

Vapor feed direct methanol fuel cells with passive thermal-fluids management system

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Abstract

The present paper describes a novel technology that can be used to manage methanol and water in miniature direct methanol fuel cells (DMFCs) without the need for a complex micro-fluidics subsystem. At the core of this new technology is a unique passive fuel delivery system that allows for fuel delivery at an adjustable rate from a reservoir to the anode. Furthermore, the fuel cell is designed for both passive water management and effective carbon dioxide removal. The innovative thermal management mechanism is the key for effective operation of the fuel cell system. The vapor feed DMFC reached a power density of 16.5 mW cm^{-2} at current density of 60 mA cm^{-2} . A series of fuel cell prototypes in the 0.5 W range have been successfully developed. The prototypes have demonstrated long-term stable operation, easy fuel delivery control and are scalable to larger power systems. A two-cell stack has successfully operated for 6 months with negligible degradation.

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1. Introduction

Miniature direct methanol fuel cells (DMFCs), which promise high energy densities and instant refueling, present beneficial opportunities for use as power sources 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 the development of miniature DMFCs in recent years, at the present time there are no truly commercial miniature DMFC products available for consumer electronic devices. 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 factors that prevents faster development of direct methanol fuel cell technology is methanol crossover. Methanol crossover is the process by which methanol is transported, by diffusion and electro-osmosis, from the anode through the electrolyte to the cathode, where it reacts directly with oxygen, so that no current is produced from the cell. Furthermore, methanol has a poisoning effect on the cathode catalyst, which results

in reduced cell performance. The methanol crossover rate is roughly proportional to the methanol concentration at the anode; therefore, in order to reduce methanol crossover it is necessary to regulate the methanol feed concentration. If the methanol concentration is too high, the methanol crossover problem will significantly reduce the efficiency of the fuel cell [1,2]. In practice, the fuel supplied to the anode of the DMFC must be a very dilute aqueous methanol solution (usually 2–6 vol.% methanol). It is very clear that carrying water in the system significantly reduces 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, and that the parasitic power losses from the blower are estimated at 20–25% of the total power output.

The conventional approaches to solving 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 [3–5]. Conversely, a passive fuel cell system supplies fuel to the anode in a passive manner requiring no external power or moving parts. A series of active DMFC prototypes have been developed at Motorola Labs [6,7]. These systems are composed of the following components: fuel cell stack, methanol sensor, CO₂ separator, electronic controls, methanol feed pump, circulation

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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 into 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 of the fuel

cell. As a result, an actively driven DMFC cannot compete with conventional battery technology in terms of cost and power output.

One alternative to an actively driven system is a passive DMFC system [8]. Certainly, a number of diverging passive methods have been developed to overcome the difficulties associated with fuel delivery issues, each with its own merits and limitations as shown in Table 1. The passive approaches to this problem can be divided into three categories:

Table 1
Selected important passive fuel delivery technologies for portable fuel cells

Technology ^a	Technology features	Advantages	Disadvantages
I. LCMSF	(a) Uses low concentrated methanol solution	(a) Very simple system design (b) Low methanol crossover	(a) Very large fuel reservoir for extended operation
II. LMC-PEM Toshiba, Hitachi, Samsung	(a) Based on the polymer membrane technology (b) Uses highly concentrated methanol solution (c) Modifies polymer electrolyte membrane to reduce methanol crossover (d) Optimizes the structure of the fuel cell's electrodes to reduce methanol concentration near the catalyst layer (e) Utilizes methanol concentration gradient to deliver the fuel to the anode catalyst layer	(a) Simple system design (b) Liquid fuel delivery	(a) No commercially available low methanol crossover electrolyte membrane thus far (b) Methanol crossover for high concentrations and mass transfer limitation for low concentrations (c) Unreliable fuel supply over the large methanol concentration range (d). Difficulties associated with recharge of fuel (e) Difficulties associated with the operation in freezing temperatures
III. PCPM MTI, Manhattan	(a) Based on the pervaporation membrane separation technology (b) Uses neat methanol (c) Vaporous fuel feeding (d) Produces the fuel vapor without heating (e) Utilizes a pervaporation membrane, or other suitable membrane, that effects a phase change from liquid methanol in the fuel reservoir to methanol vapor in the anode chamber	(a) Simple system design for micro system (b) Utilizes commercially available polymer electrolyte membranes (c) Low methanol crossover (d) Possible operation in freezing temperatures	(a) As water condenses on the surface of the methanol pervaporation membrane, the rate of fuel delivery would gradually drop (b) Unreliable operation over a large temperature range (c) Difficulties associated with extending to larger fuel cell systems (d) Difficulties associated with fuel flow rate control
IV. LFTWD, the present work	(a) Based on the thermal-fluids technology (b) Uses neat methanol (c) Vaporous fuel feeding (d) Produces the fuel vapor with heating (e) Utilizes an electrical heater (f) Reuses waste heat from the fuel cell and/or the electronic device, which is powered by the fuel cell itself (g) Utilizes hybrid heating technology of (e) and (f)	(a) Simple system design (b) Utilizes commercially available PEM (c) Low methanol crossover (d) Expandable to larger systems (e) Very reliable operation over the large temperature range (f) Simple fuel flow rate control (g) Versatile portable fuel cell platform suitable for various volatile organic fuel fed fuel cells (e.g., formic acid fuel cells)	(a) Loss of methanol fuel in CO ₂ releasing process

^a Low concentrated methanol solution feed (LCMSF); low methanol crossover polymer electrolyte membrane (LMC-PEM); phase-changing pervaporation membrane (PCPM); liquid fuel thermal-wicking dispenser (LFTWD).

