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On the consequences of methanol crossover in passive air-breathing direct methanol fuel cells

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Abstract

Passive direct methanol fuel cells (DMFC) are under development for use in portable power applications due to their enhanced energy density in comparison with active DMFCs. This study has been carried out to understand the unique properties of passive DMFCs, focusing on the internal temperature and the open circuit voltage (OCV), which change as a consequence of the methanol crossover phenomenon. The changes found in the passive DMFCs were very different from active ones because of different reactants supplying conditions. Methanol concentration in the built-in reservoir attached to the anode changed with time on stream and the OCV and the temperature changed correspondingly. Various experiments were conducted to show the unique properties of passive DMFCs at controlled conditions and configurations of the cell.
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1. Introduction

The advent of direct methanol fuel cell (DMFC) technology witnesses radical growth in meeting the demands of energy scenario for portable power applications. The DMFC has some advantages for these applications, including high energy density, operation at near ambient conditions, very low emissions, potentially renewable fuel source and fast and convenient refueling [1–3]. There are, however, many barriers that must be surmounted before DMFCs reach commercial viability. In order to mature this technology, its energy density should be increased by minimizing parasitic power losses to a pump and a fan that are needed to feed methanol and air into the cell, respectively. Towards this objective, the concept of passive-feed DMFCs has been proposed [4]. 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 [5]; the passive DMFCs operate without the help of external devices for pumping methanol and

blowing air into the cell and thus oxygen diffuses into the cathode from the ambient air by a kind of air-breathing action of the cell, and methanol diffuses into the anode from a built-in feed reservoir driven by concentration gradient between the anode and the reservoir. Because of the possibility of substantial reduction in the parasitic power loss and system volume, the passive direct methanol fuel cell is considered as a promising candidate for small-scale portable power applications.

Methanol diffusion or crossover from the anode to the cathode lowers fuel utilization, increases cathode polarization and causes excess thermal load in the cell and consequently lowers the cell performance [6–8]. The phenomena caused by methanol crossover in the active DMFCs are well summarized in the literature [9–18]. Though there are a few reports relating to passive DMFCs, the inherent properties of passive DMFCs have not been demonstrated in detail yet.

Our investigation here is primarily focused on understanding the transients in temperature and open circuit voltage (OCV) induced by methanol crossover in passive air-breathing direct methanol fuel cells. Experiments were

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conducted to show the unique properties of passive DMFCs at various conditions and configurations of the cell.

2. Experimental

The electrodes for passive DMFC were fabricated by coating a catalyst layer on a wet-proofed (20% Teflon) carbon cloth (E-Tek). The catalysts for anode (Pt-Ru black) and cathode (Pt black) were purchased from Johnson Matthey, Inc., and used 'as-received'. Nafion 115 (Du Pont) was used as the polymer electrolyte membrane. The electrodes (an anode and a cathode) were fabricated by applying catalyst slurry consisting of catalyst powder and Nafion solution on each sheet of carbon cloth, and they were placed on either side of a Nafion membrane, followed by hot-pressing at $80 \, kg \, cm^{-2}$ and at $130 \, °C$ for $150 \, s$ to make a membrane electrode assembly (MEA). The prepared membrane electrode assembly was fitted onto a small fixture to measure single cell performance under passive conditions. The schematic diagram of the passive air-breathing fuel cell is shown in Fig. 1. Active area of the electrode was $6 \, cm^2$. Single cells were operated at room temperature and ambient pressure under passive reactants supply. Temperature of the cell was measured by placing a thermocouple in the anode compartment because it was difficult to precisely measure the temperature of the cathode which was open to the atmosphere. The I–V characteristics were measured using an electronic load (Daegil Co., EL-200P) to evaluate the performances of the single cells.

