Comparison of the membrane-electrode assembly conditioning procedures for direct methanol fuel cells

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ARTICLE INFO

ABSTRACT

The effects of four conditioning procedures, i.e. methanol circulation, combination of methanol circulation and electric load, methanol circulation plus gas evolution, and H_2/O_2 PEMFC mode, on the electrochemical behaviors and performances of membrane-electrode assemblies (MEAs) in direct methanol fuel cells (DMFCs) have been comparatively investigated for maximizing their performances. The results show that the conditioning procedures do not have much influence on the catalytic activity, oxygen transport, and proton resistance in the catalyst layer. However, the conditioning procedures have significant influence on the hydration of the MEAs, which determines the electrochemical performances of the MEAs before eventually reaching their maximum performances. Among the various procedures investigated, the combination of methanol circulation and electric load is a convenient and effective in situ way to activate the fresh MEAs in DMFC, which speeds up the hydration of the MEAs due to large amount of water on both electrodes.

1. Introduction

Direct methanol fuel cells (DMFCs) are potential power sources for portable electronic devices such as cellular phones and laptops as well as for vehicle applications due to their high energy density and simple system configurations [1,2]. Membrane-electrode assembly (MEA) is a key part in DMFC, and it is comprised of electrolyte membrane, catalyst layers, and gas diffusion media. Typically, these components are fabricated individually and hot-pressed together at high temperature and pressure to strengthen interfacial contact between the catalyst layers and the electrolyte membrane. The effects of hot-pressing conditions like temperature, pressure, and duration on the electrochemical performances of MEAs have been studied extensively in the literature [3–8]. At a temperature higher than the glass transition temperature, Nafion membrane undergoes microstructural changes and irreversible water loss, resulting in much lower proton conductivity. High pressure can provide enough binding force between the catalyst layers and Nafion membrane, but it leads to severe deformation in the electrode structure, resulting in low porosity, large reactant transport resistance, and slow start-up. Some catalysts in the catalyst layer could also be enclosed and become "dead" zones dur-

ing MEA fabrication. Therefore, activation treatment, termed as conditioning, is usually required for a fresh MEA to reach its full performance.

Some conditioning procedures have been proposed to regain the inherent characteristics of the MEAs and their PEMFC performance in a relatively short period. For instance, Qi and Kaufman [9] steamed or boiled the hot-pressed MEAs in water for 10 min to humidify the Nafion membrane and activate the "dead" zones in the catalyst layer. They also presented another activation method by potential cycling of the MEAs in the range of open-circuit potential (OCV) to 0 V under elevated temperatures and pressurized gases, which was especially effective for low Pt loading MEAs with carbon-supported catalyst [10]. In addition, H_2 evolution and "CO oxidative stripping" have been used to activate the MEAs and to improve the catalyst utilization and oxygen transport in the cathode [11,12].

In DMFC, in order to improve the methanol oxidation reaction (MOR) kinetics, enhance methanol tolerance, and reduce methanol crossover to the cathode, larger amounts of catalysts, higher ionomer loading, and thicker Nafion membranes are usually employed, which make the DMFC to require more conditioning time than a PEMFC. Moreover, the process is possibly more rigorous and complicated due to the swelling of Nafion membrane and the dissolution of the Nafion ionomer in the catalyst layers in methanol solution. Scott et al. [2,13] circulated over the anode and the cathode with methanol solution and water, respectively, for 24–48 h after hot-pressing the MEA. Then the MEA was further

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conditioned at the cell voltage of 0.3 V to reach the full performance under the operating conditions. Kho et al. [14] immersed the MEAs in pure water for more than 100 h and obtained steady-state performance for passive DMFCs. They found that the MEAs pretreated with methanol solution exhibited higher power density than that pretreated with pure water. They also developed a "shut-down method" to break-in the MEAs by supplying the reactants at intervals [15]. Dinh et al. [16] preferred to break in a fresh MEA in hydrogen/air PEMFC mode before switching to methanol/air DMFC mode. They found that the Ru and Pt oxides in the catalyst layer were reduced in humidified hydrogen at 80 °C for 2–5 h, which led to better alloying and better activity toward methanol oxidation. This procedure was also adopted by Go'mez de la Fuente et al. [17] to initialize the MEA performance at open circuit with 100% humidified and pressurized gases.

