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Two-phase flow in anode flow field of a small direct methanol fuel cell in different gravities

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An *in-situ* visualization of two-phase flow inside anode flow bed of a small liquid fed direct methanol fuel cells in normal and reduced gravity has been conducted in a drop tower. The anode flow bed consists of 11 parallel straight channels. The length, width and depth of single channel, which had rectangular cross section, are 48.0, 2.5 and 2.0 mm, respectively. The rib width was 2.0 mm. The experimental results indicated that when the fuel cell orientation is vertical, two-phase flow pattern in anode channels can evolve from bubbly flow in normal gravity into slug flow in microgravity. The size of bubbles in the reduced gravity is also bigger. In microgravity, the bubbles rising speed in vertical channels is obviously slower than that in normal gravity. When the fuel cell orientation is horizontal, the slug flow in the reduced gravity has almost the same characteristic with that in normal gravity. It implies that the effect of gravity on two-phase flow is small and the bubbles removal is governed by viscous drag. When the gas slugs or gas columns occupy channels, the performance of liquid fed direct methanol fuel cells is failing rapidly. It infers that in long-term microgravity, flow bed and operating condition should be optimized to avoid concentration polarization of fuel cells.

direct methanol fuel cells, microgravity, two-phase flow, visualization, bubble behavior

1 Introduction

Direct methanol fuel cell (DMFC) is a promising power source for small unaided device because of its feature of quick refueling, low temperature and pressure operation, low cost of fuel, etc. However, slow anode kinetics, methanol crossover through the polymer membrane, gas and liquid management inside fuel cells are critical problems remaining to be solved to improve the DMFC performance.

In DMFC, the following electrochemical reactions take place,

$$\text{anode: } CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

$$\text{cathode: } 6H^+ 6e^- + \frac{3}{2}O_2 \rightarrow 3H_2O$$

There is aqueous methanol solution (reactant) and carbon dioxide (product of electrochemical reaction) on the anode side of liquid fed direct methanol fuel cells. On the anode side, there is a liquid-gas two-phase system consisting of methanol solution and carbon dioxide bubbles. At present, several researchers reported their two-phase flow studies in the anode of DMFC. Scott and his colleagues are pioneers in this field. They reported several visual observations in the anode flow bed of DMFC[1–4]. Argyropoulos et al. researched carbon dioxide gas evolution and behavior in the anode of two

