Transient Capillary Blocking in the Flow Field of a Micro-DMFC and Its Effect on Cell Performance

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We studied the performance and CO_2 bubble behavior in an in-house fabricated direct methanol fuel cell (DMFC, 1.0 × 1.0 cm in the active area) with the anode flow field consisting of various-sized microchannels down to 400 μm. We found that the flow field was blocked periodically by elongated gas slugs due to the increased capillary force in microchannels. This transient capillary blocking caused CO_2 bubbles to be evolved in the flow field and to be removed from the cell periodically. We further found that with a reduction in channel size, both the residence time and the CO_2 bubble size became longer. As a result, the effective mass-transfer area of methanol solution on the diffusion layer became smaller, causing the cell performance to decline. At the same fuel feed rate, a smaller flow channel led to a higher mass-transfer coefficient. The competition between the favorable effect of the increased mass-transfer coefficient and the adverse effect of the reduced effective mass-transfer area results in an optimal channel size that gives the best cell performance.

Because of its unique advantages such as high energy-conversion efficiency, easy storage of liquid fuel, ambient-temperature operation, and simple construction, the liquid-feed direct methanol fuel cell (DMFC) has received much attention and the different fundamental aspects of the DMFC have been studied extensively. In particular, miniaturized or micro-DMFCs have emerged as a candidate to compete with conventional batteries according to opportunity in terms of market size and growth rate for the requirement of small power supply to portable electronic devices.

Kelley et al. designed a miniaturized (0.25 cm² active area) methanol-air DMFC. The electrodes were constructed on standard microelectromechanical systems (MEMS) and microelectronic fabrication techniques using silicon substrates. With 0.5 M methanol solution, testing results showed that the mini-DMFC yielded a current density similar to that of large-scale DMFCs. Maynard and Meyers proposed a design for a miniaturized proton exchange membrane (PEM) methanol-based fuel cell for powering 0.5-20 W portable telecommunications and computing devices. In their subsequent paper, they used a silicon substrate to leverage advanced silicon processing and MEMS technology, and discussed key integration issues related to all miniaturized fuel cell systems: thermal management, humidification control, water recirculation, air movement, fuel delivery, and power conditioning. Blum et al. studied water loss and recycling in a micro-DMFC. They found that when the loss of water molecules (to the air) per molecule of methanol consumed in the cell reaction equals two, there is no need to add water to the DMFC and the cell can operate under water-neutral conditions. Water must be removed from the cell if this number is smaller than two, and water must be added if it is larger than two. Most recently, Lu et al. built a micro-DMFC with an active area of 1.625 cm² assembled by sandwiching the membrane electrode assembly (MEA) between two silicon wafers in which 750 μm wide and 400 μm deep flow channels were fabricated. Their micro-DMFC demonstrated a maximum power density of 50 mW cm² using 2 M methanol feed at 60°C, and a maximum power density of about 16 mW cm² with both 2 and 4 M at room temperature. They also found that the micro-DMFC still produced reasonable performance with 8 M methanol solution at room temperature.

The anode flow field design is a critical issue in DMFCs, through which, methanol solution is distributed to the diffusion layer and diffuses to the catalyst site. In the meantime, the reaction-produced gas CO_2 at the catalyst layer transports backward into the anode flow field through the gas diffusion layer (GDL). Therefore, unlike the single-phase gas flow in the flow field of hydrogen PEM fuel cells, the anode flow field of a DMFC involves liquid-gas two-phase flows. The design of the anode flow field of DMFCs is to ensure higher mass-transfer rates of diluted methanol solution from the flow channel to the reaction zone. Because the mass-transfer rate is affected by evolved gas, it is important to study the gas bubble evolution behavior in the flow channels.