- (1) Those utilizing a dilute methanol solution contained in larger fuel reservoirs.
- (2) Those utilizing an optimized structure for the fuel cell's electrodes and polymer electrolyte membrane to reduce methanol crossover, permitting the use of highly concentrated methanol solution.
- (3) Those utilizing a pervaporation membrane, which effects the phase change from the liquid methanol contained within a fuel reservoir to a vaporous fuel that is presented to the anode aspect of the catalyzed membrane electrolyte.

The simplest of these methods involves utilizing reservoirs containing methanol/water mixtures at the anode [9–11]. This passive method has the advantage of system simplicity. The disadvantage of this passive method is that carrying a dilute methanol solution results in a significant penalty to the energy density of the fuel cell. Kim et al. developed a passive DMFC system having a total active area of 27.0 cm², which is composed of a fuel reservoir sandwiched between two planar stacks [9]. With a 4.0 M aqueous methanol solution, the system produced a power output of 1.0 W at room temperature. Han and Park used a 4.0 M methanol solution to feed the fuel cell stack. For operation over an extended period of time, they used a large reservoir to eliminate the effect of the changing of methanol concentration [10]. The problem with this approach is that it requires that the system carry a significant amount of water along with the methanol in the cartridge.

In a U.S. patent granted to Toshiba in 2003, the company disclosed a mechanism used to deliver liquid methanol fuel into the cell by capillary action. The fuel is then vaporized by heat within the cell, and supplied to the fuel electrode, thereby generating electric power [12]. The liquid fuel tank is equipped with a pressure control mechanism for introducing the required amount of the liquid fuel into the unit cell from a liquid outlet port. Chang from Samsung developed a low methanol crossover electrolyte membrane, which maintained the same proton conductivity and 30% crossover versus Nafion[®] when a 5 M or higher concentration of methanol was used [13].

MTI MicroFuel Cells Inc. has actively pursued passive fuel delivery technology for micro DMFCs. In the MTI design, a non-porous thin film of silicone is used as a methanol vapor delivery membrane (see Fig. 1A). The silicone thin film used in the MTI invention is a polydimethylsiloxane (PDMS) membrane [14,15]. This membrane has an excellent processing ability for making ultra-thin composite membranes. 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 [16–19]. The permeation of methanol through a PDMS membrane involves three physical processes: (1) sorption of liquid methanol molecules at the feed side of the membrane, (2) diffusion of the dissolved methanol through the membrane, and (3) desorption of methanol vapor from the permeate side. Methanol vapor condenses at the anode and keeps the concentration of methanol next to the catalyzed anode surface at about 3% (1 M), or lower, which is the concentration level for the anode reaction to proceed with minimal methanol loss due to crossover.

Fuel cell systems based on this pervaporation membrane fuel delivery technology can be completely passive as long as water produced in the system can be reused by means of materials and structures. However, there are two fundamental limitations with this approach. First, as methanol evaporates from the permeate side of the methanol pervaporation membrane, the membrane will cool down. If its temperature is below the saturation temperature, water will condense on the permeate side of the membrane, so that a thin film of water will be formed on the surface. This will drop the fuel vapor pressure and reduce the rate at which fuel can vaporize out. Secondly, the fuel supply rate is difficult to control. Such controlled adjustment of the rate of liquid fuel delivery is an important key for achieving high fuel utilization in a passive DMFC. To overcome these disadvantages, a new fuel delivery system was proposed by the company (see Fig. 1B). “By using a parallel network of tubes of a sufficiently small diameter, relatively high linear flow of methanol within each narrow tube is achieved at some given overall fuel feed rate demanded by the anode. The linear liquid flow rate could then be made much greater than the linear rate of water diffusing back into the feed tube from any liquid water, which may collect in the evaporation pad during cell operation. This effectively prevents diffusion of water generated at the cell electrode back to the fuel reservoir, which back diffusion, if left unchecked, could result in dilution of the highly concentrated fuel, causing feed of fuel of vari-