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DMFCs and one of them had 9 cm^2 active area and the other had 270 cm^2 area. They found that the carbon dioxide was not uniformly produced on the surface of gas diffusion layer (GDL) and there were a number of point sources of gas release[1]. The two-phase flow patterns found in their researches were bubble flow, slug flow and annular flow. Channel blocking was believed to restrict the supply of methanol to gas diffusion layer. The bubbles produced on carbon paper membrane electrode assembly (MEA) were bigger than those produced on the carbon cloth MEA[1–3]. Scott et al. reported a visual experiment of carbon dioxide gas evolution and flow behavior with flow beds of stainless steel mesh. They presented that the gas accumulation was in the form of small bubbles or bubbles swarms flowing in the anode channel[4]. Zhao's group reported visual investigations in the anode of DMFC, including conventional DMFC and micro-DMFC[5–9]. To understand the morphology of gas-liquid two-phase flow in the anode flow field of DMFC, Yang et al. visually investigated the flow pattern in both vertical and horizontal rectangular channels with 5.0 mm ×5.0 mm square cross section. The gas was injected uniformly into the test section along a porous plate, which acted as a sidewall of test section[5]. Yang et al. also reported the bubble behaviors in different experimental conditions including current densities, operation temperature, cell fixing orientation and methanol solution flow rate[6,8]. Yang et al. showed that more carbon dioxide bubbles existed in the parallel flow field than in the single serpentine flow field at same current density. As a result, it led to poorer performance of fuel cell[7]. Wong et al. visually studied the carbon dioxide bubbles evolution in a micro-DMFC fabricated in-house with various sizes of micro channels, at the same open ratio 49%, in 1.0 cm × 5.0 cm active area. For the increased capillary force in micro channels, the flow field was blocked periodically by elongated gas slugs. They also found that the slug length and residence time varied with different flow channel width and operation conditions including temperature, methanol solution feeding flow rate[9]. With the aid of video microprobe, Mench et al. investigated the gas bubble's growth and ejection from the backing layer/flow channel interface region. They found that the bubbles, whose diameter varied from 0.1 to 0.5 mm, were ejected high frequently on the surface between current collection ribs, and the bubbles growing near the stainless steel rib/backing layer interface became larger bubbles before their detachment from the backing layer[10]. Lu et al. found that the small bubbles were produced uniformly on the hydrophilic carbon cloth diffusion layer and those bubbles evolved into a larger one at certain locations, and discrete slug bubbles were produced on the hydrophobic carbon paper backing[11]. Bewer et al. simulated two-phase flow in DMFC using aqueous H_2O_2 solution. They investigated the influence of flow field on bubble formation and flow homogeneity[12]. Using sodium bicarbonate and sulfuric acid, Fu et al. simulated two-phase flow in DMFC and took picture with a high speed video camera[13]. Nordlund et al. designed a transparent DMFC, using stainless grid mesh with gold layer as bipolar plate. They reported that the carbon dioxide bubbles were not produced homogeneously on the surface of MEA[14]. Zhang et al. visually investigated the influence of the anode gas diffusion layer (GDL) on a low temperature DMFC including performance, properties of mass transport and carbon dioxide removal from the GDL surface. Uniform small carbon dioxide bubbles formed on the hydrophilic GDL and large bubbles formed on the hydrophobic GDL[15]. Yang et al. reported bubbles behaviors in a passive micro DMFC with perforated current collector and that with parallel collector. The performance of fuel cell with parallel current collector was better than that with perforated[16]. A fact worthy of remark is that all the work in the above-mentioned literature is conducted in normal gravity condition.

In Iguchi's two-phase flow experiment under different gravity environments, the gravity has strong effect on the bubble behavior[17]. Zhao conducted a serial of two-phase flow experiments under reduced gravity environment and they also found that the gravity affected two-phase flow strongly[18]. For their high energy density, fuel cells have been thought to fit for space application especially for short-term mission[19]. Considering the potential application to vehicle and large spacecraft, Sone et al. have developed a 100 W fuel cell and had operated it for 28 h without humidifying reactant gases[20]. After a trade-off analysis of regenerative fuel cell (RFC), Barbir et al. believed that RFC was a viable option for weight sensitive application such as aerospace[21]. The authors reported micro-gravitational experiments of direct methanol fuel cells with gold plated stainless steel bipolar plates[22] and graphite bipolar plates[23], respectively. The results showed that the operation behaviors of fuel cells in the reduced gravity environment were different from those in normal gravity.

However, microgravity experiments of two-phase flow in direct methanol fuel cells are still lacking in the open literature. In this paper, the carbon dioxide bubbles behavior in anode flow fields of DMFC under normal gravity and micro gravity environments were visually observed. The influence of gravity on two-phase flow and mass transfer in DMFC was analyzed and discussed.

2 Experimental

2.1 Test loop

Figure 1 schematically shows our experimental set-up that consists of methanol solution and oxygen supply units, electric load and data acquisition system, video recording unit, and temperature control and heating units. Here, 1 is Oxygen cylinder, 2 regulator, 3 filter, 4 flow controller, 5 one-way valve, 6 direct methanol fuel cell, 7 one-way valve, 8 flow rate meter, 9 filter, 10 peristaltic pump, 11 liquid storage bag, 12 high speed video camera, 13 current transducer, 14 waste liquid retriever, 15 data acquisition system, 16 electric resistors, 17 container, and 18 temperature control and heating unit.

