

# A passive fuel delivery system for portable direct methanol fuel cells

Z. Guo, Y. Cao\*

*Department of Mechanical and Materials Engineering, Florida International University, Miami, FL 33174, USA*

Received 5 December 2003; received in revised form 26 December 2003; accepted 26 December 2003

## Abstract

A passive device is utilized for transferring methanol into water through a wick material. The wick material preferentially has a higher wicking capability with respect to methanol than water, and operates in a siphon fashion with the intake end in contact with methanol and the discharge end in contact with water. Due to the difference of wicking capabilities, a net amount of methanol is pumped into water. The device described above is used as a fuel delivery component for a liquid-feed fuel cell system, such as a direct methanol fuel cell (DMFC), which directly utilizes a liquid fuel without an intermediate reforming process. In the present experimental study, methanol and water are stored separately in two containers and a wick is positioned between the containers as a siphon, with the aqueous methanol solution communicating with the anode of the DMFC. Methanol is siphoned from the methanol container to the water container in situ when the methanol in the water is consumed during the operation of the fuel cell. Through a proper selection of the wick and the containers, the methanol concentration near the anode of the DMFC was maintained within a preferred range.

© 2004 Elsevier B.V. All rights reserved.

*Keywords:* Direct methanol fuel cell; Passive pump; Capillary action

## 1. Introduction

The direct methanol fuel cell (DMFC) has emerged as an attractive power source for portable devices because of its high-energy density in generating electric power from fuel. Currently, one of the most fundamental limitations of direct methanol fuel cells is that the fuel supplied to the anode of the DMFC must be a very dilute aqueous methanol solution (usually 0.5–2.0 M, which is translated into a methanol mass concentration of 1.6–6.4%) [1]. If the methanol concentration is too high, methanol crossover would occur, which could significantly reduce the efficiency of the fuel cell. If a DMFC is fueled with a dilute aqueous methanol solution, the fuel cell operation time per refuel would be very short, which would considerably diminish the advantage of a DMFC over a conventional battery. To overcome this difficulty, complex fuel delivery systems based on modern microsystem technology were proposed. The proposed fuel delivery systems would include micro-pumps, a methanol sensor, and a control unit. The fuel delivery system adds considerable cost to the fuel cell system and consumes a considerable amount of electricity from the fuel cell, which in turn significantly reduces the net power output of the fuel cell. As a result, the

DMFC would have tremendous difficulty to compete with the conventional battery technology in terms of cost and power output [2].

In this paper, a novel pumping device based on the concept proposed by Guo and Cao [3] is described as a passive means to transferring methanol into water. The pumping device is then used in a passive fuel delivery system for direct methanol fuel cells. Experimental results are presented for a DMFC with and without incorporating this fuel delivery system.

## 2. Capillary pump

It is well known that a liquid wets some solids and not others. The contact angle, which is the angle between the edge of the liquid surface and solid surface, measured inside the liquid, is a measure of the degree of wetting. We normally say that a liquid wets a surface if the contact angle is less than 90° and does not wet if the contact angle is more than 90°. Values of contact angle less than 20° are considered strong wetting, and values of contact angle greater than 140° are strongly nonwetting. Water on clear glass represents a wetting case. Water on Teflon or mercury on clean glass represents a nonwetting case. It is found that generally liquids with low surface tension easily wet most solid surfaces resulting in a zero contact angle, which means that the

\* Corresponding author. Tel.: +1-305-348-2205; fax: +1-305-348-1932.  
E-mail address: [yiding.cao@fiu.edu](mailto:yiding.cao@fiu.edu) (Y. Cao).

