



Structural control and impedance analysis of cathode for direct methanol fuel cell

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Received 25 March 2004; received in revised form 21 June 2004; accepted 21 June 2004

Available online 25 September 2004

Abstract

The effect of the Nafion content and loading method in the catalyst layer of the cathode for a Direct Methanol Fuel Cell (DMFC) was investigated. The impedance of the full cell and cathode were determined by ac impedance spectroscopy. The Nafion content of 1.0 mg cm^{-2} improved the current density at a cell voltage of 0.4 V up to 258 mA cm^{-2} versus 128 mA cm^{-2} at a content of 0.5 mg cm^{-2} . The increase in the Nafion content decreased the diameter of the arc at low frequencies. For the electrode prepared by the spray method (SME), the cell performance and cathode performance using a dynamic hydrogen electrode (DHE) as the reference electrode was higher than those of the electrode prepared by the paste method (PME) by decreasing the cathode potential. From the ac impedance measurement of the cathode, the diffusion resistance of the SME electrode had the lowest interfacial resistance of the cathode electrodes. The higher cell performance was mostly dependent on the diffusion resistance. The SME with a porous structure and a catalyst layer thickness of $50 \mu\text{m}$ were characterized by SEM and BET adsorption measurements.

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Keywords: DMFC; Ionomer; MEA; Electrode; Impedance

1. Introduction

Direct Methanol Fuel Cells (DMFCs) are very attractive power sources for electric vehicles and portable applications. The DMFC has several advantages that suit its application for transportation, including a high efficiency, very low emissions, a potentially renewable fuel source and fast and convenient refueling. The thermodynamic reversible cell potential for the overall cell reaction is 1.214 V at 298 K , which compares to 1.23 V for the PEFC using hydrogen, which has generated much interest in the DMFC. Meanwhile, DMFC shows a lower performance than PEFC using hydrogen. In a particular cathode for the DMFC, the electrode reaction mechanism is complicated to be O_2 reduction and crossover methanol oxidation decreased the cathode potential because of the mixed potential. The cathode flooding is easily

caused by the cathode produced water and crossover water and methanol different from the PEFC cathode. So, we believe the structural and reactant analysis of the membrane electrode assembly (MEA) including the DMFC cathode is remarkable study. The structure of the MEA for the DMFC is a composite of two porous, electro catalytically active electrodes on either side of a polymer electrolyte membrane (PEM). In the DMFCs catalyst, Pt-Ru/C is the typically utilized as the anode catalyst, and Pt/C is utilized as the cathode catalyst. Increasing the reaction sites in the catalyst layer is important for improving the electrode performance. [1,2] Since the polymer membrane like the Nafion 117 membrane used for the electrolyte is a solid phase, the membrane cannot deeply penetrate into the electrode as does a liquid one, therefore, the reaction area is limited to the contact surface between the electrode and membrane. Furthermore, the conductivity of the Nafion 117 membrane is 10 S/m at 298 K . [3–5] The cell resistance using the Nafion 117 membrane as described by Gatefold et al. was

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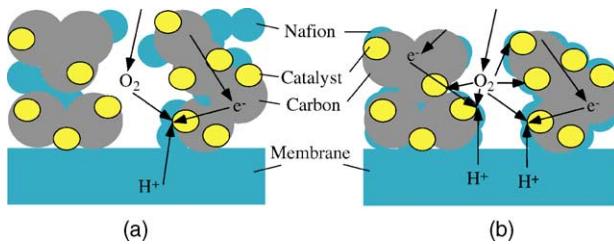


Fig. 1. Schematic diagram of Nafion loading method; (a) paste method (PME) and (b) spray method (SME).

$0.17 \Omega \text{ cm}^2$, a lower contact resistance. [6] For the purpose of improving the resistance and increasing the contact surface area, an ionomer like Nafion is added to the surface of the catalyst particle [7,8]. Here, the Nafion loading method can be classified into the following two methods (PME: paste method, SME: spray method). [9,10] For the PME, the loading method is a general and well-known method in which the PME ink includes Nafion and the catalyst load on a carbon cloth. As can be seen from Fig. 1a, the oxygen can easily reach the reaction sites, but the catalyst utilization is low and the cell performance is also low. Therefore, we suggested the new SME loading method. In the SME, the catalyst ink with no Nafion is loaded on the carbon cloth. Nafion is then sprayed on the surface of the catalyst layer. As can be seen from Fig. 1b, both the electronic and ionic conductivities are increased due to the better contacts. Meanwhile, the excess Nafion polymer hinders gas diffusion to the reaction sites. In a particular cathode, the excess of Nafion polymer on the catalyst surface is caused by flooding in the reaction sites [6,11].

