

Application of Sulfonated Carbon Ionomer to Catalyst Layers of Polymer Electrolyte Fuel Cells

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Abstract : We have developed a sulfonated carbon ionomer and applied it to the anode and cathode catalyst layers (CLs) of polymer electrolyte fuel cells (PEFCs). The above ionomer can be prepared by the thiol group oxidation method, while its ion exchange capacity (IEC) can be controlled by changing the proportions of carbon black, 3-mercaptopropyltrimethoxysilane, and H_2O_2 used in the synthesis. The sulfonated carbon ionomer can be used in both anode and cathode CLs of PEFCs, leading to their decreased performance, as compared with that of PEFCs utilizing the perfluorinated sulfonic acid (PFSA) ionomer at 80 °C and a relative humidity (RH) of 100%. The performance of PEFCs employing the sulfonated carbon ionomer hardly depends on its IEC and decreases with decreasing RH at 80 °C. These performance decreases are larger than those observed for the PFSA ionomer. On the other hand, PEFCs using the sulfonated carbon ionomer are superior to those based on the PFSA ionomer at temperatures above 100 °C and RHs below 100%.

Key Words : Polymer electrolyte fuel cell, Sulfonated carbon ionomer, Catalyst layer, Gas diffusion electrode, Operation at temperatures above 100 °C and RHs below 100%

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are considered a promising technology for clean and efficient power generation and are becoming increasingly important as alternative power sources for stationary, transportation, or portable applications, in particular for residential co-generation systems or electric vehicles, due to their high efficiency, rapid start-up, and low emission profile. The operation of PEFCs above 100 °C provides numerous advantages, like reducing the affinity of the Pt catalyst to carbon monoxide, which is a by-product of the reforming process, and thus increasing CO tolerance. As a result, the operation of PEFCs above 100 °C allows using impure fuel streams and simplifies fuel processing. High-temperature operation also increases the heat transfer rate because of a larger temperature gradient between the fuel cells and external environment, supplying waste heat that can be easily utilized by other processes (e.g., co-generation of heat and power or on-board reforming). Therefore, the heat management system is simplified, increasing the weight- and volume-specific energy densities and the overall energy density

of PEFC systems. The electrochemical kinetics of both electrode reactions are also enhanced by increasing the PEFC operation temperature. In particular, the rate of the oxygen reduction reaction is significantly increased, improving the performance of PEFCs as a whole. These factors result in increased efficiency and simplification of PEFC systems.

The perfluorinated sulfonic acid (PFSA) ionomer has been commonly used as both a polymer electrolyte membrane (PEM) and proton conductor in anode and cathode catalyst layers (CLs) of state-of-the-art PEFCs due to its high proton conductivity and high chemical and mechanical stability. However, this ionomer is not applicable to PEFCs operating above 100 °C, since it leads to losses of proton conductivity and mechanical strength, also causing considerable permeation (crossover) of fuel, hydrogen, and oxidants, air or oxygen, above its glass transition temperature (~ 110 °C). Alternative ionomers based on non-fluorinated materials, showing stability above 100 °C, processability, environmental adaptability, and low production cost, in addition to chemical and electrochemical stability, are in high demand. Intensive research efforts have been devoted to developing alter-

native dual-use ionomers (as both PEMs and proton conductors in catalyst layers) for the PEFCs. Recently, a sulfonated silane ionomer¹⁾ and non-fluorinated hydrocarbon ionomers, such as sulfonated polyether (SPE)²⁾, sulfonated polyether ether ketone (SPEEK)^{3)–7)}, sulfonated polyether ketone (SPEKK)⁸⁾, sulfonated polyarylene ether (SPAЕ)^{9), 10)}, and sulfonated polysulfone (SPS)¹¹⁾ have been developed for cost reduction, elevation of the operating temperature, and avoiding environmental pollution by fluoride after disposal. However, the application of hydrocarbon ionomers as catalyst layer (CL) ionomers often decreases the performance of PEFCs. In general, the proton conductivity of hydrocarbon ionomers is high under high humidity conditions but decreases steeply with decreasing humidity, leading to low catalyst utilization in the gas diffusion electrodes (GDEs) of PEFCs.

In this work, we have prepared a sulfonated carbon ionomer and applied it to both anode and cathode CLs of PEFCs, supposing that this ionomer with high proton conductivity exhibits no harmful effects on the performance and stability of PEFCs above 100 °C, because carbon material is usually used as a Pt catalyst support in CLs of phosphoric acid fuel cells at 200 °C and possesses high heat durability. We have evaluated the effects of using the sulfonated carbon ionomer in the anode and/or cathode CLs of PEFCs, its ion exchange capacity (IEC), and the relative humidity (RH) of the reactant gases on PEFC performance by conducting the single PEFC tests at 80 °C and RH of 100%. Subsequently, we have also evaluated the effects of temperatures above 100 °C and RHs below 100% on the performance of PEFCs utilizing the sulfonated carbon ionomer by conducting single PEFC tests.

2. Experimental

2.1 Preparation of the sulfonated carbon ionomer

The sulfonated carbon ionomer was prepared by using the thiol group (SH) oxidation method used by Munakata et al. for the surface sulfonation of a porous silica membrane¹²⁾. The surface sulfonation of carbon black (Aqua-Black® 162, Tokai Carbon Co., Ltd., Japan) was conducted as shown in Fig. 1, covalently attaching

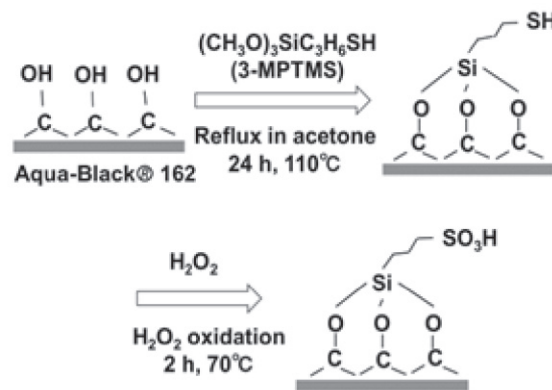


Fig. 1 Outline of surface sulfonation procedure by SH oxidation method.

