A study on fabrication of sulfonated poly(ether ether ketone)-based membrane-electrode assemblies for polymer electrolyte membrane fuel cells

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Abstract

The porosity effect of catalyst electrodes in membrane-electrode assemblies (MEAs) using a hydrocarbon-based polymer as electrolyte and ionomer was investigated on physical and electrochemical properties by varying the content of ionomer binder (dry condition) in the catalyst electrodes. The MEAs were compared with the Nafion®-based MEA using Nafion® 112 and 5 wt.% ionomer solution (EW = 1100) in terms of porosity values, scanning electron microscopic images, Nyquist plots, dielectric spectra and *I–V* polarization curves. In this study, sulfonated poly(ether ether ketone) (SPEEK) membranes with $25 \pm 5\,\mu m$ of thickness and 5 wt.% ionomer solutions have been prepared. The prepared membranes were characterized in terms of FT-IR, DSC and proton conductivity. Proton conductivity of the SPEEK membranes was compared with one of the Nafion® membranes with relative humidity. The porosity of the catalyst electrodes was calculated using the properties of catalyst, ionomer solution and solvent. As a result, the performance of the new type polymer (i.e., SPEEK in this study)-based MEA with the similar membrane conductivity and porosity of the catalyst electrode in the Nafion® MEA was similar to that of the Nafion® MEA.
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1. Introduction

A membrane-electrode assembly (MEA) is one of key components in polymer electrolyte membrane fuel cells (PEMFCs) since it is an essential unit to make an energy conversion device that generates electricity and heat by electrochemically combining hydrogen and oxygen from the air. It is a composite of a polymer electrolyte membrane sandwiched between catalyzed electrode layers. The fabrication of the MEA has typically involved the following processes: The catalyst slurry for electrodes is prepared as the mixture of electrocatalyst (e.g., Pt/C or Pt/Ru/C) and perfluoro-sulfonated ionomer dispersed in lower alcohols (e.g., Nafion® solution). The catalyst slurry is applied to either the surface of a sheet of PTFE-impregnated carbon paper or a polymer membrane (e.g., Nafion® membrane). The membrane is sandwiched between the carbon papers, and thereafter the sandwich is pressed at a temperature and a pressure.

Much attention has been paid to develop optimized MEAs for PEMFC in terms of the methods of optimizing the composition of catalyst slurries [1,2], lowering the amount of the catalyst loaded on the electrode [3] or assembling MEAs [4–9]. Those studies were, however, carried out based on perfluoro-sulfonated polymers (e.g., Nafion®) as an electrolyte and an ionomer binder. For the fabrication of MEAs using newly prepared membranes [10–12], optimization of the composition of catalyst slurry has to be made since the ionomer binder in the catalyst slurry is the same kind of material to the membrane.

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It is needed to mitigate both poor adhesion and performance problems at the membrane–catalyst interface, arising from using dissimilar polymers in the membrane and electrode. Moreover, the optimization should satisfy other important criteria for PEMFC operations, which are proton accessibility to proton-conducting membranes from the surface of catalyst layers, gas accessibility to catalysts as much as possible and electronic path continuity. Those criteria significantly depend on slurry composition, resulting in the configuration of catalyst layers. Many researchers reported that the effects of ionomer content were significant on the electrode configuration which differed PEMFC performance [13–17]. The studies suggested different optimal ionomer loadings in the electrodes they studied. Accordingly, the ionomer content is not enough for a critical parameter of developing electrode configuration for MEAs. Thus, it is needed to find a criterion to be able to provide the optimal electrode condition.

In this study, the sulfonated poly(ether ether ketone) (SPEEK) polymeric membrane and the new ionomer binder, which is the SPEEK dispersed in an organic solvent, were newly prepared. Various catalyst slurries with different contents of the SPEEK ionomer and the same loading of electrocatalyst were prepared and were then applied to PTFE-impregnated carbon papers. The MEAs were fabricated using the SPEEK membranes with the same degree of sulfonation and the electrode-loaded carbon papers and were evaluated to determine the optimal composition of the catalyst slurry by means of physical and electrochemical characterizations as well as single cell tests. Especially, this study shows an attempt to suggest the optimization of electrode configuration for PEMFCs in terms of porosity of the catalyst layers.

2. Experimental

2.1. Chemicals

Poly(ether ether ketone) (PEEK, Victrex®, UK) was dried overnight at 130 °C under vacuum and used for the reaction. Sulfuric acid (95%), N,N-dimethylacetamide (DMAc), methanol (99%) all from Junsei Chemicals Co. Ltd., Japan were used as received without further purification.

2.2. Sulfonation of PEEK

Sulfonation of PEEK was carried out in a four neck round bottom flask fitted with a mechanical stirrer. About 500 mL of 95% H_2SO_4 was transferred to the reaction flask and heated over an oil bath to 50 °C under N_2 atmosphere. Then, 25 g of PEEK was slowly added under stirring. The mass remained heterogeneous initially and the polymer was completely dissolved in 1 h. The reaction was varied to control the degree of sulfonation (DS). The polymer solution was cooled to 10 °C to arrest the reaction and dropped over ice-cold deionized water using a separating funnel as a thin stream. The fibers were then washed with deionized water until the neutral pH and stirred overnight to remove the residual acid. The polymer was dried at 60 °C for 12 h followed by overnight drying at 110 °C under vacuum.
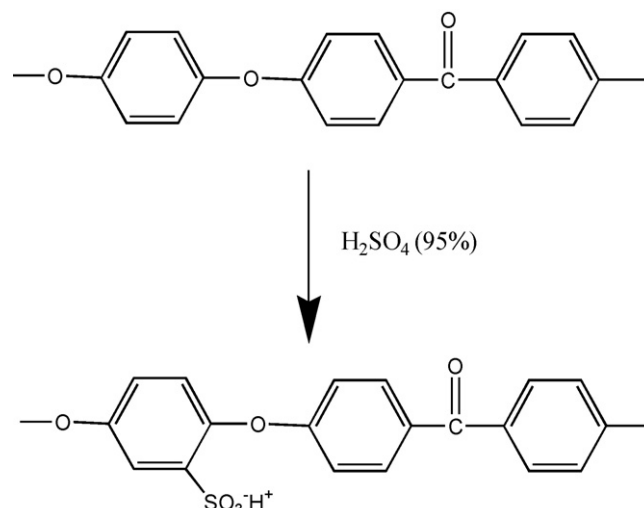

