvent.^{6,20,21} Heptane showed the highest grafting efficiency among the aliphatic hydrocarbon solvents applied, suggesting that heptane is a suitable solvent for the simultaneous radiation grafting of CEVE onto an ETFE film.

Figure 4(A) shows the variations of the DOG with an irradiation dose at various CEVE concentrations (30, 50, 70, and 100% in heptanes) during a simultaneous irradiation grafting of CEVE onto ETFE films. The CEVE grafting solutions containing the ETFE film were irradiated at total doses of 100, 200, and 400 kGy with a dose rate of 10 kGy/h. As shown in the Figure 4(A), the DOG increases as the CEVE monomer concentration increases. This behavior can be explained easily by considering that as the monomer concentration increases, the monomer availability to the grafting sites also increases, and this leads to a higher DOG. To investigate the effects of the dose rate on a simultaneous irradiation grafting of CEVE, the grafting samples containing an ETFE film

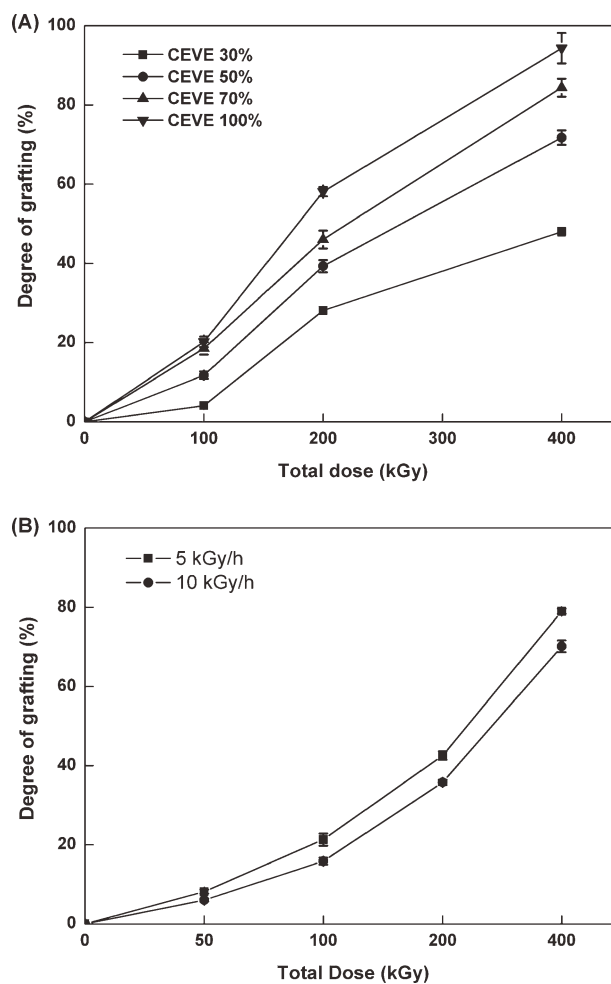


Figure 4 (A) The DOG vs. total dose at different CEVE concentrations (dose rate, 10 kGy/h). (B) The DOG vs. the total dose at different dose rates [CEVE: heptane 50: 50 (v/v)].

and a mixture of CEVE and heptanes (volume ratio, 50 : 50) were irradiated at dose rates of 5 and 10 kGy/h. As shown in Figure 4(B), the DOG had no significant differences with an increasing dose rate when the same irradiation dose was employed. This result can be considered to have arisen from the relatively lower reactivity of CEVE monomer toward radiation and therefore the amount of irradiation dose determines the overall graft rate regardless of the CEVE monomer diffusion rate in the inner side of the film.