3. Results and discussion

In a direct methanol fuel cell, methanol is crossing over from anode to cathode by concentration gradient and it leads to a decrease in open circuit voltage. At first, we observed the changes in OCV and cell temperature with time on stream in a passive DMFC cell, as shown in Fig. 2, starting just from the moment of injection of a methanol solution into the built-in reservoir attached to the anode side of the cell
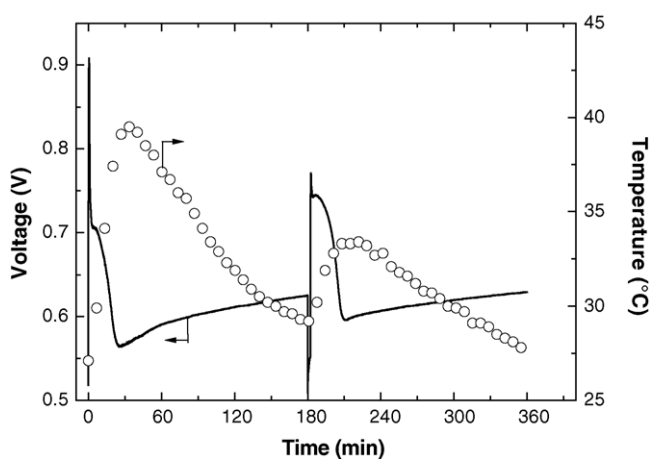

Fig. 2. Variations in voltage and temperature with a supply of MeOH at a state of open circuit: 4 M MeOH/air, room temperature.

while the cathode side was open to ambient air to take in oxygen through the holes present in the cathode plate at room temperature.

In view of the figure, when the methanol was injected in to the reservoir, the OCV experienced an abrupt jump from 0 to 0.9 V and then it dropped immediately to 0.72 V after 2 min duration and it decreased steadily down to 0.57 V over the next 25 min. After passing through the lowest voltage it increased again slowly up to 0.63 V after 3 h. But, the cell temperature went through a reverse track to that of the OCV and it rapidly increased from 25 to 40 °C during the first 30 min and then it decreased steadily. The changes found in OCV and temperature are directly related to the methanol crossover phenomenon from the anode to the cathode, which leads to a decrease in OCV by producing a mixed potential through an anodic oxidation of methanol at the cathode and an increase in temperature by combustion of methanol to release heat and water at the cathode compartment. The reversal of the OCV and the temperature at 30 min is estimated to be caused by reduced methanol crossover rate due to decreased methanol concentration in the anode methanol reservoir. As the methanol crossover rate decreases, the temperature declines and the OCV rises.
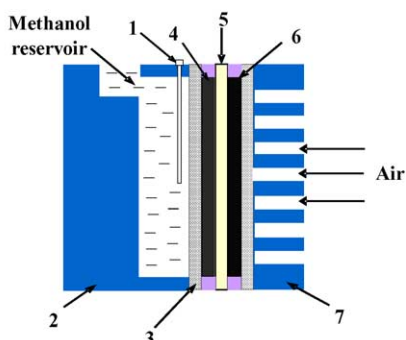
1. Thermocouple 2. Anode plate 3. Current collector 4. Anode 5. Membrane 6. Cathode 7. Cathode plate

Fig. 1. A schematic view of an air-breathing passive DMFC.
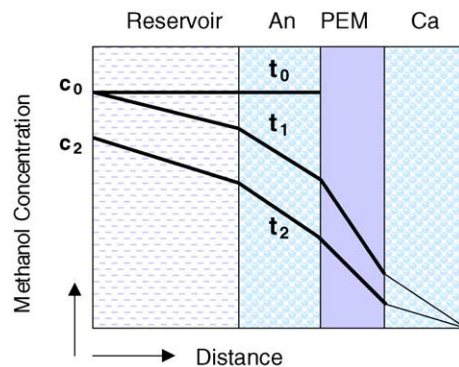

Fig. 3. Concentration gradient in a passive cell developed by consumption of methanol crossed-over from anode to cathode at an open circuit state.

In the second cycle of Fig. 2 that started by refueling a methanol solution at 180 min after evacuating the remaining methanol solution, the OCV and the temperature were recovered and then they started changing by showing similar patterns of the curves as the first ones. But at this time, the maximum values of the OCV and the temperature were much lower than those of the first cycle. This observation might be attributed to the accumulation of water in the cathode, which limited access of oxygen to the catalytic sites and led to a decrease in the methanol oxidation rate. The water came from the anode and was also produced by reduction of oxygen with protons and electrons at the cathode during the first cycle.

The change in methanol concentration in the anode compartment is a unique feature of the passive DMFC and it could be visualized as shown in Fig. 3. At time zero, t_0, the methanol concentration may be assumed to be at a point of C_0 in the anode compartment, though it is somewhat different from the real situation. When the methanol starts to diffuse into the cathode and is consumed there, the cathode potential decreases and the temperature increases even at open circuit state. The oxygen is supplied from the ambient air through the holes in the cathode plate as shown in Fig. 1. At time t_1, as the combustion reaction of methanol proceeds on the cathode and methanol is consumed, the methanol concentration in the reservoir decreases and a concentration gradient sets in across

the membrane, reducing the methanol crossover rate. At time t_2, a further decrease in methanol concentration at the reservoir results in a significant reduction in methanol crossover rate, consequently leading to the reversal of changes in OCV and temperature as can be seen in Fig. 2.

