GAS–LIQUID TWO-PHASE FLOW IN PARALLEL CHANNELS OF A DIRECT METHANOL FUEL CELL

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The CO$_2$ gas bubble behavior in an anode channel and the performance of a transparent direct methanol fuel cell (DMFC) were experimentally investigated. To observe the gas–liquid two-phase flow, the transparent anode plate was made of polycarbonate, and the anode end plate possessed a 70 mm × 70 mm window. The emergence, growth, and coalescence of the CO$_2$ bubbles were recorded by a high-speed camera at 250 frames/s$^{-1}$. The DMFC was tested and observed at different current densities, methanol flow rates, and temperatures, which exhibited an obvious influence on the CO$_2$ gas bubbles’ behavior. It was observed that the bubble size increased with the current density and temperature, while the bubble number obviously decreased downstream in the channel. On the other hand, the bubble behavior, particularly its size and gas volume, affected the internal mass transfer of the DMFC and therefore affected the cell performance.

KEY WORDS: direct methanol fuel cell, visualization method, CO$_2$ gas bubble behavior, two-phase flow, cell performance

1. INTRODUCTION

A fuel cell is a device that directly converts chemical energy into electric energy. Theoretically, the energy conversion efficiency of the fuel cell is higher than that of the heat engine because the fuel cell efficiency is not limited by the Carnot cycle as demonstrated by Ostwald (1894) (Ogden et al., 1999; Chalk et al., 1998). The fuel cell also has the advantages of environment friendliness, low noise, and high reliability (Outeiro et al., 2009; Wesselmark et al., 2010; Carton and Olabi, 2010). In the 1960s, the fuel cell was successfully applied to the GEMINI spacecraft and APOLLO mission (Sone et al., 2006; Guo et al., 2014, 2016), and it has received widespread attention because of great successes in space flight and the energy and environmental crises concerns during this period (Guo et al., 2014, 2016; Chen and Wu, 2010). The direct methanol fuel cell (DMFC) uses a proton exchange membrane as an electrolyte and directly uses methanol as fuel. Methanol has the advantages of being liquid at normal temperature and pressure, high specific energy density, convenient transportation, and low cost (Bahrani and Faghihi, 2010; Masdar et al., 2010). The DMFC is considered an early commercially available fuel cell (Dillon et al., 2004).

The oxidation of methanol at the anode generates CO$_2$, and the CO$_2$ gas, and methanol aqueous solution will flow simultaneously in the anode catalyst and diffusion layers and plate channel to form gas–liquid two-phase flow (Falcao et al., 2016; Atacan et al., 2017). To ensure the normal operation of the DMFC, the CO$_2$ gas needs to be discharged as soon as possible (Fang et al., 2017; Mallick and Thombre, 2017). Accordingly, the methanol solution can continuously enter the catalytic layer and undergo oxidation reaction. The gas emissions in the anode channel are important; in particular, when the DMFC is operating under large current density and low liquid flow rate, the volume
ratio of CO$_2$ gas in the flow channel is very large (Mench et al., 2001; Liu et al., 2017). When the active area of the DMFC increases the amount of CO$_2$ gas increases accordingly (Argyropoulos et al., 1999b). In the DMFC stack, CO$_2$ can easily accumulate in the cell because of uneven distribution of liquid fuel, thereby resulting in short- and long-term performance instability of the DMFCs (Argyropoulos et al., 1999c). Oliveira et al. (2010) experimentally investigated the effect of three different anode and cathode flow field designs on the performance of a DMFC. Using multi-serpentine and mixed parallel and serpentine channels as the flow field design can enhance cell performance. Hsieh et al. (2010) proposed and tested a new and novel arrangement for a DMFC, and the test results indicated that cell performance was improved greatly by the reduction in CO$_2$ gas and water produced in the channels.