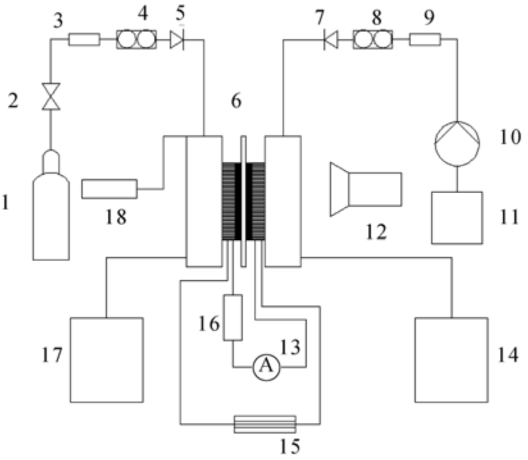


Figure 1 Experimental set-up.

Oxygen gas with purity of 99.999%, without humidification, was used as oxidant reactant. The oxygen gas flow rate was controlled by a mass flow controller (Cole Parmer, CZ-32907-67) combined with an indicator, which could control the oxygen flow rate from 0 to 1000 mL/min., with a precision of 1% of full scale. Before flowing into the cathode channel, oxygen gas has been heated up. The excess oxygen gas and produced water were discharged to a container. The prepared methanol solution was stored in a storage bag and was driven by a peristaltic pump (BT01) and sent to a liquid flow meter (Cole Parmer, CZ-32908-43) combined with an indicator, which had measurement range of 0—50 mL/min with a precision of 2% of full scale. Similar to the oxygen gas, the methanol solution was also heated up before flowing into the anode channels. The mixture of carbon dioxide gas and methanol solution from DMFC was sent to the container.

2.2 Transparent fuel cell

As schematically shown in Figure 2, a small DMFC with transparent window was designed and fabricated. A commercially available MEA was sandwiched between two graphite bipolar plates with sealing gasket. The MEA with an active area of 5.0 cm × 5.0 cm consists of a Nafion 117 membrane and two carbon cloth gas diffusion layers. The catalyst loading was 4 $\mathrm{mg\cdot cm^{-2}}$ Pt/Ru on the anode side and 4 $\mathrm{mg\cdot cm^{-2}}$ Pt on the cathode side.

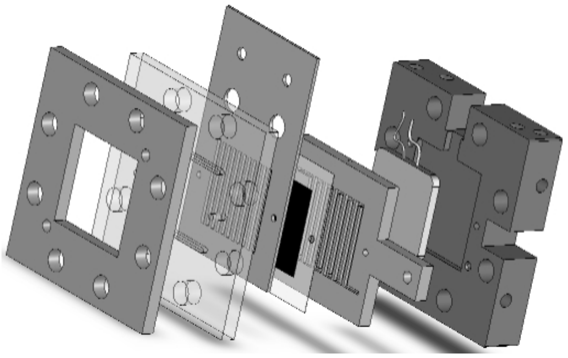


Figure 2 Assembly of a DMFC with transparent window.

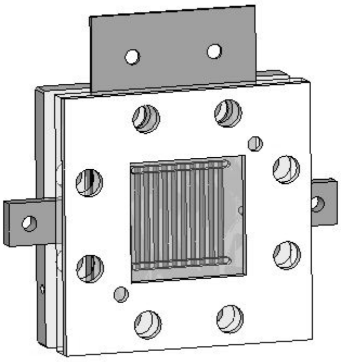
Both the anode and the cathode bipolar plates were made of graphite. The cathode bipolar plate consisted of channel area, extension area and location pinholes. A single serpentine channel, which had rectangular cross section of 2.0 mm in depth and 2.5 mm in width, was fluted in cathode flow field. The rib width is 2.0 mm and the channel length was 566 mm. Extension area of both the anode and the cathode plates was used as current connector. The channel area of anode bipolar plate had 2 manifolds and 11 parallel straight channels, whose length was 48.0 mm. Each channel had rectangle cross-section with depth of 2.0 mm and width of 2.5 mm. The width of rib, which was between two adjacent channels, was 2.0 mm. For the purpose of visual observation, the end plate of the anode side was made of transparent polycarbonate (PC). In order to preheat the fuel cell, a heater was stuck to the cathode bipolar plate.

