Development of new PEFC membrane by means of EB grafting

Masakazu WASHIO*, Fumihiro MUTO, Jingye LI, Takaharu MIURA and Akihiro OSHIMA

Advanced Research Institute for Science and Engineering, Waseda University

3-4-1, Okubo, Shinjuku-ku, Tokyo, 169-8555, JAPAN

*** E-mail: washiom@waseda.jp**

Abstract

Polymer electrolyte fuel cell (PEFC) membranes based on thin film of crosslinked perfluorinated polymer-alloys (RX-FA) have been fabricated by electron beam (EB) grafting with reactive styrene monomers using EB irradiation under nitrogen atmosphere at room temperature (RT). The characteristic properties of styrene-grafted materials (GRX-FA) and sulfonated materials (SRX-FA) have been measured by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and FT-IR spectroscopy, ion conductivity, and so on. The glass transition temperatures of SRX-FA was about 105°C±1°C, which is higher than Nafion®.

The ion exchange capacities of SRX-FA have been achieved about 3.3meq/g. The ion conductivity of obtained SRX-FA (grafting yield: 98%, IEC: 3.3meq/g) had showed 0.023S/cm at 20°C and 0.083 at 60°C with relative humidity (RH) of ~95%. The ion conductivity of the obtained SRX-FA was much higher than that of conventional PFSA.

Fabricated membrane electrode assemblies (MEAs) based on the obtained SRX-FA and SRX-FE have shown encouraging performance in the PEFC, compared with the conventional PFSA. The power density of obtained MEA based on the SRX-FA was about 340mW/cm^2 under 500mA/cm^2 at 60°C. On the other hand, the power density of MEA based on Nafion®112 was about 320mW/cm^2 at 60°C.

Keywords: PEFC, crosslinked perfluorinated polymer-alloys, MEA, EB-grafting, glass transition temperature, power density, OCV,

1. Introduction

Fuel cell is in focus as a very low exhaust dynamo system. Especially polymer electrolyte fuel cells (PEFC) using proton exchange membranes (PEM) have attracted much attention for the electrical vehicle and other mobile applications such as cellar phone, personal computer [1,2]. The conventional perfluoro-sulfonic acid membranes (PFSA) such as Nafion® (DuPont de Nemours LTD.) and Flemion® (Asahi Glass Co., LTD.) have been the popular PEM used in PEFC. However there are still several problems such as insufficient gas barrier properties, mechanical properties, low thermal resistance, and their high costs.

Our research group has studied the partially fluorinated PEM by electron beam (EB) grafting onto crosslinked polytetrafluoroethylemne (RX-PTFE) or fluorinated co-polymer films (FEP, PFA, ETFE) with reactive styrene monomers using pre-irradiation grafting method in gas and in liquid phase, respectively [3-7]. The fabricated PEM based on crossliked PTFE (SRX-PTFE) showed the high ion exchange capacity (IEC), reducing the crossover of fuels such as hydrogen gas, and improved thermal properties, compared with conventional PFSA. However, slufonated RX-PTFE showed the deterioration of mechanical properties and higher water uptake compared with conventional PFSA when those have the higher grafting yields [8].

Further, it was difficult to obtain the crosslinked FEP and crosslinked PFA with high network densities due to low viscosity at its molten state, and sample shape of obtained crosslinked FEP and crosslinked PFA were not kept initial shape [9].

In this study, we have fabricated thin crosslinked perfluorinated polymer-alloys by wire-bar coater and EB irradiation system. Thus, we have fabricated PEM by EB grafting of styrene onto crosslinked perfluorinated polymer-alloys by liquid phase reaction method and subsequent sulfonation. The characteristic properties of obtained materials have been discussed.

2. Experimental procedure

2.1 Materials

The materials used for the experiments were the aqueous dispersions of PTFE (FLUON® XAD911; Asahi Glass Fluoropolymers Co., LTD. average particle diameter: 0.25μm, concentration: 60wt%), and perfluoroalkylvinyleter (PFA: FR03; Sun Chemicals Co., LTD. average particle diameter: < 0.5μm, concentration: 30wt%), respectively.

The thin films obtained from per-fluorinated polymer-blend dispersion (PTFE and PTFE/PFA polymer-blend: FA) were fabricated by using wire-bar coater, as described in previous paper [8]. Blending ratio of FA is controlled by amount of PFA contents and is listed in Table 1.

