

EMBEDDED SELF-CIRCULATION OF LIQUID FUEL FOR A MICRO DIRECT METHANOL FUEL CELL

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ABSTRACT

This paper introduces a micro direct methanol fuel cell (μ DMFC) with an embedded self-pumping mechanism to deliver liquid fuel. The fuel is propelled by the CO_2 bubbles generated by the fuel-cell electrochemical reaction, and the bubbles are removed from the system during the self-pumping process. Furthermore, the pumping rate is self-regulated by the reaction, i.e., by the electric load. By eliminating the need for a pump and gas/liquid separator, our design allows much simpler fuel-cell systems, which is especially beneficial for miniaturization. Although we test with μ DMFC in this paper, the mechanism applies to other membrane electrode assembly (MEA)-based fuel cells with organic liquid fuels as well.

INTRODUCTION

The development of micro power sources or power micro electromechanical systems (MEMS) has gained momentum recently. A big driving force comes from portable consumer electronics, such as cell phones, global positioning systems (GPS), digital cameras and laptop computers. More and more functions with a faster computing capability are being integrated into a single device, which demands small power sources with higher energy density to support a reasonable working time. At the same time, the advancement of MEMS technologies has provided numerous individual micro systems in millimeters or smaller scales with wireless communication ability. Although the distributed applications of these systems are very attractive, the road block exists in their power sources, which are currently much larger and heavier than other parts of the microsystem. Due to its much higher energy density than traditional batteries, micro direct methanol fuel cell (μ DMFC) has been widely considered as the next generation power source for portable electronic devices. μ DMFC has been anticipated to be one of the first fuel cells to fully enter the consumer market in the near future [1], with a few products already announced [2-4]. However, several technical hurdles still need to be cleared to make the μ DMFC mature and finally accepted by the consumer market, including the cost, the performance of membrane electrode assembly (MEA), and the complexity compared with traditional batteries.

The working principle of μ DMFC is illustrated in Fig. 1. The aqueous methanol solution is fed into the anodic channel while air flows through the cathodic channel. A series of electrochemical reactions are enabled by the proton exchange membrane (PEM) and the catalyst layers. Protons migrate from anode to cathode through the PEM, while electrons are collected by the anodic electrode and consumed in the cathodic electrode. The accumulated

electrons provide the continuous current for the external circuit. An external pump is usually used to provide a continuous flow of methanol fuel to the anode and maintain the fuel concentration there.

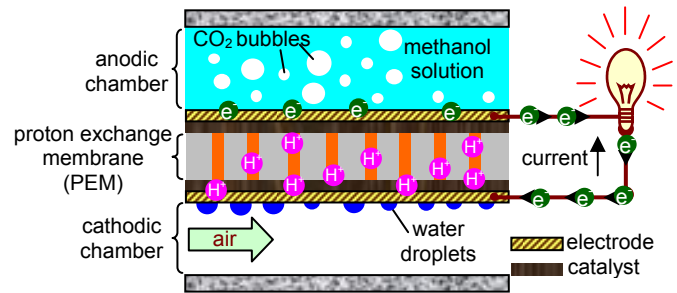
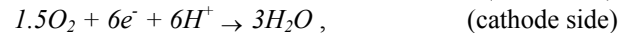


Fig. 1. Working principle of direct methanol fuel cell

In the fuel stack of a DMFC, the electrochemical reactions are:



According to this reaction, all DMFCs intrinsically generate CO_2 gas bubbles. If not promptly removed for μ DMFCs, these bubbles will clog the anodic microchannels and aggravate the deleterious methanol crossover. The current common practice is to use an external pump to deliver the fuel and push the gas bubbles to downstream. Then an open tank (gas/liquid separator) can be used to release CO_2 gas into the environment [5]. This approach is impractical in a portable device due to the danger of fuel leakage. Meanwhile, using an external pump to deliver fuel not only takes up space and complicates the microsystem, but also claims a significant portion of the power output of μ DMFC. Since most reported micropumps require 100 mW or higher of power input, about 10% of the fuel cell total power output (usually ~ 1 W) has to be consumed by pumping. This percentage can be even higher if the fuel cell is not working at the maximum power capability.

We have previously proved that a nanoporous membrane can remove gas bubbles while holding liquid with satisfactory pressure tolerance. Combined with virtual check valves, the venting mechanism has also enabled a new bubble-driven pumping mechanism [6]. The gas bubbles generated by electrolysis were employed to circulate liquid in a microfluidic loop [7].

