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Sulfonated poly(ether ether ketone) as an ionomer for direct methanol fuel cell electrodes

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ABSTRACT

Sulfonated poly(ether ether ketone) has been investigated as an ionomer in the catalyst layer for direct methanol fuel cells (DMFC). The performance in DMFC, electrochemical active area (by cyclic voltammetry), and limiting capacitance (by impedance spectroscopy) have been evaluated as a function of the ion exchange capacity (IEC) and content (wt.%) of the SPEEK ionomer in the catalyst layer. The optimum IEC value and SPEEK ionomer content in the electrodes are found to be, respectively, 1.33 meq. g⁻¹ and 20 wt.%. The membrane-electrode assemblies (MEA) fabricated with SPEEK membrane and SPEEK ionomer in the electrodes are found to exhibit superior performance in DMFC compared to that fabricated with Nafion ionomer due to lower interfacial resistance in the MEA as well as larger electrochemical active area. The MEAs with SPEEK membrane and SPEEK ionomer also exhibit better performance than that with Nafion 115 membrane and Nafion ionomer due to lower methanol crossover and better electrode kinetics.

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1. Introduction

Direct methanol fuel cells (DMFC) are drawing much attention as a power source for portable devices due to their potential advantages compared to lithium ion batteries [1,2]. They can provide continuous power without requiring an electrical outlet to recharge them. DMFC currently employs Nafion as the proton conducting electrolyte membrane, but Nafion is expensive. More importantly, the high methanol permeability through the Nafion membrane, resulting in a high crossover of methanol fuel from the anode to the cathode, remains a serious problem to realize a widespread commercialization of the DMFC technology. In this regard, there has been intensive research on the development of alternative membranes that can lower the cost and suppress methanol crossover. However, with the new membranes, Nafion is often used as an ionomer in the catalyst layer to fabricate the membrane-electrode assemblies (MEAs). The incompatibility between the polymeric membrane and the ionomer in the catalyst layer can lead to high interfacial resistance and performance loss in fuel cells [3,4]. While Zhao and co-workers [5–7] have suggested different hot-pressing methods and anode structures to have better interfacial contact in MEAs fabricated with Nafion membrane and Nafion ionomer in the catalyst layer (electrode ionomer), it is desirable to use the

same or similar polymers as both the membrane and the electrode ionomer to have a better compatibility at the interface between the membrane and electrode ionomer.

There have been a few reports on the use of alternative polymers as electrode ionomer in proton exchange membrane fuel cells (PEMFC). Mukerjee and co-workers [8] have attempted to prepare electrodes containing sulfonated poly(arylene ether sulfone)s (SPES) as electrode ionomer for PEMFC. It was shown that the fuel cell performance of the MEAs fabricated with SPES ionomer and SPES membrane is lower than that fabricated with Nafion ionomer and Nafion membrane due to poor kinetics of oxygen reduction reaction with the electrodes containing SPES ionomer. Recently, sulfonated poly(ether ether ketone) (SPEEK) has been explored as electrode ionomer for PEMFC and DMFC with SPEEK membrane [9,10]. However, the performance of the MEA fabricated with SPEEK membrane and SPEEK ionomer was lower than that fabricated with Nafion membrane and Nafion ionomer. This could be related to the lack of effective methods for the dispersion of SPEEK ionomer in the catalyst ink as well as a lack of optimization of the parameters like ion exchange capacity (IEC) and content (wt.%) of the SPEEK ionomer in the electrode.

Considering that SPEEK is known to be thermally stable and it exhibits lower methanol crossover than Nafion in DMFC [11–13], we present here the optimization of SPEEK as an ionomer in the catalyst layer, employing SPEEK as the membrane. The impregnation of SPEEK ionomer into the catalyst electrode was carried out by completely dispersing SPEEK in a water/alcohol based catalyst ink.

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The performance of the MEAs is evaluated by cyclic voltammetry, ac impedance analysis, and polarization studies in single cell DMFC as a function of the IEC and weight% of the SPEEK ionomer in the electrodes.

2. Experimental

2.1. Membrane preparation and characterization

A series of SPEEK samples were prepared by sulfonating commercially available poly(ether ether ketone) (PEEK450 PF, Victrex) with concentrated sulfuric acid at room temperature for different periods of time [11]. 5 g of PEEK powder was dissolved in 150 mL of concentrated sulfuric acid (95.9%, Fisher Scientific) by vigorous stirring at room temperature for a specified time (25–40 h). After the sulfonation is complete, SPEEK was isolated by precipitation in ice-cold water while stirring, and the precipitated SPEEK was washed thoroughly with de-ionized water and dried at 60 °C for 24 h. The IEC was measured by soaking 0.1–0.2 g of SPEEK in 30 mL of 2 M NaCl solution for 24 h, followed by titrating the solution with 0.05 N NaOH solution using phenolphthalein as an indicator. The SPEEK membranes were prepared by dissolving SPEEK in *N,N'*-dimethylacetamide (DMAc) and casting the resultant solution onto a glass plate, followed by drying at 90 °C.

