

## Recent progress in passive direct methanol fuel cells at KIST

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### Abstract

This paper describes recent advances in passive direct methanol fuel cells (DMFCs) at the Korea Institute of Science and Technology (KIST). At KIST, we have been developing passive micro-DMFCs with capacities under 5 W that are expected to be used as portable power sources. Research activities are focused on development of membrane–electrode assemblies (MEAs) and design of monopolar stacks operating under passive and air-breathing conditions. The passive cells showed many unique features, much different from the active ones. Single cells with active area of 6 cm<sup>2</sup> showed a maximum power density of 40 mW/cm<sup>2</sup> at 4 M of methanol concentration at room temperature. A six-cell stack having a total active area of 27 cm<sup>2</sup> was constructed in a monopolar configuration and it produced a power output of 1000 mW (37 mW/cm<sup>2</sup>). Effects of experimental parameters on the performance were also examined to investigate the operation characteristics of single cells and monopolar stacks. Application of micro-DMFCs as portable power sources were demonstrated using small toys and display panels powered by the passive monopolar stacks.

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**Keywords:** Passive DMFC; Air-breathing DMFC; Monopolar stack; Portable power source; MEA

### 1. Introduction

At the Fuel Cell Research Center of Korea Institute of Science and Technology (KIST), we have been working on various types of fuel cells and fuel processors, including direct methanol fuel cells (DMFCs) for portable power, polymer electrolyte membrane fuel cells (PEMFCs) for electric vehicles, molten carbonate fuel cells for large scale power plants, solid oxide fuel cells for stationary power, and microfuel processors as a hydrogen source for portable PEMFCs. In this paper we present recent achievements specifically in passive DMFCs made in our laboratory.

Direct methanol fuel cell is a very attractive option for portable power sources because of its simplicity, high energy density, easy recharging and presumably long life. Many research efforts are underway to enhance its performance by improving characteristics of the components, viz. polymer electrolyte membranes [1,2], catalysts [3], membrane–electrode assemblies (MEAs) [4,5], stack assembly, and packaging technology [6,7]. DMFCs are flexible in power output from sub-watt to several hundred watts and thus are considered to be applicable to various portable electronics such as cellular phones, laptop computers, or TV

sets. DMFCs are roughly classified by their electric capacity and micro-DMFCs are generally defined as those with less than 5 W [8]. R. Hockaday, who established a venture company named Energy Related Devices Inc., firstly proposed a concept of “microfuel cell” that ran on air and methanol [9]. The microfuel cells could be potentially used as power sources for portable electronics. Recently, many companies including Motorola, Samsung, Toshiba, DuPont, Polyfuel, NEC, MTI (Mechanical Technologies Inc.), LG Chem, Casio, Smart Fuel Cell, etc. entered into this business.

In order for the DMFC to be commercially viable, its energy density should be increased by eliminating parasitic power loss to a pump and a fan that are needed to feed methanol and air into the cell. Towards this objective, the concept of passive-feed DMFCs has been proposed. The configurations of single cells and stacks of passive-feed DMFCs are very different from those of active ones into which methanol and air are fed by force. Passive DMFCs operate without the help of external devices for pumping methanol and blowing air into the cells and thus oxygen is diffused into the cathode from the ambient by a kind of air-breathing action of the cell, and methanol is diffused into the anode from a built-in feed reservoir driven by concentration gradient between the anode and the reservoir. The stack generally has a monopolar configuration which is much different from a conventional bipolar arrangement [10,11]. A monopolar stack is assembled by placing electrodes with the same

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polarity on the same plane of the membrane and then electrically connecting anodes and cathodes in series. Substantial improvements in active DMFCs have been made in terms of the performance of MEAs, flow field of bipolar plate, stack design, and system integration. However, only a few experimental results have been presented on the air-breathing DMFCs for use in portable applications [16,17].

In this paper, we present experimental results and achievements in developing high-performance single cells and monopolar stacks of micro-DMFCs under passive-feed conditions. Unique features of passive DMFCs were discussed based on experimental data obtained under different experimental conditions. The micro-DMFC stacks made at KIST were successfully applied to portable power sources for an LCD panel and a toy car.

## 2. Experimental

The electrodes for micro-DMFCs were fabricated by coating a catalyst layer on a wet-proofed (20% Teflon) carbon cloth (E-Tek). The catalyst power for anode (Pt–Ru black) and cathode (Pt black) was purchased from Johnson–Matthey and used ‘as-received’. Nafion 115 (Du Pont) was used as the polymer electrolyte membrane. The electrodes (an anode and a cathode) which were fabricated by applying catalyst slurry consisting of catalyst powder and Nafion solution were placed on either side of a Nafion membrane, and the membrane–electrode assembly was hot-pressed at 80 kg/cm<sup>2</sup> and at 130 °C for 150 s. The prepared MEA was fitted onto a small fixture to measure single cell performance under passive conditions as shown in Fig. 1. Active area of the MEA was 6 cm<sup>2</sup>.