The objective of this study is to clarify the effect of the Nafion content and loading methods (PME and SME) on the surface of the cathode catalyst layer for improving the cell performance. By using the method of alternate current impedance spectroscopy [12,13], the variable resistances of an equivalent circuit for the MEA were determined.

2. Experimental

The membrane electrode assemblies (MEAs) were prepared as follows: the anode consisted of a carbon cloth

support (E-TEK, type A) on which was spread a thin 2.0 mg cm^{-2} layer loading of 53.1% Pt-Ru/C (Tanaka Precious Metals Co.) bound with a 20 wt.% Nafion solution dissolved in butyl acetate [14]. The cathode was constructed using a method similar to the anode using a diffusion layer bound with 2.0 mg cm^{-2} of 47.0% Pt/C (Tanaka Precious Metals Co.) as the catalyst layer. A Nafion solution for the spray method electrode (SME) was applied to the surface of the cathode catalyst layer that included no ionomer. Furthermore, the cathodes used in the experiments was also the as-received ELAT electrode (E-TEK, ELAT/NC/DS/V3) and T-1 electrode [15] for comparative purposes. Details of the experimental conditions for cathode catalyst layer are shown in Table 1. The electrodes were placed on either side of a pre-treated Nafion 117 membrane. This pre-treatment involved boiling the membrane for 1 h in 3 vol.% H_2O_2 , 1 h in deionized (DI) water, 1 h in 0.5 kmol m^{-3} H_2SO_4 and 1 h in deionized (DI) water, followed by washing in deionized (DI) water [16]. The assembly was hot-pressed at 10 MPa for 2 min at 398 K. The resulting MEA was installed in the cell after pressing, and supplied with water on the anode side and $2.5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ O_2 on the cathode side aged at 363 K for several hours. The morphology of some fabricated electrodes was observed using scanning electron microscopy (JEOL JSM-5600, JSM-6401F).

Investigations of the DMFC were performed using an experimental setup. The cell was fitted with a MEA sandwiched between two graphite blocks having serpentine channel flow paths cut out for the methanol and oxygen flows. The cell was held (6 Nm) together between two backing plates using a set of retaining bolts positioned around the cell. The anode flow-field through the vaporizer heated at 473 K was 2.0 kmol m^{-3} and the flow rate of the methanol solution was $5.0 \times 10^{-8} \text{ m}^3 \text{ s}^{-1}$. The outlet flows could be controlled in order to impose the desired amount of back pressure at 0.1 MPa. Oxygen was supplied from a cylinder at ambient temperature. The flow rate was $5.9 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. The cell temperature was maintained at 363 K. The outlet flows could be controlled to impose the desired amount of back pressure at 0.2 MPa. In addition to the usual cell hardware, our cells also contained a dynamic hydrogen electrode (DHE) as a reference electrode to resolve the anode and cathode performances in the DMFCs. The DHE electrode was a 0.5 mm diameter

Table 1
Experimental conditions for cathode catalyst layer

Abbreviation	Metal loading (mg cm^{-2})	Nafion sol. Concentration (wt.%)	Nafion content (mg cm^{-2})	Catalyst: Nafion	Loading method
Nafion content of cathode					
PME2-20-0.5	2.0	20	0.5	1:0.1	Paste
PME2-20-1.0	2.0	20	1.0	1:0.2	Paste
PME2-20-3.5	2.0	20	3.5	1:1	Paste
Various cathode electrode					
ELAT	0.5	–	–	–	–
PME	0.5	5	0.28	1:0.2	Paste
SME	0.5	5	0.28	1:0.2	Spray
T-1	0.5	5	0	–	–

Pt-black coated Pt wire. The center of the DHE electrode was separated from the fuel cell electrode edges by 5 mm.

The cell performance and electrochemical properties of the DMFC system were investigated using the electrochemical measuring system (Scribner Associates Inc., series 890B, Solatron SI 1250, Hokuto Denko HZ-3000 and Solartron SI 1287/SI 1260). The impedance spectra were usually obtained at frequencies between 65 kHz and 3 mHz [17].

