Effect of methanol concentration on passive DMFC performance

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A passive, air-breathing, liquid-feed direct methanol fuel cell (DMFC), with no external pumps or other auxiliary devices, was designed, fabricated and tested with different methanol concentrations. It was found that the cell performance was substantially improved with an increase in methanol concentration; a maximum power density of 20 mW/cm² was achieved with 5.0 M methanol solution. The measurements indicated that the better performance with higher methanol concentrations was mainly attributed to the increase in the cell operating temperature caused by the exothermic reaction between permeated methanol and oxygen on the cathode. This finding was subsequently confirmed by the fact that the cell performance was degraded when the cell running with higher methanol concentrations was cooled to room temperature.

The direct methanol fuel cell (DMFC) has attracted extensive interest from scientists and engineers worldwide because its system is simple (without reformers and humidifiers), and the theoretical energy density of methanol (6100 W h/kg at 25°C) is much higher than that of gaseous fuels.[1–6] Recently, the so-called ‘passive’ DMFC, in which external pumps or other ancillary devices for fuel and oxidant supply are removed, has been proposed and investigated.[7–14]

Since passive DMFCs have much simpler structures than conventionally active DMFCs (with fuel pumps and oxidant suppliers), and the parasitic power loss from ancillary devices is eliminated, they have been considered as more promising power sources for future advanced electronic devices. Many prototypes such as toy cars,[7] cell phones,[8, 9, 11] and other portable devices powered by passive DMFCs have been demonstrated. Some giant electronics companies – including Motorola, Toshiba, Samsung, NEC etc. – have also undertaken the research and development of passive DMFCs.

US-based MTI MicroFuel Cells, as a leading company in the commercialization of DMFCs, demonstrated several prototypes of passive DMFCs in 2001–2003, and claimed that it would enter the mass market with its own Mobion™ technology for cell phones in 2004 or 2005.[15] [In fact MTI Micro made its first production shipment of Mobion™ technology in December 2004; see Main News (page 2) in this issue.]

Presently, one of the most challenging problems for both active and passive DMFCs that employ Nafion® membranes is methanol crossover from the anode to the cathode, which causes a mixed potential on the cathode and thus reduces the overall cell voltage. For this reason, one of the most important parameters that affects the performance of DMFCs is the methanol concentration, which has been widely studied. In an active DMFC with a methanol pump and an oxygen/air compressor/blower, the maximum power density can usually be achieved with 1.0–2.0 M methanol.[16, 17]
In contrast, in a passive DMFC with a built-in methanol solution reservoir, since the access of methanol to reactive sites relies on diffusion only, the optimal concentration of the methanol solution might be different from that in active counterparts. Some researchers[10, 11] have reported that the optimal methanol solution appeared at 4.0 M in passive DMFCs. It was thought that better performance with a higher methanol concentration was because of the improved mass transfer of methanol from the reservoir to the anode catalyst layer.

Similar opinions about the effect of methanol concentration on the performance of passive DMFCs can also be found in the literature.[12–14] However, an important aspect of a passive DMFC, which has not been mentioned in previous studies, is that the operating temperature of a passive DMFC is inherently linked to the methanol concentration. A higher methanol concentration leads to a higher methanol permeation rate from the anode to the cathode, and almost all the permeated methanol reacts with oxygen on the cathode. This exothermic reaction will cause a higher cell operating temperature.

Therefore, when a passive DMFC is operated under a given ambient environment, a higher methanol solution will lead to a higher operating temperature, which in turn causes faster electrokinetics of both the methanol oxidation and the oxygen reduction reactions, and thereby a higher cell performance. This point has not been addressed in previous papers related to the study of passive DMFCs.

The objective of this paper is to study the effect of methanol concentration on the performance of a passive DMFC. We measured the operating temperature of the DMFC that was tested with different methanol concentrations. We found that a higher methanol concentration caused a higher operating temperature, and thus a better cell performance. This point was further demonstrated by the fact that the cell performance was degraded when the cell running with higher methanol concentrations was cooled to room temperature. The effect of methanol concentration on the cell efficiency was also investigated, and the results revealed that the Faradic efficiency and energy efficiency decrease with increasing methanol concentration.