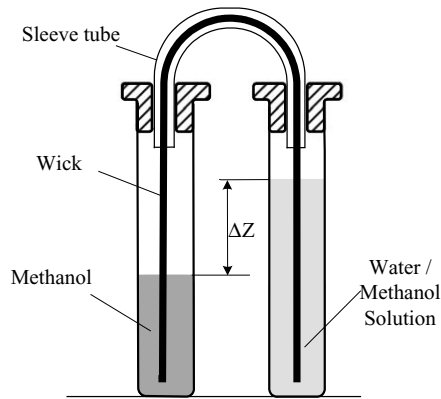


Fig. 1. A wick used for transferring methanol into water.

molecular adhesion between solid and liquid is greater than the cohesion between the molecules of the liquid. Liquids with high surface tension mostly give a finite contact angle, and here the cohesive forces become dominant. The surface tension of water is 72.75 mN/m at 20 °C; and common organic liquids have surface tensions around 20–30 mN/m. We can expect that organic liquids, such as methanol and ethanol, preferentially wet most solid surfaces better than water. For example, Teflon is highly hydrophobic (not wetted by water), but it can be completely wetted by a low surface tension liquid (such as methanol and ethanol).

As mentioned in Section 1, one of the objectives of the present work is to provide a device for transporting methanol into water through a wick material. As shown in Fig. 1, a wick material is disposed in a siphon fashion with an intake end in contact with methanol, which preferentially wets the wick, and a discharge end in contact with water, which wets the wick material weakly. The wick comprises a porous material from a group of materials consisting of ceramic, fiberglass, carbon fiber, polymers, and cotton. The net mass transfer between containers will thus be determined by two competing capillary-pressure driven flows in the wick. Be-

cause the wicking capability of the wick for methanol is higher than for water, it is expected that the apparent velocity of methanol in the wick is higher than that of water. Therefore, methanol will reach the top portion of the wick first. Then gravity will accelerate the movement of methanol and sweep water down into container. Apparently, the transportation process of methanol dominates the liquid movement in the wick, and, as a result, methanol is pumped from the methanol container to the water container.

The experiment setup used to prove the above concepts is shown in Fig. 1. Two glass tubes, with an outer diameter of 13 mm, an inner diameter of 10 mm, and a length of 100 mm, were arranged vertically side by side. Methanol and water were added to the two containers respectively to the same vertical level. The experiment was done at room temperature, 20 °C. Within the first few hours of the experiment, the liquid level in methanol container decreased, and the liquid level in water container increased. The vertical difference of the two liquid levels was denoted as  $\Delta Z$  herein as shown in Fig. 1. This indicated that methanol was pumped into the water container. In the first few weeks, the vertical difference of the two liquid levels reached its maximum value, which was followed by a very slow process of decrease. After about 2 months, the vertical difference of the two liquid levels became nearly stable.

Fig. 2 is a plot of the vertical differences of the two liquid levels measured with a number of wicks versus time. The plateaus of vertical differences of the two liquid levels are of principal interest. The wicks used in the test are made of a wide variety of materials ranging from high-energy surface to low-energy surface media, which include fiberglass, Nextel<sup>®</sup>440 ceramic fiber, polyethylene fiber and PTFE tape. Some specifications of these wicks are shown in Table 1. Fiberglass is hydrophilic (small water contact angle), whereas Nextel<sup>®</sup>440 ceramic fiber, polyethylene fiber and PTFE tape are usually considered hydrophobic (large water contact angle). In theory, liquids having surface

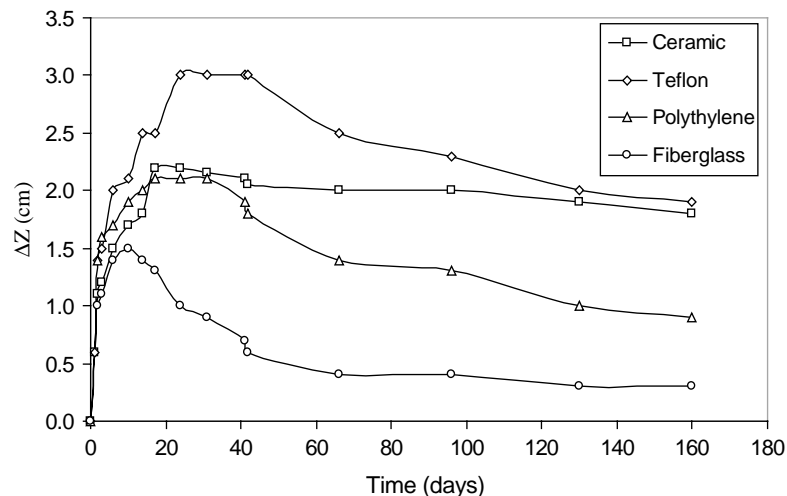


Fig. 2. Vertical differences of the two liquid levels measured with a number of wicks vs. time.