A number of papers have been reported on the study of CO_2 bubble behavior in the anode flow field of conventional DMFCs with relatively large MEAs. Argyropoulos et al. studied the CO_2 bubble flow characteristics in a DMFC based on two different flow-field designs: one consisted of a series of parallel flow channels with 2.0 mm channel width, 2.0 mm channel depth, and 30.0 mm channel length, and the other consisted of cross-flow channels with 0.5 M methanol solution at room temperature. What’s more, the gas slugs transport in the parallel flow channels in the central region, including triangular enlarging inlet and outlet sections. It was observed that there were three two-phase flow patterns, including bubbly, slug, and annular flow, according to different levels of gas fraction. The gas slugs which blocked the flow channels were observed during the DMFC operating at low flow rates and high current density. Scott et al. investigated visually the CO_2 bubble removal characteristics related to the cell performance under a number of flow designs based on stainless steel mesh. Mench et al. observed the order of 0.1-0.5 mm CO_2 bubble growth and ejection from the different locations within the backing layer/flow channel interface region with video microscopy. They found that these small CO_2 bubbles grew and coalesced with the slug, resulting in a pulsed growth behavior. Bewer et al. investigated the influence of the flow field on bubble formation and on flow homogeneity, as well as the influence of manifold on flow homogeneity with the aid of a novel method of simulating two-phase flow in a DMFC using an aqueous H₂O₂ solution. Recently, Lu and Wang developed a 5 cm² transparent DMFC to visualize the flow behavior in both the anode and cathode flow channels. In the anode flow channel, with the hydrophobic carbon cloth backing, it was observed that CO_2 bubbles nucleated at various locations and formed large and discrete bubble plugs in the channel; with the hydrophilic carbon cloth backing, it was shown that bubbles were produced more uniformly and of smaller size. In the cathode flow channel, it was shown that liquid droplets appeared more easily on the surface of carbon paper due to its reduced hydrophobicity at elevated temperature. With the single-side ELAT carbon cloth, liquid droplets tend to form in the corner between the current-collecting rib and the GDL because ELAT is highly hydrophobic and the rib (stainless steel) surface is hydrophilic. Most recently, Yang et al. studied the CO_2 bubble behavior in the anode flow field of an in-house fabricated transparent DMFC with 4.0 × 4.0 cm active area of MEA. The effects of cell orientations, methanol solution flow rates, and operation temperatures were investigated.

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Although the liquid-gas two-phase flow behavior in the anode flow field of relatively large DMFCs has been studied over the past few years, this issue has not yet been addressed in miniaturized DMFCs. When a DMFC is scaled down, the effect of surface forces on the behavior of two-phase flows in miniaturized channels becomes more critical and some atypical phenomena may arise, which certainly impact the performance of fuel cells. In this work, we designed and fabricated a micro-DMFC with an active area of 1.0 × 1.0 cm. We investigated the bubble evolution and removal behavior in the anode flow field consisting of microchannels of different sizes in this micro-DMFC. We show that the cell performance is closely correlated with the bubble evolution and removal behavior in microchannels.

Experimental

The micro-DMFC.—The micro-DMFC consisted of an MEA, with an active area of 1.0 × 1.0 cm, sandwiched between an anode and a cathode bipolar plate, which were then assembled by two fixture plates. Figure I shows the anode bipolar plate, in which the anode flow field was formed by wire-cut technique. Table I lists the design of five anode flow fields, samples I - V, with different channel widths (410, 480, 580, 730, and 1000 μm) while keeping the same depth (500 μm). To keep the same open ratio (channel area/active area of the MEA) of 49% for all the anode flow fields, rib width was altered. As a result, for the same active area, rib number and channel length also had to be varied, as shown in Table I. To avoid corrosion and to reduce the contact resistance, the bipolar plates were made of 316L stainless steel and were electroplated with a thin layer of gold (0.1 μm in thickness). For the purpose of visualization of the bubble behavior in the anode flow channel, the anode fixture plate was made of transparent Lucite material. In the cathode polar plate, an interdigital flow field with 500 μm channel width and 500 μm rib width was machined, which was used for all the experiments in this work.

The MEA consisted of a Nafion 115 membrane and two E-TEK single-side ELAT electrodes. The carbon cloth (E-TEK, type A) with 30 wt % poly(tetrafluoroethylene) (PTFE) wet-proofing treatment was used as the backing support layer in the anode and cathode electrodes. 4.0 mg cm⁻² with unsupported [PtRu] Ox (1:1 atom %) and 2.0 mg cm⁻² using 40 wt % Pt on Vulcan XC-72 were used as the catalyst loading on the anode and cathode side. Furthermore, 0.8 mg cm⁻² Nafion was applied onto the catalyst layer surface of each electrode. The membrane was pretreated by following the standard procedure: (i) boiling membrane in 5 wt % H₂O₂ solution at 80°C for 1 h; (ii) rinsing with DI water at 80°C for 1 h; (iii) boiling membrane in 0.5 M H₂SO₄ solution at 80°C for 1 h; and (iv) rinsing with deionized water at 80°C for 1 h. Finally, the MEA was formed by hot pressing under the condition of 135°C and 4 MPa for 2 min.

