

Performance of a direct methanol polymer electrolyte fuel cell

Doo Hwan Jung*, Chang Hyeong Lee, Chang Soo Kim, Dong Ryul Shin

Fuel Cell Research Team, Korea Institute of Energy Research, Yusong-Ku, 71–2, Jang-dong, Taejeon, 305–343, South Korea

Abstract

The performance of a direct methanol fuel cell based on a polymer electrolyte membrane electrolyte was investigated. Pt–Ru/C (60 wt.%) and Pt/C (60 wt.%) catalysts were employed for methanol oxidation and oxygen reduction, respectively. Morphology of the catalysts was investigated using X-ray powder diffraction, electron diffraction patterns and transmission electron microscopy. *I–V* characteristics of the fuel cell were tested by changing the methanol concentration, temperature, and Nafion types as a polymer electrolyte membrane electrolyte. The performance of the single cell was enhanced by increasing cell temperature. High cell voltage was obtained from 2.5 M methanol. The cell fabricated with Nafion 112 membranes with a current density of 230 mA/cm² at 0.55 V was obtained from 2.5 M methanol. Heat-treating of the Pt–Ru/C catalyst at 500°C for 4 h affected the performance of the direct methanol fuel cell (DMFC) single cell resulting in particle agglomeration and crystal growth. © 1998 Elsevier Science S.A.

Keywords: Direct methanol fuel cell; Single cell; Stack; *I–V* characteristics

1. Introduction

Direct methanol fuel cells (DMFCs) using polymer electrolyte membranes are promising candidates for the application of portable power sources, electric vehicle and transport applications because they do not require any fuel processing equipment and can be operated at low temperatures of 60–130°C [1]. Elimination of the fuel processor results in simpler design and operation allowing higher reliability, lower weight volume, and lower capital and operating costs.

Platinum and co-deposited Pt-based binary alloy electrodes have been extensively studied for methanol electro-oxidation in acid electrolytes at ambient and elevated temperatures. Pt–Ru/C catalyst, in particular was found to be superior to the anode of a DMFC comprising a polymer electrolyte membrane electrolyte (Nafion) [2].

Surampudi et al. [3] considers a DMFC working with a liquid feed of methanol in pure water varying from 0.5 to 4.0 M, at a working temperature in the range of 60–90°C. The authors found a high performance DMFC (250 mA/cm² at 0.5 V) under the conditions of 88°C, 5 mg/cm², 2.0 M methanol. Ren et al. [4] constructed and tested a DMFC under pressurized conditions. The electrodes were prepared

by the transfer printing technique. Three Nafion membranes, Nafion 117, 115 and 112 were used as polymer electrolyte membranes. The best performance (670 mA/cm² at 0.5 V) is obtained with Nafion 112 and 2.2 mg Pt–Ru/cm², at 130°C, with 5 atm oxygen. With a similar system, Shukla et al. [5] and Arico et al. [6] found a power density around 200 mW/cm² at 95°C, with a 2 M concentration of methanol. Effects of methanol crossover were studied under various operating conditions and membrane types [3,4]. The morphology of electrode material as anode and cathode were also studied for optimal catalyst composition [7].

The objective of this study was to develop the high performance DMFC. This paper summarizes the effects of methanol concentration and operating temperature on the DMFC single cell. Heat-treated anode and cathode catalysts at 500°C for 4 h are discussed also to understand the heat-treatment effects on the cell performance. The changing morphology of the heat-treated anode and cathode catalysts are also discussed by using X-ray diffraction and transmission electron microscopy (TEM). The *I–V* characteristics and amounts of methanol crossover using three kinds of Nafion membranes, 117, 115 and 112 at constant temperature are also discussed. The performance of a 3-cell stack, having a single cell area of 150 cm², was tested at a constant temperature of 90°C.

* Corresponding author.

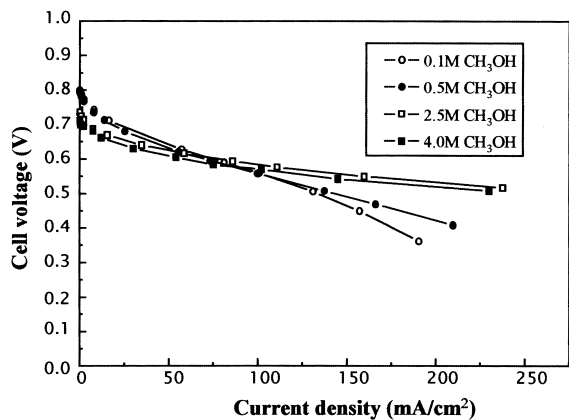


Fig. 1. *I*-*V* characteristics of a DMFC single cell at various methanol concentrations and at a constant operating temperature of 120°C. Anode: 60 wt.% Pt-Ru/C (3.0 mg Pt/cm²), 2.5 M methanol, 9 ml/min, 1 kgf/cm². Cathode: 60 wt.% Pt/C (3.0 mg Pt/cm²), O₂: 105 sccm, 3 kgf/cm².

