

Preparation of a Crosslinked Polyelectrolyte Membrane for Fuel Cells with an Allyl Methacrylate Based Two-Step Reaction

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ABSTRACT: In this study, a proton-exchange membrane for fuel cells was prepared via a two-step reaction with an allyl methacrylate (AMA) as an asymmetric crosslinking agent. First, a linear-chain polymer was synthesized, consisting of hydrophilic 2-acrylamido-2-methylpropanesulfonic acid (AMPS), hydrophobic 2,2,2-trifluoroethyl methacrylate (TFEMA), and AMA. Subsequently, we crosslinked the linear-chain polymer by reacting the remaining allyl group during dry heating. The proton conductivity of the prepared membrane was 7×10^{-2} S/cm at room temperature. The membrane was characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry, and atomic force microscopy. The polymer electrolyte membrane fuel cell (PEMFC) perform-

ance was evaluated for a membrane electrode assembly composed of the crosslinked AMPS-TFEMA-AMA/fluoroalkyl graft polymer (FGP) membrane. As a result of a power-generation test, a maximum power density of 174 mW/cm² at a current density of 400 mA/cm² was observed for a PEMFC single cell. Consequently, it was confirmed that the AMPS-TFEMA-AMA/FGP membrane for PEMFC could easily be prepared via a two-step reaction at a low cost and that PEMFC exhibited a cell performance and that of cells with the Nafion membrane. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3343–3350, 2009

Key words: composites; crosslinking; membranes; polyelectrolytes; step-growth polymerization

INTRODUCTION

Recently, polymer electrolyte membrane fuel cells (PEMFCs) have attracted much attention as lightweight, environmentally friendly, and highly efficient power-generation systems.^{1–4} Proton-exchange membranes (PEMs) are one of the key materials in PEMFC development. In particular, perfluorinated polymer electrolyte membranes, such as Nafion, Flemion, and Aciplex, are widely used for commercial PEMFCs because these membranes have a high proton conductivity, high mechanical strength, and high chemical stability. Generally, perfluorinated PEMs for fuel cells are expensive because of their complex multistep synthesis process. For the purpose of PEMFC commercialization, a PEM that can easily be prepared is required.^{5–11} One idea to obtain a PEM with a simple process is to use a crosslinked polymer consisting of a proton-conductive monomer and a bifunctional monomer.¹² The reason for the utilization of a crosslinked polymer is to prevent the dissolution of the PEM in water.¹³ The use of a

crosslinking agent with the same functional units produces a gel; however, it is difficult to obtain a uniform PEM by the recasting of such a gel.¹⁴

In this article, we propose a two-step polymerization method in which a linear-chain polymer is first synthesized; then, the polymer solution is recast on a substrate, and the linear-chain polymer is crosslinked by the reaction of the remaining allyl group during dry heating. Consequently, a 2-acrylamido-2-methylpropanesulfonic acid (AMPS)-2,2,2-trifluoroethyl methacrylate (TFEMA)-allyl methacrylate (AMA) membrane is easily prepared via a two-step reaction at a low cost compared with the Nafion membrane. The PEM prepared by the proposed method was characterized by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), atomic force microscopy (AFM), and proton conductivity measurement. Next, to enhance the mechanical strength of the membrane, the linear-chain AMPS-TFEMA-AMA was crosslinked in a fluoroalkyl graft polymer (FGP) solution. The obtained AMPS-TFEMA-AMA/FGP was characterized by scanning electron microscopy (SEM), energy dispersion X-ray spectrometry (EDS), and proton conductivity measurement. Finally, the performance of the PEMFC with the AMPS-TFEMA-AMA/FGP membrane was evaluated with a PEMFC single cell.

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EXPERIMENTAL

Preparation of the AMPS–TFEMA–AMA membrane

AMPS (Tokyo Chemical Industry, Tokyo, Japan, 20–50 wt %), TFEMA (Tokyo Chemical Industry, 40–70 wt %), and AMA (Tokyo Chemical Industry, 10 wt %) were copolymerized in *N,N*-dimethylformamide (DMF; Wako Pure Chemical Industries, Osaka, Japan, solvent : monomer weight ratio = 9 : 1) with 2,2'-azobisisobutyronitrile (AIBN; Kanto Chemical, Tokyo, Japan, 2 wt % with respect to all monomers) as an initiator at 48°C for 23 h to obtain a linear-chain polymer as a precursor for the crosslinked polymer. The linear-chain polymer solution was recast on a glass plate and subsequently dried at 120°C for 15 min. Thus, the obtained membrane was insoluble in DMF and water, which indicated that the precursor was crosslinked.¹⁵