Poly((vinyl)oxy)ethanesulfonic acid)-grafted ETFE membrane

The grafted film was sulfonated to prepare a new poly(vinyl ether)-grafted polymer electrolyte membrane as shown in Figure 1, in which the chlorine group of ETFE-g-PCEVE is replaced with a sulfonic acid group using three steps. Already, a similar methodology for the conversion of the chloride group of FEP-g-PVBC film into the sulfonic acid group was reported by our group.²² The prepared ETFE-g-PCEVE film was reacted with thiourea in an NMP solution at 140°C for 6 h to give the desired ETFE-g-PVETS film with thiouranium salt. Geng et al. showed that the thiouranium salt can be obtained with thiourea in ethanol at 40°C. However, for the ETFE-g-PCEVE, no reaction was observed in the film according to FTIR measurements at the same reaction conditions. The reason for the failure might be owing to the low reactivity of the alkyl chloride of PCEVE as compared to the benzyl chloride of PVBC. To find the optimum reaction conditions, different solvents such as NMP, DMF, acetone, and THF, along with various reaction temperatures have been attempted. In all the reaction conditions, a noticeable reaction progress was observed in case of NMP at high temperature (140°C). The prepared ETFE-g-PVETS film was then subjected to hydrolysis by immersing it in an aqueous solution of sodium hydroxide at 40°C. In the final step, the oxidation of thiol was performed using a 30% hydrogen peroxide/acetic acid solution at 30°C to obtain the ETFE-g-PVESA membranes with a desired sulfonic acid group. The color of the membrane became brownish during the sulfonation reaction.¹⁵

The reaction progress for the desired membrane can be easily monitored by FTIR spectroscopy [Fig. 5(A–C)]. The spectrum of original ETFE base film shows strong absorption bands in the range of 1000–1400 cm^{-1} owing to the presence of CF_2 groups, and stretching vibration bands at 2870 and 2969 cm^{-1} owing to the presence of CH_2 groups. Also, the spectra of ETFE-g-PCEVE film showed all bands assignable to the ETFE base film and grafted PCEVE (around 2900 cm^{-1} related to C–H stretching vibra-

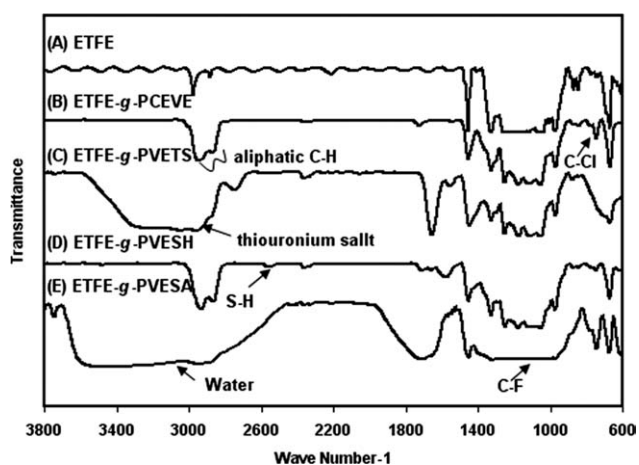


Figure 5 FTIR spectra of (A) ETFE, (B) ETFE-g-PCEVE, (C) ETFE-g-PVETS, (D) ETFE-g-PVESH, and (E) ETFE-g-PVESA.

tion and 742 cm^{-1} for C–Cl stretching vibration). After reaction with thiourea, a new absorption band resulting from the formation of thiouranium salt (1643 cm^{-1} for C=N stretching and a very broad band around 3200 cm^{-1} for N–H stretching and O–H stretching from water present as an impurity) appeared, whereas a characteristic C–Cl band of ETFE-g-PCEVE disappeared as shown in Figure 5(C). In the spectrum of the ETFE-g-PVESH sample [Fig. 5(D)], the characteristic absorption bands of thiouranium salt completely disappeared, and a very similar spectral pattern to that of ETFE-g-PCEVE [Fig. 5(B)], except an absorption band at 2543 cm^{-1} (S–H stretching vibration), was observed. Finally, the successful conversion into the desired ETFE-g-PVESA film was confirmed by the formation of a broad absorption band at 3100–3600 cm^{-1} for O–H stretching from sulfonic acid and the remaining water in the membranes.

Figure 6 shows the binding energies of four nuclides (Cl, S, O, and N) in the prepared membrane and the intermediates measured by X-ray photoelectron spectroscopy. Figure 6 also shows the reaction progress of the samples for each chemical transformation step. XPS data for ETFE-g-PCEVE film shows the binding energy peaks for Cl 2p at 199 eV and O 1s at 530 eV, indicating the successful grafting of CEVE monomer onto ETFE film. In the ETFE-g-PVETS film, peaks for S 2p, Cl 2p, and N 1s were observed at 161, 196, and 397.5 eV, respectively, owing to the formation of thiouranium salts. In this case, peak for Cl 2p is shifted to low energy as a result of a formation of Cl^- ion. In the ETFE-g-PVESH film, peaks for Cl and N 1s disappeared, whereas S 2p orbits are remained. In the final step, peak for S 2p is shifted to lower binding energy with increasing the intensity of O 1s peak, indicating successful preparation of the desired ETFE-g-PVESA membranes.

