Miniature DMFCs with passive thermal-fluids management system

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Abstract

A new miniature DMFC system that includes a fuel cell stack, a fuel tank and a passive ancillary system (termed "thermal-fluids management system" in this paper) is presented. The thermal-fluids management system utilizes passive approaches for fuel storage and delivery, air breathing, water management, CO_2 release and thermal management. With 5.1 g of neat methanol in the fuel cartridge, a prototype has successfully demonstrated 18 h of continuous operation with total power output of 1.56 Wh.
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1. Introduction

Miniature direct methanol fuel cells (DMFC), which promise high energy densities and instant refueling, present beneficial opportunities for use as a power source for small mobile devices (e.g., notebook computers, personal digital assistants, music systems and cellular telephones). Although extensive research and industrial efforts have focused on development of miniature DMFCs in recent years, there is still no truly commercial miniature DMFC product available for consumer electronic devices so far. Typically, it has been difficult to provide an ancillary system that ensures effective power generation processes in a miniature DMFC platform. One of the fundamental limitations to faster development of direct methanol fuel cell technology is methanol crossover. Methanol crossover is the process by which methanol transports by diffusion and electro-osmosis from the anode through the electrolyte to the cathode, where it will react directly with oxygen, producing no current from the cell. Furthermore, methanol has a poisoning effect on the cathode catalyst, which will reduce the performance of the cell. The methanol crossover rate is roughly proportional to the methanol concentration at the anode, therefore the regulation of methanol feed concentration is needed to reduce methanol crossover. In practice, the fuel supplied to the anode of the DMFC must be a very dilute aqueous methanol solution (usually 2–6 vol% methanol). If the methanol concentration is too high, the methanol crossover problem will significantly reduce the efficiency of the fuel cell [1]. This effect raises the difficulties associated with the need for a sufficient water supply to the anode. It is very clear that carrying water in the system significantly reduce the overall system energy density. It is also well known that a forced air design with an external blower is unattractive for use in small fuel cell systems, as the parasitic power losses from the blower are estimated at 20–25% of the total power output.

The conventional approaches to these problems can be divided into two categories: "active" and "passive". An active system requires moving parts such as a pump or fan to feed fuel and oxygen into the fuel cell stack. Conversely, a passive fuel cell system supplies fuel to the anode in a passive method requiring no external power or moving parts. A series of active DMFC prototypes has been developed at Motorola Labs [2]. These systems are composed of the following components: fuel cell stack, methanol sensor, CO_2 separator, electronic controls, methanol feed pump, circulation pump and pump drivers. The appropriate methanol concentration is maintained by dosing neat methanol from a methanol cartridge into the recirculation anode liquid. This DMFC design is difficult to create because of the complexity in miniaturizing all the required system components and integrating them in a small unit required for portable applications. In addition, system components add considerable cost to the fuel cell system and consume considerable electricity from the fuel cell, in turn significantly reducing the net power output

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Table 1
Summary of technologies used by selected miniature-micro DMFC developers

Fuel cell developers	Technology	Advantages	Disadvantages	Operation mode	Power output
Motorola [2]	The DMFCs developed at Motorola operate in an actively driven mode. The active components used in the system include: methanol sensor, CO_2 separator, electronic controls, methanol feed pump, circulation pump and pump drivers	• A complete system	○ Overall system energy density	Active	0.1 W to a few watt
		• Flexible in design	○ Reliability and maintenances		
		• Pure methanol fuel • Methanol sensor	○ Costs ○ Manufacture problems		
		• Control circuitry			
MTI MicroFuel Cells [7]	The system uses effluent gases (CO_2) to drive liquids (methanol and water) among elements of the fuel cell system. A number of valves are used to control this operation	• Self-driven	○ CO_2 driving pump	Passive	A few watts
		• No Micro-pumps • Neat Methanol	○ Reliability ○ Manufacture of valves		
Manhattan Scientific Inc. [8]	A fuel ampoule is use to deliver fuel by diffusion through the ampoule walls. The methanol vapor condenses at the anode surface and combines with water to form a water/methanol solution	• No moving parts	○ Low power density	Passive	Less than 1 W
		• Ambient operation	○ Water management		
		• Flexible assemblies	○ Idle loss		
Toshiba [11]	A wick structure is used to deliver liquid methanol solution into the cell. The fuel is vaporized within the cell and supplied to the anode. The liquid fuel tank is equipped with a pressure control mechanism for controlling the fuel flow rate	• High methanol concentration solution	○ Thermal management	Passive	0.1 W to tens watt
		• No moving parts	○ Slow starting ○ No pure methanol		
Samsung [12]	A low methanol crossover membrane was developed at Samsung. The membrane could maintain the same proton conductivity and near 30% crossover vs. Nafion when 5 M or higher concentrations of methanol were used	• Simpler design	○ New electrolyte membrane	Passive or active	A few watt to tens watt
		• Cost reduction • High power density	○ Endurance ○ Fuel supply system		
KIST[a] [13]	A dilute methanol solution (4 M) is directly fed to the fuel cell stack	• Simple design	○ Not a complete system	Passive	Sub-watt to a few watt
		• High power density	○ Short Runtime per refueling		
		• Low cost			
Florida International University [14]	In this passive system, methanol fuel and water are stored separately in two containers. A wick is disposed between these containers in a siphon fashion, with the container of the aqueous methanol solution communicating with the anode of the DMFC. Methanol is siphoned from the methanol container to the aqueous solution container in situ	• Very Simple design	○ Initial research stage	Passive	Sub-watt to a few watt
		• Low cost • No moving parts	○ Carrying water ○ Methanol concentration control		

Table 1 (*Continued*)

Fuel cell developers	Technology	Advantages	Disadvantages	Operation mode	Power output
Present Paper [15,16]	This proposed research concerns the development of miniature passive DMFCs with a new thermal-fluids management system and a new integrated methanol sensor. The thermal-fluids management system utilizes passive approaches for fuel storage and delivery, air breathing, water management, CO_2 releasing and thermal management. Based on the response of the sensor, the control of the methanol concentration to the desired level can be achieved	• Simple design	○ New technology	Passive	0.1 W to 20 W
		• Low cost • Methanol sensor • No moving parts • Neat methanol storage • High power density • A complete self-sustainable system	○ High risk		

[a] Korea Institute of Science and Technology.

of the fuel cell. As a result, the actively driven DMFC is not competitive, relative to the conventional battery technology, in terms of cost and power output.

One alternative to actively driven systems is passive DMFC systems. Certainly, a number of diverging passive methods have been taken to overcome the difficulties associated with thermal-fluids management issues, each with its own merits and limitations as shown in Table 1. The simplest method involves utilizing reservoirs containing methanol/water mixtures at the anode [3–5]. This method, which is passive in nature, has the advantage of system simplicity. The problem with this approach is that carrying a dilute methanol solution results in a significant penalty in energy density of the fuel cell. Kim et al. developed a passive DMFC system having a total active area of $27\,cm^2$, which composes two planar stacks [3]. A fuel reservoir was sandwiched between these two planar stacks. With 4 M aqueous methanol solution, the system produced a power output of 1 W at room temperature. Han and Park used 2 M methanol solution to feed the fuel cell stack [4]. For operation over an extended period of time, they used a large reservoir to eliminate the effect of changing of methanol concentration. An external pump is usually needed to supply the dilute methanol solution to DMFC stacks [5].

Gottesfeld at MTI MicroFuel Cells described the DMFC system that has two features: on-board neat methanol and water recycling [6]. The system uses effluent gases (CO_2) to drive fluids among elements of the fuel cell system. This passive fuel delivery system includes a number of valves to control liquid and gas flow, which is difficult to implement on a miniature scale.