Preparation of the AMPS–TFEMA–AMA/FGP composite membrane

The crosslinked AMPS–TFEMA–AMA membrane was chemically stable; that is, it was insoluble in water and many organic solvents; however, it had poor mechanical strength. To enhance the mechanical strength of the membrane, the linear-chain polymer solution (AMPS : TFEMA : AMA = 50 : 40 : 10, 40–70 wt %), FGP (Central Glass, Yamaguchi, Japan, Cefral Soft; CAS no. 89823-13-2), AIBN (1 wt % with respect to all monomers), and DMF were mixed to obtain a solution with a solid content of 11.1 wt %. The solution was recast onto a glass plate and subsequently dried at 120°C for 15 min. Then, the desired AMPS–TFEMA–AMA/FGP composite was obtained, in which AMPS–TFEMA–AMA was crosslinked.

Characterization of the polymer membrane

The membrane characteristics were investigated by FTIR (PerkinElmer, Waltham, MA, Spectrum Spotlight 200S), DSC (Shimadzu, Kyoto, Japan, DSC-60), and AFM (Shimadzu, SPM-9500 J3 model). The IR spectra of KBr pellets containing AMPS–TFEMA–AMA were recorded with a spectrometer with a wave number resolution of 4 cm⁻¹ in the range 450–4000 cm⁻¹. The measurement was conducted for the precursor and crosslinked PEM. A thermal analysis of the polymer membranes was performed by DSC. The samples were loaded into aluminum pans. DSC measurement was carried out in a dry nitrogen atmosphere with heating from 30 to 150°C at a rate of 5°C/min. The second heating curve was recorded because the first heating curve showed a significant effect of residual water.¹⁶ The surface morphology of the membranes was observed with an AFM system equipped

with a 55-μm scanning head and operated in tapping mode. In this mode, we used silicon probes (Olympus, Tokyo, Japan) with a spring constant of 42 N/m and a resonance frequency of 300 kHz. AFM was conducted at room temperature and room humidity. The membrane surface morphologies were imaged immediately at a scan rate of 1 Hz and a 512 × 512 pixel resolution. The piezoscanner of the AFM system was calibrated by the imaging of a gold grating sample from Shimadzu Co.

The surface morphology of the AMPS–TFEMA–AMA/FGP membrane was observed by SEM (JEOL, Tokyo, Japan, JSM-6060A) in combination with EDS (JEOL, JED-2300) after it was coated with Au by sputtering.

Measurement of the proton conductivity and water uptake

We considered that the prepared membrane had a proton conductivity, the same mechanism as that of the Nafion membrane, because the membrane also contained a sulfonic acid group. The proton conductivity of the PEMs in the thickness direction was measured by the alternating-current impedance method at room temperature and 100% RH.^{17,18} Before the measurement, the membranes were surface-dried with tissue paper and then immediately inserted between the two Au electrodes and pressed with a micrometer. The alternating-current impedance spectrum was recorded from 2 MHz to 100 Hz with a Solartron 1260 impedance/gain-phase analyzer (Hampshire, England) and Zplot software (Scriber Associates, Lake City Starke, FL) for Windows. The membrane resistance was determined by extrapolation of the complex impedance diagram at high frequency to the real axis. The proton conductivity was calculated as follows:

$$\text{Proton conductivity} = l/RS \quad (1)$$

where *l*, *R*, and *S* denote the sample thickness, membrane resistance, and sample area, respectively.¹⁹

The membranes were soaked for 1 day in deionized water to determine the water uptake. The weight of a dry membrane was measured after the sample was dried overnight *in vacuo* at 80°C. Water uptake is defined as the water mass per mass of a water-containing membrane:

$$\text{Water uptake} = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{wet}} \times 100 \quad (2)$$

where *W*_{wet} and *W*_{dry} are the masses of the water-swollen membrane and dry membrane, respectively.²⁰

Ion-exchange capacity (IEC) was calculated as follows:

$$\text{IEC} = n/W \quad (3)$$

where n and W are the milliequivalents of sulfonic acid groups and the mass of the membrane, respectively.²¹

Membrane electrode assembly (MEA) preparation and PEMFC performance

An electrocatalyst dispersion for air spraying was prepared as follows. Pt/C (Tanaka Kikinzoku, Tokyo, Japan, 45.9 wt % Pt) and Nafion solution (Wako Pure Chemical Industries, Ltd., 5 wt % Nafion) were mixed in a Pt/C:Nafion weight ratio of 6 : 1 and then diluted to a 3 wt % solid content by the addition of a methanol : 2-propanol : water solution with a weight ratio of 1 : 1 : 1.