Equilibrium water swelling W_s was determined at room temperature from the weight gain by first measuring the weight of the wet membrane (during wetting with water any residual DMAc solvent present in the membrane might be removed) and then the weight of the dry membrane as

$$W_s = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

where W_{wet} and W_{dry} are, respectively, the weight of the wet and dry membranes. Proton conductivity of the water-equilibrated membranes was measured in the lateral direction (i.e. in plane) using an open window framed two platinum electrode cell [14] with an HP 4192A LF impedance analyzer.

2.2. MEA fabrication and electrochemical evaluation

SPEEK was first dissolved in *N,N*-dimethylformamide (DMF) and a desired amount of the SPEEK/DMF solution (14.5 wt.%) was transferred into a water/iso propyl-alcohol (IPA) mixture and sonicated for 30–50 min until the SPEEK polymer was solubilized completely in the water/IPA mixture. The resultant homogeneous solution was mixed with the catalyst powder, followed by sonication for 1–2 h. The catalyst layer was prepared by brushing the anode or cathode catalyst inks onto a gas diffusion layer (A-6 ELAT/SS/NC/V2 carbon cloth E-TEK Inc.). This alcohol/water based catalyst-SPEEK ink preparation provided an easy coating of the catalyst ink onto the gas diffusion layer due to the use of a lower amount of aprotic organic solvents like DMF (9 wt.% DMF in the catalyst ink). In the case of electrodes containing Nafion ionomer, the catalyst powder was dispersed in a water/IPA mixture, followed by mixing with Nafion solution by sonication for 1 h and painting the resultant ink onto the gas diffusion layer. The anode catalyst layer consisted of 40 wt.% 1:1 Pt–Ru alloy on Vulcan XC-72 carbon black (ETEK Inc.) with either SPEEK or Nafion ionomer. The cathode catalyst layer consisted of 20 wt.% platinum on carbon black (ETEK Inc.) with either SPEEK or Nafion ionomer. The Pt–Ru and Pt loadings in the anode and cathode were 1.0 mg cm⁻². For MEA fabrication, the anode and cathode electrodes were hot-pressed onto either Nafion or SPEEK membrane. Hot-pressing conditions were 140 °C, 80 psi for 2.5 min and 100 °C, 40 psi for 3 min, respectively, with Nafion and SPEEK membranes. The resultant MEAs were

soaked in 1 M H₂SO₄ solution and rinsed with de-ionized water to remove any remaining organic solvent and convert the SPEEK ionomer in the electrodes into acid form completely. Fuel cell tests were performed using a single cell hardware (active area of 5 cm²) at 65 °C with 1 M methanol at a flow rate of 2.5 mL min⁻¹ and humidified oxygen at a flow rate of 200 mL min⁻¹ without back-pressure.

Methanol crossover was determined by a voltammetric method as reported elsewhere [15]. The measurement was carried out by supplying methanol solution at a flow rate of 2.5 mL min⁻¹ into the anode side of the MEA, while the cathode side was kept in an inert humidified N₂ atmosphere. By applying a positive potential at the cathode side, the flux rate of permeating methanol was determined by measuring the steady-state limiting current density resulting from complete electro-oxidation at the membrane/Pt catalyst interface at the cathode side.

Impedance analysis was performed with a Volta Lab 80 potentiostat (PGZ 402 Universal potentiostat) at room temperature. The anode and cathode were supplied, respectively, with 1 M methanol (at a flow rate of 2.5 mL min⁻¹) and hydrogen (at a flow rate of 10 mL min⁻¹). The cathode was used as a dynamic hydrogen electrode (DHE) for the measurement of anode impedance. The frequency range was from 100 mHz to 5 kHz and the amplitude of the sinusoidal current signal was 5 mV. Cyclic voltammetry was also performed using the Volta Lab 80 potentiostat at room temperature. The anode (working electrode) and cathode were supplied, respectively, with humidified nitrogen and hydrogen at a flow rate of 10 mL min⁻¹. The potential was scanned between –0.15 and 1.2 V at a sweep rate of 50 mV s⁻¹. The impedance and cyclic voltammetry data obtained at room temperature were analyzed to explain the DMFC performance at 65 °C with an assumption that the trends in the impedance and cyclic voltammetry data are the same regardless of temperature [16].

3. Results and discussion

3.1. Effect of the ion exchange capacity of SPEEK ionomer

A series of SPEEK polymers was prepared by a sulfonation of PEEK using sulfuric acid for different reaction times. Their IEC, proton conductivity, and water swelling values are given in Table 1. It is seen that the IEC of SPEEK increases from 1.27 to 1.51 meq.g⁻¹ as the sulfonation time increases from 26 to 37 h. The proton conductivity of the SPEEK membranes at room temperature also increases from 0.05 to 0.09 S cm⁻¹ with sulfonation time. This proton conductivity values presented here are higher than those reported previously by our group [11]. The lower proton conductivity value in our previous study is due to the contact resistance between the membrane and the electrodes as well as due to a decrease in proton conductivity in the water vapor environment as the measurement was carried out in the transverse direction (i.e. through-plane) using a closed window two stainless steel electrode cell with water vapor at each relative humidity. In the case of water swelling at room temperature, while the SPEEK membranes with IECs values of 1.27–1.33 meq.g⁻¹ exhibit water swelling comparable to that of Nafion, the SPEEK membranes with IEC values of 1.37–1.51 meq.g⁻¹ show greater swelling than Nafion. Also, the water swelling values presented here are higher than those reported previously by our group [11]. This could be related to the residual DMAc solvent present in the dry membrane in our previous study as it involved first the measurement of the weight of the dry membrane prepared from DMAc solution and then the weight of the wet membrane in contrast to the procedure described in Section 2.