Hockaday disclosed a passive fuel delivery system involving a fuel ampoule for delivering fuel by diffusion through the silicone rubber film walls [8]. The silicone rubber film is composed of polydimethylsiloxane (PDMS) as well as silica filler, which has excellent processing ability for making ultra-thin composite membranes [9]. PDMS membranes exhibit selective transport for organic molecules with respect to polar molecules such as

water and low molecular weight gases such as nitrogen, oxygen, and helium [8,10]. The permeation of methanol through a PDMS membrane involves three physical processes: absorption of liquid methanol molecules at the feed side of the membrane, diffusion of the dissolved methanol through the membrane, and desorption of methanol vapor from the permeate side. Methanol vapor condenses at the anode and keeps the local methanol concentration next to the catalyzed anode surface at about 3%, or below, which is the concentration level for the anode reaction to proceed with minimal methanol loss due to crossover. By using the vapor fuel delivery, the silicone rubber films require no physical contact with the fuel cell; orientation-independent operation is guaranteed.

In a US patent granted to Toshiba in 2003, the company disclosed a mechanism to deliver liquid methanol fuel by capillary action into the cell. The fuel is then vaporized by heat within the cell and supplied to the fuel electrode, thereby generating electric power [11]. The liquid fuel tank is equipped with a pressure control mechanism for introducing a required amount of the liquid fuel from a liquid outlet port into the unit cell.

Chang developed a low methanol crossover electrolyte membrane, which maintained the same proton conductivity and near 30% crossover versus Nafion® when 5 M or higher concentrations of methanol were used [12].

While the trend towards passive techniques is becoming an attractive choice for driving miniature DMFCs, the above-mentioned passive techniques focus mainly on one aspect in the DMFC, namely fuel delivery. Fuel storage, CO_2 release, water and thermal management, and orientation-independent operation are some of the other unresolved issues in such systems. In designing a complete power system these issues must also be addressed.

In this paper, we present a new miniature passive DMFC that includes a fuel cell stack and an ancillary system (termed "thermal-fluids management system" in this paper). The thermal-fluids management system utilizes passive approaches

for fuel storage and delivery; air supply, water management, CO_2 release and thermal management. In the thermal-fluids management system, methanol and water are stored in hydrophobic and hydrophilic porous media, respectively. The water storage medium is positioned close to the anode of the fuel cell stack. A methanol concentration gradient, established between the neat methanol storage medium and the anode catalyst layer, delivers methanol to the anode catalyst layer. Capillary action dominates the liquid movement in the porous media; therefore, gravitational effects can be ignored. This enables the DMFC to work in any direction, without any moving parts. A hydraulic pressure, which is developed in the region between the cathode catalyst layer and gas diffusion layer (GDL), will force some of the liquid water to the anode side. The fuel cell stack used in this study incorporates a window-frame structure that provides a large open area for more efficient passive fuel and air delivery. Furthermore, the modular design of the stack makes it possible to fabricate the fuel cell stack separately from the thermal-fluids management system [17].

2. Operation of DMFCs with passive thermal-fluids management system

In a low temperature range, DMFCs are operated with a liquid water–methanol mixture at the anode and air at the cathode. The electrochemical reactions are listed as follows:

At the anode, oxidation of methanol takes place:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{1}$$

And the oxygen is reduced at the cathode according to:

$$6H^+ + 6e^- + 1.5O_2 \rightarrow 3H_2O \tag{2}$$

The overall reaction in the cell is:

$$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O \tag{3}$$

Fluids involved in a miniature DMFC operation are:

Reactants: $CH_3OH_{(l)}$, $H_2O_{(l)}$, $O_{2(g)}$
Byproducts: $CO_{2(g)}$, $H_2O_{(l)}$

It is important to notice that the fuel supplied to the anode of the DMFC must be a very dilute aqueous methanol solution due to the methanol crossover problem. There are many challenges relative to miniature direct methanol fuel cell systems, which include:

- Providing an efficient thermal-fluids management system.
- Providing passive methods for fluids transport in a miniature DMFC, specifically intended for:
  ○ Supplying neat methanol to the cell with uniform distribution.
  ○ Transporting water from the cathode (air) side to the anode (fuel) side.
  ○ Supplying oxygen (O_2) to the cell with uniform distribution across the cell.
  ○ Releasing CO_2 from the cell.

- Providing a storage mechanism for reactants (methanol and water).
- Providing a mechanism for efficient operation and high stability in various physical orientations.
- Providing a mechanism for controlling the methanol concentration.
- Providing a mechanism for operation in extreme environmental conditions, such as sub-freezing and dry, hot weather.
- Providing a mechanism for starting and shutting down the fuel cell system.

The key challenge relating to miniature DMFCs is how to achieve the desired power performance while operating in a passive mode in order to miniaturize the whole system and reduce cost. An innovative design of the thermal-fluids management system is conceived to overcome the above-mentioned challenges and control methanol concentration at the anode thereby reducing methanol crossover.

2.1. Proposed passive methanol delivery system

Methanol, with a low surface tension ($22.65\,\mathrm{mN\,m^{-1}}$ at $20\,^\circ C$), wets most solid surfaces. For instance, methanol can wet Teflon®, one of most hydrophobic materials. In contrast, water, with a relatively high surface tension of $72.88\,\mathrm{mN\,m^{-1}}$ at $20\,^\circ C$, is a non-wetting liquid for these hydrophobic materials. If said materials are porous, methanol fills these hydrophobic media.

Hydrophobicity is an inherent property for many polymers, notably polyethylene and polytetrafluoroethylene (Teflon). These hydrophobic porous media can be used as neat methanol carriers because methanol preferentially wets the surfaces of the media and is drawn within the media by capillary action (the capillary pressure of methanol is negative in these porous media). In contrast, hydrophobic porous media repels water naturally (the capillary pressure of water is positive in hydrophobic media).

Other materials, such as carbons and inorganic oxides, are hydrophilic. The hydrophilicity of porous media can also be achieved by hydrophilic treatments. Hydrophilic porous media are good water or water/methanol mixture carriers.