**Experimental**

Membrane-electrode assembly

A membrane-electrode assembly (MEA) with an active area of 4.0 cm² was fabricated in-house employing single-side ELAT electrodes from ETEK and a pretreated Nafion® 115 membrane. This pretreatment involved boiling the membrane for 1 h in 5 vol% H₂O₂ and for 1 h in 0.5 M H₂SO₄ before washing in boiling deionized water. Both anode and cathode electrodes used carbon cloth (E-TEK, Type A) as the backing support layer with 30 wt% PTFE wet-proofing treatment. The catalyst loading on the anode side was 4.0 mg/cm² with PtRu black (1:1 a/o), while the catalyst loading on the cathode side was 2.0 mg/cm² using 40 wt% Pt on Vulcan XC-72. Furthermore, 0.8 mg/cm² dry Nafion® ionomer was applied onto the surface of each electrode. Finally, the MEA was formed by hot pressing at 135°C and 5.0 MPa for 3.0 min. More detailed MEA fabrication procedures can be found elsewhere.[18]

Single cell fixture

As shown in Figure 1a, the MEA described above was sandwiched between two electrical

<table>
<thead>
<tr>
<th>Methanol concentration, M</th>
<th>Open-circuit voltage, V</th>
<th>Current density at 0.4 V, mA/cm²</th>
<th>Current density at 0.2 V, mA/cm²</th>
<th>Max. power density, mW/cm²</th>
<th>Maximum temperature, °C</th>
<th>Internal resistance, Ω cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.576</td>
<td>12.1</td>
<td>57.8</td>
<td>10.7</td>
<td>23.5</td>
<td>0.58</td>
</tr>
<tr>
<td>2.0</td>
<td>0.553</td>
<td>11.1</td>
<td>75.4</td>
<td>15</td>
<td>25.4</td>
<td>0.56</td>
</tr>
<tr>
<td>3.0</td>
<td>0.532</td>
<td>8.7</td>
<td>84</td>
<td>17</td>
<td>28.5</td>
<td>0.55</td>
</tr>
<tr>
<td>4.0</td>
<td>0.513</td>
<td>7.8</td>
<td>97.6</td>
<td>19.7</td>
<td>32</td>
<td>0.53</td>
</tr>
<tr>
<td>5.0</td>
<td>0.495</td>
<td>5.1</td>
<td>97</td>
<td>20</td>
<td>36.5</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Table 1. Performance of the passive DMFC using different methanol concentrations.
current collectors, which were made of 316 stainless-steel plates of 1.0 mm in thickness. Multiple 3.0 mm diameter holes were drilled in both current collectors, to serve as the passages for fuel and oxidant, which resulted in an open ratio of 44.2%. A 200 nm thick platinum layer was sputtered onto the surface of the current collectors to reduce the contact resistance with the electrodes.

The cell was held together between an anode and a cathode fixture, both of which were made of transparent acrylic plates. A 3.0 ml methanol solution reservoir was built in the anode fixture. Methanol was diffused into the catalyst layer through the opening of the surrounding air – was diffused into the cathode catalyst layer through the opening of the cathode fixture.

To control the cell operating temperature, a water tank was attached to the anode side of the cell, as shown in Figure 1b. The water tank and the methanol solution reservoir were separated by a 0.1 mm thick stainless-steel plate. The cell operating temperature was varied and maintained by circulating warm or cold water, the temperature of which was controlled outside the cell by a bath circulator (Polyscience 9105). The cell temperature was measured by a miniature (0.0005 inch/13 µm thick) thermocouple (Omega CO-1T), installed between the anode current collector and the MEA.

**Results and discussion**

Figure 2 shows the performance of the passive DMFC operated with various methanol concentrations from 1.0 to 5.0 M. It is seen that both the limiting current density and the peak power density exhibit a tremendous increase when the methanol concentration was increased from 1.0 to 2.0 M. In the cases when the methanol concentration was increased from 2.0 to 5.0 M, although the cell performance kept improving, the increments became progressively smaller toward the highest methanol concentration. A maximum power density of 20 mW/cm² was obtained with 5.0 M methanol solution.

More detailed performance parameters measured with different methanol concentrations are listed in Table 1. It is found from Table 1 that the current density at 0.2 V (column 4) and the maximum power density (column 5) increase with increasing methanol concentration. However, both the OCV and the current density at 0.4 V decrease with increasing methanol concentration. Apparently, the lower performance at low current densities can be attributed to the fact that methanol crossover from the anode to the cathode increases with increasing methanol concentration.