In this paper, a similar pumping mechanism is applied to a μ DMFC, using the intrinsically generated CO_2 gas bubbles as the gas source. Therefore, the fuel delivery requires no separate pumping component and no power. The design

solves the bubble clogging and fuel delivery problems at the same time. Both the gas/liquid separator and external pump are eliminated from the system, allowing an integrated, simple and economic design of a μ DMFC system.

PUMPING BY HYDROPHOBIC VENTING

The gas removal approach is implemented by microscopic hydrophobic venting holes, which allow the gas to pass through relatively undeterred while the liquid menisci block the liquid from flowing out. Fig. 2 represents an idealized model to illustrate how liquid can be restricted from leaking by its own meniscus. On the sharp corner of the venting hole's entrance, this meniscus balances with the varying pressure across the meniscus (transmeniscus pressure) according to the Laplace-Young equation:

$$P_l - P_o = 2\sigma_l \cdot \cos(\pi - \alpha) / r, \quad (1)$$

where P_l is the pressure of the liquid fuel, P_o is the ambient pressure, σ_l is the surface tension of the liquid fuel, α is the angle between meniscus and the capillary wall, and r is the radius of the capillary.

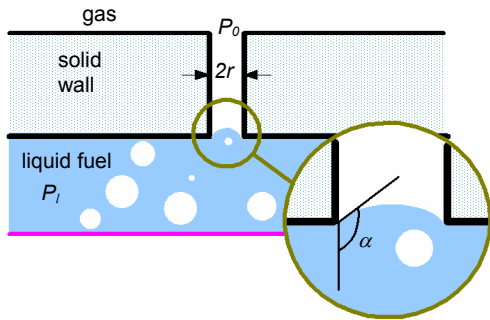


Fig. 2. Hydrophobic venting by a microscopic venting hole

Due to the intrinsic hydrophobicity and small pore size of the hydrophobic nanoporous membranes, they can provide a high leakage onset pressure. The successful venting of gas bubbles has been achieved for both pure water and methanol fuel with a concentration as high as 10 M, by employing a porous polypropylene membrane with a nominal pore radius of 0.1 μ m (from Chemplex[®]). The fuel is proven to be contained without leakage under the pressure as high as 200 kPa for both pure water and 10 M methanol [8].

A new bubble-driven pumping mechanism [7] has been developed utilizing hydrophobic venting, as Fig. 3 illustrates. A group of small hydrophilic capillaries are fabricated on the left side of the bubble source to serve as a virtual check valve for gas bubbles. When a bubble grows at a location close to this virtual check valve (as Fig. 3-a shows), expansion of the left meniscus of the bubble is hindered due to its capability to provide a higher capillary pressure than the right meniscus does. Consequently, the bubble only grows to the right and pushes the liquid rightward. The bubbles generated in the middle of the microchannel can be pushed by the leftmost one to the right. This rightward bubble motion can also be promoted by the

proper design of the channel shape, e.g., a diverging hydrophilic shape [9]. By making the microchannel hydrophilic (e.g., SiO₂), a surface energy difference between its hydrophilic surface and the hydrophobic membrane can make the latter a “bubble trap” [10]. Once a bubble reaches the hydrophobic nanoporous membrane, it will be drawn into the membrane region (Fig. 3-b). Through the venting holes in the membrane, the bubble is vented out without liquid loss. The liquid then fills into the section symmetrically to replace the vacancy left by the gas bubble. A pumping cycle is thus completed and a net pumping to the right is achieved.

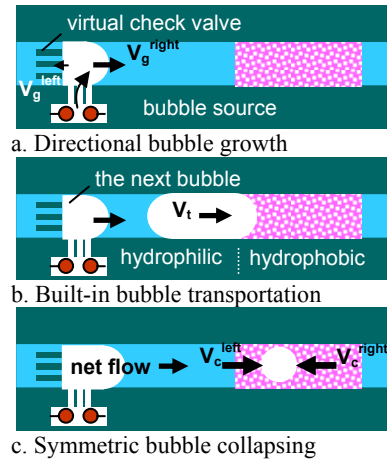


Fig. 3. Micropumping by directional growth and hydrophobic venting of bubbles

By using this self-pumping method, liquid circulation in a sealed closed-loop microchannel has been demonstrated by using electrolytic gas bubbles (H₂ and O₂) [7]. Compared with the similar thermal-bubble-driven pump, the electrochemical-bubble-driven micropump exhibits better controllability and biocompatibility with 10-100 times higher power efficiency.