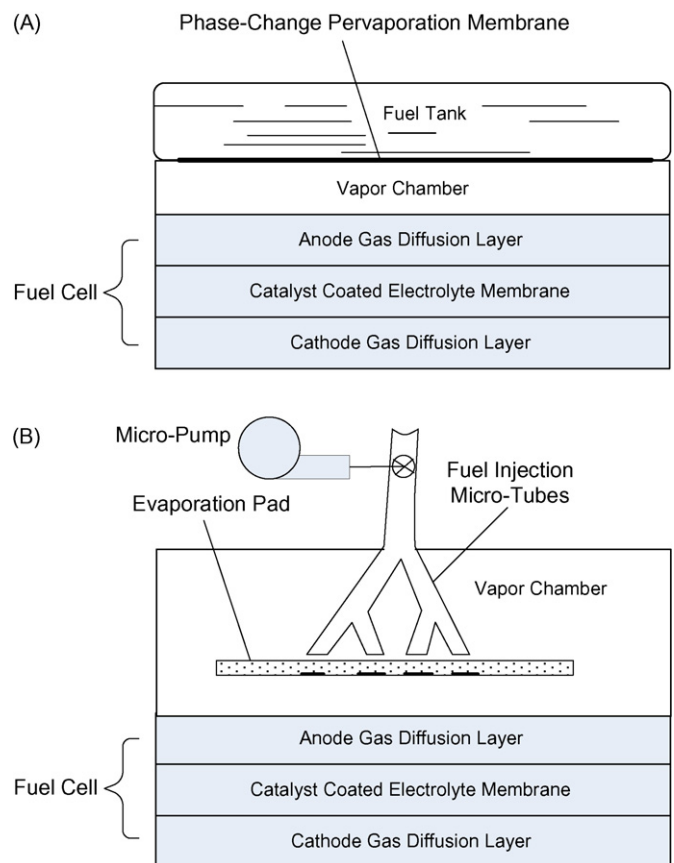


Fig. 1. MTI Microfuel Cells Inc.'s technology for fuel delivery. (A) Passive phase-change pervaporation membrane technology; (B) active liquid fuel injection technology.

able concentration” [20]. This fuel delivery system is actually an actively driven system.

Manhattan Scientifics Inc. also utilizes “selectively permeable membrane” technology. This membrane is highly permeable to fuel over water. The inventors in U.S. Patent No. 6,630,266 also called this process as “per-evaporation” [17]. “The process of enhancing the selective vaporization of fuel from a membrane is called per-evaporation. It essentially increases the evaporation of that fuel. Thus, the ampoule membrane uses this effect when the fuel concentration is low. It keeps the fuel concentration higher at the fuel cell than it would be without the fuel ampoule selectively permeable barrier.”

While the trend toward passive techniques is becoming an attractive choice driving miniature DMFCs, the above-mentioned passive techniques focus mainly on one aspect in the DMFC, fuel delivery. Fuel storage, CO₂ 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 be addressed.

2. System architecture

In the miniature DMFCs proposed in this study, liquid methanol is introduced, through a wick structure, to an evaporation pad in the anode chamber, as shown in Fig. 2. Methanol vapor condenses at the anode and mixes with water to provide a dilute methanol/water mixture at the anode feed. Water is transferred from the cathode internally, across the thickness of the cell, reducing the amount of water needed from an external source. This new DMFC architecture provides an attractive combination of easily controllable pure methanol feed and passive

water self-supply. Furthermore, the simplicity of the hardware makes it possible to fabricate and operate miniaturized fuel cells both cost-effectively and with promising stability and duration.

In the vapor chamber, methanol evaporates from the evaporation pad and water evaporates from the anode diffusion layer. Therefore, a miscible binary vapor mixture is present in the vapor chamber, along with some noncondensable gases such as air and carbon dioxide. As methanol evaporates, the evaporation pad may cool below the saturation temperature of the binary vapor mixture. If this happens, the less volatile component (water) in the system will condense on the surface of the evaporation pad. In other words, water condenses more rapidly than methanol does, therefore, methanol in the evaporation pad will become diluted. The temperature of the liquid in the evaporation pad must be increased in order to continue the evaporation process. In the subsequent evaporation process, methanol preferentially evaporates from the binary liquid system in the evaporation pad [21]. As a result, water tends to accumulate in the evaporation pad.

In practice, a DMFC must be operated at variable temperatures. If the operational temperature of the DMFC is reduced, the temperature drops in the vapor chamber. If the vapor mixture in the evaporation chamber is sufficiently supercooled, a fog may be formed and fall on the evaporation pad. This also causes water accumulation in the evaporation pad.

Some important results can be seen by observing Fig. 3. First, methanol vapor pressure increases exponentially with increases in the temperature of the liquid fuel source; therefore, small temperature increases can cause significant increases in methanol vapor pressure, resulting in greater production of methanol vapor in the anode chamber. Secondly, methanol vapor

