

# Behavioral pattern of a monopolar passive direct methanol fuel cell stack

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## Abstract

A passive, air-breathing, monopolar, liquid feed direct methanol fuel cell (DMFC) stack consisting of six unit cells with no external pump, fan or auxiliary devices to feed the reactants has been designed and fabricated for its possible employment as a portable power source. The configurations of the stack of monopolar passive feed DMFCs are different from those of bipolar active feed DMFCs and therefore its operational characteristics completely vary from the active ones. Our present investigation primarily focuses on understanding the unique behavioral patterns of monopolar stack under the influence of certain operating conditions, such as temperature, methanol concentration and reactants feeding methods. With passive reactants supply, the temperature of the stack and open circuit voltage (OCV) undergo changes over time due to a decrease in concentration of methanol in the reservoir as the reaction proceeds. Variations in performance and temperature of the stack are mainly influenced by the concentration of methanol. Continuous operation of the passive stack is influenced by the supply of methanol rather than air supply or water accumulation at the cathode. The monopolar stack made up of six unit cells exhibits a total power of 1000 mW ( $37 \text{ mW cm}^{-2}$ ) with 4 M methanol under ambient conditions.

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**Keywords:** Passive direct methanol fuel cell; Monopolar stack; Methanol crossover; Portable power source; Stack temperature; Feed conditions

## 1. Introduction

Fuel cell power sources have reached a defining moment after a long journey towards commercialization, especially for portable applications [1,2]. A tremendous growth in unit sales of portable electronic devices coupled with an increasing burden on battery capacity has created a serious concern among scientists and engineers about power requirements. The energy density argument is clear for direct methanol fuel cell (DMFC) in portable electronics—the energy density of the liquid fuel methanol ( $6.1 \text{ Wh g}^{-1}$  at  $25^\circ\text{C}$ ) is much higher than that of gaseous fuels [3–6], in spite of the molecular simplicity and ease of oxidation of hydrogen in proton exchange membrane fuel cell (PEMFC) that has specific energies of  $33 \text{ Wh g}^{-1}$ . Hydrogen suffers from low storage density, and a lack of storage, generation and distribution infrastructure. The concept of a passive feed, air-breathing DMFC with no external pump or fan to feed the reactants has been proposed to simplify the system, and to minimize the associated parasitic power losses [7]. It

could offer the potential for longer run-times than batteries and convenient recharging via fuel cartridge replacement. Liu et al. [8] have summarized the performance achievement of air-breathing DMFCs by various groups [9–16] around the world between the years 2002 and 2003. There are also several reports in the literature, where the performance of the passive DMFC has been tested under various experimental conditions [17–22].

Presently, numerous companies around the globe are involved in the portable fuel cell business and a few of them have reportedly obtained remarkable achievements. For example, both Mechanical Technologies, Inc. and Samsung Advanced Institute of Technology (SAIT) have developed mobile phones with built-in fuel cells with power of about 3 W. There are also other companies that are now developing fuel cells for portable electronics, e.g. LG Chemicals, Smart Fuel Cell, Toshiba, NEC, Hitachi, etc. At KIST, we have been developing passive micro-DMFCs with power under 5 W for portable applications. Research activities are set to develop membrane–electrode assemblies (MEAs) and designing of monopolar stacks to operate under passive and air-breathing conditions.

For DMFC-based systems to reach their commercial potential, they must be rugged, compact and have long run-times. These goals require advances in the stack design and compo-

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nents, as much of the size and weight is due to the bipolar plates that are employed to connect several cells in series to form a stack.

With the monopolar pack, it is possible to realize a small system size and simple design factors in a passive DMFC, where the electrodes of a polarity, anodes or cathodes, are placed on the same surface of the polymer electrolyte membrane. For this reason, the passive monopolar DMFCs have attracted attention among the researchers involved in the development of portable fuel cells. However, there have been only a few reports regarding this subject. Chang et al. have reported on the monopolar DMFC stack with 12 cells which had a peak power of  $23 \text{ mW cm}^{-2}$  (560 mW at 2.8 V) [13]. Chen and Yang tested an air-breathing DMFC pack with four unit cells and achieved a maximum power density of  $10.5 \text{ mW cm}^{-2}$  (342 mW at 1 V), which was much lower than the performance of single cells with  $21.3 \text{ mW cm}^{-2}$ . They attributed the lower performance to the assembly problem, such as contact resistance losses [11]. Recently, Liu et al. fabricated an air-breathing monopolar stack with 12 cells and obtained a peak power of  $26.1 \text{ mW cm}^{-2}$  (1.88 W at 2.2 V) and reported on an operation of a mobile phone with this DMFC stack. The higher performance with the stack than that with a single cell observed in this study was attributed to the effect of increased cell temperature due to heat generation by oxidation of crossover methanol.