Table 1. Blending ratio of PTFE/PFA blend polymers

PTFE/PFA blend polymer	FA
PTFE concentration	89 wt%
PFA concentration	11 wt%

The per-fluorinated polymer-blend thin film was crosslinked by EB (NHV Corp., CURETRON®, acceleration voltage: 200kV, current: 1mA, installed at RISE, Waseda University) irradiation at 335°C±3°C in nitrogen atmosphere, as described in previous paper [10]. The thicknesses of obtained crosslinked perfluorinated polymer-alloy (RX-FA) films were about 5~15μm. with smooth surface.

2.2 Grafting and Sulfonation

The RX-FA were irradiated up to 15kGy and 30kGy using EB in nitrogen atmosphere at 25°C. After irradiation, all trapped radicals were converting to peroxy radicals by exposing in air. Reactive styrene monomer has been graftedonto thin film of crosslinked perfluorinated polymer-alloys in liquid phase at 80°C under vacuum.

The yields of grafting was determined as the weight gain according to the following equation:

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

Where, W_g and W_0 are the weight of materials after and before grafting, respectively.
The styrene-grafted materials (GRX-FA) were sulfonated with a mixture of chlorosulfonic acid and carbontetrachloride (CCl_4) (1 : 99 volume %) at room temperature with a period of 24 hours.

2.3 Measurements

The chemical structures of before and after styrene grafting onto RX-FA and slufonated RX-FA (SRX-FA) were analyzed by fourier transform infrared spectroscopy (FT-IR: JEOL JES-6000) for the study of grafting and slufonating mechanism. The resolution of IR wavenumber was 4cm^{-1}. The glass transition temperature of SRX-FA was measured by DSC (Perkin Elmer: PYRIS Diamond DSC) under nitrogen atmosphere. The heating rate was 10°C /min. Ion exchange capacity (IEC) was determined by acid-base titration (Ion analysis: Metrohm: 716 DMS Titrino). From the volume of the acid (HCl solution) consumed in the titration, the IEC per unit mass (meq/ g) was calculated. Ion conductivity was determined by four point AC impedance method using electrochemical measurement system (HOKUTO DENKO Corp.: HZ-3000; Frequency: 100mHz~100KHz).

2.4 Fuel Cell properties

The obtained membrane was laminated with the electrodes (Electro Chem: EC-20-10-7) to form membrane electrode assemblies (MEAs) using press machine (Tester Industry Co.) at 110°C during 3min with presser of 0.8MPa. The platinum loading density was 1.0mg/cm^2. The MEA was assembled in to single cell unit with an effective area of 1.0cm^2, the fuel gases were flew into the serpentine flow filed. The cell was operated at various temperatures using H_2 humidified in bubblers and dry O_2. The gas pressure at the cell inlet was 0.2MPa, and the flow rates of both H_2 and O_2 were 50cc/min.

3. Results and discussion

3.1 Styrene grafting onto crosslinked perflurinated polymer-alloys

Reactive styrene monomer has been grafting onto the very thin film (thickness: 5~15µm) of FA polymer-alloys (RX-FA) in liquid phase by EB pre-irradiation method. Figure 1 shows the yields of grafting as a function of reaction periods for styrene grafting onto RX-FA with various crosslinking doses. The yields of grafting (Yg) showed the initial rapid increase, and then tended to saturate above 5–8hours. In addition, the higher network density gives the higher grafting yields at early reaction stage.

According to our electron spin resonance (ESR) spectroscopy, a major radical trapped in crosslinked perfluorinated polymer-alloys exposed in air by after EB irradiation at room temperature under nitrogen atmosphere has been assigned to tertiary type peroxy radical ($-\mathrm{CF_2}-\mathrm{C}R_f(\mathrm{OO}\cdot)-\mathrm{CF_2}-$) at network point due to dissociative electron attachment. Further, it has been found that the number of trapped radicals in crosslinked perfluorinated polymer-alloys is much larger than that in non-crosslinked one, and the decay of free radicals trapped in crosslinked one takes place mainly at the temperature range of α-relaxation (Tα: 100~130°C). As the results, it has been concluded that the grafting reaction would be taking place at tertiary radicals below the Tα of the crosslinked perfluorinated polymer- alloys.

These behaviors could be explained by the yields of trapped radicals in crosslinked matrix, hence, the higher network densities give the higher number of trapped free radicals in crosslinked system.