To assess the PEMFC single-cell characteristics, electrocatalyst layers of 5 cm² area were deposited on both surfaces of the membrane by air-spraying. The Pt loads at the anode and cathode were 1 mg/cm². Then, the catalyst-coated membranes were dried in a vacuum oven at 140°C for 1 h. The MEA thus produced was installed in a PEMFC single cell (Electrochem, Inc., Woburn, MA, EFC05-01SP) to measure its current–voltage (I - V) characteristics with a cell operation system (FC Development Co., Ibaraki, Japan, HPE-1000). The measurements were carried out at a cell temperature of 80°C. Hydrogen gas for the anode and oxygen gas for the cathode were humidified by an 80°C humidifier and supplied to the cell both at a rate of 40 cm³/min. The I - V polarization curves presented were recorded after a 3 h of preconditioning.

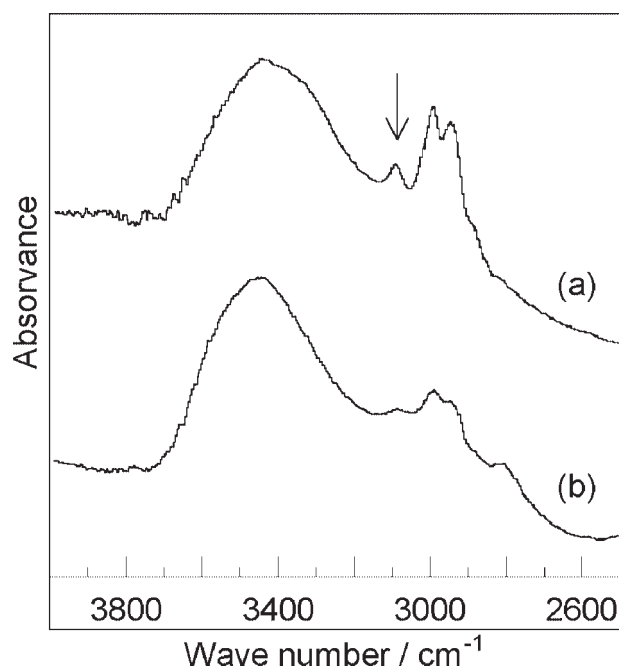


Figure 1 FTIR spectra of the AMPS-TFEMA-AMA membrane (a) before and (b) after crosslinking. The arrow denotes the 3080-cm⁻¹ peak.

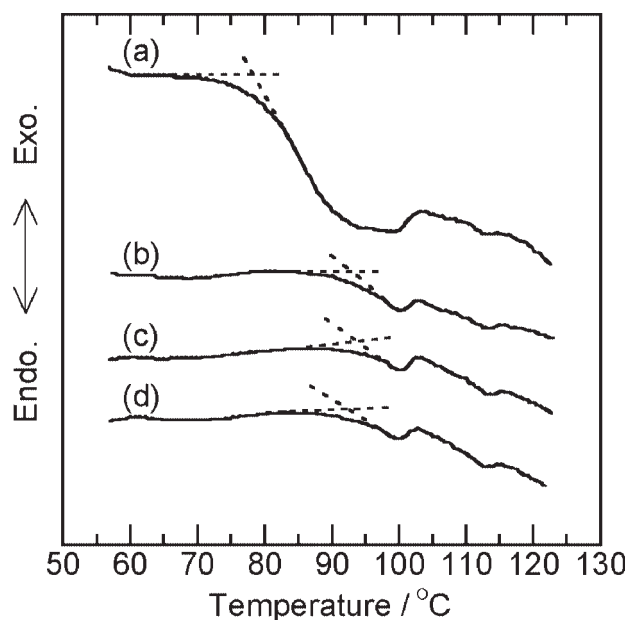


Figure 2 DSC curves for crosslinking AMPS-TFEMA-AMA membranes as a function of the AMA content: (a) 0, (b) 10, (c) 20, and (d) 30 wt %. Dashed lines indicate the endothermic temperature.