Table 1
Characterization data of the SPEEK membranes

Sample ^a	Sulfonation time (h)	IEC (meq. g ⁻¹)	Proton conductivity (S cm ⁻¹)	Water swelling (%)
SPEEK 1.27	25	1.27	0.046	35.0
SPEEK 1.33	31	1.33	0.050	36.1
SPEEK 1.37	33	1.37	0.062	45.1
SPEEK 1.51	37	1.51	0.091	56.3
Nafion 115	–	0.92	0.090	34.0

^a The numbers refer to the IEC value for each SPEEK sample.

For the use of the sulfonated polymer as an ionomer in the electrode, the water swelling of sulfonated polymer needs to be taken into account carefully to prevent the electrodes containing sulfonated polymer from being flooded under the fuel cell operating environment. Although impregnation of a sulfonated polymer with a high IEC into the catalyzed electrode may be preferred with respect to ensuring good proton transfer capability in the electrode, the electrode could suffer from flooding during fuel cell operation due to the excessive swelling of the SPEEK ionomer, resulting in a hindrance in the access to oxygen and removal of products (carbon dioxide or water) from the catalyst layer. To investigate the effect of the IEC of the SPEEK ionomer in the electrodes on the fuel cell performance, a series of electrodes (anode and cathode) containing SPEEK ionomer with different IECs (1.27–1.51 meq. g⁻¹)

was prepared and evaluated in DMFC. The MEAs were fabricated with Nafion 115 to rule out the variations in fuel cell performance that could be caused by the differences in the thickness or IEC values of the SPEEK membrane. Fig. 1(a) shows the dependence of the DMFC performances on the IEC values of the SPEEK ionomer impregnated into both the anode and cathode electrodes. The content of SPEEK ionomer was kept at 20 wt.% in these experiments. As seen in Fig. 1(a), the fuel cell performance improves slightly as the IEC value of the SPEEK ionomer increases from 1.27 to 1.33 meq. g⁻¹, which could be attributed to better proton conductivity in the catalyst layers. However, a decrease in DMFC performance is seen on using SPEEK ionomers with IEC > 1.33 meq. g⁻¹, which is due to a higher water swelling (45–56%) observed with SPEEK having IEC values of 1.37–1.51 meq. g⁻¹ compared to that found with Nafion (34%) as seen in Table 1. This indicates that the impregnation of SPEEK ionomers with high IEC values (>1.33 meq. g⁻¹) into the electrodes may result in a decrease in the hydrophobic properties of the electrodes and consequent limitations in the transfer of reactants and products through the catalyst layer.

3.2. Effect of SPEEK ionomer content

Fig. 1(b) compares the performances in DMFC as a function of SPEEK ionomer (IEC = 1.33 meq. g⁻¹) content in both the anode and cathode electrodes. For a reference, the fuel cell performance of a MEA fabricated with the Nafion ionomer in the catalyst layers is also shown. The Nafion content in the anode and cathode catalyst layers was 30 wt.%, which is known as an optimum content for carbon supported catalyst electrodes [17,18]. As seen in Fig. 1(b), the MEAs with 20 or 25 wt.% of SPEEK ionomer in the catalyst layers show better performance than that with 30 wt.% Nafion ionomer although a mass transfer limitation at high cur-