The MEA for a monopolar stack was made by assembling six sets of anode and cathode pairs on each side of the membrane, and then sandwiched between two plastic plates through which methanol and air were diffused into the electrodes as depicted in Fig. 2. Active area of each electrode was 4.5 cm<sup>2</sup> and hence the total active area was 27 cm<sup>2</sup>. The cathode side plate had many holes for air diffusion and the anode side plate had channels and large open spaces for delivering and storing methanol solution. The monopolar stack was assembled by connecting the anodes and cathodes in se-

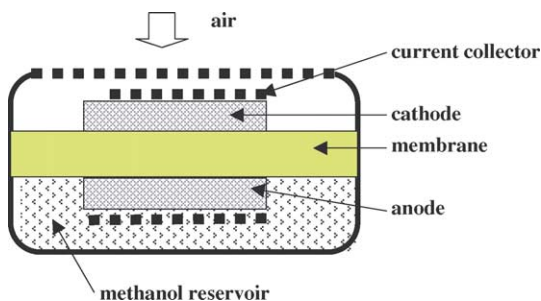


Fig. 1. A schematic diagram of the single cell of micro-DMFC operating under passive conditions.

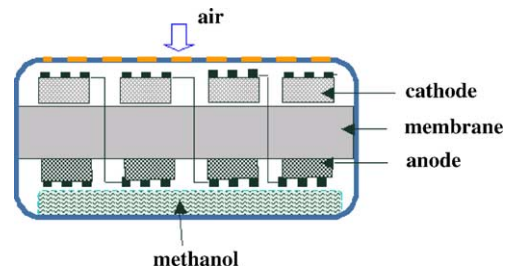


Fig. 2. A schematic diagram of a passive monopolar stack with a built-in methanol reservoir.

ries using wires as shown in Fig. 2. The single cells and the monopolar stacks were operated at room temperature and ambient pressure under passive conditions unless mentioned otherwise. The *I*–*V* characteristics were measured using an electronic load (Daegil Co. EL-200P) to evaluate the performances of single cells and monopolar stacks.

## 3. Results and discussion

Single cells were tested to investigate the effects of experimental parameters on their performances under passive-feed conditions. Fig. 3 shows the effect of methanol feed concentration on the performance of a passive cell. Power density of the cell increased with increasing methanol concentration up to 4 M and then decreased exhibiting a maximum value at a concentration of around 4 M. The optimum methanol concentration was very high compared to that found with active DMFC cells, which usually had a maximum performance at around 1 M of methanol concentration [12,13]. However, being fed with 1 M methanol solution, the passive cell showed a very poor performance and the voltage dropped sharply at current densities above 30 mA/cm<sup>2</sup>. This is due to methanol shortage in the anode catalytic layer caused by mass transfer limitation. To obtain a high performance in the passive-feed

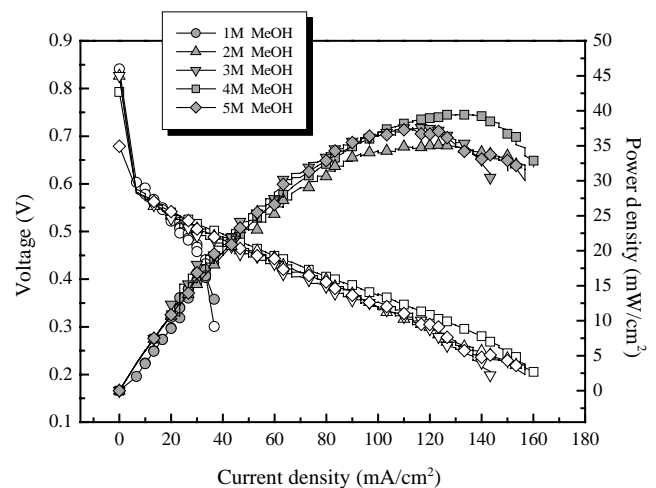


Fig. 3. Effect of methanol concentration on the performance of a single cell operating under passive conditions at room temperature.

configuration, a high methanol concentration gradient should be built up between the anode and the methanol reservoir because methanol migrates from the reservoir to the anode only by diffusion driven by the concentration gradient. Thus, high methanol concentration facilitates methanol transport to overcome the methanol shortage in the anode side. On the other hand, a high methanol concentration also facilitates methanol crossover through the membrane and degrades the cell performance, particularly at methanol concentrations above 5 M [14]. Therefore, DMFCs exhibit the highest performance at an optimum methanol concentration.