3. Results and discussion

3.1. Nafion content of cathode

Fig. 2 shows the effect of the MEA preparation on the cell performance at 363 K. By increasing the Nafion content of the cathode, the current density at a cell voltage of 0.4 V was increased to 258 mA cm^{-2} for a 1.0 mg cm^{-2} (PME2-20-1.0) content when compared to 128 mA cm^{-2} for a 0.5 mg cm^{-2} (PME2-20-0.5) content. Meanwhile, an excess Nafion content decreased the cell performance and cell voltage in the short circuit current region. The limiting current density is ascribed to the high concentration over-voltage during cathode flooding to the cathode reaction sites. **Fig. 3** shows an equivalent circuit for the ac impedance analysis. Here, R_1 is the cell resistance including the electrolyte and membrane resistances. R_2 is the charge-transfer resistance at the interface of the catalyst layer. R_3 is the diffusion resistance of the oxygen dissociative

chemisorption at the catalyst reaction site. C_2 is the capacitance of the double layer and C_3 is the capacitance of the adsorption [18,19]. Generally, the R_3C_3 circuit is treated as the diffusion impedance. However, the diffusion impedance is completely analogous to the wave transmission in a finite length RC transmission line. Therefore, the equivalent circuit can be approximately expressed by a RC circuit. Furthermore, the charge-transfer reaction and the chemisorption reaction was described by Kamiya et al. [20].

From the impedance measurements, the measured values were well fitted using the parameters depicted by **Fig. 3**. The diameter of the arc at low frequency decreased by increasing the Nafion content. Meanwhile, for the 3.5 mg cm^{-2} Nafion content (PME2-20-3.5), the diameter became larger than that of the 1.0 mg cm^{-2} Nafion content (PME2-20-1.0). **Fig. 4** shows the effect of the Nafion content on the variable resistances (R_1 , R_2 and R_3) and capacitances (C_2 and C_3) at dc potential 0.4 V. The cell resistance (R_1) for the excess Nafion content was lower than that of the lower Nafion content due to the good contact between the membrane and electrode. The charge-transfer resistance (R_2) decreased more than that of the higher Nafion content and the double layer capacitance (C_2) became higher than that of the excess Nafion content. Since the dispersion of the Nafion polymer increased, the reaction site of the catalyst layers increased the area of the three-phase boundary. The diffusion resistance (R_3) and capacitance (C_3) also decreased. Meanwhile, the excess Nafion content increased R_3 and C_3 due to the increased Nafion polymer thickness at the reaction sites in the catalyst layers. The larger volume of the ionomer suppressed the oxygen chemisorption on the catalyst site. The diffusion resistance (R_3) shown in **Fig. 4** was reasonably correlated with the cell performance shown in **Fig. 2**. This correlation clearly suggests that a low ionomer content in the catalyst layer is beneficial.

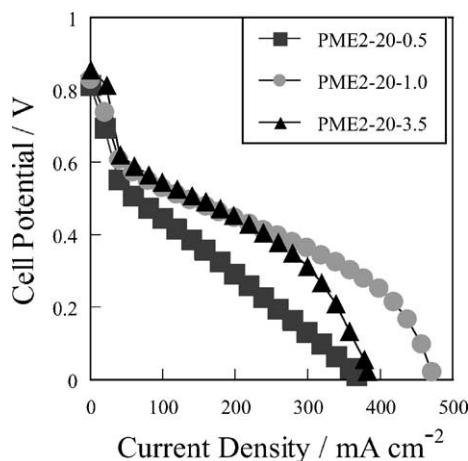


Fig. 2. Effect of Nafion content on the cell performance at 363 K.

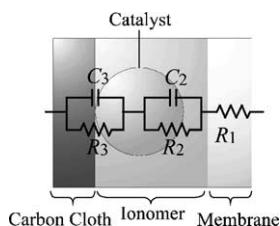


Fig. 3. Equivalent circuit for the ac impedance analysis.