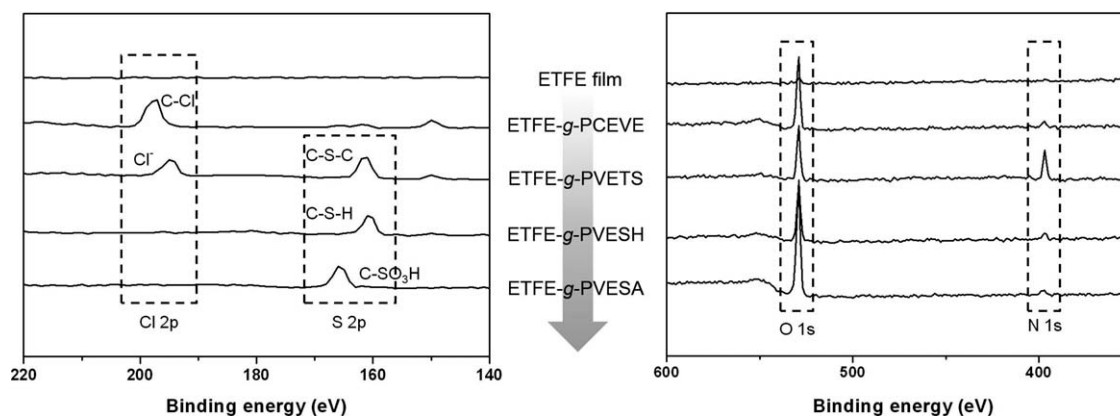


Figure 6 XPS spectra of ETFE, ETFE-g-PCEVE, ETFE-g-PVETS, ETFE-g-PVESH, and ETFE-g-PVESA.

The reaction progress of each chemical step from original ETFE film to sulfonated ETFE-g-PVESA can also be confirmed by SEM images and EDX profiles of the characteristic atom as shown in Figure 7. Figure 7(A) shows the element distribution profile over the cross section of the original ETFE film. The ETFE-g-PCEVE film [Fig. 7(B)], showing an even chlorine atom distribution profile over the cross section of the grafted film, was employed to prepare the desired ETFE-g-PVESA membrane in this study. The nearly identical distribution profiles of the chlorine and sulfur atoms are shown in Figure 7(C), and this result indicates an effective conversion process to the desired ETFE-g-PVETS through the inner por-

tion of the film. Furthermore, the reduction of chlorine atoms to a very low level (possibly noise level), as shown in Figure 7(D), also indicates that the thio-uranium chloride salt in the grafted film was effectively converted to the desired ETFE-g-PVESH through the inner portion of the film. Finally, as shown in Figure 7(E), the distribution profile of oxygen atom with sulfur atom supports the successful formation of the sulfonic acid group in the grafted film. SEM images of original ETFE film to sulfonated ETFE-g-PVESA do not show any significant morphological change.

The thermal stabilities of the ETFE membranes were determined by TGA (Fig. 8). The original ETFE