Fig. 1 shows a miniature DMFC with the thermal-fluids management system presented in this study. Seven points of interest in the miniature DMFC are denoted by the reference letters A, B, C, D, E, F, and G, respectively. These points represent interfaces between layers. A methanol storage layer (between points A and B) is hydrophobic and used to store neat methanol (serving as a methanol carrier). Through a methanol distribution layer (between points B and C), methanol can be distributed uniformly to a hydrophilic medium (between points C and D), which is positioned adjacent to the anode gas diffusion layer (between points D and E). Water from the reaction will be transferred from the cathode to the hydrophilic medium simultaneously (as discussed below). The mixture of methanol and water is formed in the region of the hydrophilic medium next to the anode catalyst layer. Methanol is supplied to the anode, thereby generating electric power. Besides liquid components (water and methanol), water and methanol vapors, and CO_2 released from electrochemical reactions also exist in this porous media.
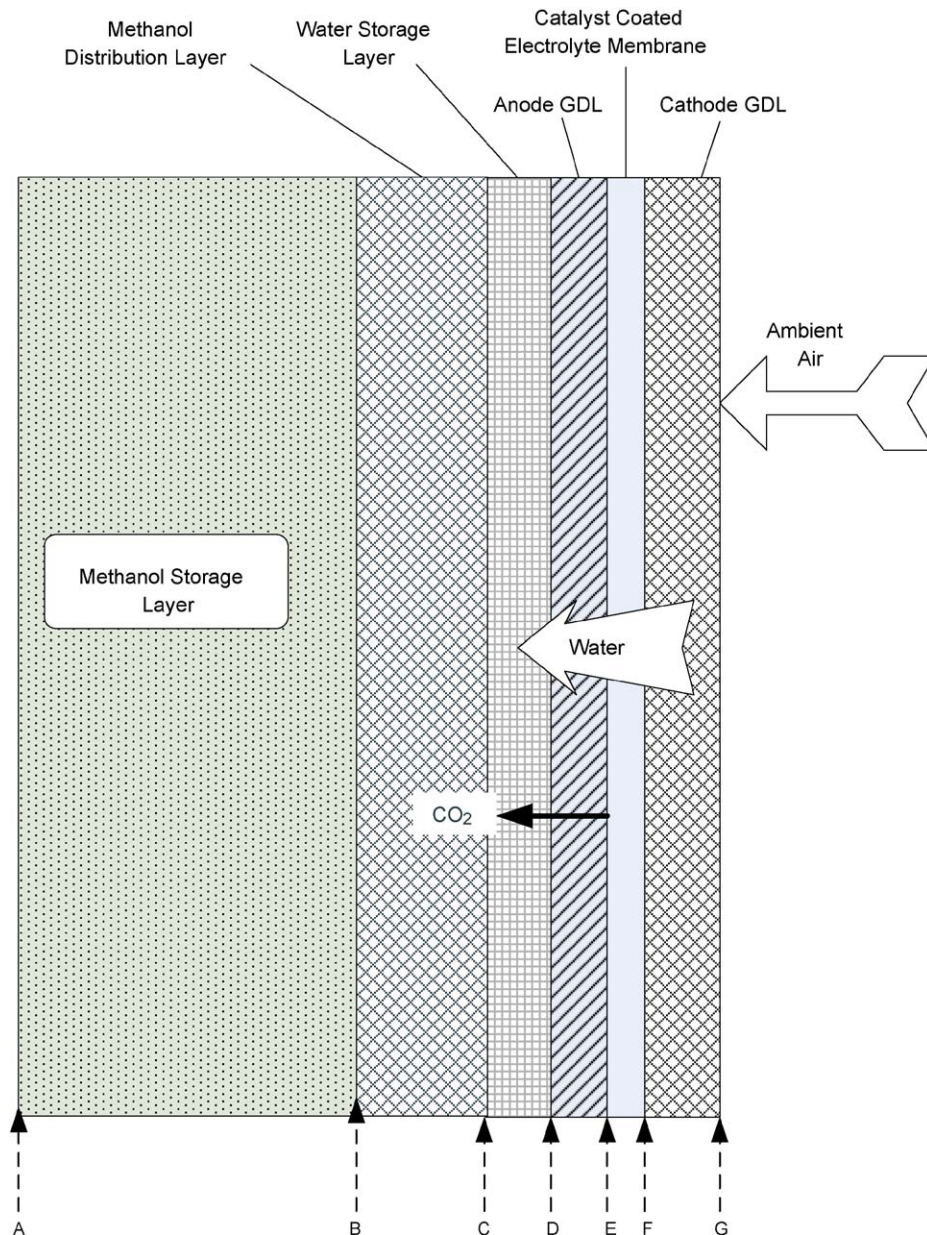
Fig. 1. Schematic of the thermal-fluids management system for a passive miniature DMFC.

Referring now to Fig. 2, one may see how capillary pressure varies from points A to G with water and methanol. Methanol thoroughly wets the methanol storage and methanol distribution layer. The methanol capillary pressure in these regions is negative. As a result, methanol can be drawn into the porous media. The methanol storage layer, with extremely high porosity, functions as neat methanol storage. The methanol distribution layer, with extremely small and evenly distributed pores, serves as a methanol distributor. The water storage layer (between points C and D) is hydrophilic and has negative capillary pressure for both water and methanol, thus the water–methanol mixture can be trapped in the hydrophilic medium.

Fig. 3 shows that the concentration of methanol varies at points A–G under typical operating conditions. This methanol concentration gradient can be used to deliver methanol to the

anode catalyst layer (point E). As expected, the methanol concentration is highest in the methanol storage layer (between points A and B) and lowest in the cathode GDL (between points F and G), with a significant reduction in concentration caused by the electrochemical reactions. While the methanol concentration at point F (cathode catalyst layer) is low, it is not zero, meaning some methanol has crossed over the membrane electrolyte layer (between points E and F) and reached the cathode catalyst layer without supplying any power.

2.2. Proposed water management in the passive DMFC

Observing Eqs. (1)–(3) it is important to notice that water is needed for the reaction at the anode, but there is a net production of water in the overall reaction. This means that a DMFC can
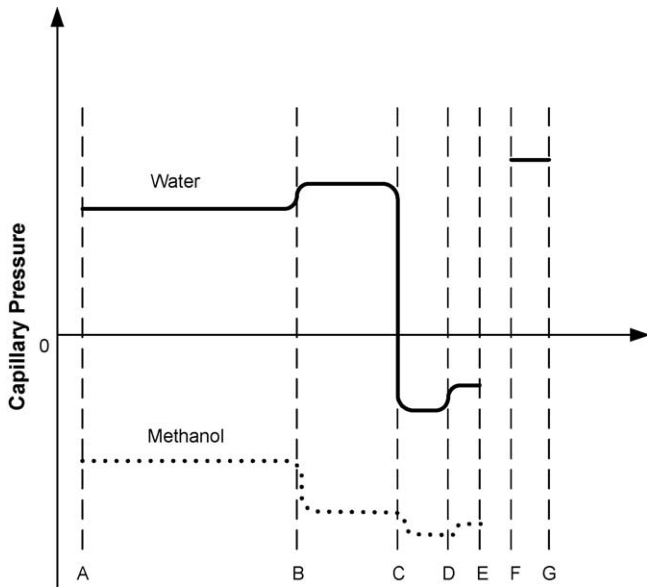
Fig. 2. Capillary pressure distributions in the miniature passive DMFC.

Fig. 4. The air breathing DMFC cathode structure for water recirculation and air filtration.

and/or a higher water contact angle, a higher hydraulic pressure is generated and more water is forced back to the anode side. An optimal design of the GDL can achieve a water balance operation of the miniature DMFC, eliminating the need to add water to the cell.

The proposed water management system is schematically shown in Fig. 4. The combination of the well laminated micro porous sub-layer, the hydrophobic backing and the deep filter layer, together defines a cathode structure of unique water management capacity. This water management system enables to operate a DMFC with direct pure methanol, without the need for any external supply or pumping of water.

2.3. Proposed air filtration in the passive DMFC

At a certain small scale, DMFC's system simplicity is more important than system efficiency. While air breathing mode provides the simplest mechanism for supplying air to the cathode, it also poses challenges for DMFC operation. Firstly, too much air access would quickly dry out the membrane and the cell would cease producing useful output power. On the other hand, if not enough air access is allowed, performance suffers due to oxygen reduction reaction deficiencies. Secondly, air access also effects system start-up from dry conditions. When a dry cell slowly starts to produce water (both from methanol electro-oxidation at the anode and chemical oxidation at the cathode) performance slowly improves as the level of hydration and temperature increases; too much air access will evaporate the water and hinder the start-up process. Thirdly, dirt in air may damage the cathode as the fuel cells are exposed to air.

An air filter will be attached to the outer surface of the cathode, which is permeable to air and impermeable to liquid and airborne environmental contaminants, such as dust and other particulate matter. Its required properties follow from their functions, namely:

(1) Protection for the fuel cell itself against airborne dust—therefore it must have micro pore size.
(2) Preventing external liquids (rain, etc.) from contemning cathode—it must be hydrophobic.
(3) Preventing loss of water vapor in the fuel cell—it must have sufficient thickness.
(4) Preventing loss of heat when the fuel cells are operated in cold environment—it must have low thermal conductivity.

Filtration is the process of separating particles in suspension from a carrier fluid by passing the fluid through a permeable material which may be larger particles, granular, porous or

self-supply water by reusing the water produced at the cathode [18].