The passive monopolar stack has several unique features. The reports available in the literature on passive monopolar stacks are insufficient to gain a full understanding of various interesting aspects. The present study deals with the fabrication of a monopolar DMFC stack with six unit cells and the performance measurements made under passive feed conditions. The effects of various operating conditions on its performance have also been investigated.

## 2. Experimental

### 2.1. Membrane and electrode assembly

The electrodes for monopolar passive DMFC were fabricated by coating a catalyst layer on to a wet-proofed (20% Teflon) carbon cloth (E-Tek). Electro-catalysts used in the anode and

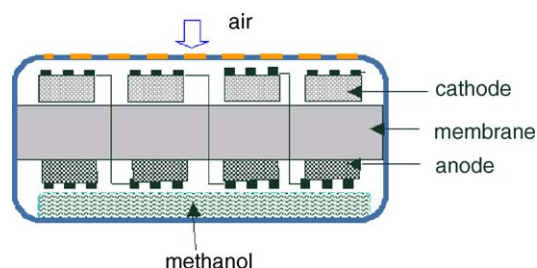


Fig. 2. A schematic diagram of monopolar passive air-breathing DMFC stack.

the cathode were Pt–Ru black (50:50 at.%) and Pt black (Johnson Matthey), respectively. The catalysts were then mixed with Nafion™ solution (Dupont Co.), water and isopropyl alcohol (IPA) to form a catalyst ink. The catalyst ink was applied on to carbon cloth gas diffusion medium, and the catalyst loadings in each electrode were  $8 \text{ mg cm}^{-2}$  based on the total metal weight. The electrodes were then hot-pressed on Nafion 115 membrane at 8 MPa and at  $130^\circ\text{C}$  for 150 s to make a membrane–electrode assembly. The MEA used in the stack was composed of six pairs of electrodes having an active area of  $4.5 \text{ cm}^2$  per electrode and thus total active area was  $27 \text{ cm}^2$  as shown in Fig. 1.

### 2.2. Monopolar stack fixture

All experiments were carried out using a passive monopolar DMFC stack which was designed and fabricated in our laboratory. The prepared MEAs were sandwiched between two plates to make a stack. The cathode side plate had many holes for air diffusion and the anode side plate had channels and large open space for delivering and storing methanol solution. Basically, the monopolar stack that is schematically depicted in Fig. 2 was operated under passive feed conditions unless mentioned otherwise. That is, the oxygen diffused into the cathode side from ambient air without any help of external devices, such as a pump or fan, and the methanol solution was stored in the reservoir attached to the anode side plate and the methanol also diffused into the anode driven by concentration gradient set between the reservoir and anode. The volume of the methanol reservoir was  $18 \text{ cm}^3$ . A porous metal mesh was used as a current collector. The  $I$ – $V$  curves were collected using an electric load (Daegil Co. EL-200P) to measure the stack performance.



Fig. 1. A monopolar membrane–electrode assembly consisting of six pairs of electrodes.

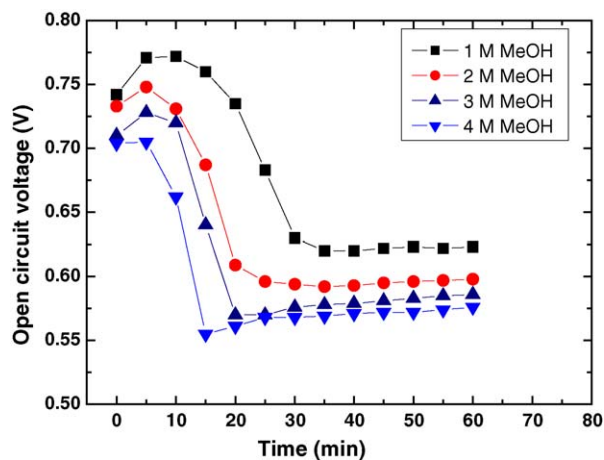


Fig. 3. Variations in open circuit voltage (OCV) with methanol concentration under passive feed conditions at room temperature in the monopolar stack.

