Sulfonated polyimide hybrid membranes for polymer electrolyte fuel cell applications

Ken-ichi Okamoto*, Kazuaki Yaguchi, Hajime Yamamoto, Kangcheng Chen, Nobutaka Endo, Mitsuru Higa, Hidetoshi Kita

Graduate School of Science & Engineering, Yamaguchi University, Tokiwadai 2-16-1, Ube, Yamaguchi 755-8611, Japan

ARTICLE INFO

ABSTRACT

Sulfonated Si-MCM-41 (SMCM) with an ion exchange capacity (IEC) of 2.3 mequiv. g^{-1} was used as a hydrophilic and proton-conductive inorganic component. Sulfonated polyimide (SPI) based on 1,4,5,8-naphthalene tetracarboxylic dianhydride and 2,2′-bis(3-sulfophenoxy) benzidine was used as a host membrane component. The SMCM/SPI hybrid membrane (H1) with 20 wt% loading of SMCM and an IEC of 1.90 mequiv. g^{-1} showed the high mechanical tensile strength and the slightly higher water vapor sorption than the host SPI membrane (M1) with an IEC of 1.86 mequiv. g^{-1}. H1 and M1 showed anisotropic membrane swelling with about 10 times larger swelling in thickness direction than in plane one. The proton conductivity at 60 °C of H1 was lower in water than that of M1, but comparable at 30% RH. At 90 °C, H1 showed the rather lower performance of polymer electrolyte fuel cell (PEFC) at 82% RH than M1 and fairly better performance at 30% RH. On the other hand, at 110 °C and low humidity less than 50% RH, H1 showed the much better PEFC performance than M1 and Nafion 112. This was due to the promoted back diffusion of produced water by the superior water-holding capacity of SMCM. The SMCM/SPI hybrid membranes have high potential for PEFCs at higher temperatures and lower humidities.

© 2010 Published by Elsevier B.V.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been attracting great attention as clean energy sources of residential cogeneration, vehicular transportation and other applications. Polymer electrolyte membrane (PEM) is a key component playing a critical role on PEFC performance. Perfluorosulfonic acid polymer membranes such as Nafion (DuPont) are state-of-the-art membranes because of their high proton conductivity and excellent chemical stability [1,2]. However, they have some disadvantages such as low operational temperatures below 80 °C and high fuel gas and oxygen crossover and high cost. Much research has been done in the development of alternative PEMs based on sulfonated aromatic polymers [3–20]. Generally, the aromatic PEMs have some shortcomings such as relatively low proton conductivity at a low relative humidity and lower membrane durability in PEFC operation.

To improve both the cell efficiency and feasibility, it is desirable to operate PEFCs at high temperatures above 100 °C and low relative humidities below 50% RH [6]. Recently we reported on side-chain-type sulfonated polyimides (SPIs) derived from 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and 2,2′-

bis(3-sulfophenoxy) benzidine (BSPOB) and their SO_2-crosslinked membranes. They showed high performance and durability for PEFCs operated at 90 °C and 0.3 MPa in wide humidity range of 84% RH to 30% RH [18,19]. The reasonably high PEFC performance at 30% RH was attributed to the effective back diffusion of water molecules formed at the cathode. In a previous paper, we investigated their PEFC performance at a higher temperature of 110 °C and the low relative humidities [21]. The PEFC performances at 110 °C and low relative humidities of 49 and 33% RH were much lower than those at 90 °C and 48 and 27% RH due to the less effective back diffusion of water at the higher temperature.

To improve the proton conductivity at high temperatures and low relative humidities, organic–inorganic composite (hybrid) membranes have been investigated [22–24]. Yamaguchi et al. developed nano-hybrid membranes composed of zirconium hydrogen phosphate and sulfonated poly(ether sulfone), which showed high proton conductivity of 19 mS cm^{-1} at 90 °C and 50% RH [23].

Recently, Wark et al. reported on the synthesis and proton conductivity of sulfonic acid functionalized Si-MCM-41 (SMCM) [25,26]. The SMCM materials exhibited high proton conductivities at temperatures above 100 °C and 100% RH. These materials have an advantage of the higher water storage capability even at high temperatures above 100 °C. Therefore, it is interesting to prepare the hybrid membranes composed of SMCM and BSPOB-based SPI

* Corresponding author. Tel.: +81 836 85 9660; fax: +81 836 85 9601.
  E-mail address: okamotok@yamaguchi-u.ac.jp (K.-i. Okamoto).

Fig. 1. Chemical structure of SPI, NTDA-BSPOB/BAPBz.

and to investigate their PEFC performance at high temperatures and low relative humidities.

