IMPEDANCE ANALYSIS ON THE TRANSIENT BEHAVIOR OF DMFC ANODE DURING PRE-CONDITIONING PERIOD

Joon-Hee Kim, Ho-In Lee, and Heung Yong Ha

aSchool of Chemical Engineering and Research Center for Energy Conversion and Storage, Seoul National University, Seoul 151-744, Korea

bFuel Cell Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

ABSTRACT

The transient behavior of direct methanol fuel cell (DMFC) during pre-conditioning period of the membrane electrode assembly (MEA) has been investigated using an impedance analysis technique. Conditioning period is essential to the MEA using a supported catalyst in order to attain a maximum performance and this period is dependent on the conditioning methods. Conditioning temperature had substantial influence on the behaviors of MEAs, to which room-temperature treatment was more favorable than high-temperature one. Also, application of electric load was found to accelerate the hydration of electrolyte, and thus reduced the time to approach the full performance. Equivalent circuit of the DMFC anode was constructed to deconvolute impedance data and three kinds of resistances in the MEA such as resistances of charge transfer ($R_{ct}$), electrolyte ($R_e$), and pore electrolyte ($R_p$) were investigated. All these three resistances decreased at early stage and then maintained stable values during the conditioning period. Resistance of the recast ionomer ($R_p$) in the catalyst layer was found to be significantly affected by temperature.

INTRODUCTION

In the last two decades, tremendous research interests have been focused on the improved performance of direct methanol fuel cell (DMFC) based on polymer electrolyte membrane. To improve the performance of DMFC, it is important to establish an appropriate conditioning method of a membrane electrode assembly (MEA). Several methods have been employed in conditioning the MEA for the stable operation and the improved performance of the DMFC. For polymer electrolyte membrane and ionomer, sufficient hydration process is necessary to obtain stable proton conductivity, which needs about 24 to 48 hr. According to Aricò et al., after installing an MEA, water was supplied to both the anode and the cathode backing layers and the cell was warmed-up step-wise to the maximum operating temperature of 95 °C. The internal humidification was achieved by operating the fuel cell with methanol (0.5 M) and oxygen at high currents for 24 hr. Shukla et al. began to operate the single cell after hydrating the MEA for 24 hr by circulating 2 M methanol solution through the anode compartment at 80 °C. Scott et al. adopted both the above methods. He et al. suggested that hydrogen evolution
on electrodes improve DMFC performance by reducing the overpotential of both oxygen reduction and methanol oxidation.

However, a definite explanation has not been reported on the mechanism of the change in single cell performance during the conditioning period though various methods are used for conditioning the MEA. Polymer electrolyte membrane fuel cell (PEMFC) as well as DMFC needs conditioning period for about 24 hr, which is mentioned only as to hydrate proton conducting material (polymer electrolyte membrane and ionomer in the catalyst layer).

In this study, we investigated the effect of various MEA conditioning methods on the DMFC performance by using impedance analysis technique. Further, in order to evaluate the measured anode impedance data, we proposed an appropriate equivalent circuit which contains various impedance elements representing the reaction steps involved methanol oxidation and the electrode structure.

**IMPEDANCE ELEMENTS IN EQUIVALENT CIRCUIT**

**Basic elements**

The impedance of a solid electrode having a smooth surface may be described by a simple model consisting of two impedance elements: charge transfer resistance ($R_p$) and double layer capacitance ($C_d$). To represent an electrolyte resistance ($R_e$), one may additionally append a resistor. To describe porous DMFC anode and methanol electro-oxidation a few additional steps are required.