Fig. 1. Schematic principle for the sulfonation of poly(ether ether ketones).

As shown in Fig. 1, the sulfonation of PEEK is an electrophilic substitution reaction. The sulfonic acid group ($-SO_3H$) is substituted for a proton in the electron-rich position of the aromatic ring. Since sulfonation with concentrated H_2SO_4 (95–98%) avoids degradation and cross-linking of the polymer, we have employed the same as sulfonating agent. However, the reaction is heterogeneous until reaching 40% sulfonation level. The rate of reaction slows down with time. The polymers having sulfonation degree above 70% swell excessively in the presence of water. Even though the conductivity of highly sulfonated PEEKs is higher than that of Nafion membrane, the highly sulfonated polymers are not useful in fuel cell applications due to reduced mechanical stability and high swelling property. Thus, we selected the polymers having the sulfonation degrees of ∼57% for fuel cell testing. The above levels of sulfonation were reached in 6 h at 50 °C.

2.3. Membrane preparation and characterization

2.3.1. Membrane preparation

The dry SPEEKs were first dissolved in DMAc to prepare a 10 wt.% solution which was thereafter cast onto a glass plate. The samples were dried in an oven at 80 °C for 12 h and then under vacuum at 100 °C for 1 day. Dry membranes were peeled off from the substrate with deionized water. Most thickness of the membranes was 25 ± 5 μm. Thinner SPEEK membranes than Nafion® 112 used in this study as a reference membrane made membrane resistance similar and enable to significantly exclude a membrane effect in comparison of cell performance.

2.3.2. FT-IR

The FT-IR spectra were recorded on a JASCO FT/IR-4000 spectrophotometer (Jasco Inc., USA). The spectra of pristine polymers were recorded as KBr pellets. For the sulfonated polymers, about 10 μm transparent films were made and spectra were recorded on these films. The FT-IR spectra recorded for the pristine polymers as well as sulfonated polymers are given in Fig. 2. The absorption of the corresponding functional
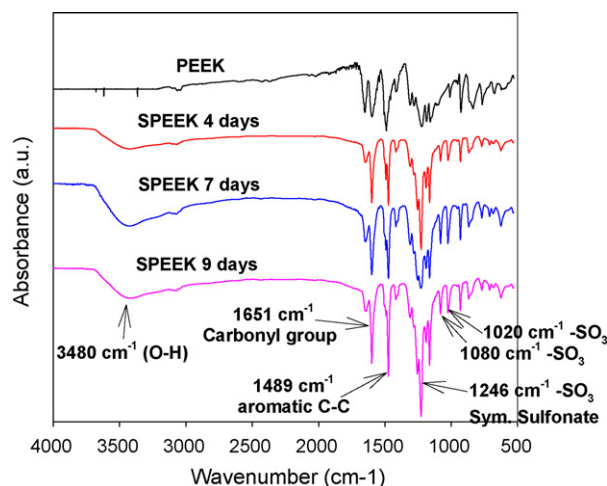
Fig. 2. FT-IR spectra of PEEK and SPEEKs.

Table 1
Degree of sulfonation and ion-exchange capacity of the SPEEKs

Sulfonation time (h)	Degree of sulfonation (%)	Ion exchange capacity (mequiv. g^{-1} of dry membrane)
36	48.4	1.48
48	57.5	1.72
77	72.4	2.09
96	89.3	2.48
120	100	2.74

groups is marked in the figure. The appearance of a broad band around 3460 cm^{-1} in the sulfonated samples was assigned to O–H vibration from sulfonic acid groups interacting with water molecules. The new absorptions at 1255, 1080 and 1020 cm^{-1} which appeared upon sulfonation were assigned to the sulfonic acid groups in SPEEKs. It was observed that their intensities increased with the sulfonation time. There is no change in the carbonyl band at 1651 cm^{-1} for SPEEK compared with PEEK.

2.3.3. Thermal properties of SPEEKs

A differential scanning calorimetry (DSC) (TA2010, Dupont, USA) was employed to study the thermal transition behavior of the samples. The samples ($\sim$10 mg) were preheated under nitrogen from the room temperature to 160 °C at 10 °C min^{-1} to remove moisture, then cooled to 90 °C and reheated from the temperature to 280 °C. The DSC results of PEEK and SPEEK are given in Fig. 3. The PEEK and SPEEK have T_g values of approximately 150 and 180 °C, respectively. The figure clearly shows the increase in the T_g value of the SPEEK. The increase