Test rig.—The experiments were carried out in the test rig detailed elsewhere. On the anode, aqueous methanol solution was fed by a digital high-pressure liquid chromatography (HPLC) micro-pump (series III). On the cathode, 99.999% high-purity oxygen was supplied without humidification. A mass flow meter (Omega FMA-7105E), along with a multiple channel indicator (Omega FMA-5876A), was used to control and measure the flow rate of oxygen. The CO₂ bubble behavior in the anode flow field was observed and captured by an image recording system consisting of a JVC charge coupled device (CCD), a Navitar 6X CCD C-Mount Lens, and a digital camcorder (Sony DCR-TRV900E).

The Arbin BT2000 (Arbin Instrument) electroload interfaced with a computer was employed to control the cell operation condition and to measure voltage-current (polarization) curves. All the experiments were performed using the same cathode interdigital flow field fed with a constant oxygen gas flow rate of 10 sccm at atmospheric pressure and with the anode flow field fed with 1 M aqueous methanol solution. The operating temperature was controlled at 30 and 60°C, respectively, by two heating rods installed in the cell fixture plates. The heating rods were connected to a temperature controller (Digi-Sense).

Results and Discussion

The performance of the cells with the flow fields of different channel sizes.—Figure 2 compares the performance of the cells with the flow field consisting of different channel sizes (samples I-V). The experiments were conducted with 1.0 M methanol solution fed at a flow rate of 0.1 mL min⁻¹ and at a fixed temperature of 60°C. It is seen that the performance upgraded with decreasing channel size from 1.0 mm to 730 and 580 μm. A further reduction in channel width from 580 to 480 and 410 μm, however, caused the performance to decline. The cell with the 580 μm flow channel width exhibited the best performance among all the channels tested, however.
achieving a peak power density of 80.8 mW cm\(^{-2}\). Figure 3 compares the peak power densities of the cells with the five flow channels; the peak power density of the 580 \(\mu\)m channel width is about 21.7\% higher than that of the 1.0 mm channel width, and 19.0\% higher than that of the 410 \(\mu\)m channel width.

The design of the anode flow channel of a DMFC generally affects the cell performance in three aspects. The first is the mass transport of reactants. The flow channel design is required to ensure the transport of reactant molecules from the bulk flow in the channel to the diffusion layer at a higher mass-transfer rate. Second, the design of the flow channels is required to minimize the bubble coverage on the surface of the diffusion layer; larger bubble coverage will reduce the effective mass-transfer area, thereby reducing the mass-transfer rate. Third, the flow channels should ensure reactants to distribute on the surface of the entire MEA as uniformly as possible. Because the distribution of reactants on the MEA is a minor issue in such a small MEA tested in this work, we now focus on examining how channel size affects the mass-transport and bubble coverage in the flow field to explain the effect of channel size on cell performance presented in Fig. 2 and 3.

**Channel size vs mass-transfer coefficient.** The mass-transfer rate of aqueous methanol solution, \(m\), from the channel bulk flow to the diffusion layer can be evaluated by

\[
m = Ah(c_a - c_w)
\]

where \(A\) represents the effective mass-transfer area, \(c_a\) and \(c_w\) denote methanol concentration in the channel bulk flow and at the surface of the diffusion layer, and \(h\) represents the mass-transfer coefficient. Under typical fuel cell operating conditions, because of the disturbance of gas bubbles/slugs in the anode flow channel, the liquid flow of methanol solution can never be fully developed. Under such a circumstance, the mass-transfer coefficient is the function of the liquid flow velocity; a higher flow velocity leads to a higher mass-transfer coefficient. For the same methanol solution flow rate, a narrower channel width leads to a higher flow velocity and thereby a higher mass-transfer coefficient. Therefore, according to Eq. 1, a narrower channel gives a higher mass-transfer rate. This explains why narrower channels (580 \(\mu\)m) led to a better performance than did the wider channels (1.0 mm to 730 \(\mu\)m). It should be recognized from Eq. 1, however, that the mass-transfer rate also depends on the effective mass-transfer area between the bulk methanol solution and the diffusion layer surface. As presented in the subsequent section, the effective mass-transfer area is strongly affected by the bubble evolution behavior in the flow channel.