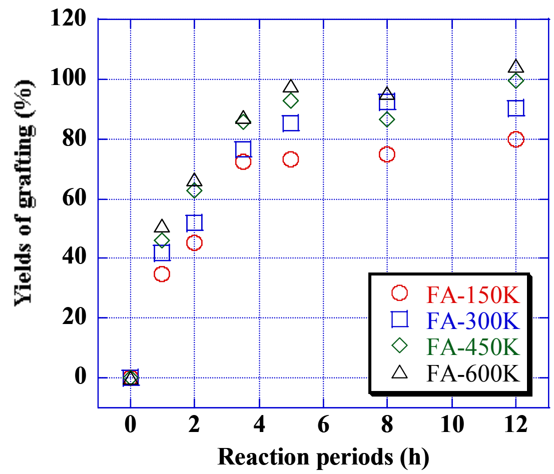

Figure 1 The yields of grafting as a function of reaction periods for styrene grafting onto crosslinked fluorinated-polymers (RX-FA) thin films with various crosslinking doses at reaction temperature of 80°C

Figure 2 shows FT-IR spectra of base materials (RX-FA), styrene grafted materials (GRX-FA) and slufonated materials (SRX-FA). For RX-FA, the bands due to $-CF_2-$ stretching vibrations observed at around 1100cm^{-1} ~ 1250cm^{-1}. These bands with high intensities have been observed for all spectra (grafted and slufonated materials). After styrene grafting onto RX-FA (GRX-FA), the presence of aromatic rings due to styrene grafting was confirmed by the =C-H stretching vibration at 3050cm^{-1} and the C-C in-plane stretching vibrations at 1500cm^{-1} and 1600cm^{-1}, respectively. C-H out of plane bending overtone and combination band patterns were in the region around 1660 ~ 2000 cm^{-1}. The absorption bands at 2800 ~ 2900 cm^{-1} and at 2900 ~ 3000 cm^{-1} were assigned to the symmetric and the asymmetric stretching of CH_2 group, respectively. The signal intensities of aromatic rings due to GRX-FA depend on the grafting yields. Thus, the higher grafting yields give the higher signal intensities of aromatic rings. For the IR spectra of SRX-FA, the absorption bands at 1165 ~ 1150 cm^{-1} and at 1350 ~ 1342 cm^{-1} were assigned to the symmetric and the asymmetric stretching of S = O with aromatic ring, respectively.

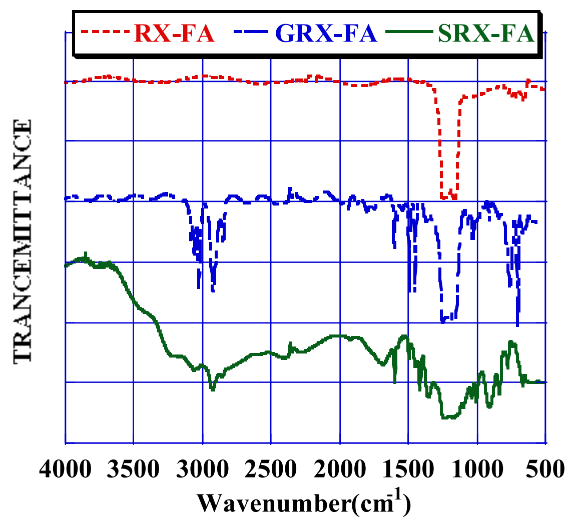

Figure 2 FT-IR spectra of base materials (RX-FA), styrene grafted materials (GRX-FA) and su l fonated materials (SRX-FA).

3.2 Properties of slufonated materials

Although the initial thickness of RX-FA are 7µm ~15µm, thickness comes about two times of initial materials after EB-grafting and sulfonation process. The thickness of obtained PEM was about 15µm ~30µm, which are half or less of Nafion®112 (52µm).

By DSC analysis, the glass transition temperature (Tg) of SRX-FA was hardly dependent on network densities and the grafting yields, and Tg for SRX-FA showed about 105°C±1°C. On the other hand, Tg of Nafion®112 and slufonated RX-PTFE (SRX-PTFE) was about 92°C and 102°C±2°C, respectively. Tg values for all obtained SRX-FA showed higher values than Nafion®112 and SRX-PTFE.

