Fabrication of the hybrid PEM consists of perfluoro-sulfonic acid and sulfonated PS-g-FEP using EB-grafting

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Abstract

The performance of polymer electrolyte fuel cell (PEFC) is affected by an interfacial property between proton exchange membrane (PEM) and electrodes. Thus, development of well-laminated membrane electrode assemblies (MEAs) has been carried out. The hybrid PEM consists of perfluoro-sulfonic acid (PFSA) ionomer and sulfonated polystyrene grafted tetrafluoroethylene-co-hexafluoropropylene (sulfonated PS-g-FEP) synthesized by soft electron beam (soft-EB) induced grafting method, was fabricated by mixing sulfonated PS-g-FEP with PFSA ionomer which is applied to coat the interface of the PEM and electrodes. The obtained hybrid PEM was characterized in terms of water uptake, ion exchange capacity, polarization performance and electrochemical impedance.

Keywords: Hybrid PEM, Soft-EB, EB-grafting, sulfonated PS-g-FEP, Power density

Introduction

Fuel cells (FCs) have been paid much attention as the efficient and green energy sources. The inherent advantages such as high efficiency and low CO_2 emissions have stimulated the development of FCs. 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 and so on [1,2]. The conventional perfluoro-sulfonic acid membranes (PFSA) such as Nafion[®] (DuPont de Nemours LTD.) and Flemion[®] (Asahi Glass Co., LTD.) have been often used for PEMs owing to their chemical stability in PEFC. However there are still several problems such as insufficient gas barrier properties, mechanical properties, low thermal resistance, and their high costs [3].

The radiation-induced grafting of styrene and its derivatives into fluorinated polymer membranes and successive sulfonation were designed as an alternative way to synthesize the PEM with low cost for the PEFC [4-18].

Our research group has studied the partially fluorinated sulfonic acid membrane (part-FSA) by soft

electron beam (soft-EB) grafting onto crosslinked polytetrafluoroethylene (RX-PTFE) or fluorinated co-polymer films (FEP, PFA, ETFE) with styrene monomers using pre-irradiation grafting method in gas and in liquid phase, respectively [7,11,13-18]. The fabricated PEM *e.g.* sulfonated polystyrene grafted crosslinked PTFE showed reducing the crossover of fuels such as hydrogen gas, and improved thermal properties, compared with conventional PFSA. Although ion exchange capacities (IEC) of obtained PEMs were 1.3 ~ 2.2 times higher than that of Nafion[®] 112, their cell performance were same or lower than Nafion[®] 112 [15-18].

The low cell performance should have been caused by a poor interface between the PEM and carbon electrodes with catalyst, because chemical reaction takes place between the catalysts and a PEM with hydrogen or oxygen [19]. Hence, the catalysts should show higher performance and efficiency to achieve high cell performance, by improving the interface between the PEM and the electrodes.

Two approaches have been considered to improve the performance of a membrane electrode assembly (MEA). One is to apply hot-pressing above glass transition temperature of the PEM, another is to use ionomer such as Nafion[®] dispersion which coated the interface between the PEM and electrodes [20]. However, when we use a PEM prepared by a radiation grafting method, the different chemical nature of the PEM and the ionomer on the catalyst layers should induce delamination between the PEM and electrodes [21].

In this study, PEMs were prepared by mixing part-FSA with Nafion[®] dispersion to get a well-laminated interface between the PEM and electrodes with holding high IEC. The resulting PEMs were characterized in terms of water uptake, IEC, polarization performance and electrochemical impedance.

Experimental procedure
Materials

Tetrafluoroethylene-co-hexafluoropropylene (FEP, FLON INDUSTRY CO., LTD.) with thickness of 25 μm was used for the experiments. FEP was irradiated by soft-EB with the absorbed dose of 15 kGy under nitrogen atmosphere at room temperature with the low energy electron accelerator, (CURETRON[®], NHV Corp. acceleration voltage: 200 kV, current: 1 mA, installed at RISE, Waseda University). After irradiation, almost all trapped radicals in FEP were converting to peroxy radicals by exposing in air. The irradiated samples were grafted with styrene in liquid phase at 80 °C under vacuum with a period of 2 hours.

The yields of grafting were 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 samples after and before grafting, respectively.

