

Ameliorating effect of silica addition in the anode-catalyst layer of the membrane electrode assemblies for polymer electrolyte fuel cells

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Abstract Incorporation of silica particles through a sol-gel process into the anode-catalyst layer with a sol-gel modified Nafion-silica composite membrane renders easy retention of back-diffused water from the cathode to anode through the composite membrane electrolyte, increases the catalyst-layer wettability and improves the performance of the Polymer Electrolyte Fuel Cell (PEFC) while operating under relative humidity (RH) values ranging between 18% and 100% with gaseous hydrogen and oxygen reactants at atmospheric pressure. A peak power density of 300 mW cm^{-2} is achieved at a load current-density value of 1200 mA cm^{-2} for the PEFC employing a sol-gel modified Nafion-silica composite membrane and operating at 18% RH. Under similar operating conditions, the PEFC with a Membrane Electrode Assembly (MEA) comprising Nafion-silica composite membrane with silica in the anode-catalyst layer delivers a peak power density of 375 mW cm^{-2} . By comparison, the PEFC employing commercial Nafion membrane fails to deliver satisfactory performance at 18% RH due to the limited availability of water at its anode, acerbated electro-osmotic drag of water from anode to cathode and insufficient water back diffusion from cathode to anode causing the MEA to dehydrate.

Keywords Polymer electrolyte fuel cell · Silica-Nafion composite membrane · Wettability · Humidification · Anode-catalyst layer

1 Introduction

In general, Polymer Electrolyte Fuel Cells (PEFCs) are operated under high relative humidity (RH) conditions, but, for many applications, it is desirable to operate them at low RH. To this end, Williams et al. [1] modified the gas-diffusion layer, making it less hydrophobic. Other studies [2–5] have reported self-humidifying membranes obtained by embedding Pt catalyst particles into the membrane. The catalyst particles act as water-generation sites by recombination of permeated gaseous hydrogen and oxygen reactants. This, however, gives rise to the problem of short-circuits due to the electrically conducting path formed by the embedded metal particles. Other researchers [6–9] have reported Nafion-silica composite membranes to improve cell performance at high temperatures. The incorporation of silica as inorganic additives enhances thermal stability and water uptake of the composite membrane, besides retaining its inherent property. Sacca et al. [10] have reported a Nafion-titania composite membrane and have found that induction of titania particles as inorganic fillers endows the composite membrane with good mechanical and thermal resistance. This composite membrane also exhibits higher water uptake and ion exchange capacity in relation to commercial Nafion membranes. Nafion-composite membranes suitably modified with ceramic/inorganic fillers, namely SiO_2 , TiO_2 , ZrO_2 , etc., are widely used [11–17] due to their water retention characteristics; these composite membranes facilitate proton conductivity at elevated temperatures even under low RH conditions.

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Recently, a novel method for incorporating silica particles into Nafion ionomer so as to fabricate a Nafion-silica composite membrane that facilitates PEFC operation under low humidity conditions has been reported [18]. These studies have stressed the importance of prudent water management within the fuel cell to maximize its performance. Besides the membrane, the catalyst layer is also a complex and versatile component of PEFC, as it provides the three-phase contact to electrochemical reaction. Any attempt to modify the catalyst layer and corresponding MEA fabrication should address the aforesaid issues.

The present study provides a novel methodology to accomplish improved PEFC performance under low RH conditions. It is demonstrated that the incorporation of silica particles through a sol-gel process into the anode-catalyst layer with a sol-gel modified Nafion-silica composite membrane renders easy retention of back-diffused water from the cathode to anode through the composite membrane electrolyte, increases wettability and ameliorates the performance of PEFC while operating under low RH conditions. While a peak power density of only 300 mW cm^{-2} is achieved at a current-density value of 1200 mA cm^{-2} for the PEFC employing a sol-gel modified Nafion-silica composite membrane and operating at 18% RH, the PEFC with a membrane electrode assembly comprising Nafion-silica composite membrane and silica in its anode-catalyst layer is able to deliver a peak power density of 375 mW cm^{-2} at a similar current-density and RH. By contrast, a PEFC employing commercial Nafion membrane fails to deliver satisfactory performance at 18% RH.

