

## Development of Two-layer Electrode for Direct Methanol Fuel Cell

Doo-Hwan Jung<sup>†</sup>, Seong-Hwa Hong, Dong-Hyun Peck, Rak-Hyun Song,  
Dong-Ryul Shin, and Hyuk-Nyun Kim\*

Advanced Fuel Cell Research Team, Korea Institute of Energy Research Jang-dong 71-2, Yuseong-gu, Daejeon 305-600, Korea  
\*Fuel Cell Team / Battery Research Institute, LG Chem, Ltd., Research Park P.O. Box 61, Yuseong Science Town, Daejeon 305-380, Korea

(Received October 30, 2002 : Accepted February 6, 2003)

**Abstract:** The performance of the Direct Methanol Fuel Cell (DMFC) using multi-layer electrode, which prepared by various anode catalysts and Nafion membranes, was studied for reducing the amount of the metal catalyst loaded in the MEA system. The amount of the catalyst used in this experiment was 3-4 mg/cm<sup>2</sup> in cathode and 1-2 mg/cm<sup>2</sup> in anode, respectively. The best performance was to be 230 mW/cm<sup>2</sup> of MEA3 at 90°C and 2 bar in this experiment. However, the overall performance of the DMFC was maintained almost the same compared to the general commercial catalyst systems.

**초 록 :** 전지 성능을 저하시키지 않고 연료극 및 공기극의 귀금속 촉매량을 줄이기 위하여 다층막 전극을 이용한 직접메탄올 연료전지의 성능특성을 조사하였다. 다층막 전극 즉, 연료극과 공기극에 사용된 촉매사용량과 나피온 막의 종류를 변화시키며 최종성능을 측정하였다. 본 실험에서 사용된 촉매량은 연료극이 3-4 mg/cm<sup>2</sup> 공기극이 1-2 mg/cm<sup>2</sup> 이다. 본 실험에서는 나피온 115를 사용한 MEA3의 90°C, 2기압에서 측정 결과 최대 전력밀도인 230 mW/cm<sup>2</sup>를 나타내었다. 이 결과는 현재 시판되고 있는 상용전극과 거의 같은 수준의 성능을 보여주고 있는 반면, 금속 촉매의 양은 기존의 상용전극과 비교하여 약 50% 정도 감소된 것이다.

**Key words :** Methanol crossover, Direct methanol fuel cell, Nafion membrane, Metal incorporation

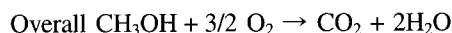
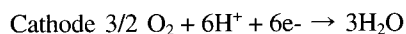
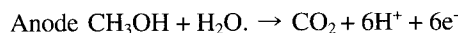
### 1. Introduction

Direct methanol fuel cell (DMFC) is one of the prime candidates for the small power sources and future electric vehicle applications because of its high power density and low temperature operation<sup>1-3</sup>). In contrast with the polymer electrolyte membrane fuel cell (PEMFC), the DMFC system does not require either hydrogen as a fuel or fuel reforming devices for the fuel cell stack. Reformer also increases the overall system weight. Generally, hydrogen may be carried in a form of hydride. Presently most of the fuel cell vehicles are using compressed hydrogen in a cylinder as fuel although it is not safe perfectly. From the safety of the fuel storage, the researchers are trying to alter the hydrogen as a fuel for the methanol.

The DMFC has some problems, yet as followings. 1) Methanol crossover through the membrane to the cathode side decreases the oxygen kinetics<sup>1</sup>) and the cell potential in turn affecting the efficiency of the system. 2) The removal of carbon monoxide, which poisons the catalyst, is essential in the catalyst system to improve the overall performance of the DMFC<sup>4,5</sup>). 3) The formation of CO<sub>2</sub> at the anode side blocks the active site of the catalyst<sup>6,7</sup>).

The methanol is oxidized at the anode and releases proton, which combines with oxygen to form water and generates the energy as shown in Fig. 1. The electrochemical reactions

occurring in a DMFC, which contains a polymer electrolyte membrane, are as following:



The significance of the DMFC is due to overall simplicity and a liquid fuel where the gases need not to be humidified.

Many researchers have reported the catalysts to promote the methanol oxidation reaction, as following: (1) noble metals, (2) noble metal alloys, (3) noble metal alloys with non-noble metals, (4) chemisorbed layers on Pt, (5) platinum with inorganic material, and (6) redox catalysts<sup>4-11</sup>). Pt-Ru appears to be the best methanol oxidation catalyst in acidic electrolytes as reported in the literature<sup>14</sup>).