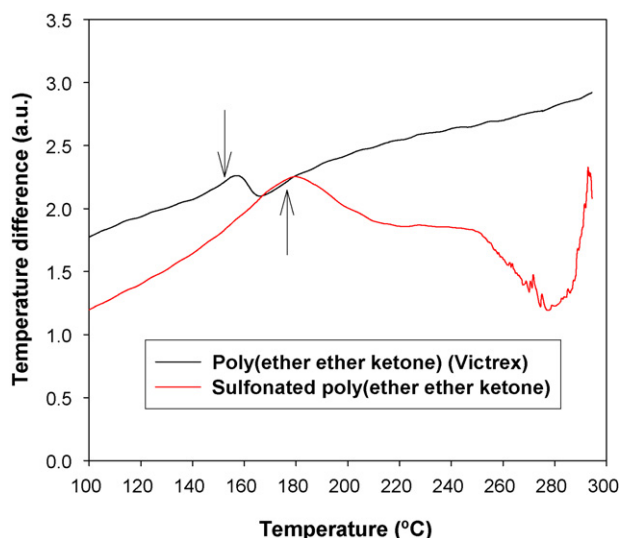in T_g value is due to strong interaction between sulfonic acid groups [18].

2.3.4. Degree of sulfonation (DS) and ion-exchange capacity (IEC)

The DS was determined by titration. About 1–2 g of SPEEK membranes in the acid form (H$^+$) was placed in the 0.1 M NaCl solution for 24 h to exchange the H$^+$ ions with Na$^+$ ions. Then it was back titrated with 0.01 M NaOH solution using phenolphthalein as an indicator. The IEC is expressed as the milliequivalents of sulfonic acid per gram of dry polymer. The degree of sulfonation is calculated according to the formula (1) [19]:

$$x = \frac{M_{w,p} \cdot \text{IEC}}{(1000 - M_{w,f} \cdot \text{IEC})} \qquad (1)$$

where $M_{w,p}$ is the molecular weight of the nonfunctional polymer repeating unit, $M_{w,f}$ the molecular weight of the functional group with the counter ions (–SO$_3$H) and x is the degree of sulfonation. Table 1 summarizes the DS and IEC of the SPEEKs with sulfonation time. As summarized in Table 1, the DS of the membranes linearly increase with sulfonation time after the homogeneous mixing was achieved ($\sim$1 h). In this study, it was found that the DS was able to be controlled quite well by varying sulfonation time.

2.3.5. Proton conductivity

The proton conductivity of the membranes was measured by an ac impedance spectroscopy using a Solarton 1260 frequency response analyzer interfaced to an EG&G 270 multistat. The measurement was carried out in the potentiostatic mode over the frequency range 1 Hz to 1 MHz with oscillating voltage of 5 mV. The home made four-probe conductivity cell configuration is similar to that reported in the literature [19]. The cell had two platinum foils for carrying the current and two platinum wires at 1 cm apart to sense the potential drop. The membrane sample (2 cm length, 1 cm wide) was placed over the platinum foils in the lower compartment, the upper compartment along with the potential sensing platinum wires was clamped. The cell was kept in a temperature- and relative humidity-controlled sealed off vessel. The conductivity of the samples was calculated by the formula (2):

$$\sigma = \frac{L}{RWd} \qquad (2)$$

where σ is the proton conductivity, L the length between two potential sensing platinum wires, R the membrane resistance
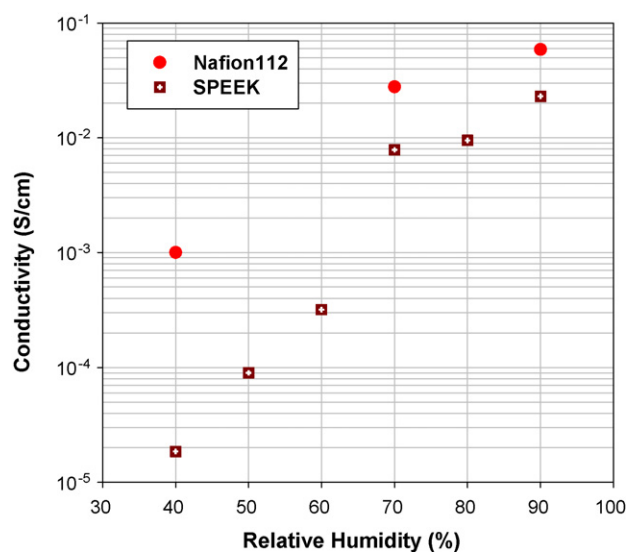

Fig. 3. DSC curves of PEEK and SPEEKs.

Fig. 4. Proton conductivity of Nafion® 112 and SPEEKs with different relative humidity (RH) at 70 °C.

Table 2
The properties of Nafion and SPEEK solutions

Ionomer solution	Concentration (wt.%)	Polymer density (g cm^{-3})	Equivalent weight (mg mequiv.$^{-1}$)	T_g (°C)
Nafion	5	1.989	1100	140
SPEEK	5	1.067	574	178

powder. The properties of solutions are summarized in Table 2. The mixtures were then sonicated for 1 h and were kept being mixed on a stirrer for 3 days. Each catalyst slurry was applied to PTFE-impregnated Toray 250 carbon paper (waterproof by 8 wt.% PTFE) by a spraying method. The carbon papers were dried in the oven at 100 °C to determine the amount of catalyst loading. The carbon papers sandwiched the membranes by hot pressing at 135 °C and 50 kgf cm^{-2} for 3 min. The electrodes used in this study were well laminated onto the carbon paper as shown in Fig. 5. The morphology of the electrodes and MEAs made in this study was investigated using a scanning electron microscope (JSM-849, JOEL). Surface of the electrodes was vacuum sputtered with a thin layer of Au/Pd prior to the analyses.