Water at the cathode arises from:

- Electrochemical reaction at the cathode as shown in Eq. (2).
- Electro-osmotic drag of water through the membrane from the anode to the cathode.
- Chemical reaction of air and methanol, which permeates through the membrane from the anode (methanol crossover) to the cathode.

In the low-temperature range, liquid water will accumulate in the cathode catalyst layer and the cathode GDL. Several commercial gas diffusion layers are available for DMFC operation. Some of them are very hydrophobic and coated with a thick micro porous sub-layer, which can function as a liquid water barrier layer. A hydraulic pressure, which is developed in the region between the cathode catalyst layer and GDL will force some of the liquid water to the anode side and some of the liquid water to the cathode GDL. This process depends on the properties of the GDL. If the GDL has a smaller average pore size
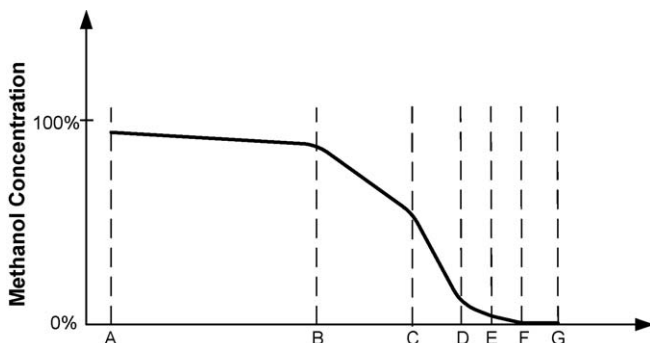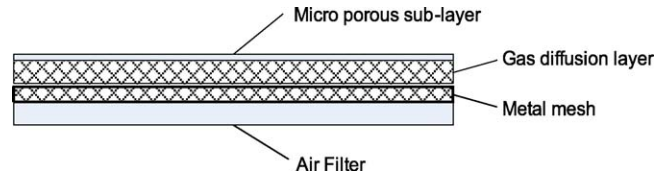

Fig. 3. Methanol concentration distribution in the miniature passive DMFC.

fibrous media. The separated solids may be collected as a cake on the surface of the filtration medium (*surface filtration*) or trapped within the pores of the medium when trying to pass through the tortuous path (*deep filtration*) [19]. A surface filter, like an expanded PTFE membrane (ePTFE) filter, can fill requirement (1) by filtering particles on its surface and requirement (2) by its hydrophobic property. It is hard for a surface filter to fill requirements (3) and (4). In order to fulfill requirements (1–4) deep filtration may be the only functional solution.

3. Experiments and results

The selection of materials used for the thermal-fluids management system was based on experiments which tested methanol storage and distribution, and water storage in porous media. Once the materials were chosen, the methanol delivery portion of the thermal-fluids management system was assembled and tested for proper operation and methanol delivery. Passive tests were run on a fuel cell using dilute methanol solutions to determine the performance of the cell without a thermal-management system for comparison. The thermal-fluids management system was then assembled and tested on a fuel cell.

3.1. Liquid retention in porous media

The methanol storage medium and methanol distribution medium must have substantial hydrophobic characteristics. If a methanol distribution medium is included, the methanol storage medium has to have a porosity that is greater than or equal to the porosity of the methanol distribution medium. The methanol storage medium should ideally have porosity in the range of about 0.7–0.9. The desirable liquid holding capability of methanol storage medium needs to be about 8.0–10.0 g (methanol) per gram of the dry material used to construct methanol storage medium. The desirable average pore size range of the methanol storage medium is from about 10 to 50 μm. The methanol storage medium can be constructed of any inert material or combination of materials having the aforementioned characteristics.

The methanol distribution medium has to have porosity in the range of about 0.1–0.3. The desirable liquid holding capability of methanol distribution medium is in the range of about 0.1–0.3 g (methanol) per gram of the dry material used to construct methanol distribution medium. The contact angle between water and methanol distribution medium should be greater than about 105°. The contact angle between methanol and the methanol distribution medium needs to be less than 50°. The desirable

average pore size range of the methanol distribution medium is about 10–20 μm. The methanol distribution medium can be constructed of any inert material or combination of materials having the aforementioned characteristics.

The water storage medium has to have a porosity that is in the range of about 0.7–0.9. The desirable liquid holding capability of the medium should be in the range of about 15.0–20.0 g (water) per gram of the dry water storage medium. The desirable average pore size range of water storage is about 10–50 μm.

Liquid distribution and mass transfer in porous media play an important role in the proposed thermal-fluids management system. The selected materials that will be used in the subsequence experiments are listed in Table 2. The liquid retention, which was determined by Eq. (4), was first measured for these porous media.

$$R = \frac{M_w - M_d}{M_d} \qquad (4)$$

where R (g g^{-1}) is the liquid retention of the medium, M_d the dry sample weight and M_w is the "wet" mass of the sample (100% saturated liquid). The sample was first dried thoroughly in an incubator and weighted. Then the sample was submerged in the testing liquid for 24 h and weighted again to obtain the "wet" mass of the sample.

To gain information on liquid transport in SPC^{TM} Oil Sorbents, we measured the liquid retention along a vertically hung sample with the lower end immersed in a reservoir of test liquid. The SPC Oil Sorbent samples were used as received and cut into 6.0 cm long specimens. A small brass rod with a diameter of 0.6 mm was sewn to each end of the specimen to prevent them from curling during the test. The specimen was suspended vertically in a sealed tube with the test liquid inside as shown in Fig. 5. The bottom end of the specimen is submerged 1.0 cm in the test liquid. Tests were conducted at room temperature of 20 °C for 24 h to establish an equilibrium state. The lid of the tube was then removed and the specimen was quickly cut into 1.0 cm long pieces. Each piece was then sealed in a plastic bag for weighing. The bags used to hold the sample pieces were weighed before being used and then weighed with the specimen pieces still sealed inside. The difference between these two weights was referred to as the "wet" mass, M_w, of the piece. Specimens were removed from the plastic bags and dried thoroughly in an incubator, then weighed again after drying. This second weight was referred to as the "dry" mass, M_d, of the piece.

The SPC^{TM} Oil Sorbents had the highest liquid retention density when the liquid is 90% methanol solution, as shown in Fig. 6.