2.3 Video recording system

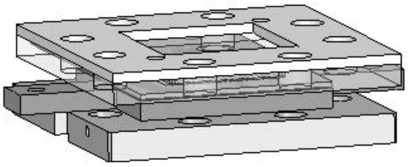
A high-speed video camera (VITcam CTC) with a CCTV C-mount lens (SE2514, AVENIR) was employed to capture two-phase flow images in the anode flow field. In our experiment, the micro gravity environment was obtained by free fall of a drop capsule, which contained our fuel cells experimental system. A shutter speed of 3996 μs and a recording speed of 250 frames/s were set to visualize and record two-phase flow in the anode flow field. The camera could record 2096 frames of pictures with 1280×1024 pixels resolution. With the aid of AOS Imaging Studio program, bubbles moving velocities were measured from consecutive images.

2.4 External circuit and test condition

Electric resistors were employed as external circuit load and two current transducers (LEM, LTS 25NP and LTS 6NP) were adopted to measure the current. All data, including fuel cell temperature, current and voltage, flow rate and gravity signal, were collected into a data acquisition system (AQU1216), which could store the data in an integrated hardware. All the experiments reported in this paper were performed in following condition: oxygen gas flow rate was kept constant of 400 mL/min. Methanol solution with molarity of 0.5 kmol/m^3 was supplied to anode flow bed at flow rate of 10 mL/min. Temperature of fuel cell was maintained at 80℃. Our experiments were performed in two different orientations: horizontal and vertical (Figure 3).



(a) Vertical



(b) Horizontal

Figure 3 Orientations of the tested DMFC.

2.5 Micro gravity environment

The micro gravity environment was provided by free fall of a drop capsule, in which our experimental rig was fixed, in a drop tower of National Micro Gravity Laboratory, Chinese Academy of Sciences. Falling in the air, the residual gravity acceleration of experimental rig was less than $10^{-2}g_0$ (ground gravity acceleration, 9.81 m/s^2). The effective micro gravity environment could last 3.6 s. The capsule was released after the fuel cell ran at 80℃ for 70 min.

3 Results and discussion

Figure 4 shows two-phase flow in anode flow bed of a liquid fed direct methanol fuel cell under different gravities. The orientation of the fuel cell kept vertical (Figure 3(a)). The inlet manifold was in the bottom, and the outlet manifold was on the top of the flow bed. The *in-situ* images were captured at 0.040 s before releasing capsule, 1.0000 s, 2.000 s and 3.000 s after free falling of capsule, respectively. In this paper, the starting time of microgravity was set as the moment of releasing capsule.

In normal gravity environment, the carbon dioxide bubbles were produced uniformly with tiny shape. The bubbles detachment diameter is influenced by buoyancy, momentum flux, surface tension, inertia force and drag force. In normal gravity environment, the gravitational buoyancy is the principal detaching force[24]. The diameter of most bubbles, which were detached from the MEA surface, ranged from 0.05 to 0.3 mm in our experiments.

After detaching from the MEA surface, the carbon dioxide bubbles moved fast. Table 1 shows the bubbles rising speed in anode channels, while methanol solution flow rate was 10 mL/min. Considering that the mean velocity of liquid at the entry of channel was 3.03 mm/s, which was calculated from the inlet flow rate of methanol solution, the speed of bubbles removal was quite fast because of buoyant lift force.

In normal gravity, the big bubbles with fast velocity would push the small ones anterior. When the bubbles collided with each other, coalescence took place and it was a dominative way of bubbles growth. The typical flow pattern in the anode flow channels in normal gravity was bubbly flow.