In DMFC,  $\text{CO}_2$  is produced at the anode side by oxidation of methanol. In this study, transparent plastic plates were used as a cell frame and thus we could see  $\text{CO}_2$  bubbles coming out of the anode and flowing upward along the channels by a buoyant force [15] and water droplets accumulating on the cathode side. Fig. 4 shows the  $\text{CO}_2$  bubbles that were produced at the anode side. The  $\text{CO}_2$  bubbles should be removed immediately from the anode to reduce the negative effect of the bubbles that block diffusion of methanol to the active catalytic sites. Under air-breathing conditions, water also accumulates at the cathode side to limit access of oxygen to the catalytic sites. Therefore, both anode and cathode separators should be designed to facilitate removal of  $\text{CO}_2$  bubbles and water from the passive cell.

Temperature of fuel cells generally increases by the heat released during electrochemical reaction. However, in the DMFCs, heat is not produced by only electrochemical reaction but also by methanol oxidation. Fig. 5 shows temperature change in the passive DMFC cell at an OCV state at methanol concentrations of 1 and 5 M. The cell temperature at 5 M methanol concentration was higher than that at

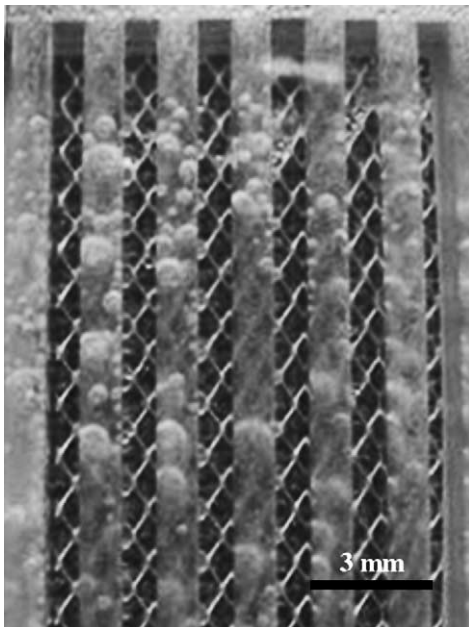


Fig. 4.  $\text{CO}_2$  bubbles generated and accumulated in the channels of the separator at the anode side of the passive cell.

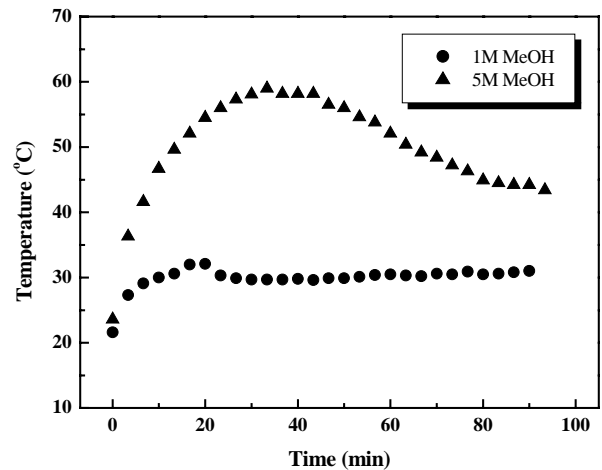


Fig. 5. Change in cell temperature at OCV state.

1 M methanol concentration though they varied with time as shown in Fig. 5. In the case of the cell using 5 M methanol, the cell temperature rose up to  $60^\circ\text{C}$  in the initial 30 min, and then cooled down slowly. The increase in cell temperature even at a state of OCV is due to oxidation of methanol crossing over to the cathode, not due to electrochemical reaction. At the cathode the methanol is oxidized in the presence of oxygen to produce carbon dioxide, water, and heat by combustion reaction. The reaction is purely chemical and not electrochemical and thus produces only heat, not electricity.