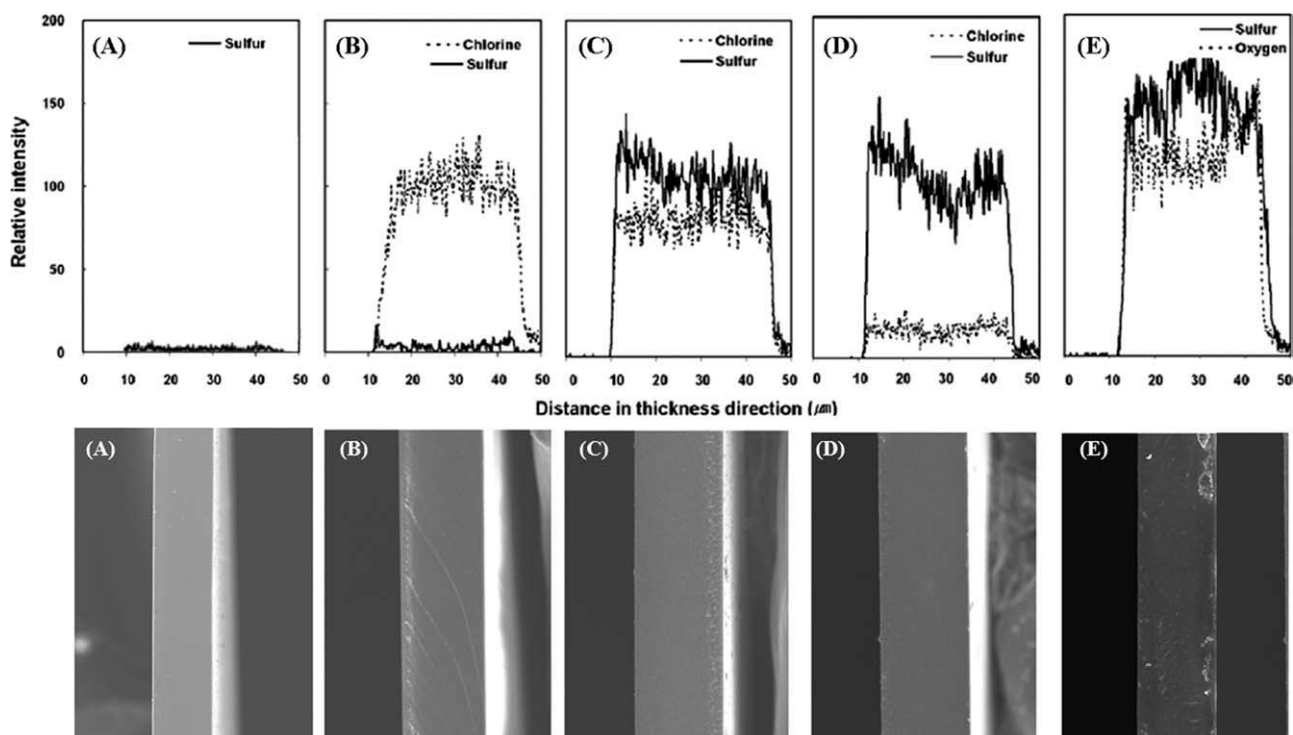


Figure 7 SEM image and element distribution profiles of (A) original ETFE film, (B) ETFE-g-PCEVE, (C) ETFE-g-PVETS, (D) ETFE-g-PVESH, and (E) ETFE-g-PVESA.

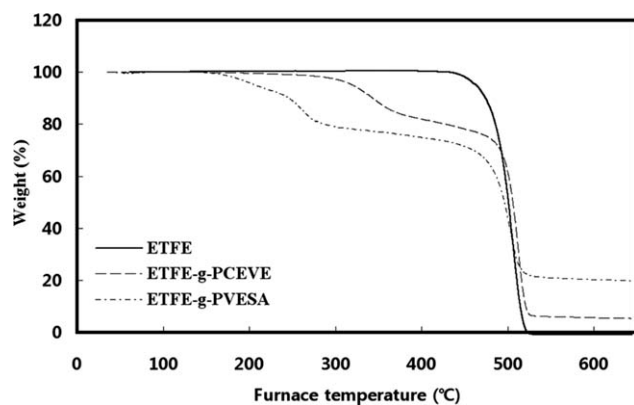


Figure 8 TGA curve for original ETFE (A), grafted ETFE-g-PCEVE (B), and sulfonated ETFE-g-PVESA (C).

film has only one sharp weight loss at 490°C, which can be ascribed to the decomposition of the main polymer chain. For the grafted ETFE, there are two decomposition steps. The first one is attributed to the grafted PCEVE graft polymer, the decomposition of which begins at 310°C, and the second is the ETFE backbone polymer chain decomposition. The sulfonated membrane exhibits three different steps of thermal degradation: (1) in the first degradation step, the weight loss starts below 150°C and is related with the desorption of water from the membrane; (2) the second degradation step occurs between 245 and 335°C and is related with the sulfonic acid group and CEVE grafted decomposition simultaneously; and (3) the last thermal degradation that starts between 450 and 545°C is assigned to the degradation of the main polymer chain. The initial degradation temperature for the PCEVE graft polymer of the grafted film is 310°C, but for the polymer matrix in the sulfonated membrane it is speculated that the graft chain degradation of grafted polymer occurs early. The reason for early degradation could be considered owing to the sulfonic acid group that can facilitate the thermal degradation of the graft chain.