**Porous layer**

Porous electrodes in PEMFC may be described using different models. In general, there exists a correlation between the geometry of the model and the simplicity of the impedance elements used. The second step to discuss a porous electrode is offered by mathematics. A model may be very descriptive for the real conditions in the porous regions, but the same model may be ineffective when it can not be defined by simple mathematical elements. Thus, the model used here is based on a relatively simple geometry, assuming a system of ‘homogeneous’ pores as suggested by Göhr. The impedance of the porous layer may be expressed in terms of the macroscopic impedance elements such as:

- $Z_p$: Impedance of the pores filled with electrolyte;
- $Z_m$: Impedance of the porous metal catalyst
- $Z_q$: Impedance of the interface (porous layer | pore)

The impedance $Z_p$ and $Z_m$ can reduce to resistive elements ($R_p$ and $R_m$). In this study, the term $R_m$ can be neglected assuming a value of zero. The expression for the total impedance ($R_{pl}$) in the porous layer may appear complex, but can be calculated by using the approach of Göhr as given in eqn. (1):

$$Z_{pl} = \frac{\sqrt{R_p Z_q}}{\tanh(\sqrt{R_p / Z_q})}$$

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Relaxation impedance

According to Schiller et al., impedance spectra of the Pt anode in a PEMFC show a strong time dependence and exhibit a pseudo-inductive contribution at the low frequency region of the spectra due to the influence of carbon monoxide poisoning. The pseudo-inductive behavior can be attributed to a surface relaxation process of the anode. It is already known that oxidation of adsorbed carbon monoxide in the mechanism of methanol oxidation is the rate-determining step. Thus, the same phenomena may be found in the DMFC anode and a relaxation impedance term ($Z_r$) should be included.

The relaxation impedance may be included in a model of Faradaic impedance ($Z_F$) at non equilibrium potential. The Faradaic impedance, which describes either the mass transport or the reaction mechanism at the electrode, is composed of a potential-dependent charge transfer resistance ($R_{ct}$) and a time-dependent relaxation impedance as given in eqn. (2):

$$Z_F = \frac{R_{ct}Z_r}{R_{ct} + Z_r} \quad (2)$$

Therefore, total impedance ($Z$) and equivalent circuit of DMFC anode in this study have been proposed as given in eqn. (3) and shown in Fig. 1:

$$Z = R_{ct} + Z_F + \frac{1}{1/Z_p + j\omega C_d} \quad (3)$$

EXPERIMENTAL

Membrane electrode assembly (MEA)

Cathode catalyst used for oxygen electro-reduction was 47 wt% Pt/C (Tanaka) and anode catalyst used for methanol electro-oxidation was 53 wt% PtRu/C (Tanaka). Catalyst ink was prepared by dispersing appropriate amounts of catalyst in deionized water with 5% Nafton® solution (1100 EW, Du Pont) and isopropyl alcohol (IPA) for the cathode and dipropyl ketone (DPK) for the anode. The catalyst ink was sprayed onto a 10 cm² of carbon paper (TGPH-060, Toray) to make an electrode. The metal (Pt or PtRu) loading was 3 mg/cm² in each electrode and the total ionomer loading was 30 wt% to catalyst (ratio of dry ionomer to catalyst multiplied by 100) for the cathode and 60 wt% to catalyst for the anode. A pair of electrodes (cathode and anode) was hot-pressed on both sides of the polymer electrolyte membrane (Nafton® 117, Du Pont) at a temperature of 140 °C and with a pressure of 70 kg/cm² for 150 sec.

Operation of single cell

All experiments including electrochemical measurements were conducted with cells which consisted of MEAs sandwiched between two graphite plates with serpentine flow field. In all the experiments operated in a fuel cell mode: 2 M methanol solution was pumped through the anode side at 5 mL/min and oxygen to the cathode side at a flow rate of 250 sccm. The temperature and the pressure of single cells were held at 90 °C and atmospheric pressure, respectively. Oxygen gas was humidified by passing through a
humidifier maintained at a temperature of 65 °C. Current-voltage curves were measured galvanostatically by using an electric load (EL-500P, Daegil Electronics).

**Conditioning of MEA**

In this investigation during the conditioning period of MEAs, temperature (25 or 90 °C) and electric load (applied or not) were selected as variables to study their effects on the performance of the DMFC (Table 1). Single cell performances were measured at 90 °C at every 6 or 12 hr during the MEA conditioning. After measuring the cell performance, impedance analysis was conducted subsequently. During each of the conditioning process, the whole system was under the corresponding conditioning state (Table 1) until the next measurement. For example, in case of experiments with MEA3, the cell was maintained at 25 °C at a load of 100 mA/cm² while feeding methanol solution to the anode and oxygen to the cathode for 6 hr, and then its temperature was raised to 90 °C to record an i-V curve and impedance data. After that the temperature was dropped to 25 °C again while the load was maintained at 100 mA/cm² until the next cycle.