In microgravity, the carbon dioxide bubbles could not get away from the MEA surface in time. At the begin-

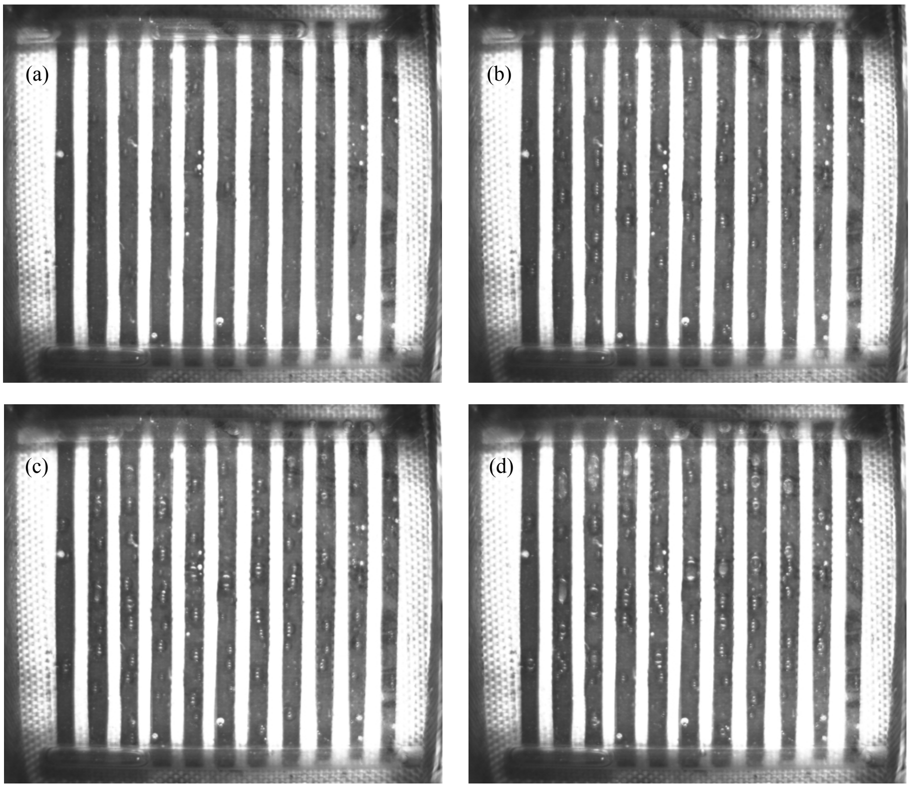


Figure 4 Two-phase flow in anode channel of the vertical DMFC. (a) —40 ms; (b) 1000 ms; (c) 2000 ms; (d) 3000 ms.

Table 1 Bubbles moving velocity in vertical parallel channels of DMFC in normal gravity

Channel No.	Bubble moving speed (mm/s)		
	(−1836 ms)—(−1820 ms)	(−1820 ms)—(−1804 ms)	(−1804 ms)—(−1788 ms)
3	162	144	143
4	124	133	145
5	104	128	129
6	145	150	143
7	155	123	132
8	136	121	123

ning, the bubbles accreted on the wall of carbon cloth surface. Then, the bubbles on the surface grew gradually because of producing carbon dioxide by anode electrochemical reaction. The longer the time was, the bigger the bubble was (Figure 4). The gravity affects not only detaching diameter, but also bubbles rising velocity[25]. The *in-situ* observation showed that once the capsule was released, the bubbles move was slowed down immediately. Bubbles, which were detached from MEA, almost suspended in methanol solution.The average rising velocity of bubbles in channels are shown in Table 2. The speed of bubbles moving in micro gravity was obviously slower than that in normal gravity because buoyancy lift was very weak and the bubbles removal was governed by viscous drag of fluid in the reduced gravity. Some bubbles coalesced with each other and formed larger bubbles. Those large bubbles decreased the effective area of fuel mass transfer and hence the DMFC performance deterioration took place.