RESULTS AND DISCUSSION

AMPS-TFEMA-AMA membrane

Characterization of AMPS-TFEMA-AMA

Figure 1 shows the FTIR spectra of the AMPS-TFEMA-AMA membranes before and after crosslinking. An absorption peak at 3080 cm⁻¹, which was attributed to the C-H stretching of the alkene group,²² was observed before the crosslinking (precursor), whereas no absorption peak was observed after the crosslinking (PEM). The first-step reaction produced a linear-chain polymer that still had an allyl group. The disappearance of the 3080-cm⁻¹ peak meant that the remaining vinyl group participated in the crosslinking. In addition, the first-step reaction product [Fig. 1(a)] dissolved in water, whereas the second-step reaction product [Fig. 1(b)] was insoluble in water. It was, therefore, apparent that crosslinking occurred in the second step.

Figure 2 shows the DSC curves of the AMPS-TFEMA-AMA membranes containing 0, 10, 20, and 30 wt % AMA as a crosslinking agent. From the DSC data, the initiation endothermic temperatures were 78°C for the noncrosslinked AMPS-TFEMA

TABLE I
Water Stability of the AMPS-TFEMA-AMA Membranes Before and After Crosslinking

| | IEC = 0.97 | IEC = 2.4 |
|---------------------|------------------|-----------|
| Before crosslinking | Dissolved | Dissolved |
| After crosslinking | Slightly swollen | Swollen |

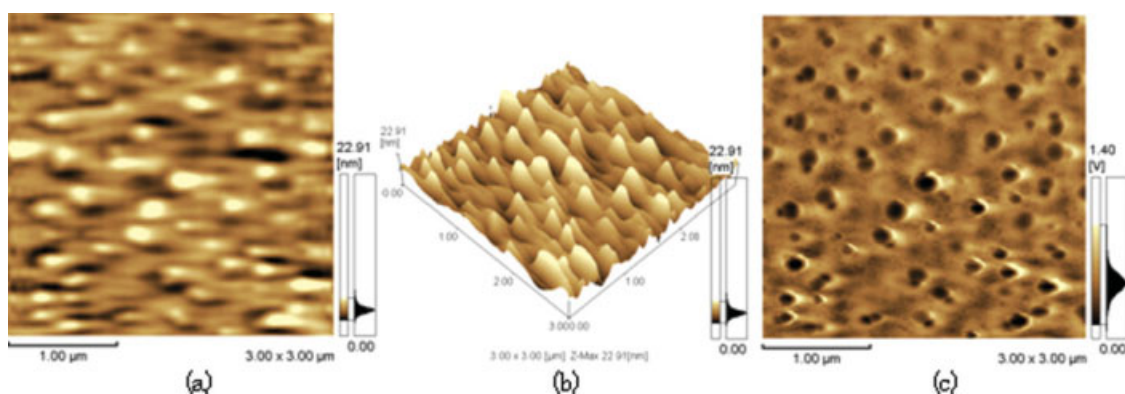


Figure 3 (a,b) AFM topography and (c) corresponding phase image of the AMPS-TFEMA-AMA membrane (AMPS : TFEMA : AMA = 20 : 30 : 70 w/w). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

membrane [Fig. 2(a)] and 94°C for the crosslinked AMPS-TFEMA-AMA membrane [Fig. 2(b-d)]. The shift in temperature indicated that the crosslinking agent enhanced the thermal stability of the polymer structure.²³ From the FTIR and DSC results, we concluded that the crosslinking occurred in two steps.

Table I demonstrates the AMPS-TFEMA-AMA membrane stabilities in water before and after the crosslinking. The copolymer before the crosslinking was soluble in water, whereas the copolymers after the crosslinking were insoluble in water. The crosslinking made the polymer insoluble regardless of the magnitude of IEC. On the other hand, the sample with a 2.4 mmol/g IEC showed good membrane quality, although its large AMPS percentage induced swelling.

Figures 3 and 4 show the AFM topography and corresponding phase image of the crosslinked AMPS-TFEMA-AMA membrane, respectively. It is clear from the figures that the high spots in the topography corresponded to the hard regions in the phase image, and the low spots in the topography corresponded to the soft regions in the phase image,

respectively.¹¹ In the phase image, the bright spots correspond to the soft domains of the membrane, and the dark spots correspond to the hard domains. This indicates that the membrane had a phase separation consisting of these two types of domain. The soft domains were considered to be hydrophilic clusters because the AMPS-based hydrophilic domain absorbed water to soften the domain.^{19,24-27} When we compared Figure 4 to Figure 3, containing many and few hydrophilic AMPS's, respectively, the soft domains of the former were smaller but more numerous. The average hydrophilic domain sizes in Figures 3 and 4 were approximately 200 and 100 nm, respectively. Therefore, a hydrophilic domain based on phase separation in a crosslinked AMPS-TFEMA-AMA membrane was approximately 10 times larger than that in the Nafion membrane.^{19,27}