IEC, proton conductivity, and WU

The theoretical and experimental IEC values of the obtained polymer electrolyte membrane, as a function of the DOG, are listed in Table I. The IEC values of the prepared membranes with 48 and 71% DOG were observed at 1.48 meq/g with 72% DOS and 2.28 meq/g with 81% DOS, respectively. These observed

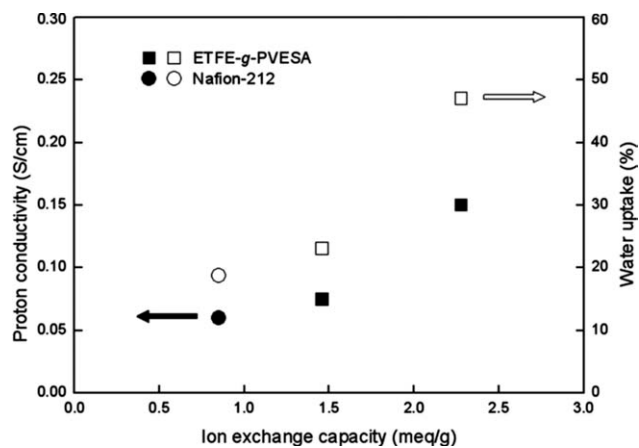


Figure 9 The proton conductivity and WU of the prepared ETFE-g-PVESA membranes as a function of the IEC compared with Nafion 212.

high IEC values can be attributed to the efficient chemical conversion of the chloride of the graft into the sulfonic acid group. The IEC increased with the increase in DOG and this tendency is owing to an increased number of ionic sites in a membrane available for sulfonation with an increase in the DOG. Therefore, the IEC of the prepared membranes could be controlled with a desired ionic content by controlling the DOG. This value far exceeds that of Nafion 212 membrane, which is equal to 0.85 meq/g.

IEC has also a direct relationship with the proton conductivity and WU. Generally, the higher IEC of a membrane results in a higher WU, and consequently higher proton conductivity. Figure 9 shows the proton conductivity and WU of the membranes as a function of IEC. It can be seen that both the WU and the proton conductivity increased with an increase in IEC, indicating that more hydrophilic sulfonic acid groups were incorporated in the membrane with a higher IEC and led to higher WU and proton conductivity. In this study, the WUs of the membranes with 48 and 71% DOGs were measured to be 23 and 47%, respectively, whereas the Nafion 212 membrane was at 18% under the same experimental conditions, and they also have higher proton conductivity than a Nafion 212 membrane.

Methanol permeability

Nafion[®] membranes have been widely used as polymer electrolyte membranes in fuel cell application

TABLE I
Preparation Conditions for the ETFE-g-PVESA Membranes

Sample name	Total dose (kGy)	Monomer conc. (%)	DOG (%)	IEC _{theor} (meq/g)	IEC _{exp} (meq/g)	DOS (%)
Nafion 212	—	—	—	—	0.85	—
ETFE-g-PVESA	400	50	48	2.05	1.48	72
ETFE-g-PVESA	400	70	71	2.28	2.28	81

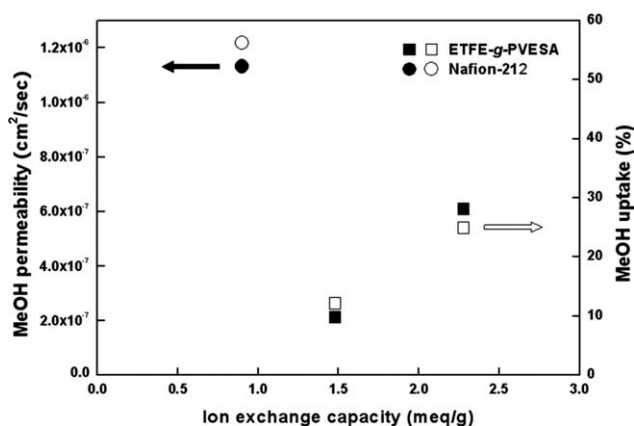


Figure 10 The methanol permeability and MU of the prepared ETFE-g-PVESA membranes as a function of the IEC compared with Nafion 212.

owing to its thermal, chemical, and oxidative stable properties, but a high methanol crossover has been a major issue for a Nafion[®] membrane in DMFC applications. Figure 10 shows the relationship of the methanol permeability and MUs of the prepared membranes as a function of IEC, and the methanol permeability and MU of the prepared membranes increased with increasing IEC values. The results of MU were well in conformity with the methanol permeability results. Figure 10 also shows that the methanol permeability of the prepared membranes is comparatively lower than the Nafion 212 membrane, and the prepared membranes even have higher IEC, WU, and proton conductivity. The lower methanol permeability of the prepared membranes is attributed to the hydrocarbon-based graft chain because hydrocarbon polymer has a lower MU than fluorinated polymer.