At higher current densities, however, the mechanism leading to better performance of the passive DMFC with a higher methanol concentration is more complicated. Performance behavior similar to that shown in Figure 3 and Table 1 has also been reported in numerous previous papers studying the effect of methanol concentrations on the performance of passive DMFCs. The higher performance at higher current densities was traditionally attributed to the improved mass transfer with higher methanol concentration.

The operating temperature variation of passive DMFCs with methanol concentration, however, has never been reported in the literature. In the present study, a tiny thermocouple was installed between the anode current collector and the electrode to monitor the cell operating temperature. Figure 3 shows the cell operating temperature variation with time after the methanol solution with different concentrations was injected into the reservoir. Note that the temperatures shown in Figure 3 and Table 1 (second column from right) were measured under open-circuit conditions; we found that under discharging conditions, the cell operating temperature was 1–3 °C higher than under open-circuit conditions, depending on current densities.

It is interesting to note from Figure 3 that the cell fed with lower methanol concentrations (1.0 and 2.0 M) was operated at close to room temperature (22–23°C). With 4.0 and 5.0 M methanol concentrations, however, the cell operating temperature rose to 32.0 and 36.5°C, respectively, implying that the cell was operating...
at an elevated temperature. A higher temperature leads to improved electrochemical kinetics in the methanol oxidation and oxygen reduction reactions. Moreover, the internal resistance of the cell listed in Table 1 (rightmost column) decreased as a result of the temperature increase with higher methanol concentrations, which can also benefit the performance of passive DMFCs.

Therefore, higher cell temperature is the major factor that leads to higher performance of the passive DMFC when operated with higher methanol concentrations. This finding has not previously been addressed clearly in the literature. A higher methanol concentration leads to a higher rate of methanol crossover from the anode to the cathode. The exothermic reaction between the permeated methanol and oxygen on the cathode generates more heat with higher methanol concentration, leading to a higher operating temperature.

The above discussion indicates that the better performance of passive DMFCs with a higher methanol concentration is caused by a higher operating temperature resulting from the exothermic reaction between the permeated ethanol and oxygen on the cathode. We now show how the performance changes when the heat generated in the cell is removed by the cooling water as shown in Figure 1, which can maintain a desired cell operating temperature. As such, the effect of temperature variations can be minimized when the cell is tested with different methanol concentrations.

We tested the cell with 2.0 and 4.0 M methanol solutions for the cases without and with cooling. The results are shown in Figure 4. It is seen that in the case without cooling, the maximum power density of the cell with 4.0 M methanol was nearly 20 mW/cm², which was about 5 mW/cm² higher than that with 2.0 M methanol. However, the power density with 4.0 M methanol was reduced to only 11.5 mW/cm² when the cell was cooled to 22.5°C. The performance degradation in the case with 2.0 M methanol solution is also observed from Figure 4 when the cell is cooled. This suggests that better performance with a higher methanol concentration is primarily as a result of the increase in operating temperature resulting from a higher methanol permeation rate.

The importance of the temperature effect on the cell performance can be further demonstrated by the following test. As we described above, the maximum operating temperature of the cell with 5.0 M methanol without cooling was 36.5°C. We tested the performance of the cell with 3.0 M methanol by heating the cell using hot water to an operating temperature of 36.5°C, which is the same as the case with 5.0 M methanol but without cooling. The results are compared in Figure 5, which shows that at the same temperature the 5.0 M methanol operation did not lead to better performance than the 3.0 M methanol operation. Clearly, the improved performance with a higher methanol concentration was mainly as a result of the temperature increase.

Figure 6 shows the transient discharge current at a constant voltage (0.35 V) with a start from the cell to be fueled with 3.0 ml methanol solution at different concentrations. It is seen that the discharge current for all methanol concentrations increases rapidly in the early stage, reaches a peak, and decreases gradually toward zero as the methanol concentration in the reservoir decreases. The peak current value increases with methanol concentration; a maximum current of 0.11 A was obtained with 5.0 M methanol solution.

The operating temperature of the passive DMFC corresponding to the operating condition presented in Figure 6 is shown in Figure 7. It is interesting to note that the transient cell operating temperature varies with a trend similar to the transient discharge current shown in Figure 6. This behavior indicates that the current differences among different methanol concentrations can be attributed to the temperature variation caused by methanol crossover. A higher concentration methanol solution in the reservoir increases the rate of methanol crossover, thereby generating more heat by the exothermic reaction of methanol oxidation on the cathode, and causing a higher cell temperature and higher cell performance.