2. Experimental

2.1. Preparation of SPI membrane

A random copolyimide was prepared from NTDA, BSPOB and 1,3-bis(4-aminophenoxy) benzene (BAPBz) according to the reported method [18]. The SPI prepared was NTDA-BSPOB/BAPBz(2/1) where the data in parentheses refer to the molar ratio of BSPOB to BAPBz. The chemical structure of SPI is shown in Fig. 1. SPI membranes were prepared by casting the 5–6 wt% m-cresol solutions (in triethylamine (TEA) form) onto glass plates, followed by residue extraction in methanol, proton exchange and curing [18].

2.2. Preparation of SMCM/SPI hybrid membranes

In this study, the SMCM sample was prepared using 30 mol.% of 3-mercapto-trimethoxysilane (MPMS), as follow. Thiol-functionalized Si-MCM-41 was prepared by a hydrothermal synthesis according to the literature method [26]. 2.61 g (7.16 mmol) of cetyltrimethylammonium bromide (CTAB) was dissolved in 400 ml of deionized water. 2.0 g (15.3 mmol) of sodium metasilicate and 1.29 g (6.59 mmol) MPMS were added into the CTAB solution with stirring, and then 4 ml of ethyl acetate was added into the mixture with vigorously stirring. After being stood at 30 °C for 24 h, the mixture was heated at 100 °C for 24 h. The white powder was filtrated from the mixture and washed with ethanol and then with hot water, and dried in vacuo. The powder was treated with ethanol (500 ml) containing hydrochloric acid (18 g) at 70 °C for 8 h to remove the template.

Thus-obtained sample of thiol-functionalized Si-MCM-41 was oxidized with a 30% H_2O_2 solution (45 ml) at 30 °C for 24 h according to another literature [27]. The solid was filtrated and washed with deionized water and then suspended in a 10 wt% H_2SO_4 for 1 h. The solid was filtrated, washed with deionized water and dried. Overall yield: 50%.

SMCM/SPI hybrid membranes were prepared by casting the m-cresol solutions of NTDA-BSPOB/BAPBz(2/1) and SMCM onto glass plates followed by the similar pos-treatment mentioned above.

2.3. Membrane characterization

X-ray diffraction (XRD) was measured with a Rigaku diffractometer. FT-IR spectra were recorded on a Horiba FT-200 Spectrometer by ATR (attenuated total reflection). Mechanical tensile tests were performed on a universal testing machine (Orientic, TENSILON TRC-1150A) at 25 °C and around 60% RH. Scanning electron microscopy (SEM) was performed using a JEOL JSM-6335F instrument. Ion exchange capacity (IEC) was evaluated by a titration method.

Water vapor sorption isotherms were measured at 60 °C and water vapor activities a_w less than 0.93 using a sorption apparatus (BEL-18SP) by means of a volumetric method. The weight of membrane sample used was 80–100 mg. Water uptake and dimensional change of membrane were measured according to the methods described elsewhere [18,19]. Water uptake (WU) was calculated from the following equation:

$$WU = \frac{W_s - W_d}{W_d} \times 100\% \tag{1}$$

where W_d and W_s are the weights of dry and corresponding water-swollen membranes, respectively. Dimensional changes in thickness (Δt_c) and in plane direction (Δl_c) were calculated from the following equation:

$$\Delta t_c = \frac{t - t_d}{t_d}$$
$$\Delta l_c = \frac{l - l_d}{l_d} \tag{2}$$

where t_d and l_d are the thickness and length of the dry membrane, respectively; t and l refer to those of the membrane swollen in water.

In-plane proton conductivity ($\sigma_{//}$) was determined using an electrochemical impedance spectroscopy technique over the frequency from 10 Hz to 100 kHz (Hioki 3532-80) from the following equation:

$$\sigma_{//} = \frac{d}{t_s w_s R} \tag{3}$$

where d is the distance between the two electrodes, t_s and w_s are the thickness and width of the membrane at a standard condition of 70% RH and 25 °C, respectively, and R is the resistance value measured.

2.4. Fabrication of membrane electrode assembly (MEA) and measurements of cell performance

An MEA was fabricated from a membrane sample by hot-pressing an electrode/membrane/electrode sandwich at 150 °C for 5 min under 60 kgf cm^{-2}. Prior to the hot-pressing, both surfaces of the membrane and Pt/C electrodes (Johnson Matthey Plc., #45372) were impregnated with a small amount of Nafion solution as a binder. The effective electrode area was 5 cm^2. The MEA was set in a single cell test fixture and mounted into an in-house fuel cell test station (NF Inc., model As-510), which was supplied with temperature-controlled humidified gases. The PEFC performance was evaluated at cell temperatures of 90 and 110 °C and

Table 1
Physicochemical properties of SPI (M1), SMCM/SPI hybrid (H1 and H2) and Nafion 112 membranes.