Applying electric load to a single cell and making it operate at constant current is also a procedure to activate the MEAs. Arico et al. [18] first circulated the anode and the cathode with water to achieve a good humidification of the MEA with low cell resistance, and then operated the cell at high current density for 1 or 2 days until it reached a steady-state performance. Liu et al. [19] kept the single cell running at a constant current density of 100 mA cm^{-2} to incubate the MEA for about 5 h. Sherazi et al. [4] controlled the potential of the single cell at 0.4 V to break-in the MEA for 2 h at 40 °C. Actually, this procedure is the combination of methanol circulation and electric load. Its activation rate and effectiveness are limited by the current density and voltage generated by the MEA. Besides, He et al. [11] developed a fast procedure to condition the MEAs in DMFC. The catalyst utilization and mass transport were much improved in less than 1 h through H$_2$ evolution and CO$_2$ evolution by methanol oxidation. It should be noted that the methanol circulation is also involved in the process.

Overall, the following procedures: methanol solution circulation [2,13–15], gas evolution or the combination of methanol circulation and gas evolution [11,12], H$_2$/O$_2$ PEMFC mode [10,16,17], and methanol circulation plus electric load [4,14,18,19] have been employed to maximize the MEA performance in fuel cells. The advantages, time involved, and effectiveness of each procedure seem to depend on the operating conditions, MEA components (e.g., type of catalyst and membrane, thickness of the catalyst layer and membrane, and ionomer/carbon ratio), fuel cell types, and even researcher's preference. A unified consensus on the activation mechanism of the MEAs has not yet been achieved in the fuel cell community.

We present here a systematic investigation of the effects of four conditioning procedures, i.e. methanol circulation, combination of methanol circulation and electric load, methanol circulation plus gas evolution, and H$_2$/O$_2$ PEMFC mode, on the electrochemical performances of the MEAs in DMFC. The aim of this paper is to clarify the discrepancies in the effectiveness of the activation modes and to find the most effective conditioning procedure for DMFC.

2. Experimental

2.1. Membrane-electrode assembly (MEA) fabrication

Nafion 115 membranes (Dupont) were pretreated sequentially in 5 vol.% H$_2$O$_2$, deionized (D.I.) water, 0.5 M H$_2$SO$_4$, and D.I. water at 80 °C for 1 h and kept in D.I. water prior to use. Commercial PtRu/C (40 wt.% Pt and 20 wt.% Ru, Johnson Matthey) and Pt/C (60 wt.% Pt, Johnson Matthey) were used, respectively, as the anode and cathode catalysts. The catalysts were first wetted by a small amount of D.I. water and then mixed with a required amount of solvent and Nafion solution (5 wt. % solution, EW1000, Dupont). The weight ratio of dry Nafion ionomer to carbon was fixed at 0.8. The mixture was sonicated (sonication bath, Branson 1510) for 60 min for homogenizing at room temperature. The resultant ink was sprayed onto the gas diffusion layer (35 BC, SGL) on a hotplate. The catalyst loadings on both the anode and cathode were 2.5 mg cm^{-2}. The electrodes were bonded with Nafion 115 by hot-pressing at 135 °C with a pressure of 50 kg cm^{-2} for 3.0 min. The geometrical active area of MEA is 5 cm^2.

2.2. MEA assembling and single cell testing

The obtained MEAs were assembled in a single cell fixture (Electrochem Inc.) consisting of two graphite plates with serpentine channels. Electrical heaters and a thermocouple were embedded into the plates and connected to a fuel cell test station (Scribner, 850 C) to control the cell temperature at 65 °C in this study. A peristaltic pump (IPC4, Ismatec) was employed to supply aqueous 1.0 M methanol solution to the anode at a flow rate of 1.0 mL min^{-1}. O$_2$ was humidified by passing through the humidifier built in the test station and then fed to the cathode at the flow rate of 200 mL min^{-1} without backpressure. Current–voltage curves were automatically recorded with an electrical load bank, and the cell resistances were monitored by an impedance analyzer built in the test station.

2.3. Conditioning procedures

Considering the performance discrepancies that could occur due to the small variations in the fabrication of MEAs even when they are prepared under identical conditions and to avoid the after-effects from different types of measurements, twelve MEAs were prepared for the four pretreatment procedures. Each pretreatment procedure had three MEAs; the first MEA was used for electrochemical measurements, the second MEA was used for cathode polarization measurements in PEMFC, and the third MEA was used for the polarization measurement in DMFC mode. The fresh MEAs were pretreated in a single cell by the following procedures.