**Channel size vs bubble behavior.** In our previous visual study of the bubble behavior in the anode single-serpentine flow field with larger channels (>1.0 mm),\(^{27}\) we found that the CO\(_2\) bubble evolved in a relatively steady fashion at a specific current density. For smaller channels tested in this work, the most remarkable difference from the larger channel in our previous work\(^{27}\) was that the bubble evolution and removal from the flow field behaved in a cyclic manner. Figure 4 shows a sequence of images of the CO\(_2\) bubble evolution behavior in the flow field with 410 \(\mu\)m channel width over a cycle when the cell was discharged at a current density of 40 mA cm\(^{-2}\) with 1 M methanol fed at 0.1 mL min\(^{-1}\) at 60°C. The images, 1 s apart, were captured from the recorded video, with a shutter speed of 1/250 s. The lighter areas represent the gas bubbles, while the dark areas represent the aqueous methanol solution. The bubble evolution cycle under this particular condition lasted about 16 s. Initially, it was observed that a number of discrete tiny CO\(_2\) bubbles were evolving from the surface of the diffusion layer. These small bubbles grew and departed from the surface of the diffusion layer with the help of the crosscurrent flowing methanol solution. Traveling along the flow channel toward the channel outlet, the bubbles gradually grew up due to coalescing with the newly produced small bubbles from the surface of the GDL. As a result, some gas slugs formed in the channel downstream region; because of being confined by channel dimensions, these gas slugs grew lengthwise while moving toward the channel outlet. These elongated gas slugs were stuck at the channel walls and continued to grow as time went by. Once the gas slugs became sufficiently long (see the image at 15 s, which is also shown in Fig. 5e with a larger magnification), they were suddenly removed from the flow channel and a follow-up cycle began (see the image at 16 s). As such, the bubble evolution and removal repeated periodically. As shown in Fig. 5, under the same operating conditions it was found that the critical gas slugs increased with decreasing channel width, and the longest critical gas slugs appeared in the narrowest channel width (410 \(\mu\)m).

To explain why the gas slugs are suddenly removed from the flow channel, when their length becomes critically long (referred to
as the critical length hereafter), we sketch a gas slug in Fig. 6. As can be seen from Fig. 6, when the gas slug forms in the flow channel, methanol solution is virtually forced to flow through the channel corner regions (see the sketched cross section on the right side in Fig. 6). The liquid flow across the gas slug can be treated as Poiseuille flow and the pressure drop can be approximated by

$$\Delta P_l = p_1 - p_2 = \frac{128 \mu L Q}{\pi D_{\text{eff}}^4}$$ \[2\]

where $Q$ is the mass flow rate of methanol solution, $\mu$ the viscosity of the fluid, $L$ the length of the slug, and $D_{\text{eff}}$ the effective dynamic diameter of the liquid flow. It is clear from Eq. 2 that the pressure drop across the gas slug becomes larger with gas slug length. In the meantime, this pressure drop also tends to push the gas slug toward downstream. However, as the outward motion of the gas slug is initiated, the contact angles at the right and left side of the slug must be the receding $\theta_2$ and advancing $\theta_1$ values, respectively, as indicated in Fig. 6. As a result, a smaller mean radius of curvature exists at the right side of the slug than at the left side, creating a capillary force resisting the motion of the liquid flow with a pressure drop of $\Delta P_c = p_1 - p_2$. With the aid of the Young-Laplace equation, this capillary force can be approximated by

$$F_c = 2\alpha \left( \frac{1}{W} + \frac{1}{H} \right) (\cos \theta_2 - \cos \theta_1)$$ \[3\]

For the still gas slug, the pressure drop is balanced by the capillary force, i.e.

$$\Delta P_l = p_1 - p_2 = F_c$$ \[4\]