2 Experimental

Nafion-1135 (DuPont) membrane was boiled with 30 vol.% nitric acid for 1 h to expel metal and organic impurities followed by copious rinsing and washing with distilled water. The membrane was subsequently boiled in 5 vol.% H_2O_2 for 30 min followed by rinsing and washing in distilled water. Finally, the membrane was boiled in 1 M H_2SO_4 for 1 h followed by washing with distilled water. All cleaned membranes were stored in deionized water for later use.

Tetraethylorthosilicate (TEOS) (98%, Acros Organics), iso-propyl alcohol (IPA) (99%, Merck) and deionized water (H_2O) were used as the starting materials. A silica sol comprising TEOS + IPA + H_2O was obtained by mixing the constituents in the respective molar ratio of 1:4:4. The mixture was sonicated for 15 min to obtain a visibly homogeneous and transparent colloidal suspension. The required amount of sol was then impregnated with 5 wt.% commercial Nafion solution (DuPont) and Nafion-silica

composite membranes were fabricated as reported elsewhere [18].

Toray carbon paper (thickness = 0.27 mm) was used as backing layer. To the backing layer, diffusion layer comprising 1.5 mg cm^{-2} of Vulcan XC-72R carbon slurry was applied by brushing method. In-house prepared 40 wt.% Pt catalyst [19] supported onto Vulcan XC-72R carbon was mixed with iso-propyl alcohol and sonicated for 15 min. To this mixture, a required amount of silica sol mixed with 5 wt.% Nafion ionomer was added and further sonicated for about 20 min. The silica mixed catalyst slurry was coated onto the diffusion layer in a similar manner as above to form the anode of the Membrane Electrode Assembly (MEA). The presence and distribution of silica particles in the catalyst layer of the anode was ascertained with the help of a JEOL JSM 5400 Scanning Electron Microscope (SEM) coupled with Electron Dispersive Spectroscopy Analysis by X-ray (EDAX) facility. By contrast, no silica was added to the catalyst slurry for the cathode. However, the catalyst loading on both the anode and the cathode (active area: 25 cm^2) was kept at 0.5 mg cm^{-2} . MEAs were obtained by sandwiching the membrane between anode and cathode and hot pressing at 125°C under 15 kN ($\sim 60 \text{ kg cm}^{-2}$) for 3 min. The compositions of the MEA types employed in the present study are given in Table 1. To conduct the polarization studies, MEAs were coupled with Teflon gas-sealing gaskets and placed in the single-cell test fixture. The performance evaluation of the PEFCs with MEA types was conducted at varying RH values between 18% and 100% at 60°C using gaseous hydrogen and oxygen reactants at atmospheric pressure.

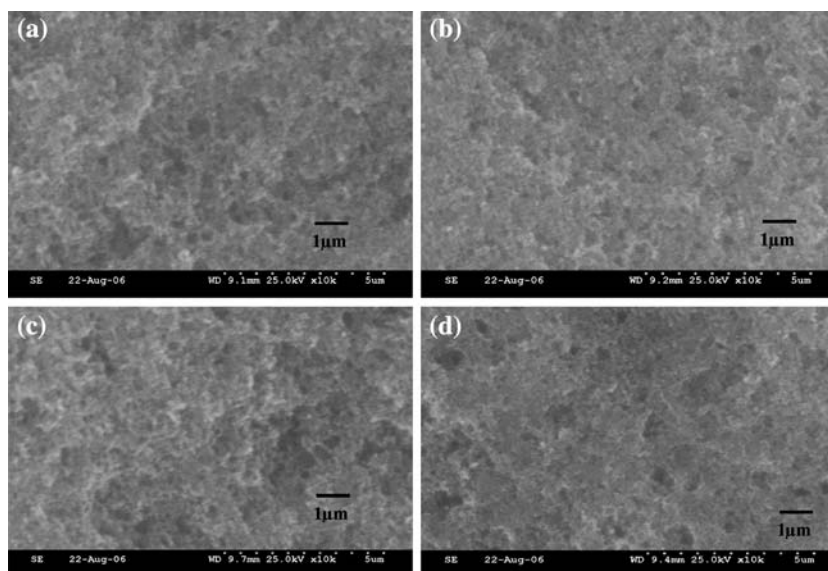
The high RH value in the PEFC (100% RH) was maintained by passing humidified hydrogen and oxygen gases to its anode and cathode sides, respectively, at a flow rate of 1.5 L min^{-1} controlled by a mass-flow controller, through a humidification bottle containing deionized water maintained at 65°C . In order to operate the PEFC at varying RH values, parameters like Dew Point Temperature (DPT), Gas Temperature (GT)/Gas Supply Temperature (GST) and Dew Point Humidification Temperature (DPH) were adjusted using an Arbin Fuel Cell Test Station (Model PEM-FCTS-158541) as reported elsewhere [18]. After establishing the desired experimental conditions, the polarization data on the PEFCs were obtained under steady-state conditions. Reproducibility of the data was ascertained by repeating the experiments.