Table 2
Some specifications of the porous media used in the work

| Porous media	Mean pore dia. (μm)	Liquid retention ratio R (g g^{-1})	Functionality in this work	Manufacturer
Versi-dry-super	N/A	8.20 (water)	Water storage	Parmer Instrument Co.
SPC Oil Sorbents	18.8	4.41 (methanol)	Methanol storage	Parmer Instrument Co.
Porous polyethylene I	80–100	1.02 (methanol)	Air filter	Small Parts Inc.
Porous polyethylene II	10–20	0.12 (methanol)	Methanol distribution	Small Parts Inc.
Porous PTFE	20	0.08 (methanol)	Methanol distribution	Small Parts Inc.
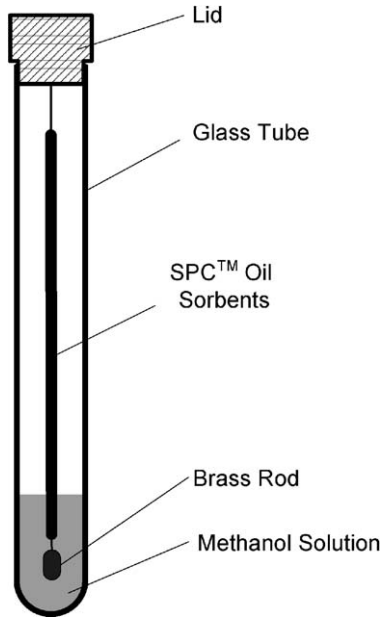
Fig. 5. An experimental setup for testing liquid distribution in a vertically suspended porous medium.
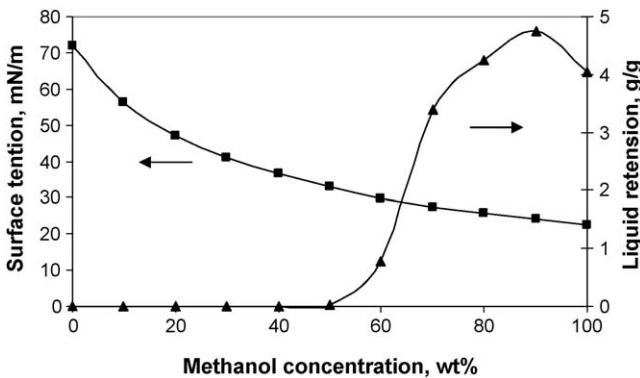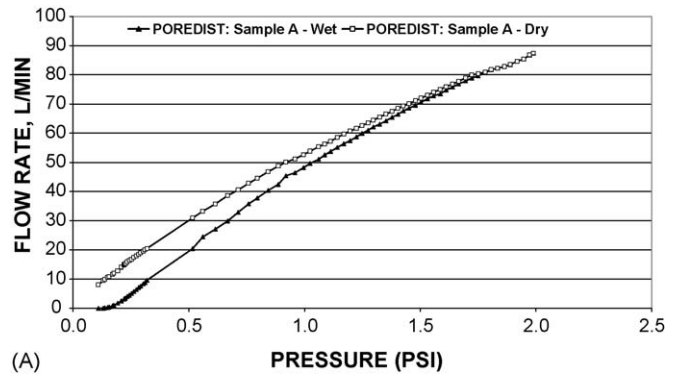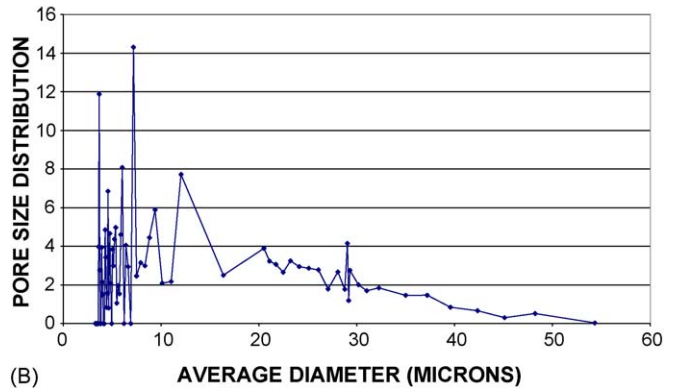

Fig. 6. Liquid retention density above liquid level and surface tension of methanol in water at 25 °C (Lide, 2001).

For pure methanol, the liquid distribution in the vertically hung fiberglass wick was nearly uniform. Liquid retention densities were much lower for those solutions in which the methanol concentrations were less than 40%. For SPC^{TM} Oil Sorbents, the

Fig. 7. (A) Flow rate verse pressure in SPC Oil Sorbents (fluid used: galwick; sample diameter: 2.5 cm; sample thickness: 0.35 cm). (B) Pore size distribution (%) of SPC Oil Sorbents.

water flow rate versus pressure, and pore size distribution are shown in Fig. 7A and B, respectively.

3.2. Passive fuel delivery system demonstrations

Fig. 8 shows an experimental setup for demonstrating the working mechanism of the passive methanol delivery system in a DMFC. Dry air is forced underneath the surface of the water storage medium. An electric heater placed underneath the water surface supplies heat to simulate fuel cell operating conditions. When liquid evaporates from the water storage medium, water and methanol are replenished from the water tank and methanol
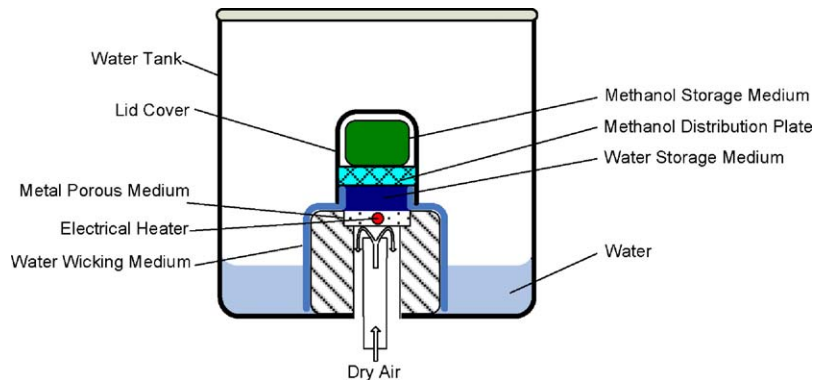

Fig. 8. An experimental setup for demonstrating the working mechanism of the passive methanol delivery system in a DMFC.
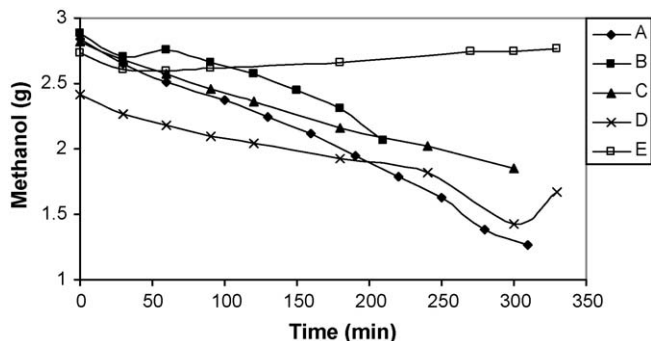
Fig. 9. Methanol weight variations in the methanol storage medium over time under different wet conditions of the water storage medium.

storage medium, respectively. In this experiment, the evaporated liquid is used to demonstrate the water/methanol mixture at the anode of a DMFC, which is consumed by the fuel cell. The purpose of the experimental setup is to show:

- Methanol being able to diffuse from methanol storage medium to the water storage medium.
- How to block water back diffusion from the water storage medium to the methanol storage medium.
- By changing the thickness and properties of the methanol distribution plate, the methanol flow rate can be controlled.

Fig. 9 shows the results of the tests when using 3 methanol storage layers and one distribution layer. These tests were run with a temperature of about 30 °C and a flow rate of air between 80 and 90 ml min^{-1}. The five different cases are for different water saturation of the water storage layer. Case A shows the methanol change when the water storage layer absorbed only about 0.0426 g of water. This case had the most methanol loss due to the very dry conditions of the water storage layer. In case B the water storage layer absorbed about 1.5 g of water by the end of testing. The methanol storage layers did not lose as much methanol in this case because there was more water in the water storage layers. The second measurement during this test actually showed an increase in weight meaning that some water back diffusion had taken place. In case C the water storage layer absorbed about 0.6 g of water by the end of the test. This test displayed very consistent linear results for the methanol loss during the test. The water storage layers in case D absorbed about 2.0 g of water by the end of the test. The rate of methanol loss in this case was lower than the previous cases, 0.0025 g min^{-1} compared to 0.005 g min^{-1} for the greatest methanol loss. This test also shows some water back diffusion at the end of testing when the methanol in the storage layers was becoming depleted. The water absorbed in the storage layer in case E was about 2.46 g. This test shows that the weight of the fuel delivery system increases. This is caused by water back diffusion. The fuel delivery system increased in weight by about 0.0004 g min^{-1}, which is the amount of water diffusing into the system minus the amount of methanol leaving the system.

These tests show that the amount of water in the water storage medium plays an important role in methanol diffusion and cell performance. When the water storage medium was dry, methanol diffused from the storage layer at much faster rate. When the water storage medium was very wet, methanol diffused from the storage layer very slowly. Also, when the water storage medium was very wet, the weight of the methanol storage assembly increased in weight. This shows that some water back diffusion takes place when there is too much water in the water storage layers.