Code	NTDA-based SPIs	Membrane thickness (μm)	IEC[a] (mequiv. g^{-1})	WU[b] (%)	Size change[b]		$\sigma_{//}$[c] (mS cm^{-1})				M[d] (GPa)	S[e] (MPa)	E[f] (%)
					Δt_c	Δl_c	30	50	70	Water			
M1-1	BSPOB/BAPBz(2/1)	46 (40)[g]	(1.96) 1.86	76	0.47	0.039	1.0	8.7	35	170	2.6	128	51
M1-2	BSPOB/BAPBz(2/1)	26	(1.96)	72	0.47	0.038	1.1	9.4	38	178	–	–	–
H1	(20 wt%) SMCM/M1 hybrid	27	1.90	90	0.52	0.044	0.8	6.9	32	152	2.5	79	25
H2	(40 wt%) SMCM/M1 hybrid	37	1.93	96	0.56	0.047	1.2	8.6	20	124	1.6	41	12
Nafion 112		53	(0.91) 0.89	39	0.14	0.13	9.8	30	59	141	0.2	37	410

[a] By titration method, data in parentheses are the calculated ones.
[b] At 30 °C.
[c] Proton conductivity at 30% RH, 50% RH, 70% RH and in water at 60 °C.
[d] Young's modulus.
[e] Stress at break.
[f] Elongation at break.
[g] See in Table 2.

gas pressures of 0.2 and 0.3 MPa and different gas humidification temperatures of 90–59 °C. The gas flow was controlled to keep constant utilization of H$_2$ at 60, 70 or 80% and of air at 15, 30 or 50%, depending on the humidification condition. The cell resistance (R_c) and electrode reaction resistance (R_{el}) were determined by the AC impedance cole–cole plots. The *through-plane* proton conductivity ($\sigma_{\perp,FC}$) was evaluated by assuming that the membrane resistance is approximately equal to the cell resistance. It is noted that the $\sigma_{\perp,FC}$ value is evaluated to be smaller for the thinner membrane when the resistance other than the membrane resistance is not negligibly small. Therefore, the comparison of the $\sigma_{\perp,FC}$ value should be limited between the membranes with the similar thickness.

3. Results and discussion

3.1. Physicochemical properties

Table 1 lists the physicochemical properties of host SPI membranes (M1-1 and M1-2), SMCM/SPI hybrid membranes (H1: 20 wt% doping and H2: 40 wt% doping) together with those of Nafion 112 membrane. The IEC value of the SMCM powder sample was 2.3 mequiv. g^{-1}, which was a little higher than the reported one [26]. XRD pattern of the sample showed a peak at 2.4° corresponding to the (1 0 0) reflection with the absence of the (1 1 0) and (2 0 0) reflections, which was similar to those reported [26]. The IR spectra of the SMCM sample showed small bands around 3000 cm^{-1} attributed to the C–H stretching vibrations of aliphatic CH$_2$-groups and two bands at 1160 and 1200 cm^{-1} for sulfonic acid groups. M1-1 and M1-2 had the same chemical composition but the different membrane thickness.
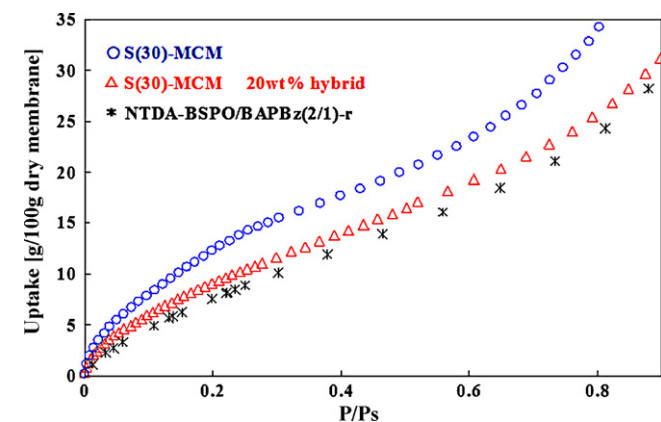
The SMCM/SPI hybrid membrane (H1) doped with 20 wt% SMCM was not so transparent as the host SPI membranes (M1). SEM observation of H1 showed the rather homogeneous dispersion of SMCM particles of 1–3 μm in size in the membrane. H1 showed reasonably high mechanical tensile strength, namely, Young's modulus (M) of 2.5 GPa, maximum stress (S) of 79 MPa and elongation at break (E) of 25%, although these S and E values were 40 and 50%, respectively, smaller than those of M1-1. H2 with 40 wt% SMCM showed the lower mechanical strength than H1, but still kept the membrane toughness.