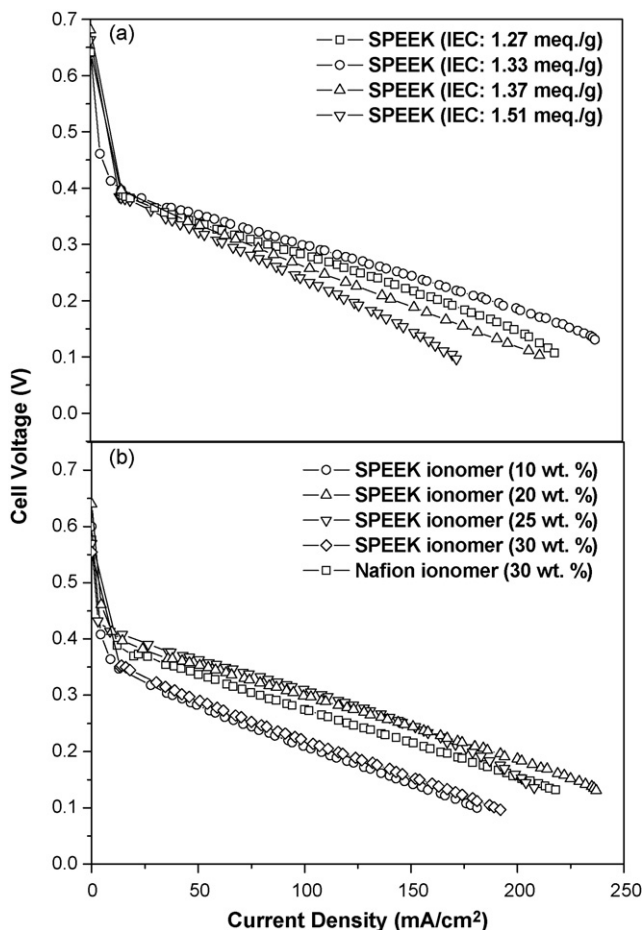


Fig. 1. Variations of the performances in DMFC of the MEAs fabricated with Nafion 115 membrane and SPEEK ionomer as a function of (a) the IEC value of the SPEEK ionomer with a constant 20 wt.% ionomer and (b) SPEEK ionomer content with a constant IEC of 1.33 meq. g⁻¹. The wt.% values in (b) refer to the amount of SPEEK ionomer in the electrodes. Methanol concentration: 1 M, cell temperature: 65 °C, and humidified oxygen flow rate: 200 Sccm.

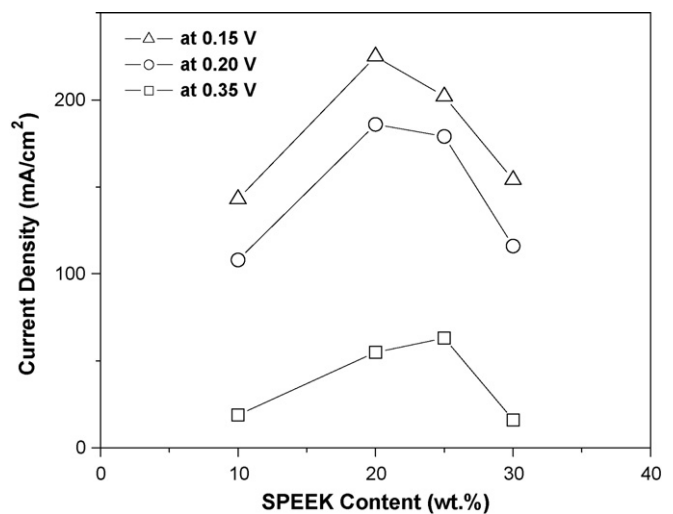


Fig. 2. Variations of the current density with SPEEK content (IEC = 1.33 meq. g⁻¹) at different cell voltages.

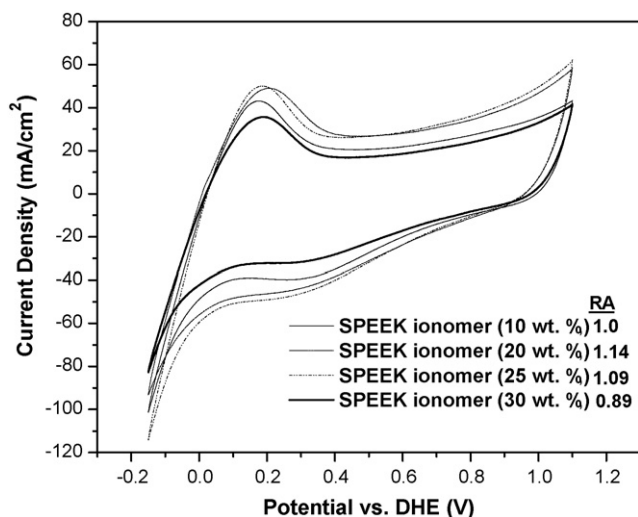


Fig. 3. Cyclic voltammograms of the anode electrodes having various SPEEK ionomer ($\text{IEC} = 1.33 \text{ meq. g}^{-1}$) content. The wt.% values refer to the amount of SPEEK ionomer in the electrodes. The relative hydrogen desorption peak areas (RA) are also indicated for each ionomer content.

rent densities is observed with 25 wt.% SPEEK ionomer. On the other hand, relatively poor performance is seen when the SPEEK ionomer content is too low (10 wt.%) or too high (30 wt.%). To have a better comparison, the current densities at different cell voltages are displayed in Fig. 2 as a function of SPEEK ionomer ($\text{IEC} = 1.33 \text{ meq. g}^{-1}$) content in the catalyst layers. As seen, the current density at a given voltage increases as the loading of the SPEEK ionomer increases from 10 to 20 or 25 wt.% and then decreases with further increase in SPEEK ionomer content. This suggests that the proton conductivity in the catalyst layer is a critical factor in determining the fuel cell performance particularly at low ionomer content. At higher cell voltages (0.35 V), the current density increases up to 25 wt.% SPEEK ionomer and then decreases at 30 wt.% SPEEK ionomer, while at lower cell voltages (0.15 and 0.2 V), the current density increases up to 20 wt.% SPEEK ionomer and then decreases. The latter is because of the water flooding in the catalyst layer on drawing higher current densities (i.e. at lower cell voltages).