### 3. Results and discussion

It is known that the open circuit voltage (OCV) of the DMFC is much lower than that of the polymer electrolyte fuel cell (PEFC) which uses hydrogen as a fuel. Also, the OCV pattern in the passive DMFC system is different from that found in the active DMFC system. In passive DMFC system, the OCV varies with time while in the active DMFC it maintains a fairly stable value [19]. Fig. 3 shows the changes in the OCV of the monopolar stack with time under passive feed conditions. The OCV undergoes significant variations with time. It decreases with an increase in the concentration of methanol indicating that it is inversely proportional to the methanol crossover rate. The methanol crossover is driven by physical diffusion of methanol due to concentration gradient as well as by electro-osmotic drag of protons [23]. The crossover of methanol not only results in a loss of fuel, but also lowers the cell performance due to the formation of mixed potential [19,24–27]. In addition, a reaction intermediate, such as carbon monoxide, adsorbs onto the catalyst surface to poison the catalyst and this further lowers the performance of the cathode [28,29]. The time dependence of the OCV is due to a change of the methanol concentration in the methanol reservoir of the anode compartment. As described in our previous study [19], when a methanol solution is injected into the reservoir of the passive DMFC fixture, the OCV experiences a change as time passes by. At first, the OCV increases to 0.9 V and then drops to around 0.75 V in 5 min and it further drops down to the lowest value due to the methanol crossover from the anode to cathode compartment through the polymer electrolyte membrane. As the methanol crossover proceeds, the methanol concentration in the anode reservoir decreases and the methanol crossover rate declines. Hence, the OCV rebounds and steadily rises again. In this experiment, the reservoir and the anode chamber were first filled with water and then the methanol solution was injected into the reservoir after removing the water. Therefore, the methanol diffused slowly into the anode and then crossed over to the cathode. Consequently, the change in methanol concentration in the cell was not that quick but rather slow. The time interval to collect the voltage data was relatively

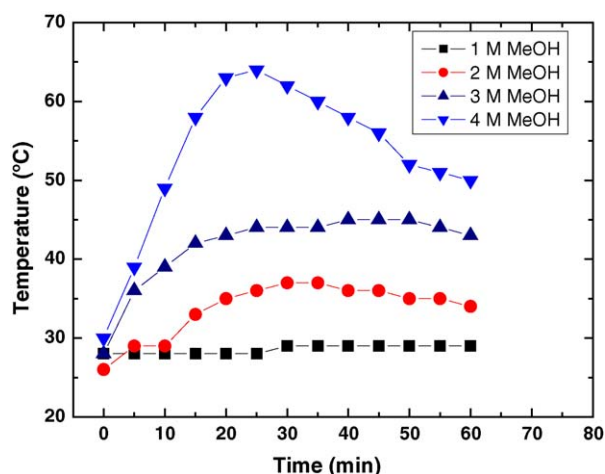


Fig. 4. Variation in stack temperature with methanol concentration under passive feed conditions at room temperature.

long as shown in Fig. 3, therefore, we could not get the same patterns of curves as with single cells, which showed a very sharp change in the voltage during the initial period of the operation [19]. However, the unique shape of the curves indicates the characteristic OCV pattern in the passive DMFC stack.

When a methanol feed is introduced into the anode compartment of the DMFC, the cell also experiences a change in the internal temperature. The pattern of temperature change in the passive DMFC is different from the active one. Fig. 4 shows the temperature change in the monopolar stack at an open circuit state with various methanol concentrations. In case of a 4 M methanol feed, for example, the temperature increases with time as the crossed-over methanol gets oxidized, releasing heat at the cathode. It marks a maximum in nearly 30 min and then it gradually falls off again. The time at which the highest temperature appears coincides with that of the lowest OCV point shown in Fig. 3. It decreases further indicating that the crossover rate decreases as the methanol concentration in the anode is declining.