#### 2.3.1. Procedure 1 – methanol circulation
The anode and the cathode of the first MEA were circulated with 1.0 M methanol and pure water, respectively, for 2 h at the cell temperature of 65 °C. Then water was replaced with oxygen. This MEA was denoted as Pre1-MEA.

#### 2.3.2. Procedure 2 – methanol circulation and electric load
The conditioning of the second MEA was conducted in a DMFC single cell. The cell was kept running with a constant current density of 100 mA cm^{-2} for 2 h at the temperature of 65 °C. This MEA was denoted as Pre2-MEA.

2.3.3. Procedure 3 – methanol circulation plus gas evolution
The third MEA was installed into the fuel cell fixture, and the cell was operated with 1.0 M methanol solution at the anode and nitrogen at the cathode at 65 °C. A potential of 0.5 V (vs. the cathode) was applied to the anode for 20 min with the potentiostat. CO$_2$ and H$_2$ were produced, respectively, at the anode and cathode as according to the reactions below:

$$\text{Anode}: CH_3OH + H_2O \rightarrow 6H^+ + CO_2 + 6e^{-1} \tag{1}$$

$$\text{Cathode}: 2H^+ + 2e^{-1} \rightarrow H_2 \tag{2}$$
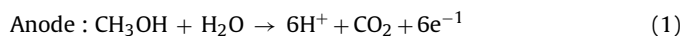
The cross-over methanol in the cathode was then oxidized by applying 0.5 V potential to the cathode for 20 min.

$$\text{Cathode}: CH_3OH + H_2O \rightarrow 6H^+ + CO_2 + 6e^{-1} \tag{3}$$

$$\text{Anode}: 2H^+ + 2e^{-1} \rightarrow H_2 \tag{4}$$
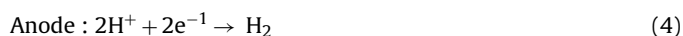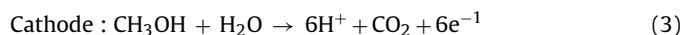
This MEA was denoted as Pre3-MEA.

2.3.4. Procedure 4 – H₂/O₂ PEMFC mode

The H₂/O₂ PEMFC mode was adopted to condition the fourth MEA by supplying humidified H₂ and O₂ at the cell temperature of 65 °C. The cell was operated at a constant current of 100 mA cm⁻² for 2 h. Subsequently, H₂ was switched to 1.0 M methanol solution and the cell was operated in DMFC mode. This MEA was denoted as Pre4-MEA.

2.4. Electrochemical measurements

Fully humidified H₂ and N₂ were fed, respectively, into the anode, as a dynamic hydrogen electrode (DHE), and cathode at a flow rate of 200 mL min⁻¹. Cyclic voltammetry (CV) data were collected with a potentiostat (Solartron 1287A, Solartron Analytical) at a scan rate of 20 mV s⁻¹ in the potential range of 0.04–0.90 V vs. DHE. The electrochemical adsorption/desorption of hydrogen on the catalyst surface was thereby monitored and the curves were recorded with the CorrWare software (Scribner Associates).

The anode polarization experiments were conducted on the potentiostat by supplying 1.0 M methanol solution with a flow rate of 1.0 mL min⁻¹ to the anode and fully humidified H₂ at 200 mL min⁻¹ to the cathode as a DHE. The polarization curves were recorded in the potential range of 0–0.5 V (vs. DHE) with a scan rate of 2 mV s⁻¹.

EIS measurements were conducted under the same operating conditions as the anode polarization on a frequency response analyzer (1260 FRA, Solartron Analytical) combined with the potentiostat. The amplitude of the sinusoidal signal for AC impedance was set as 10 mV rms over a frequency range of 4 kHz to 0.1 Hz. A bias DC potential was applied to the anode and the impedance spectra of methanol electro-oxidation were recorded with the ZPlot software (Scribner Associates).