**Characterization of electrodes**

Impedance spectra were obtained on the operating cells with a potentiostat (IM6, Zahner). The anode was supplied with 2 M methanol solution (5 mL/min) at 90 °C and the cathode with a continuous stream of dry hydrogen (200 sccm) to make a dynamic hydrogen electrode (DHE) and to facilitate removal of permeated water. All anode impedance spectra reported here were measured between the anode and the DHE in the complete fuel cell. The frequency range was varied from 50 mHz to 1 kHz and the amplitude of sinusoidal current signal was adjusted so that the potential amplitude did not exceed 5 mV. Every spectrum was measured at a dc potential of 0.4 V (vs. DHE).

The porous microstructure of anode was studied with scanning electron microscopy (SEM) using S-4200 (Hitachi).

**RESULTS AND DISCUSSION**

A stable performance of DMFC single cell can be attained only after an appropriate pre-conditioning process and the conditioning method affects time required to approach the maximum cell performance. Fig. 2 shows the single cell performance of the MEAs treated with various methods presented in Table 1 during the conditioning period. In case of MEA1 and MEA2, reactants were supplied continuously for conditioning at 25 and 90 °C, respectively. On the other hand, in case of MEA3 and MEA4, constant load (100 mA/cm²) was applied under the condition of MEA1 and MEA2, respectively. It can be seen from the performance pattern of the MEA1 that the performance increases abruptly in the first 12 hr and then no further change is observed with time. The other MEAs also show similar tendency though the extent vary depending on the conditioning methods. Fig. 3 represents the changes in the current density of all the MEAs shown in Fig. 2 in terms of duration of conditioning period at a cell voltage of 0.4 V. It can be observed that the changing rates of performance and the attainment of stable values are different from one another. These differences are caused by the conditioning temperature employed and the ongoing electrochemical reaction. MEAs treated at 25 °C (RT-treated MEAs: MEA1 and MEA3) show better performance than MEAs treated at 90 °C (HT-
treated MEAs: MEA2 and MEA4). And MEAs (MEA3 and MEA4) treated under the application of a constant load (100 mA/cm²) also show better performance than MEAs treated at OCV (MEA1 and MEA2) during the conditioning period.

Electrodes of DMFC experience changes in ionic conductivity, pore structure and contact resistance during the pre-conditioning period. And each of the single cell performance (with MEA1 to MEA4) shows difference in the increasing rate and the maximum value attained. Temperature appears as the main factor that affect the single cell performance since the structure and the property of recast ionomer in the catalyst layer are readily affected by the temperature. According to Siroma et al., recast film of Nafion® ionomer was dissolved in methanol aqueous solution at 80 °C even if the film was treated through a hot-pressing process. Hence, there may be a possibility that the recast ionomer in the anode catalyst layer is dissolved or at least the polymer structure is loosened excessively when the MEA is in contact with methanol solution. This structural change of the recast ionomer is affected by concentration and temperature of a methanol solution. And thus, the morphology and the electrochemical property of the catalyst layer can also be changed. At the initial stage, the ionomer is swollen by aqueous methanol solution and hence, the interfacial area between the ionomer and the catalyst particles increases and the ionomer network in the catalyst layer is built up well. Therefore, the activity of electrode gets increased. But the ionic conductance in the catalyst layer can be decreased by the disconnected network when the ionomer structure is loosened due to excessive swelling. The HT-treated MEAs (MEA2 and MEA4) using 2 M methanol solution might have looser ionomer structure than the RT-treated ones (MEA1 and MEA3). Though the hydration rate is faster at the higher temperature, the performance does not improve further (Fig. 3) since there is a significant change of the recast ionomer structure in the catalyst layer. On the other hand, at the low temperature, a substantial improvement in the performance was noticed and this has been attributed to the existence of the stable ionomer structure and the well-organized ionomer network in the catalyst layer though relatively long conditioning time is required. In case of MEAs to which constant current is applied (MEA3 and MEA4), electrolyte membrane and catalyst might be affected. Proceeding of electrochemical reaction improves hydration rate and proton conductivity of the membrane due to water crossovered by electro-osmotic drag. Moreover, the electrochemical reaction during the conditioning period activates the catalyst by increasing the roughness of catalyst surface and consequently improves the activity of the electrode.