Fig. 2 shows the water vapor sorption isotherms of SMCM powder, M1-1 and H1 at 60 °C. The water vapor sorption was much larger (for example, 56% at 30% RH) for SMCM and slightly larger (15% at 30% RH) for H1 than for M1-1. With increasing the loading of SMCM, IEC slightly increased from 1.86 mequiv. g^{-1} for M1-1 to 1.93 mequiv. g^{-1} for H2, and the water uptake at 30 °C fairly increased from 72 to 76% for M1 to 96% for H2. Both H1 and H2 showed the anisotropic membrane swelling with about 10 times larger *through-plane* swelling than *in-plane* one. It is noted that the hybrid membrane with a high loading of 40 wt% showed the similar anisotropic membrane swelling to that of the host membranes.

Fig. 3 shows the relative humidity dependence of proton conductivity at 60 °C. Table 1 also lists the proton conductivity data. The SPI and hybrid membranes displayed larger RH dependence of conductivity than Nafion 112. For example, the $\sigma_{//}$ values at 50 and 30%
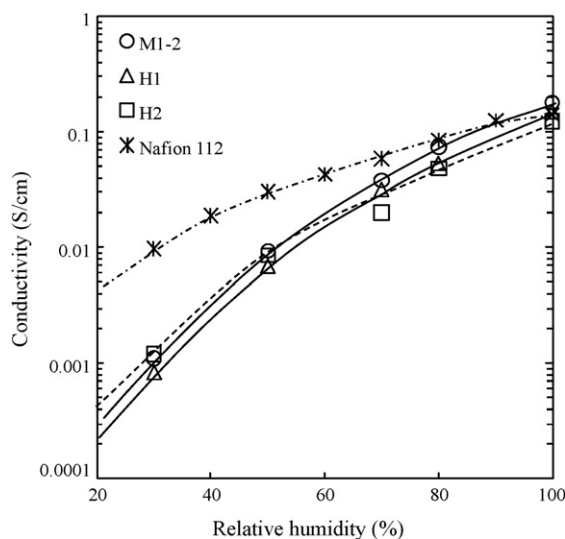
Fig. 2. Water vapor sorption isotherms of SMCM powder, M1-1 and H1 at 60 °C.

Fig. 3. Relative humidity dependence of proton conductivity ($\sigma_{//}$) of SPI (M1-2), hybrid (H1 and H2) and Nafion 112 membranes at 60 °C.

RH for M1-2 were about a tenth and a hundredth, respectively, of that (80 mS cm^{-1}) at 80% RH, whereas the corresponding $\sigma_{||}$ values for Nafion 112 were about three tenths and a tenth, respectively, of that (90 mS cm^{-1}) at 80% RH.

With increasing the SMCM loading, the proton conductivity in water decreased from 178 mS cm^{-1} for M1-2 to 124 mS cm^{-1} for H2, whereas the conductivity at low humidities of 30–50% RH hardly changed. In the high relative humidity range above 80% RH, the conductivity was in the order, M1 > H1 > H2. The proton conductivity values of the corresponding SMCM sample (in compressed tablet form) at 100% RH have been reported to be 0.2, 3 and 30 mS cm^{-1} at 60, 110 and 140 °C, respectively [26]. Therefore, it is considered that in the highly swollen hybrid membranes, the doped SMCM particles act as insulating filler to reduce the conductivity by the tortuosity effect. On the other hand, under the low humidification of 30–50% RH, the SMCM particles may act as water adsorbate to compensate the conductivity.

3.2. PEFC performance at 90 °C

Fig. 4(a) and (b) shows the PEFC performances for M1, H1 and Nafion 112 at a cell temperature of 90 °C, a feed gas pressure of 0.2 MPa and anode/cathode gas humidification temperatures of 85/80 and 59/59 °C, which correspond to 82/68% RH and 27/27% RH, respectively (here after abbreviated to 82% RH and 27% RH). Table 2 lists the PEFC performance data of open circuit voltage (OCV), cell voltage at 0.5 A cm^{-2} ($V_{0.5}$), maximum output (W_{max}), *through-plane* proton conductivity ($\sigma_{\perp,FC}$) and electrode reaction resistance (R_{el}) under PEFC operation.