3 Results and discussion

Figure 1 shows SEM photographs for the electrode without silica and with varying silica content in the anode-catalyst layer employed during the study. Fig. 1(a) shows the

Table 1 Compositions of various MEAs

MEA types	Cathode catalyst layer	Anode-catalyst layer	Electrolyte membrane
1	Pt/C	Silica (0 w/o)–Pt/C	Nafion-1135
2	Pt/C	Silica (40 w/o)–Pt/C	Nafion-1135
3	Pt/C	Silica (15 w/o)–Pt/C	Nafion-1135
4	Pt/C	Silica (5 w/o)–Pt/C	Nafion-1135
5	Pt/C	Silica (0 w/o)–Pt/C	Nafion-silica (15 w/o) composite
6	Pt/C	Silica (5 w/o)–Pt/C	Nafion-silica (15 w/o) composite

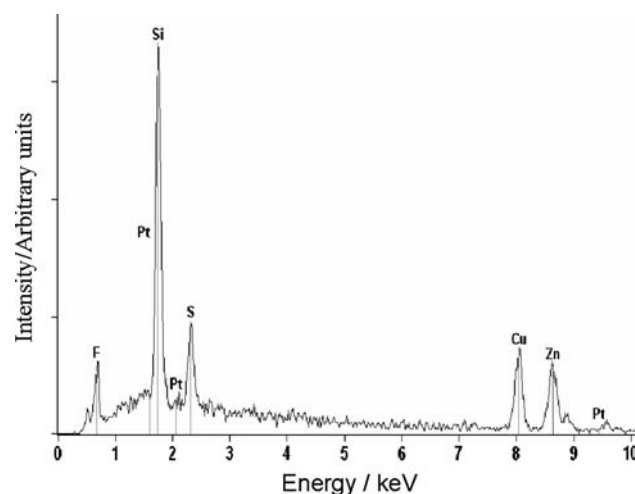
Fig. 1 SEM images for anode-catalyst layer in gas-diffusion anodes with (a) silica (0 w/o)–Pt/C, (b) silica (40 w/o)–Pt/C, (c) silica (15 w/o)–Pt/C and (d) silica (5 w/o)–Pt/C

morphological features of finished catalyst layer electrode without any silica content. SEM photographs of anode-catalyst layer for MEA types 2, 3 and 4 are shown in Fig. 1b–d, respectively. Little difference in morphological features are noticed between unmodified catalyst layer and silica incorporated catalyst layer, signifying silica to be uniformly mixed with catalyst ink, which helps retaining the microstructure of the catalyst layer and is seminal to the performance of the PEFC. Typical EDAX spectrum for the anode-catalyst layer shown in Fig. 2 confirms the presence of Si as one of its constituents. It has been documented that incorporation of silica in the anode-catalyst layer improves its wettability [20].

The performance of H_2/O_2 PEFC at varying RH values employing Nafion-silica composite membranes has been reported elsewhere [18] and it was found that the Nafion-silica composite membrane shows better performance than those with unmodified Nafion membranes. The maximum performance of PEFC was reported for Nafion-silica (15w/o) composite membrane, where silica improves water retention in the membrane electrolyte without affecting the continuity of the proton conduction path. A peak power density of 700 mW cm^{-2} for the PEFC at 83% RH has been achieved with this configuration. It is this composition

that has been chosen to evaluate the ameliorating effect of silica incorporation through the sol-gel process in the anode-catalyst layer.