The performance of a monopolar DMFC stack at various methanol concentrations under passive feed conditions is shown in Fig. 5. The performance increases with an increase in the methanol concentration and attains a maximum value of about 1000 mW ( $37 \text{ mW cm}^{-2}$  at 1.6 V) with a 4 M solution. The optimum concentration of methanol to obtain maximum performance is 4 M in the monopolar stack, and this is almost the same as that observed for a single cell tests in passive DMFCs [18]. The results obtained under passive feed conditions are quite different from those obtained under active feed conditions, where maximum performance usually appears at around 1.0 M [30,31]. This difference is mainly attributed to two reasons: (i) the mass transport rate of methanol from bulk solution to the anode catalyst layer, which depends on the methanol feeding method and (ii) the methanol crossover rate which is directly proportional to concentration of methanol. Under active feed conditions, the convective flow facilitates the mass transport of methanol. Therefore, a maximum performance is obtained at nearly 1.0 M methanol concentration, while the higher

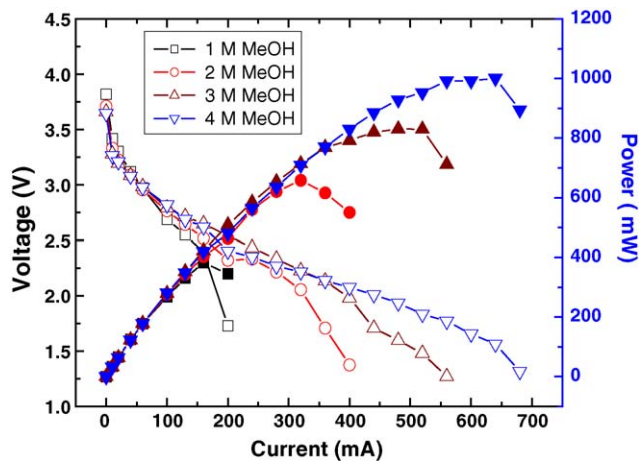


Fig. 5. Performance of a monopolar DMFC stack at various methanol concentrations under passive feed conditions.

concentrations increase the methanol crossover rate, leading to performance decay. By contrast, in the case of passive feed conditions, methanol is transported to the electrode only by a diffusion mechanism driven by the concentration gradient, and thus a higher methanol concentration than in the active system is required to supply sufficient methanol to the electrode. Thus, a maximum performance occurs at a higher concentration of methanol than in the active DMFC system.

Further, we have investigated the behavioral pattern of the passive DMFC stack under an electric load. The stack temperature varies under a load application as shown in Fig. 6. It increases with increasing methanol concentration, though the shapes of the curves vary depending on the concentration. In the case of 4 M methanol feed, for instance, a rapid rise in temperature is observed in the current range less than 50 mA, and this might be due to the heat released by the oxidation of crossed-over methanol in the cathode compartment as previously shown in Fig. 4. As the current increases further, the temperature falls in contrast to the trend observed in the active DMFC where the cell temperature increases with increasing electric load [22].

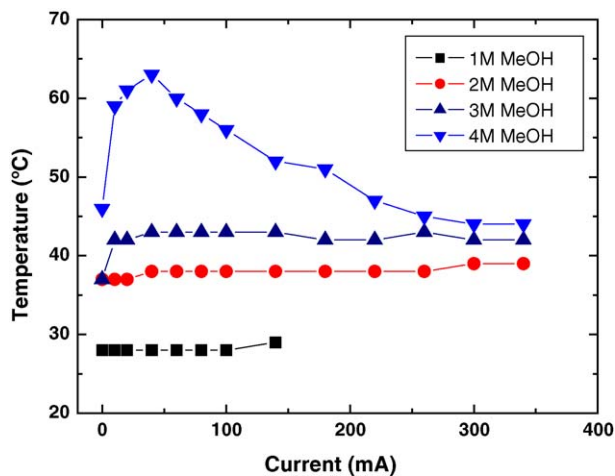


Fig. 6. Variations in system temperature with methanol concentrations under passive feed conditions at room temperature under the application of an electric load.