Argyropoulos et al. (1999a,b,c) conducted an early study on anode visualization. They observed two-phase flow in the anode channel to understand the bubble dynamics in DMFCs. Lu and Wang (2004) developed a transparent DMFC to visualize the anode bubble dynamics and cathode flooding. The visualization of bubble dynamics on the anode side showed differences between the hydrophobic and hydrophilic backing layers. Yang et al. (2005) experimentally investigated the two-phase flow pressure drop behavior in the anode flow field of a DMFC. The influence of current densities, methanol solution flow rates, and CO$_2$ gas bubble behavior in serpentine and parallel channels at different current densities was also explored. Liao et al. (2007) studied the CO$_2$ bubble dynamic behavior in the anode channel; the effect of flow rate, temperature, concentration, and the pressure on CO$_2$ gas bubble behavior; and the cell performance. The processes of emergence, growth, coalescence, and detachment of the CO$_2$ bubbles occur periodically. Burgmann et al. (2012, 2013) qualitatively and quantitatively investigated the appearance and evolution of CO$_2$ bubbles on the anode side using micro-particle image velocimetry. Yuan et al. (2015) experimentally and numerically investigated the CO$_2$ transmission behavior under different operation parameters in a micro-DMFC. The operating current, flow rate, and temperature obviously influenced the quantity and shape of CO$_2$ bubbles. Yuan et al. (2016) experimentally investigated porous patterns and their effects on reactant and product management on the basis of different flow fields. The performance of the parallel flow field showed less sensitivity to the change in methanol feed rate, and the serpentine flow field was closely influenced. Some studies have used visualization methods to observe two-phase flow. However, a wide range of working conditions is needed to prove the generality and universality of the conclusions in these studies.

This paper presents results of visual observation of the two-phase flow in the anode parallel channel of a transparent DMFC. The CO$_2$ bubble behavior in the anode channel under different current densities, methanol flow rates, and operating temperatures was observed, and its effect on cell performance was studied experimentally.

2. EXPERIMENTAL PROCEDURE

2.1 Structure of the Transparent DMFC

A transparent DMFC with a parallel channel was used to study the gas–liquid two-phase flow at the anode channel. Figure 1 shows the structure of the transparent DMFC. It consists of the membrane electrode assembly, the anode end plate, the transparent anode polar plate, the cathode polar plate, and the cathode end plate.

In the visual observation of the gas–liquid two-phase flow at the anode, a 70 mm × 70 mm window is applied in the middle of the anode end plate, and the transparent anode plate is made of polycarbonate to resist methanol corrosion. Figure 2 shows the anode end plate and transparent anode plate. The channel width is 2 mm, the depth is 2 mm, the ridge width is 2 mm, and the channel length is 52 mm. A Nafion 117 membrane is used (DuPont Company). Pt/Ru and Pt/C are used as anode and cathode catalysts, respectively, and the Pt/Ru and Pt loadings are both 4 mg/cm$^{-2}$.

2.2 Experimental System

Figure 3 shows the anode visualization experimental system of the transparent DMFC. A non-circulating methanol liquid supply system is used, and the methanol solution is used only once to keep the constant concentration of the methanol solution at the anode inlet. The excreted methanol is recycled into the recovery tank. The methanol solution is extracted from the tank by a peristaltic pump and enters the anode entrance by the buffer. The CO$_2$ gas
and the unreacted methanol solution are discharged from the fuel cell and into the gas liquid separator. The separated liquid flows enter the reclaimed methanol solution tank through the back pressure valve, whereas the separated gas is discharged through the exhaust valve. High-purity oxygen is extracted from the oxygen bottle into a mass flow controller and a pressure reducing valve, and then it enters the cathode entrance by the buffer after being heated and humidified. The water and unreacted oxygen is discharged from the fuel cell to the gas liquid separator. The separated gas is discharged through a back pressure valve, and the liquid flows out through a drain valve.

In the experiment, the $\text{O}_2$ inlet flow at the cathode was $800 \text{ ml/min}^{-1}$, the cathode outlet pressure was ambient pressure, and the concentration of methanol solution was $1.0 \text{ mol/l}^{-1}$. The programmable electronic load produced by Arbin Instruments Company of America (College Station, TX, USA) was adopted as the electronic load, and MITS Pro version 3.0.8 was used as the control software for the electronic load.