Figure 3 compares the polarization curves for PEFCs with MEA types 1, 2, 3 and 4 under high humidification

**Fig. 2** Typical EDAX spectrum for a silica added anode-catalyst layer in the gas diffusion anode

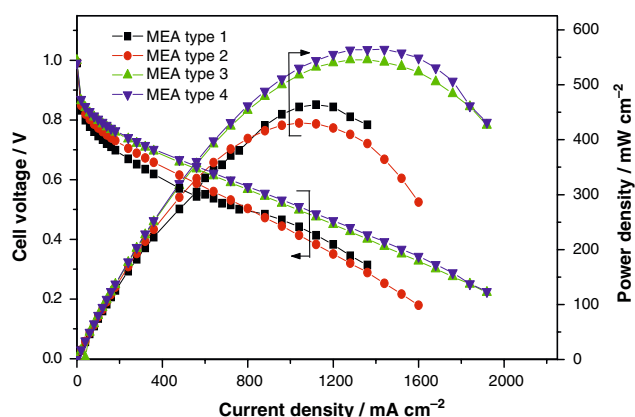


Fig. 3 Performance curves for PEFCs with MEA types 1, 2, 3 and 4 at 83% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

conditions (83% RH) at 60 °C using hydrogen and oxygen gaseous reactants at atmospheric pressure. It is seen that the PEFC with MEA type 4 gives the optimum performance. PEFC with MEA type 3 shows a little lower performance than the PEFC with MEA type 4, but it is higher than the performance for the PEFC with MEA type 1. The lowest performance is obtained for PEFC with MEA type 2, which may be due to an excess of the silica particles that affect the active Pt-sites in the catalyst. Excessive addition of silica may also exert an adverse effect on the electrical (ionic + electronic) conductivity of the catalyst layer. Accordingly, the peak power density for the PEFC with MEA type 2 is lower in relation to PEFC with MEA type 1. During PEFC operation generally product water resides in the cathode catalyst layer. Accordingly, it is inappropriate to add hydrophilic silica particles to the cathode catalyst layer as it would aggravate cathode flooding.

Figure 4 compares the polarization curves for the PEFCs with MEA types 1, 4, 5 and 6 under fully wet

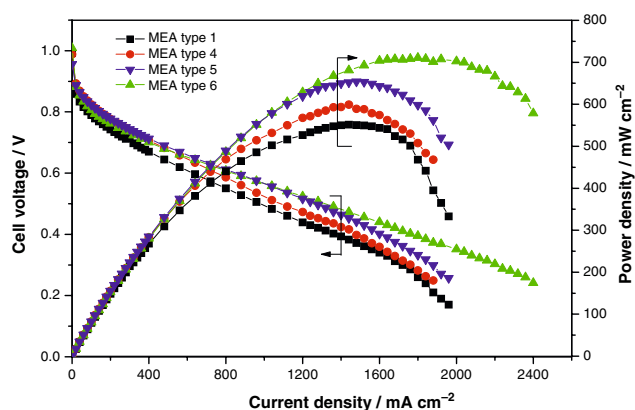


Fig. 4 Performance curves for PEFCs with MEA types 1, 4, 5 and 6 at 100% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

conditions (100%RH) at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure. It is apparent that the PEFCs with MEA types 4, 5, and 6 show lower resistance values as compared to PEFC with MEA type 1. The resistance is lowest for PEFC with MEA type 6. The maximum peak power density of 710 mW cm⁻² is achieved for the PEFC with MEA type 6 as compared to 550 mW cm⁻² realized for PEFC with MEA type 1 under identical operating conditions.