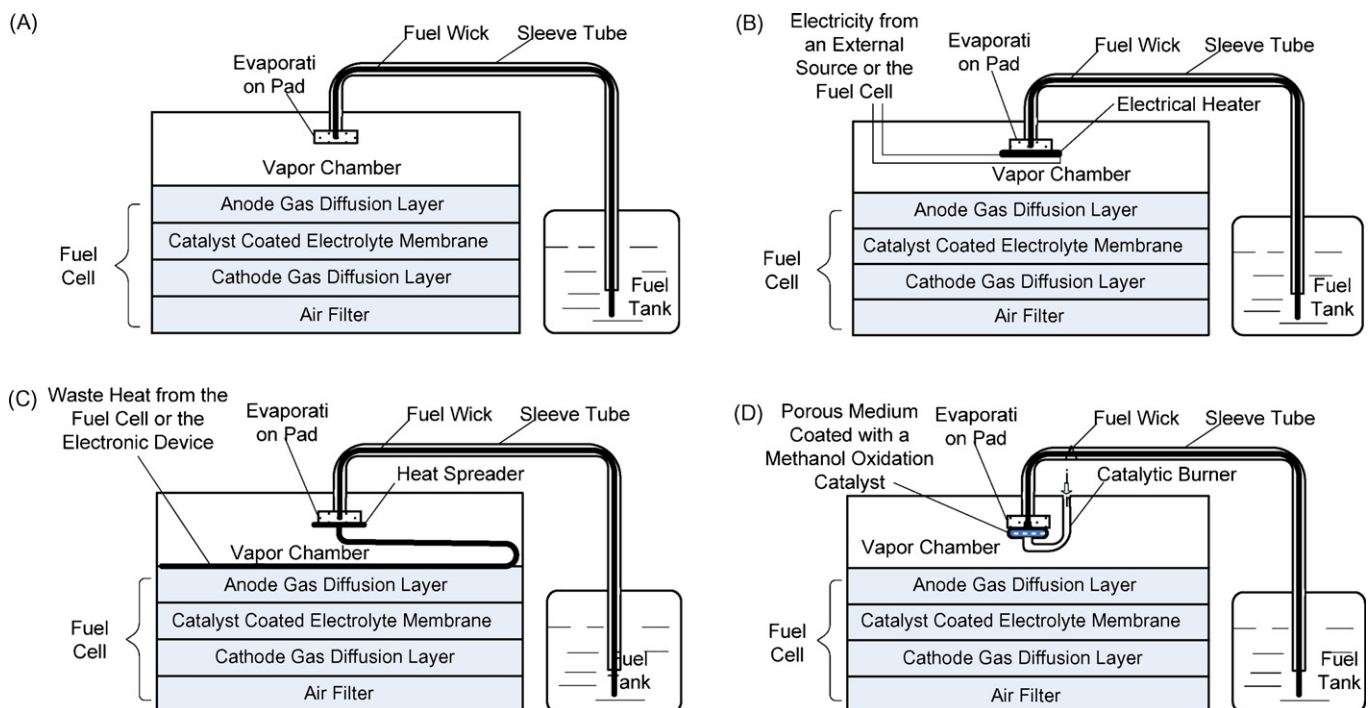


Fig. 2. Vapor fuel delivery system (A) without heating evaporation pad; (B) with an evaporation pad heated by an electrical heater; (C) the evaporation pad heated by the fuel cell and/or the electronic device; (D) the evaporation pad heated by a catalytic burner.

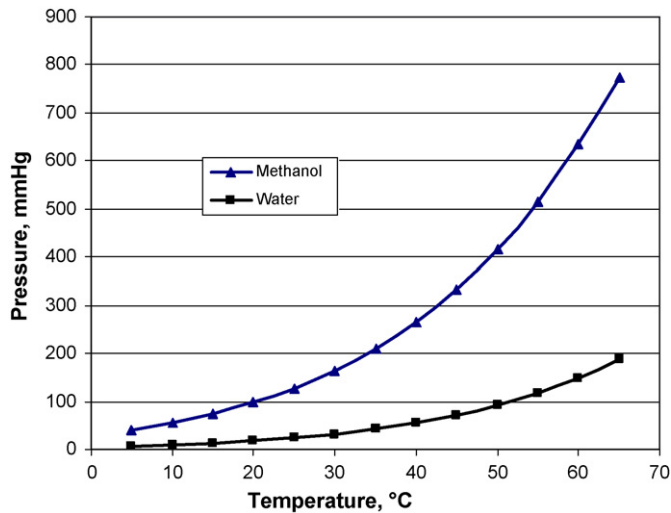


Fig. 3. A plot of methanol and water vapor pressure with temperature changes.

pressure is much higher than that of water in the temperature range of DMFC applications; the saturation pressure of the methanol/water solution is dominated by the partial pressure of methanol. Provided the total saturation vapor pressure (methanol and water vapor) exceeds the aqueous methanol solution P_{tot} , as described by Raoult's law, the total vapor pressure is: $P_{\text{tot}} = (1 - x)P_M + xP_W$, where x is the mole fraction of water in the solution, and P_W and P_M are pure water and methanol saturation vapor pressure, respectively. From this equation, it is clear that water accumulation in the evaporation pad will reduce methanol vapor pressure linearly. As more and more water accumulates, the rate of methanol evaporation from the evaporation pad will be diminished.

2.1. Passive vaporous fuel feed

As the evaporation process occurs in the evaporation pad, its temperature is decreased. It will absorb heat from surround-

ing gases by convection, which is generally a bottleneck in the evaporation processes. Additional heat may be transferred to the evaporation pad in order to: (1) heat the surface of the evaporation pad, (2) heat the liquid in the evaporation pad, or (3) remove water in the evaporation pad. To avoid vapor condensation, the surface of the evaporation pad should be heated to a temperature above the dew point. Increasing the temperature of the liquid in the evaporation pad can increase the production of the fuel vapor. Also, water can be easily vaporized at an elevated temperature if it does exist in the evaporation pad.

Additional heat can be added to the evaporation pad by several approaches. Three fundamental heating methods are proposed in this paper, namely, electrical heat, waste heat recovery, and use of a catalytic burner (see Table 2 for details). The system may employ one or a combination of these systems. A small, thin film heater can be inserted in the evaporation pad (see Fig. 4), with electricity provided either by an external source or by the fuel cell itself. To calculate the electrical energy needed in this process, we can assume that the electrical power source provides heat only for methanol vaporization. The methanol latent heat of vaporization is the dominating term in the process, which is 37.5 kJ mol^{-1} at $25 \text{ }^\circ\text{C}$. The total energy released from 1.0 mol of methanol is about 726.6 kJ under standard conditions at $25 \text{ }^\circ\text{C}$. The electric energy used to vaporize methanol is equivalent to approximately 5% of the energy content in methanol, which also means that the system conversion efficiency is reduced by at least 5%.