sulfonic acid groups (SO_3H) to the carbon black. First, the carbon black was refluxed in 3-mercaptopropyltrimethoxysilane (3-MPTMS, KBM-802, 98.9%, Shin-Etsu Chemical Co., Ltd., Japan) solution at 110 °C for 24 h to attach SH precursor groups, with acetone (99.0%, Showa Chemical Co., Ltd., Japan) used as solvent. The weight ratio of acetone to carbon black was set at 15:1. Second, the SH groups on the carbon black were converted to SO_3H groups by oxidation with 10 wt% H_2O_2 aqueous solution (30 wt% H_2O_2 aqueous solution, Showa Chemical Industry Co., Ltd., Japan) at 70 °C for 2 h. The weight ratios of 3-MPTMS and H_2O_2 to the carbon black were varied to change the IEC of the prepared sulfonated carbon ionomer. The weight ratio of 3-MPTMS to carbon black was set at 0.5 and 1, and the ratio of H_2O_2 to the carbon black was set at 2 and 3.

2.2 Characterization of the sulfonated carbon ionomer

Fourier transform infrared (FTIR) spectroscopy was performed using the FTIR Spectrum One® spectrometer and the Universal ATR Accessory® (PerkinElmer Inc., USA) to verify presence of SO_3H moieties on the prepared sulfonated carbon ionomer¹⁾, with triglycine sulfate used as a detector. The IEC of the prepared ionomer was also measured to estimate the amount of formed SO_3H groups. The sulfonated carbon ionomer samples were dried at 120 °C for 30 min in air. The samples were immersed in 20 cm^3 of a saturated NaCl aqueous solution (NaCl, 99.5%, Showa Chemicals Co., Ltd., Japan) and shaken for 24 h with a shaker to exchange the protons of SO_3H units for sodium ions. The solution was filtered,

and the filtrate was titrated against 0.01 M NaOH aqueous solution (NaOH, 93.0%, Showa Chemicals Co., Ltd., Japan) using a potentiometric titrator (AT-510, Kyoto Electronics Industry Co., Ltd., Japan) to quantify the amount of protons. Based on the obtained result and the weight of the sulfonated carbon ionomer sample, the IEC was estimated using Eq. (1)¹³⁾:

$$IEC = (V \times C) / W_{\text{dry}} \quad (1)$$

where IEC [$\text{mmol g}^{-1} = \text{meq g}^{-1}$] is the ion exchange capacity, V [L] is the volume of the NaOH solution used for titration, C [mmol L^{-1}] is the concentration of the above NaOH solution, and W_{dry} [g] is the dry weight of the sulfonated carbon ionomer.

2.3 Preparation of GDEs and membrane-electrode assemblies

GDEs with a three-layer structure, i.e., CL/microporous layer (MPL) /wet-proofed carbon paper, were prepared for each single PEFC as follows. Carbon paper (360 μm thick, TGP-H-090, Toray Industry Inc., Japan) was immersed in an aqueous dispersion of polytetrafluoroethylene (PTFE, 31-JR, 60 wt%, Du Pont-Mitsui Fluorochemicals Co., Ltd., Japan) for 2 min, dried at 60 $^{\circ}\text{C}$ for 30 min in air, and then sintered at 350 $^{\circ}\text{C}$ for 1 min. This wet-proofing procedure was repeated until a PTFE loading of 5 wt% was reached. The MPL was formed on the wet-proofed carbon paper as follows. Ultrapure water, methanol, and the PTFE dispersion were mixed with carbon black (Vulcan XC-72R, Cabot Corporation, USA). The weight ratio of ultrapure water/methanol/carbon black/PTFE was controlled at 10/10/1.0/0.84. The components were mixed under ultrasonic agitation (SU-9TH ultrasonic cleaner, Shibata Scientific Technology Ltd., Japan) until a uniform paste was obtained. The resulting paste was repeatedly coated onto one face of the wet-proofed carbon paper followed by drying at ambient temperature until reaching a loading of 10 – 15 wt%. The paste-coated wet-proofed carbon paper was then hot-pressed with a mini TEST PRESS[®]-10 hot-pressing apparatus (Toyo Seiki Seisaku-sho, Ltd., Japan) at 120 $^{\circ}\text{C}$ under 1 MPa for 1 min and heated at 350 $^{\circ}\text{C}$ in air for 1 h to form the MPL on the wet-proofed carbon paper. The gas diffusion layer (GDL) of the GDE was composed of the MPL and the wet-proofed carbon paper.

The anode and cathode CLs were deposited over the GDL surface. To prepare the catalyst paste, 500 mg of Pt-loaded carbon black catalyst powder (Pt/C catalyst; 46.7 wt% Pt supported on high-specific-surface-area carbon black, TEC10E50E, Tanaka Kikinzoku Kogyo K.K., Japan) were mechanically mixed with 2451 mg of ultrapure water and 549 mg of 1-propanol (99.5%, Wako Pure Chemical Industries, Ltd., Japan) in a planetary ball mill for 1 h using zirconia balls. The prepared sulfonated carbon ionomer or the commercial PFSA ionomer (5 wt% Nafion[®] solution; D-521, E. I. du Pont de Nemours and Company, USA) were added into the mixture, which was mechanically homogenized in the planetary ball mill for 1 h using zirconia balls. The weight ratio of the dry sulfonated carbon ionomer or the dry Nafion[®] ionomer to Pt in the catalyst paste was set to 1. The prepared catalyst paste was four times spread onto the GDLs with a surface area of 27 cm^2 . The obtained catalyst-coated GDLs were dried at 2 $^{\circ}\text{C}$ in air for 1 h. The amount of loaded Pt was adjusted to $0.45 \pm 0.02 \text{ mg cm}^{-2}$ in the anode CL and $0.30 \pm 0.02 \text{ mg cm}^{-2}$ in the cathode CL.

