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# 고온형 멤브레인을 사용한 메탄올 개질 연료전지의 개질기 일체형 평판 설계

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# Planar fuel cell design integrated with methanol reformer by using a high temperature membrane

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**Key words** : Reformed hydrogen fuel cell(개질수소 연료전지), Methanol steam reforming(메탄올 수증기 개질), High temperature membrane(고온형 멤브레인)

**Abstract** : For a mobile application such as cellular phone, micro fuel cells should be extremely compact and thin. RHFC can be an alternativesolution because RHFC gives higher power density than DMFC and does not need ahydrogen storage vessel. In this paper, RHFC using methanol fuel is made as a novel planar design without a PROX. Both reformer and cell are made closely in a same plate to share the heater of reformer with the cell. The PBI membrane is used in the cell. The reason is that high temperature of reformer can cause a performance drop when perfluorosulfonic acid membrane such as Nafion is used. Such a high temperature operation also guarantees the higher CO tolerance to MEA catalyst. The cell is designed as an air-breathing type which the cathode of the cell is opened to the air. The commercial Cu/ZnO/Al2O3 steam reforming catalyst is packed in reformer channel. The active area of MEA is 11.9 cm2 and the peak power density was 27.5 mW/cm2.

**subscript**

RHFC : reformed hydrogen fuel cell
DMFC : direct methanol fuel cell
PROX : preferential oxidation
PBI : polybenzimidazole
MEA : membrane electrode assembly
PEMFC : polymer electrolyte membrane fuel cell

## 1. Introduction

There is growing pressure on battery manufacturers to increase further the energy density for the next generation of portable electronic equipment, which will require much higher energy densities[1]. Fuel cells have the potential of providing energy storage densities several times than those possible using current state-of-the-art lithium-ion batteries[2]. Thus, fuel cells seem to be best suited to applications where significantly more energy storage is required than at present in portable devices. The hydrogen fuel is essential in the use of small fuel cells for portable applications unless the methanol is being directly used. However, hydrogen is a highly voltile and flammable gas, and in certain circumstances hydrogen and air mixtures can detonate[3]. Thus, the difficulties and hazards involved in the storage and handling of the hydrogen fuel for fuel cells in either compressed gas or liquid form have been a major impediment in miniaturizing hydrogen proton exchange membrane fuel cells[4].

Hydrogen can be produced on demand by reforming methanol, or hydrocarbon fuels derived from crude oil (e.g., gasoline, diesel, or middle distillates) without such difficulties of directly handling and storing hydrogen[5]. The reformed gas from hydrocarbon fuels contains high concentration

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of CO, which can cause substantial losses in performance because of poisoning of the platinum anode electrochemical catalyst.

There are three methods available to mitigate the effect of CO poisoning in PEMFCs. These are the use of Pt alloy catalysts, an increase in fuel cell operating temperature and the introduction of oxygen into the fuel gas stream[6]. The Pt-Ru alloys are the most promising as Pt alloys to mitigate the effect of CO poisoning. Another method to mitigate CO poisoning is to increase the cell temperature. The higher Pt-Ru catalyst loading and higher cell temperature result in better CO tolerance. One of the final methods to mitigate CO poisoning by introducing oxygen into the anode gas stream is referred to as O2 bleeding. The injection of 2-5 percent oxygen into the anode gas can result in CO tolerance at concentrations up to 500 ppm.

There are also several methods for removing CO from a mixed gas stream. These include methanation, preferential oxidation, and the use of hydrogen permeable membranes[7]. However, both methanation and preferential oxidation require hydrogen loss and are difficult to control as well. The use of hydrogen permeable membranes (ex. palladium) would require multi-stage compressor and high pressure, which is not suitable to small scale application.

In this paper, RHFC using methanol as a fuel is designed to avoid the difficulties of the storage of hydrogen and to achieve a higher power than direct methanol fuel cells do. To attenuate the effect of CO poisoning, high temperature membrane (PBI/ $H_3PO_4$) is used and reforming channel is fabricated closely to the high temperature cell. Such an arrangement is intended to reuse efficiently the heat supplied for reforming to heat the cell. The cathode plate is designed as an air-breathing type that the air is supplied by convention of atmosphere.

## 2. Experiment

### 2.1 Design of the planar reformed hydrogen fuel cell

On a base plate, both channels of reformer and anode flow field are fabricated as shown in Fig. 1. The channel dimension of reformer is 1 mm (width) × 1 mm (depth) × 295 mm (length) and the cross sectional dimension of anode flow field is 1 mm × 1 mm. Plates are made from aluminum or PEEK (Polyether Ether Ketone), which is thermostable up to about 260 °C. The gasket material for covering the reforming channel is a stainless steel and a Teflon-glass fiber sheet. The cell is assembled with PBI/H3PO4 Membrane between Teflon gaskets and two au-coated SUS current collectors.