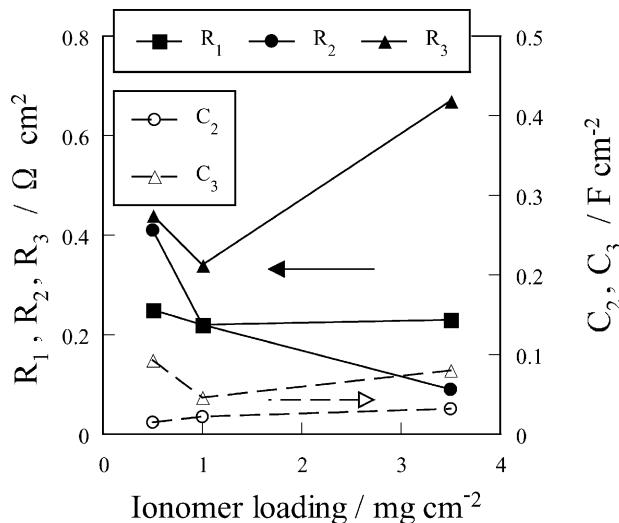


Fig. 4. Effect of the Nafion content on the internal resistances (R_1 , R_2 and R_3) and capacitances (C_2 and C_3), DC potential 0.4 V.

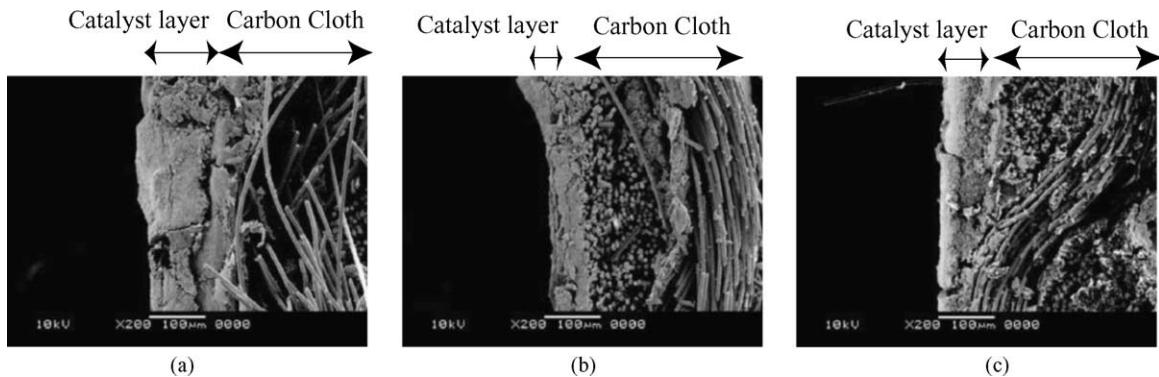


Fig. 5. SEM image of cathode cross-section ($\times 200$); (a) PME, (b) SME and (c) ELAT.

3.2. Various cathode electrodes

Cross-sectional scanning electron microscopy (SEM) micrographs of the catalyzed cathodes made by the paste method electrode (PME) and spray method electrode (SME) are shown in Fig. 5a and b, respectively. Fig. 5a shows a planar micro porous support layer with an average thickness of about 30 μm over a carbon cloth. On the surface of the micro porous support layer including the carbon cloth (the right side), a cathode layer (the left side) of about 100 μm in thickness consisting of carbon supported Pt and Nafion polymer was observed. In Fig. 5b, a SME cathode catalyst layer with a total average thickness of about 50 μm could be seen on the surface of the micro porous support layer. These two electrodes, PME and SME, had different catalyst layer sicknesses because PME was observed to be a Nafion layer and agglomerated in the catalyst layer. The SME was thin layer because the Nafion solution was sprayed on the surface of the cathode catalyst layer network without an ionomer. Fig. 5c shows a cross-sectional SEM micrograph of the as-received catalyzed ELAT electrode. A cathode catalyst layer and support layer of ELAT with an average thickness of about 50 μm could be seen on the surface of the carbon cloth.

Fig. 6 shows the polarization curves for the spray method electrode (SME) compared to the paste method electrode (PME). The best performances (921 mA cm^{-2} at the short circuit current) were obtained using the ELAT electrode with a thin catalyst layer. For the SME electrode, the cell performance was higher than that of the PME electrode because these PME and SME electrodes were different in catalyst layer thickness (Fig. 5a and b). The cell performance of the T-1 electrode was inferior to the other electrodes because the T-1 electrode used for chlor-alkaline electrolysis did not include the polymer electrolyte such a Nafion ionomer in the catalyst layer.