According to our previous experimental results, the resistances of electrolyte membrane and proton-conducting ionomer in catalyst layer were found to decrease during the conditioning period and the secondary pore size increased due to structural change of catalyst layer caused by ionomer swelling. These changes can be primary factors to improve the MEA performance during the conditioning period.

Single cell performance is affected by both mass and charge transfer processes. Mass transfer process is facilitated in the large secondary pores (0.04–1.0 μm) which originates from the space among agglomerates of catalyst and ionomer. However, in this study, mass transfer limitation in the high current density region was hardly observed in the I-V curve (Fig. 2) because relatively high concentration of methanol (2 M) was used. Actually, it was hard to find any prominent structural change in the SEM images (Fig. 4) of each electrode before and after conditioning.

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Various resistances associated with methanol oxidation on the DMFC anode can be measured using impedance analysis. Fig. 5 shows the impedance data of the anode for each MEA during the conditioning period. The measured data along with fitted data acquired from the equivalent circuit (Fig. 1) are illustrated. From the anode impedance in MEA1, electrolyte resistance ($Z_{le} = R_e$ at the point of $Z_{lm} = 0$ in high frequency range, the smaller intercept on the real part of the axis) and charge transfer resistance ($R_{ct}$, diameter of semicircle) decreased gradually over the first 12 hr, while the single cell performance was increased. These results indicate that the resistances decrease gradually due to hydration of proton conducting material during the conditioning period. The other MEAs (MEA2~MEA4) also experienced decrease in resistances in anode impedance data in almost the same pattern though the degree of change varied depending on the conditioning methods employed. It can be found that $R_e$ and $R_{ct}$ of the HT-treated MEAs in right column show slow decreasing rates, but have still higher values compared to those of the RT-treated MEAs in left column. This is because of the increased contact resistance either between the electrode and the electrolyte membrane or between the recast ionomer and catalyst particles in the catalyst layer. When the single cell fixture was disassembled after the completion of cell operation, it was found that the HT-treated MEAs were totally separated into electrodes and electrolyte membrane. On the other hand, the RT-treated MEAs were well kept up in contact just like a fresh MEA. It can be inferred that the coherence of electrodes and electrolyte membrane decreases significantly because the ionomer is swollen excessively and the polymer structure is loosened at high temperature. These structural changes of the ionomer have obvious influence on the structure of the electrode, i.e. the catalyst layer.

In order to investigate the effects of structural changes of catalyst layer on the electrochemical property of electrode, impedance data were fitted with an equivalent circuit as described in the theoretical section (Fig. 1). Fitted data matched well measured impedance data (Fig. 5), and thus it was possible to separate several resistance elements from the anode impedance data. The resistances, $R_{ct}$, $R_e$, and $R_p$, which were mentioned previously could be suggested here as the resistances directly related with the charge transfer process. First of all, $R_{ct}$ is a resistance that is involved in methanol electro-oxidation occurring at the interface of catalyst and ionomer in a catalyst layer. Therefore, it is not only related with the effective area of three-phase interface, but also reflects the mass transfer resistance. In general models, $R_e$ has included resistances of electrolyte membrane and pore electrolyte (i.e. recast ionomer) in catalyst layer, but in this study the pore electrolyte resistance $R_p$ is extracted from $R_e$. The resistance for electron ($R_m$) transferred through catalyst is excluded because of its negligibly small value.

