Direct methanol fuel cells (DMFCs) have been envisaged as potential power sources for electric vehicles and portable applications because of their high energy density and simpler operating system. However, issues such as poor methanol electro-oxidation kinetics and methanol crossover through the polymer electrolyte membranes (PEMs) from anode to cathode remain as obstacles to deploy DMFCs for their practical applications. It has been found that using the Nafion type membranes nearly 30-40% of methanol undergoes crossover, which causes not only a depolarization effect on the cathode, but also a decrease in the utilization efficiency of fuel. Under open-circuit conditions, the methanol crossover is mainly caused by diffusion as a result of the concentration difference between anode and cathode.

When used as portable power sources, DMFCs are preferred running under air breathing mode without the help of oxygen pumping and air blowing devices to achieve compact and simplified system design and low parasitic power cost. In this case, oxygen shortage and severe flooding problems are usually encountered on the cathode, which reduce not only the open-circuit voltage (OCV) but also cell performance at high current densities. Qi et al. reported that the OCV of a DMFC declined as the airflow rate decreased in the temperature range of 60 to 80°C.

During the process of testing DMFCs, we have repeatedly observed gas evolution in the anode flow field when the cell was maintained under open-circuit conditions and at low oxygen flow rates. This finding is something contrary to conventional wisdom that no gas evolution normally occurs on the anode because electrochemical reaction ceases under open-circuit conditions. We found that the onset of this gas evolution was accompanied by a decline in OCV. In this paper, we report on experimental evidence for this peculiar phenomenon and discuss the underlying mechanism leading to the phenomenon.

**Results and Discussion**

Similar to previous studies, we also found CO₂ gas bubbles in the anode flow field of the cell, when it was operated at high current densities. Surprisingly, however, we still observed gas bubbles in the anode flow field, when external load was removed and the oxygen flow rate (OFR) decreased to certain value. Figure 1 displays the gas bubbles evolved in the anode side channels under the open circuit condition, when the cell was operating at low OFRs (15, 12, 11, and 10 sccm). When OFR decreased to and maintained at 15 sccm, small bubbles started to appear near the channel downstream (see Fig. 1a). With decreasing OFR to 12 sccm, it can be seen from Fig. 1b that more gas bubbles appeared and they covered about one forth area of theMEA. At OFR of 11 sccm, the gas evolving area increased and covered about one third of the MEA, as shown in Fig. 1c. With further decreasing OFR to 10 sccm, almost two third of the MEA area was covered by the gas bubbles (see Fig. 1d). When OFR was maintained to below 10 sccm, we noted that the gas bubble generating rate decreased but the gas bubble generating area became larger.

The above mentioned gas bubble evolving process was accompanied by a decline in OCV of the cell. Figure 2 shows the variation in OCV, running with 2-M methanol concentration at 60°C, with time when OFR decreased. Initially, when OFR was maintained in the range of 50 to 20 sccm, the cell exhibited a typical and stable DMFC OCV of around 0.63 V. When decreasing OFR to 15 sccm, fluctuation in OCV (ranging from 0.63 to 0.53 V) was observed. With further decreasing OFR to 12, 11, and 10 sccm. OCV became stable and decreased to 0.48, 0.45, and 0.43 V, respectively. Note that each image shown in Fig. 1 was taken under a steady state, in which the OCV remained constant.

Because the gas bubbles on the anode were produced while lowering OFR, the gas evolution has something to do with the concentration distribution of O₂ on the cathode. Due to reaction with cross-over methanol, a decrease in OFR causes a decrease in the average concentration of O₂ over the entire channel. Because the cathodic reaction causes a decrease in O₂ concentration along the flow chan-

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nel toward the exit, a shortage of O$_2$ is likely to occur in the channel downstream region at lower OFRs. In addition to acting as oxidant on the cathode, oxygen flow stream sweeps the liquid water, resulted from the cathodic reaction and permeated from the anode, away to the channel exit, implying that water concentration becomes higher but O$_2$ concentration gets lower in the channel downstream. Moreover, water vapor and CO$_2$, resulting from the reactions on the cathode, also causes a decrease in O$_2$ concentration in the channel downstream. For these reasons, once OFR decreases just below a critical value around 15 sccm for the cell in this work, serious flooding occurs in the channel downstream region even under open-circuit conditions. The flooded region on the cathode increases with decreasing OFR, which can prevent O$_2$ from access to the cathode catalyst sites. In addition, the crossover of methanol from the anode also enhances the flooding in this region. In the meantime, in the upstream region, flooding is unlikely to occur because O$_2$ concentration is relatively high and water concentration is relatively low. As such, the MEA area can be divided into two regions: unflooded region (oxygen rich region) and flooded region (oxygen lean region), as sketched in Fig. 3. Although the two regions are connected in parallel by both electrodes and the same electrolyte (membrane), the lateral proton conduction in the electrolyte is so low that the flooded and unflooded sections of the cell act as if they were two independent cells that are connected electrically but not ionically. This explanation can be further clarified by the fact that the in-plane electrical resistivity (5 m$\Omega$ cm) of carbon cloth (E-TEK, Type ‘A’) is more than one thousand times smaller than the protonic resistivity (5.9 V cm at 80°C) of the Nafion membrane. Under this condition, the flooded regions are expected to act similarly to the methanol/inert cells (or electrolytic cells), used by Ren et al. to measure the rate of methanol crossover through the membrane. At the same time, the unflooded region of the MEA still acts as a normal DMFC (or galvanic cell) and maintains a certain voltage between two electrodes. In the flooded region, as long as the magnitude of voltage applied on the electrodes is sufficient, the following electrolytic reactions will take place:

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2\uparrow + 6\text{H}^+ + 6\text{e}^- \quad \text{(Anodic Reaction)} \quad [1]$$

$$6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\uparrow \quad \text{(Cathodic Reaction)} \quad [2]$$

These methanol electrolytic reactions consume electrical power and behave just like an internal electrical load connected to the unflooded region, where the galvanic cell is still operable. Therefore, the galvanic cell in the unflooded region does not stay in the open-circuit status, although the external load is disconnected. As evident from Fig. 2, once the gas evolution was initiated, the DMFC exhibited a potential decline from OCV to a low value, indicating that the galvanic cell was virtually discharging. Hence, the following electrochemical reactions occur in the un-flooded region:

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2\uparrow + 6\text{H}^+ + 6\text{e}^- \quad \text{(Anode)} \quad [3]$$

and

$$\frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \quad \text{(Cathode)} \quad [4]$$

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**Figure 1.** Gas bubble evolution on the anode side under typical oxygen flow rates (a) 15, (b) 12, (c) 11, and (d) 10 sccm.

**Figure 2.** Variation in OCV with different oxygen flow rates on the cathode.

**Figure 3.** Schematic representation of electrochemical reactions under open-circuit and oxygen-shortage conditions.
sured formation rates of CO₂ and H₂ gases corresponding to typical gases were measured by the water displacement method. The measurements on the catalyst sites to yield H₂, CO₂, and CO. 13 Such methanol reforming reactions, however, happen only at elevated temperatures (higher than 160°C). Therefore, for the cell operated at 60°C in this work, the possibility of gas evolution due to thermal decomposition of methanol is eliminated.

### Table I. OCV and gas flow rates in the efflux from anode under open-circuit conditions.

<table>
<thead>
<tr>
<th>Oxygen flow rate (sccm)</th>
<th>12</th>
<th>11</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCV (V)</td>
<td>0.48</td>
<td>0.45</td>
<td>0.43</td>
</tr>
<tr>
<td>Total gas flow rate (sccm)</td>
<td>1.3</td>
<td>1.3</td>
<td>1.24</td>
</tr>
<tr>
<td>H₂ flow rate (sccm)</td>
<td>0.74</td>
<td>0.76</td>
<td>0.68</td>
</tr>
<tr>
<td>CO₂ flow rate (sccm)</td>
<td>0.56</td>
<td>0.54</td>
<td>0.56</td>
</tr>
</tbody>
</table>

This discharging current, flowing between the flooded and un-flooded regions within the same MEA, can be regarded as a self-discharging current. As indicated in Fig. 3, the coexistence of Reactions 2 and 3 within the same MEA explains why gas evolution took place on the anode flow channel when external load was removed. We collected the gases generated in the anode flow channel and conducted a chromatography analysis. The result confirmed that the gas mixture principally consisted of CO₂ and H₂ with small amount of methanol and water vapor. The formation rates of CO₂ and H₂ gases were measured by the water displacement method. The measured formation rates of CO₂ and H₂ gases corresponding to typical OFRs are listed in Table I. It is seen from Table I that the measured ratio of CO₂ to H₂ is about 0.7 at different OFRs, which is larger than the theoretical ratio of 1:3 determined from the reactions given by Eq. 2 and 3. The extra CO₂ gas might be caused by CO₂ cross-over from the cathode. 12 Although the production of CO₂ gas was substantial, there were only a few of bubbles in the upstream region as seen from Fig. 1. This can be attributed to the fact that most of the CO₂ produced dissolved into methanol solution. The data in Table I also shows that the total gas flow rate on the anode is rather constant with oxygen flow rate. The total gas evolution rate depends not only on the flooded area on the cathode but also on the open-circuit potential. As the oxygen flow rate decreases, the flooded area increases by expanding upstream, but the circuit potential decreases. The competition between these two factors determined that the total gas evolution rate remained almost the same for the three oxygen flow rates listed in Table I.

It should be recognized that another possibility of gas evolution in the anode flow channel is that methanol can be thermally decomposes on the catalyst sites to yield H₂, CO₂, and CO. 13 Such methanol reforming reactions, however, happen only at elevated temperatures (higher than 160°C). Therefore, for the cell operated at 60°C in this work, the possibility of gas evolution due thermal decomposition of methanol is eliminated.

### Conclusions

Coexistence of the galvanic and methanol electrolytic reactions in a single cell has been found to be the reason why gas evolution occurs in the anode flow channel under open-circuit conditions. Although the whole cell is running under open circuit conditions, there is still self-discharging current causing methanol consumption and hydrogen evolution. This self-discharging mechanism also explains why the variation in OCV depends on oxygen flow rates. Practically speaking, the generation of hydrogen not only decreases the net output of electrical power for running cells but also consumes fuel continuously even under open-circuit conditions. Thus, it is important to maintain adequate and uniform supply of oxygen on the cathode side when DMFCs are under both running and standby conditions. In addition, produced hydrogen requires additional safety considerations for DMFC design and operation.

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