This fuel cell efficiency loss can be eliminated by reusing the waste heat from the fuel cell or the electronic device powered by the fuel cell. In a passive DMFC being operated at ambient temperature, the electrodes' temperatures can reach $30\text{--}50 \text{ }^\circ\text{C}$ and the system conversion efficiency is typically less than 30%. Therefore, more than 70% of the energy content in methanol is converted into heat and released into the ambient air, which is sufficient for vaporizing methanol even with low waste heat utilization efficiency. As waste heat is generated in the fuel cell electrodes, it is also the hottest region in a passive DMFC. As

Table 2
A comparison of different heating technologies used in the present work

Technology	Technology features	Advantages	Disadvantages
I. Without heating	The evaporation pad absorbs heat from the surrounding gases	(a) Very simple system design (b) Stable operation under low power densities	Vapor feed system is not reliable, resulting in unstable operation of the fuel cell
II. Electrical heater	The evaporation pad is heated by an electrical heater	(a) Simple system design (b) Easy control for fuel feeding rate (c) Vapor feed system is very stable as sufficient heat provided	Reduces overall system efficiency
III. Recovery of waste heat	The evaporation pad is heated by reuse of waste heat from the fuel cell itself and/or from the electronic device	(a) High overall system efficiency (b) Vapor feed system is very stable as high temperature waste heat provided	(a) An optimal design of waste recovery system is needed (b) Unreliable operation may occur at very low temperatures
IV. Catalytic burner	The evaporation pad is heated by catalytic burning of methanol	(a) The overall system efficiency is slightly reduced (b) Very stable vapor feed system (c) Very stable fuel cell operation	(a) Loss of methanol fuel (b) An optimal design of catalytic burner is needed

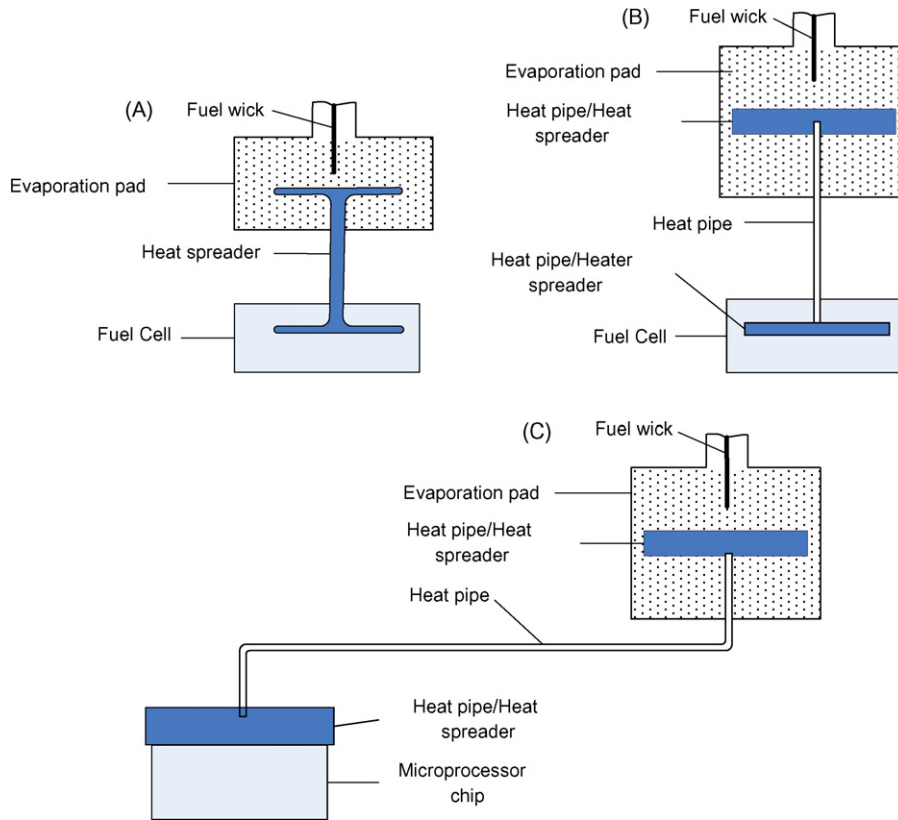


Fig. 4. Different waste heat recovery arrangements. (A) Using a heat spreader to recover heat from the fuel cell; (B) using micro heat pipes and/or heat spreaders to recover heat from the fuel cell; (C) using micro heat pipes and/or heat spreaders to recover waste heat from an electrical device.

shown in Fig. 5, heat spreaders or heat pipes are utilized to collect the waste heat from the anodic electrode and then transfer it to the evaporation pad [22]. The critical issue in this design is to transfer enough heat to vaporize methanol with a minimal temperature gradient. Electronic devices powered by the fuel cell generate heat that can also be reused in the fuel cell to vaporize liquid fuel. The waste heat from the electronic device is usually generated at a temperature greater than 80 °C, which provides a greater temperature gradient for the heat transfer process.

Fig. 4 shows different waste heat recovery arrangements. (A) Using a heat spreader to recover heat from the fuel cell; (B) using micro heat pipes and/or heat spreaders to recover heat from the fuel cell; (C) using micro heat pipes and/or heat spreaders to

recover waste heat from the electrical device. A heat pipe is essentially a passive heat transfer device with extremely high effective thermal conductivity. The heat pipe in its simplest configuration is a closed, evacuated cylindrical metal vessel with internal walls lined with a capillary structure or wick that is saturated with a working fluid. The advantage of using a heat pipe over other conventional methods is that large quantities of heat can be transported through a small cross-sectional area over a considerable distance with no additional power input. Furthermore, design and manufacturing simplicity, small end-to-end temperature drops, and the ability to control and transport high heat rates at various temperature levels are unique features of heat pipes [22].