We have been trying to enhance the performance of single cells by employing various techniques and have achieved a marked improvement as shown in Fig. 6. At the beginning of this study about 4 years ago, we could only get a single cell performance of about  $5\text{ mW}/\text{cm}^2$ . However, cell performance has been improved gradually and sometimes abruptly, and at present exhibits as high as  $43\text{ mW}/\text{cm}^2$  at room temperature and ambient pressure. The enhancement could be

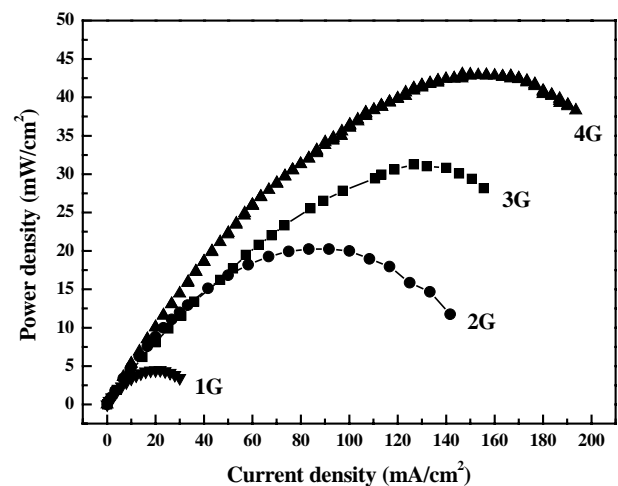


Fig. 6. Progress in the performance of a single cell at room temperature under passive conditions at KIST.

ascribed mainly to optimization of composition and structure of the membrane–electrode assemblies and the structure of separator plates. The MEA structure was optimized to reduce mass transport and charge transfer resistances. Additionally, the structures of separator plates on both anode and cathode sides were very important because they affected mass transport of methanol and  $\text{CO}_2$  in the anode side and oxygen and water in the cathode side.

A monopolar stack was fabricated by arranging electrodes with the same polarity on one side of an electrolyte membrane and by connecting the anode and cathode in series as shown in Fig. 2. The stack consisted of six cells with an active area of  $4.5 \text{ cm}^2$  per cell and a total active area of  $27 \text{ cm}^2$ . For comparison with the single cells, the effect of methanol concentration on its performance was tested under passive conditions and the results are shown in Fig. 7. Similar to the results with single cells, the stack performance increased with increasing methanol concentration up to 3 or 4 M, exhibited a maximum value at a methanol concentration around 3 and 4 M, and then decreased. Maximum power of the stack was 1000 mW and the power density based on electrode area was  $37 \text{ mW/cm}^2$ , which was much higher than those reported by others [16,17]. At methanol concentrations lower than 3 M or higher than 4 M, remarkable decreases in performances were observed due to either mass transport limitation or methanol crossover, respectively, as explained in Fig. 3.

Fig. 8 shows the changes in performance of the passive stack at a methanol concentration of 2 M and at different loads with operating time. The stack was kept under open circuit condition, during the initial 5 min, and then electric load of 200 or 300 mA was applied to the stack. Upon applying load of 200 mA to the stack, the voltage dropped sharply from 3.7 V (OCV) to 2.2 V and then remained al-

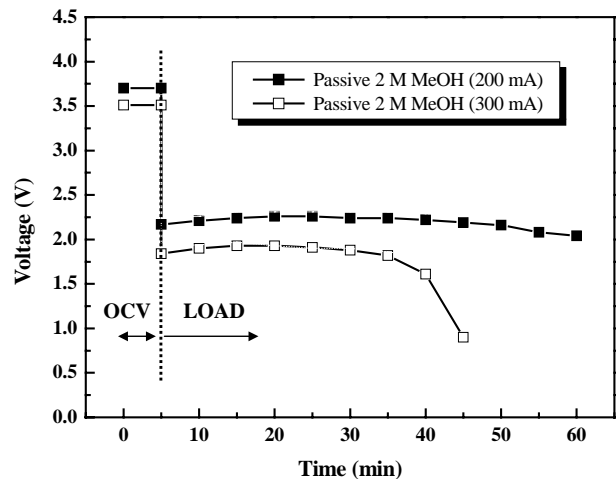


Fig. 8. Changes in voltages of the stack with time upon different electric loads under passive conditions. Electric load started to be applied at time of 5 min.

most constant over 60 min. In contrast, with the applied load of 300 mA, the voltage declined sharply in 30 min because of methanol shortage under passive conditions. These results show a unique feature of passive stacks that the total operating time with one dose is dependent on the electric load drawn from the stack.