However, as the gas slug grows longer, the pressure drop essentially increases, as indicated by Eq. 2. It is also noted from Eq. 3 that the capillary force is independent of gas slug length. Consequently, as the gas slug becomes critically long, the increased pressure drop becomes larger than the capillary force and thus the gas slug is pushed downstream until it is removed from the flow channel. Following up the removal of the old gas slugs, new gas slugs form along the channel length, creating a new cycle. The cyclic bubble evolution and removal is caused by transient capillary blocking. It is interesting to note from Eq. 3, a narrower channel creates a larger capillary force. As indicated by Eq. 2 and 4, a larger capillary force means a longer gas slug. This observation is consistent with the visualization results presented in Fig. 5, which shows that narrower channels caused longer gas slugs.

We analyzed the gas slugs by replaying the recorded video at slow motion and measured the gas slug residence time in different channels under different operating conditions. The results are shown in Fig. 7. It is seen that under all the specified operating conditions gas slugs stayed longer in narrower channels than in wider channels. This is because the capillary force is larger in narrower channels, as indicated by Eq. 2. Comparing the data represented by triangle and
The effects of methanol solution flow rates and operating temperatures.—Figure 8 shows the cell performance at the same temperature (60°C) and with the same methanol concentration (1 M) as the case shown in Fig. 2, but a higher flow rate (0.8 mL min$^{-1}$). Figure 8 indicates that at the higher flow rate, the cell performance with each flow channel is significantly higher than that shown in Fig. 2 at a lower flow rate, because of the increased mass-transfer rate with higher flow rates. It is also noticed from Fig. 8 that at this higher flow rate, the differences in the cell performance among different channel widths are still significant.

Figure 9 presents the cell performance at a lower temperature (30°C) but with the other operating conditions remaining the same as the case shown in Fig. 8. Figure 9 indicates that at the lower temperature, the cell performance with each flow channel is significantly lower than that shown in Fig. 8 at a higher operating temperature, because of the lower electrochemical kinetics at lower temperatures. It is also interesting to notice from Fig. 9 that at lower operating temperature, the differences in the cell performance among different channel widths become smaller. At lower temperatures, CO$_2$ gas has a lower evolving rate but higher dissolving rate. As a result, both the number of bubbles and gas slugs become smaller and a change in channel size becomes insensitive to the bubble behavior. Therefore, the effect of channel size on the cell performance becomes more insignificant.

**Conclusion**

The flow channel size on the performance of an in-house fabricated micro-DMFC with an active area of 1.0 × 1.0 cm was investigated experimentally. It was found that at the same fuel feed rate the cell with a medium flow channel width (580 μm) exhibited the best cell performance, either narrower or wider channels causing the performance to decline. The underlying mechanism leading to the optimal channel size has been explained based on in situ-visualized CO$_2$ bubble behavior in the flow fields. The results show that bubble evolution and removal in smaller flow channels occurred in a cyclic manner because of transient capillary blocking. Shrinking channel width resulted in not only longer gas slugs but also a longer gas slug residence time in the flow field. As a result, the effective mass-transfer area between methanol solution and the diffusion layer virtually divides the methanol solution flow into two streams. The upper stream flows adjacent to the impermeable wall, whereas the lower stream flows over the permeable surface of the diffusion layer. This means that in the elongated gas slug regions only the lower stream of methanol solution is utilized, whereas the methanol in the upper stream is virtually wasted. This explains why the cell with the narrowest flow channel (410 μm) exhibited a lower performance shown in Fig. 2 and 3.

The above discussions on the correlation between the channel size and the mass-transfer coefficient, and the correlation between the channel size and the bubble behavior can be summarized as follows: at the same methanol solution flow rate, narrower flow channels lead to higher mass-transfer coefficient, a favorable effect on cell performance. The longer gas slugs in narrower flow channels not only yield a smaller effective mass-transfer area between the methanol solution and the diffusion layer, but also cause part of methanol solution to be unused. In this context, narrower channels adversely affect cell performance. The competition between the higher mass-transfer coefficient and the smaller effective mass-transfer area results in an optimal channel size that gives the best cell performance. For the presently configured MEA, this optimal channel width is 580 μm, as shown in Fig. 2, 8, and 9.
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