Study on PEFC Membrane Based on Crosslinked FEP Using EB-Grafting

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Summary: Polymer electrolyte fuel cell (PEFC) membranes based on crosslinked tetrafluoroethylene-co-hexafluoropropylene (FEP) have been fabricated by pre-irradiation grafting method. The chemical structures of crosslinked materials have been analyzed by Differential Scanning Calorimeter (DSC) and ^{19}F solid-state Nuclear Magnetic Resonance (NMR) spectroscopy. The radical yields of irradiated samples were measued by Electron Spin Resonance (ESR), and the mechanism of grafting reaction has been discussed. The styrene grafted materials were sulfonated by chlorosulfonic acid. The ion exchange capacity of the obtained sulfonated crosslinked FEP (S-FEP-X) showed 2.0 to 2.4 meq/g, which were 2.2 to 2.7 times higher than that of Nafion®112. Glass transition temperatures (T_g) of S-FEP-X were almost independent on crosslinking dose of FEP, and show about 96 °C, which are slightly higher than that of Nafion®. The electrochemical properties of the membranes have been measured, and cell performances of them have been evaluated. Ionic conductivities (ICs) of S-FEP-X are 1.2 to 1.6 times higher than that of Nafion®. The higher network densities gave the higher open circuit voltage (OCV). The power density of S-FEP-600kGy was about 10% higher than that of Nafion® at 500mA/cm^2. Thus, the obtained sulfonated membranes can be expected to apply for high efficiency PEFC.

Keywords: crosslinking; electron beam irradiation; polymer electrolyte fuel cell; proton exchange membrane; radiation grafting

Introduction

Fuel cell (FC) is in focus as a very low exhaust new dynamo system. Especially polymer electrolyte fuel cells (PEFC) with proton exchange membranes (PEM) have attracted much attention for the electrical vehicle and other mobile applications such as cellular phone, personal computer.[1,2] Conventional perfluoro-sulfonic acid (PFSA) membranes such as Nafion® (DuPont de Nemours LTD.) have been the famous PEM used for PFEC. However there are still several problems such as insufficient gas barrier properties, mechanical properties, low thermal durability, and their high costs. Polytetrafluoroethylene (PTFE) is one of the most famous fluorinated polymeric materials in the industrial fields due to its outstanding properties. However, it had been once considered to be impossible to apply for based-materials of radiation-grafting due to main chain scission by ionizing radiation.[3]

Recently, it has been demonstrated that PTFE can be crosslinked by irradiation in its molten state around 340 °C under an oxygen-free atmosphere.[4-10] The crosslinked PTFE (RX-PTFE) shows remarkable improvements in radiation and thermal durability and mechanical properties, compared with those of non-crosslinked one.[4-7] The most outstanding advantage of RX-PTFE is its network structure. The

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formation of network structure of PTFE prevents the gas transmission.[10] Moreover, when the RX-PTFE was irradiated by ionizing radiation, the yields of trapped radicals in RX-PTFE is much higher because of dissociative electron attachment at the crosslinking sites.[11]

Our research group has studied partial-fluorinated sulfonic acid membranes (part-FSA) for PEFC by radiation-grafting onto RX-PTFE with reactive styrene monomers.[12,13] Although the obtained sulfonated membranes have showed the high performance for PEFC, it was thought that mechanical property of base material would be still inadequate. Sherer *et al.* have studied part-FSA membranes based on non-crosslinked tetrafluoroethylene-co-hexafluoropropylene (FEP) for PEFC.[14,15] However, it was thought that durability would be unsatisfied because of poor gas permeation and high swelling.

In this study, in order to produce the high performance PEFC using the part-FSA membranes, PEFC membranes based on crosslinked FEP films with high toughness have been fabricated by pre-irradiation grafting method. The chemical structures of crosslinked materials have been analyzed by Differential Scanning Calorimeter (DSC) and ^{19}F solid-state Nuclear Magnetic Resonance Spectroscopy (NMR). The radical yields of irradiated samples were measured by Electron Spin Resonance spectroscopy (ESR), and the mechanism of grafting reaction has been discussed. The electrochemical properties of the membranes have been measured, and cell performances of them have been evaluated.