At the relatively high humidification of 82% RH, M1-2 of 26 μm in thickness showed the slightly higher cell performance than M1-1 (40 μm) and Nafion 112 (53 μm). Compared to M1-2, H1 with the similar thickness of 27 μm showed the lower cell performance and $\sigma_{\perp,FC}$ value. The lower performance of H1 was attributed to the

Table 2
PEFC performance data of open circuit voltage (OCV), cell voltage at 0.5 A cm^{-2} ($V_{0.5}$), maximum output (W_{max}), *through-plane* proton conductivity ($\sigma_{\perp,FC}$) and electrode reaction resistance (R_{el}) under PEFC operation.

Conditions[a]	Code	OCV (V)	$V_{0.5}$ (V)	W_{max} (W cm^{-2})	$\sigma_{\perp,FC}$[b] (mS cm^{-1})	R_{el}[b] (mΩ)
90/0.2/82	M1-1[c]	0.99	0.69	>0.88	50	38
	M1-2	0.96	0.71	>0.96	47	30
	H1	0.94	0.67	>0.75	43	50
	Nafion	0.93	0.69	>0.86	90	39
90/0.2/48	M1-1	0.99	0.69	0.67	37	52
	Nafion	0.94	0.68	0.75	70	52
90/0.2/27	M1-1	0.98	0.68	0.51	34	84
	M1-2	1.00	0.66	0.53	25	57
	H1	0.94	0.63	0.60	30	63
	Nafion	0.96	0.66	0.57	58	96
110/0.2/49	M1-1	0.97	0.30	0.17	(7)	–
	M1-2	0.98	0.51	0.28	(8)	(69)
	H1	0.94	0.58	0.37	13	–
	H2	0.93	0.51	0.31	13	70
110/0.3/49	M1-2	0.97	0.62	0.53	20	52
	H1	0.93	0.67	0.68	30	57
110/0.3/33	M1-1	0.98	0.45	0.23	(9)	–
	M1-2	0.99	0.58	0.35	(11)	–
	H1	0.94	0.64	0.64	25	63
	H2	0.94	0.60	0.41	19	–
	Nafion	0.95	0.67	0.53	49	96

[a] PEFC operation conditions: *x*/*y*/*z* refer to cell temperature (°C), gas pressure (MPa) and relative humidity of feed gas (% RH).
[b] Measured at 1 A cm^{-2}; the data in parentheses are measured at 0.5 A cm^{-2}.
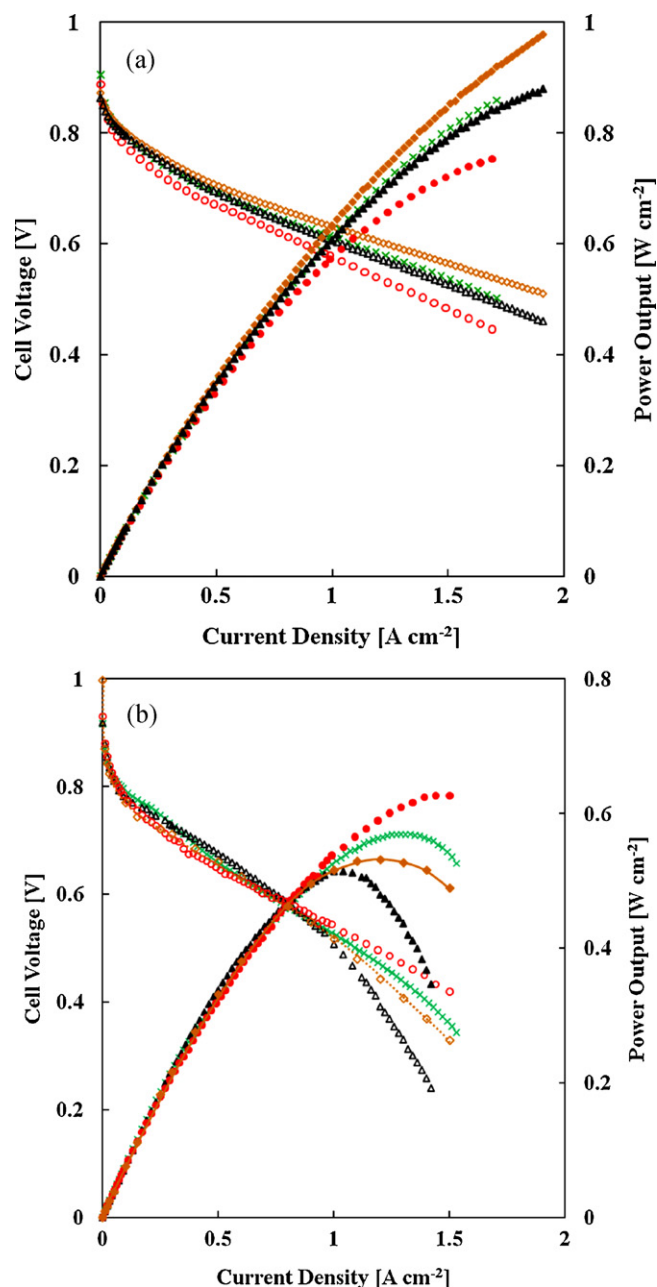[c] The membrane of 40 μm in thickness was used in this case, and the 46 μm one in the other cases.