Fig. 3 displays the cyclic voltammograms of the anode electrodes as a function of SPEEK ionomer ($\text{IEC} = 1.33 \text{ meq. g}^{-1}$) content in the electrodes. The relative hydrogen desorption peak areas (RA) determined from the cyclic voltammograms are also indicated in Fig. 3. The hydrogen desorption peak area obtained with the anode can be interpreted as the electrochemical active area of the catalyst layer in the electrode where methanol oxidation takes place [16,19]. As seen in Fig. 3, the hydrogen desorption peak area increases initially up to 20 wt.% SPEEK ionomer and then decreases. This demonstrates that the electrochemical active area of the catalyst layer is enlarged by adding SPEEK ionomer up to 20 wt.%, while further loading of the SPEEK ionomer, which is an electrical insulator, results in a lowering of the electrochemical active area due to a decrease in the electrical conductivity of the catalyst layer as well as due to the coverage of the active sites by SPEEK ionomer [9,16].

Fig. 4(a) displays the Nyquist plots obtained from the impedance measurements of the MEAs containing different amounts (10–30 wt.%) of SPEEK ionomer ($\text{IEC} = 1.33 \text{ meq. g}^{-1}$) in the electrodes. The ohmic resistance determined from the intercept of the real Z-axis at high frequency includes membrane resistance, interfacial resistance, and cell electronic resistance, which includes the electronic resistances of the electrode and the cell hardware (flow fields and current collectors). The interfacial resistance can be estimated by subtracting the membrane resistance from the

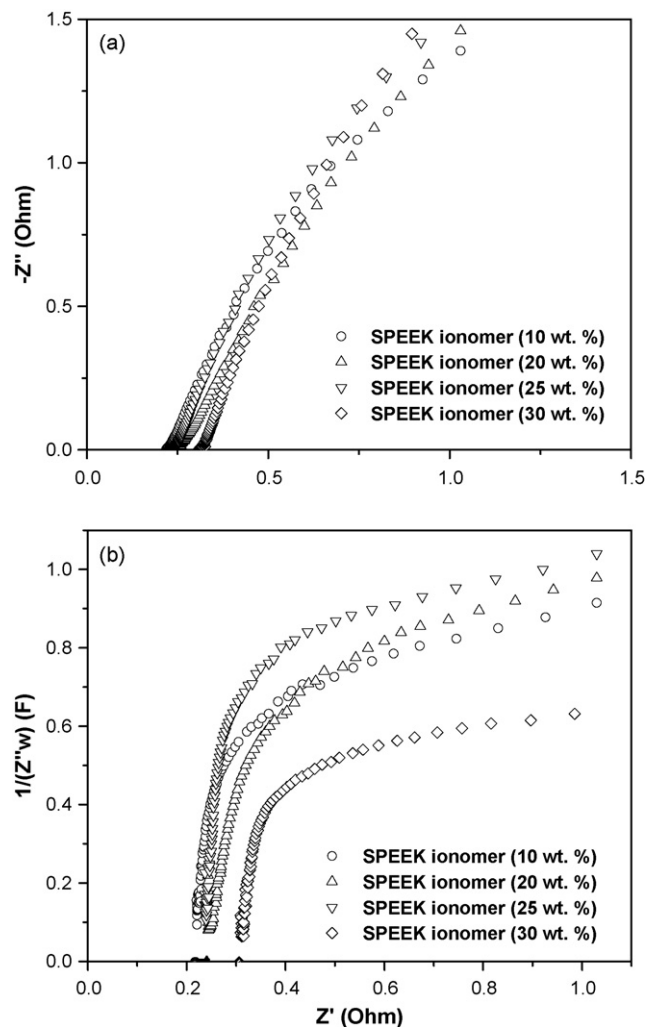


Fig. 4. Nyquist (a) and capacitance (b) plots obtained with the anode electrodes having various SPEEK ionomer ($\text{IEC} = 1.33 \text{ meq. g}^{-1}$) contents. The wt.% values refer to the amount of SPEEK ionomer in electrodes.

ohmic resistance of the MEA based on the assumption that the cell electronic resistance is constant and negligibly small [3,9]. Since Nafion 115 was employed as the membrane in all cases, the membrane resistance is constant for all the MEAs and so the interfacial resistance between the membrane and electrode is the factor that influences the high frequency ohmic resistance. From the Nyquist plots, the ohmic resistance determined from the intercept of the real Z-axis at high frequency increases with SPEEK ionomer content. This suggests that the interfacial resistance between the Nafion membrane and the electrodes containing SPEEK ionomer increases with SPEEK ionomer content due to the incompatibility between the Nafion membrane and the SPEEK ionomer in the electrode. The incompatibility between the membrane and ionomer in the electrodes results in poor interfacial contact and hindrance to proton transfer at the interface between the membrane and the electrodes. This is supported by the fact that the adhesion between Nafion membrane and the electrodes became worse (on examining the MEAs after the DMFC test) as the SPEEK ionomer content in the electrodes increases. This can be attributed to the different degrees of swelling for the two incompatible polymers (for example, 40 and 110% water swelling at 65°C , respectively, for Nafion 115 and SPEEK films). It can be concluded, as already shown in Fig. 1(b), that the improvement in the fuel cell performance as the SPEEK ionomer content increases from 10 to 25 wt.% is primarily due to an expan-

sion of the electrochemical active area in the catalyst layer, whereas the decline in fuel cell performance at 30 wt.% SPEEK ionomer content is a consequence of the combined effects of the decreased electrochemical active area of the electrodes and the relatively high interfacial resistance of the MEA (see Figs. 3 and 4(a)).