For determining the optimal configuration of electrodes based on the SPEEKs, the amount of the SPEEK ionomer binder was controlled to be 10, 20, 30 and 40 wt.% in electrodes. Table 3 summarizes the composition of the slurries and the porosity of the electrodes calculated by (i) densities of platinum, carbon, Pt/C, ionomer, solvent and water; (ii) concentrations of Pt/C and ionomer solution; (iii) assumption that each particle of carbon black has a spherical shape and its diameter is 30 nm. The density of Pt/C was calculated using the concentration of Pt/C, densities of Pt and carbon and was 3.50 g cm^{-3}. The tap density (i.e., apparent density) of Pt/C including Pt/C and pore was measured to be 0.50 g cm^{-3}. The porosity of electrodes were calculated as follows: (i) calculate the demanded amount of Pt/C; (ii) calculate the demanded amount of ionomer; (iii) calculate the volumes of
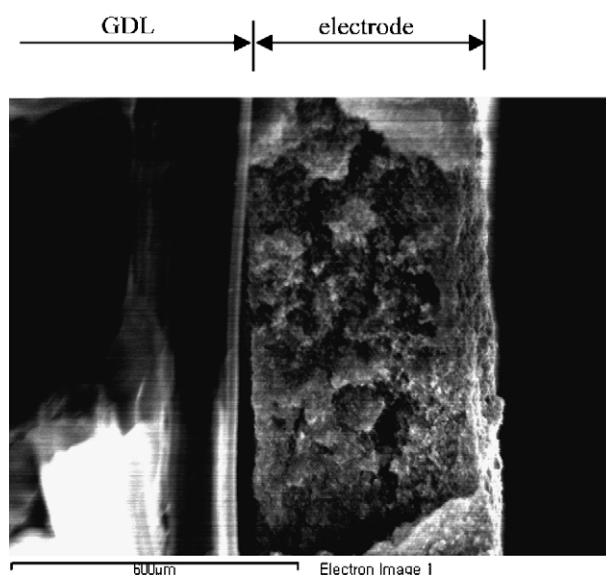
derived from the impedance value at zero phase angle, W the width of the potential sensing platinum wire and d the membrane thickness. The membranes for each measurement were prepared by the following procedures: (i) the samples were equilibrated in deionized water for 1 day and water on the surface of the samples was removed; (ii) the samples were placed in the vessel kept at various measurement conditions (i.e., temperature and relative humidity).

It is shown in Fig. 4 that the proton conductivity of the SPEEK and the Nafion® 112 membranes highly depend on the relative humidity. The proton conductivity of the SPEEKs with relative humidity is relatively lower than that of the Nafion® 112 despite the similar membrane resistance at a full hydration condition. This is because the Nafion® membranes enable to make more ion-rich domains, which allows the ions to migrate easier than the SPEEKs [20]. Although the proton conductivities of the SPEEKs are lesser than those of Nafion® membranes in all range of relative humidity, the difference in proton conductivity significantly narrows down above 70% of relative humidity due to the thinner thickness of SPEEK membranes. It is inferred that the MEAs using the SPEEK membranes might show similar PEMFC performances compared with one using the Nafion® 112 under the full hydration condition if properties of the electrodes containing a Nafion®- and a SPEEK-based ionomer are similar.

2.4. Fabrication and characterization of membrane-electrode assemblies (MEAs)

2.4.1. Fabrication of MEAs

Pt/C (40 wt.%, E-Tek, USA) was employed as a catalyst. The platinum loading for both anode and cathode was 0.4 mg cm^{-2}. The catalyst slurries for Nafion®-based and SPEEK-based MEAs were prepared by mixing Nafion® solution (5 wt.%, Sigma–Aldrich) in aliphatic alcohol and SPEEK ionomer solution (5 wt.%, lab.-made) in DMAc, respectively, with the catalyst

Fig. 5. Cross-sectional view of MEAs fabricated in this study by SEM (25,000 magnificence).

Table 3
The composition of catalyst slurries using the 5 wt.% SPEEK ionomer solution on the basis of an effective area of 100 cm^2

	Loading of ionomer binder (%)				
	10	20	30	40	45[a]
5 wt.% SPEEK (or Nafion[a]) ionomer solution (g)	0.22	0.5	0.86	1.33	1.64[a]
40 wt.% Pt/C (E-Tek) (g)	0.1	0.1	0.1	0.1	0.1
DMAc (or IPA[a]) (g)	9.68	9.40	9.04	8.57	8.26[a]
Porosity[b] (%)	80.5	74.0	65.7	54.5	65.1

[a] The 5 wt.% of a Nafion-based ionomer solution and isopropyl alcohol as a solvent were used.

[b] This value was calculated by using the following properties: (i) density of platinum (21.45 g cm^{-3}), carbon (2.25 g cm^{-3}), ionomers (see Table 2), solvents (0.782 g cm^{-3} for isopropyl alcohol; 0.937 g cm^{-3} for DMAc) and water (1.0 g cm^{-3}); (ii) tap density of Pt/C powder (0.50 g cm^{-3}); (iii) concentration of Pt/C (40 wt.%) and ionomer solution (5 wt.%); (iv) assumption that each particle of carbon black has a spherical shape and its diameter is approximately 30 nm.

Pt/C including and excluding pore; (iv) calculate the volume of dried ionomer binder; (v) calculate the porosity of the electrodes.