The membrane-electrode assemblies (MEAs) were fabricated by hot-pressing the PEM sandwiched between two GDEs (anode and cathode) using the hot-pressing apparatus at 120 $^{\circ}\text{C}$ under 1 MPa for 1 min. The commercially available PFSA membrane, Nafion[®]NRE212 (50 μm thick, E. I. du Pont de Nemours and Company, USA), and a poly (styrene sulfonic acid)-grafted poly-ether ether ketone (ssPEEK) membrane¹⁴⁾ (30 μm thick) were used as PEMs. The ssPEEK membrane was donated by IHI Corporation, Japan. The geometrical surface areas of all electrodes were 25 cm^2 . The MEA was assembled into a single PEFC unit, using carbon separators with serpentine gas-channels.

2.4 Fuel cell operation

All of single PEFCs were operated under atmospheric pressure, with the setup of the experimental system used in this study shown in Fig. 2. Humidified H_2 and air were supplied to the anode and cathode, respectively, as reactant gases. The flow rates of H_2 and air were controlled at 500 and 2000 sccm (standard cubic centimeter per minute, 20 $^{\circ}\text{C}$), respectively, using two mass-flow controllers. These flow rates corresponded to O_2 and H_2 utilization of 21.0 and 34.8% at a current density

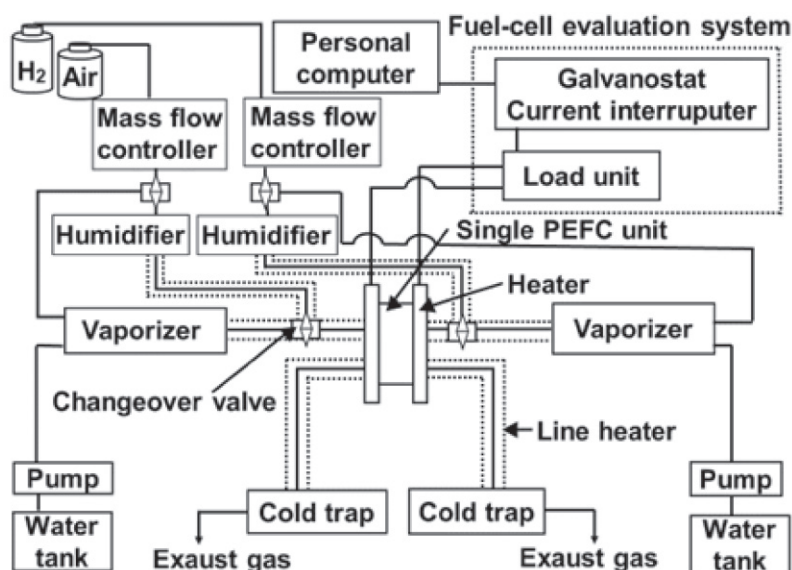


Fig. 2 Experimental setup.

of 1 A cm^{-2} . At 80°C , each reactant gas was humidified by bubbling through a humidifier prior to being fed to the single PEFC. The RHs of reactant gases were set to equal values, controlled by changing the humidifier temperature. For temperatures above 100°C , each reactant gas was mixed with vaporized water (steam) using a vaporizer prior to being fed to the single PEFC. The RHs of reactant gases were set to equal values, controlled by changing the amounts of water supplied to the vaporizer by a pump. By controlling the cathode water supply at 1.19 g min^{-1} and the anode water supply at 0.30 g min^{-1} , the RHs of H_2 supplied to the anode and air supplied to the cathode were set to 100, 72, and 53% at 100, 110, and 120°C , respectively.

Current–voltage ($I-V$) and IR drop characteristics of single PEFCs were measured using a fuel-cell evaluation system (TFC-2000G, Tsukasa Sokken Co., Ltd., Japan) under steady-state operation conditions. The IR drop characteristics were measured by applying $100\text{-}\mu\text{s}$ current-off pulses to single PEFCs and recording the resulting potential responses. The overall resistance polarization was calculated using the measured IR -drop characteristics. The current was normalized based on the electrode geometrical surface area of 25 cm^2 . The IR drop data was included in the $I-V$ characteristics reported herein.

$I-V$ characteristics were analyzed to evaluate the sources of polarization¹⁵⁾, with the overall activation po-

larization defined in Eq. (2) :

$$\eta_a = b \log (I / I_{0.90}) \quad (2)$$

where $\eta_a [\text{V}]$ is the overall activation polarization, b is the Tafel slope, $I_{0.90} [\text{A cm}^{-2}]$ is the current density at 0.90 V and $I [\text{A cm}^{-2}]$ is the measured current density. The Tafel slope was estimated by applying the least squares method to the current densities at IR -free cell voltages between 0.82 and 0.92 V .

3. Results and discussion

3.1 Characterization of the prepared sulfonated carbon ionomer

The FTIR spectrum of the prepared sulfonated carbon ionomer is shown in Fig. 3, the corresponding IEC be-

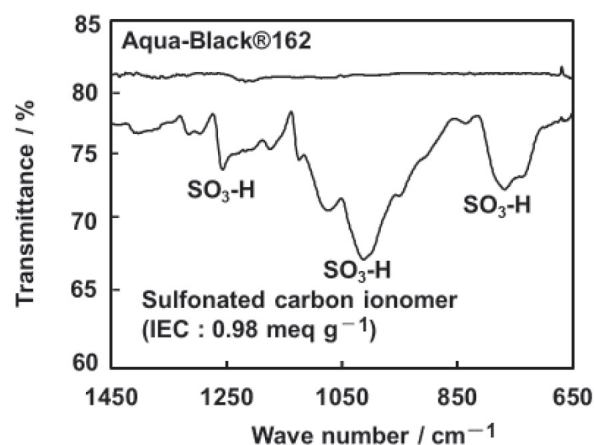


Fig. 3 FTIR spectrum of prepared sulfonated-carbon ionomer.

Table 1 Synthetical condition and IEC of sulfonated carbon ionomer.