The grafted membranes were sulfonated with a mixture of chlorosulfonic acid in carbon tetrachloride (1 : 100 vol.%) at room temperature with a period of 24 hours. Subsequently, they were soaked in deionised water at room temperature and treated in 1M HCl for 24 hours to obtain acid form

membranes.

Obtained sulfonated styrene grafted FEP (sulfonated PS-g-FEP) was milled to powder with various mills ("mixer mill", Retsch, "Speed rotor mill", FRITSCH, "Planetary Potmill", ITOH Lab.). Then, sulfonated PS-g-FEP powder was dispersed in 5 wt% Nafion® dispersion (DuPont Co., Ltd.) and 1-propanol, which was used to decrease the viscosity of the solution and prevent the PEM from being cracked. The samples prepared by changing the amount of sulfonated PS-g-FEP with Nafion® dispersion were 10 wt% (FN10), 20 wt% (FN20) and 50 wt% (FN50), respectively. The hybrid polymer electrolyte membranes (FN) were obtained by drying the solution at 110 °C for 1hour. Nafion® 112 membrane was purchased from DuPont Co., Ltd. which was used as a reference.

Characterization

IEC of FN, sulfonated PS-g-FEP and Nafion® 112 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. The glass transition temperatures were measured by DSC (Perkin Elmer: PYRIS Diamond DSC) with a temperature scanning rate of 10 °C/min under nitrogen atmosphere.

Fabrication of MEA and the cell performance

Carbon electrodes with 1 mg/cm^2 platinum loaded (Pt/C electrodes) were purchased from Electro Chem, Inc. They were cut into 2 cm×2 cm, and coated with Nafion® dispersion 0.2 mg/cm^2 for the cathode and the anode, respectively. The modified Pt/C electrodes were subsequently dried at 80 °C for 1hour. The sulfonated PS-g-FEP mixed with Nafion® dispersion (FN), with an active area of 1 cm^2, were stored in deionized water for 1hour to improve the interface between the PEM and the electrodes [18, 22]. All the MEAs were prepared by hot-pressing at 110 °C under 8 MPa for 3 minutes.

Fuel cell operation test was performed with humidified H$_2$ and dry O$_2$ supplied under 0.2 MPa, and both gas flow rates were 50 cc/min, respectively. Characterization of the MEAs was carried out by polarization performance and electrochemical impedance spectroscopy (EIS; Hokuto Denko Co,. Ltd.). The EIS was measured by the four-electrode frequency response analyzer method, and was taken at dc current density of 500 mA/cm^2 with the ac frequency ranging from 100 kHz to 0.1 Hz. The ionic conductivity was calculated from the Ohmic resistance (R$_{ohm}$) and membranes thickness.

Results and discussion

Yields of grafting and IEC of sulfonated PS-g-FEP were 39 % and 2.0 meq/g, respectively. And also, the grass transition temperature of sulfonated PS-g-FEP and Nafion® were about 98 °C and 92 °C, respectively. The obtained sulfonated PS-g-FEP was milled to powder with various mills. The average diameter of obtained particles measured by scanning electron microscope was 22 μm ± 10 μm. The hybrid polymer electrolyte membrane (FN) was prepared by mixing the obtained sulfonated PS-g-FEP with Nafion® dispersion. The grass transition temperature of FN was about 102 °C determined by DSC. Table 1 shows the characteristic properties of the obtained hybrid membranes (FN10, FN20, FN50) and Nafion® 112.

IEC values of FN50, FN20, FN10, sulfonated PS-g-FEP, Nafion®-cast and Nafion® 112 were 1.2 meq/g, 1.1 meq/g, 1.0 meq/g, 2.0 meq/g, 0.9 meq/g and 0.9 meq/g, respectively. IEC of FN50 is about 1.3 times higher than that of Nafion®. IEC of FN10 was almost same as Nafion®. Water uptake of FN50, FN20, FN10, sulfonated PS-g-FEP, Nafion®-cast and Nafion® 112 was about 72 %, 56 %, 54 %, 29 %, 34 % and 16 %, respectively. FN revealed the higher water uptake than sulfonated PS-g-FEP and Nafion®. These results would be explained by the fabrication process of FN. As FN was fabricated by a casting method, the molecular chain of FN may be isolated without any physical or chemical interaction. Thus, the motion of molecular chain would have increased and it enabled FN to swell up and to obtain water easily.