3. Results and discussion

3.1. Electrochemical surface area

As soon as the conditioning was finished, the anode and cathode were fed, respectively, with humidified H₂ and N₂. The electrochemical surface area (ESA) of the Pt cathode was measured in the potential range of 0.04–0.9 V vs. DHE at the cell operating temperature of 65 °C. This potential range was chosen to avoid H₂ evolution at low potentials and platinum oxidation at high potentials. Fig. 1 shows the CV curves of the cathodes activated by the four conditioning methods. The ESA (m² g$_{Pt}$⁻¹) values were calculated by integrating the hydrogen desorption charge on platinum, which was divided by a value of 210 μC cm⁻² (assuming hydrogen mono-
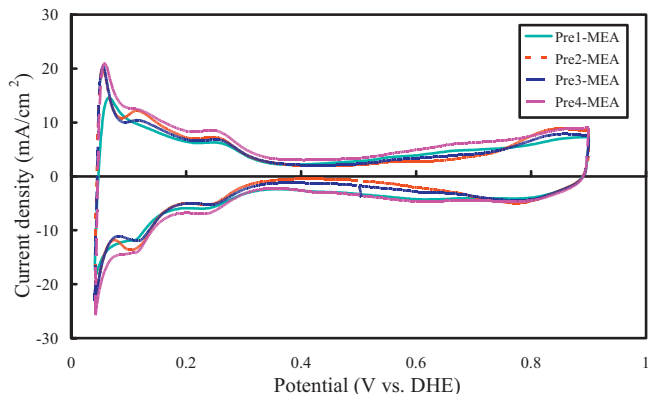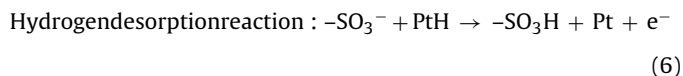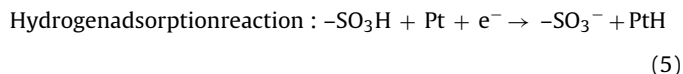
layer adsorption on Pt surface) and further divided by the catalyst loading (g$_{Pt}$ cm⁻²).

The ESA listed in Table 1 corresponding to each conditioning method are respectively 29.0, 34.9, 31.7, and 36.0 m² g⁻¹ for procedure 1–4. Compared to the total surface area of 85 m² g⁻¹ for Pt/XC-72 (provided by the manufacturer), the catalyst utilizations are 34, 41, 37, and 42%, respectively, for methods 1–4. If a 10% error in the ESA determination is considered, the conditioning procedures do not show a significant impact on ESA and catalyst utilization.

As we know, the protons dissociate from the sulfonic acid groups (−SO₃H) and combine with active Pt sites during CV measurements. The hydrogen adsorption/desorption reactions occur as follows:

$$\text{Hydrogen adsorption reaction}: -SO_3H + Pt + e^- \rightarrow -SO_3^- + PtH$$

(5)

$$\text{Hydrogen desorption reaction}: -SO_3^- + PtH \rightarrow -SO_3H + Pt + e^-$$

(6)

The hydrogen adsorption/desorption reactions on Pt surface are affected by the proton activity, which is expressed as $a_{H^+} = c_{H^+}\gamma_{H^+}$, where c_{H^+} is the concentration of protons dissociated from sulfonic acid groups and γ_{H^+} is the proton activity coefficient. Proton concentration is high at low levels of hydration, but the proton activity coefficient is low. While at high levels of hydration, proton concentration is small, but the proton activity coefficient is high. The two opposing tendencies lead to slight variations in proton activity, which might give similar values of ESA for MEAs with different degree of hydration.

Pre2-MEA and Pre4-MEA were activated at constant current density, which accelerates the hydration of Nafion membrane and ionomer in the catalyst layers. In addition to the water produced in the cathode, a lot of water also reaches the cathode from the anode through the membrane by virtue of diffusion and electro-osmosis. For example, if the electro-osmotic drag (EOD) coefficient of water is about 3.0 per proton, there are 18 moles of water transport to the cathode though Nafion membrane when one molar methanol is oxidized to produce 6 moles of protons [20]. Therefore, there is sufficient water to hydrate the Nafion membrane and the ionomer at the cathode of Pre2-MEA and Pre4-MEA. In the case of Pre1-MEA, water at the cathode comes from the anode only by diffusing under concentration gradient. Apparently, the amount of water is much less in Pre1-MEA compared to that in Pre2-MEA and Pre4-MEA. However, as discussed above, they have similar values of ESA due to the two opposing tendencies caused by the level of hydration.