The behavior of three kinds of resistances ($R_{ct}$, $R_e$, and $R_p$) in the DMFC anode during the conditioning period has been explicated with impedance data. These three resistances for the respective anodes during the conditioning period are shown in Fig. 6. In view of the changes in the resistances for the anode of MEA1, a significant decrease and an attainment of gradual stabilization are shown in 12 hr. Particularly, $R_p$ decreases dramatically compared with the other resistances though they show almost the same trend. However, all the resistances in the HT-treated MEA2 are larger than those in the MEA1, and the reduction in $R_e$ is not significant in spite of fast hydration and following stabilization. The difference (20 mΩ) between $R_p$ values of the RT-treated and the HT-treated MEAs is larger than the one (ca. 10 mΩ) between the other resistances ($R_{ct}$ and $R_e$).
values) because the recast ionomer in the catalyst layer is most significantly affected by temperature as mentioned previously. The reason for the increased values of $R_p$ and $R_{ct}$ for the HT-treated MEAs may be that the contact resistance of catalyst layer with electrolyte membrane and another contact resistance of catalyst with recast ionomer in the catalyst layer were relatively higher than those of the RT-treated MEA due to the loosened ionomer structure.

In cases of MEA3 and MEA4 to which constant load (100 mA/cm$^2$) was applied, the resistance values measured at the time of 2 hrs are very small and all the three kinds of resistances approach the steady state quickly compared with those of MEA1 and MEA2. Though there is no significant difference in the time to reach the steady state in case of $R_p$ values, $R_{ct}$ and $R_e$ values of the load-applied MEAs decrease more quickly. This observation is attributed to the fact that activation of catalyst and hydration of polymer electrolyte are accelerated by inducing electrochemical reaction with applying a constant load.

Fitted double layer capacitance ($C_d$) of each electrode also varies during the conditioning period as shown in Fig. 7. Capacitance represents the double layer formation in the interface of electrode (catalyst) and electrolyte (recast ionomer) and that value increases with an increase in the area of the double layer. The capacitance values for the RT-treated MEAs increase rapidly and then maintain almost the constant values after ca. 10 hr duration. In these cases, it is presumed that the interface area between the catalyst and the recast ionomer keeps increasing from the start of the conditioning process up to 10 hr. Therefore, the increase of capacitance implies widening of three-phase interface effective to reaction, i.e. electrochemical active surface area. However, the capacitances for the HT-treated MEAs hardly change as in the case of previous resistances, since the interface area of catalyst and recast ionomer decreases by the loosened ionomer structure at high temperature.

The result of the above investigation leads one to conclude that structural and electrochemical properties of electrodes during the pre-conditioning period change mainly due to the structural change of the recast ionomer that exists in the catalyst layer and between the electrode and the electrolyte membrane. Perfluorosulfonate ionomer such as Nafion$^\text{®}$ is composed of hydrophobic fluorocarbon component and hydrophilic ionic groups. Ionic groups lead to the formation of interconnected clusters when the ionomer is hydrated. Hydrated ionic phase determines the electrochemical properties and fluorocarbon phase determines the swelling level and the mechanical property of the ionomer depending on its extent of crystallinity. The structure and crystallinity of the recast ionomer film which is made of ionomer solution is dependent on the preparation condition, especially on the solvent of the ionomer solution. Recast ionomer with low crystallinity can be dissolved easily in water or organic solvents due to the collapsed structure. The recast ionomer prepared under the hot-pressing condition (140 °C, 150 sec, 70 kgf/cm$^2$) used for the preparation of MEAs in this study is difficult to have sufficient durability in the solvent such as water and alcohol. Consequently, the recast ionomer film made of the ionomer solution comes to have the structure easily loosened or dissolved in alcohol or water compared with commercial Nafion$^\text{®}$ membrane. And moreover stability of the recast film is affected by temperature. Therefore, the HT-treated MEAs (at 80 °C) exhibit increased contact resistances due to separation of catalyst layer.
and electrolyte membrane, and all three kinds of resistances such as $R_{ct}$, $R_e$, and $R_p$ are higher than those in case of RT-treated MEAs.