FABRICATION AND ACTIVATION OF μ DMFC

We have applied a similar pumping mechanism to a μ DMFC, with the intrinsically generated CO₂ gas bubbles as the gas source [11]. The concept has been verified by circulating the liquid fuel in an on-chip microfluidic closed-loop with a small reservoir, which supported the fuel cell operation for about 8 minutes under 80 °C. In this paper, the device has been modified so that it can be connected to an external fuel cartridge and tested for a long-term operation under room temperature. The cross-sectional views of the assembled self-pumping μ DMFC are shown in Fig. 4. Microchannels of the anode, the cathode and the breather cover are fabricated by DRIE, followed by metal evaporation (0.01 μ m Cr, 3 μ m Cu and 0.5 μ m Au). The anode and the cathode are then anodically bonded to two pieces of Pyrex[®] glass. A Plexiglas fixture is used to sandwich MEA (E-TEK[®]) between the anode and the cathode. Silicone rubber sheets are added between the Plexiglas fixture and the μ DMFC device to ensure uniform

clamping pressure. A piece of nanoporous polypropylene film (Chemplex[®]) is glued between the anode and the breather cover by epoxy to remove CO₂ gas bubbles during operation. The breather outlet is connected to a valve via tubing. The control experiment can be performed by closing the valve and stopping the venting. In order to decrease flow resistance and avoid bubble clogging, fuel inlet and

fuel outlet 2 are connected to the fuel cartridge directly to form a fluidic loop that can be driven by the self-pumping mechanism. During MEA activation (to be detailed later), an external pumping is needed to deliver methanol fuel. In this case, the whole fuel cartridge is used as an inlet, and the used fuel can be discharged through fuel outlet 1.