3.2. Anode polarization and impedance analysis

After the CV measurements, to characterize the activity of the anode electrode toward methanol oxidation, the anode polarization curves were immediately measured in half cell mode. Fig. 2 shows the anode polarization curves of the MEAs pretreated with different conditioning methods. Generally, the anodes show similar performance for the four MEAs treated by the four procedures. The polarization curves of Pre1-MEA, Pre2-MEA, and Pre3-MEA almost overlap when the current density is smaller than 100 mA cm⁻², which indicates that the three anodes exhibit the same performance. It might arise from their common characteristic that the anode is circulated with methanol solution. It implies that the processes of electric load and gas evolution did not exert much influence on the anode performance. The anode performance of Pre4-MEA is slightly superior to the other three anodes. It has been reported that the Pt and Ru oxides could be reduced and made to

Fig. 1. Cyclic voltammograms of the cathodes pretreated with various conditioning methods.

Table 1
Electrochemical surface area (ESA), Tafel slope, and current density (j) at 0.9 V for the MEAs pretreated with various conditioning methods.
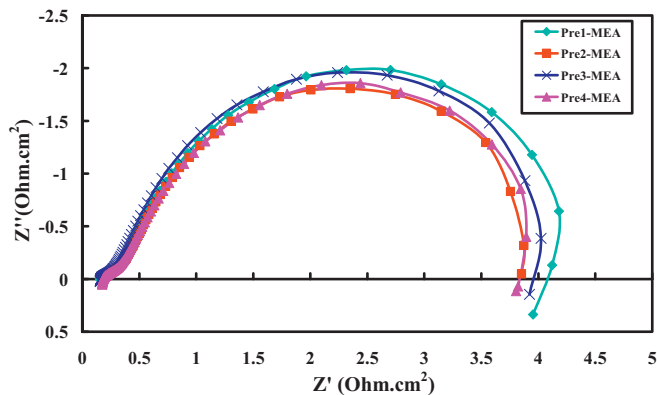
MEA	Conditioning method	ESA ($m^2\,g^{-1}$)	Tafel slope ($mV\,dec^{-1}$)	j@ 0.9 V ($mA\,cm^{-2}$)
Pre1-MEA	Methanol circulation	29.0	84.5	21.5
Pre2-MEA	Methanol circulation + electric load	34.9	83.0	43.7
Pre3-MEA	Methanol circulation + gas evolution	31.7	83.6	40.1
Pre4-MEA	PEMFC mode	36.0	79.5	54.2
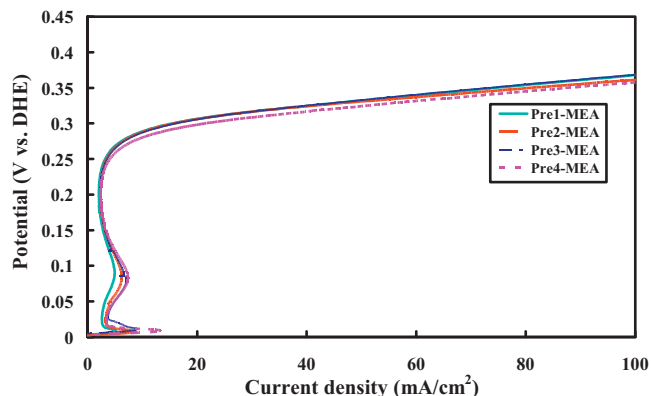
Fig. 2. Anode polarization curves of the MEAs pretreated with various conditioning methods.

Fig. 4. H_2/O_2 polarization curves of the MEAs pretreated with various conditioning methods. Cell temperature, 65 °C; hydrogen, 200 mL min^{-1} at ambient pressure; oxygen, 500 mL min^{-1} at ambient pressure.

alloy better with humidified hydrogen in single cell at 80 °C, resulting in a significantly improved activity for methanol oxidation [16]. To clarify this, a fresh MEA was installed into a single cell and both the electrodes were exposed to humidified H_2 for more than 10 h at 80 °C. The XRD data of the electrodes reveal that the composition and structure of PtRu catalyst has experienced little change before and after the hydrogen treatment. Therefore, in our experiments, the higher performance could be ascribed to the less absorbed contaminants from methanol oxidation when the MEA was treated in the H_2/O_2 PEMFC mode.