Table 1  
Some specifications of wicks

Wick	Material	Diameter (in.)	Manufacturer
Fiberglass 1286	Fiberglass	1/4	Pepperell Braiding Company
Nextel® 440 Sleeve	Ceramic	1/16	Omega Engineering Inc.
Spectra® Cable	Polyethylene	0.060	Small Parts, Inc.
PTFE thread seal tape	PTFE	–	–

tensions lower than a solid critical surface tension should uniformly and completely wet the solid. Methanol with a low surface tension of 22.65 mN/m at 20 °C is expected to wet most of these solid materials thoroughly. In contrast, water with a higher surface tension can only partially wet these solids.

From the results in Fig. 2, it is apparent that the ceramic wick used in the present test is advantageous in terms of practical applications. First, the ceramic wick exhibits a one-way transportation characteristic, i.e., it only allows methanol to flow from the methanol container to the water container and almost no water can flow back. Second, the overshooting of the test curve is very small and its quasi-equilibrium value of  $\Delta Z$  can be reached quickly. These features could allow the determination of the methanol concentration in the water container at the quasi-equilibrium condition if the capillary pump is designed in a proper way, as will be described later.

### 3. DMFC with a capillary pump

The working mechanisms and embodiments of the capillary pump have been described above. One of the most important applications of the capillary pump is the fuel storage and delivery assembly of a liquid-feed fuel cell such as a DMFC.

Fig. 3 shows a direct methanol fuel cell with which the fuel storage and delivery system of the present work is used. The fuel storage and delivery system comprises a methanol container, an aqueous methanol solution container and a wick.

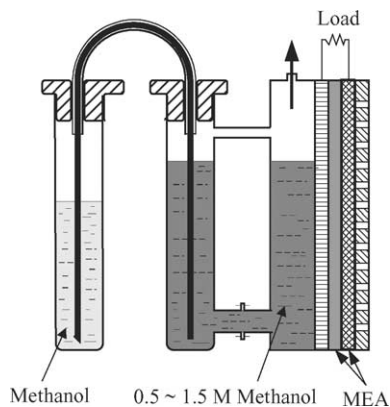


Fig. 3. The air-breathing DMFC with a passive fuel delivery system.

Methanol in the methanol container is transported through the wick to the aqueous methanol solution container, where it is mixed with the water and forms an aqueous methanol solution. The aqueous methanol solution container was connected to a fuel reservoir at the anode of the fuel cell. Therefore, an aqueous methanol solution is supplied to the anode of the membrane electrode assembly (MEA) which includes an anode, a membrane electrolyte and a cathode. As the mixture of methanol and water is introduced into the anode while oxygen (air) is introduced into the cathode from the holes in a fixture plate, reactions occur at anode and cathode. As a result, electrons flow from the anode through the external load to the cathode, while hydrogen ions flow from the anode through the membrane electrolyte to the cathode. As long as the chemical reactions continue, a current is maintained through the external load. Because of the chemical reactions, carbon dioxide will accumulate in the reservoir as a reaction product. A CO<sub>2</sub> release mechanism can be used to release carbon dioxide. The CO<sub>2</sub> release mechanism could be a release valve. As the pressure is built up to a certain level, the release valve is opened momentarily, which releases the carbon dioxide to the atmosphere. To operate direct methanol fuel cells at optimal conditions, the concentration of methanol in the reservoir should be kept in a certain range (e.g., 0.5–2.0 M). In theory, the consuming ratio between the methanol and water at an anode is 1:1. Departures from this value in practice occur frequently for many fuel cells. The value of this ratio for a particular fuel cell can be obtained from experimental studies. To maintain a preferred methanol concentration near the anode, the ratio of the methanol and water supplied to the anode of a fuel cell should be equal to the consuming ratio of the methanol and water at the anode. If the ratio of the cross-sectional areas of the methanol and water containers are chosen to be equal to the consumption ratio of the methanol and water by the fuel cell, the consumed methanol could be compensated with the same amount. As a result, an approximately constant methanol concentration can be maintained at the anode.