When electrochemical reaction proceeds by applying an electric load to a DMFC, the amount of water passing through an MEA by electro-osmotic drag\textsuperscript{13} increases compared to the MEA maintained at OCV. Thus the ionic conductivity of the whole MEA increases due to the substantial hydration of electrolyte membrane and electrode. In addition, roughening of catalyst owing to the electrochemical reaction helps increase the active area.\textsuperscript{14} And thus, $R_{ct}$ decreases quickly by the increase of active sites for methanol oxidation. Though all the resistances are initially almost the same as shown in Fig. 6(a), the $R_p$ value decreases more rapidly than the others and reflecting the performance ability of the MEAs

The changes that are occurring during conditioning period can be summarized as follows. First of all, $R_e$ decreases as electrolyte membrane is hydrated with the supplying of aqueous methanol solution to the anode, and then pore electrolyte resistance, $R_p$, in electrode also decreases due to the formation of ionomer network when recast ionomer in the electrode is hydrated and swollen. In addition, $C_d$ increases and $R_{ct}$ decreases as the interface of catalyst and recast ionomer enhances. However, at high temperature, the recast ionomer tends to be dissolved or loosened structurally when the MEA is in contact with a methanol solution. Therefore, $R_e$ and $R_p$ do not decrease substantially due to the collapsed ionomer network and the reduced contact area between catalyst and the ionomer. Applied electric load helps to accelerate hydration of electrolyte membrane and the activation of catalyst.

**CONCLUSIONS**

The influence of steps and methods involved in the pre-conditioning processes of MEA in DMFC on the single cell performance and the anode impedance was investigated. The MEAs treated at room temperature showed more improved single cell performance than the MEAs treated at a high temperature of 90°C and had advantage in reinforcing the contact of catalyst layer with electrolyte membrane. Charge transfer, electrolyte and pore electrolyte resistances were deconvoluted separately from the measured impedance data by using an equivalent circuit for DMFC anode impedance. Resistances associated with the RT-treated MEAs showed lower values than the ones with the HT-treated MEAs. Particularly, it can be explained from the significant difference in $R_p$ value that recast ionomer in the catalyst layer was affected mainly by conditioning temperature. An electric load applied to the cell while conditioning an MEA accelerated hydration of electrolyte because the amount of water crossovered by electro-osmotic drag has been increased. In this case, $R_e$ and $R_{ct}$ appeared to become stabilized more quickly though their ultimate values are rarely affected. From the fact that double layer capacitance increased during conditioning period, it could be deduced that the interface area (electrochemical active surface area) between catalyst and recast ionomer increase. The capacitance for the HT-treated MEAs showed no change because excessively swollen and loosened recast ionomer could not increase the interface area any more.

Consequently, optimization of conditioning method is necessary in order to improve DMFC performance because MEAs undergo structural and electrochemical changes depending on the conditioning methods.
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Table 1. Conditions applied to the cell during conditioning period

|                | MEA1 | MEA2 | MEA3 | MEA4 |
|----------------|------|------|------|------|
| Temperature (°C) | 25   | 90   | 25   | 90   |
| Current (100 mA/cm²) | x    | x    | o    | o    |

Fig. 1. Equivalent circuit for evaluation of the DMFC anode impedance data.
Fig. 2. Performances of MEAs treated by different pre-conditioning methods during the conditioning period: (a) treated at 25 °C and OCV, (b) treated at 90 °C and OCV, (c) treated at 25 °C and 100 mA/cm², (d) treated at 90 °C and 100 mA/cm².

Fig. 3. Performances at cell voltage of 0.4 V as a function of the conditioning time: Rearrangement of the data in Fig. 2.
Fig. 4. SEM images of anodes before and after conditioning: (a) as-prepared, (b) MEA1, (c) MEA2, (d) MEA3, (e) MEA4.
Fig. 5. Impedance data of anode in MEAs during different pre-conditioning methods. Symbols: Measured data, Lines: Fitted data.

Fig. 6. Fitted impedance data of anodes with MEAs treated by different pre-conditioning methods during the conditioning period: □ and ■; Charge transfer resistance (R_{ct}), ○ and ●; Electrolyte resistance (R_e), □ and ▲; Pore electrolyte resistance (R_p).
Fig. 7. Fitted double layer capacitances of anodes in MEAs treated by different pre-conditioning methods during the conditioning period.