We have made efforts to increase the performance of the monopolar stacks and we have achieved some improvements during the last 4 years, as shown in Fig. 9. At first the stack performance was lower than  $5 \text{ mW/cm}^2$  and has been improved to  $40 \text{ mW/cm}^2$ , with progress both in the performance of monopolar MEAs and techniques for stack assembling. One of the most difficult techniques in stack assembly is to connect the monopolar MEAs in series without

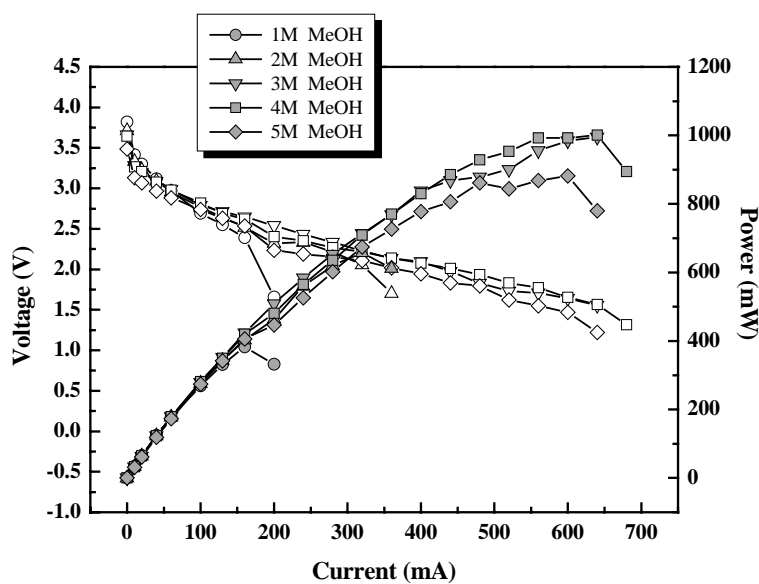


Fig. 7. Effect of methanol concentration on the performance of a six-cell monopolar stack with a total active area of  $27 \text{ cm}^2$  operating under passive conditions at room temperature.

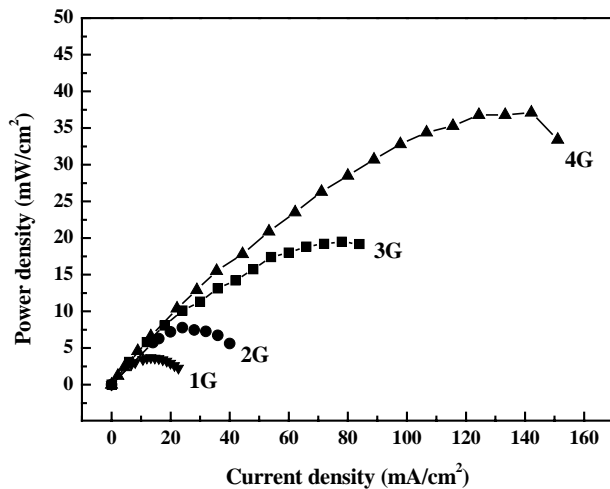
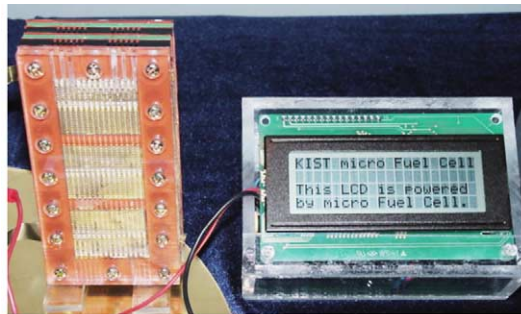


Fig. 9. Progress in performances of six-cell stacks made at KIST. The stacks operated under passive conditions and at room temperature.

methanol leakage. Our current techniques for stack assembly are considered to be at an early stage for commercialization and much more improvement should be made in this regard.

In our laboratory, we have fabricated various types of micro-DMFC packs to demonstrate their feasibility as portable power sources. For example, an LCD panel and a toy car shown in Fig. 10 operated successfully using electric power from DMFC packs. They may look crude, but we



(a)



(b)

Fig. 10. (a) An LCD panel (600 W) and (b) a toy car (2400 W) powered by micro-DMFC stacks made at KIST.

see the bright future of DMFCs as portable power sources that could generate electricity using stored methanol.

#### 4. Conclusions

In this study we presented unique features of single cells and monopolar stacks of micropassive DMFCs and some achievements made at KIST. The DMFC single cell under a passive condition produced different characteristics upon varying methanol concentration from an active one, exhibiting a maximum performance of 43 mW/cm<sup>2</sup> at around 4 M methanol concentration. Methanol crossover caused a temperature increase by direct oxidation of methanol at the cathode side releasing heat of combustion.

A six-cell monopolar stack with a total active area of 27 cm<sup>2</sup> behaved almost in the same manner as the single cells upon changing methanol concentration and produced a power of 1000 mW and a power density of 37 mW/cm<sup>2</sup>. It was also demonstrated that the micro-DMFCs could be used as a power source for small electronic devices. The performances of both single cells and monopolar stacks under passive conditions were higher than the results reported by others.

This paper was written to introduce our activities on passive DMFCs. Further progress will be presented in separate papers soon.

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