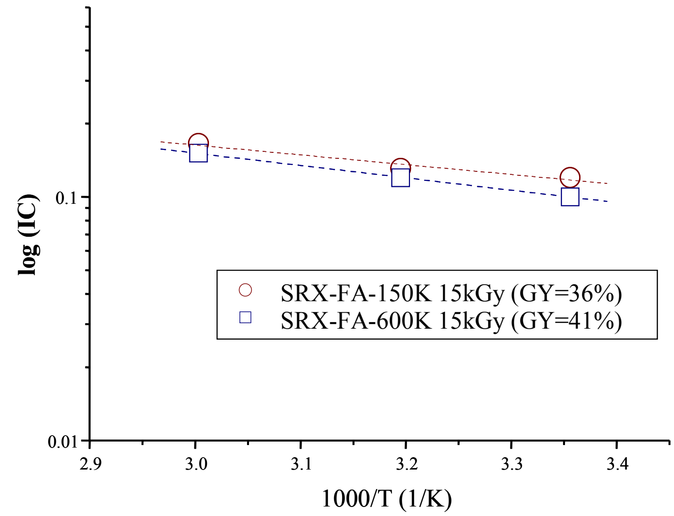

Figure 3 Arrhenius plot of ion conductivity (IC) of obtained sulfonated SRX-FA

The IEC value of sulfonated materials based on perfluorinated polymer-alloys have been achieved 3.3 meq/g. It means that the yields of subsequent sulfonation for all obtained sulfonated materials were closed to about 100% and obeyed the expected curve. The IEC values of obtained materials are about 3 times higher than the conventional PFSA. The ion conductivity (IC) of obtained SRX-FA has showed about 0.17S/cm at 60°C with relative humidity (RH) of ~95%, as shown in Figure 3. The IC of the obtained SRX-FA was higher than that of Nafion®112 in our experimental condition.

3.3 Fuel cell properties

Fabricated MEAs based on the obtained SRX-FA have shown encouraging performance in the PEFC, compared with Nafion®112. The SRX-FA membrane was laminated with the electrodes to form MEAs, and pressed with 0.8MPa at 110°C. The platinum loading density was 1.0mg/cm^2. The

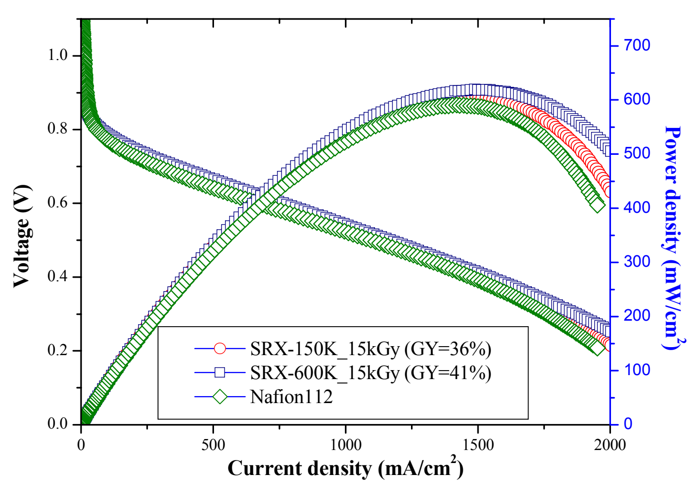

Figure 4 The polarization curves at 60 C for SRX-FA. Gas flow: H_2/O_2 50ml/min, Gas pressure: H_2/O_2 0.2MPa
Bubbler temperature: 60°C

MEA was assembled in single cell unit with an effective area of $1.0cm^2$, the fuel gases were flew into the serpentine flow filed.

Figure 4 shows the polarization curves at 60 °C for SRX-FA. The open circuit voltage (OCV) of obtained SRX-FA shows the 910~920mV. On the contrary, OCV of Nafion®112 showed 980mV at 60°C with R.H. ~95%. The OCV of our obtained SRX-FA was lower than that of Nafion®112. It would be due to the insufficient bonding between membrane and electrode for SRX-FA system, because Nafion® dispersion was used for the adhesive to form the MEAs.

The power density of obtained MEA based on the SRX-FA was about $330\sim340mW/cm^2$ under $500mA/cm^2$ at 60°C. On the other hand, the power density of MEA based on Nafion®112 was about $320mW/cm^2$ at 60°C. The power density of the obtained SRX-FA was higher than that of Nafion®112 in our experimental condition.

4. Conclusions

PEFC membranes based on crosslinked perfluorinated polymer-alloys (RX-FA) have been fabricated by EB-grafting with reactive styrene monomers using EB irradiation under nitrogen atmosphere at room temperature, and subsequent sulfonation. The glass transition temperatures of SRX-FA were hardly dependent on network densities and the grafting yields, and showed about 105°C±1°C, respectively. The IECs of SRX-FA have been achieved about 3.3meq/g. Fabricated MEAs based on the obtained SRX-FA have shown encouraging performance in the PEFC, compared with the Nafion®112. Although the OCV of obtained SRX-FA shows the 920mV, the power density of obtained MEA based on the SRX-FA shows about $340mW/cm^2$ at 60°C with a current density of $500mA/cm^2$.

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