Jung et. al. have reported the anode catalyst to improve the overall performance in the DMFC cells<sup>12</sup>). In most of their studies, they used commercially available carbon as a support material. Pt-Ru samples and catalyst for anode were prepared in their laboratories. Loading amount of the anode catalyst varies from 5 to 10 mg/cm<sup>2</sup> in the previous paper. The present work is mainly concentrated on low loading noble metals and operating at low temperature and pressure. A DMFC is operated at normal atmospheric pressure and between room temperature to 90°C. Comparative studies were carried out using various commercially available anode

<sup>†</sup>E-mail: doohwan@kier.re.kr

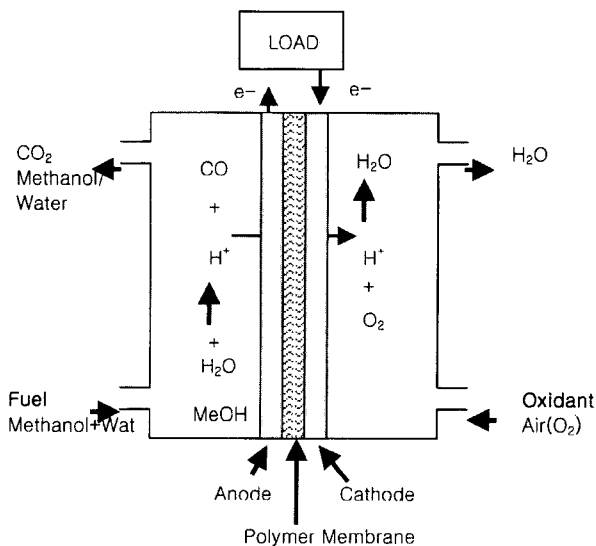


Fig.1. Schematic diagram of DMFC single cell.

catalysts for DMFC.

### 2. Experimental

The performance of the DMFC using multi-layer electrode was examined in this study. The schematic diagram of the multi-layer electrode was shown in Fig. 2. The membrane electrode assemblies (MEA) used in this study had an active area of 25 cm<sup>2</sup>. The membrane and electrode were assembled using graphite plates that have flow channel machined into the surface for the supply of fuel and oxidant, which acts as electrical connection for the cell. The cell was assembled using gold-coated copper end plate. 2.0 M methanol was used and was passed through the anode side of the cell using programmable mass flow controller with a flow rate of 2 ml/min in all the experiments. The flow rate of oxygen was kept at 2 bar on the cathode side. The anodes prepared using various catalysts were i) 60% Pt-Ru on carbon, ii) unsupported Pt-Ru black. The loading of the catalyst was varied on the electrodes as shown in Table 1. The Pt-Ru catalysts were from E-TEK (USA), having an atomic ratio of 1:1. The catalyst slurry was prepared by adding a Nafion ionomer into a mixture of iso-

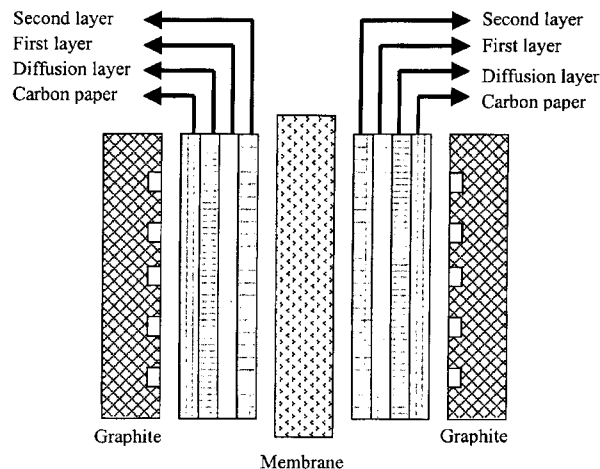


Fig. 2. Schematic diagram of multi-layer electrode used in this experiment.

propyl alcohol and distilled water. The additions of ionomer in the catalyst partially reduced catalyst particles in intimate contact with other catalyst particles to provide electronic conductivity. It also provides good ionic conductivity within the electrode structure and a continuous ionic path to the membrane electrolyte. The cathode catalyst is Pt black and the loading varied from 3 to 4 mg/cm<sup>2</sup>. Cathode is a gas-diffusion type consisting of two layers. The single cell assembled was operated at various temperatures.

### 3. Results

Fig. 3 shows the single cell performance of MEA1 under the ambient (Fig. 3a) and 2 bar oxygen pressure (Fig. 3b). The maximum power density of MEA1 was shown to be 115 and 130 mW/cm<sup>2</sup> under the ambient and 2 bar oxygen pressure at 0.4 V, 60°C, respectively. As expected, the overall power density of MEA1 increased with increasing the temperature at the same operating voltage.