Fig. 4 illustrates schematically a fuel cell system with an enhanced fuel delivery mechanism, in which a water permeating layer is positioned approximately to the anode and the wick is attached at the water permeating layer. In this case, no separate aqueous methanol solution container is needed; the fuel reservoir also serves as an aqueous methanol solution container. The water permeating layer is made of a material selected from a group of materials consisting

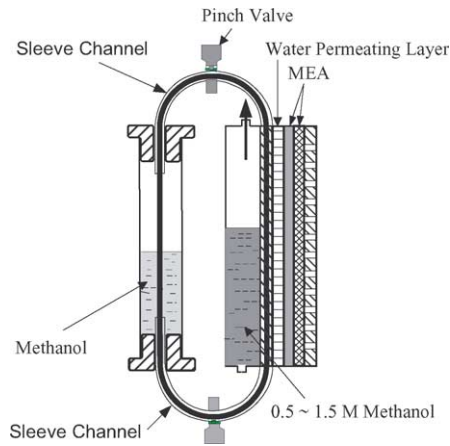


Fig. 4. A DMFC with an enhanced passive fuel delivery system.

of screen materials, non-woven fabrics, and woven fabrics as long as it has a capability of wicking a carbonaceous fuel/water mixture and has a large proportion of pores to allow the carbon dioxide to vent out of the surface of the anode. Inside the water permeating layer, dilute methanol aqueous solution moves upward due to the capillary action and methanol moves downward through the wick. The diffusion of the methanol from the wick to the water permeating layer will keep the methanol concentration in the liquid permeating layer constant. The wick is placed inside a Teflon sleeve channel, so that evaporation of methanol into air is prevented. The Teflon sleeve channel was designed to compress the wick tight enough to block the free flow of methanol and water when the wick is positioned downward, but not too tight to stop the capillary action. The advantage of the configuration in Fig. 4 compared to the configuration in Fig. 3 is that the fuel delivery system can work in any orientation. Two flow control pinch valves are mounted on the outer wall of the sleeve tubes. Through fine adjustments of the pinch valve, the compressive force upon the wick and consequently the permeability of the wick can be adjusted. As a result, the flow rate through the wick can be easily and repeatedly controlled if it is desired.

To validate the fuel storage and delivery system according to the previous descriptions, a direct methanol fuel cell having a fuel storage and delivery assembly similar to that shown in Fig. 3 was used in a validation experiment. The tested fuel cell was based on a single cell with a square action electrode area of  $16\text{ cm}^2$ . It was made by H-TEC, a Germany company. Originally, it had only one liquid container with an inner diameter of 16 mm, and the cell used 3% methanol–water solution. To determine the methanol–water consuming ratio, experiments were conducted as following: a solution of 3% methanol concentration was added the container. After a 3-h operation, a small amount of solution sample was taken out to measure its methanol concentration. According to the methanol concentration measured, a certain amount of methanol was added to the container for compensation of the methanol consumed. After a total 12-h

operation, the water consumed was also measured. The consumed methanol in each 3-h operation is added to obtain the total methanol consumption. Through this procedure, the methanol–water consuming could be determined. It was found that the methanol and water consuming ratio for the H-TEC fuel cell used in this study is about 3:5. So we select a glass tube with an inner diameter of 12.5 mm as methanol container (the cross-sectional area ratio of the methanol container to water container therefore is roughly equal to the methanol and water consuming ratio). This glass tube was positioned side by side in the original liquid container and connected by a wick in a capillary siphon fashion as shown in Fig. 3. During the operation of the modified fuel cell system, methanol was siphoned to the water container in situ to maintain the methanol concentration near 3%, as shown in Fig. 3. A fuel loading of 12 ml pure methanol was placed in the methanol container and 20 ml of de-ionized water was in the water container. A small fan was used as the external load in the experiment. The output voltage of the fuel cell was shown in Fig. 5. The data reported here were obtained at a temperature of  $20\text{ }^\circ\text{C}$ . With prolonged operation, the cell temperature became stable at  $22\text{ }^\circ\text{C}$ . The fuel cell operated more than 260 h until the methanol in the fuel container was completely consumed. A comparative experiment was done without using the present fuel storage and delivery assembly. The same fuel cell was used to power the same small fan. A fuel load of 20 ml of 1.5 M aqueous methanol solution was directly added to the fuel reservoir, and the fuel cell output voltage was recorded until the voltage was too low to power the fan. It is apparent from Fig. 5 that the fuel cell according to the present work produced a stable output voltage for 11 days, whereas the same fuel cell in comparative experiment produced an output voltage only for less than 24 h. The reason for the poor performance of the comparative experiment is that the methanol concentration of the aqueous methanol solution in the fuel reservoir continued to decrease as the methanol was consumed at the anode. In the validation experiment, however, methanol can be transferred continuously from the methanol container to the fuel