Sample	Weight ratio			IEC (meq g ⁻¹)
	Aqua-Black® 162	3-MPTMS	H ₂ O ₂	
A	1	0.5	2	0.98
B	1	0.5	3	2.67
C	1	1	3	4.37

ing 0.98 meq g⁻¹. The presence of sulfonic groups on the sulfonated carbon ionomer was confirmed by peaks at 767, 1012, and 1257 cm⁻¹ corresponding to the SO₃H bond. However, these peaks were not observed for Aqua-Black® 162. This qualitative study suggests that the sulfonated carbon ionomer can be successfully prepared by the SH oxidation method.

Table 1 shows the synthetic condition and the IEC of the sulfonated carbon ionomer. The weight ratio of Aqua-black® 162/3-MPTMS/H₂O₂ was controlled. The IEC equaled to 0.98 meq g⁻¹ at a weight ratio of 1/0.5/2, 2.67 meq g⁻¹ at a weight ratio of 1/0.5/3, and 4.37 meq g⁻¹ at a weight ratio of 1/1/3, respectively. Increasing the weight ratio of H₂O₂ from 2 to 3 promoted the oxidation of SH groups to SO₃H moieties, increasing the IEC from 0.98 to 2.67 meq g⁻¹, respectively. Increasing the weight ratio of 3-MPTMS from 0.5 to 1 promoted the formation of SH groups on Aqua-black® 162, and the IEC increased from 2.67 to 4.37 meq g⁻¹, respectively. These results indicate that the IEC of the sulfonated carbon ionomer

can be controlled by changing the weight ratio of carbon black/3-MPTMS/H₂O₂.

3.2 Application of the sulfonated carbon ionomer in CLs

I – *V* and *IR* drop characteristics of single PEFCs were measured at 80 °C and an RH of 100%. Nafion® NRE212 was used as the PEM and the prepared sulfonated carbon and Nafion® ionomers were used in the CLs. The IEC of the used the sulfonated carbon ionommer was 0.98 meq g⁻¹. Figure 4 (a) shows the *I* – *V* characteristics of a single PEFC with (i) the sulfonated carbon ionomer in both anode and cathode CLs; (ii) sulfonated carbon ionomer in the cathode CL and the Nafion® ionomer in the anode CL; and (iii) the Nafion® ionomer in the cathode CL and the sulfonated carbon ionomer in the anode CL. For comparison, the *I* – *V* characteristics of a single PEFC with the Nafion® ionomer in both anode and cathode CLs are also shown in Fig. 4 (a). The PEFC with the sulfonated carbon ionomer in the anode and/or cathode CLs showed decreased performance, as compared with that with the Nafion® ionomer in both anode and cathode CLs. Figure 4 (b) shows the activation polarization characteristics of the single PEFCs derived from the *I* – *V* characteristics shown in Fig. 4 (a). The activation polarization of the single PEFC with the sulfonated carbon ionomer in the anode and/or cathode CLs increased in comparison with the value displayed by the PEFC with the Nafion®

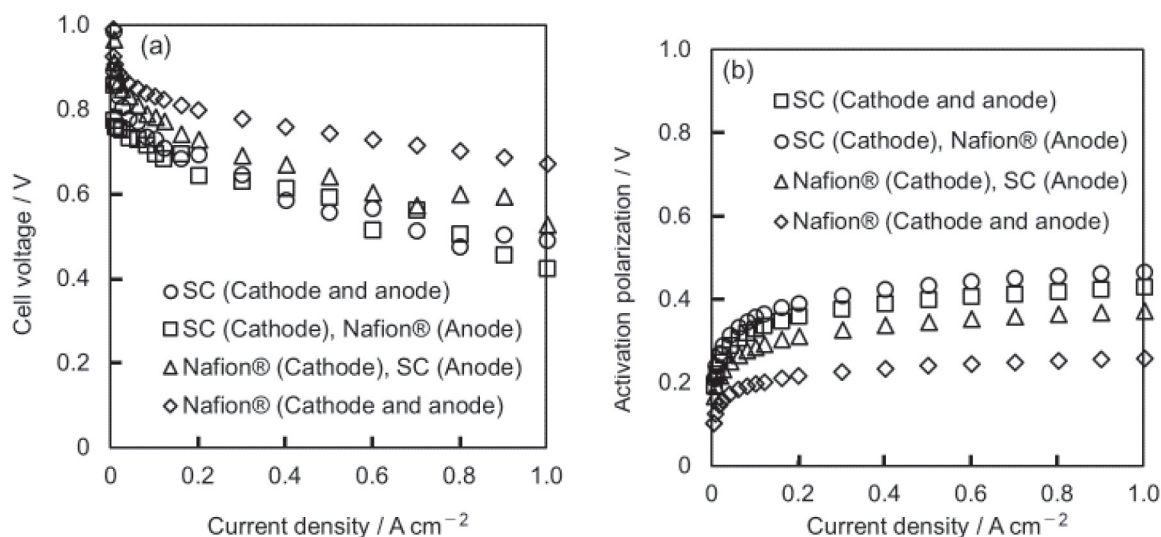


Fig. 4 Effect of application of sulfonated carbon ionomer (SC) to anode and/or cathode CLs on *I* – *V* and activation polarization characteristics of single PEFC at 80 °C and RH of 100%: (a) *I* – *V* characteristics, (b) activation polarization characteristics.

ionomer in both anode and cathode CLs. The resistance polarization of the single PEFC with the sulfonated carbon ionomer in the anode and/or cathode CLs slightly increased compared with that of the PEFC with the Nafion[®] ionomer in both anode and cathode CLs. In single PEFC with the sulfonated carbon ionomer in the anode and/or cathode CLs, no large increases of resistance polarization due to the increased interfacial resistance occurred, despite the ionomer different from the PEM.

These results indicate that the sulfonated carbon ionomer can be used for both anode and cathode CLs of PEFCs and that the performance of PEFCs with the sulfonated carbon ionomer in the anode and/or cathode CLs decreases due to the increase of activation polarization, as compared with that of the PEFC with the Nafion[®] ionomer in both cathode and anode CLs at 80 °C and an RH of 100%. The decrease of the activation polarization is required to improve the performance of the PEFCs with the sulfonated carbon ionomer.