Proton conductivity and water uptake

Table II shows the water uptake of the membranes containing 0, 10, 20, and 30 wt % AMA as a

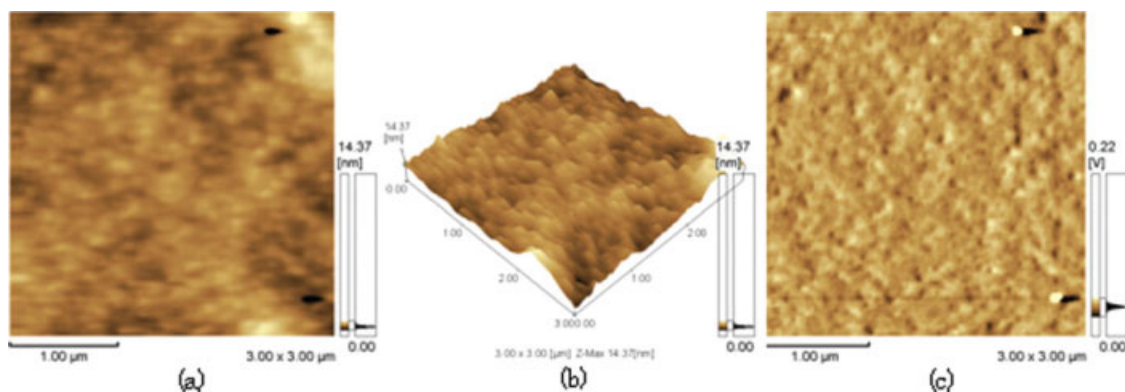


Figure 4 (a,b) AFM topography and (c) corresponding phase image of the AMPS-TFEMA-AMA membrane (AMPS : TFEMA : AMA = 50 : 40 : 10 w/w). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Water Uptake of the AMPS–TFEMA–AMA Membranes
as a Function of the AMA Content

| | 0 wt % | 10 wt % | 20 wt % | 30 wt % |
|--------------|-----------|---------|---------|---------|
| Water uptake | Dissolved | 88.6 | 83.6 | 83.1 |

The AMPS content was fixed at 50 wt %.

crosslinking agent with a fixed amount of used AMPS. As seen in Table II, the water uptake was not measured for the membrane without the AMA. The water uptake of the samples containing 20 and 30 wt % AMA was not much different from that of the sample containing 10 wt % AMA. In addition, the mechanical stability of the membrane containing 10 wt % AMA was found to be good. From the DSC results shown in Figure 2, the thermal stability did not change with respect to the AMA content. Consequently, in the following experiments, the AMA content was fixed at 10 wt %.

Figure 5 shows the relationship between the IEC and proton conductivity of the crosslinked PEM. As shown in the figure, at IEC = 2.4 mmol/g, the proton conductivity was as high as that of the Nafion membrane.²¹ When we compared PEM with the Nafion membrane at a proton conductivity of 0.08 S/cm, the IEC of the Nafion membrane was 0.9 mmol/g, and that of the crosslinked PEM was 2.4 mmol/g. The difference in IEC indicated that the proton-conductive domain structures of the Nafion membrane and PEM markedly differed. Affoune et al. reported that the hydrophilic domain size of the Nafion membrane was within approximately 7–15 nm on the basis of the phase image obtained by AFM.^{19,27} As pointed out in Figures 3 and 4, the hydrophilic domain of the crosslinked AMPS–TFEMA–AMA membrane was approximately 10 times larger than that of the Nafion membrane. The marked difference in the hydrophilic domain size induced a difference in the magnitude of proton conductivity between the AMPS–TFEMA–AMA and Nafion membranes. Figure 6 shows the relationship between the IEC and water uptake of the crosslinked PEM. For comparison, the data of Nafion 117 is also plotted. From the figure, the water uptake of the crosslinked PEM proportionally increased with IEC. This was because the large number of sulfonic acid groups of the crosslinked PEM promoted water uptake.