2.4.2. Electrical impedance spectroscopy (EIS)

EIS experiments for the fabricated MEAs were carried out in a single cell with the effective area of 10 cm^2. Bipolar plates in the single cell were made of graphite plates with gas channels. Two gold-coated copper end plates with attached heaters were used to clamp the graphite plates. Humidified fuel and oxidant gases were supplied by means of mass-flow controllers. A four-electrode system was used to measure the voltage between both end plates of the single cell and symmetric gas flow supply was fed into the cell using H$_2$ and air pre-humidified in a water chamber at 70 °C. The temperature of the single cell was kept at 75 °C. The impedance measurements were carried out using the aforementioned instruments (see the Section 2.3.5). The frequency range scanned was from 0.01 Hz to 1 MHz with oscillating voltage of 5 mV.

2.4.3. Cell performance

Prior to the PEMFC operation, the MEAs were fully hydrated by feeding N$_2$ pre-humidified in a water chamber into the single cell for about 4 h. During the operation, pre-humidified H$_2$ and air at 70 °C were fed into the anode and cathode, respectively. The temperature of the single test cell was kept at 75 °C. The stoichiometry of hydrogen to air was maintained to be 1.5/2 and the relative humidity 100/100%. Performance was evaluated by plotting the current–potential (I–V) polarization curves.

3. Results and discussion

In fabrication of MEAs, the amount of ionomer binder and Pt/C can optimize the configuration of their electrodes in consideration of gas permeability and a direct connection between catalyst and electrolyte except the gas diffusion layer. The ionomer binder, which is the same to electrolyte material, spreads out over the catalyst. It does not fully cover the catalyst, but makes a direct connection between catalyst and electrolyte for proton conduction as well as supports carbon particles impregnated by Pt (i.e., Pt/C) to form the electrode onto either the electrolyte or gas diffusion layer. This enables to promote 'three-phase contact' between reactant gas, electrolyte and electrode catalyst. The composition of ionomer binder and Pt/C

determines the porosity of electrodes in MEAs. The porosity might be a main parameter to optimize the three-phase contact. Evidently, the catalyst type [13,14] or pre-treatment conditions [21,22] may play an important role in determining electrode performance. However, their effects are excluded in this study.

The SPEEK-based electrodes with the different contents, 10, 20, 30 and 40 wt.% were prepared. The Nafion®-based electrode with the content of 45 wt.% was also prepared as a reference. It was selected to be the optimal content for the PEMFC performance in this study (not shown here). For the preparation of the SPEEK-based ionomer solution, DMF, DMSO, NMP, DMAc can be organic solvents which enable to dissolve SPEEK polymers prepared in this study. The previous study [23] reported that DMF enters in strong hydrogen bonding with sulfonic acid groups of SPEEK, reducing the number of protons available for charge transfer, which dramatically bring down the PEM conductivity and the SPEEK membranes prepared using DMAc showed better conductivity than DMF. In this study, DMAc was employed as a solvent for the SPEEK polymers. All of the electrodes prepared in this study contained the same catalyst loading of 0.4 ± 0.03 mg Pt cm^{-2} at both anode and cathode. As summarized in Table 3, porosity of the electrodes decreases with an increase in the SPEEK-based ionomer content. It is noted that porosity can be different despite the similar loading of the SPEEK- and Nafion®-based ionomer. In fact, the SPEEK-based ionomer loading of 30% and the Nafion®-based one of 45% have similar porosity. In other words, consideration in terms of ionomer content for expecting electrode configuration is not enough because the ionomers used for preparing electrodes have different properties (e.g., density, equivalent weight) as summarized in Table 2.

As discussed earlier, the SPEEK-based ionomer content of 30% and the Nafion®-based ionomer content of 45% have similar porosity. This can be confirmed roughly in Fig. 6 which shows the surface views of the electrodes prepared by the simulated catalyst slurries. The much agglomeration for the SPEEK-based electrodes was taken place as the amount of ionomer binder increased. Accordingly, the porosity decreased with increasing the amount of ionomer binder. It is inferred that the electrochemical properties of the MEAs and the performance of the PEMFC may significantly depend on porosity in accordance with the three-phase contact concept.
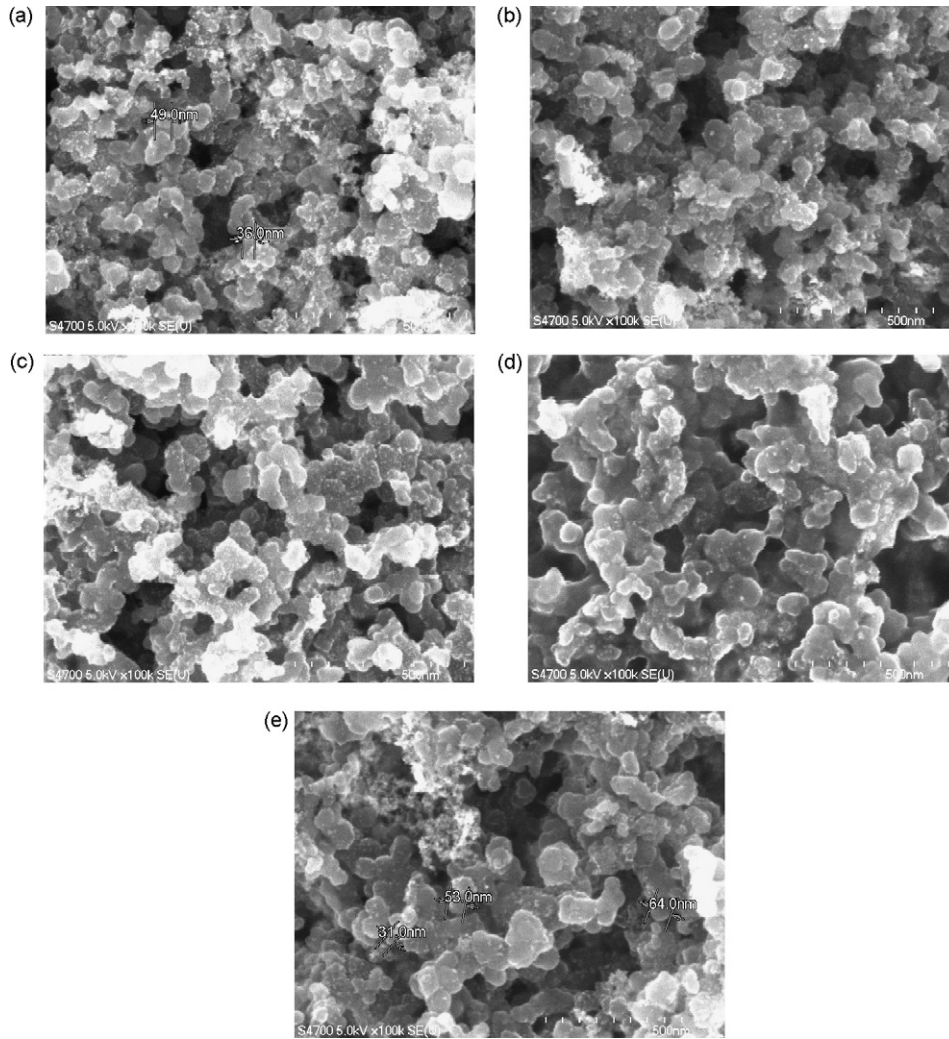
Fig. 6. Surface views of electrodes in the fabricated MEAs with ionomer contents and types of (a) 10% (SPEEK), (b) 20% (SPEEK), (c) 30% (SPEEK), (d) 40% (SPEEK), and (e) 45% (Nafion®) by SEM (100,000 magnificence).

