Impedance Analysis on the DMFC Anode with an Equivalent Circuit during the MEA Pre-Conditioning

MEA 전처리 과정의 DMFC 산화극에 대한 등가회로를 이용한 임피던스 분석

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1. Introduction

Recently a great deal of research have focused on the direct methanol fuel cell (DMFC) [1,2]. To improve the performance of DMFC, it is important to establish appropriate methods of conditioning the cells. There are many methods employed in conditioning the membrane electrode assembly (MEA) before operating the DMFC [3-5]. In this study, we investigated the effect of the MEA-conditioning method on the performance of DMFC using an impedance technique.

2. Experimental

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% Nafion® 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 cm^2 of carbon paper (TGPH-060, Toray) to make an electrode. The metal (Pt or PtRu) loading was 3 mg/cm^2 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 (Nafion® 117, Du Pont) at a temperature of 140 °C and with a pressure of 70 $\mathrm{kg_f/cm^2}$ for 150 sec.

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).

In this study, temperature (25 or 90 °C) and electric load (applied or not) were selected as variables during the conditioning period to study their effects on the performance of the DMFC (Table 1). Cell performances were measured at every 6 or 12 hr during the MEA conditioning. After the measurement of cell performance, impedance measurement was made immediately. In this conditioning process, the whole system was under the corresponding conditioning state (Table 1) until the next measurement after measuring the performance.

Table 1. Conditions applied to the cell during conditioning period

	MEA1	MEA2	MEA3	MEA4
Temperature (°C)	25	90	25	90
Current-loading (100 mA/cm^2)	×	×	○	○

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 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).

3. Results and discussion

Fig. 1 shows the single cell performance of the MEAs treated with the methods presented in Table 1 during the conditioning period. In case of MEA1 and MEA2, reactants were supplied continuously for

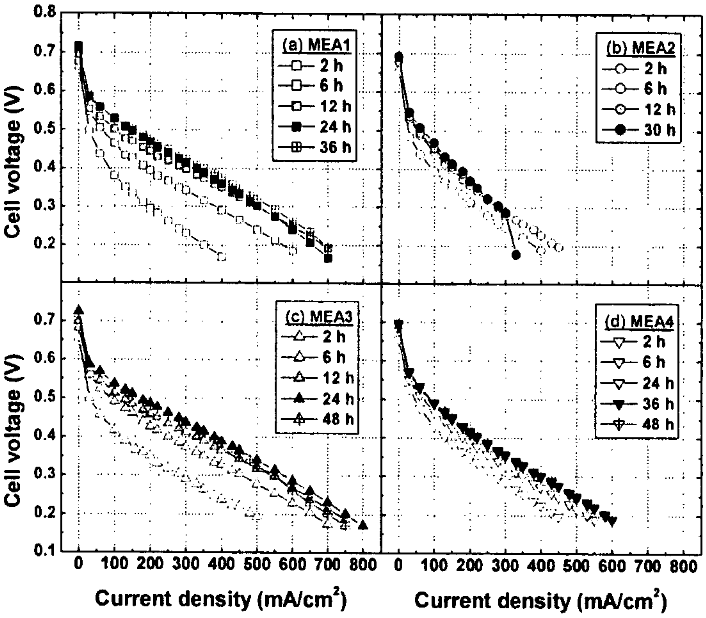

Fig. 1. Performances of MEAs treated by different pre-conditioning methods during the conditioning period: (a) treated at 25 °C and OCV, (b) treated at 90 °C and OCV, (c) treated at 25 °C and 100 mA/cm^2, (d) treated at 90 °C and 100 mA/cm^2.

conditioning at 25 and 90 °C, respectively. On the other hand, in case of MEA3 and MEA4, constant load (100 mA/cm^2) was applied under the condition of MEA1 and MEA2, respectively. It can be seen from changes in the performance of the MEA1 that the performance increases abruptly in the duration of 12 h and then is stabilized to constant value. The other MEAs also show similar tendency though the extent may vary depending on the conditioning methods. MEAs treated at 25 °C (RT-treated MEAs; MEA1 and MEA3) show the better performance than MEAs treated at 90 °C (HT-treated MEAs; MEA2 and MEA4). And constant load-applied (100 mA/cm^2) MEAs (MEA3 and MEA4) also show the more increased performance than MEAs treated at OCV (MEA1 and MEA2) during the conditioning period.

The origin of various resistances associated with methanol oxidation on the DMFC anode can be measured using impedance analysis. Fig. 2 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 are illustrated. From the anode impedance in MEA1, electrolyte resistance ($Z_{\mathrm{Re}} = R_e^*$ at the point of $Z_{\mathrm{Im}} = 0$ in high frequency range, the smaller intercept on the real part axis) and charge transfer resistance (R_{ct} , diameter of semicircle) decreased gradually up to the first 12 h as the single cell performance increased, and then decreased slightly. These indicate that the resistances decrease gradually due to the hydration of proton conducting material during the conditioning period. In cases of the other MEAs (MEA2~MEA4), resistances in anode impedance data also decreased but each one exhibited a different trend 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 partly because of the increased contact resistance between the electrode and the electrolyte membrane. When the single cell frame was taken to pieces after the cell operation was completed, it was found that the HT-treated MEAs were totally separated into electrode and electrolyte membrane. On the other hand the RT-treated MEAs were well kept up just as after hot-pressing process. 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 [6]. These structural changes of the ionomer have obvious influence on the structure of electrode, i.e. catalyst layer.

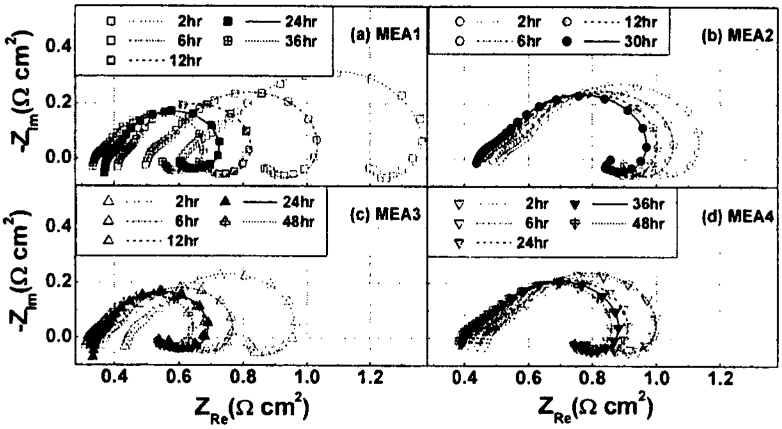

Fig. 2. Impedance data of anode in MEAs treated by different pre-conditioning methods during the conditioning period: Symbols; Measured data, Lines; Fitted data.

4. Conclusions

The pre-conditioning effect of MEA in DMFC on the single cell performance and the anode impedance was investigated. The RT-treated MEAs showed the more improved single cell performance than the HT-treated MEAs 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 with the equivalent circuit for DMFC anode impedance. Resistances associated with the RT-treated MEAs showed the lower values than ones with the HT-treated MEAs. Particularly, it can be explained from more difference in R_p value that recast ionomer in the catalyst layer was affected mainly by conditioning temperature. Applied current accelerated the hydration of electrolyte because the amount of water crossovered by electroosmotic drag has been increased. In this case, R_e^* and R_{ct} decreased quickly and approached the lower values though R_p was hardly affected. Based on the result that double layer capacitance increased during conditioning period, it can be considered that the interface area (electrochemical active surface area) between catalyst and recast ionomer increases. 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.

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