Fig. 4. shows the single cell performance of MEA2 under the ambient (Fig. 4a) and 2 bar oxygen pressure (Fig. 4b). The maximum power density of MEA2 was shown to be 40 and 50 mW/cm<sup>2</sup> at 0.4 V, 60°C under the ambient and 2 bar oxygen pressure, respectively. The overall performance

Table 1. Sample preparation condition in this experiment.

MEA No.	cathode electrode				anode electrode	
	diffusion layer	1st layer	2nd layer	diffusion layer	1st layer	2nd layer
1	C/B + teflon binder	2 mg/cm <sup>2</sup> Pt black + teflon(25%)	2 mg/cm <sup>2</sup> Pt black + Nafion(15%)	C/B + Nafion binder	1 mg/cm <sup>2</sup> Pt-Ru/C + Nafion (33 %)	1 mg/cm <sup>2</sup> Pt-Ru black + Nafion(25 %)
2						0.3 mg/cm <sup>2</sup> Pt-Ru/C + Nafion(33 %)
3						1 mg/cm <sup>2</sup> Pt-Ru black + Nafion(25 %)
4			1 mg/cm <sup>2</sup> Pt black + Nafion binder(15 %)		0.5 mg/cm <sup>2</sup> Pt-Ru/C + Teflon(20 %)	0.5 mg/cm <sup>2</sup> Pt-Ru black + Nafion (25 %)

MEA No. 1, 2, 4: Nafion 117, and pressured at 34 Kgf/cm<sup>2</sup> for 3 min.

MEA No. 3: Nafion 115, and pressured at 34 Kgf/cm<sup>2</sup> for 3 min.

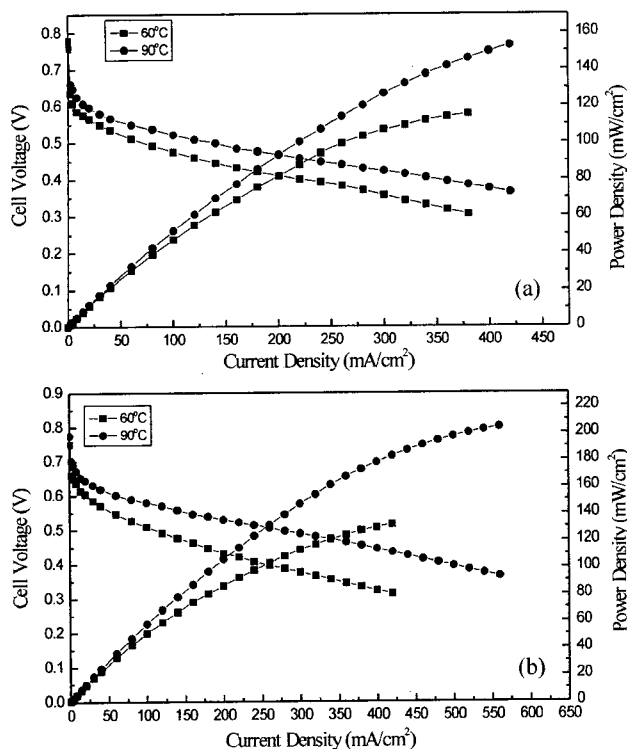


Fig. 3. Single cell performance of MEA1 at the (a) ambient and (b) 2 bar of oxygen pressure.

decrease compared to the MEA1 should be due to decrease of the amount of catalyst in anode.

Fig 5. shows the single cell performance of MEA3 used the Nafion 115 membrane under the ambient (Fig. 5a) and 2 bar oxygen pressure (Fig. 5b). The maximum power density of MEA3 was shown to be 65 and 140 mW/cm<sup>2</sup> at 0.4 V, 60°C under the ambient and 2 bar oxygen pressure, respectively. The maximum power density examined at 90°C under 2 bar oxygen pressure was shown to be 230 mW/cm<sup>2</sup>, and it is the best performance in this experiments. The maximum power density examined at 60°C under ambient oxygen pressure was much smaller than that of the MEA1. This should be due to the thickness of the Nafion membrane.

Fig 6 shows the single cell performance of MEA4 under the ambient (Fig. 6a) and 2 bar oxygen pressure (Fig. 6b). The maximum power density of MEA4 was shown to be 22 and 28 mW/cm<sup>2</sup> at 0.4 V, 60°C under the ambient and 2 bar oxygen pressure, respectively. The sample prepared using the MEA4, which contained the smallest amount of catalyst in this experiment, showed the lowest value of the maximum power density in this experiments.