Fig. 3 shows the anode Nyquist plots at the bias potential of 0.3 V vs. DHE. According to the studies of Müller and Urban [21,22], there is only one semicircle at medium frequency, reflecting the kinetics of methanol-oxidation. No low frequency arc related to mass-transport limitations is observed in the Nyquist plots. The size of the semicircles for the Pre2-MEA and Pre4-MEA is smaller than those of others, but the differences are insignificant. The trend agrees well with the anode polarization.

3.3. ORR kinetics and cathode transport polarization

According to impedance studies [21], DMFC performance is also dominated by ORR and oxygen diffusion at the cathode. The cathode polarization curves of the four MEAs were immediately measured in a H_2/O_2 single cell after conditioning, which can reflect the effectiveness of the conditioning procedures. The partially humidified H_2 and O_2 were supplied to the anode and cathode, respectively. The gases were not fully humidified in order to embody the impacts of the degree of hydration from conditioning process on the cathode performance. Fig. 4 shows the whole polarization curves with 50% relative humidity (RH) on both sides. In the kinetically controlled regime ($E > 0.8$ V), the cell performance is determined by cathode activation polarization. Fig. 5 shows the Tafel plots for ORR of the MEAs pretreated by various methods. They were obtained by plotting the IR-corrected electrode potential against the logarithm of current density that was compensated for H_2 cross-over current. In the absence of ohmic and mass transport losses in the
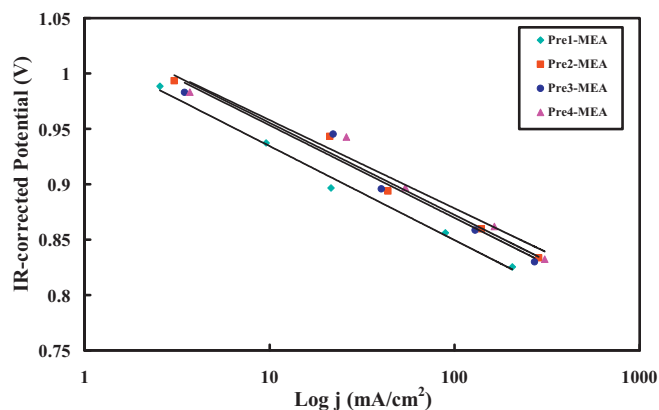

Fig. 3. Impedance spectra of the methanol electro-oxidation for the MEAs pretreated with various conditioning methods at the cell potential of 0.3 V vs. DHE.
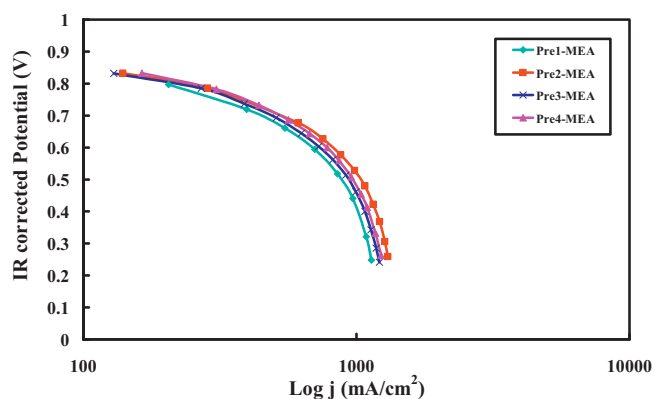

Fig. 5. Tafel plots of MEAs pretreated with various conditioning methods at the cell temperature of 65 °C and 50% RH for the anode and cathode. Hydrogen, 200 mL min^{-1} at ambient pressure; oxygen, 500 mL min^{-1} at ambient pressure.

Fig. 6. The H_2/O_2 polarization curves of the MEAs pretreated with various conditioning methods at high current density. Cell temperature, 65 °C; hydrogen, 200 mL min^{-1} at ambient pressure; oxygen, 500 mL min^{-1} at ambient pressure.

Fig. 7. Nyquist plots of the MEAs operated under H_2/N_2 at 65 °C and RH 50%.

cathode, the Tafel slope reflects the inherent electrode kinetics. As seen in Table 1, the Tafel slopes for Pre1-MEA, Pre2-MEA, Pre3-MEA, and Pre4-MEA are, respectively, 84.5, 82.9, 83.5 and 79.5 mV dec^{-1}. These values deviate from the theoretical value of 2.303 RT/α_cnF, assuming the transfer coefficient and the number of electrons are 0.5 and 2, respectively, suggesting that the conditioning procedures did not pose any influence on the kinetic mechanism. It should be pointed out that the study of Tafel slope in MEA is still risky although some empirical equations have been widely used in fuel cell for years [23]. The factors such as reactant humidity, proton activity, electronic resistance, and anode polarization could influence the Tafel slope even after IR compensation [24].