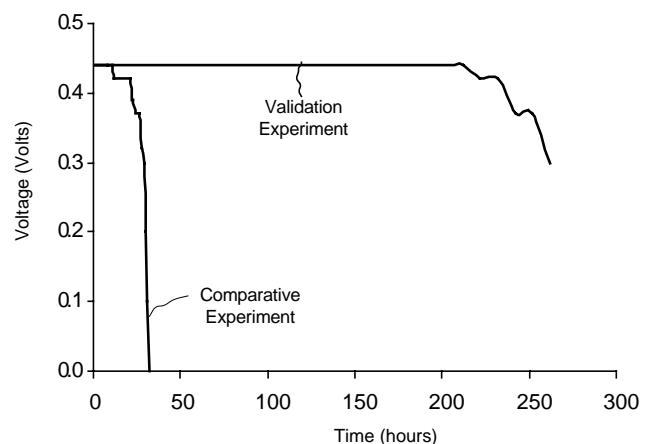


Fig. 5. Comparison of DMFC output voltages.

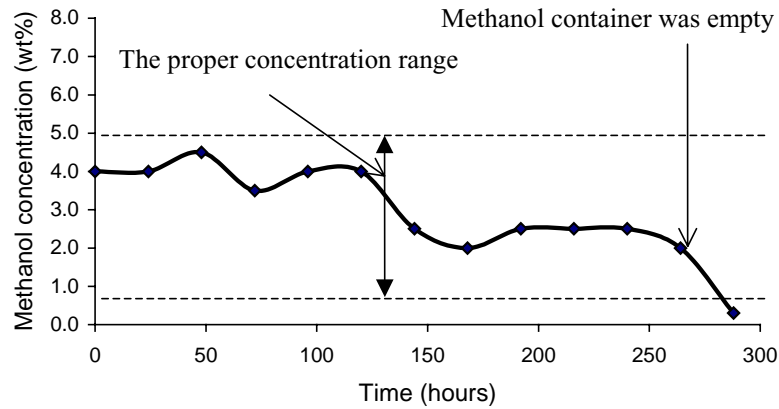


Fig. 6. Methanol concentration during the operation of the fuel cell.

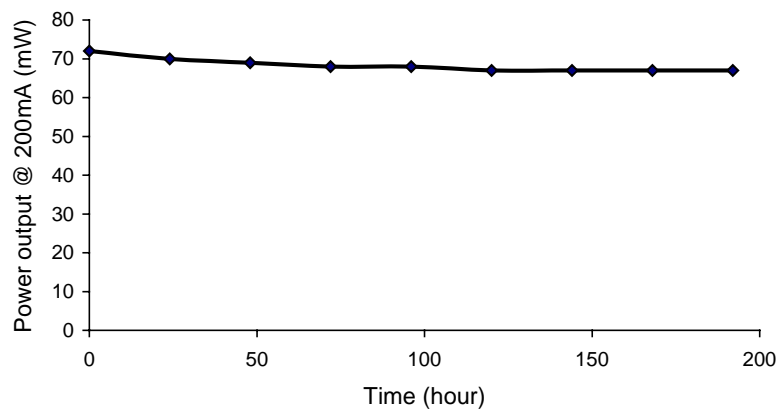


Fig. 7. Fuel cell power output at 200 mA with a loading of 40 ml methanol and 50 ml water.

reservoir through the wick. As a result, the methanol concentration in the fuel reservoir could be maintained within a preferred range for a prolonged period of time until the methanol in the fuel container is completely used by the fuel cell. Fig. 6 shows the change of methanol concentration during the validation fuel cell operation. It can be seen that methanol concentration was kept in the proper concentration range before the methanol was depleted.