#### 4. Discussions

In the present study, performance of the multi-layer electrode for the DMFC was investigated to reduce the amount of the catalyst actually loaded in the MEA system without decreasing the overall performance of the DMFC. The amount of the catalyst used in this experiment was 3-4 mg/cm<sup>2</sup> in cathode and 1-2 mg/cm<sup>2</sup> in anode. The MEA prepared by a

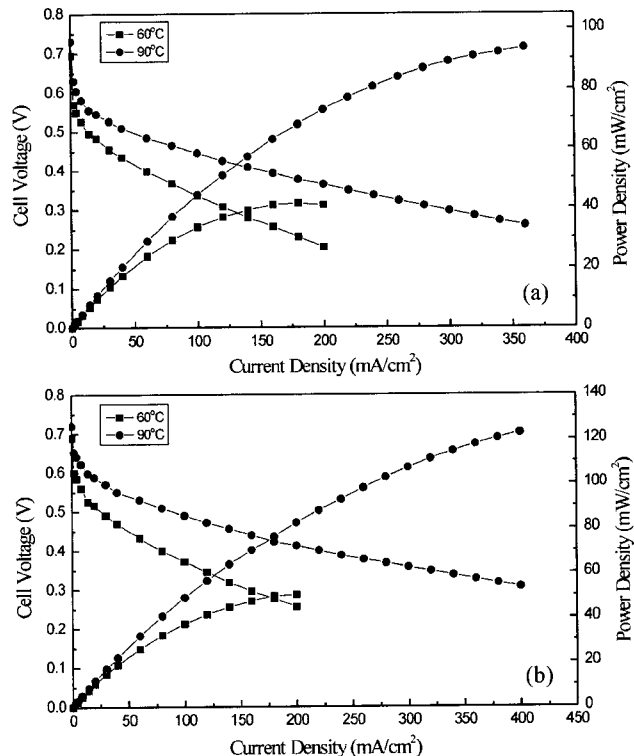


Fig. 4. Single cell performance of MEA2 at the (a) ambient and (b) 2 bar of oxygen pressure.

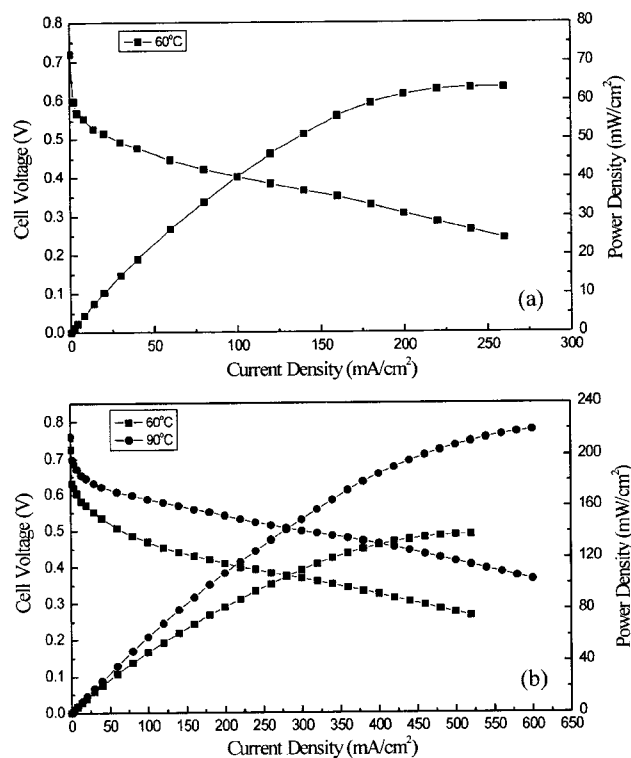


Fig. 5. Single cell performance of MEA3 at the (a) ambient and (b) 2 bar of oxygen pressure.

multi-layer electrode could reduce the amount of the catalyst about 1/2-1/4 compared to the general commercial product,