3.3 Effect of the IEC of the sulfonated carbon ionomer

$I - V$ and IR drop characteristics of single PEFCs were measured at 80 °C and an RH of 100%. Nafion[®]NRE212 was used as the PEM, and the sulfonated carbon ionomers were used in both anode and cathode CLs. The IECs of the employed sulfonated carbon ionomers were 0.98, 2.67, and 4.37 meq g⁻¹. Figure 5 (a) shows the $I - V$

characteristics of single PEFC employing sulfonated carbon ionomers with different IECs. The PEFC performance obtained for the sulfonated carbon ionomer decreased in comparison with that obtained for the Nafion[®] ionomer and the former slightly increased with increasing the IEC of the sulfonated carbon ionomer. Figure 5 (b) shows the activation polarization characteristics of the single PEFC using sulfonate carbon ionomers with different IECs, derived from the $I - V$ characteristics shown in Fig. 5 (a). The activation polarization of the single PEFC with the sulfonated carbon ionomer increased compared with that of the PEFC with the Nafion[®] ionomer and the former slightly decreased with increasing the ionomer IEC. The resistance polarization of the single PEFC with the sulfonated carbon ionomer hardly depended on the ionomer IEC and was similar to the values obtained for the Nafion[®] ionomer.

These results suggest that the proton conduction between the SO₃H groups of the sulfonated carbon ionomer and the Pt particles of the Pt/C catalyst is inferior to that between the SO₃H groups of the Nafion[®] ionomer and the Pt particles. We presume that this difference of the proton conduction is caused by the contact between the ionomer and Pt particles. The Nafion[®] ionomer is composed of the PFSA polymer and uniformly contacts the Pt particles. On the other hand, the sulfonated carbon ionomer is composed of the carbon black particles and does not uniformly contact the Pt particles. Thus,

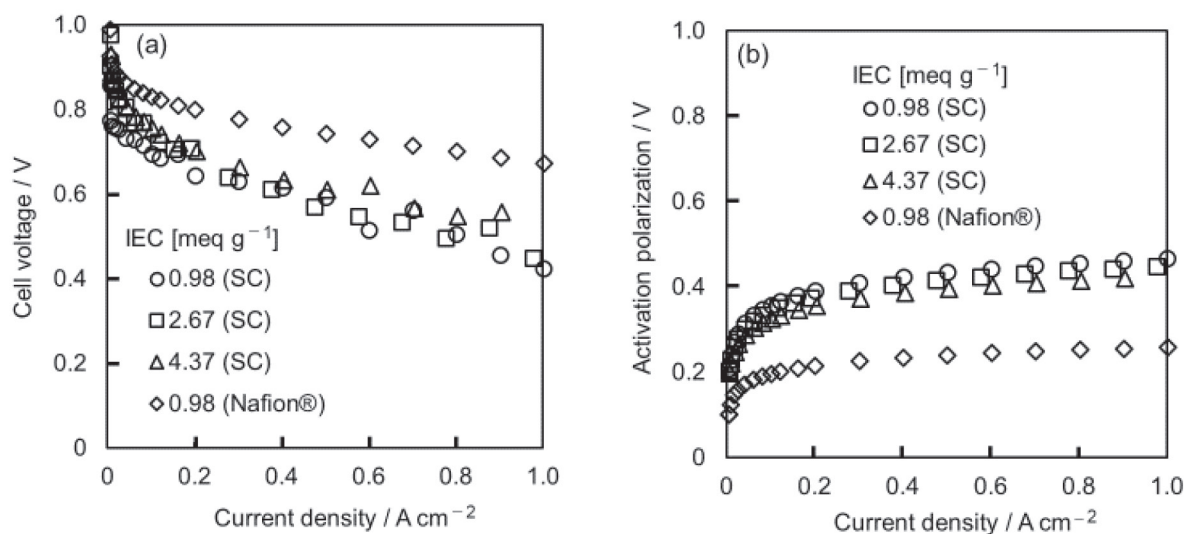


Fig. 5 Effect of IEC of sulfonated carbon ionomer (SC) in both anode and cathode CLs on $I - V$ and activation polarization characteristics of single PEFC at 80 °C and RH of 100%: (a) $I - V$ characteristics, (b) activation polarization characteristics.

the proton conduction between the SO_3H groups of the sulfonated carbon ionomer and the Pt particles is more preventable than that between the SO_3H groups of the Nafion[®] ionomer and the Pt particles. These results also suggest that increasing the IEC of the sulfonated carbon ionomer hardly improves the PEFC performance.

3.4 Effect of the RH of reactant gases

$I-V$ and IR drop characteristics of single PEFCs were measured at 80 °C. Nafion[®]NRE212 was used as the PEM and the sulfonated carbon and Nafion[®] ionomers were used in both cathode and anode CLs. The IEC of the used sulfonated carbon ionomer was 0.98 meq g^{-1} . The RH of the reactant gases was set to 40, 60, 80, and 100% by adjusting the humidifier temperature to 59, 68,

75, and 80 °C, respectively. Figure 6 (a) shows the $I-V$ characteristics of single PEFCs with the sulfonated carbon and Nafion[®] ionomers. The performance of the PEFCs with both sulfonated carbon and Nafion[®] ionomers decreased with decreasing RH, however, the decreases for the former was larger than that for the latter. Figure 6 (b) shows the activation polarization characteristics of the single PEFCs derived from the $I-V$ characteristics shown in Fig. 6 (a). The activation polarization of the single PEFC with the sulfonated carbon ionomer was larger than that of the PEFC with the Nafion[®] ionomer. The values for both PEFCs increased with decreasing RH, the increases of the former being larger than that of the latter. This indicates that the proton conduction of the sulfonated carbon ionomer highly depends on the RH