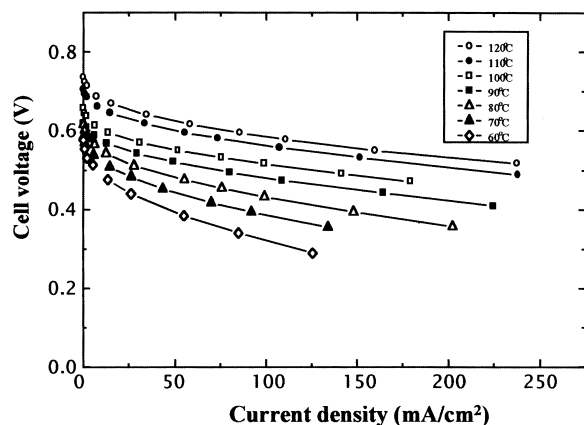


Fig. 2. *I*-*V* characteristics of a DMFC single cell at various operating temperatures. Anode: 60 wt.% Pt-Ru/C (3.0 mg Pt/cm²), 2.5 M methanol, 9 ml/min, 1 kgf/cm². Cathode: 60 wt.% Pt/C (3.0 mg Pt/cm²), 2.5 M methanol, 9 ml/min, 1 kgf/cm².

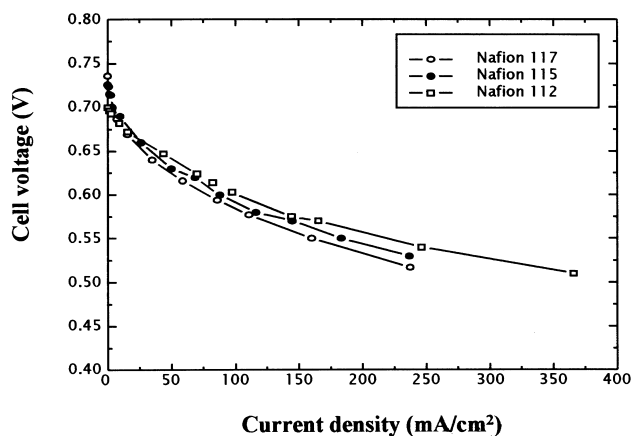


Fig. 3. *I*-*V* characteristics of a DMFC single cell at various methanol concentrations and at a constant operating temperature of 120°C. Anode: 60 wt.% Pt-Ru/C (3.0 mg Pt/cm²), 2.5 M methanol, 9 ml/min, 1 kgf/cm². Cathode: 60 wt.% Pt/C (3.0 mg Pt/cm²), O₂: 105 sccm, 3 kgf/cm².

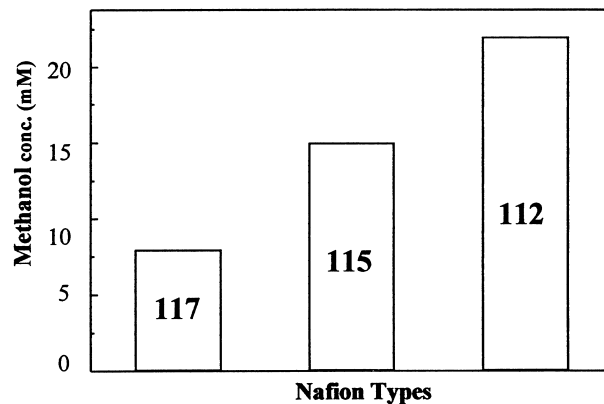


Fig. 4. Concentration of methanol crossover for various Nafion types at an operating temperature of 90°C. Anode: 60 wt.% Pt-Ru/C (3 mg Pt/cm²), 2.5 M CH₃OH, 9 ml/min, 1 kgf/cm². Cathode: 60 wt.% Pt/C (3 mg Pt/cm²), O₂: 105 sccm, 3 kgf/cm².