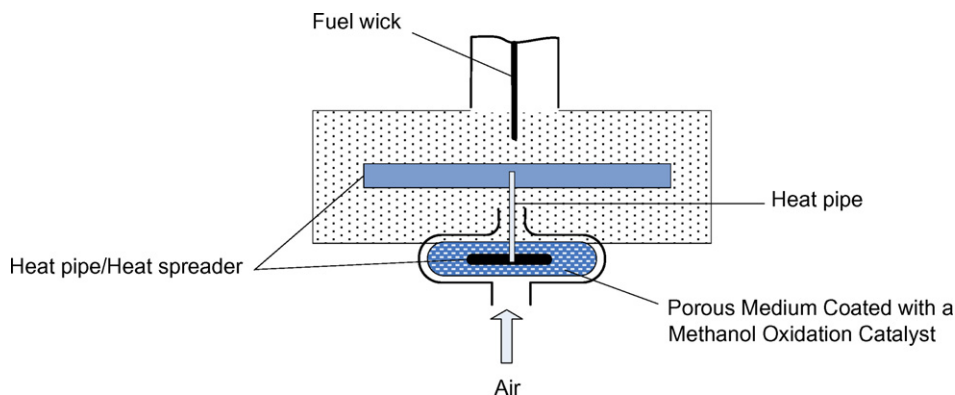


Fig. 5. The evaporation pad is heated by catalytic burning of methanol.

In one embodiment, a heat transfer system uses multiple micro heat pipes to transport heat from the fuel cell to the evaporation pad (see Fig. 4B). One end of the micro heat pipes is in close contact with the fuel cell; the other end is attached to a thermal spreader or a flat heat pipe, which is embedded in the evaporation pad.

In another embodiment, the heat pipes are used for transporting heat from an electronic device (e.g., a notebook computer, especially a notebook computer powered by a DMFC) to the evaporation pad. In such an application, it is desirable to maintain junction temperatures below 125–150 °C. A thermal spreader or a flat heat pipe is attached to a waste heat source (e.g., a micro-processor chip) for heat absorption. The multiple heat pipes are attached to the thermal spreader or the flat heat pipe to assist with the dissipation of heat generated by the waste heat source and with release of heat to the evaporation pad. This can be accomplished by using a thermal spreader or a flat heat pipe embedded in the evaporation pad (see Fig. 4C).

Fig. 5 is a schematic side view of one embodiment of the low temperature methanol burner used in a direct methanol fuel cell. The fuel (methanol) diffuses through a wick structure and is exposed to a catalyst that oxidizes the fuel as air is provided. The burner includes a catalyst-coated porous medium, which defines the catalyzed area. A combustion chamber provided over the catalyzed area includes an aperture to restrict oxygen access, and to consequently control the catalytic reaction. A number of catalysts can be used to oxidize methanol in the presence of oxygen. By way of illustration, platinum and platinum/ruthenium blends are typical materials whose uses as catalysts are well known, although, other metallic catalysts may be used to allow for the air oxidation of methanol. A variety of porous media can be used as the catalyst carrier in the burner. However, carbon cloth coated with a Pt/Ru catalyst was used in an initial qualitative experiment. The catalyst (Pt/Ru) was combined with a PTFE solution and thoroughly stirred. The carbon cloth was immersed in the mixture for 5 min and dried in an oven at 300 °C for 1–2 h. With limited air access, the temperature of the catalyzed area can be controlled in the range of 30–80 °C.

A convenient way to control the methanol feed rate is to control the flow rate in the wick structure that is used to transfer methanol from the methanol tank to the evaporation pad. This wick can be made of flexible materials as in the present study. A micro-actuator, ideally constructed using Micro Electro Mechanical System (MEMS) fabrication techniques, can be located either proximity to, or possibly within the wick structure, to control the cross-section area of the wick and therefore control methanol flow rate.

2.2. Water recycling

Water at the cathode arises from: (i) the electro-chemical reaction at the cathode; (ii) the electro-osmotic drag and diffusion of water through the membrane from the anode to the cathode; (iii) the chemical reaction of air and methanol, which permeates through the membrane from the anode (methanol crossover) to the cathode [23].

In the low-temperature range, liquid water will accumulate in the region between the cathode catalyst layer and the cathode gas diffusion layer (GDL). Several commercial gas diffusion layers are available for DMFC operation. Most of them are hydrophobic and function as liquid–water barrier layers. Hydraulic pressure, which is developed in the region between the cathode catalyst layer and GDL, will force some liquid water to the anode side and some liquid water to the cathode GDL. This process depends on the properties of the GDL. If the GDL has a smaller average pore size and/or a higher water contact angle, higher hydraulic pressure is generated and more water is forced back to the anode side. An optimally designed GDL can reduce the amount of water needed to add to the cell.

The micro porous sub-layer 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 vapor to escape out of the cell. However, 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 to reduce the escape of water vapor while ensuring sufficient oxygen supply.