From the results shown in Figures 5 and 6, water taken up participated in the ionization of the sulfonic acid groups, which induced proton conduction. In Figure 6, when we compared the AMPS–TFEMA–AMA and Nafion membranes at an IEC of approximately 0.9 mmol/g, the percentages of water uptake were found to be almost the same. We con-

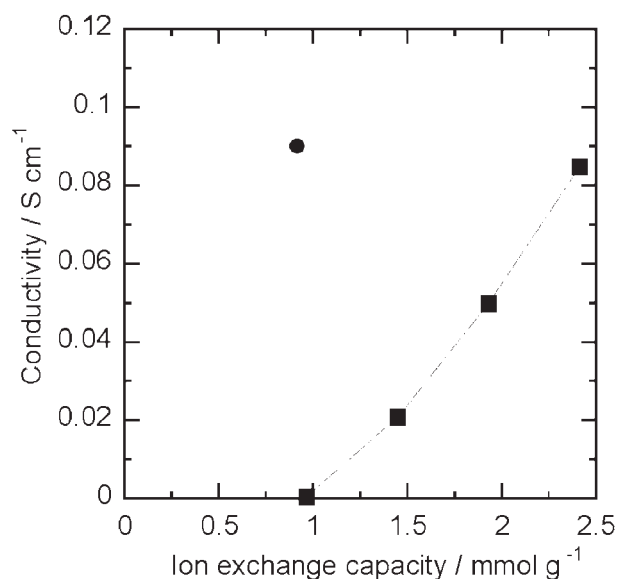


Figure 5 Proton conductivity versus the IEC: (■) cross-linked AMPS–TFEMA–AMA and (●) Nafion 117.

cluded that the difference in proton conductivity between the two membranes was due to the difference in the number of charge carriers or in mobility.

The proton conductivity was defined as follows:²⁸

$$\text{Proton conductivity} = n \times e \times \mu \quad (4)$$

where n is the number of charge carriers, e is the elementary electric charge, and μ is the mobility. By comparing the two membranes in Figure 5 at IEC \approx 0.9 mmol/g, we discovered that the conductivity

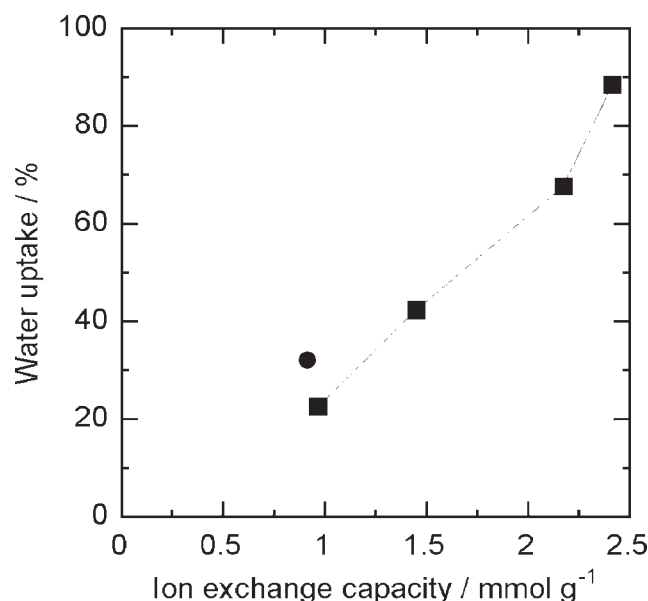


Figure 6 Water uptake versus the IEC: (■) cross-linked AMPS–TFEMA–AMA and (●) Nafion 117.