Ren et al. [21] studied the cell performance based on the anode and cathode performances, with a DHE reference electrode. One of the problems of the previously reported DHE within the fuel cell structure was a serious potential drift when the cell was operated at a high current density. This was explained by the changes in the water activity in the vicin-

ity of the reference electrode, caused by the electro-osmotic drag of water. This problem was solved in our DHE by sufficiently separating the DHE from the edge of the fuel cell electrodes (4 mm as compared to the membrane thickness of about 0.2 mm). In the present study, the measurement of the cathode polarization behavior using the DHE was employed to diagnose the polarization behaviors of the unit cell without modifications of the operating cell fixture and MEA. In Fig. 6, the polarization curves of cathode using the PME and SME electrodes were confirmed to have significantly different waves. For the SME electrode, the cathode performance was higher than that of the PME electrode. Meanwhile, the polarization curves of the cathode using the PME and SME electrodes was confirmed to have voltage drops over a 600 mA cm^{-2} current density because of the higher mass transfer resistances. The limiting current density is ascribed to the high concentration over-voltage for the cathode flooding to the cathode reaction sites.

Fig. 7(1) shows the cathode impedance spectra (DC current: 200 mA cm^{-2}) for the spray method electrode (SME) and also the paste method electrode (PME) using the equiv-

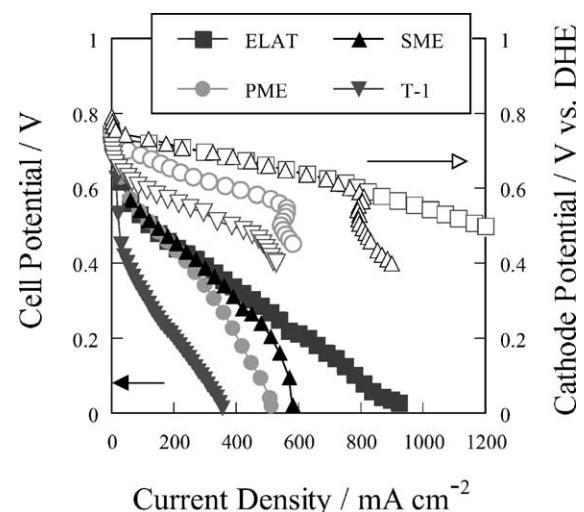


Fig. 6. Polarization curves for spray method electrode (SME) compared to paste method electrode (PME).

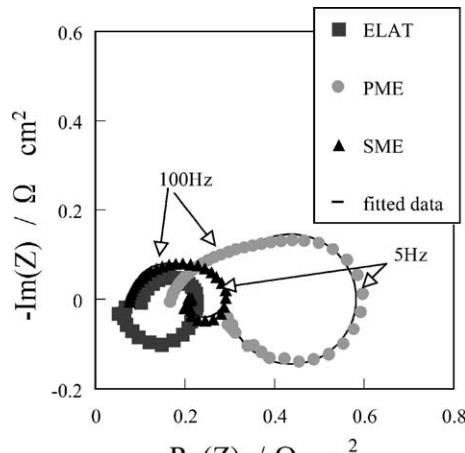


Fig. 7. (1) Cathode impedance spectra of spray method electrode (SME) compared to paste method electrode (PME), DC current 200 mA cm^{-2} . (2) Equivalent circuit for the cathode impedance analysis.

alent circuit shown in Fig. 7 (2). Here, the inductance L_1 and R_4 are characteristics of this equivalent circuit, and thus deserve an explanation with respect to its mechanistic significance. Inductive behavior means that the current signal follows a voltage perturbation with a phase delay. The inductive behavior can be explained using the kinetic theory for reactions involving intermediate adsorbates [12]. In Fig. 7 (1), the measured values were well fitted using the parameters depicted by Fig. 7 (2). The impedance parameters of the PME and SME are listed Table 2. All the resistance parameters of the SME decreased in comparison to that of the PME. The cell resistance (R_1) of the SME was lower than that of the PME due to the thin catalyst layer and the good connection between the membrane and electrode. The charge-transfer resistance (R_2) of the SME became lower than that of PME. Since the dispersion of the Nafion polymer using the spray treatment increased, the reaction site of the catalyst layers increased the area of the three-phase boundary. The diffusion resistance (R_3) was also decreased. The Nafion content of the PME increased R_3 due to the increased Nafion polymer thickness of the reaction site in the catalyst layers. The larger volume of the ionomer suppressed the oxygen chemisorption on the catalyst site. The diffusion resistance (R_3) shown in Table 2 was reasonably correlated with the cell performance