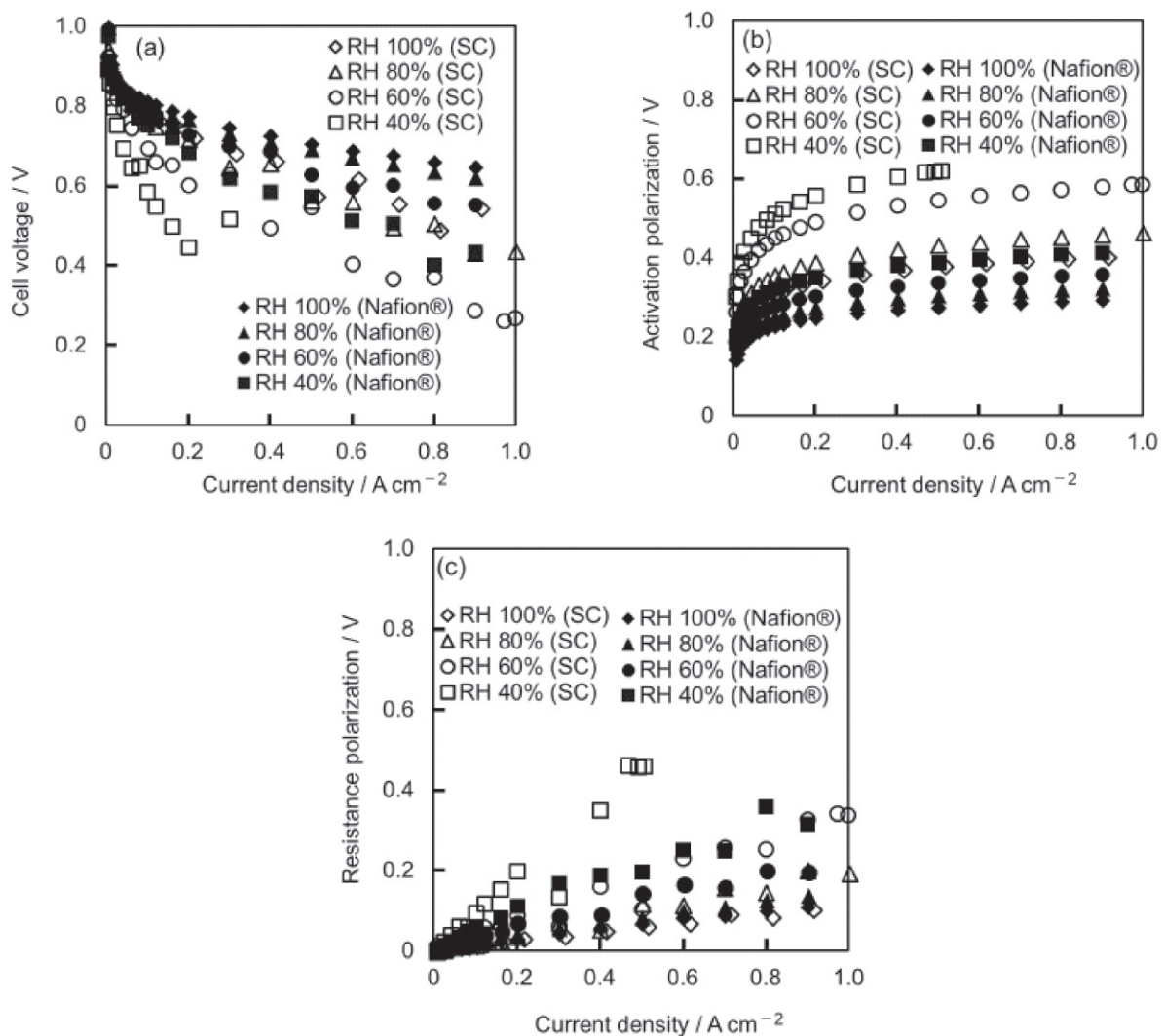


Fig. 6 Effect of RH of reactant gases on $I-V$ and polarization characteristics of single PEFC with sulfonated carbon ionomer (SC) in both anode and cathode CLs at 80 °C: (a) $I-V$ characteristics, (b) activation polarization characteristics, (c) resistance polarization characteristics.

of the reactant gases, and that the water reserve characteristics of the Nafion[®] ionomer are superior to those of the sulfonated carbon ionomer.

Figure 6 (c) shows the resistance polarization characteristics of the single PEFCs. The resistance polarization of the single PEFC with the sulfonated carbon ionomer was similar to that of the PEFC with the Nafion[®] ionomer at an RH of 100%. The values for both PEFCs increased with decreasing RH, the increases of the former being larger than that of the latter. The larger increase of the PEFCs with the sulfonated carbon ionomer is attributed to the characteristics of water transportation from the cathode CL to the PEM. In the single PEFCs with the Nafion[®] ionomer, an extensive water transportation network is present in the PEM and the above ionomer, since they consist of the same material. Therefore, water produced in the cathode CL during the cathode reaction is easily transferred to the PEM through the Nafion[®] ionomer, and the PEM drying at low RHs can be suppressed. Conversely, in the single PEFC with the sulfonated carbon ionomer, the water transportation network in the PEM and sulfonated carbon ionomer is not extensive, because the PEM and ionomer in the CLs consist of different materials. The water produced in the cathode CL, therefore, is not easily transferred to the PEM through the sulfonated carbon ionomer, and the PEM drying at low RHs cannot be suppressed.

3.5 Effect of PEFC operation above 100 °C

$I - V$ and IR drop characteristics of single PEFCs were measured at 100, 110 and 120 °C. The ssPEEK membrane was used as the PEM, and the sulfonated carbon and Nafion[®] ionomers were used in both anode and cathode CLs. The IEC of the sulfonated carbon ionomer was 0.98 meq g⁻¹. Figure 7 (a) shows the $I - V$ characteristics of the single PEFC with the sulfonated carbon ionomer at temperatures of 100, 110, and 120 °C and RHs of 100, 73 and 52%, respectively. The RHs at 110 and 120 °C were set to keep the steam amounts constant at the saturated steam amount at 100 °C, supposing PEFC operation under atmospheric pressure. The PEFC with the sulfonated carbon ionomer performed better than that with the Nafion[®] ionomer at temperatures of 100 and 110 °C and RHs of 100 and 73%, respectively. These results indicate that the performance of PEFCs with the

sulfonated carbon ionomer is superior to that of PEFCs with the Nafion[®] ionomer above 100 °C. Both the single PEFC with the sulfonated carbon ionomer and that with the Nafion[®] ionomer could not generate power at 120 °C and an RH of 52%, which was attributed to the low water-reserve characteristics of the ssPEEK membrane used under this condition.