2.3. Air-breathing

While air-breathing provides the simplest mechanism for supplying air to the cathode, it also poses challenges for DMFC operation. First, too much air access would dry out the membrane quickly so that the cell would cease producing a useful power output. On the other hand, if there is insufficient air access, performance suffers due to oxygen reduction reaction deficiencies, and cross-over methanol begins to wet the cathode structure, further limiting performance. Second, air access also affects 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. Third, airborne particulates may damage the cathode as the fuel cells are exposed to air. In an attempt to solve these problems, two kinds of air filters were used. The first one was a porous polyeth sheet (mean pore size 80–120 μm , thickness: 0.08 in.). The second one was a porous PTFE sheet (pore size: 25 μm , thickness: 1/16 in.).

2.4. CO₂ releasing

In the operation of the cell, CO₂ is produced at the anode and accumulates in the anode chamber. CO₂ must be released

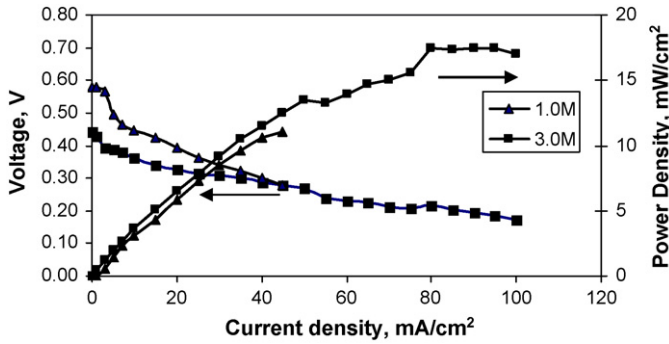


Fig. 6. The polarization and power density curves.

to the ambient air when the pressure of the anode chamber is increased to a certain level. A one-way check valve can be used to facilitate this release. Once the pressure in the anode chamber reaches a predetermined level, the valve opens for a short time to release CO₂. A semi-gas-permeating membrane is also needed to prevent the loss of liquid fluids (methanol and water) in the process of releasing CO₂.

3. Experiments and results

A single fuel cell was built, consisting of a Nafion® 117 membrane, platinum-clad niobium-expanded mesh, gas diffusion layers, and fiberglass fixtures. The gas diffusion layer at the cathode side was made of hydrophobic-treated carbon cloth (available from Electrochem, Inc.). Untreated carbon cloth was used as the GDL at the anode side. The cell was assembled by sandwiching (from anode to cathode) metal mesh, carbon cloth, Nafion 117 membrane (with a catalyst layer at both sides), treated carbon cloth, and metal mesh between two fiberglass fixtures using 12 screws. The DMFC has a square active area of 9.0 cm². A vapor chamber constructed of Teflon was attached by bolts and nuts to the fuel cell.

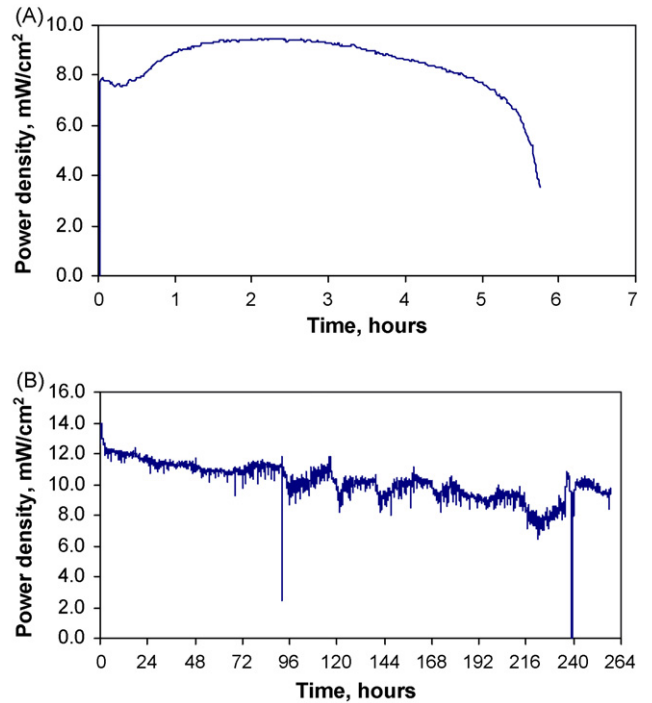


Fig. 7. Typical power density vs. time curves for different DMFC systems: (A) without heating evaporation pad as shown in Fig. 2A; (B) with an electrical heater to heat the evaporation pad as shown in Fig. 2B.

3.1. Single cell performance evaluation

The single cell performance evaluation was carried out with a dilute methanol solution first. Two different methanol concentrations were examined: 1.0 and 3.0 M. The cell was operated at a room temperature of 19.6 °C and a relative humidity of 27%. The testing results are shown in Fig. 6. The fuel cells operated well for 1.0 M methanol solution, but do not achieve