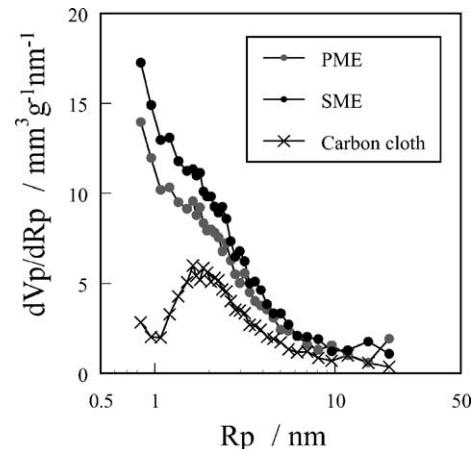


Fig. 8. Pore size distribution for the DMFC cathode electrodes.

shown in Fig. 6. The intermediate adsorbate resistance (R_4) increased due to the larger intermediate adsorbate coverage at the reaction site of the catalyst surface [19]. Thus, the cell performance of the SME with the smallest interfacial resistance was recorded to have a power density of 130 mW cm^{-2} .

Since the catalyst layer porosity is one of the key factors that govern the gas diffusion properties inside the electrode, the porosity of the catalyst layers was measured [21]. There are also the BET adsorption measurements [22,23] that allow one to obtain the specific surface area and the pore size distribution from the amount of adsorbed gas measured at different gas pressures. The specific surface areas and pore volumes of the cathode were determined by N_2 gas adsorption at 77 K. The surface areas and micro pore volumes of the samples were evaluated using the BET and DH method, respectively. The amount of N_2 adsorbed at relative pressures was employed to determine the total volume, which corresponds to the sum of the micro pore and mesopore volumes. In Fig. 8, the pore size distribution inside the catalyst layer of the PME and SME including the carbon cloth was calculated from the DH method. The pore radii of the carbon cloth were mostly within the range of 1–10 nm with an average radius of 1.7 nm. The pore size and size range of the PME and SME decreased in comparison with that of the carbon cloth including the non-catalyst layer. Thus, the catalyst layer was confirmed to be porous. The pore size and size range of the SME was the smallest for the electrodes. In the PME, the pore volume in the catalyst layer was covered by a polymer electrolyte such as the Nafion ionomer. The pore volume in the micropores of the SME and PME was $32 \text{ mm}^3 \text{ g}^{-1}$ and $24 \text{ mm}^3 \text{ g}^{-1}$, respectively. Thus, the SME of the higher pore volume compared to that of the PME was confirmed to have a porous structure and thin Nafion layer on the catalyst particle.

Table 2
Impedance parameters of MEA with various cathode electrodes

Abbreviation	$R_1 (\Omega \text{cm}^2)$	$R_2 (\Omega \text{cm}^2)$	$R_3 (\Omega \text{cm}^2)$	$R_4 (\Omega \text{cm}^2)$
PME	0.17	0.14	0.28	0.16
SME	0.08	0.12	0.12	0.25

4. Conclusion

The Nafion content of the cathode improved the current density at a cell voltage of 0.4 V up to 258 mA cm^{-2} for the

1.0 mg cm⁻² content in comparison to the 128 mA cm⁻² for the 0.5 mg cm⁻² content. The Nafion solution in the catalyst layers is available for high cell performance and lower interfacial resistance (R_1 and R_2). Based on the ac impedance measurement results, the increase in the Nafion loading decreased the arc diameter at low frequencies. The higher cell performance depended on the diffusion resistance (R_3) of the oxygen dissociative chemisorption. The presence of a slight amount of ionomer on the catalyst surface is necessarily the key for the higher cell performance of the DMFC.

For the SME electrode, the cell performance and cathode performance using a DHE reference electrode was higher than that of the PME electrode. Based on the ac impedance measurements of the cathode, the diffusion resistance of the SME electrode had the lowest interfacial resistance of the cathode electrodes. The higher cell performance was mostly dependent on the diffusion resistance. The SME with a porous structure and a catalyst layer thickness of 50 µm was evaluated by SEM and BET adsorption measurement. The SME was confirmed to have a porous structure and thin catalyst layer.

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