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A self-pumping and self-breathing micro direct methanol fuel cell with polymer bipolar plates

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ABSTRACT

A passive micro direct methanol fuel cell (DMFC) for reducing volume and parasitic power is designed and fabricated using several integrated technologies. New bipolar plates with tapered channels at the anode and a pillar array at the cathode are first applied to a passive micro-DMFC. The substrate of the bipolar plates made of acrylonitrile butadiene styrene (ABS) is hot embossed with two molds, fabricated by UV-LIGA and micro machining. To make the bipolar plates conductive and hydrophilic, a nickel layer is electroplated on the ABS plates, and three PDDA/PSS bi-layers are self-assembled onto the nickel layer. The bipolar plates are produced using hot embossing, a low cost, highly accurate batch process. A single cell is assembled to verify the self-pumping function, and it can generate a peak power density of 7.4 mW cm^{-2} with a 3 M methanol solution. The fuel cell is verified to work in three different orientations. When the fuel cell is placed horizontally, the self-pumping rate is about 0.1–0.15 mL h^{-1}. And the fuel cell can work through self-pumping for 5 h under this condition.

1. Introduction

Recently, with the demands of high energy density for commercial electronics and micro devices, micro direct methanol fuel cells (micro-DMFC) have been considered as a promising power source candidate instead of lithium-ion batteries. The investigation of micro-DMFC system is a hot topic both in academia [1–3] and industry [4–6]. Some companies even have launched their products or prototypes, such as Toshiba's Dynario in 2010 [6]. In theory, methanol has a dramatic energy density, 4878 Wh L^{-1} in volume and 6098 Wh kg^{-1} in weight. Based on the state-of-the-art, the fuel volume-based energy density of micro-DMFC prototypes could be 620–1420 Wh L^{-1}, much higher than the energy density of the Li-ion battery (about 350 Wh L^{-1}) [7]. However, the system volume-based energy density is quite low, normally 77–325 Wh L^{-1} [7]. One of the reasons for the low system volume-based energy density is that the ancillary components in the system consume part of the overall energy, and increase the entire volume and weight. The pump used to deliver liquid fuel in an active micro-DMFC is normally the main energy consuming source, especially when the scale of micro-DMFC is reduced to fit small portable devices. Sometimes, a pump may even use more energy than the fuel cell can generate. A passive micro-DMFC [8,9] may be an alternative choice, but the output power is limited by the low fuel delivering rate. Moreover, the fuel is mainly delivered by diffusion in a passive mode, so the anode electrode needs to be directly attached to the fuel reservoir, making the system incompatible and limited to a certain orientation.

In fact, the CO_2 bubbles generated from the electrochemical reactions contain some energy which can further push the capillary-driven liquid movement. Different approaches had been done to improve the mass transportation in micro-DMFC by using the energy [1,10–12]. Zhao and Ye [12] developed a passive fuel delivery system with the liquid fuel self-pumping by the CO_2 bubbles in a single serpentine flow field. By combining the theoretical and experimental results, they found that the methanol feeding system was capable of achieving a performance comparable to an active pump system for 0.5–4.0 M methanol. However, this micro-DMFC could have a selectivity of orientations, because the movement of bubbles is only along the effects of buoyancy. Their system requires a vertical pipe, and the effective height strongly affected the movements of bubbles. This problem was solved by applying some special microstructures in the flow fields. Meng and Kim [1] developed a silicon based self-pumping micro-DMFC. They built a gas-blocking element to make the bubbles moving towards one direction and venting through a porous silicon membrane. With the removal of CO_2 bubbles, a little fresh methanol solution will be vented into a flow field. Paust et al. [10,11] had a concept of degassing bubbles and self-pumping by the difference of capillary pressures. High feeding rate, 13 times higher than the methanol oxidation rate, was achieved

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by applying parallel tapered channels with T-shape cross sections.

The self-pumping technique allows the designers to reconsider the design of a passive micro-DMFC from several aspects, including arrangement in a stack, series interconnection, materials, and fabrication. Since the reservoir need to be attached directly to the electrode in a passive micro-DMFC as mentioned above, each single cell was typically put into the same plane in traditional designs [8]. This made the stack incompact and complex in series interconnection. A bipolar plate structure can make the system compactable and easily interconnected without ultra wires. The bipolar plate structure means that the bipolar plate acts as an anode for one cell and a cathode for the next cell in a stack structure. This structure was applied to an active micro-DMFC stack [13,14]. However, it was considered very hard to be utilized in a passive stack [8,12], because the liquid fuel is difficult to be delivered into a flow field only by diffusion. The self-pumping technique can deliver the methanol solution into the flow field at a high rate without an ancillary pump. If the self-pumping technique can be integrated with the bipolar plate structure, the passive micro-DMFC would be more compactable and the series interconnection would be much easier.

