**Electrochemical Analysis of the Pre-Conditioning Effects on DMFC Performance**

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Recently a great deal of researches 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 [3,4]. In this study, we investigated the effect of MEA-conditioning method on the performance of DMFC using an impedance technique.

A catalyst ink containing a Pt/C (Tanaka) for the cathode and a PtRu/C (Tanaka) for the anode, respectively, was mixed with 5% Nafion® solution diluted with a solvent, and then was sprayed on a backing material (carbon paper). An MEA was obtained by hot-pressing the anode and the cathode on both sides of the membrane, Nafion®117 (DuPont). The fuel cell was fed with a methanol solution of (2 M, 5 mL/min) and oxygen (250 sccm) at 90 ºC and 1 atm. Cell voltage vs. current density was measured galvanostatically. Impedance measurement of the anode was conducted on the single cell using an impedance analyzer (IM6, Zahner).

In this study, temperature (25 or 90 ºC) 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 conditioning the MEA. After the measurement of cell performance, impedance measurement was made immediately. In this process, the whole system was under the corresponding conditioning state until the next measurement after measuring the performance.

Fig. 1 shows the changes in the current density of all the MEAs in terms of duration of conditioning period at the cell voltage of 0.4 V. It can be observed that the changing rates of performance and the attainment of stable values are found to vary. These differences are generated by the conditioning temperature and the electrochemical reaction. 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 current-applied (100 mA/cm$^2$) MEAs (MEA3 and MEA4) during conditioning period also show the more increased one than MEAs treated at OCV (MEA1 and MEA2).

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 MEA1 during 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) and charge transfer resistance ($R_{ct}$, diameter of semicircle) decrease gradually during the first 12 hr as the single cell performance increases, and then decrease slightly. These indicate that the resistances decrease gradually due to the hydration of proton conducting material during conditioning period.

**REFERENCES**

1. P. Argyropoulos, K. Scott, and W. M. Taama, *Electrochim. Acta*, **45**, 1983 (2000).
2. A. S. Aricò, P. Cretì, E. Modica, G. Monforte, V. Baglio, and V. Antonucci, *Electrochim. Acta*, **45**, 4319 (2000).
3. A. K. Shukla, P. A. Christensen, A. J. Dickinson, and A. Hamnett, *J. Power Sources*, **76**, 54 (1998).
4. K. Scott, W. M. Taama, P. Argyropoulos, and K. Sundmacher, *J. Power Sources*, **83**, 204 (1999).

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$^2$) | × | × | ○ | ○ |

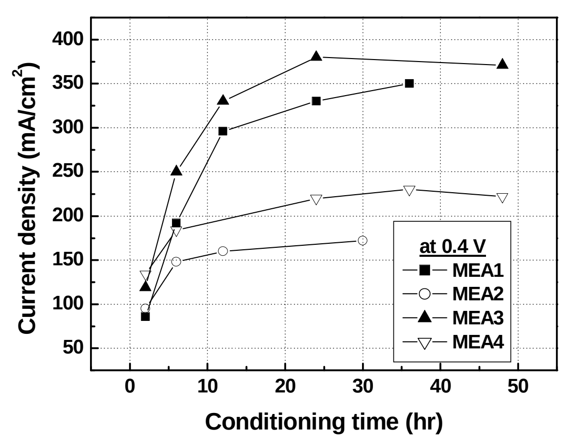


Fig. 1. Performances at the cell voltage of 0.4 V as a function of conditioning time.

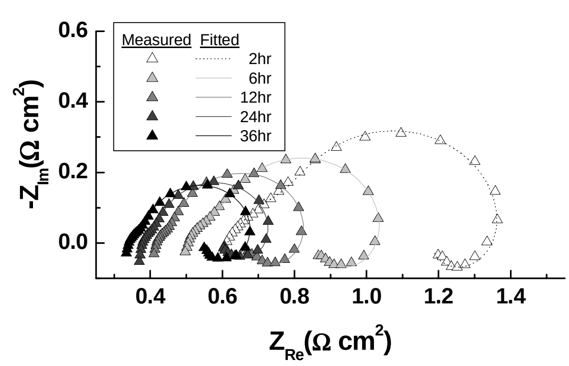


Fig. 2. Impedance data of the anode in MEA1 during conditioning period.