Fig. 4(b) shows the capacitance plots of the anode electrodes as a function of the SPEEK ionomer ($\text{IEC} = 1.33 \text{ meq. g}^{-1}$) content. The limiting capacitance determined from the low frequency plateau in the capacitance plot is proportional to the electrochemically effective interfacial area between the catalyst particles and the ionomer, where an electric double layer is formed [20,21]. As seen in Fig. 4(b), the limiting capacitance increases gradually as the SPEEK content increases from 10 to 25 wt.% and then drops drastically at 30 wt.% SPEEK ionomer. This implies that the interfacial area between the catalyst particles and the SPEEK ionomer increases with SPEEK ionomer content up to 25 wt.%, and decreases upon further increase in SPEEK ionomer content (30 wt.%) as the latter does not lead to any further increase in interfacial area but only results in a decrease in the electrical conductivity of the catalyst layer due to the excessive loading of the SPEEK ionomer (electrical insulator).

3.3. Characterization of MEAs with SPEEK membrane

To investigate the dependence of the fuel cell performance of SPEEK membranes on the types of ionomer (SPEEK vs. Nafion) used in the electrodes, the MEAs consisting of SPEEK membrane and either SPEEK or Nafion ionomer in the electrodes were prepared and characterized in DMFC. The polarization curves of such MEAs are displayed in Fig. 5. The SPEEK membrane used was kept identical in all the MEAs with a constant thickness of $90 \mu\text{m}$ and a constant IEC of 1.51 meq. g^{-1} . As seen in Fig. 5, the MEA with SPEEK ionomer (20 wt.% and $\text{IEC} = 1.33 \text{ meq. g}^{-1}$) in the electrodes exhibits distinctly better performance than that with Nafion ionomer (30 wt.%). To understand the origin of the differences in the fuel cell performances of the different MEAs, ac impedance spectroscopy was performed with the MEAs to evaluate their ohmic resistances and limiting capacitances. Fig. 6(a) shows the Nyquist plots obtained with the MEAs containing SPEEK membrane ($\text{IEC} = 1.51 \text{ meq. g}^{-1}$ and thickness = $90 \mu\text{m}$) and either SPEEK (20 wt.% and $\text{IEC} = 1.33 \text{ meq. g}^{-1}$) or Nafion (30 wt.%) ionomer in the electrodes. Using the ohmic resistance determined from the intercept of the real Z -axis in the high frequency range, the esti-

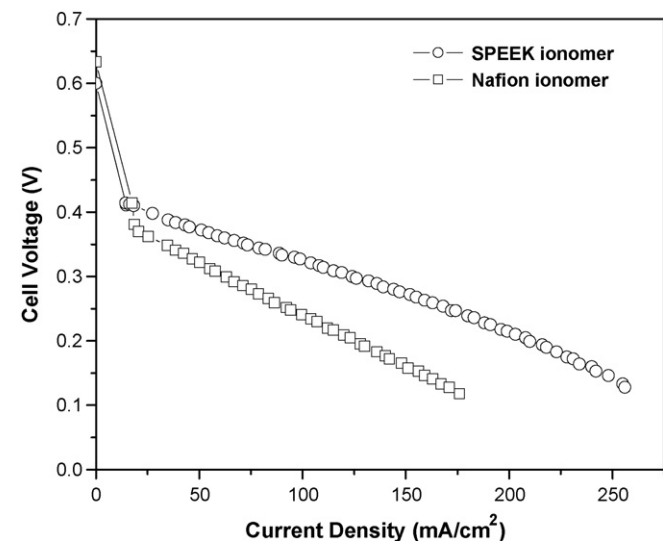


Fig. 5. Comparison of the performances in DMFC of the MEAs fabricated with the SPEEK membrane ($\text{IEC} = 1.51 \text{ meq. g}^{-1}$ and thickness = $90 \mu\text{m}$) and 20 wt.% SPEEK ionomer ($\text{IEC} = 1.33 \text{ meq. g}^{-1}$) or 30 wt.% Nafion ionomer in the electrodes.