Figure 5 compares the performance curves for the PEFCs at 83% RH conditions with MEA types 1, 4, 5 and 6 at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure. The performance for PEFCs with MEA types 1 and 4 at 83% RH are lower as compared to their performance at 100% RH (see Fig. 4). By contrast the PEFCs with MEA types 5 and 6 at 83% RH deliver peak power densities of 680 mW cm⁻² and 740 mW cm⁻², respectively, which are higher in relation to the power density values obtained at 100% RH. The increase in peak power densities for PEFCs with MEA types 5 and 6 suggests that the water management in the PEFC is appropriate. Under fully humidified conditions (100% RH), the high silica content makes the MEA prone to water flooding, which impedes oxygen from accessing the catalyst layer and lowers the cell performance. At relatively lower RH values near 83% RH the water flooding recedes improving the performance of the PEFC as seen from Fig. 5.

The performance data for PEFCs with MEA types 1, 4, 5 and 6 at RH values 66% and 31% at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure are shown in Figs. 6 and 7, respectively. The PEFC with MEA type 1 exhibits lowest performance in relation to the PEFCs with MEA types 4, 5 and 6, as the former is poor in retaining water within its framework at these RH values. The peak power densities obtained for PEFC with MEA type 1 at 66% and 31% RH values are 300 mW cm⁻² and

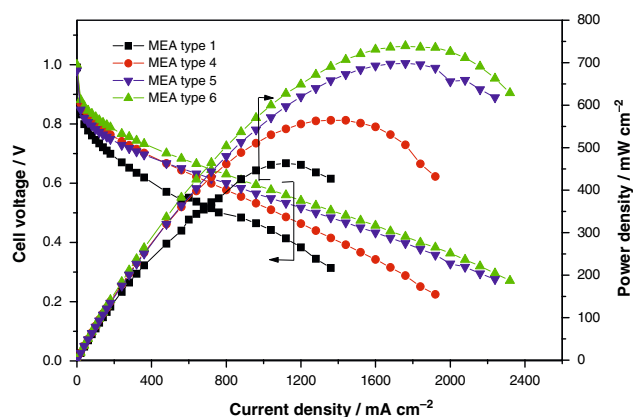


Fig. 5 Performance curves for PEFCs with MEA types 1, 4, 5 and 6 at 83% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

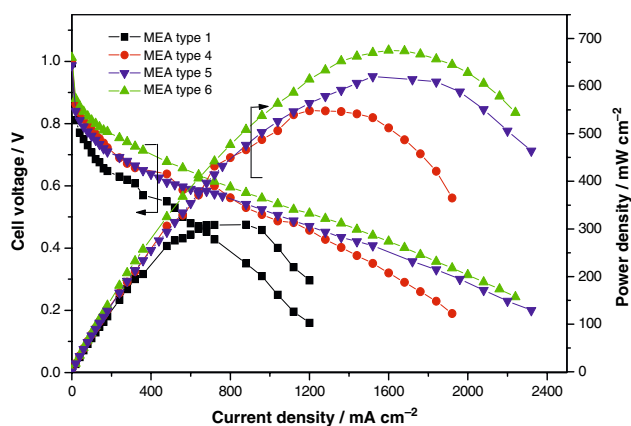


Fig. 6 Performance curves for PEFCs with MEA types 1, 4, 5 and 6 at 66% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

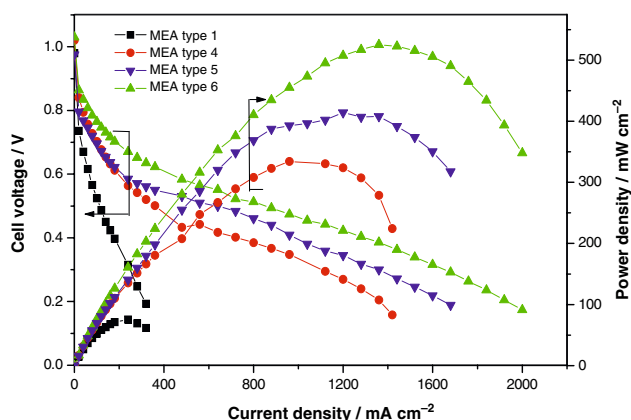


Fig. 7 Performance curves for PEFCs with MEA types 1, 4, 5 and 6 at 31% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

80 mW cm⁻², respectively. By comparison, PEFCs with MEA types 4, 5 and 6 yield much better performance at similar RH values. The maximum peak power densities of 675 mW cm⁻² at 66% RH and 525 mW cm⁻² at 31% RH are realized for PEFC with MEA type 6.