Experimental Part

Preparation of the RX-FEP Membranes

The FEP films (Teflon®FEP, FLON INDUSTRY, Thickness: 25 μm) were put in an irradiation vessel with a heating device. It was heated up to 280 °C in nitrogen gas atmosphere, and the temperature during irradiation was kept at $280 \pm 5\,^{\circ}$C. The materials were irradiated up to 600 kGy with a dose rate of 15 kGy/pass (acceleration voltage: 200 kV, current: 1 mA, pass speed: 2 m/min) by the electron beam accelerator (NHV Co., CURETRON®).[16]

Grafting and Sulfonation

Radiation crosslinked FEP (RX-FEP) membranes were irradiated up to 15kGy under nitrogen gas atmosphere at room temperature by electron beam (EB). RX-FEP membranes were grafted by styrene in liquid phase at 80 °C.[17] The grafting yields (GY) were determined as the weight increase of the samples according to the following equation;

$$\mathrm{GY}(\%) = 100 \times (\mathrm{W_g} - \mathrm{W_0})/\mathrm{W_0}$$

Where, W_g and W_0 are the weight of the samples after and before grafting, respectively.

The grafted RX-FEP membranes were sulfonated by chlorosulfonic acid in carbon tetrachloride (1:100, vol.) at room temperature for 24 hours. The sulfonated crosslinked FEP membranes (S-FEP-X) were washed by deionized water for several times.

Measurements

Melting temperatures and heat of melting for irradiated samples were measured by DSC (Perkin Elmer Co.: PYRIS Diamond DSC) under nitrogen atmosphere with the heating and cooling rate of 20 °C/min. Glass transition temperatures (T_g) of S-FEP-X were measured by DSC. The heating rate was 10 °C/min.

The chemical structures of irradiated samples were analyzed by ^{19}F solid-state magic angle spinning NMR (Bruker AV600 wide-bore spectrometer, proton frequency: 600 MHz) spectroscopy with the MAS rates of 25 and 32 kHz, respectively.

Obtained samples were irradiated under vacuum at room temperature. After irradiation, the radical yields of the samples were measured by X-band ESR (JEOL Co. JES-TE200).

The ion exchange capacities (IEC) of the PEMs were determined by acid-base titration method with 716 DMS Titrino automatic titrator. (Metrohm herisau Co., Ltd.).

The water uptake of the PEMs was determined by the difference between the wet and the dry mass of the membranes.

MEA Fabrication and Single Cell Testing

The membranes were laminated with the Pt/C electrodes (Pt:1.0 mg/cm^2) to form a membrane electrode assemblies (MEA) in a hot press (8 MPa, 110 °C, 3 min). The MEA was assembled into standard fuel cell with an active area of 1 cm^2. Fuel cell tests were performed with humidified H_2 and dry O_2 supplied under 0.2 MPa at room temperature, and both gas flow rates were fixed at 50 ml/min.

The fuel cell was controlled by a electrochemical analysis system (Hokuto Denko Co.). Under different fuel cell test conditions, the MEAs were firstly activated by running under different current density continuously until the cell voltage were constant. Thus, the polarization curves were obtained. The open circuit voltage (OCV) of the MEAs under different test conditions was taken at the beginning of the polarization curve measurement. The electrochemical impedance spectroscopy (EIS) was measured by the four-electrode frequency response analyzer method, and was taken at DC current density of 500 mA/cm^2 with an AC frequency ranging from 100 kHz to 0.1 Hz.

Results and Discussion

Figure 1 shows the DSC melting thermograms of irradiated FEP at 280 °C in nitrogen gas atmosphere. For non-irradiated FEP (FEP-Blank), the peak temperature with endothermic reaction observed at around 267 °C, which is melting point of FEP. With increasing crosslinking dose of FEP, the peak shifts to a lower temperature, *i.e.* the crystal size becomes smaller with increasing crosslinking dose.[5] In addition, the peak area which is related with crystallinity is decreasing with increasing crosslinking dose. Therefore, crystallinity is decreasing with increasing crosslinking dose, *i.e.* materials become amorphous.

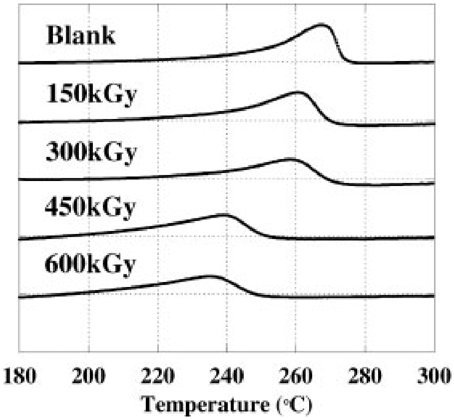

Figure 1.
DSC thermo-grams of RX-FEP (Crosslinking dose: 0 ~ 600 kGy).