A second type of test cell was a single cell with a square active electrode area of  $25\text{ cm}^2$  as shown in Fig. 4. The MEA and gas diffusion layers were purchased from Lynntech Industries, Ltd. The catalyst used in the anode was Pt/Ru black with a loading of  $4.0\text{ mg/cm}^2$  and carbon cloth was used as a gas diffusion layer on the anode side. The catalyst used in the cathode was Pt black with a loading of  $4.0\text{ mg/cm}^2$  and ELAT (carbon cloth based material) was used as a gas diffusion layer on the cathode side. Two porous polyethylene sheets (obtained from Small Parts, Inc.), one with hydrophilic treatment and the other without, were used as water permeating layer and wick material respectively. Both sheets have a thickness of  $1/16\text{ in.}$  and a mean pore size ranging between  $15\text{ and }45\text{ }\mu\text{m.}$  A series of  $3\text{ mm}$  diameter holes were made on these porous polyethylene sheets to allow the passage of fuel and carbon dioxide. The MEA and gas diffusion layers were then sandwiched between

two current collectors, which were made from  $0.5\text{ mm}$  stainless steel plates with a series of  $1\text{ mm}$  diameter holes for the passage of fuel and ambient air. The wick material (porous polyethylene) and water-permeating layer (porous polyethylene with hydrophilic treatment) were attached to the current collector on the anode side. Finally, the cell was held together between two acrylic plates by means of a set of eight retaining bolts positioned around periphery of the cell. The air cathode is operated by natural diffusion of oxygen in the ambient air to the cathode catalyst layer. The anode directly contacts with the liquid permeating layer that contains methanol diffused from the methanol wick with no active mechanical device required for reactant supply. Fig. 7 shows the power output of the fuel cell at  $200\text{ mA}$  over a period of  $190\text{ h}$  with  $40\text{ ml}$  methanol and  $50\text{ ml}$  water. The experimental results reported here were obtained at a room temperature of  $23\text{ }^\circ\text{C.}$  Under prolonged operation, the cell temperature became stable at  $26.5\text{ }^\circ\text{C.}$  The overall efficiency of energy conversion in the operation period was about  $6.5\%.$

#### 4. Conclusions and discussions

By incorporating the capillary pump of the present study in the DMFC, methanol and water can be carried separately

and mixed in situ during fuel cell operation, which provides a much simpler, cost effective and reliable fuel delivery system for direct methanol fuel cells. Experiments have shown that the passive fuel delivery system significantly extends the fuel cell operation time per refill. The 70 mW fuel cell sustained stable performance for approximately 10 days, without refueling. It is expected that, with an improved design, a prolonged operation beyond 10 days could be achieved with the same fuel loading.

DMFC power densities in the range of 10–30 mW/cm<sup>2</sup> of membrane active area, using air-breathing cathodes and with cell temperatures close to the ambient have been achieved recently. The power density in our design was only 3 mW/cm<sup>2</sup>. Analysis has shown that the capillary pump has sufficiently large capability to supply methanol to the anode. Future effort will be focused on the improvement of the MEA and the hardware related to the fixture to improve the power density of the passive fuel cell.

The capillary pump adds almost no cost and volume; the fuel and water containers are needed anyway. With the passive pump, no ancillary power consumption and no external power source as starter are needed by the DMFC, which could produce an ideal DMFC that is a truly stand alone, maintenance free, complete passive fuel cell.

## References

- [1] A. Heinzel, V.M. Barragán, A review of the state-of-the-art of the methanol crossover in direct methanol fuel cells, *J. Power Sources* 84 (1999) 70–74.
- [2] C.R. Korpella, W.J. Ooms, D.L. Wilcox, J.W. Bostaph, Direct Methanol Fuel Cell System and Method of Fabrication, US Patent 6387559 B1.
- [3] Z. Guo, Y. Cao, Passive Fluid Pump and its Application to Liquid-Feed Fuel Cell System, US Patent Pending, 2002.