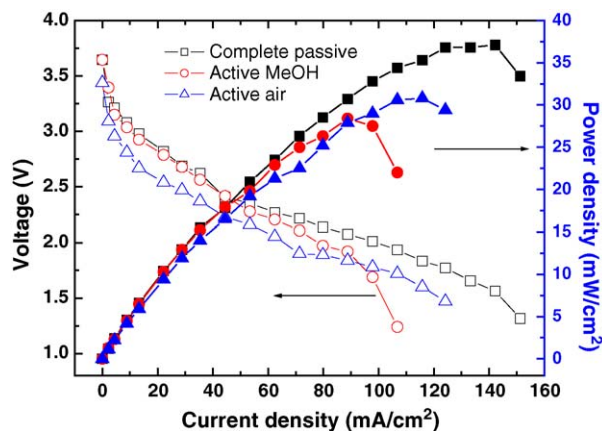
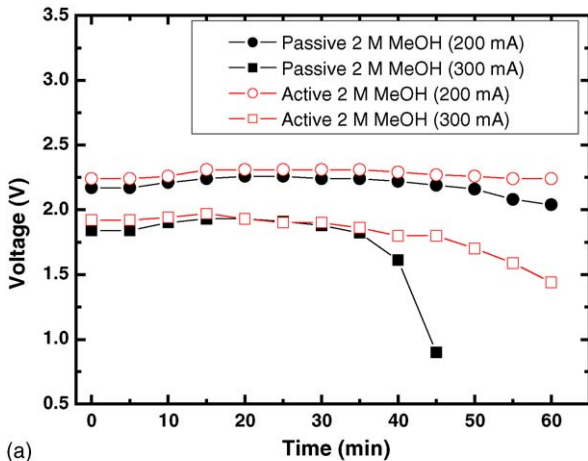


Fig. 7. Monopolar DMFC stack performance under various feed conditions with a 4 M methanol solution.

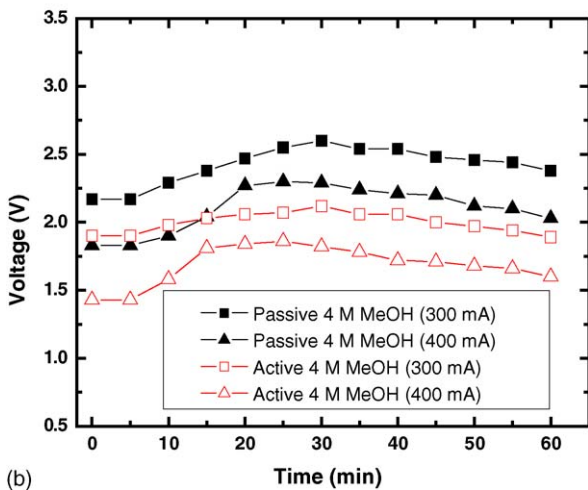
The decrease in stack temperature is attributed to the drop in the methanol concentration in the anode due to the consumption of methanol by the ongoing electrochemical reaction at the anode that reduces the methanol crossover rate [18,19]. One can infer from Fig. 6 that the heat contribution by oxidation of the crossed-over methanol is higher than that released by oxygen reduction at the cathode under the given conditions. By contrast, at low methanol concentrations the stack temperature is maintained almost at a constant value even with the application of an electric load, presumably because, though the heat contribution by methanol crossover is reduced, there is an increased heat release from the oxygen reduction reaction at the cathode.

Fig. 7 shows the performance of the monopolar DMFC stack under various operating conditions, by regulating the air and methanol flows to observe the effects of the feeding conditions. In this figure, “passive” means completely passive conditions, and “active methanol” means the feeding of a methanol solution using a pump at  $3 \text{ cm}^3 \text{ min}^{-1}$  while the air supply is in the passive state, and “active air” means the feeding of air using a small fan while the methanol is in a passive state. Among the various feeding conditions tested, the highest power was attained under completely passive conditions. Lower cell performances observed with the active methanol supply or active air feed conditions are speculated to be caused by an increased methanol crossover rate and a decrease in stack temperature that results as a consequence of heat dissipation by the flowing reactants.