The current density at 0.9 V IR-corrected potential was selected to evaluate the catalytic activity toward ORR, i.e. the higher the current density is, the higher the catalytic activity is. As listed in Table 1, the Pre4-MEA has the highest catalytic activity while the Pre1-MEA has the lowest activity. As we discussed, the four cathodes have similar ESA, so they should exhibit similar activity. The ESA of Pt catalyst measured by CV reflects the total area of the catalyst sites that are in contact with the electrolyte, and the electrode reactions occur only on the accessible sites to the reactants (reactant-catalyst-electrolyte sites). The number of reactant-catalyst-electrolyte sites is, therefore, smaller than the catalyst-electrolyte sites due to the inaccessibility of some sites to the reactants.

The catalytic activity is also associated with the level of hydration in the electrodes. This relationship was addressed in the work of Xu et al. [25]. The catalytic activity increases with water uptake in Nafion ionomer. However, at very high water uptake, the catalytic activity decreases because of diluted proton concentration. During conditioning, the amount of water going through the cathode might be in following sequence: Pre2-MEA > Pre4-MEA > Pre3-MEA > Pre1-MEA. Thus, too much water in Pre2-MEA led to the decreased catalytic activity.

Fig. 6 shows the ORR polarization curves at high current density after correcting for cell resistances. It is observed that the variations in cathode potential with current density are not very pronounced between the MEAs pretreated with the above mentioned procedures. The four polarization curves almost overlap in the limiting current region, indicating that the process of conditioning did not
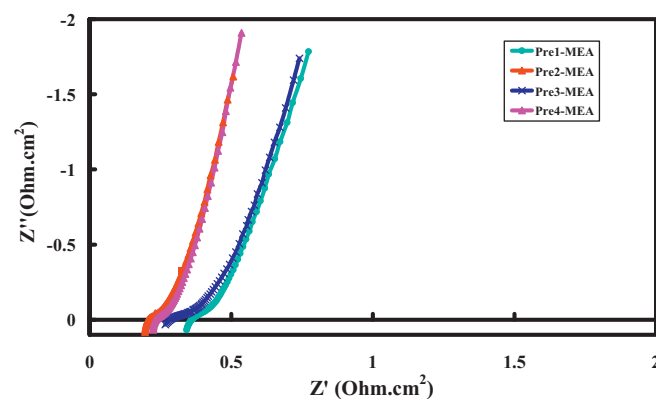
have much effect on oxygen transport in the catalyst layer. As reported by He et al. [11], Pre3-MEA should produce the higher limiting current than the other MEAs due to its increased porosity and reduced tortuosity after H_2 and CO_2 evolution in the cathode layer, which is not in accordance with our investigations. Jaouen et al. [26] and Ihonen et al. [27] proposed an agglomerate model to predict the effect of mass-transport limitations on the polarization curves in PEMFC. The limiting current could be controlled by the following transport processes: proton migration in the ionomer or dissolved oxygen diffusion in the agglomerates. The proton resistances in the cathode catalyst layers were measured according to the method proposed by Pickup et al. [28] under H_2/N_2 atmosphere. Fig. 7 gives the impedance spectra of the cathode catalyst layers without electrochemical reaction. The proton resistance (R_p) and cell ohmic resistance (R) of the cathode catalyst layers were estimated by fitting the EIS data with the transmission-line model, which has been used to estimate the proton resistance of catalyst layers by many researchers [28–30]. As listed in Table 2, the proton resistances in the cathode catalyst layers for the four MEAs are very close, which seems to have little influence on the mass transport in the high current density region. The similar proton resistances also indicate that the hydrating catalyst layer is much easier than the Nafion membrane. Thus, the different performances in Fig. 4 mainly result from the cell ohmic resistances. That is why the four MEAs show similar performances after compensating the ohmic resistance loss as seen in Figs. 5 and 6.