The increase in cell temperature at open circuit state is due to oxidation of methanol on the cathode as mentioned previously. At the cathode the methanol is oxidized in the presence of oxygen to produce carbon dioxide and water along with heat by a combustion reaction as described in the following equation. This reaction is not electrochemical, but purely chemical, and thus it produces only heat, not electricity:

$$CH_3OH + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2H_2O,$$
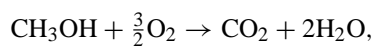
$$\Delta H_f = -725.51 \, \text{kJ mol}^{-1}$$

In order to verify the oxidation reaction of methanol at the cathode, complementary experiments have been conducted. As shown in Fig. 4, two electrodes with platinum catalyst layer were placed separately in two beakers containing a methanol solution: one of them was completely immersed and the other was half immersed in the methanol solution. Fig. 4c shows the temperature changes that were observed
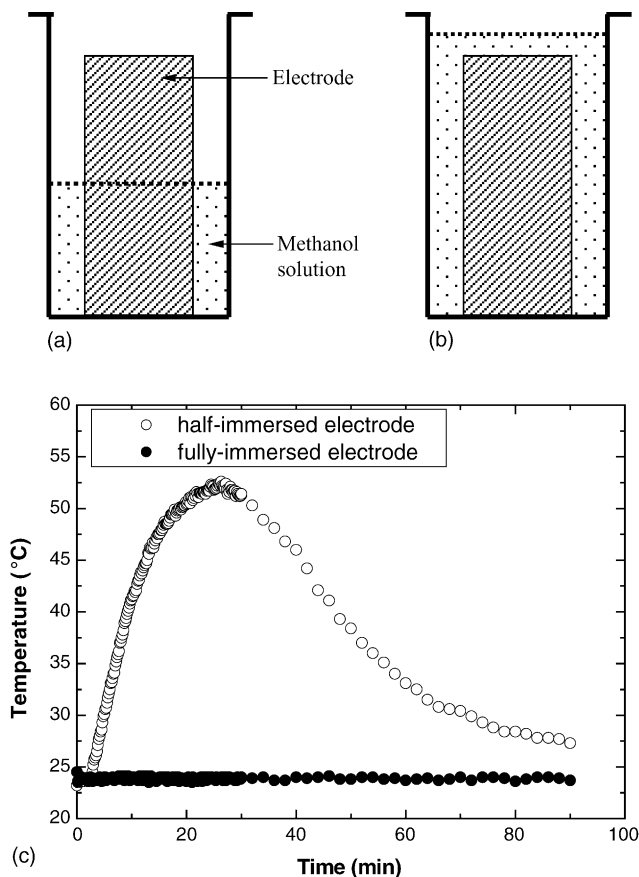

Fig. 4. (a) An electrode half-immersed in a methanol solution; (b) an electrode fully-immersed in a methanol solution; (c) temperature change of methanol solution in the presence of Pt catalyst (5 M MeOH/air, R.T.).

in these two beakers. The fully immersed electrode showed no change in temperature and, on the other hand, the half-immersed electrode experienced a significant increase in temperature that showed a convex curve. This observation indicates that in case of the half-immersed electrode methanol diffused upward into the area that was in contact with air and got oxidized to release heat in the presence of platinum catalyst while in the case of fully-immersed electrode the electrode could not get into contact with oxygen coming from the ambient air to effect a methanol oxidation reaction on the electrode.

A second complimentary experiment was carried out to confirm the combustion of crossed-over methanol at the cathode. Fig. 5 shows the changes in temperature of the two cells, the one (open symbol) equipped with a complete membrane electrode assembly and the other (closed symbol) with an MEA in the absence of platinum catalyst in the cathode side. When a methanol solution was injected into the anode side reservoir while the cathode side was kept open to the atmosphere, the two cells behaved very differently in terms of temperature. The cell with a complete MEA showed a large increase in temperature following a similar track as in Figs. 2 and 4 while the temperature of the cell without cathode catalyst remained unchanged. This experiment showed that the crossed-over methanol could be oxidized on the cathode only in the presence of platinum catalyst.