3.3. Operation of the DMFC with predetermined dilute methanol solution

A DMFC was fed with a predetermined dilute methanol solution. A reservoir was created and attached to the anode side of the fuel cell. This reservoir was then filled with a certain amount of dilute methanol solution. The DMFC can only produce stable power output over a short period of time before methanol is depleted in the solution.

The cell was tested with a dilute methanol solution first to see how the cell performed over a period of time so that when the fuel delivery tests were run, there would be some previous data to compare to. At the start of the test, 5.0 g of predetermined methanol solution was poured into the reservoir. During the test, measurements were taken every 5 min of the stack's current, the stack's temperature, and the ambient temperature. This cell was tested using 1.0, 2.0 and 5.0 M methanol solutions, under the ambient conditions of 25 °C and a relative humidity of 52%. The cell ran in a constant current density mode, where the discharging current density was selected as 40 mA cm^{-2}. The operational voltage ranged from 0.5 to 0.25 V at this current density for the cell tested, which is the passive DMFC normal operational voltage under the ambient conditions. The testing results are shown in Fig. 10. The cell ran for 3 min on 1.0 M methanol solution. The power output was not stable over the testing period due to the methanol transport limitation. The 2.0 M solution had an average operating power density of about 12.2 mW cm^{-2} and stayed consistent for 40 min, after which point the power density decreased as the methanol concentration was depleted. At 5.0 M concentration, the power curve declined from 13.0 to 10.0 mW cm^{-2} in 200 min before the solution was depleted.
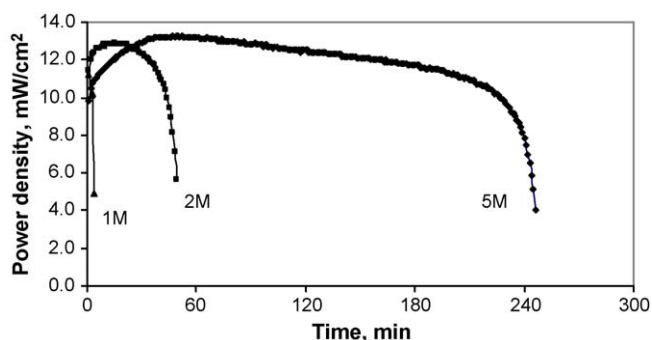

Fig. 10. DMFC constant current operation curves with different concentrations of methanol solution.

The power density is a little low because the current density was not run at the optimal power density range, which is generally 80–100 mA cm^{-2}.

3.4. Operation of the DMFC with passive methanol delivery system

Fig. 11 shows different testing setups for the proposed micro DMFC with the passive methanol delivery system. Fig. 11A is a simple setup with only one methanol storage layer. Fig. 11B has an additional methanol distribution layer. Fig. 11C has an exter-

nal supply of methanol and water. The micro DMFC has an active area of 9.0 cm^2. A porous material (water storage medium) is placed next to the anode gas diffusion layer to wet the anode gas diffusion backing with liquid methanol–water solution. Another porous material (methanol storage medium) is positioned on the top of the water storage medium to hold neat methanol so that methanol can diffuse into the water storage medium. Therefore, the methanol concentration in the water storage medium can be kept stable, and lengthen the operation time of the fuel cell. The methanol and water storage media are SPC^{TM} Oil Sorbents and Super Absorbents Lab Soakers, respectively. It is important to
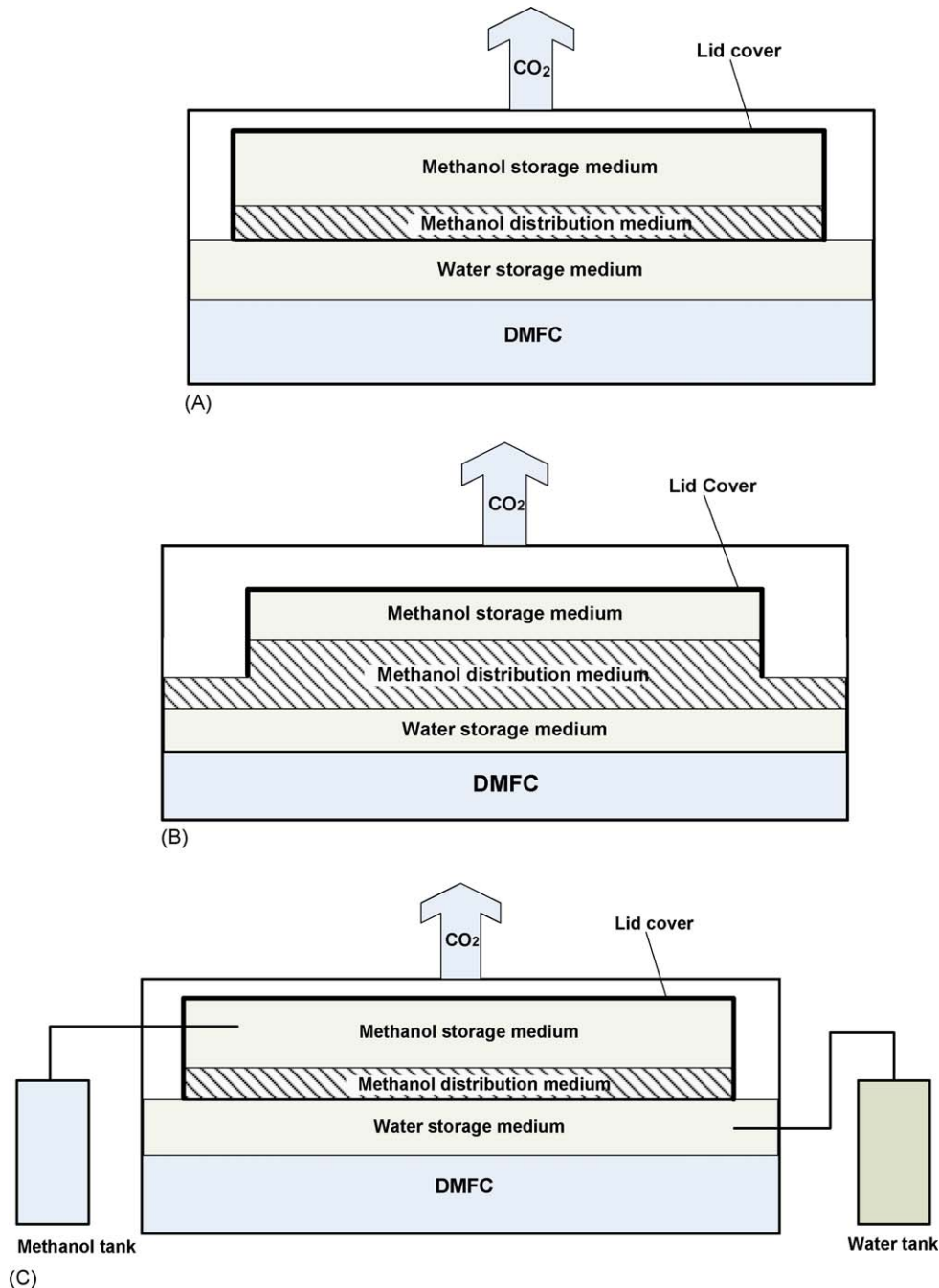

Fig. 11. Methanol and water are stored in separated media, and methanol is delivered to the anode through a methanol distribution medium in situ. (A) Simple fuel delivery setup. (B) Fuel delivery setup with an extended methanol distribution layer. (C) Fuel delivery with auxiliary methanol and water tanks.
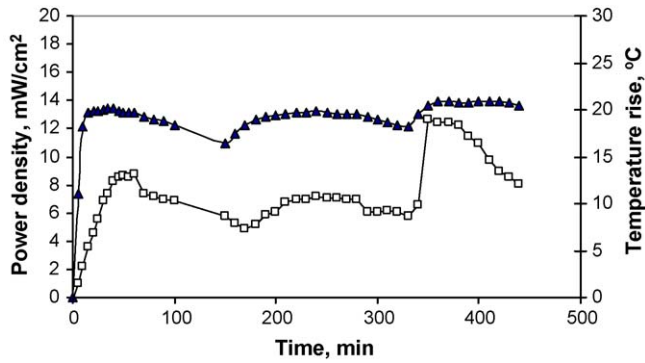
Fig. 12. Performance plots of the DMFC with the passive fuel delivery system. (▲) Power density and (□) temperature rise above room temperature.