To investigate the effects of porosity on the electrochemical properties of the SPEEK-based electrodes, their electrochemical impedance spectra were measured in the experimental setup as shown in Fig. 7(a). Fig. 7(b) shows a typical complex plane representation of an electrochemical impedance spectroscopy (EIS). All of the impedance spectra have two regions with frequency: one is the semicircle arising from the resistance of the electrolyte membrane, electrodes and charge transfer processes at high frequencies and another is the Warburg impedance (linear behavior) arising from mass-transfer limitation, i.e., diffusion, at low frequencies. These properties of the MEAs suggest that the system can be described electrically by the equivalent circuit illustrated as follows:
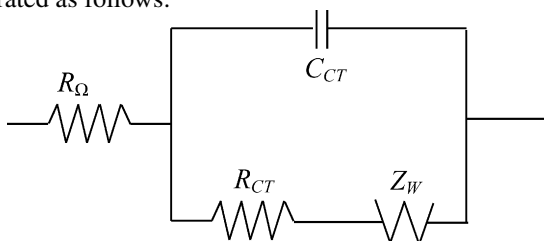
where R_Ω is the resistance of the electrolyte membrane and electrodes (i.e., anode and cathode), R_{CT} and C_{CT} the charge transfer resistance and capacitance, respectively, and Z_W is the Warburg impedance. The impedance data obtained from MEAs with different ionomer contents and types were quantitatively analyzed by the equivalent circuit. Impedance data were processed by ZSimpWin (Princeton Applied Research, USA) software employing a down-hill simplex fitting method. More details are found elsewhere [24]. The Nafion®-based MEA has the smaller semicircle diameter than the SPEEK-based one due to higher conductivity of the electrolyte and ionomer binder. A decrease in semicircle diameter at high frequencies is clearly shown with ionomer content. As a result of the quantitative analyses, the resistances (R_Ω) of the electrolyte membrane and electrodes were 0.0429, 0.0273, 0.0214 and 0.0211 $\Omega\,cm^{-2}$ for the ionomer contents of 10, 20, 30 and 40%, respectively. In case of the MEA using the Nafion®-based ionomer, it was 0.0198 $\Omega\,cm^{-2}$ due to the higher proton conductivity. The resistance (R_Ω) decreased with an increase in the SPEEK content. However, a slight decrease in the resistance for the 40% SPEEK-ionomer content arises from the more coverage of ionomer on
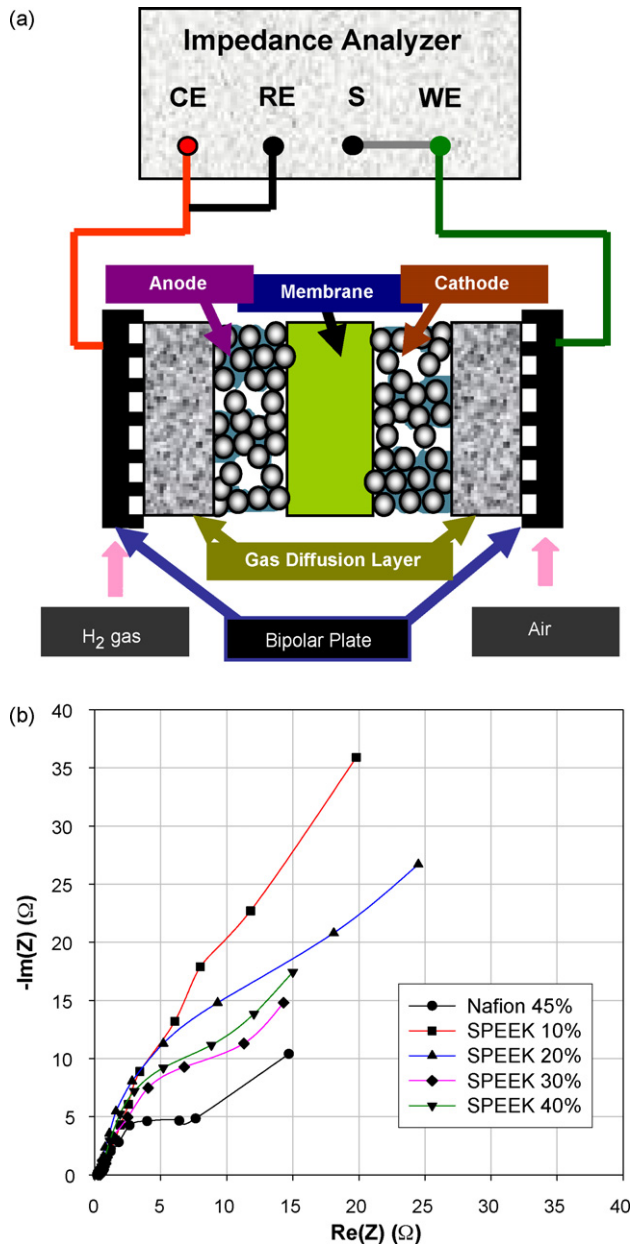
Fig. 7. Measurement of Nyquist plots of PEMFC single cells using the MEAs fabricated in this study: (a) a measurement set-up; (b) Nyquist plots of the MEAs with different ionomer contents and types (cell temperature of the single cell: 75 °C; stoichiometry of H$_2$/air: 1.5/2 under ambient pressure; relative humidity of anode/cathode: 100/100%).