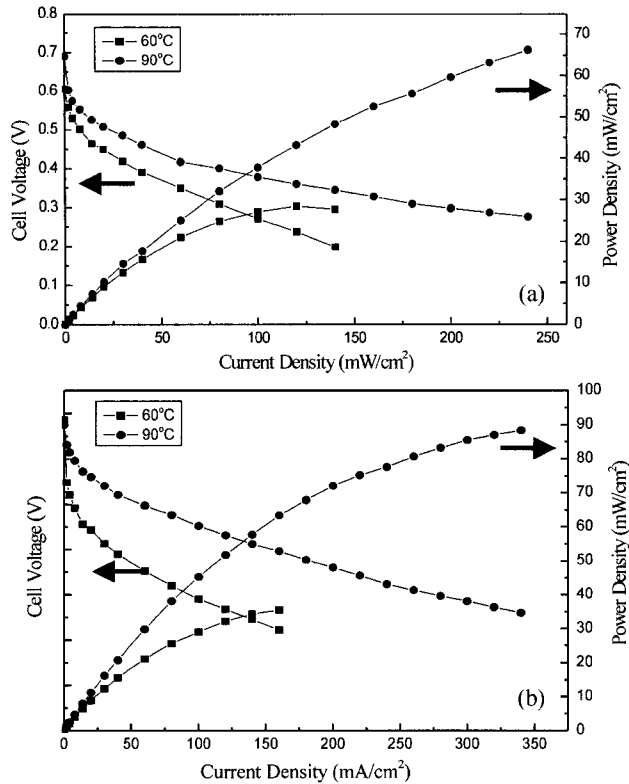


Fig. 6. Single cell performance of MEA4 at the (a) ambient and (b) 2 bar of oxygen pressure.

without the loss of the performance<sup>1,8)</sup>.

It is better to reduce the amount of the catalyst in anode than cathode catalyst without the performance decrease. The best performance was shown in this experiment to be 230 mW/cm<sup>2</sup> of MEA3 using Nafion 115 at 90°C. However, the overall performance of the DMFC was maintained almost the same compared to the general commercial catalyst systems<sup>15)</sup>. It should be that the diffusion of methanol was occurred easily in the multi-layered electrode and the effect of the teflon and Nafion binder, because the oxidation reaction of methanol appeared between the surface of Nafion membrane and the second layer.

The effect of membrane thickness on the DMFC performance was also examined in this experiment. At lower current density

under 150 mA/cm<sup>2</sup>, there was not any appreciable change of the cell performance. With thinner membrane, higher performance is expected but this behaviour was suppressed due to increasing the amount of the methanol cross over on the cathode side. However, there is difference of 50 mA/cm<sup>2</sup> in the higher current density region at the same operating voltage. It should be that most of the methanol was consumed in the reaction and then the methanol cross over was very low. This improvement was observed due to thinner membrane.

The performance of DMFC was determined by many factors such as methanol diffusion and CO<sub>2</sub> evolution, especially, dealt with in this experiment. The methanol diffusion and CO<sub>2</sub> evolution were affected by the hydrophobic, hydrophilicity and pore size distribution of diffusion layer. These factors should reduce the amount of catalyst without the performance decrease of DMFC. More detailed studies are needed continuously to clarify the factors and their mechanisms.

## References

1. H. Dohle, H. Schmitz, T. Bewer, J. Mergel, and D. Stolten, *J. Power Sources*, in press.
2. A. Heinzel and V. M. Barragan, *J. Power Sources*, **84**, 70 (1999).
3. S. Wasmus and A. Kuver, *J. Electroanal. Chem.*, **461**, 14 (1999).
4. B. Rohland and V. Plzak, *J. Power Sources*, **84**, 183 (1999).
5. T. J. Schmidt, H. A. Gasteiger, and R. J. Behm, *J. Electrochem. Soc.*, **146**, 1296 (1999).
6. H. A. Gasteiger, N. Markovic, P. N. Ross, Jr., and E. J. Cairns, *J. Phys. Chem.*, **97**, 12020 (1993).
7. A. Parthasarathy, B. Dave, S. Srinivasan, A. J. Appleby, and C. R. Martin, *J. Electrochem. Soc.*, **139**, 1634 (1992).
8. K. A. Friedrich, K. P. Geysers, A. J. Dickinson, and U. Stimming, *J. Electroanal. Chem.*, in press.
9. K. A. Starz, E. Auer, Th. Lehmann, and R. Zuber, *J. Power Sources*, **84**, 84 (1999).
10. C.-H. Lee, C.-W. Lee, D.-H. Jung, C.-S. Kim, and D.-R. Shin, *J. New Mat. Electrochem. Systems*, **2**, 125 (1999).
11. T. Toda, H. Igarashi, H. Uchida, and M. Watanabe, *J. Electrochem. Soc.*, **146**, 3750 (1999).
12. 정두환, 이창형, 신동열, *한국에너지공학회지*, **7**, 35 (1998).
13. A. Hamnett, *Catalysis today*, **38**, 445 (1997).
14. B. R. Rauhe, Jr., F. R. McLarnon, and E. T. Cairns, *J. Electrochem. Soc.*, **142**, 1073 (1995).
15. C. Lim, and C. Y. Wang, *J. Power Sources*, **113**, 145 (2003).