Fig. 13. Plot of constant current a single cell with an active area of $9.0\,cm^2$ at the ambient conditions.

note that the liquid evaporation is a major source of fuel loss during long term operation of the cell. A plastic cover was used to prevent liquid from evaporating in air.

The test started with dipping water storage medium in deionized water for 1 min. The wetted water storage was then transferred to the anode of the micro DMFC. The methanol storage medium was dipped in pure methanol for 1 min before it was transferred to the top of the water storage medium. In about 2 min, the methanol diffusion front reached the anode of the micro DMFC. As a result, the cell voltage and operation temperature rose quickly. In another 5 min, the cell reached a stable operation state.

Fig. 12 shows typical long term operation curves of the DMFC with the passive fuel delivery system. One layer of Super Absorbent Lab Soakers (paper only) was used as a water storage medium. Three layers of SPC Oil Sorbent were used as a methanol storage medium. The cell was operated under the constant current of $40\,mA\,cm^{-2}$. As shown in Fig. 12, the cell operating temperature increased rapidly in the first 35 min. The internal resistance was $56\,m\Omega$. As the internal resistance increased to $70\,m\Omega$ at 150 min, 0.5 g water was added to the system. The internal resistance generally increases as the membrane dries out, which is why water is added to the system. To increase the power density, 0.53 g methanol was added at 330 min. The cell temperature and power density increased slowly. The total amount of methanol added to the system was 2.12 g.

One methanol distribution layer was added for blocking water back diffusion – "Developmental ELAT(R) Gas Diffusion Layer Type 33, very thick, standard ELAT architecture" – was used in this test. The power density increased very quickly and the cell temperature increased slowly. After 7 h operation, the system was opened, the methanol consumption was 1.34 g. Water consumption was 2.04 g. The water storage medium was kept saturated. 1.54 g methanol was added and the system was reassembled. Water and methanol were added as necessary to keep the cell operational for a total of 27 h as shown in Fig. 13.

Fig. 14A shows a graph of power density in mW cm^{-2} versus time, during a 36 h test of this cell. The room temperature varied from 21 to $26\,°C$, and the relative humidity was 80%. Both cell temperature and the room temperature were recorded. The temperature difference between the cell temperature and the room temperature is also shown in Fig. 14A. Fig. 14B is a
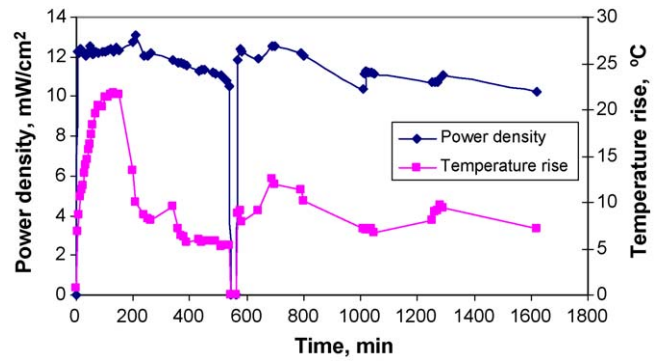
graph of the cell resistance during the test. At the start of the run, neat methanol and water were placed in the methanol storage medium and water storage medium, respectively. Additional methanol and water were added as needed during the test. The cell had an applied load of $40\,mA\,cm^{-2}$. A slow increase of the cell internal resistance was observed after the start of the test, accompanied by a decrease in cell power output, showing the slow process of dehydration of the membrane. A small amount of water was added to the water storage medium when the internal resistance reached $70.0\,m\Omega$. The lower cell operation temperature and low power density were associated with lower methanol concentration at the anode. Methanol was added to the methanol storage medium when the cell operation temperature was lower than $30\,°C$ and the internal resistance was less than $70.0\,m\Omega$. Over the course of the test, 6.0 g of methanol and 4.0 g of water were added to the methanol storage medium and the water stor-
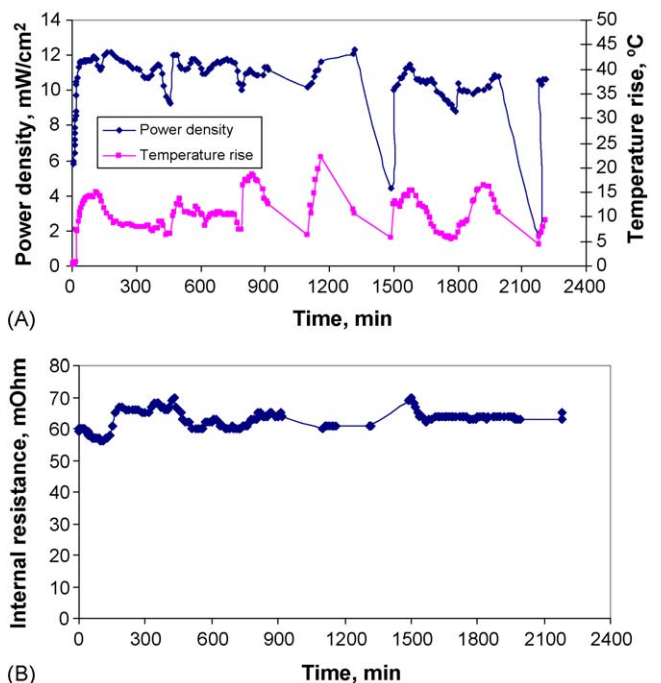

Fig. 14. Plot of constant current a single cell with an active area of $9.0\,cm^2$ at the ambient conditions. (A) Power density and temperature rise. (B) Internal resistance.
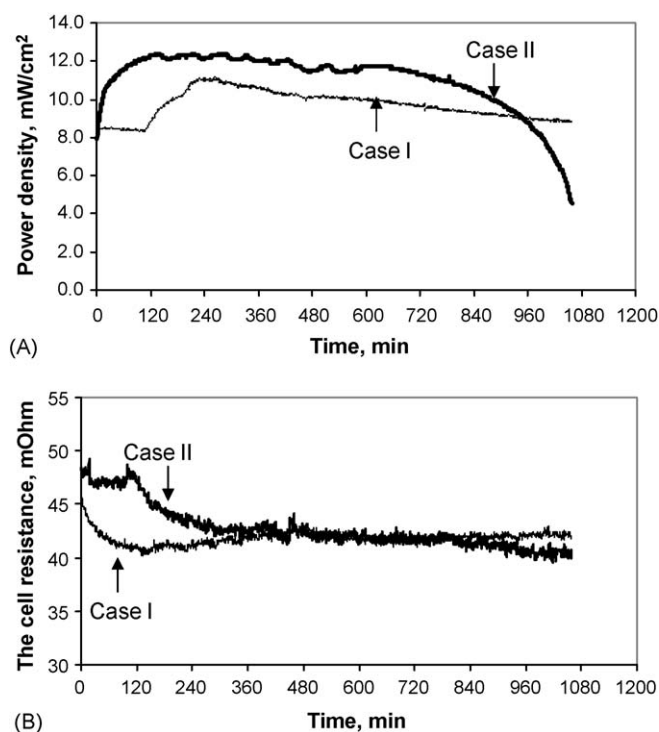
(A)

(B)

Fig. 15. Performance plots of a DMFC operating with passive fuel delivery system. (A) Power output vs. time; (B) the cell resistance vs. time.

age medium, respectively. Only a slight decrease in cell power density was observed towards the end of the test, showing the stability of the fuel delivery system.