Table 1 Characteristic properties of obtained the hybrid membrane

Membrane	Amount of sulfonated PS-g-FEP (wt%)	Thickness at wet state (μm)	IEC (meq/g)	Water uptake (%)	Ionic conductivity at 60 °C (S/cm)
FN50	50	58	1.2	72	0.12
FN20	20	74	1.1	56	0.12
FN10	10	78	1.0	54	0.16
sulfonated PS-g-FEP	100	49	2.0	29	0.07
Nafion®-cast	0	50	0.9	34	0.09
Nafion®112	0	53	0.9	16	0.07

The ionic conductivities at 60 °C with relative humidity (RH) of ~ 95 % for FN50, FN20, FN10, sulfonated PS-g-FEP, Nafion®-cast and Nafion® 112 were 0.12 S/cm, 0.12 S/cm, 0.16 S/cm, 0.07 S/cm, 0.09 S/cm and 0.07 S/cm, respectively. The ionic conductivity of FN10 showed the higher than any other obtained PEMs in our evaluation condition.

The ionic conductivity of sulfonated PS-g-FEP was almost same value though IEC is two times higher compared with Nafion®-cast and Nafion® 112. On the other hand, the ionic conductivity of FN10 was about two times higher than that of Nafion® though IEC of FN10 showed the nearly equal to Nafion®. This is suggesting that the ion conductive mechanism of PEM based on grafted type would be different from perfluoro sulfonic acid type such as Nafion® and Flemion®.

Figure 1 shows the results of the fuel cell performance tests where the operating temperature was 60 °C. The values of open circuit voltage (OCV), power densities at the maximum and at 500 mA/cm^2 are listed in Table 2. The power densities at a current density of 500 mA/cm^2 of MEA based on FN50, FN20, FN10, sulfonated PS-g-FEP, Nafion®-cast and Nafion® 112 were 308 mW/cm^2, 343 mW/cm^2, 349 mW/cm^2, 325 mW/cm^2, 336 mW/cm^2 and 320 mW/cm^2, respectively. The maximum power densities of MEA based on FN50, FN20, FN10, sulfonated PS-g-FEP, Nafion®-cast and Nafion® 112 were 523 mW/cm^2, 806 mW/cm^2, 1003 mW/cm^2, 674 mW/cm^2, 899 mW/cm^2 and 467 mW/cm^2, respectively.

The power densities of maximum and 500 mA/cm^2 of MEA based on Nafion®-cast showed higher than those of Nafion® 112. It was thought that the cell performance would be affected by the difference of water uptake in Nafion®, as sown in Table 1. In the case of the prepared Nafion®-cast
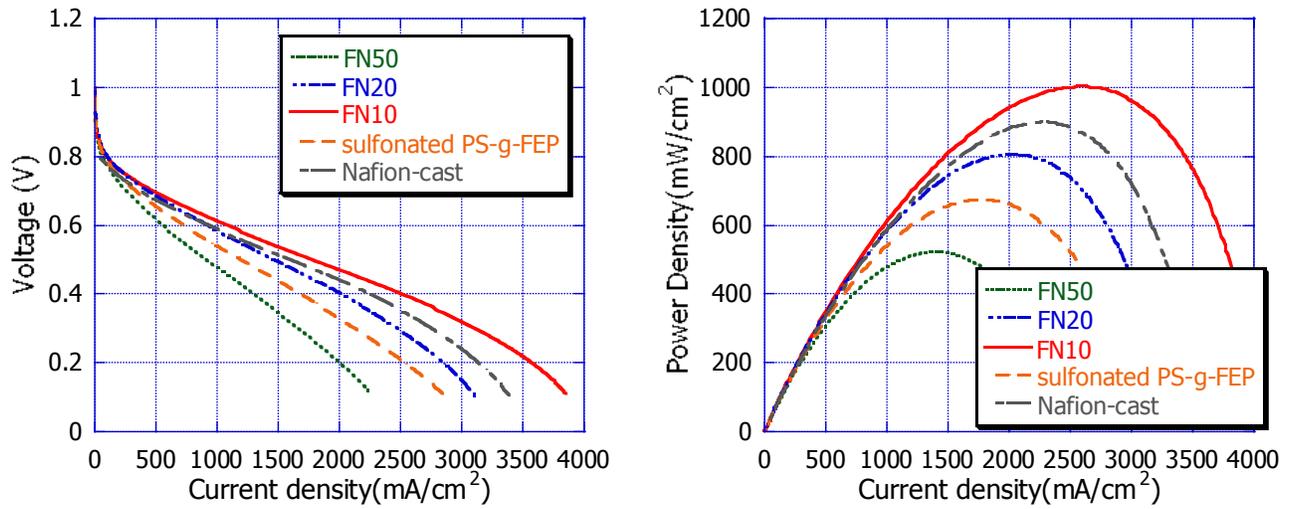
Figure 1 Polarization curves of obtained PEMs. Cell temperature :60 °C, H_2/O_2 Gas flow: 50 cc/min, Gas pressure: 0.2 MPa, H_2 : humidified, O_2: dry. (a): I-V curve (b) Power density