3.4. DMFC performance

After the MEAs were conditioned as described in Section 2.3, the first polarization curves of the MEAs in DMFC were recorded immediately. Fig. 8 shows a comparison of these polarization curves. It can be seen clearly that Pre2-MEA and Pre4-MEA exhibit slightly better performances than the other two MEAs. The inset in Fig. 8 shows the variations in high frequency resistance (HFR) with current density. Pre2-MEA and Pre4-MEA have smaller resistances than the other MEAs. Based on the results of the anode impedance and cathode polarization, it is concluded that the cell resistances bring about the discrepancies in the performance of the MEAs. Fig. 9 shows the polarization curves of the MEAs after they were

Table 2
Fitting parameters from Fig. 7 based on the transmission-line model.

MEA	Conditioning method	R (Ω cm^2)	R_p (Ω cm^2)
Pre1-MEA	Methanol circulation	0.362	0.272
Pre2-MEA	Methanol circulation + electric load	0.212	0.246
Pre3-MEA	Methanol circulation + gas evolution	0.292	0.268
Pre4-MEA	PEMFC mode	0.239	0.227
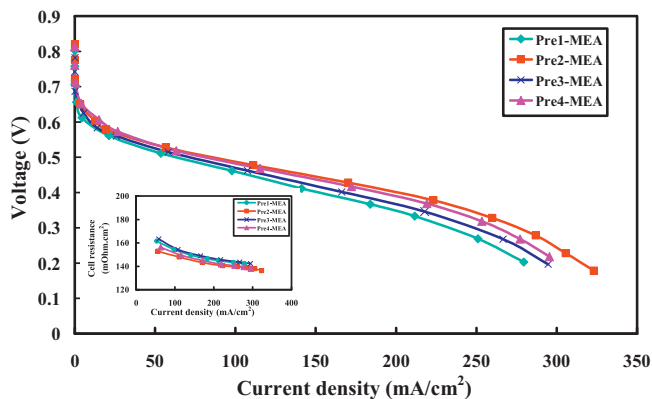
Fig. 8. The first polarization curves of the MEAs pretreated with various conditioning methods after conditioning. Cell temperature, 65 °C; methanol concentration and flow rate, 1.0 M and 1.0 mL min^{-1}; dry oxygen, 200 mL min^{-1} at ambient pressure.
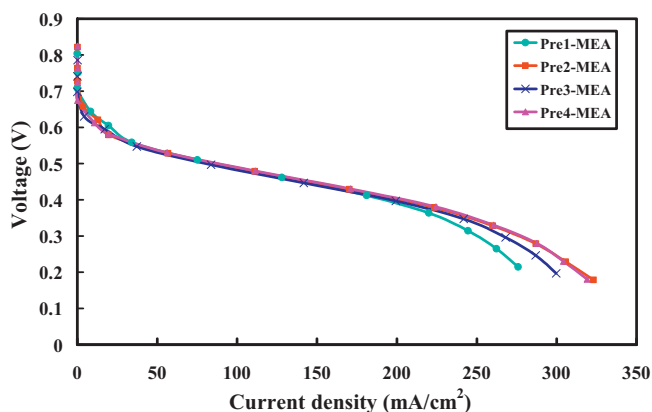
Fig. 9. Polarization curves of the MEAs after 10 h of continuous operations. Cell temperature, 65 °C; methanol concentration and flow rate, 1.0 M and 1.0 mL min^{-1}; dry oxygen, 200 mL min^{-1} at ambient pressure.

kept running for more than 10 h. The MEAs almost show the same performance, which seem not directly related to the specified conditioning procedure. The very small differences in the polarization plots result likely from the discrepancies in the MEA fabrication and structures, rather than from the pretreatment procedures, although they were prepared in the same batch.

4. Conclusions

The effects of four conditioning methods, viz., methanol circulation, combination of methanol circulation and electric load, methanol circulation plus gas evolution, and H$_2$/O$_2$ PEMFC mode, on the electrochemical performances of fresh MEAs in DMFC have

been investigated systematically. It is found that the hydration in MEAs is the most important factor for their electrochemical performances. As long as the MEA is fully hydrated, it can reach its maximum performance. The conditioning procedures do not seem to have much impact on the catalyst activity, oxygen transport, and proton resistance in the catalyst layer. The combination of methanol circulation and electric load is a simple and effective conditioning procedure for DMFC.

Acknowledgement

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