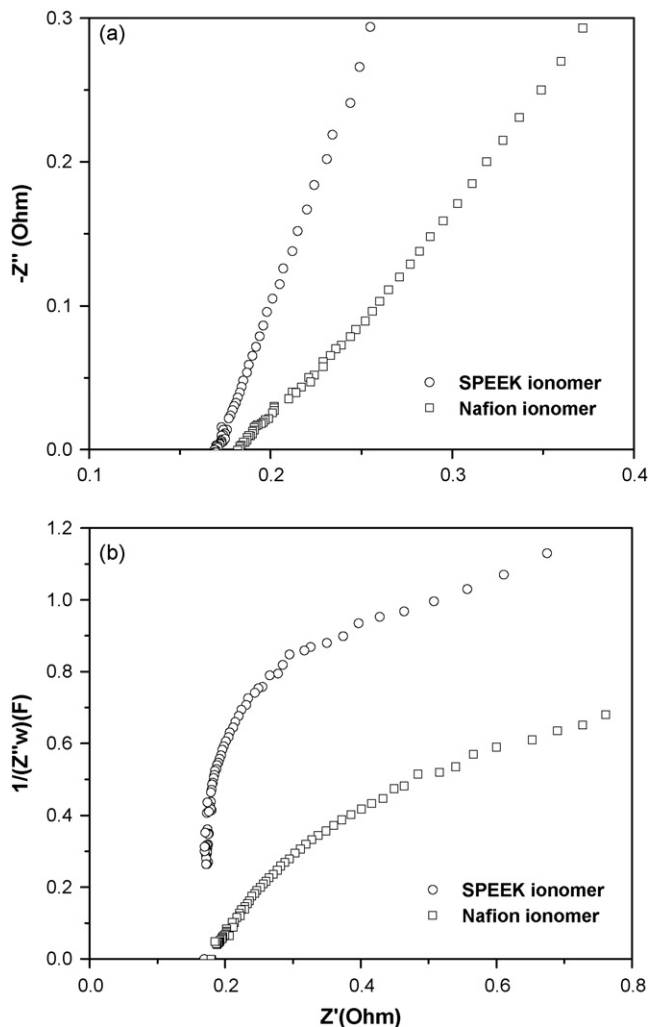


Fig. 6. Nyquist (a) and capacitance (b) plots obtained with the anode electrodes of the MEAs fabricated with SPEEK membrane ($\text{IEC} = 1.51 \text{ meq. g}^{-1}$ and thickness = $90 \mu\text{m}$) and 20 wt.% SPEEK ionomer ($\text{IEC} = 1.33 \text{ meq. g}^{-1}$) or 30 wt.% Nafion ionomer in the electrodes.

mated interfacial resistances of the MEAs are found to be 0.069 and $0.092 \Omega \text{ cm}^2$, respectively, for the SPEEK and Nafion ionomers. This indicates the realization of a lower interfacial resistance between the SPEEK membrane and electrodes on replacing the Nafion ionomer by the SPEEK ionomer in the electrodes. In parallel, to evaluate the interfacial active area of the electrodes depending on the ionomer, the capacitances of the anode electrodes containing either SPEEK or Nafion ionomer were determined and are displayed in Fig. 6(b). As seen in Fig. 6(b), the limiting capacitance of the electrodes containing SPEEK ionomer is almost two times higher than that of the electrodes containing Nafion ionomer. This can be taken to imply that the SPEEK ionomer is evenly distributed and interconnected through the catalyst layer of the electrode, which results in a large interfacial area where the catalyst particles are in contact with the ionomer network in the catalyst layer.

Fig. 7 compares the performances in DMFC of the MEAs prepared with SPEEK membranes having two different IECs (1.33 and 1.51 meq. g^{-1}) as well as Nafion 115 membrane. 20 wt.% of a SPEEK ionomer with an IEC of 1.33 meq. g^{-1} was used for preparing the electrodes of the MEAs fabricated with the two SPEEK membranes. The MEA with the Nafion 115 membrane was prepared with Nafion ionomer (30 wt.%) in the electrodes. As seen in Fig. 7, the SPEEK membranes with SPEEK ionomer in the electrodes exhibit superior performance in DMFC regardless of the membrane IEC compared

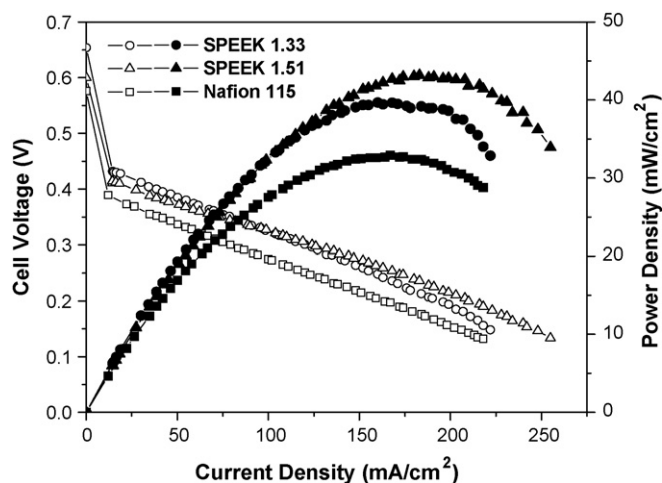


Fig. 7. Comparison of the performances in DMFC of various MEAs: MEAs fabricated with SPEEK membrane (IEC = 1.33 meq. g⁻¹ and thickness = 70 μm) and 20 wt.% SPEEK ionomer (IEC = 1.33 meq. g⁻¹), SPEEK membrane (IEC = 1.51 meq. g⁻¹ and thickness = 90 μm) and 20 wt.% SPEEK ionomer (IEC = 1.33 meq. g⁻¹), and Nafion 115 membrane and 30 wt.% Nafion ionomer.