Figure 8 shows the polarization curves for PEFCs with MEA types 1, 4, 5 and 6 under near-dry conditions (18%RH) at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure. At this RH value the humidification of hydrogen gas is inappropriate for operating PEFCs with MEA type 1, as the PEFC yields a peak power density of only about 30 mW cm⁻² at 100 mA cm⁻², primarily due to the poor conductivity of the Nafion membrane. The PEFC with MEA type 1, due to the limited availability of water at the anode, suffers dehydration due to exacerbated electro-osmotic drag of water from anode to cathode and insufficient water back diffusion from cathode to anode. The membrane dehydration is manifested by an

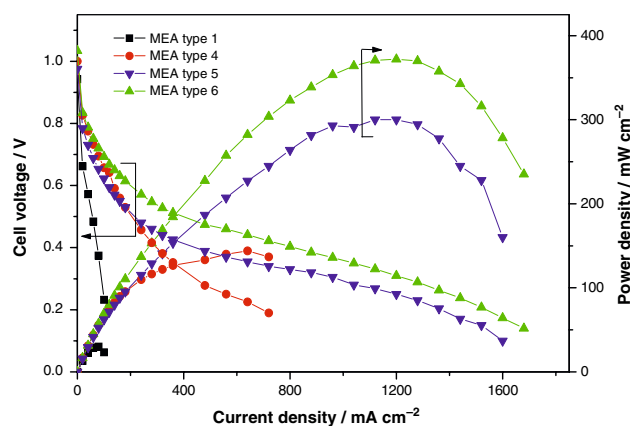


Fig. 8 Performance curves for PEFCs with MEA types 1, 4, 5 and 6 at 18% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

increase in ohmic resistance of the cell leading to decreased cell performance [21]. By contrast, for a PEFC employing MEA type 5 this problem is obviated due to the good water retention characteristics of silica in the membrane. Thus, under identical conditions, a PEFC employing MEA type 5 yields a peak power density of 300 mW cm⁻² at 1200 mA cm⁻². On the other hand, the PEFC with MEA type 6 delivers a peak power density of 375 mW cm⁻² at the same current density. The amelioration in the performance of the PEFC with MEA type 6 appears to be related to the retention of back-diffused water by silica particles present in the anode catalyst layer. Accordingly, PEFC with MEA type 6 performs better than the PEFC with MEA type 5 at low RH values.

To complement the polarization data on PEFCs with various MEA types under varying RH values, the electrochemical kinetic parameters of the cells were estimated as described elsewhere [7, 18, 22]. Assuming the mass-transfer limitations to be negligible and the hydrogen oxidation reaction to be fast, the cell potential (V) vs. current density (i) plot for PEFCs is expressed by,

$$V = V_o - b \log i - iR$$

where V_o is the observed open-cell potential, b is the Tafel slope for the oxygen reduction reaction, and R accounts for the linear variation of overpotential with load current density primarily due to the ohmic resistance of the cell. Table 2 shows the electrochemical kinetic parameters of the PEFCs with MEA types 1, 2, 3 and 4 at 83% RH. The ohmic resistance (R) for PEFCs with MEA types 2, 3, and 4 decreases with decreasing silica content in anode-catalyst layer in relation to the PEFC with MEA type 1. The lowest resistance is observed for PEFC with MEA type 4. The electrochemical kinetic parameters for PEFCs with MEA types 1, 4, 5 and 6 at varying RH values are given in

Table 2 Electrochemical kinetic parameters for PEFCs with MEA types 1, 2, 3 and 4 at 83% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

MEA types	V_0/V	b/V	$R/\Omega \text{ cm}^2$	Current density/ mA cm^{-2}	
				at 0.7 V	at 0.4 V
1	0.991	0.049	0.35	180	1160
2	0.994	0.044	0.36	240	1040
3	0.999	0.039	0.30	320	1360
4	0.991	0.037	0.28	360	1360