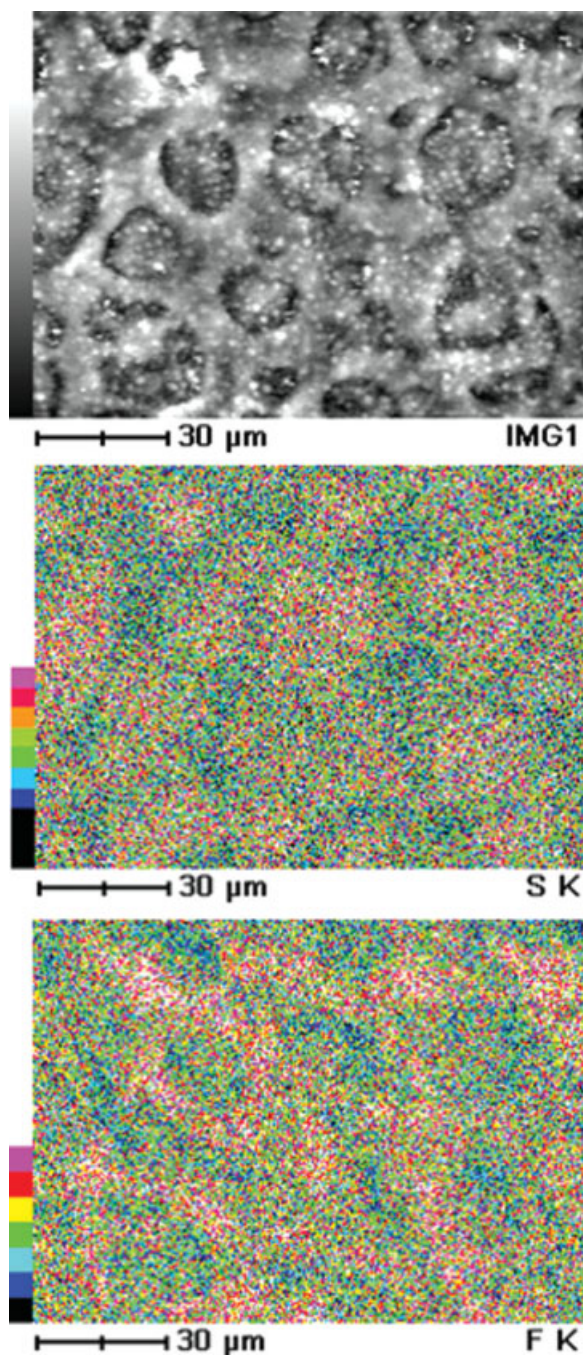


Figure 7 SEM and EDS images of the surface morphology of the AMPS-TFEMA-AMA/FGP membrane.

of the crosslinked AMPS was smaller than that of the Nafion membrane. When one takes eq. (3) into account, the difference in conductivity indicates that the number of charge carriers in the crosslinked AMPS was larger than that in the Nafion membrane or that the mobility of the charge carriers of the Nafion membrane was larger than that of the crosslinked AMPS. Because the same IEC means the same magnitude of n , we concluded that this difference was due to the difference in mobility, which

could be affected by the hydrophilic domain size determined on the basis of phase separation.

AMPS-TFEMA-AMA/FGP composite membrane

Characterization of AMPS-TFEMA-AMA/FGP

Although the crosslinked AMPS-TFEMA-AMA membrane was chemically stable, that is, it was insoluble in water, it had been poor tensile and tearing strengths. To enhance the mechanical strength of this membrane, a noncrosslinked polymer was mixed with FGP and then cured in an FGP matrix. Figure 7 shows SEM and EDS surface images of the AMPS-TFEMA-AMA/FGP composite membrane (AMPS-TFEMA-AMA : FGP weight ratio = 50 : 50 wt %). As shown in the figure, the membrane had a typical sea-island structure, in which 10–20- μ m layers of the AMPS-TFEMA-AMA polymer island and FGP sea domains were observed. This island domain consisted of the AMPS-TFEMA-AMA polymers (Figs. 3 and 4) because AMPS contained sulfur.

Proton conductivity and water uptake

Figure 8 shows the dependences of the proton conductivity and water uptake on the AMPS-TFEMA-AMA polymer content of the AMPS-TFEMA-AMA/FGP composite membranes. Although the proton conductivity of the AMPS-TFEMA-AMA/FGP membrane proportionally increased with AMPS-TFEMA-AMA polymer content, the magnitude of the conductivity was smaller than that of the AMPS-TFEMA-AMA polymer without FGP. This indicated

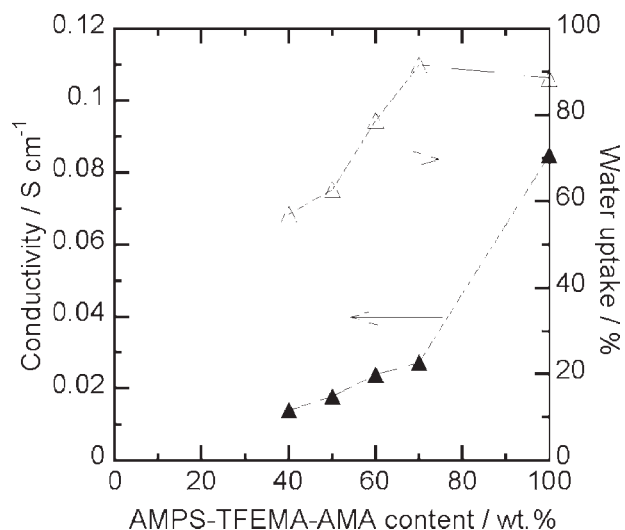


Figure 8 AMPS-TFEMA-AMA content in the AMPS-TFEMA-AMA/FGP system versus (▲) the proton conductivity and (△) the water uptake of AMPS-TFEMA-AMA/FGP membranes.