### 2.3 High-Speed Video Recorder System

To complete the visualization experiment of the DMFC anode, a digital camera and a high-speed camera were used in this experiment. The high-speed camera was the FASTCAM Super 10K series produced by the Photron Company (Tokyo, Japan). The high-speed camera was used to record the change in gas–liquid two-phase flow at 250 frames/s$^{-1}$. 
3. RESULTS AND DISCUSSION

3.1 Effect of the Current Density on the Cell Performance

Figure 4 shows the CO$_2$ bubble behavior under different current densities. The methanol solution inlet flow at the anode was 10 ml/min$^{-1}$ and the operating temperature was 70°C. The experimental results presented in Fig. 4 show that the gas volumes in the flow channel and the bubble size increase with the current density. At low current density, small bubbles escape slowly and attach to the flow channel wall. Occasionally, the bubbles detach quickly from the flow channel wall into the outlet manifold. When the current density is 40 mA/cm$^2$, the bubbles in the flow channel obviously increase. A few bubbles that are bigger than 1 mm in the channel top can be observed clearly in Fig. 4. Small bubbles are attached to the channel in the channel bottom, and the gas elastohydrodynamic flow is applied in the outlet manifold. When the current density is 60 mA/cm$^2$, the gas discharges quickly because of high gas generation, and the number of small bubbles in the channel top decreases. When the current density is 100 mA/cm$^2$, the number of large bubbles in the channel increases and the bubbles are dense in the upper part of the flow channel. A few small gas slugs appear in the channel, small bubbles mix in the methanol solution in the channel, and nearly no bubbles attach to the channel wall. At high current densities, the bubbles’ movement rate drops after entering the outlet manifold. Thus, a large bubble is easily formed at the joint between the channel and the manifold.

The bubble’s movement in the channel is not vertical under high current density. Figure 5 shows photographs of a bubble moving through a channel at 150 mA/cm$^2$, captured by a high-speed camera shooting at 250 frames/s. As shown in Fig. 5, the bubble moves up the channel with a swinging motion. When the bubble moves to one side of the channel wall, it will collide with the channel wall. In experiments, this phenomenon is obvious when the bubble size is approximately 1 mm. The swinging motion of CO$_2$ bubbles shows that the formation rate is fast at high current density. The two-phase flow in the channel is disturbed, and the methanol reaction rate is smaller than the low current density.
FIG. 4: Effect of current density on the CO$_2$ bubble behavior: (a) 10 mA/cm$^{-2}$; (b) 20 mA/cm$^{-2}$; (c) 40 mA/cm$^{-2}$; (d) 60 mA/cm$^{-2}$; (e) 80 mA/cm$^{-2}$; (f) 100 mA/cm$^{-2}$; (g) 120 mA/cm$^{-2}$; (h) 150 mA/cm$^{-2}$

Figure 6 shows the change in the cell voltage and power density with the current density during the experiment. The performance of the transparent DMFC is relatively stable. When the current densities are 100 and 120 mA/cm$^{-2}$, the performance of the cell slightly fluctuates. The increase in the amount of gases affects the mass transfer of methanol. The large bubbles prevent methanol from entering the diffusion layer and slow down the rate of reaction.

### 3.2 Effect of the Methanol Flow at the Anode Inlet on the Cell Performance

Figure 7 shows the CO$_2$ bubble behavior under different methanol inlet flow rates. The cell current density was 150 mA/cm$^{-2}$ and the operating temperature was 70°C. As can be seen in Fig. 7, the number of bubbles in the channel is low and the average size of the bubbles decreases with an increase in the flow rate. As shown in Figs. 7(a) and 7(b), several large bubbles appear and few small gas slugs cross the flow channel on the top of the channel. However,
all bubbles move significantly fast such that no blockage occurs. When the methanol flow rate is 20 ml/min$^{-1}$, the number of large bubbles in the channel obviously decreases. The length of the gas slug in the outlet manifold shortens and the movement speed accelerates. When the flow rate is 30 ml/min$^{-1}$, the number of bubbles in the channel decreases and the large bubbles only appear near the outlet manifold. No large bubble is observed at the lower part of the channel. When the methanol flow rate reaches 60 ml/min$^{-1}$, no bubble larger than 1 mm is found in the channel.
and the number of small bubbles is very low. The gas slug in the outlet manifold is very small and the manifold is filled with large bubbles.