to the MEA fabricated with the Nafion 115 membrane and Nafion ionomer. The polarization loss in the kinetic region at low current densities (10–50 mA cm⁻²) is smaller for the MEAs fabricated with SPEEK membrane and SPEEK ionomer in Fig. 7 compared to that found with the Nafion membrane and Nafion ionomer, suggesting better electrode kinetics in the former. This is also consistent with that found in Fig. 1(b) where the polarization loss at low current densities is smaller for the MEA fabricated with Nafion membrane and SPEEK ionomer (20 wt.% and IEC = 1.33 meq. g⁻¹) than that for the Nafion membrane and Nafion ionomer (30 wt.%). Fig. 8 compares the methanol crossover current densities for the MEAs as described in the experimental section. To see the effect of methanol crossover on DMFC performance, the steady state crossover current densities should be compared. As seen in Fig. 8, the MEAs fabricated with the SPEEK membranes (IEC = 1.33 and

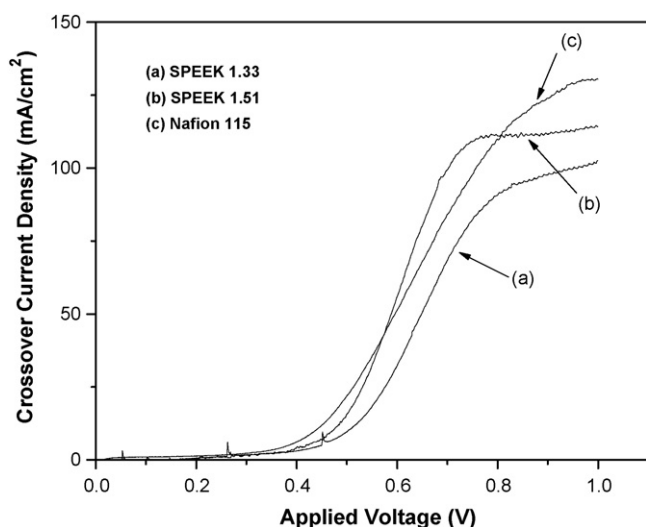


Fig. 8. Comparison of the methanol crossover current densities of various MEAs: MEAs fabricated with SPEEK membrane (IEC = 1.33 meq. g⁻¹ and thickness = 70 μm) and 20 wt.% SPEEK ionomer (IEC = 1.33 meq. g⁻¹), SPEEK membrane (IEC = 1.51 meq. g⁻¹ and thickness = 90 μm) and 20 wt.% SPEEK ionomer (IEC = 1.33 meq. g⁻¹), and Nafion 115 membrane and 30 wt.% Nafion ionomer.

1.51 meq. g⁻¹) and SPEEK ionomer (20 wt.% and IEC = 1.33 meq. g⁻¹) exhibit lower steady state crossover current density (i.e. lower methanol crossover) than the MEAs fabricated with Nafion 115 membrane and Nafion ionomer (30 wt.%). This demonstrates that the better performance found in DMFC with the SPEEK membranes and SPEEK ionomer compared to that with Nafion membrane and Nafion ionomer is a result of the combined effects of lower methanol crossover and better electrode kinetics with SPEEK membrane and SPEEK ionomer.

Looking at the power density values in Fig. 7, the SPEEK membrane with an IEC of 1.33 meq. g⁻¹ exhibits slightly lower (by 9%) power density than the SPEEK membrane with an IEC of 1.51 meq. g⁻¹. This can be attributed to the higher membrane resistance (0.14 Ω cm²) of the SPEEK membrane with an IEC of 1.33 meq. g⁻¹ compared to that of the SPEEK membrane with an IEC of 1.51 meq. g⁻¹ (0.1 Ω cm²). In addition, ac impedance analysis gave interfacial resistance values of 0.042 and 0.069 Ω cm², respectively, for the two SPEEK membranes with the IEC values of 1.33 and 1.51 meq. g⁻¹. This indicates a decrease in the interfacial resistance when the SPEEK membrane and the SPEEK ionomer have the same IEC values (1.33 meq. g⁻¹) due to a better compatibility between the membrane and the electrode ionomer.

4. Conclusions

A series of SPEEK with different IECs values have been prepared and explored as an ionomer in the electrodes of MEAs. The electrodes containing SPEEK ionomer have been characterized as a function of the IEC value and content of the SPEEK ionomer by single cell DMFC tests, cyclic voltammetry, and ac impedance spectroscopy. The optimum IEC value and SPEEK ionomer content in the electrodes are found to be, respectively, 1.33 meq. g⁻¹ and 20 wt.%. The MEAs fabricated with SPEEK membrane and SPEEK ionomer exhibit better performance in DMFC than that fabricated with Nafion ionomer, which is attributed to lower interfacial resistance in the MEA and increased electrochemical active area of the catalyst layer. The MEAs fabricated with SPEEK membrane and SPEEK ionomer also show superior performance in DMFC compared to that with Nafion 115 membrane and Nafion ionomer due to lower methanol crossover and better electrode kinetics. Replacement of Nafion ionomer by SPEEK ionomer in the catalyst layer can also provide significant cost savings as Nafion is expensive.

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