Pt/C particles. In other words, more ionomer connects the ionic conduction well, but slightly blocks the electronic conduction in that the charge transfer resistance (CTR) increases. The CTRs (R_{CT}) in the equivalent circuit were 4.8, 2.6, 1.6 and 1.7 Ω cm^{-2} for the ionomer contents of 10, 20, 30 and 40%, respectively (when CTR is 0.56 Ω cm^{-2} in case of the Nafion® ionomer). The CTR decreased with an increase in the SPEEK content except the 40% SPEEK-ionomer content. The CTR means how well electronic conducting pathway is built up in catalyst layers. Thus, the behavior (i.e., a slight increase in CTR for the 40% SPEEK-ionomer content) was due to the high loading of the SPEEK ionomer, which blocked the catalyst sites as an elec-

tronic insulator. The blockage resulted in reducing the electronic conductivity and gas permeability in the catalyst layer. The CTR value of the Nafion® ionomer (i.e., 0.56 Ω cm^{-2}) was lower than all cases of the SPEEK ionomer despite high loading of the Nafion® ionomer. However, density of the Nafion® ionomer is higher than the SPEEK one. The high loading does not result in much more occupancy in pore volume of catalyst layers as seen in Table 3. The slightly more blockage can be confirmed by the results of dielectric spectra as shown in Fig. 8. The Nafion®-based electrodes resulted in less tortuous pathway for proton. This property can be quantitatively analyzed by a dielectric loss spectroscopy which represents the following equation [25]:
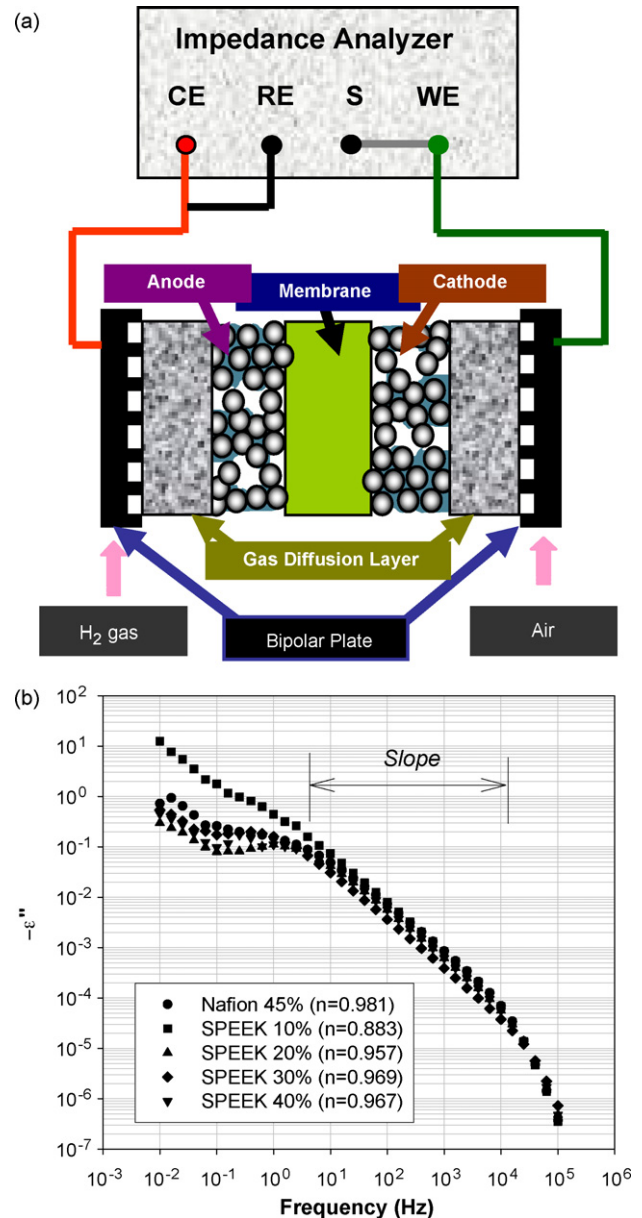
$$-\varepsilon'' = a \cdot f^n \qquad (3)$$

Fig. 8. Measurement of dielectric spectra of PEMFC single cells using the MEAs fabricated in this study: (a) a measurement set-up; (b) dielectric spectra of the MEAs with different ionomer contents and types (cell temperature of the single cell: 75 °C; stoichiometry of H$_2$/air: 1.5/2 under ambient pressure; relative humidity of anode/cathode: 100/100%).