2. Experimental

For a single cell performance test, carbon supported 60 wt.% Pt-Ru/C binary metal powders (E-TEK, atomic ratio 1:1) and 60 wt.% Pt/C powders (E-TEK) were used as anode and cathode catalysts, respectively. Both the 60 wt.% Pt-Ru/C and Pt/C catalysts are characterized by XRD (X-ray diffraction patterns) obtained on a JEOL JDX-8P X-ray diffractometer. The XRD patterns were collected at the scan rate of 2°/min in the range of $2\theta = 30\text{--}50^\circ$. TEM analysis was performed using a Philips CM20 transmission electron microscope. Specimens were prepared by grinding the raw catalysts and ultrasonically suspending the particles in methanol. Drops of the suspension were deposited onto a standard Cu grid covered with carbon film (300 mesh) and

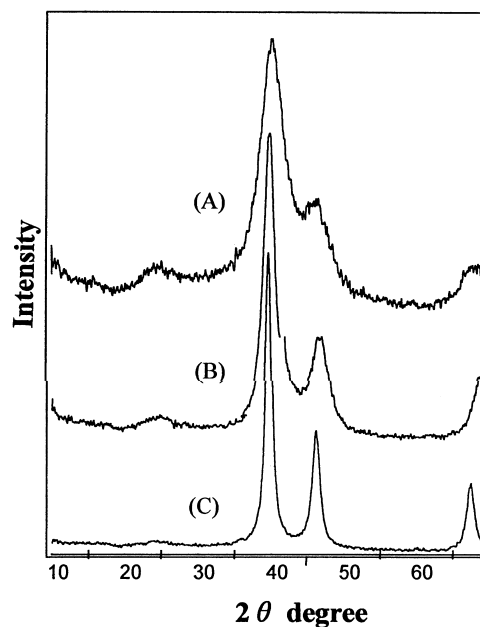


Fig. 5. X-ray diffraction patterns for as-received 60 wt.% Pt-Ru/C (A), heat-treated 60 wt.% Pt-Ru/C (B) and 60 wt.% Pt/C at 500°C for 4 h (C).

allowed to dry before being inserted into the microscope. Catalyst inks were prepared by grinding the water-wetted metal catalysts with a ball mill having two kinds of alumina ball (9 and 6 mm) for 12 h. After mixing the catalysts, 20 wt.% of PTFE solution was added to the catalyst inks by agitating in an ultra sonic bath for 5 min. Suitable drying ink compositions were 80 wt.% Pt–Ru/C with 20 wt.% PTFE for the anode ink, and 80 wt.% Pt/C with 20 wt.% PTFE for the cathode ink. In order to prepare the catalyst layer, appropriate amounts of anode and cathode ink were uniformly applied to carbon paper of 7.6 cm² area to give a metal catalyst loading of approximately 3 mg Pt/cm² and then dried at 80°C for 1 h.

Nafion membranes (117, 115, 112) were cleaned and converted into the acid form by boiling the membrane in 3%

H₂O₂, deionised water, 5% H₂SO₄, and then deionised water again for over 1 h for each step.

Membrane electrode assembly (MEA) was carried out by hot pressing at 120°C and 100 kg/cm² for 2 min after applying about 0.6 mg/cm² of 5 wt.% Nafion solution (900 equivalent weight, Aldrich) onto the surface of the anode and cathode electrodes. The MEAs were inserted into the fuel cell hardware which consisted of a graphite block with machined serial flow channel, gold-coated copper current collectors, and stainless steel for compression plates.

Methanol solution with pure water was pumped into the anode channel of the cell through the vaporizer controlled at the same temperature as the cell, and pure oxygen gas as a cathode fuel was supplied into the cathode channel. Cell performances were evaluated over the range of 60–120°C