Tables 3, 4, 5, 6, 7. The PEFC with MEA type 4 has lower resistance in relation to the PEFC with MEA type 1 at all RH values, and the resistance of the PEFC with MEA type 5 is even lower. The PEFC with MEA type 6 exhibits least resistance at all RH values, a clear manifestation of the ability of silica to reduce membrane resistance due to its water retention properties. Among PEFCs with various

Table 3 Electrochemical kinetic parameters for PEFCs with MEA types 1, 4, 5 and 6 at 100% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

MEA types	V_0/V	b/V	$R/\Omega \text{ cm}^2$	Current density/ mA cm^{-2}	
				at 0.7 V	at 0.4 V
1	0.990	0.040	0.27	320	1400
4	0.988	0.030	0.25	400	1480
5	0.956	0.032	0.22	480	1640
6	1.009	0.034	0.21	420	1760

Table 4 Electrochemical kinetic parameters for PEFCs with MEA types 1, 4, 5 and 6 at 83% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

MEA types	V_0/V	b/V	$R/\Omega \text{ cm}^2$	Current density/ mA cm^{-2}	
				at 0.7 V	At 0.4 V
1	0.991	0.048	0.35	180	1160
4	0.991	0.037	0.28	360	1420
5	0.980	0.040	0.20	360	1760
6	1.0	0.033	0.20	480	1840

Table 5 Electrochemical kinetic parameters for PEFCs with MEA types 1, 4, 5 and 6 at 66% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

MEA types	V_0/V	b/V	$R/\Omega \text{ cm}^2$	Current density/ mA cm^{-2}	
				at 0.7 V	at 0.4 V
1	0.994	0.056	0.40	110	750
4	1.0	0.038	0.30	220	1360
5	0.987	0.046	0.24	220	1550
6	1.012	0.034	0.23	400	1680

Table 6 Electrochemical kinetic parameters for PEFCs with MEA types 1, 4, 5 and 6 at 31% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

MEA types	V_0/V	B/V	$R/\Omega \text{ cm}^2$	Current density/ mA cm^{-2}	
				at 0.7 V	at 0.4 V
1	0.980	0.073	2.00	30	180
4	1.02	0.044	0.72	100	720
5	0.975	0.057	0.28	100	970
6	1.03	0.037	0.27	180	1280

Table 7 Electrochemical kinetic parameters for PEFCs with MEA types 1, 4, 5 and 6 at 18% RH at 60 °C using gaseous hydrogen and oxygen reactants at atmospheric pressure

MEA types	V_0/V	b/V	$R/\Omega \text{ cm}^2$	Current density/ mA cm^{-2}	
				at 0.7 V	at 0.4 V
1	0.942	0.072	4.30	15	80
4	1.0	0.044	1.67	80	300
5	0.975	0.070	0.38	50	440
6	1.034	0.048	0.27	90	800

MEA types studied here, the Tafel slope (b) of the polarization curve for PEFC with MEA type 6 is lowest. This signifies that an increase in the contact area between silica added anode-catalyst layer in contact with the Nafion-silica composite membrane improves the hydration of the ion-conducting phase in the electrode with concomitant increase in the wettability of the anode, which facilitates electrochemical reaction at the electrode.

In brief, the present study demonstrates that incorporation of hydrophilic silica particles in the anode-catalyst layer increases hydration at low RH values and thus improves proton conduction in the medium. Moreover, at high current densities, the drying out effect on the anode side of the cell is mitigated by the presence of silica particles in the anode-catalyst layer, which helps retaining back-diffused water with concomitant increase in wettability. The present study provides a Nafion-silica composite membrane with silica particles in the anode catalyst layer which absorbs water and acts as a water reservoir to keep the membrane wet, even at low RH values. This helps PEFCs to sustain periods of inlet-stream draught without excessive loss in membrane conductivity. Consequently, the humidification exigencies for PEFCs are reduced, which in turn will help cutting system complexity and hence cost.

4 Conclusions

It has been clearly established that silica incorporation into the anode catalyst layer of the membrane electrode

assembly ameliorates the performance of PEFCs. The effect is, however, more pronounced with Nafion-silica composite electrolyte membranes. The study provides a new protocol for designing PEFCs operating under low humidification.

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