Fig. 4. PEFC performances for M1-1 (△▲), M1-2 (◇◆), H1 (○●) and Nafion 112 (× ×) at 90 °C and 0.2 MPa and (a) 82% RH and (b) 27% RH.

same reason mentioned above for the lower proton conductivity $\sigma_{||}$ at the high relative humidities above 80% RH. On the other hand, at 27% RH, in the range of high load current density above 1 A cm^{-2}, where both the formation of water at cathode and the feed gas flow rates became larger, the cell performance was in the order of H1 > Nafion 112 > M1-2 > M1-1. The difference in cell performance among H1, M1-2 and M1-1 seemed due to the difference in the effect of back diffusion of water molecules formed at the cathode. At 90 °C, the effect of doping of SMCM was limited in the range of low relative humidity and the higher load current densities.

3.3. PEFC performance at 110 °C

Fig. 5 shows the PEFC performances at 110 °C, 0.2 MPa and a gas humidification temperature of 90/90 °C (corresponding to 49% RH). At 90 °C, 0.2 MPa and 48% RH, M1-1 (46 μm) showed the fairly
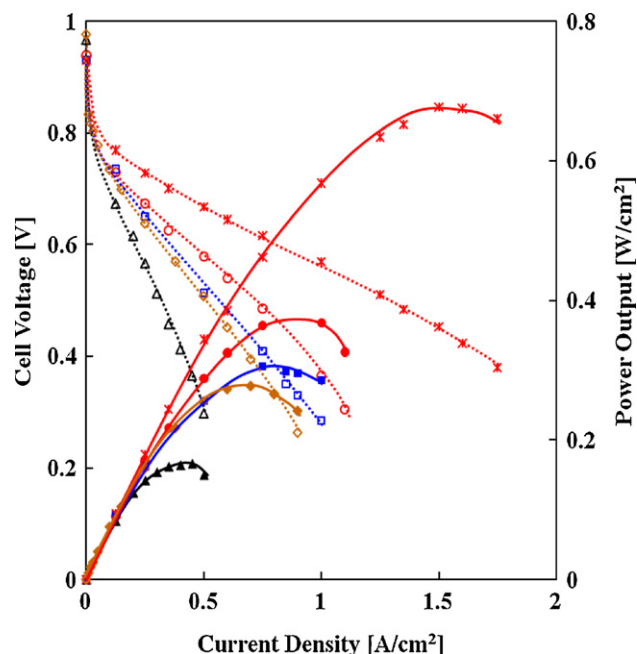
Fig. 5. PEFC performances for M1-1 (△▲), M1-2 (◇♦), H1 (○●) and H2 (□■) at 110 °C, 49% RH and 0.2 MPa, and for H1 (✳✳) at 0.3 MPa.

Fig. 6. PEFC performances for M1 (△▲), M1-2 (◇♦), H1 (○●), H2 (□■) and Nafion 112 (× ×) at 110 °C, 0.3 MPa and 33% RH.

high PEFC performance of $V_{0.5}$ of 0.69 V and W_{max} of 0.67 W cm^{-2}, as listed in Table 2. On the other hand, at 110 °C, M1-1 showed the low performance; that is, the cell voltage largely decreased with increasing load current density, resulting in low values of $V_{0.5}$ and W_{max} (0.30 V and 0.17 W cm^{-2}, respectively). This was due to the much lower $\sigma_{\perp,FC}$ value (7 mS cm^{-1}) at 110 °C compared with the value (37 mS cm^{-1}) at 90 °C. Compared to M1-1, M1-2 (26 μm) showed much higher performance of $V_{0.5}$ of 0.51 V and W_{max} of 0.28 W cm^{-2} at 110 °C. These results indicate that the back diffusion of produced water was more effective for the thinner membrane, but became less effective at the higher temperature. Furthermore, H1 showed the much higher performance than M1-2, namely, $V_{0.5}$ of 0.58 V and W_{max} of 0.37 W cm^{-2}. This was due to the 60% larger $\sigma_{\perp,FC}$ value (13 mS cm^{-1}) for H1 than for M1-2, indicating the enhanced effect of back diffusion of produced water for the hybrid membrane.