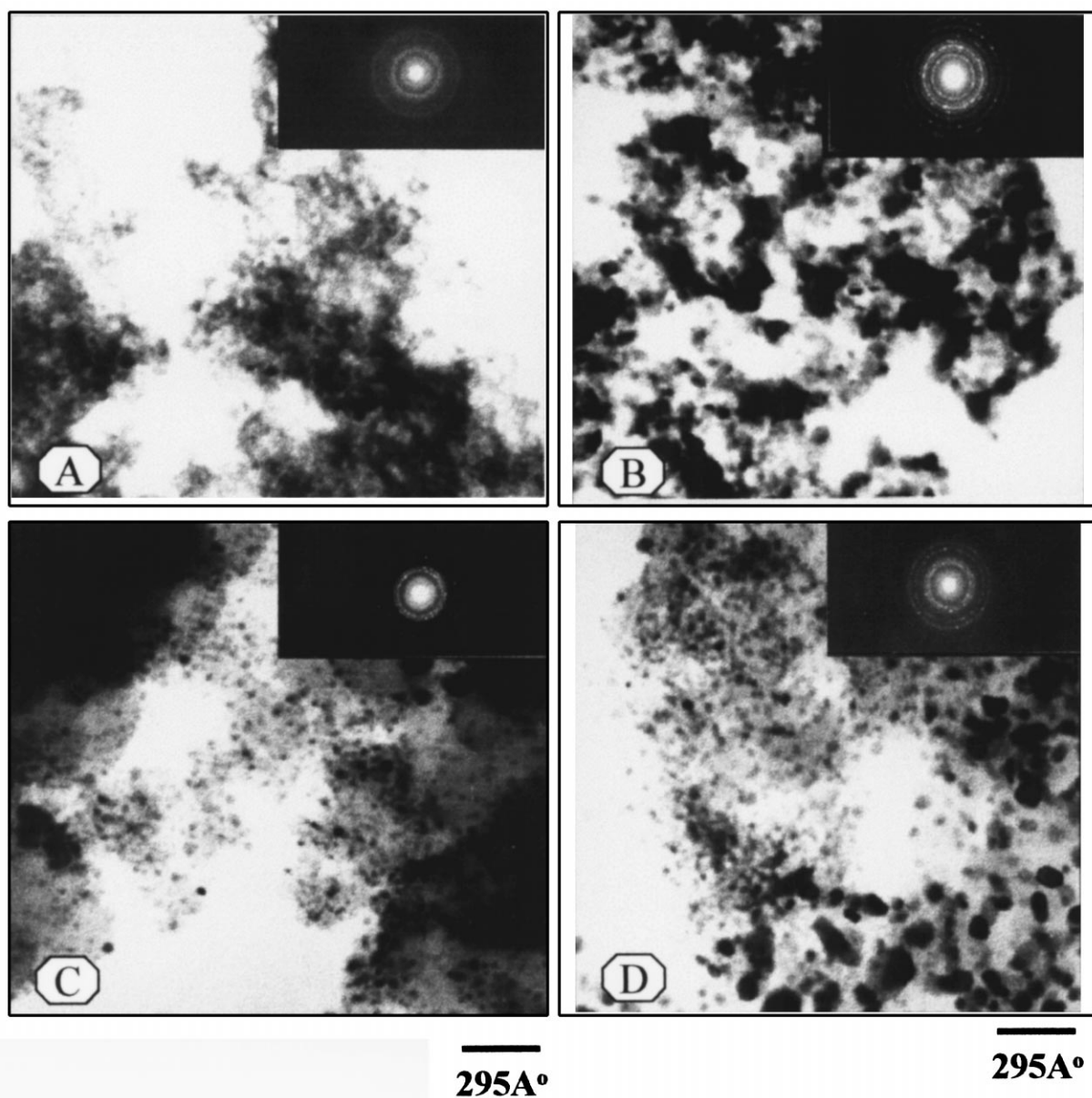


Fig. 6. TEM and electro diffraction patterns for the electrode catalysts: as-received (A) and heat-treated 60 wt.% Pt–Ru/C at 500°C for 4 h (B), as-received (C) and heat-treated 60 wt.% Pt/C at 500°C for 4 h (D).

with methanol concentrations of 0.5–4.0 M, flow rates of 9 ml/min, and an oxygen saturation of 105 sccm.

The methanol concentration remaining in the drain water coming from the cathode outlet was tested by gas chromatography (Shimadzu 8A) with a Porapak Q (1.5 m, 1/8 inch, stainless steel) column.

A 3-cell stack, having a single cell area of 150 cm² fabricated with Pt–Ru/C (3.0 mg Pt/cm²) and Pt/C (3.0 mg Pt/cm²) as anode and cathode electrode catalysts, respectively, was tested by using the same experimental apparatus as the single cell test. Methanol (2.5 M) with a flow rate of 30 ml/min and pure oxygen at 300 sccm were used as anode and cathode fuel, respectively.