Further, the effect of oxygen on the methanol oxidation in the passive cell was studied by blocking the cathode side to prevent oxygen supply from the environment. As shown in Fig. 6, the OCV and cell temperature were found to be very low during the first 100 min when the cathode side was closed with a cover. Subsequently, after the cover was removed to allow oxygen to diffuse into the cathode, the OCV and temperature rose steeply and the curves follow the similar track as found in Fig. 2. This observation indicates that methanol oxidation at the cathode proceeds only in the presence of oxygen.
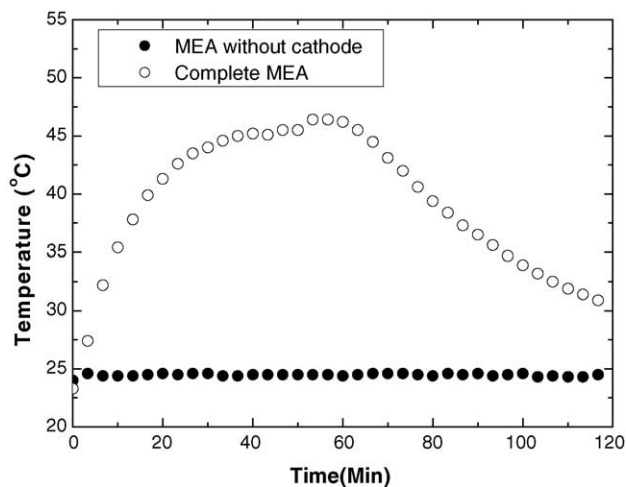
From the inferences of experimental results shown in Figs. 2–6, it could be confirmed that the crossed-over methanol is oxidized to produce heat and undergoes anodic oxidation to generate a mixed potential at the cathode, consequently leading to an increase in cell temperature and a decline of cathode potential only in the presence of oxygen and platinum catalyst.

Since methanol crossover rate is dependent on the methanol concentration in the reservoir, it is expected that OCV and temperature vary with methanol concentration [19,20]. Experiments were carried out with various concentrations of methanol in the reservoir from 1.0 to 5.0 M. As shown in Fig. 7a and b, it was observed that the OCV has decreased and the temperature has increased with increasing methanol concentration. They all have the same shape of curves though the extent of change varies depending on methanol concentration.

Fig. 8 shows the change in voltage and temperature in the complete DMFC while the cell was at an open circuit state during the first 20 min followed by the application of an electric load of $5 \, mA \, cm^{-2}$ to effect a fuel cell reaction. At a state of open circuit during the first 20 min, the cell temperature rose and the OCV declined. Subsequently, when an electric load was applied to the cell, there occurred abrupt changes in temperature and voltage. The sharp decrease in temperature might be attributed to two reasons: (1) heat loss by endothermic oxidation of methanol in the anode; (2) reduction of heat production rate due to instantaneous depletion of methanol and oxygen in the cathode. The abrupt decrease in the cell voltage might be caused by an activation overpotential as well as instantaneous depletion of the reactants (methanol and oxygen) at the catalytic sites of the anode and cathode. But the temperature and cell voltage were recovered gradually as time passed by. And at the time of 60 min, the temperature started to drop again because the heat production rate was not enough to maintain the cell temperature due to reduced methanol crossover rate, but the voltage increased steadily higher than the OCV value

Fig. 5. Changes in temperature with time on stream for the cells with a complete and a cathode-absent MEA, respectively (4 M MeOH/air, R.T.).
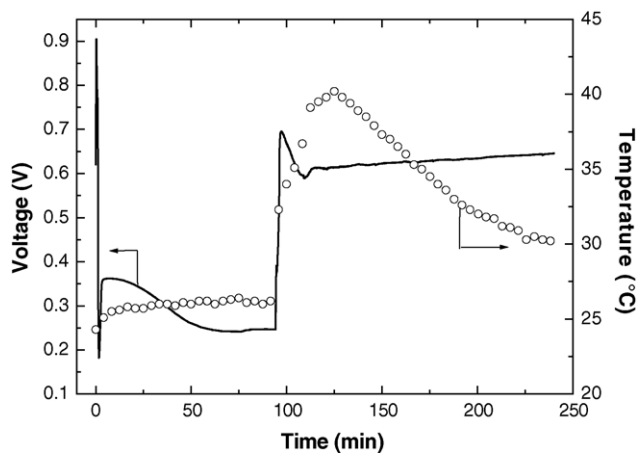