membrane, the entanglement of molecular chains might be poor, compared with commercially available Nafion[®] 112.

When the amount of sulfonated PS-g-FEP mixed with Nafion[®] dispersion was decreased, the cell performances showed the better results. The maximum power density of obtained FN10 is about 1.5 times higher than that of sulfonated PS-g-FEP, and about 1.1 times higher than that of the prepared Nafion[®]-cast, and about 2 times higher than that of a Nafion[®] 112. The MEA based on FN10 shows the higher power densities of maximum and at 500 mA/cm^2 than any other tested membranes. However, in the case of the high temperature cell operation (80 °C), the power density of the fabricated FN10 was slightly decreased, compared with that of operation at 60 °C. In the high current density region, it was considered that the flooding would occur on the cathode layer. Consequently, it is thought that the water management becomes very important in the operation at higher temperatures.

Table 2 Cell performance of obtained the hybrid membrane at 60 °C operation

Membrane	OCV (mV)	Power Density (mW/cm^2)	
		at 500 mA/cm^2	Maximum
FN50	948	308	523
FN20	972	343	806
FN10	956	349	1003
sulfonated PS-g-FEP	952	325	674
Nafion[®]-cast	822	336	899
Nafion[®] 112	970	320	467

Though, the cell performance of the MEA based on FN20 showed the higher than that of Nafion[®]-cast in the low current density region less than 1000 mA/cm^2, FN20 was worse than that of

Nafion®-cast in the high current density region above 1000 mA/cm². These results would be explained that both diffusion polarization and activation polarization of FN would be changed by the mixing of sulfonated PS-g-FEP and Nafion®. In generally, the cell performance is deteriorated by Ohmic resistance, diffusion polarization and activation polarization. Activation polarization takes place at a low current density region, while diffusion polarization takes place at a high current density region [23]. Thus, the FN10 would be decreasing diffusion polarization by its high IEC value and high ionic conductivity. On the other hand, the apparent activation polarization of FN50 and sulfonated PS-g-FEP would have been caused by the poor interface between the PEM and electrodes.

The OCV values of FN's showed the 950 mV ~ 970 mV. On the other hand, OCV values of Nafion®-cast and Nafion® 112 showed 822 mV and 952 mV, respectively. Although the OCV values of obtained FN's were as same as commercially available Nafion® 112, Nafion®-cast showed lower OCV value than those of any other PEMs in spite of their high power densities. It would be due to the insufficient entanglement of molecular chain in Nafion®-cast. That is, it is considered that the mobility of the molecular chain would increase gas crossover and that would decrease its OCV value. In the case of the FN, the thermal treatment at 110 °C above glass transition temperature of the FN would prevent from gas crossover and decreasing OCV value.

Conclusion

In order to fabricate the well laminated interface between radiation grafted PEM and Pt/C electrodes, the hybrid PEM consists of PFSA and sulfonated PS-g-FEP synthesized by soft-EB induced grafting method, was fabricated by mixing sulfonated PS-g-FEP with sulfonic ionomer which is applied to coat the interface of the PEM and electrodes.

The IEC value of the fabricated PEM was 1.0 meq/g ~ 1.2 meq/g. Water uptake of the FN was 54 % ~ 72 %, and is considerably high compared with the commercially available PFSA. It is explained that the casting method enhanced the molecular chain motion of the FN and resulted in large amount of water uptake. The polarization curve and electrochemical impedance of the FN, the sulfonated PS-g-FEP and a Nafion® was analyzed. As a result, ionic conductivity of FN10 showed 0.16 S/cm and is the highest in the tested PEMs. The maximum power density of FN10 is 1003 mW/cm², which is 1.5 times higher than commercially available Nafion® 112.

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