3. Results and discussion

Fig. 1 shows the performance of the single cell (7.6 cm²) for various methanol concentrations at a constant temperature of 120°C with a 60 wt.% Pt–Ru/C (3 mg Pt/cm²) catalyst and a 60 wt.% Pt (3 mg Pt/cm²) catalyst as anode and cathode electrode catalysts. Each data point represents typical steady state voltages that were taken after continuous operation for 5 min at the indicated current density. It can be seen that the open circuit voltages decrease with increasing methanol concentration. This agrees well with the experimental results reported by Surampudi et al. [7]. It has been noted that the open circuit voltage of the DMFC at higher methanol concentrations is attributed to the higher methanol crossover than the lower methanol concentration. These results show that at high operating current densities, the highest cell voltages are obtained with 2.5 M methanol while somewhat lower voltages are obtained with both the higher concentration, 4 M methanol, and lower concentration, 0.5 M. The lower performance of the cell at concentrations less than 0.5 M is due to the concentration polarization effects. The lower performance of the cell at higher methanol concentrations is attributed to the fuel crossover phenomenon [7,8].

Fig. 2 shows the *I*–*V* characteristics of a DMFC single cell at various operating temperatures (60–120°C) using Nafion 117 and 2.5 M methanol. It can be seen that at a potential of 0.5 V, the current densities are 130, 230, and over than 250 mA/cm² at 100, 110 and 120°C. At high temperatures, the high performance is attributed to the combined effects of a reduction of ohmic resistance and polarization [6].

Fig. 3 shows the *I*–*V* characteristics of the cell using Nafion 117 (0.18 mm thickness), 115 (0.13 mm thickness) and 112 (0.05 mm thickness) as electrolytes which have different membrane thicknesses at the operating temperature of 120°C. It can be seen that the highest cell current density using Nafion 112 at a constant cell voltage of 0.55 V could achieve 230 mA/cm² with a fuel conversion value of 0.87% in the first pass. On the other hand, the highest cell current densities of single cells using Nafion 115 and 117 at

a constant cell voltage of 0.55 V represent the values of 183 and 160 mA/cm² with fuel conversions of 0.68 and 0.59%, respectively. This is due to the reduction of resistance of charge transfer from the anode side to the cathode side and the reduction of concentration polarization in the polymer electrolyte with the decreasing of membrane thickness. Nevertheless, the open circuit voltages shown in Fig. 3 decrease from 0.73 to 0.70 V with increasing membrane thickness. This can be attributed to the reduction of methanol crossover with increasing mass transfer resistance in the membrane.

Fig. 4 shows the weight percent of methanol remaining in the drain water coming from the cathode outlet. The methanol concentration is about 3 times higher for the MEA using the Nafion 112 membrane than for the MEA using the Nafion 117 membrane. As a result the methanol permeation rates through the membranes are expected to be higher in the thinner membranes.

The X-ray diffraction patterns of Pt/C and Pt–Ru/C samples are shown in Fig. 5. It is found that as-received Pt–Ru/C catalyst is X-ray amorphous. Heat-treated Pt–Ru/C in nitrogen flow at 500°C for 4 h is found to be crystalline (Fig. 5B) and shows the presence of a cubic phase similar to Pt (Fig. 5C), with peak positions shifted toward higher angles, typically associated with the formation of a Pt–Ru alloy [3,5].

Fig. 6 shows the TEM photographs and X-ray diffraction patterns of as-received Pt–Ru/C (Fig. 6A), Pt/C catalysts (Fig. 6C), and heat-treated Pt–Ru/C (Fig. 6B), Pt/C (Fig. 6D) at 500°C for 4 h. It can be seen that the heat-treated Pt–Ru/C catalyst represent the increasing of particle agglomeration and crystal growth due to the changing of the chemical composition and structural features of the catalyst. By contrast, there is no changing of particle configuration and crystallinity in the Pt/C catalyst.

The *I*–*V* characteristics of the cell using heat-treated Pt–Ru/C catalyst is shown in Fig. 7. The cell using the heat-treated catalyst shows the lower performance than the as-

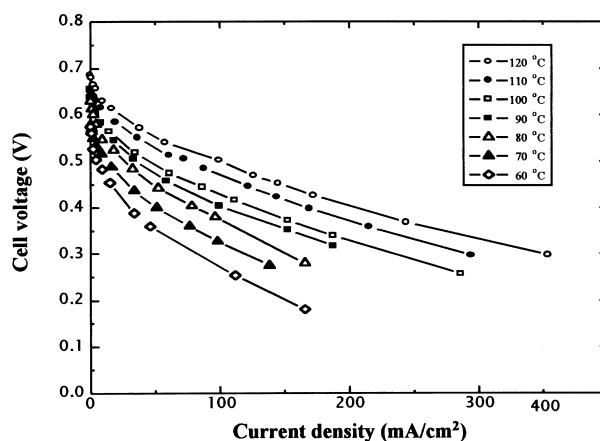


Fig. 7. *I*–*V* Characteristics of a DMFC single cell at various operating temperatures. Anode: heat-treated 60 wt.% Pt–Ru/C at 500°C for 4 h (3.0 mg Pt/cm²) 2.5 M CH₃OH, 9 ml/min, 1 kgf/cm². Cathode: as-received 60 wt.% Pt/C (3 mg/cm²), O₂: 105 sccm, 3 kgf/cm².