CONCLUSIONS

In this study, a CEVE monomer with a reactive chloride functional group was successfully grafted onto the ETFE film using a simultaneous radiation grafting method. Heptane was found to be the most preferable diluent for the grafting. The ETFE-g-PCEVE film was successfully sulfonated using thiourea to form thiuronium salt, hydrolysis for the formation of thiol, and oxidation with hydrogen peroxide. FTIR, XPS, TGA, and EDX were utilized to characterize the desired membranes and intermediates. The physiochemical properties of the prepared

membranes for DMFC application including IEC, WU, MU, proton conductivity, and methanol permeability were also studied. The proton conductivity and WU were increased with an increase in the IEC. Membranes with an IEC of 1.48 and 2.28 meq/g showed high proton conductivities (0.75 and 0.15 S/cm, respectively) and remarkably decreased methanol permeability than that of the Nafion 212 membranes. Therefore, ETFE-g-PVESA can be expected to be a promising material for DMFC applications.

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References

- Kuver, A.; Vogel, L.; Vielstich, W. *J Power Sources* 1994, 52, 77.
- Cruikshank, J.; Scott, K. *J Power Sources* 1998, 70, 40.
- Kuver, A.; Vielstich, W. *J Power Sources* 1998, 74, 211.
- Lyons, B. J. *Radiat Chem* 1995, 45, 159.
- Nasaf, M. M.; Saidi, H.; Dessouki, A. M. *Polym Int* 2000, 49, 399.
- Shin, J.; Geng, F.; Kang, S. A.; Ko, B. S.; Kang, P. H.; Nho, Y. C. *J Appl Polym Sci* 2009, 113, 2858.
- Gubler, L.; Prost, N.; Gürsel, S. A.; Scherer, G. G. *Solid State Ionics* 2005, 176, 2849.
- Brack, H. P.; Bührer, H. G.; Bonorand, L.; Scherer, G. G. *J Mater Chem* 2000, 10, 1795.
- Chapiro, A. *Radiation Chemistry of Polymeric Systems*, Wiley-Interscience: New York, 1962.
- Geng, F.; Sohn, J. Y.; Lee, Y. S.; Nho, Y. C.; Shin, J. *Polymer (Korea)* 2010, 34, 464.
- Dargaville, T. R.; George, G. A.; Hill, D. J. T.; Whittaker, A. K. *Prog Polym Sci* 2003, 28, 1355.
- Hegazy, E. A.; Ishigaki, I.; Rabie, A.-G. M.; Dessouki, A. M.; Okamoto, J. *J Appl Polym Sci* 1981, 263, 871.
- Taher, N. H.; Hegazy, E. A.; Dessouki, A. M. *Radiat Phys Chem* 1989, 33, 129.
- Jeun, J. P.; Hua, Z. J.; Kang, P. H.; Nho, Y. C. *J Appl Polym Sci* 2010, 115, 222.
- Chen, J.; Asano, M.; Yamaki, T.; Yoshida, M. *J Membr Sci* 2005, 256, 38.
- Abdel Aal, A.; Khutoryanskiy, V. V.; Nurkeeva, Z. S.; Mun, G. A. *J Mater Chem* 2002, 12, 2692.
- Safran, A.; Omishi, H.; Okamoto, J. *Radiat Phys Chem* 1986, 27, 447.
- Bhattacharya, A.; Mishra, B. N. *Prog Polym Sci* 2004, 29, 767.
- Kabanov, V. Ya.; Kubota, H.; Stannett, V. *ibid* 1979, A13, 807.
- Park, K. R.; Kang, P. H.; Nho, Y. C. *React Funct Polym* 2005, 65, 47.
- Nasef, M. M. *Polym Int* 2001, 50, 338.
- Geng, F.; Shin, J.; Kang, S. A.; Ko, B. S.; Kang, P. H.; Lee, Y. S.; Nho, Y. C. *J Polym Sci Part A: Polym Chem* 2010, 48, 563.