Fig. 6. Changes in voltage and temperature by varying oxygen supply into the cathode (4 M MeOH/air, R.T.).
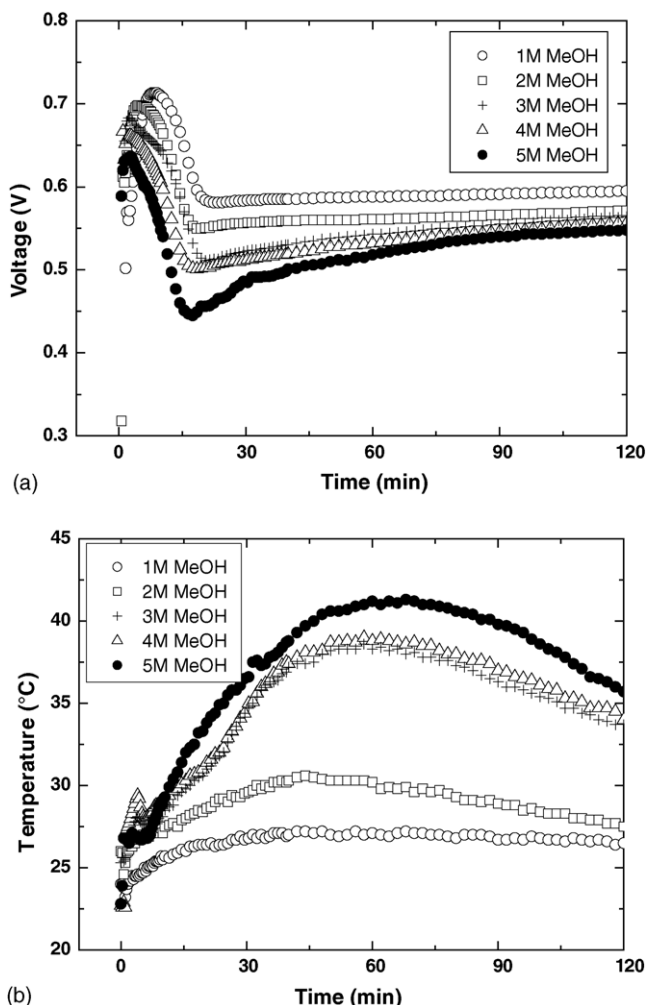
Fig. 7. Variations in (a) OCV and (b) temperature with different concentrations of methanol.
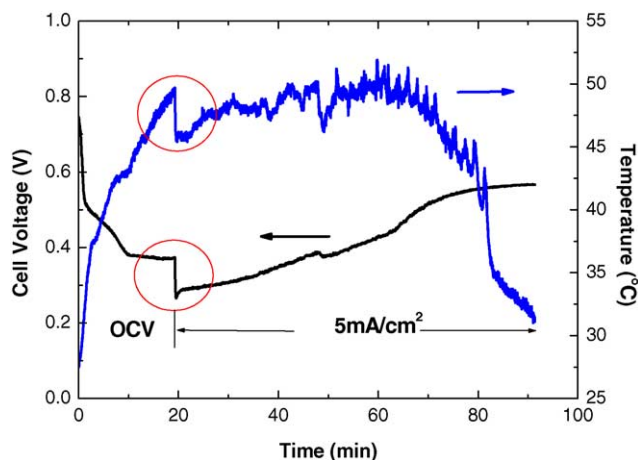
at the time of 20 min because of lowered overpotential at the cathode.

4. Conclusions

In this study, the unique properties of the passive air-breathing DMFC have been investigated by conducting various experiments. In a passive cell with a built-in methanol reservoir, the temperature and the electric potential varied with time even at open circuit state and the changes were dependent on the methanol concentration in the reservoir. It has been confirmed through various experiments that the unique properties of the passive DMFC were caused by the methanol crossover phenomenon and these variations were subjected to changes in methanol concentration in the built-in reservoir with respect to time. That is, since the passive DMFC is operated at a transient state due to the change in anode methanol concentration with time, the behaviors of the cell in terms of temperature and electric potential are much different from the active one that is operated at a steady state.

As the passive DMFC is being researched intensively for its application in portable power sources, this kind of preliminary study could help one understand the unique characteristics of passive DMFC and be a starting point to develop advanced and energy-efficient portable DMFC systems.

Acknowledgements

Fig. 8. Variations in voltage and temperature caused by changing the electric load from 0 to 5 mA cm^{-2} (5 M MeOH/air, R.T.).

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