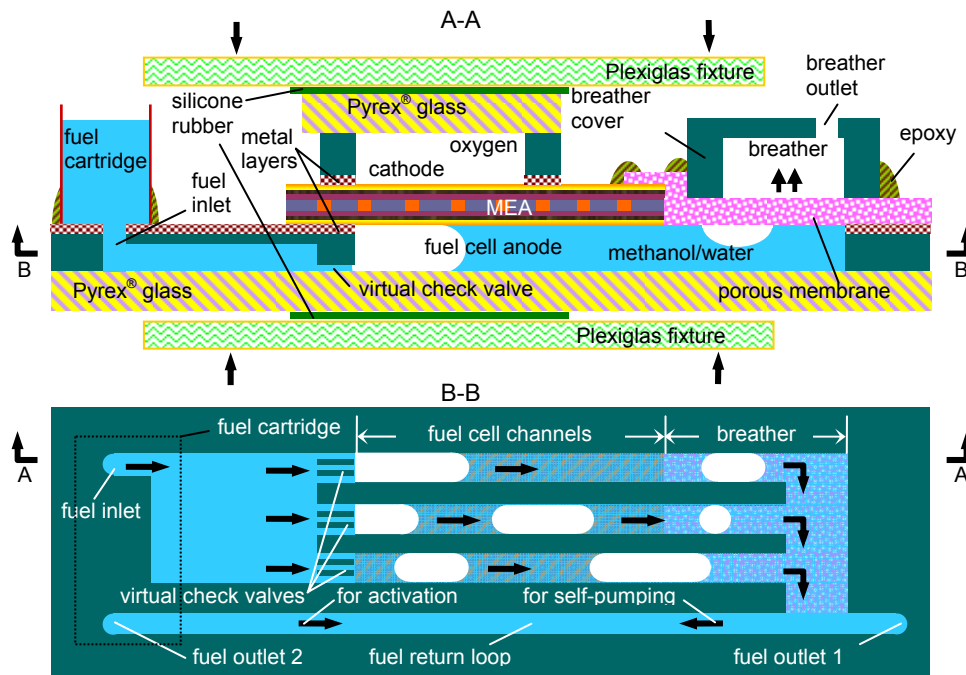


Fig. 4. The cross-section of assembled self-pumping μ DMFC

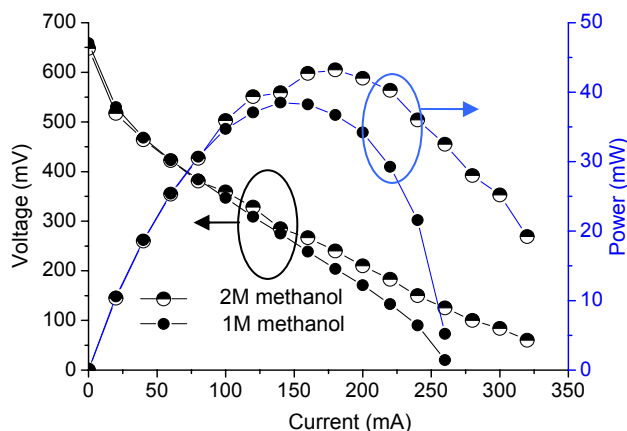


Fig. 5. Polarization and power density curves of the assembled μ DMFC after MEA activation

After assembly, the MEA of the fuel cell is activated according to the procedure provided by the manufacturer. Hot DI water at 90 °C is first flowed through the anode microchannels with a flow rate of 3 mL/min for 1.5 hours to activate the PEM. Then, 2 M methanol at 80 °C is flowed through the anode microchannels with a flow rate of 3 mL/min for 3 hours. Meanwhile, oxygen is flown through the cathode channel at ~100 mL/min. The cell voltage is controlled at ~0.25 V by a variable resistor connected to it.

This second step activates the catalyst. During activation, an external pump (Masterflex[®] C/L[®] variable-speed tubing pump by Cole-Parmer[®]) is used to deliver the anodic liquid from the “fuel cartridge” to the “fuel outlet 1” in Fig. 4. A pressurized gas tank is used to provide the cathodic gas flow. The measured polarization and power density curves of the μ DMFC after activation are shown in Fig. 5. This test has been performed with 3 mL/min 2 M methanol flow at anode, ~100 mL/min oxygen flow at cathode, and under room temperature.

VERIFICATION OF FUEL CIRCULATION

After activation, the fuel cell was cooled down to room temperature and brought to the operation condition with “fuel outlet 1” closed. The gas bubbles generated by the electrochemical reaction are used as the gas source in a self-pumping mechanism, as Fig. 3 indicated, to circulate the fuel. This fuel circulation mechanism does not require any external power input.

In order to verify the fuel circulation, the μ DMFC is tested by loading it with a 1.3 Ω resistor and measuring the power output over time, as shown in Fig. 6. The self-sustained fuel cell operation has been observed under room temperature, with 1.2 mL of 2 M methanol in the anode and 53 mL/min oxygen flow in the cathode. Both the cartridge and the cathode are pressurized at 11 kPa over atmosphere.

The operation time span (~60 minutes) confirmed the sufficient fuel delivery. As a reference, a control experiment was performed by closing the valve connected to the breather outlet, i.e., blocking CO₂ venting and disabling the self-pumping mechanism. In the control experiment, gas bubbles were observed to grow and fill the entire anodic microchannel, and the power output dropped rapidly after about 3 minutes.

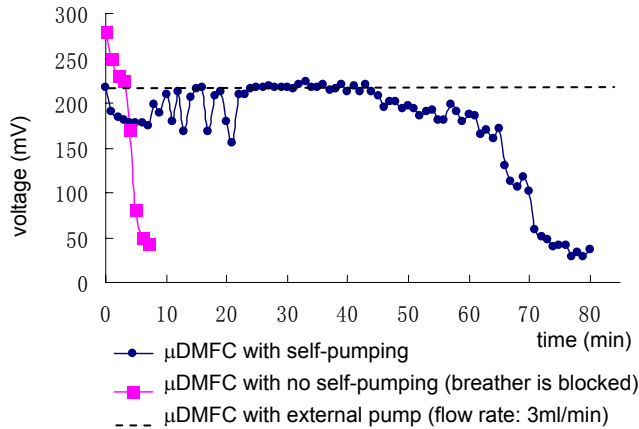


Fig. 6. Self-sustainability of the self-pumping μ DMFC

The anodic microchannels have also been visualized to further confirm the self-pumping. Similar bubble motion pattern as in [7] has been observed throughout the flow field. Fig. 7 demonstrates the bubble motion at the end of an anodic microchannel, as well as the successful bubble removal.