Figure 2 shows the ^{19}F solid-state NMR spectra of RX-FEP and FEP-Blank. For FEP-Blank, an intense peak at −124 ppm and side peaks at −114 and −128 ppm were observed, and have been already assigned.[8,18] The peaks at −124 ppm and −114 ppm were assigned to the fluorine signals of internal $–C\underline{F_2}–$ and $–C\underline{F_2}–CF(CF_3)–C\underline{F_2}–$, respectively. The signal at −128 ppm corresponds to $–C\underline{F_2}–CF_3$, and the peak intensity of FEP-600 kGy showed higher intensity than that of FEP-Blank. In case of FEP-600 kGy, the new peaks appeared at −85, −87,−110 ppm, respectively. The signals at −85 and −87 ppm were assigned to the fluorine signal of molecular chain end CF_3 (end-CF_3 crystal and amorphous, respectively) including chain end of perfluoroalkylvinylethr.[18] The signal at −110 ppm corresponds to $–C\underline{F_2}–CF(–R_f–)_n$ $–C\underline{F_2}–$, which are network structures in the polymer matrix.[18] The peak at around −188 ppm became broader. It is indicating that the new signal of tertially carbon due to crosslinking site would be appeared.[18] These results are indicating that network formation has been taken place by EB irradiation under nitrogen gas atmosphere at melting temperature.

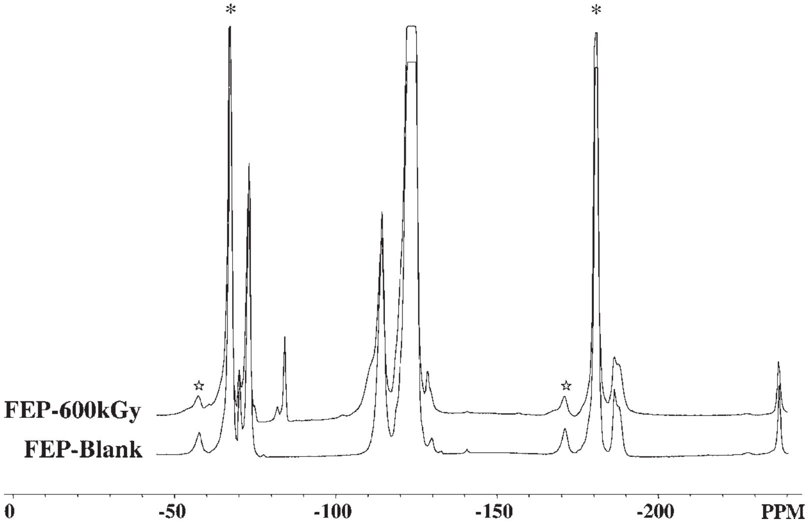

Figure 2.
^{19}F solid-state NMR spectra of RX-FEP (MAS: 32 kHz, Crosslinking dose: 0, 600 kGy).

Figure 3 shows the grafting yields as a function of reaction periods for styrene grafting onto RX-FEP with various crosslinking dose. For all RX-FEP with various network density, the grafting yields showed initial rapid increase, and then tended to saturate above 3.5 hours.

Figure 4 shows the relationship between crosslinking dose, grafting yields with the reaction period of 5 hours, and radical yields. The samples with higher crosslinking dose give the higher grafting yields, and radical yields. For FEP-600 kGy, the grafting yields were about 20% higher than that of FEP-Blank. These behaviors could be explained by the yields of trapped radicals in crosslinked matrix. That is, the higher network densities give the higher number of trapped free radicals in crosslinked system.[17,19,20,21]

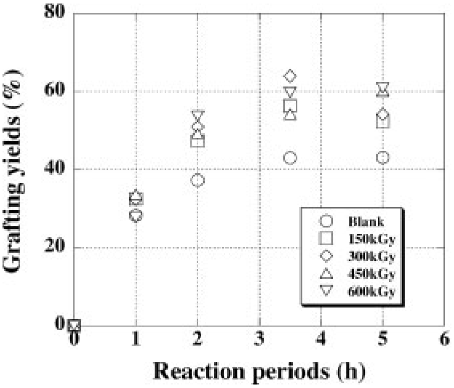

Figure 3.
Grafting yields as a function of reaction periods (Reaction temperature: 80 °C).