Fig. 5 and Table 2 also show the effect of pressure on the cell performance for H1 and M1-2. With an increase in pressure from 0.2 to 0.3 MPa, both H1 and M1-2 showed the significantly enhanced performances; for example, $V_{0.5}$ of 0.67 V and W_{max} of 0.68 W cm^{-2} for H1. This was due to more than 2-fold increases in $\sigma_{\perp,FC}$, indicating that the back diffusion of water was more effective at the higher pressure.

Fig. 6 shows comparison of the PEFC performances at 110 °C, 0.3 MPa and a gas humidification temperature of 80/80 °C (corresponding to 33% RH) among M1, H1, H2 and Nafion 112. H1 showed the much higher PEFC performance than M1-2. For example, the W_{max} value for H1 (0.64 W cm^{-2}) was about two times larger than that for M1-2 (0.35 W cm^{-2}). The $\sigma_{\perp,FC}$ value of H1 (25 mS cm^{-1}) was also about two times larger than that of M1-2 (11 mS cm^{-1}). The PEFC performance of H2 (40 wt% loading and 37 μm) was much lower than that of H1 but higher than that of M1-2. Even if taking the difference in membrane thickness into account, the 20 wt% loading seemed to be better than the 40 wt% loading. The PEFC performance of Nafion 112 was much higher than that of M1. This is not due to the effect of back diffusion of water, but due to the much higher proton conductivity in the low relative humidity range.

Thus, the PEFC performance at 110 °C was in the order, H1 > Nafion 112 > H2 > M1-2 > M1-1. It is noted that H1 could main-
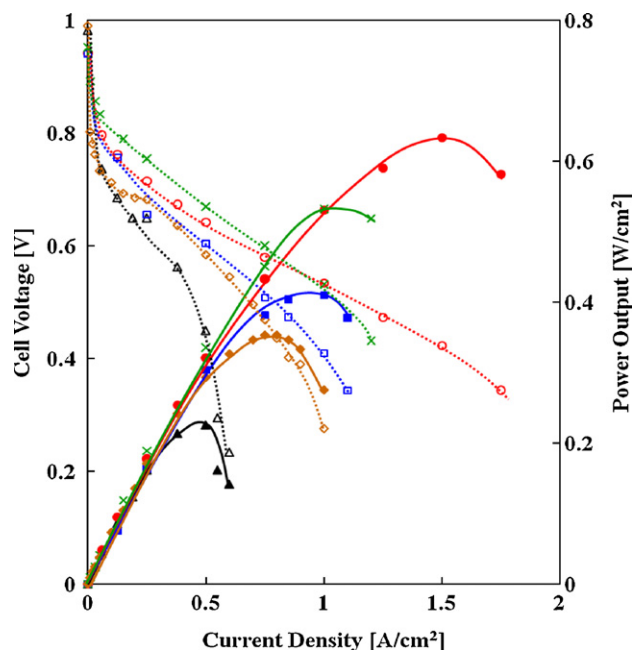
tain the PEFC performance at 110 °C and 50–33% RH in a relatively high level due to the effective back diffusion of produced water. In other words, SMCM particles enhanced the water-holding capacity at high temperature and low humidity.

For a durability test, a PEFC with H1 was operated at 110 °C, 0–1.7 A cm^{-2} and 33–50% RH for 300 h. During the operation, a slight decrease in the cell performance was observed. On the other hand, in the OCV durability test at 110 °C, 0.2 MPa and 50% RH, the OCV for Nafion 112 decreased very rapidly and became less than 0.2 V after 75 h. These results indicate that H1 had fairly good durability in PEFC operation at 110 °C and 33–50% RH, but Nafion 112 had very poor durability.

Thus, SMCM/SPI hybrid membranes have high potential as PEMs for PEFCs operated at high temperatures and low relative humidities. The further study on the effects of sulfonation degree and loading of SMCM and membrane morphology on the cell performance is under progress.