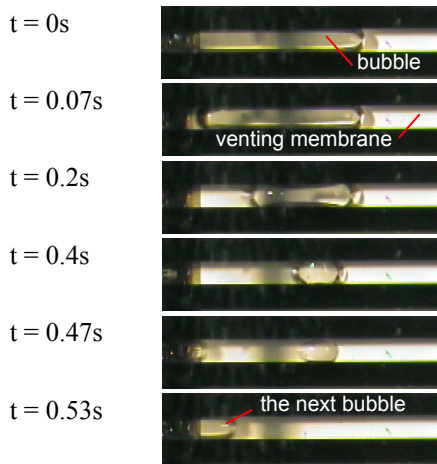


Fig. 7. Bubble removal by the breather

An interesting and useful feature of the self-pumping is that it can be self-regulated by the reaction of μ DMFC. Since the bubble generation rate is directly connected to the electrochemical reaction rate, the pumping rate will increase with a faster reaction rate, the pumping rate will increase with a faster reaction rate, when the external load is larger, and the pumping rate will decrease when the load is smaller.

CONCLUSIONS

A self-pumping mechanism was integrated into a μ DMFC to circulate liquid fuel in the anode microchannel without any pumping component. By employing the directional growth of CO₂ gas bubbles by the intrinsic electrochemical reaction and removal of them by hydrophobic venting, a compact design of μ DMFC was implemented. The complexity and cost of the system can be reduced by eliminating the gas/liquid separator and the external pump. Without the external fuel pump, significant portion of power consumption on fuel delivery (estimated to be more than 10%) can be saved. The fuel circulation has been verified both by visual confirmation and by the self-sustainability test of the fuel cell.

ACKNOWLEDGEMENT

The authors would like to thank Professors C.-M. Ho, T. J. Yen and Dr. T. Cubaud for their discussions and suggestions, as well as Mr. J. Jenkins and Ms. A. Lee for their help with the manuscript.

REFERENCES

- [1] E. Sakaue, "Micromachining/Nanotechnology in Direct Methanol Fuel Cell," *Proc. IEEE Int. Conf. MEMS*, Miami, FL, 2005, pp. 600-5.
- [2] MTI micro fuel cell: "<http://www.mticrofuelcells.com/>".
- [3] IBM & Sanyo's μ DMFC: "<http://www.ibm.com/news/be/en/2005/04/11.html>".
- [4] Toshiba's μ DMFC: "http://www.toshiba.co.jp/about/press/2004_06/pr2401.htm".
- [5] K. Yoshida, Y. Hagihara, S. Tanaka, and M. Esashi, "Normally-Closed Electrostatic Micro Valve with Pressure Balance Mechanism for Portable Fuel Cell Application," *Proc. IEEE Int. Conf. MEMS*, Istanbul, Turkey, Jan. 2006, pp. 722-5.
- [6] D. D. Meng, J. Kim, and C.-J. Kim, "A degassing plate with hydrophobic bubble capture and distributed venting for microfluidic devices," *Journal of Micromechanics and Microengineering*, 2006, vol. 16, pp. 419-24.
- [7] D. D. Meng and C.-J. Kim, "Micropumping by Directional Growth and Hydrophobic Venting of Bubbles," *Proc. IEEE Int. Conf. MEMS*, Miami, FL, Jan. 2005, pp. 423-6.
- [8] D. D. Meng, T. Cubaud, C.-M. Ho, and C.-J. Kim, "A Methanol-Tolerant Gas Permeable Microchannel for Micro Direct Methanol Fuel Cell," *Journal of Microelectromechanical Systems*, 2007 (To appear).
- [9] U.-C. Yi and C.-J. C. Kim, "Soft Printing of Droplets Pre-Metered by Electrowetting," *Sensors and Actuators A*, 2004, vol. 114, pp. 347-54.
- [10] D. D. Meng and C.-J. Kim, "Self-aligned Micro Bubble Arrays by Using Surface Tension," *ASME Int. Mechanical Engineering Congress and Exposition*, Anaheim, CA, Nov. 2004, CD: IMECE 2004-62182.
- [11] D. D. Meng and C.-J. Kim, "A Micro Direct Methanol Fuel Cell with Self-Pumping of Liquid Fuel," *Tech. Dig. Solid State Sensor, Actuator and Microsystems Workshop*, Hilton Head Island, SC, 2006, pp. 120-3.