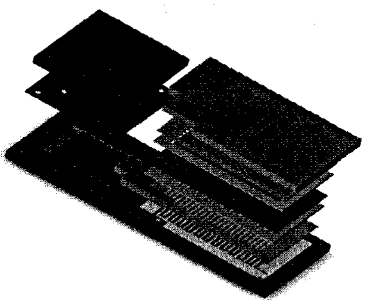

**Fig. 1 Model of a planar reformed hydrogen fuel cell that reformer is placed closely to the high temperature cell, whose cathode is the air-breathing type.**

### 2.2 Experimental set-up

To measure the performance of both reformer and cell, experimental equipment is set up as shown in Fig. 2. The produced gas stream and exhaust gas outward the cell was passed to an on-line micro gas chromatograph for analysis of reformed gas or exhaust gas from cell. The micro-gas chromatograph (Varian CP-4900) was equipped with a Molecular Sieve 5A and Porapak Q column and a TCD detector using Argon as the carrier gas. The electric performance is analyzed by an electric load (KIKUSUI PLZ-70UA) of minimum 0.010 mA resolution. A Piston pump (Youngin solvent delivery pump SP30D) supplies the methanol and water mixture to the reformer, whose temperature is controlled and recorded.

## 3. Results and discussion

Real fabricated planar system is shown in Fig. 3. Total dimension of reformer and cell is 50 mm (width) × 120 mm (height) × 7 mm (height) and volume is about 42 ml. As the temperatures are observed carefully to prevent the cell from being overheated beyond 200 °C, various flow rate of methanol - water mixture and temperature combination was tried.

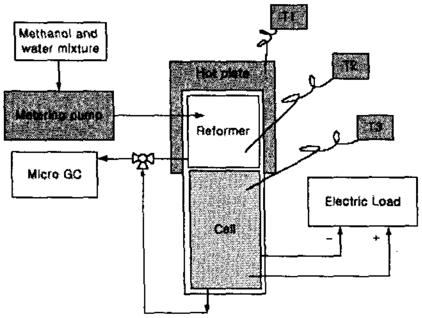


**Fig. 2. Experimental set-up with an electric load of KIKUSUI PLZ-70 UA and Varian CP-4900 Micro GC.**

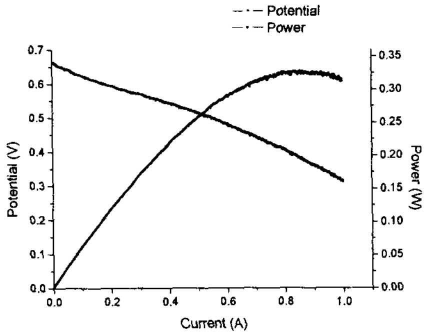


**Fig. 4 Performance at 0.05 ml/min flow rate of methanol (1) and water (1.2) mixture. Surface temperature of reformer and cell is 245 °C and 175 °C respectively.**

When flow rate of methanol-water mixture (1:1.2) is 0.05 ml/min, maximum power density is measured as shown in Fig. 4. The OCV (open circuit voltage) is 0.664 V and maximum power density is calculated as 27.5 $mW/cm^2$ at 0.868 A, 0.327 W because Mean's active area is 11.9 $cm^2$.

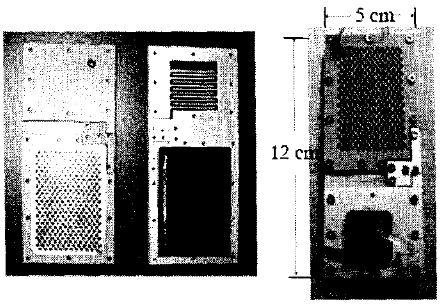


**Fig. 3. The fabricated plates with reforming catalyst and membrane and the final view integrated with micro fuel pump.**

The lower OCV in RHFC performance measurement than value of the MEA performance measurement may mean that contact resistance between current collector and electrode is little bit high. Moreover, it is suspected that CO poisoning causes the degradation of fuel cell and increases the anodic resistance and diffusion impedance during temperature combination changing[8].

## 4. CONCLUSION

The specific structure that reformer as well as cell is placed in a plate closely is originally suggested in order to be able to miniaturize the fuel cells. The planar reformed hydrogen fuel cells using a $PBI/H_3PO_4$ high temperature membrane was successfully made as a very small volume and its performance is measured. Cathode flow field is designed as an air breathing type that the air is supplied by atmospheric convection. It is demonstrated that air breathing cathode flow field is able to be properly adapted not only in low temperature fuel cell, but also in high temperature fuel. It is recognized that to use the high temperature membrane in reformer fuel cell system gives advantages of high CO tolerance and no humidification necessary. Nevertheless, there remain some technical issues to improve the performance of planar reformed hydrogen fuel cell.

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