With the integration of the self-pumping technique, bipolar plates may be much more different from the traditional one. Suitable material and fabrication methods will be required to meet the requirements for strength, accuracy, weight, and cost. Although microfabrication on silicon wafers is an attractive approach for its maturity and high accuracy, this method has been refuted many times because of its fragility, low conductivity, and high cost [8,15]. Stainless steel and titanium alloy may be suitable for the bipolar plates after a proper corrosion protection. Using wet chemical etching, micro structures can be efficiently fabricated at low cost [8,15], but the aspect ratio of the structures is limited. Compared with silicon and metal, polymer is an alternate material due to its manufacturing flexibility, chemical stability, and low cost. Using hot embossing, micro structures can be duplicated on polymer plates with high accuracy and low cost [16,17]. Although most of polymers are insulating, high conductivity can be achieved after a metallization on the polymers. Nguyen et al. [18] assembled a micro fuel cell with gold-sputtered polymethyl methacrylate (PMMA) substrates, on which the gas flow channels were formed by laser micromachining. Litterst et al. [10] used the hot embossing technique to fabricate transparent PMMA plate to observe the bubble development and movement. Due to the insulation of PMMA, stainless steel sheets machined by laser were used as a current collector in their experiments. However, sputtering is an expensive way to make polymer conductive, and the application of an extra current collector, stainless steel sheet, makes the assembly process more complex. Alternatively, a low cost metal layer can be easily deposited on a polymer substrate by an electrochemical deposition, especially on ABS (acrylonitrile butadiene styrene) [19].

In this paper, a new conception of a self-pumping micro-DMFC stack, assembled with metalized polymer bipolar plates, is presented. A simple model was used to explain the mechanism of self-pumping. New bipolar plates were fabricated using several techniques, including UV-LIGA, metallization of polymer, and nano self-assembly. With the bipolar plates, micro-DMFCs were assembled, and tested under different methanol concentrations along different orientations. In addition, the self-pumping rate was characterized.

2. Self-pumping mechanism and design of fuel cell stack

2.1. Self-pumping mechanism

When a CO_2 bubble is generated from the electrochemical reaction, it enters into a channel through a gas diffusion layer, and moves towards an open area of the channel to minimize surface energy. Fresh fuel can be sucked into the channel from the narrow end, when the bubble is traveling along the channel like a piston. This mechanism is similar to the oxygen bubble movement presented by Maharbiz et al. [20].

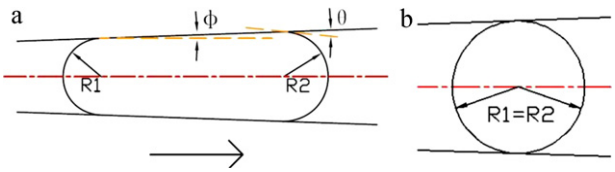

Fig. 1. Tapered micro-channel bubble geometry: (a) nonequilibrium state and (b) equilibrium state.

When a bubble is introduced into a tapered channel with hydrophilic surface, as shown in Fig. 1, two opposite but unbalanced forces are applied to each end of the bubble. The difference is due to the change of channel cross section. The following equations describe the force on each ends of the bubble

$$F_1 = 2R_1\pi\sigma \cos(\theta + \phi) \quad (1)$$

$$F_2 = 2R_2\pi\sigma \cos(\theta - \phi) \quad (2)$$

where F_1 and F_2 are the forces on each end of the bubble, R_1 and R_2 are the radius of gas/liquid interface, σ is the surface tension, θ is the contact angle, and Φ is the angle between the channel wall and the channel axis. By combining Eqs. (1) and (2), the total force along the central line is:

$$F = 2\pi\sigma[R_2 \cos(\theta - \phi) - R_1 \cos(\theta + \phi)] \quad (3)$$

For a completely hydrophilic material ($\theta = 0^\circ$), the net driving force is given by

$$F = 2\pi\sigma \cos(\phi)[R_2 - R_1] \quad (4)$$

From Fig. 1a, it is obvious that F will be more than 0 until R_2 is equal to R_1. The bubble will continue to move until the two radiuses, R_1 and R_2, are the same, as shown in Fig. 1b.

Moreover, the continuous generation of CO_2 bubbles will also push the liquid moving due to the expansion of volume. Although the bubble may be blocked in the channel when it is in an equilibrium state ($R_1 = R_2$), other bubbles will be generated from the continuous electrochemical reaction. The volume of the bubble will be expanded due to the coalescence, thus the bubble will continue to move until the next equilibrium state. If the bubble reaches an open end, it will be no longer limited by the channel and float out.

2.2. Structure of bipolar plates

The bipolar plates used in a micro-DMFC were metalized polymer plates with anode and cathode flow fields on each side, as shown in Fig. 2a. ABS was formed by hot embossing, followed by electroplating of nickel. The anode flow field consisted of 15 parallel tapered channels with 250 μm depth. Each channel was a straight channel (110 μm wide and 4.3 mm long) with a tapered channel (110 μm wide at narrow end, 580 μm wide at wide end, and 26.7 mm long), as shown in Fig. 2b. For the cathode, there is a pillar array (1 mm in diameter and 1 mm high with a pitch of 1.5 mm) in the middle of a plate. Four screw holes, 2.7 mm in diameter, were used to assemble and seal the fuel cell, and another four vias (0.5 mm in diameter) were used to connect the nickel layer on each side of the plate.

2.3. Stack design

Fig. 3 shows the structure of the micro-DMFC assembled with bipolar plates. Membrane electrode assemblies (MEAs) with