As shown in Figs. 3 and 4, the stack temperature and cathode overpotential change with time due to the change in the methanol concentration in the anode reservoir. This observation implies that the performance of the passive stack is hard to be maintained with a steady value as the methanol concentration varies with time. In order to assess the performance of the passive stack with the passage of time, continuous operation of the stack was conducted under the application of a constant electric load. Fig. 8(a) compares the changes in voltage under the application of the electric load of 200 mA and 300 mA, with a 2 M methanol under passive or active methanol feed conditions while the air supply was in the passive state. At a load of 200 mA, the active methanol feeding condition gives a slightly higher voltage and the voltage remained constant without an appreciable change



(a)

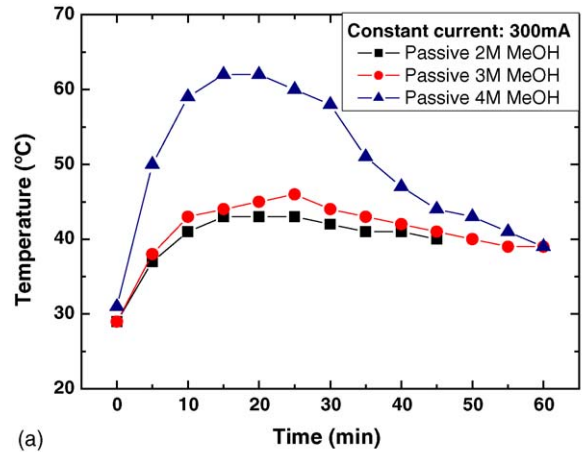


(b)

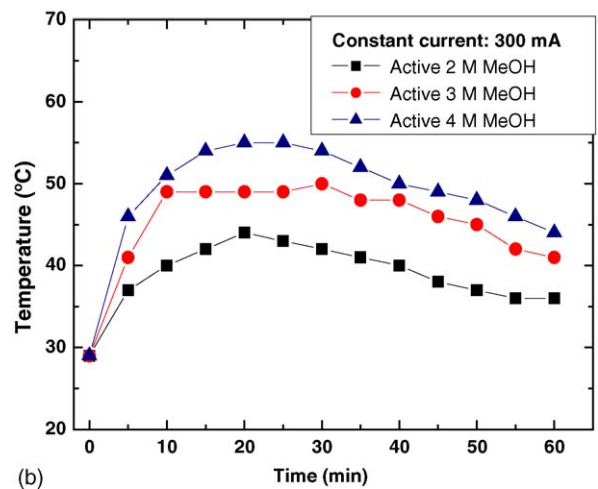
Fig. 8. Voltage profiles during continuous operation of the monopolar stack at constant loads under various feed conditions: (a) 2 M MeOH and (b) 4 M MeOH.

during the first 60 min of operation regardless of the methanol feeding method. But under the passive feed conditions with a load of 300 mA, the stack experiences a fall in performance during a period of 40 min presumably due to shortage of methanol in the reservoir while the change in voltage with active methanol feed is not significant. However, as shown in Fig. 8(b), when a 4 M methanol solution is used, there is no substantial change in the voltages during the first 60 min under the higher loads of 300 mA and 400 mA irrespective of the mode of methanol feed that was employed. These observations suggest that a higher methanol concentration is required to operate the stack for a long time without a power failure that might arise from methanol shortage. The problems of air supply and water flooding in the cathode may not be serious to the extent that may arise from shortage of methanol during continuous operation even under the passive air condition.

Fig. 9 shows the change of temperature in the stack during continuous operation at a load of 300 mA with various methanol concentrations. When the stack is operated in the passive feed conditions (Fig. 9(a)), the temperature of the stack varies and reaches peak values through different patterns. The magnitude of change in temperature and the maximum value attainable



(a)



(b)

Fig. 9. Variations in monopolar DMFC stack temperature with methanol concentration during continuous operation at a load of 300 mA under (a) passive and (b) active feed conditions.

increases with an increase in methanol concentration. With a 4 M methanol, the temperature climbs as high as 62 °C and it then declines rapidly to about 40 °C as the methanol is consumed from the reservoir for the reactions. Ultimately, the temperatures became almost the same irrespective of the initial concentration of the methanol feed. On the other hand, when the methanol is pumped continuously into the stack (Fig. 9(b)), the temperature rises swiftly during the first 20 min to mark a highest value which is directly proportional to the methanol concentration. But it then drops steadily to reach a stabilized value. The maximum stack temperature attained with the active methanol feed is lower than that with the passive feed for all the concentrations due to the heat removal by the flowing methanol solution.