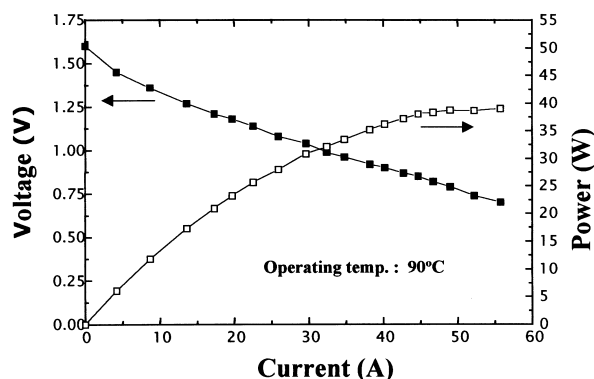


Fig. 8. I - V characteristics and out power of 3-cell stack (active electrode area of 150 cm^2) at operating temperature of 90°C . Anode: 60 wt.% Pt-Ru/C (3.0 mg Pt/cm^2), $2.5\text{ M CH}_3\text{OH}$, 30 ml/min , 1 kgf/cm^2 . Cathode: 60 wt.% Pt/C (3.0 mg Pt/cm^2), O_2 : 300 sccm , 3 kgf/cm^2 .

received Pt-Ru/C catalyst represented in Fig. 1. This behavior is due to the changing morphology which was mentioned in the previous results, such as particle size, crystallinity and chemical composition of the anode catalysts [7].

Fig. 8 shows the performance of a 3-cell stack having a single cell area of 150 cm^2 at a constant operating temperature of 90°C . At that time, 2.5 M methanol with the flow rate of 30 ml/min , and 300 sccm oxygen were supplied as anode and cathode fuels, respectively. The highest cell power of about 38 W (0.26 W/cm^2) was obtained at a constant cell voltage of about 0.8 V . The open circuit voltage and cell current at a constant cell voltage are somewhat lower than the single cell values represented in Fig. 1. To overcome this problem, optimization of operating conditions, cell design with flow patterns and water management produced at the cathode side will be further studied for the scale up of a DMFC having a large cell area of electrode.

4. Conclusions

By changing methanol concentration, temperature and Nafion types, optimal operating conditions were revealed, and also the heat-treatment effects on the electrode catalyst were evaluated. The performance of a single cell was enhanced with increasing cell temperature. It was found that 2.5 M methanol was a suitable fuel concentration reducing diffusion polarization and methanol crossover. The single cell was fabricated with a Nafion 112 membrane. A current density of 230 mA/cm^2 at 0.55 V was obtained from 2.5 M methanol. The cell using heat-treated catalysts showed the lower performance than the as-received catalyst, due to the changing morphology such as particle size, crystallinity and chemical composition. The highest 3-cell stack ($150\text{ cm}^2/\text{single cell}$) performance gave a power of 38 W with a lower open circuit voltage and current density than the small size single cell.

References

- [1] N.A. Hampson and M.J. Wilars, *J. Power Sources*, 4 (1979) 191.
- [2] J.B. Goodenough, A. Hamnett, B.J. Kennedy, R. Manoharan and S.A. Weeks, *J. Electroanal. Chem.*, 240 (1988) 133.
- [3] Surampudi et. al., *J. Power Sources*, 47 (1994) 377.
- [4] X. Ren, M.S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.*, 143 (1996) L12.
- [5] A.K. Shukla, P.A. Christensen, A. Hamnett and M.P. Hogarth, *J. Power Sources*, 55 (1995) 87.
- [6] A.S. Aricò, P. Cretì, H. Kim, R. Mantegna, N. Giordano and V. Antonucci *J. Electrochem. Soc.*, 143 (1996) 3950.
- [7] M.K. Ravikumar and A.K. Shukla, *J. Electrochem. Soc.*, 143 (1996) 2601.
- [8] J.T. Wang, S. Wasumus and R.F. Savinell, *J. Electrochem. Soc.*, 143 (1996) 1233.