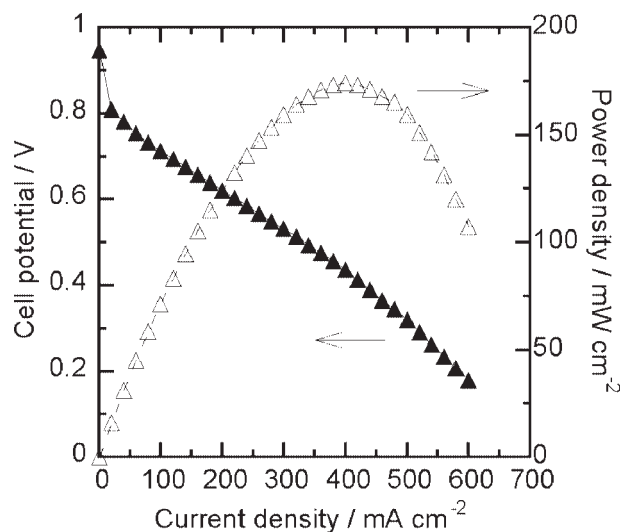


Figure 9 I-V curves for a PEMFC with MEA based on AMPS-TFEMA-AMA/FGP.

that the use of insulating FGP decreased the conductivity of the AMPS-TFEMA-AMA/FGP composite membrane. In addition, the water uptake of the AMPS-TFEMA-AMA/FGP membrane increased with AMPS-TFEMA-AMA polymer content. The water uptake at a 70 wt % AMPS-TFEMA-AMA content exceeded that at 100 wt %. From the result, water uptake occurred not only at the hydrophilic domain but also in the space between the AMPS-TFEMA-AMA polymer and FGP. The AMPS-TFEMA-AMA/FGP composite membrane had a higher film-forming ability and water uptake than the AMPS-TFEMA-AMA membrane. In general, the higher water uptake caused the polymer to dissolve in water, which accelerated the decrease in the membrane's stability. Furthermore, the AMPS-TFEMA-AMA membrane broke easily when folded under dry conditions. On the other hand, the AMPS-TFEMA-AMA/FGP membrane did not break, even when the membrane was folded under dry conditions. The flexibility was attributed to the characteristics of FGP.

PEMFC performance

Finally, the MEA consisting of the polymer blend PEM (AMPS-TFEMA-AMA/FGP weight ratio = 50 : 50; the membrane stability and proton conductivity were relatively high) was installed in a PEMFC single cell. We evaluated the I-V characteristics of the single cell by feeding oxygen gas to the cathode and hydrogen gas to the anode. The results are shown in Figure 9. The maximum power density in the case of the AMPS-TFEMA-AMA/FGP composite membrane was found to be 174 mW/cm² at a current density of 400 mA/cm². Next, when the

humidifier temperature was changed from 80 to 50 and 30°C, the maximum power density decreased from 174 to 16 and 9 mW/cm². Simultaneously, the magnitude of relative humidity (RH) of the supplied gases decreased from 97.2% RH to 84.1 and 79.1% RH. When the PEM was sufficiently humidified, the maximum power density improved. From the result, we knew that the proton conductivity of the PEM was enhanced by higher humidification. The AMPS-TFEMA-AMA/FGP composite membrane was easily prepared by a two-step reaction at a low cost compared with the Nafion membrane.

CONCLUSIONS

A novel crosslinked PEM was successfully prepared with AMA and a two-step reaction. The main results are summarized as follows.

1. A crosslinked AMPS-TFEMA-AMA membrane was synthesized by two-step polymerization.
2. The synthesized membrane had a crosslinked structure, as determined from the results of FTIR and DSC.
3. The hydrophilic domain size of AMPS-TFEMA-AMA was within 0.1–0.2 μm.
4. The proton conductivity of the crosslinked PEM measured could reach that of the Nafion membrane because the IEC at the same proton conductivity was different.
5. The water uptake of the crosslinked PEM increased proportionally with IEC.
6. A maximum power density of 174 mW/cm² was obtained at a current density of 400 mA/cm² with an AMPS-TFEMA-AMA/FGP membrane. The proton conductivity of the PEM was enhanced by higher humidification.
7. An AMPS-TFEMA-AMA/FGP composite membrane was easily prepared at a low cost compared with the Nafion membrane.

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