The passive fuel delivery system as shown in Fig. 11C was used in the extended tests. One layer of Super Absorbent Lab Soakers (paper only) was used as a water storage medium. One layer of SPC Oil Sorbent was used as a methanol storage medium. A cover was used to prevent methanol from evaporating. A neat methanol bottle was connected to the methanol storage medium through a hydrophobic wick (porous polyethylene, obtained from Small Parts Inc.). A water bottle was connected to the water storage medium through a hydrophilic wick (Product #461 from Pepperell Braiding Co.). As methanol and water are consumed in the anodic reaction, more methanol and water will be transported into the methanol and water storage media, in such a way that stable operation of the fuel cell can be expected.

The first test (case I) was performed under a constant current of $30 \, mA \, cm^{-2}$ and an ambient temperature of $25 \, ^{\circ}C$. As shown in Fig. 15A, the cell power density increased to

about $11.2 \, mW \, cm^{-2}$ and then declined slowly in the following 800 min. The internal resistance was kept nearly constant during 18 h of testing indicating good hydration condition of membrane. The total amount of water consumed during testing was 11.9 g and methanol consumption was 5.1 g. The total power output was 1.56 Wh and the overall efficiency was 5.0%.

The second test (case II) was performed in a temperature controlled chamber set at $32 \, ^{\circ}C$. The results in Fig. 15A and B were obtained under a constant current of $40 \, mA \, cm^{-2}$. The total amount of water consumed during testing was 7.9 g and the methanol consumption was 4.9 g. The total power output was 1.79 Wh at an overall efficiency of 6.0%.

The cell internal resistance was determined by the current-interrupt technique. The good agreement of the internal resistance between two cases was obtained at steady state operation, which also indicates the validity of the measurement technique (see Fig. 15B).

3.5. Operation of the DMFC with passive water management system

The micro porous sub-layer shown in Fig. 4 is formed by coating and bonding carbon particles together with PTFE compounds. The layer has micro pores with a pore diameter between about 1.0 and 0.1 μm in order to block liquid water. These pores allow oxygen from the ambient air to pass through to the cathode aspect of the sub-layer, and they allow a limited amount of water in vapor form to escape out of the cell. The pores are too small and hydrophobic to allow liquid water to pass through the sub-layer, so the liquid water that accumulates is pushed back in the other direction across the sub-layer, to the anode as is required for the anode reaction of the fuel cell. The gas diffusion layer consists of several layers of carbon backing medium. The added cathode filter, which may include a layer of expanded PTFE, helps curb water vapor escape while ensuring sufficient oxygen supply. Thus, water mass is balanced within the cell to allow neat, or highly concentrated methanol feed without active external recirculation.

Measurements of water loss in fuel cells operating with the cathode backing are described by the following examples. Three cells (nos. 22, 24 and 25) with different cathode diffusion layer structure were run in a temperature controlled chamber set at $32 \, ^{\circ}C$. Each case was allowed to operate for 3 days. The water and methanol were added to water tank and methanol tank as needed. The testing results were summarized in Table 3. The following conclusions can be drawn from the table:

Table 3
Comparison of cell performance and water loss with different cathode structures

Cell ID	Electrolyte membrane	Number of anode backing layers	Number of cathode backing layers	Air filter	Average power output (mW cm^{-2})	R_{cell} (mΩ)	H$_2$O loss/MeOH (mole mole^{-1})
DMFC#22	Nafion 117	1	1	No	8.2	59	3.28
DMFC#24	Nafion 117	1	2	No	8.0	45	1.72
DMFC#25	Nafion 112	2	4	No	11.5	32	0.94
DMFC#25	Nafion 112	2	4	Polyeth	11.5	32	0.68
DMFC#25	Nafion 112	2	4	PTFE	11.2	32	0.22

1. Despite the reducing of cathode permeability with thicker backing layer, there is no significant loss of cell performance.
2. With thinner electrolyte membrane, the cell internal resistance decreases.
3. With a layer of cathode backing layer, water loss is greater than 3:1 ($water_{mole}$:$MeOH_{mole}$).
4. With a thicker cathode backing layer, water loss is reduced to near 1:1 ($water_{mole}$:$MeOH_{mole}$).
5. With a deep air filter, water loss is significantly reduced to 0.22:1 ($water_{mole}$:$MeOH_{mole}$).

To further reduce the water loss, an air filter was used. This air filter was made of porous PTFE sheet (pore size: 25 μm, thickness: 1/16 in.). The edge of porous PTFE sheet was covered with soft PTFE foam. The air filter was tightly inserted into the cathode chamber. The cell with serial number 25 were operated in our lab for 24 h. The water tank was removed from the system and weighed. It was found that there was no water loss in the testing course. The whole water supply sub-system was then removed from the fuel cell system. The 100% methanol was delivered to fuel cell for 48 h. The cell internal resistance was kept near constant in this total 72 h, which indicated the cell was well hydrated.

3.6. Operation of the DMFC with air filtration

An air breathing management layer is attached to the cathode to control air access into the cathode. It also serves as a filter to keep the cathode clear when the cell operates in dirty air. Four filter materials and their combinations were tested in seven experiments. These porous materials are expanded PTFE membrane (ePTFE), PTFE sheet (PTFE), porous polyeth sheet (PV), and Oil Sorbents (OS). All testing was performed on a single cell with referencing no. 25. Each test lasted at least 24 h. The testing results are listed in Table 4.

The effectiveness of the ePTFE membrane (mean pore size 0.5 μm, thickness: 0.01 in.) owes its function to the microporous property. The ePTFE membrane stays clean by filtering particles on its surface. Excellent release characteristics give the ePTFE membrane a high air permeability. The polyethylene sheet (mean pore size 80–120 μm, thickness: 0.08 in.) owes a high air permeability to its relative large pore size. Since both of these filters had high water vapor permeability, the water loss was relatively high. But the power loss due to the effect of the air block was

negligible. The porous PTFE sheet (pore size: 25 μm, thickness: 1/16 in.) can provide additional deep effectiveness and better results for trapping water vapor. It caused 5–7% performance loss in terms of power density. A high degree of vapor trapping is achieved by SPC^{TM} Oil Sorbents. It also provided high air penetration. Therefore the power loss is less than 1%. The combination of ePTFE membrane and porous sheet produced high filtration efficiency since the filtration mechanism is doubled. But the performance loss due to limited air access to cathode was also increased.

4. Conclusion

Overall, this work provided a simple and inexpensive design for micro DMFCs for battery replacement applications. Some of the technological novelties of the present proposal include: a thermal-fluids management system for miniature DMFCs, passive methods for fluids transport, a mechanism for controlling the methanol concentration by using a methanol distribution layers, transport of water from the cathode to the anode, supplying oxygen to the cell with a uniform distribution across the cell. The thermal-fluids management system has allowed cells to be run for 36 h at an average power density of 11 mW cm^{-2} under a constant load of 40 mA cm^{-2}. From a system design viewpoint, many challenges remain, such as self-sustainable operation, low cost, sustained performance over a range of exterior humidity, pressure and temperature, endurance and reliability and packaging.

Acknowledgments

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Table 4
Comparison of cell performance loss and water loss with different filter materials

Experiment	Filter materials	H$_2$O loss/MeOH (mole mole^{-1})	Filter type	Power output loss (%)
#1	ePTFE	0.12	Surface	<1.0
#2	PTFE	0	Deep	<5.0
#3	PV	0.22	Deep	<1.0
#4	OS	0.1	Deep	<1.0
#5	PV + OS	0	Deep	<1.0
#6	ePTFE + PTFE	0	Deep	<6.0
#7	ePTFE + PV	0	Deep	<7.0

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