Figure 7 (b) shows the activation polarization characteristics of the single PEFCs derived from the $I - V$ characteristics shown in Fig. 7 (a). The activation polarization of the single PEFC with the sulfonated carbon ionomer decreased at 100 and 110 °C compared with that of the PEFC with the Nafion[®] ionomer. Thus, the application of the sulfonated carbon ionomer to both anode and cathode CLs can presumably decrease the activation polarization above 100 °C. This indicates that the proton conductivity of the sulfonated carbon ionomer is superior to that of the Nafion[®] ionomer above 100 °C.

Figure 7 (c) shows the resistance polarization characteristics of the single PEFCs. The resistance polarization of the single PEFC with the sulfonated carbon ionomer was nearly equal to that of the PEFC with the Nafion[®] ionomer at 100 °C and an RH of 100%. On the other hand, the resistance polarization of the PEFC with the sulfonated carbon ionomer decreased compared with that of the PEFC with the Nafion[®] ionomer at 110 °C and an RH of 73%. Thus, the application of the sulfonated carbon ionomer to both anode and cathode CLs presumably suppresses water discharge from the PEM at temperatures above 100 °C and RHs below 100%, which contrasts the experimental results described above. At 80 °C, the resistance polarization of the PEFC with the Nafion[®]NRE212 and the sulfonated carbon ionomer increased with decreasing RH. This indicates that the sulfonated carbon ionomer suppresses water discharge from the PEM at temperatures above 100 °C and RHs below 100%. We presume that a larger amount of formed water is preserved in the sulfonated carbon ionomer compared to the Nafion[®] ionomer, preventing the PEM from drying under these conditions and suppressing the increase of the resistance polarization.

We used the SH oxidation method for the preparation of the sulfonated carbon ionomers. This method was used for the sulfonation of the porous silica membrane and a hydrothermal treatment was conducted at 170 °C

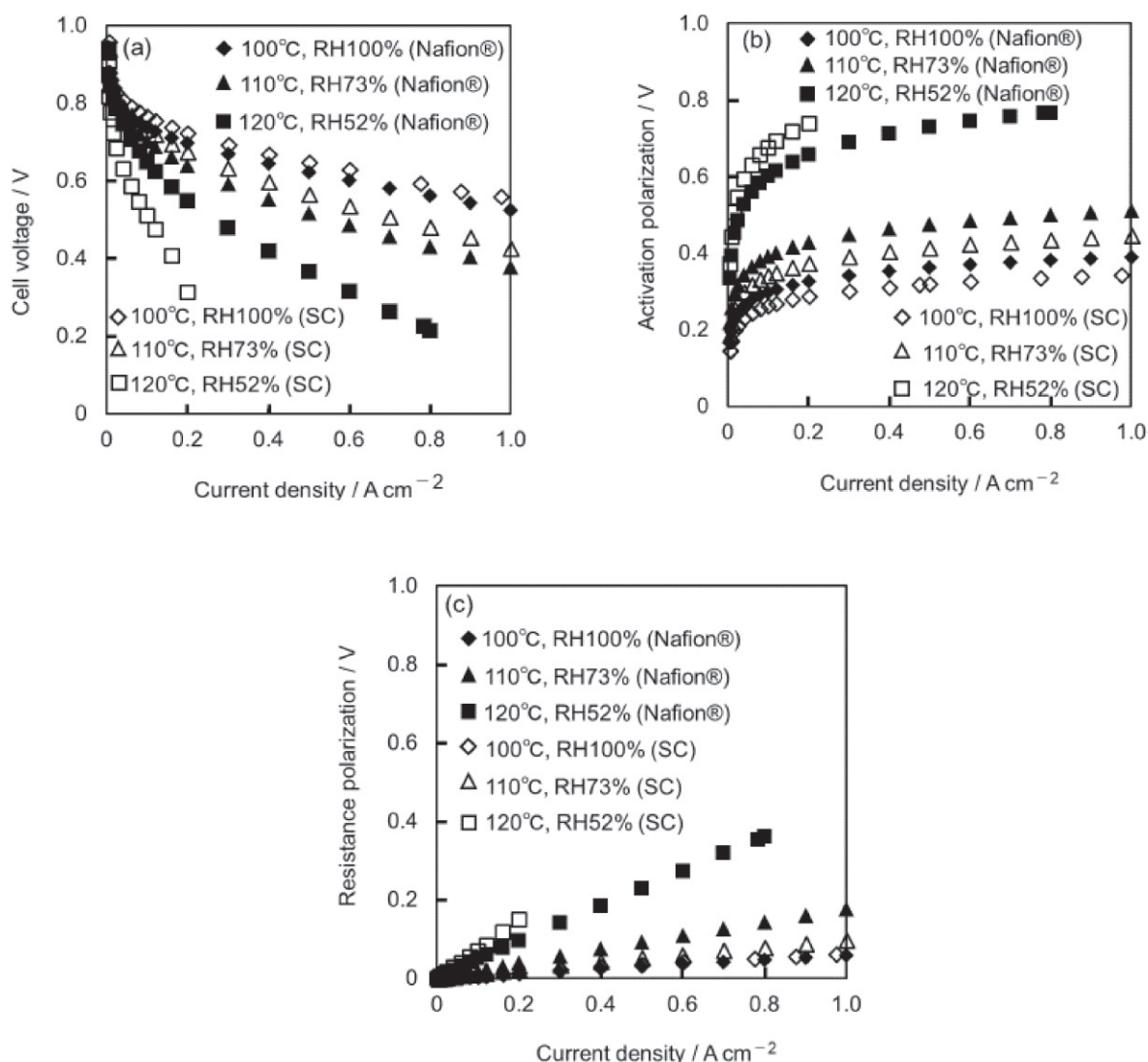


Fig. 7 Effect of operation above 100 °C on I – V and polarization characteristics of single PEFC with sulfonated carbon ionomer (SC) in both cathode and anode CLs: (a) I – V characteristics, (b) activation polarization characteristics, (c) resistance polarization characteristics.

in order to increase silanol groups on the silica surface¹²⁾. The FT-IR spectra of the porous silica membranes before and after the hydrothermal treatment at 170 °C showed that the peak intensity of silanol groups was increased with increasing duration for hydrothermal treatment. We, therefore, presume that the sulfonated carbon ionomer is stable at 170 °C.