Figure 8 shows the performance curves of the DMFC under different methanol flow rates. The cell voltage drops in the ohmic polarization region as the flow rate increases. In the concentration polarization region, the cell voltage
rises when the flow rate increases from 5 to 20 ml/min$^{-1}$ and the cell voltage drops from 20 to 60 ml/min$^{-1}$. The flow velocity and static pressure in the channel increase with the flow rate. The crossover of methanol from the anode through the proton exchange membrane to the cathode is exacerbated, thereby decreasing the performance of the DMFC in the ohmic polarization region. In the area of concentration polarization, the main factors that affect the cell performance are the lack of feed to the catalytic layer and the removal of reactions from the catalytic layer. An increase in the flow velocity and pressure can alleviate the problem.

### 3.3 Effect of Temperature on the Cell Performance

Figure 9 shows the CO$_2$ bubble’s behavior at different temperatures. The cell current density was 80 mA/cm$^{-2}$ and the methanol flow at the anode inlet was 10 ml/min$^{-1}$. As shown in Fig. 9, when the cell operating temperature is 30°C several small bubbles are observed on the top of the channel. Meanwhile, small bubbles adhere to the channel wall and combine with other bubbles to form large bubbles. The large bubbles move slowly and combine with other bubbles to form a gas slug. A comparison of Figs. 9(a)–9(d) shows that the number and size of the bubbles increase with temperature due to the decrease in the gas solubility and surface tension of the methanol solution.

Figure 10 shows the performance curves of the DMFC at different operating temperatures. The cell performance increases greatly with temperature. The improvement in cell performance is obvious in the polarization region of the cell. The voltage drops slowly when the temperature increases in the concentration polarization region with increasing current density. This is due to the fact that the catalyst activity and the diffusion coefficient of methanol increase with temperature, and the latter is important for improving the performance of the DMFC in the concentration polarization region. After the increase in temperature, the molecular motion increases and the diffusion coefficient enlarges, thereby enhancing the process of the reactants. The mass transfer of the DMFC in the concentration polarization region improves. When the cell temperature rises, the increase in gas volume affects the mass transfer of methanol and reduces the reaction rate. However, the influence on cell performance is less and nearly negligible with the increase in the catalyst activity and the methanol diffusion coefficient. Therefore, the increase in gas volume and bubble size does not decrease the performance of the DMFC after the increase in temperature.

### 4. CONCLUSIONS

The cell performance and CO$_2$ gas bubble behavior characteristic in the anode channel at different current densities, methanol flow rates, and temperatures of the DMFC were reported in this paper. The major experimental conclusions were as follows:

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*Figure 8: Effect of the methanol solution flow rate on the cell performance*
FIG. 9: Effect of temperature on the CO₂ bubble behavior: (a) 30°C; (b) 50°C; (c) 70°C; (d) 85°C

FIG. 10: Effect of temperature on the cell performance

1. With increasing current density, the gas flow in the channel increases and the bubble size enlarges. The bubbles move in the channel accompanied by the oscillation. When the current density is increased to 100 mA/cm⁻², the performance of the DMFC slightly fluctuates.

2. The number, average size, and length of bubbles in the channel obviously decrease with an increase in the methanol flow rate. The cell voltage drops in the ohmic polarization region, and the voltage rises first and then decreases in the concentration polarization region.
3. As the temperature increases the number and size of the bubbles in the channel increase, a long gas slug appears in the outlet manifold, and the performance of the DMFC greatly improves.

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