Fig. 9. The *I–V* polarization curves of unit cells using the fabricated MEAs with different ionomer contents and types (cell temperature of the single cell: 75 °C; stoichiometry of H_2/air: 1.5/2 under ambient pressure; relativ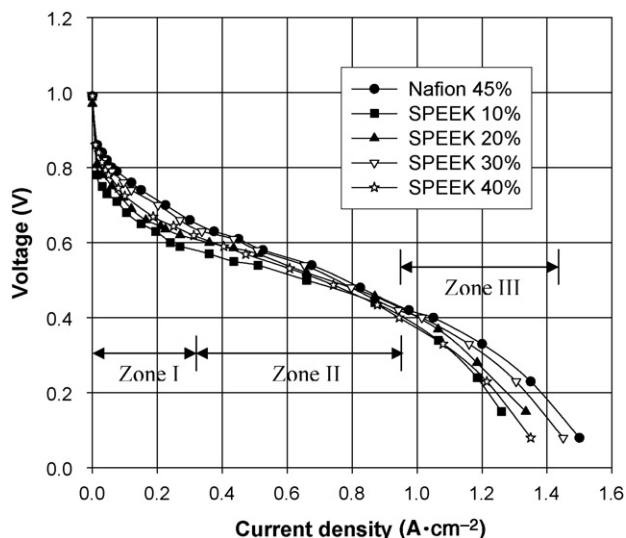e humidity of anode/cathode: 100/100%). "*Zone I*" arises from the major influence of charge transfer kinetics, "*Zone II*" the major influence of ohmic resistance and "*Zone III*" the major influence of mass transport.

where *a* is the arbitrary constant, *f* the frequency, ε'' the imaginary dielectric constant and *n* is the degree of tortuosity of the conductive path. The results of fitting are shown in Fig. 8(b). The *n* values for the SPEEK ionomer were in the range of 0.8–1.0, which increased with an increase in the ionomer content except the 40% SPEEK-ionomer content. It indicates that the ionic transport pathway is less tortuous as the ionomer content increases. At 40% ionomer content, *n* value slightly decreased. Thus, in accordance of the CTR result, ionomer blockage became pronounced and resulted in being more tortuous. It is expected that it might influence the fuel cell performance.

All of the MEAs were also tested at the same operating condition. Fig. 9 shows the results of the single cell tests. Noting that the Nafion® ionomer content of 45% was a critical value, a decrease in performance above the Nafion® ionomer of 45% was due to a decrease in gas permeability as well as the aforementioned reason such as ionomer blockage. Thus, it can be expected that the performance at the SPEEK ionomer content of 40% might decrease due to the lowered porosity as well as more ionomer blockage than the Nafion® ionomer of 45% as discussed earlier. The CTR (R_{CT}) and the resistance (R_{Ω}), however, decreased gradually up to the SPEEK ionomer content of 30%. Accordingly, the performances at Zone I and II gradually improved due to the lowered CTR (R_{CT}) and the resistance (R_{Ω}), respectively. As shown in Fig. 9, the performances at the SPEEK ionomer contents of 40% decreased due to the aforementioned reasons. In addition, a decrease in the performance at Zone III arises from the lowered gas permeability. The performance for the SPEEK ionomer content of 30% (the porosity of 65.7%) was similar to the Nafion® ionomer of 45% (the porosity of 65.1%) at the similar porosity of electrodes.

4. Concluding remarks

So far, the study on optimizing catalyst layer has been mainly carried out in recent years, especially, for the optimum amount of Nafion® ionomer in the catalyst layer. However, there are so many types of commercially available Nafion® ionomers in markets, which have individual properties. In particular, fabrication of their MEAs using newly prepared membranes also has the same problem to have no critical indicator. In addition, newly prepared polymers have a bunch of different properties by their synthesis methods and conditions even though they are originated from the same main polymer. Thus, it was suggested that the porosity of the electrode layers was used as a controlling parameter so as to find out the optimal slurry composition and finally to give the optimal electrode configuration.

In this study, the hydrocarbon-type electrolyte membrane using SPEEK was prepared as a proton-conducting membrane. For the application of polymer electrolyte membrane fuel cells, it was needed to fabricate new membrane-electrode assemblies, and accordingly to optimize electrode configuration since the SPEEK should be also used as an ionomer binder to prepare catalyst slurries. According to the results of SEM and porosity calculation, the electrodes using 45 and 30% loading of Nafion® and SPEEK ionomer, respectively, might have the similar electrode configuration in terms of porosity. Improvement on electrochemical properties (i.e., impedance spectra and *I–V* polarization curves) was shown up to the SPEEK ionomer content of 30% in the catalyst layers. The Nafion® and SPEEK-based MEAs with the similar porosity showed the similar electrochemical properties and finally the similar fuel cell performance because the porosity control enables to provide the same volume of ionomer to electrodes, then the weight of ionomer calculated by its density and then the approximately same equivalent mole of sulfonic acid group. It is believed that a porosity control suggested in this study can be one of main parameters to design MEA's electrodes prepared by various polymers.

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