Table 2 Mean rising speed of bubbles in vertical parallel channels of DMFC

Channel No.	In normal gravity (mm/s)	In microgravity (mm/s)
3	134	4.1
4	138	9.3
5	122	2.7
6	140	6.6
7	135	6.6
8	134	4.9

When DMFC is oriented in horizontal (Figure 3(b)), the typical flow pattern is the elongated slug flow (Figure 5). Two-phase flow in the reduced gravity has almost the same bubbles behaviour as that in normal gravity. This result implies that the influence of gravity on two-phase flow has been reduced. Like in the condition

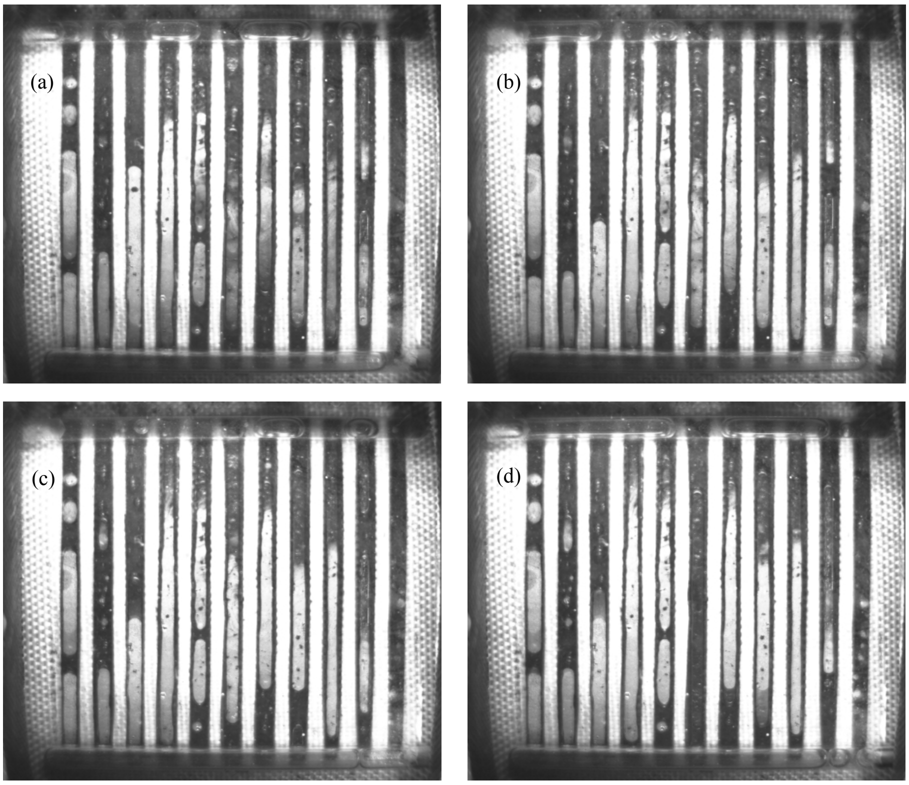


Figure 5 Two-phase flow in anode channel of the horizontal DMFC. (a) –40 ms; (b) 1000 ms; (c) 2000 ms; (d) 3000 ms.

of vertical orientation of fuel cell, once the gas slugs or even gas columns occupy channels, the performance of liquid fed direct methanol fuel cells will fall rapidly. The phenomena infer that in long-term microgravity condition, flow bed, fuel cell orientation and operation condition should be optimized to ensure timely discharge carbon dioxide bubbles and avoid concentration polarization.

4 Conclusions

Two-phase flow behaviors in the anode flow field with parallel channels of a liquid fed direct methanol fuel cell are studied experimentally in normal gravity and short-term reduced gravity.

(1) When the fuel cell orientation is vertical, the detachment diameter of bubbles range from 0.05 to 0.3 mm in normal gravity. However, the size of bubbles in the reduced gravity is bigger. The flow pattern in anode channels of liquid fed direct methanol fuel cells can change from bubbly flow in normal gravity to slug flow in microgravity.

(2) The bubbles rising velocity in vertical channels in microgravity is obviously slower than that in normal gravity. It is because buoyancy lift is very weak and the bubbles removal is governed by viscous drag in the reduced gravity.

(3) The influence of gravity on two-phase flow is nonsignificant when the fuel cell lies flat. The slug flow in the reduced gravity has almost the same bubbles behaviour as that in normal gravity.

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