We have showed that sulfonated carbon ionomer is available to PEFCs as proton conductor of anode and cathode CLs in this paper. The sulfonated carbon ionomer increases PEFC performance over 100 °C compared with the PFSA ionomer. The performance of the PEFC with the sulfonated carbon ionomer over 100 °C, however, is lower than that with the PESA ionomer at 80 °C.

We suppose that the performance of the sulfonated carbon ionomer must be improved further by studying surface treatment of carbon, alternative carbon material, and so on.

4. Conclusion

The sulfonated carbon ionomer can be prepared by using the SH oxidation method, and its IEC can be controlled by changing the weight ratio of carbon-black/3-MPTMS/H₂O₂. The sulfonated carbon ionomer can be used for both anode and cathode CLs of PEFCs. The performance of PEFCs with the sulfonated carbon ionomer decreases in comparison to that of PEFCs with the

PFSA ionomer at 80 °C and an RH of 100 %, and hardly depends on the IEC of the sulfonated carbon ionomer. The performance of the PEFCs with both sulfonated carbon and PFSA ionomers at 80 °C decreased with decreasing RH, however, the decreases for the former was larger than that for the latter. On the other hand, the performance of PEFCs with the sulfonated carbon ionomer is superior to that of PEFCs with the PFSA ionomer at temperatures above 100 °C and RHs below 100%. We conclude that PEFCs with the sulfonated carbon ionomer can generate power and achieve higher performance compared with that of the PFSA ionomer at temperatures above 100 °C and RHs below 100%.

Acknowledgement

The authors thank IHI Corporation, Japan, for the donation of the ssPEEK membrane and also thank Ms. Emi Sindou of Nanotechnology Research Center, Tokyo City University for her help in FTIR measurements.

References

- 1) J. I. Eastcott, E. B. Easton : Sulfonated silica-based fuel cell electrode structures for low humidity applications, *J. Power Sources*, **245**, 487 – 494 (2014)
- 2) A. B. Beleke, K. Miyatake, H. Uchida, M. Watanabe : Gas diffusion electrodes containing sulfonated poly-ether ionomers for PEFCs, *Electrochim. Acta*, **53**, 1972 – 1978 (2007)
- 3) E. B. Eastone, T. D. Astill, S. Holdcroft : Properties of gas diffusion electrodes containing sulfonated poly (ether ether ketone), *J. Electrochem. Soc.*, **152**, A752 – A758 (2005)
- 4) J. -S. Park, P. Krishanan, S. -H. Park, G. -G. Park, T. -H. Yang, W. -Y. Lee, C. -S. Kim : A study on fabrication of sulfonated poly (ether ether ketone)-based membrane-electrode assemblies for polymer electrolyte membrane fuel cells, *J. Power Sources*, **178**, 642 – 650 (2008)
- 5) T. Astill, Z. Xie, Z. Shi, T. Navessin, S. Holdcroft : Factors influencing electrochemical properties and performance of hydrocarbon-based electrolyte PEMFC catalyst layers, *J. Electrochem. Soc.*, **156**, B499 – B508 (2009)
- 6) K. A. Sung, W. -K. Kim, K. -H. Oh, J. -K. Park : The catalyst layer containing sulfonated poly(ether ether ketone) as the electrode ionomer for polymer electrolyte fuel cells, *Electrochim. Acta*, **54**, 3446 – 3452 (2009)
- 7) J. Peron, D. Edwards, A. Besson, Z. Shi, S. Holdcroft : Microstructure-performance relationships of sPEEK-based catalyst layer, *J. Electrochem. Soc.*, **157**, B1230 – B1236 (2010)
- 8) V. Ramani, S. Swier, M. T. Shaw, R. A. Weis, H. R. Kunz, J. M. Fenton : Membranes and MEAs based on sulfonated poly (ether ketone) and heteropolyacids for polymer electrolyte fuel cells, *J. Electrochem. Soc.*, **155**, B532 – B537 (2008)
- 9) T. Yoda, T. Shimura, B. Bae, K. Miyatake, M. Uchida, H. Uchida, M. Watanabe : Gas diffusion electrodes containing sulfonated poly (arylene ether) ionomer for PEFCs Part 1. Effect of humidity on the cathode performance, *Electrochim. Acta*, **54**, 4328 – 4333 (2009)
- 10) T. Yoda, T. Shimura, B. Bae, K. Miyatake, M. Uchida, H. Uchida, M. Watanabe : Gas diffusion electrodes containing sulfonated poly (arylene ether) ionomer for PEFCs Part 2. Improvement of the cathode performance, *Electrochim. Acta*, **55**, 3464 – 3470 (2010)
- 11) S. von Kraemer, M. Puchner, P. Jannasch, A. Lundblad, G. Lindbergh : Gas diffusion electrodes and membrane electrode assemblies based on sulfonated polysulfone for high-temperature PEMFC, *J. Electrochem. Soc.*, **153**, A2077 – A2084 (2006)
- 12) H. Munakata, H. Chiba, K. Kanamura : Enhancement on proton conductivity of inorganic-organic composite electrolyte membrane by addition of sulfonic acid group, *Solid State Ionics*, **176**, 2445 – 2450 (2005)
- 13) S. Sambandam, V. Ramani : Effect of cathode binder IEC on kinetic and transport losses in all-SPEEK MEAs, *Electrochim. Acta*, **53**, 6328 – 6336 (2008)
- 14) Japanese Unexamined Patent Application Publications, No. 2016 – 193987.
- 15) M. V. Williams, H. R. Kunz, J. M. Fenton : Analysis of polarization curves to evaluate polarization sources in hydrogen/air PEM fuel cells, *J. Electrochem. Soc.*, **152**, A635 – A644 (2005)