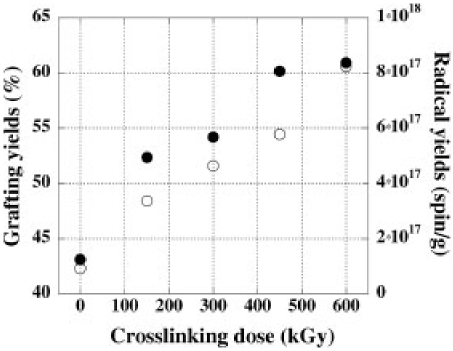

Figure 4.
The relationship between crosslinking dose, grafting yields, and radicals yields. (Grafting yields:●, Radical yields:○) ESR measurement condition; Absorbed dose:13.9 kGy, Temperature: 25 °C, Modulation Width: 0.2 mT, Fr: 9.43 GHz, Center magnetic field: 335 mT, Grafting reaction condition; Absorbed dose:15 kGy, Reaction periods:5h, Reaction temperature:80 °C.

Table 1.
Membrane properties of S-FEP-X and Nafion®112.

PEM	Thickness (μm)*	Water Uptake/mass-%	Grafting yields/mass-%	Ion exchange capacity (meq/g)
S-FEP-Blank	43	61	39	2.0
S-FEP-150kGy	51	68	47	2.2
S-FEP-600kGy	47	60	54	2.4
Nafion®112	58	17	–	0.9

*wet.

Grafted membranes with the reaction periods of 2 hours were sulfonated by chlorosulfonic acid solution. Table 1 shows the membrane properties of S-FEP-X and Nafion®112. IEC of S-FEP-X has been achieved 2.0 to 2.4 meq/g, which is 2.2 to 2.7 times higher than that of Nafion®. Water uptake of S-FEP-X is 2.4 to 3.0 times higher than that of Nafion®. The water uptake of S-FEP-150 kGy is 7% higher than that of S-FEP-Blank. The higher grafting yields result in the higher concentration of the sulfonic acid groups in the membranes, and S-FEP-150 kGy has higher hydrophilicity. On the contrary, the water uptake of S-FEP-600 kGy is 8% lower than that of S-FEP-150 kGy. It is thought that permeation of water would be prevented by higher network densities.

T_g of S-FEP-X showed about 96 °C, which were almost independent on crosslinking dose. On the other hand, T_g of Nafion®112 showed about 92 °C. T_g of the obtained membranes showed slightly higher than that of Nafion®.

MEAs were fabricated by the obtained membrane and Pt/C electrodes, and assembled into fuel cell. Figure 5 shows the EIS curves of the MEAs of S-FEP-X and Nafion®112 under room temperature operation. The impedance spectra are quantified using model parameters from an equivalent circuit such as Nyquist presentation.[22,23] Figure 5(B) shows the enlarged view of Figure 5(A). The ohmic resistances (R_{ohm}) of S-FEP-X are lower than that of Nafion® and decreasing with increasing of crosslinking dose. The R_{ohm} is given by the ionic resistance of the membrane. The ionic resistances of the membranes are decreasing with increasing of crosslinking dose.

Table 2 shows the electrochemical properties of the S-FEP-X and Nafion®112. The ionic conductivity (IC) was calculated by dividing the thickness of the PEMs by the R_{ohm}. IC of S-FEP-Blank was almost same as that of Nafion®, though IEC of S-FEP is 2.2 times higher than that of Nafion®. It was thought that the ionic

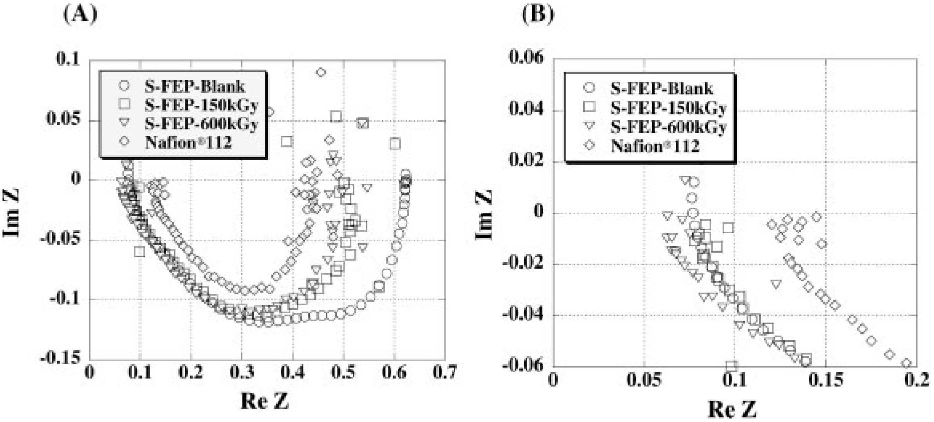

Figure 5.
The EIS of the MEAs at room temperature. (Fig. B is the enlarged view of Fig. A).