Fig. 10 shows the voltage profiles over the stack under the application of varied electric load in 4 M methanol solution. Though the OCV of cell no. 6 has an abnormally higher value than all the other cells in the stack, the voltage profiles are relatively uniform in all the cells under various load conditions chosen for test in our study. The voltage profile in the stack is affected by several factors including the performances of individual MEAs, reactants distribution, temperature profile over the stack and accumulation of the products, such as CO<sub>2</sub> and water

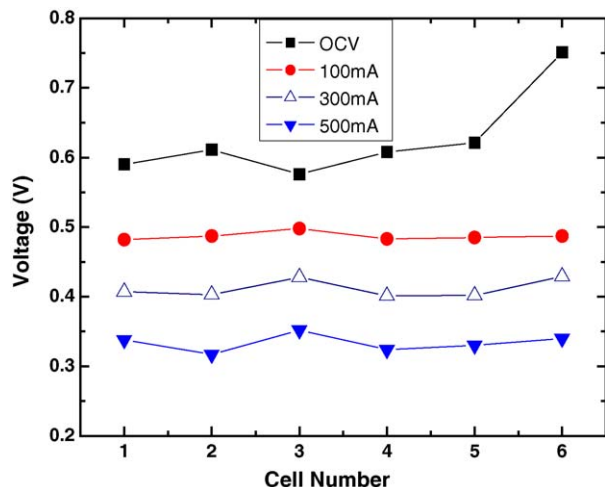


Fig. 10. Voltage distribution over the unit cells of the monopolar stack with passive MeOH/air at room temperature.

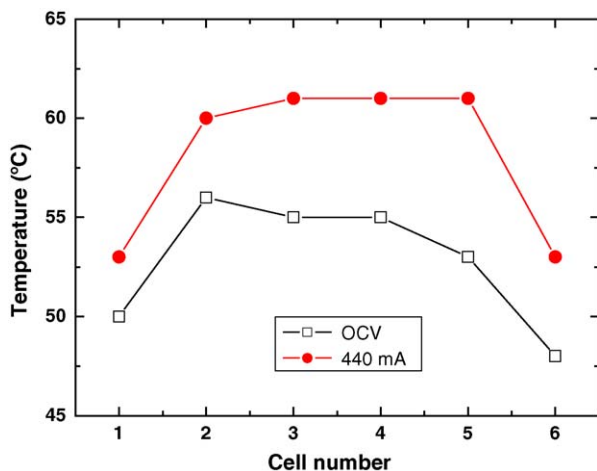


Fig. 11. Temperature profiles of the unit cells in the monopolar stack under passive MeOH/air feed conditions at room temperature.

in the electrodes. When a non-uniform voltage profile develops over the stack, it could lead to a rapid performance deterioration that might be caused by local corrosion [32]. And the stack performance as well as the durability could be determined by the worst cell. Therefore, it is a challenging task to make a stack with a uniform voltage profile.

The temperature profiles of the stack at various loads are shown in Fig. 11. They have a reversed U-shape, and are completely different from the voltage profiles in Fig. 10. The temperature of the cells No. 1 and 6 is much lower than those of the cells which are present in the inner regime of the stack. This is because the outer cells 1 and 6 are more vulnerable to heat loss than the cells placed in the inner regime (cells 2–5).

#### 4. Conclusions

A small direct methanol fuel cell for a portable power source is sought and hence, a passive air-breathing monopolar DMFC stack made up of six unit cells has been designed, fabricated and tested for its performance to understand its behavioral pattern at

various operating conditions, such as variation in methanol concentration, feeding methods and applied load conditions. The stack showed the highest performance in terms of power density at 4 M methanol concentrations under passive feed conditions. The improved performance of passive DMFCs with higher concentrations of methanol is partly attributed to the heat released from the exothermic reaction of crossed-over methanol and oxygen reduction at the cathode. The performance of the monopolar DMFC stack varied depending on the feeding conditions, but the forced air-blowing or methanol-pumping to the stack had rather negative effects of decreasing temperature and resulted in lower performance than that under passive feed conditions. Continuous operation of the passive stack was dependent on the concentration of methanol solution and was not affected appreciably by the air supply or by water accumulation in the cathode. From this study, we could see that a higher methanol concentration is essential to extend the operating time of the stack for portable power applications.

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