4. Conclusions

SMCM/SPI hybrid membrane (H1) with 20 wt% loading of SMCM had the high mechanical tensile strength and showed the slightly higher water vapor sorption and water uptake than the host SPI membranes (M1-1 and M1-2). H1 and M1 showed the anisotropic membrane swelling with about 10 times larger swelling in thickness direction than in plane one. The proton conductivity at 60 °C of H1 was lower in water than that of M1, but comparable at 30% RH. At 90 °C, H1 showed the rather lower PEFC performance at 82% RH than M1-1 and M1-2 but fairly better performance in the range of the higher load current density at 30% RH. On the other hand, at 110 °C and low humidity less than 50% RH, H1 showed the much better PEFC performance than M1-1, M1-2 and Nafion 112. This was due to the promoted back diffusion of produced water by the superior water-holding capacity of SMCM at higher temperatures and lower humidities. H1 had fairly good durability in PEFC operation at 110 °C and 33–50% RH, but Nafion 112 had very poor durability. The SMCM/SPI hybrid membranes have high potential as PEMs for PEFCs at higher temperatures and lower humidities.

Acknowledgements

References

[1] O. Savadogo, J. New Mater. Electrochem. Syst. 1 (1998) 47–66.
[2] K.A. Mauritz, R.B. Moore, Chem. Rev. 104 (2004) 4535–4586.
[3] M. Rikukawa, K. Sanui, Prog. Polym. Sci. 25 (2000) 1463–1502.
[4] J.A. Kerres, J. Membr. Sci. 185 (2001) 3–27.
[5] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29–39.
[6] Q. Li, R. He, J.O. Jensen, N. Bjerrum, Chem. Mater. 15 (2003) 4896–4915.
[7] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chem. Rev. 145 (2004) 4587–4612.
[8] W.L. Harrison, M.A. Hickner, Y.S. Kim, J.E. McGrath, Fuel Cells 5 (2005) 201–212.
[9] Y. Yin, O. Yamada, K. Tanaka, K. Okamoto, Polym. J. 38 (2006) 197–219.
[10] C. Marestin, G. Gebel, O. Diat, R. Mercier, Adv. Polym. Sci. 216 (2008) 185–258.
[11] K. Goto, I. Rozhanskii, Y. Yamakawa, T. Otsuki, Y. Naito, Polym. J. 41 (2009) 95–105.
[12] N. Asano, M. Aoki, S. Suzuki, K. Miyatake, H. Uchida, M. Watanabe, J. Am. Chem. Soc. 128 (2006) 1762–1769.
[13] K. Miyatake, Y. Chikashige, E. Higuchi, M. Watanabe, J. Am. Chem. Soc. 129 (2007) 3879–3887.
[14] A. Roy, H.-S. Lee, J.E. McGrath, Polymer 49 (2008) 5037–5044.
[15] M.L. Einsla, Y.S. Kim, M. Hawley, H.-S. Lee, J.E. McGrath, B. Liu, M.D. Guiver, B.S. Pivovar, Chem. Mater. 20 (2008) 5636–5642.
[16] H. Bai, W.S. Winston Ho, J. Membr. Sci. 313 (2008) 75–85.
[17] C.H. Lee, C.H. Park, Y.M. Lee, J. Membr. Sci. 313 (2008) 199–206.
[18] Y. Sutou, Y. Yin, Z. Hu, S. Chen, H. Kita, K. Okamoto, H. Wang, H. Kawasato, J. Polym. Sci., Chem. Ed. 44 (2009) 1463–1477.
[19] N. Endo, K. Matsuda, K. Yaguchi, Z. Hu, K. Chen, M. Higa, K. Okamoto, J. Electrochem. Soc. 156 (2009) B628–B633.
[20] Z. Hu, Y. Yin, K. Yaguchi, N. Endo, M. Higa, K. Okamoto, Polymer 50 (2009) 2933–2943.
[21] K. Yaguchi, K. Chen, N. Endo, M. Higa, K. Okamoto, J. Power Sources, in press.
[22] G. Alberti, M. Casciola, Annu. Rev. Mater. Res. 33 (2003) 129–154.
[23] G.M. Anilkumar, S. Nakazawa, T. Okubo, T. Yamaguchi, Electrochem. Commun. 8 (2006) 133–136.
[24] M.H. Woo, O. Kwon, S.H. Choi, M.Z. Hong, H.-W. Ha, K. Kim, Electrochim. Acta 51 (2006) 6051–6059.
[25] R. Marschall, I. Bannat, J. Caro, M. Wark, Micropor. Mesopor. Mater. 99 (2007) 190–196.
[26] R. Marshall, J. Rathousky, M. Wark, Chem. Mater. 19 (2007) 6401–6407.
[27] E. Cano-Serrano, G. Branco-Brieva, J.M. Campos-Martin, J.L.G. Fierro, Langmuir 19 (2003) 7621–7627.