Table 2.
Electrochemical properties of S-FEP-X and Nafion®112 at room temperature.

PEM	Thickness*	R_{ohm}	R_{ct}	Ionic conductivity
	(μm)	(mΩ)	(Ω)	(mS/cm)
S-FEP-Blank	43	77	0.56	56
S-FEP-150kGy	51	72	0.46	71
S-FEP-600kGy	47	63	0.43	75
Nafion®112	58	122	0.31	48

*wet.

conductive channel of part-FSA could be different from that of Nafion®. That is, ion exchange site of part-FSA should be the grafted side chain. On the other hand, in case of Nafion®, ion exchange site should be the end of branched chain. For S-FEP-150 kGy, and -600 kGy, ICs were increased with increasing of IEC, and were about 1.2 to 1.6 times higher than that of Nafion® at room temperature.

Figure 6 shows the polarization curves of the MEAs for S-FEP-150 kGy and Nafion®112 in the operation at room temperature. The OCV, power density at 500 mA/cm^2, maximum power density are listed in Table 3. Increasing of crosslinking dose improved the OCV values. The higher crosslinking dose gives the higher network densities, which would prevent fuel gases from crossover. In addition, power density at 500 mA/cm^2 and maximum power density are increasing with increasing of crosslinking dose. The power density of S-FEP-600 kGy at 500 mA/cm^2 showed 296 mW/cm^2, which is about 10% higher than that of Nafion®. Thus, it is expected to apply for high efficiency PEFC using the obtained sulfonated membrane.

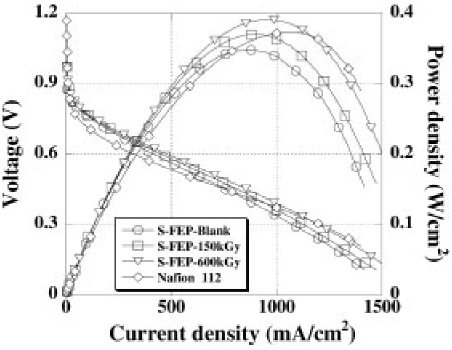

Figure 6.
The polarization curves of the MEAs at room temperature operation. (Gas flow rate [H_2/O_2]: 50 ml/min, H_2: wet, O_2:dry).

Conclusion

RX-FEP were grafted with styrene monomers using EB irradiation under nitrogen atmosphere at room temperature. For all RX-FEP membranes, the grafting yields showed the initial rapid increase, and then tend to saturate above 3.5 hours. The higher network density gives the higher grafting yields. These behaviors could be explained by the yields of trapped radicals in crosslinked matrix. The styrene grafted materials were sulfonated by chlorosulfonic acid, and membrane properties of them were evaluated by IEC, water uptake, and T_g. The IEC value of S-FEP-X achieved 2.2 to

Table 3.
MEA characterization of S-FEP-X and Nafion®112 at room temperature.

PEM	Thickness	Open Circuit Voltage	Power density @500 mA/cm^2	Maximum Power density
	(μm)	(mV)	(mW/cm^2)	(mW/cm^2)
S-FEP-Blank	43	887	280	348
S-FEP-150 kGy	51	969	291	370
S-FEP-600 kGy	47	978	296	392
Nafion®112	58	1018	265	374

2.7 meq/g, which is more than two times higher than that of Nafion®112. T_g of S-FEP-X were almost independent on crosslinking dose of FEP, and showed about 96 °C, which were slightly higher than that of Nafion®.

MEAs were fabricated by the obtained membranes and Pt/C electrodes, and assembled into fuel cell with an active area of 1 cm^2. ICs of S-FEP-X were 1.2 to 1.6 times higher than that of Nafion®. The higher network densities give the higher OCV and power densities at 500 mA/cm^2. The power density of S-FEP-600 kGy at 500 mA/cm^2 was 10% higher than that of Nafion®. Thus, the obtained sulfonated membranes are expected to apply for high efficiency PEFC.

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