It is also found from Figure 7 that the cell operating temperature decreases rapidly after the peak point. This might be attributed to evaporation of water generated by diffusion from the anode, oxidation of methanol in the cathode and electrochemical reaction.

To investigate the effect of methanol concentration on the fuel utilization, we define the Faradic efficiency $\eta$ as:

$$\eta = \frac{\text{Discharging capacity (A h)}}{\text{Theoretical discharging capacity (A h)}} = \frac{\int_0^t i(t)dt}{6C_MV_MF}$$

where $i(t)$ is the time of the discharging process, $i(t)$ represents the transient discharge current, $C_M$ is the methanol concentration, $V_M$ is the methanol solution volume, and $F$ is the Faraday constant. The Faradic efficiency
defined in Equation 1 indicates the ratio of the actual discharging capacity to the theoretical discharging capacity.

In addition, the efficiency of a passive DMFC can also be assessed on the basis of energy (Wh) by taking both the voltage and current into account. It follows that the energy efficiency $\xi$ can be defined as:

$$\xi = \frac{\text{Discharging energy (Wh)}}{\text{Theoretical discharging energy (Wh)}} = \frac{\int \Phi_i(t)\,dt}{\phi_M V S FE}$$

(2)

where $V$ is the working voltage of a passive DMFC; the theoretical voltage $E = 1.18$ V at 25°C.

The Faradic efficiency and energy efficiency determined by Equations 1 and 2 with different methanol concentrations are shown in Figure 8.

It is seen that the Faradic efficiency decreases from 52.0% to 22.8% when the methanol concentration increases from 1.0 to 5.0 M. The lower Faradic efficiency was primarily caused by the higher rate of methanol crossover with higher methanol concentrations. It is also noted that the energy efficiency is much lower than the Faradic efficiency, because of the deviation of working voltage from the theoretical voltage. The energy efficiency was only about 10% when 2.0 M or higher methanol concentration was used.

However, it should be pointed out that, despite such a low energy efficiency, the actual specific energy (Wh) of methanol is 610 Wh/kg (calculated based on the theoretical specific energy of about 6100 Wh/kg with an energy efficiency of 10%), which is still comparable to the theoretical specific energy of lithium-ion batteries (410 Wh/kg).[19] In this context, passive DMFCs illustrate their advantage in the application of portable power sources.

The above experimental results indicate that a higher methanol concentration can improve the performance of passive DMFCs at high current densities because of the increased cell operating temperature. It should be pointed out, however, that the cell operated at high methanol concentration would also suffer from lower fuel utilization because of serious methanol crossover. Therefore, the trade-off between cell performance and fuel utilization needs to be considered in practical applications. It should also be emphasized that a more feasible method to elevate the cell operating temperature of a passive DMFC is to reduce the heat loss to the surrounding air. This can be achieved by selecting low thermal conductivity materials and through innovative design of passive DMFC stacks.

Concluding remarks

A passive feed, air-breathing DMFC was fabricated and tested with different methanol concentrations. The experimental results indicate that the power density of the cell increases with methanol concentration, and a maximum power density of 20 mW/cm² was achieved with 5.0 M methanol. The experiments also reveal that the operating temperature increases with increasing methanol concentration. Therefore, the improved performance of passive DMFCs running with higher concentrations can be attributed primarily to the higher temperature caused by the exothermic reaction between the permeated methanol and oxygen on the cathode.

The results presented in this work suggest that better performance of a passive DMFC can be achieved when the cell is operating at an elevated temperature. Therefore, thermal management in passive DMFCs is critical for improving the performance of this type of fuel cell.

Moreover, the experimental results also indicate that the methanol utilization and energy efficiency of the passive DMFC decrease with increasing methanol concentrations. More than 50% methanol in the reservoir was wasted by methanol crossover, and the energy efficiency was lower than 15% when 2.0 M or higher methanol was used in the passive DMFC. This result indicates that the passive DMFC can work only for a limited time with one charge of fuel. In this context, the concept of the passive DMFC is just like a conventional battery, which can discharge for a limited time with one charge.

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**Pt-Co/C electrocatalysts by reduction with borohydride in acid and alkaline media, and effect on catalyst performance**


**Thermodynamic analysis of hydrogen production from ethanol using CaO as CO2 sorbent**


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