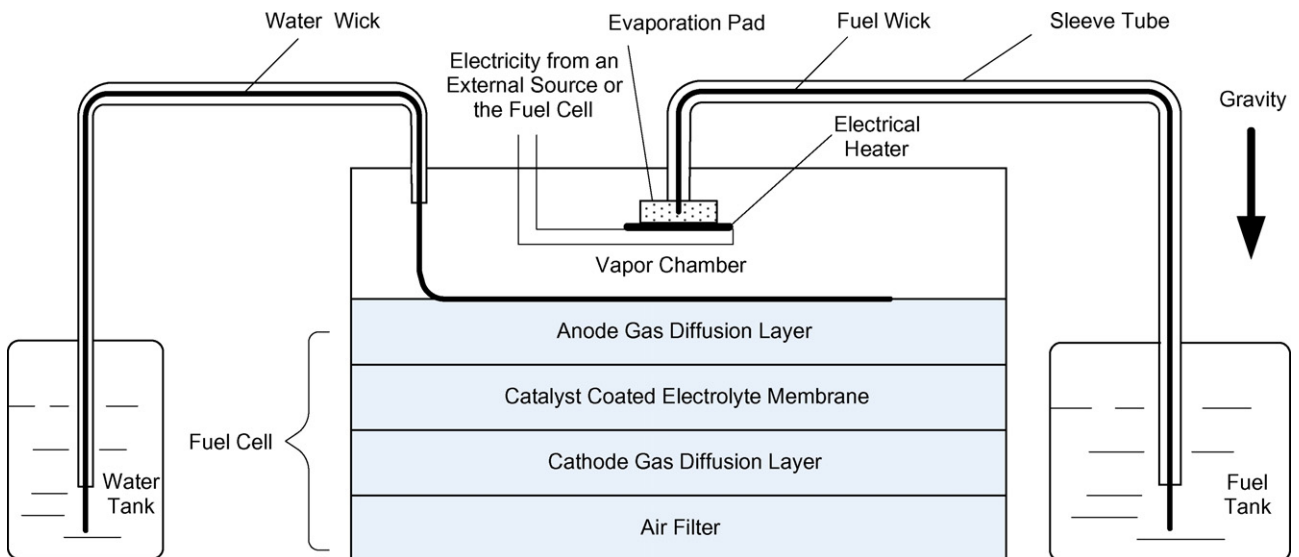


Fig. 8. Vapor fuel delivery system with an evaporation pad heated by an electric heater. The fuel cell is positioned at the bottom of the vapor chamber.

high power densities due to the low mass transport limitation of 1.0 M solution, which restricts the fuel cell from operating at high current densities (greater than 50.0 mA cm^{-2}). The fuel cell can only operate for short periods of time because the methanol in the solution is depleted quickly. The cell does not experience a high temperature rise, due to the lower methanol crossover and lower electro-chemical reaction. If the cell is operated at current densities less than 40 mA cm^{-2} , 1.0 M solution is acceptable.

The cell is capable of reaching over 17.5 mW cm^{-2} with 3.0 M methanol solution and under these conditions the cell experiences moderate temperature rises. The mass transport limitation shifts to higher current densities as the concentration of methanol is increased in the solution. The overall performance of 3.0 M solutions is generally higher than 1.0 M solution for current densities greater than 40 mA cm^{-2} , as shown in Fig. 6. The maximum power density for 3.0 M solutions occurs at current densities between 80.0 and 100.0 mA cm^{-2} , which is significantly higher than the current densities reached with 1.0 M solutions.

The next single cell evaluation experiment was carried out on a vapor feed DMFC system as presented in Fig. 2A. A fuel tank contained neat liquid methanol and a wick structure connects the fuel tank to an evaporation pad, which is placed in the evaporation chamber. Methanol is vaporized in the vapor chamber and supplied to the anode. The cell operated at a constant load of 40 mA cm^{-2} and a room temperature of 25°C . A typical power density versus time curve (see Fig. 7A) is shown from when methanol is filled in the tank. At the beginning the power density increased from zero to about 8.0 mW cm^{-2} . As the cell temperature increased, the power density also increased to about 9.0 mW cm^{-2} and remained at this level for 2–3 h. Then the power density dropped gradually and went to zero after about 6 h. Some liquid remained in the fuel tank and the evaporation pad was saturated with liquid, suggesting that water vapor had condensed in the evaporation pad. As a result, the fuel vapor pressure dropped and reduced the rate at which fuel could evaporate from the evaporation pad. Thus, the rate of fuel delivery gradually dropped and the evaporation pad gradually filled with a mixture of methanol and water. As the methanol vapor pressure decreased in the anode chamber, the fuel transfer limitation occurred at the anode catalyst layer and resulted in a decrease in the power density.

The results described above were noted for cells operating at relatively steady temperatures. In many practical applications, the device is more likely to experience rapid temperature changes. To observe the fuel cell behavior under such operating conditions, one experiment was conducted in which the room temperature was increased from 20 to 28°C in about 10 min and then remained constant. In this case, the cell attained an even higher power density than before. In another experiment, the room temperature was decreased from 28 to 20°C in about 10 min. The cell power density decreased quickly to zero, demonstrating that water condensed on the evaporation pad surface when the cell experienced a sudden temperature decrease.

3.2. Heating evaporation pad with an electrical heater

Previous runs had shown evidence of water condensation on the surface of the evaporation pad; this condensation eventually reduced the fuel evaporation rate. To resolve this issue, various approaches were used in subsequent experiments to heat the evaporation pad to a temperature above the dew point of water and the methanol vapor mixture in the anode chamber (see Table 2). In Fig. 2B, an electrical film heater with a resistance of 14.4Ω was attached to the evaporation pad and a primary battery (size D and OCV of 1.5 V) was used as the power source. In a long-term test the cell power output became very stable. Fig. 7B shows that the power density remained stable for more than 10 days with several fuel recharges. The two lower spikes in the figure, one near 96 h and the other near 240 h, represent the points at which the fuel supply was interrupted because of depletion of methanol in the fuel tank. After recharging the fuel tank, the power output was resumed.

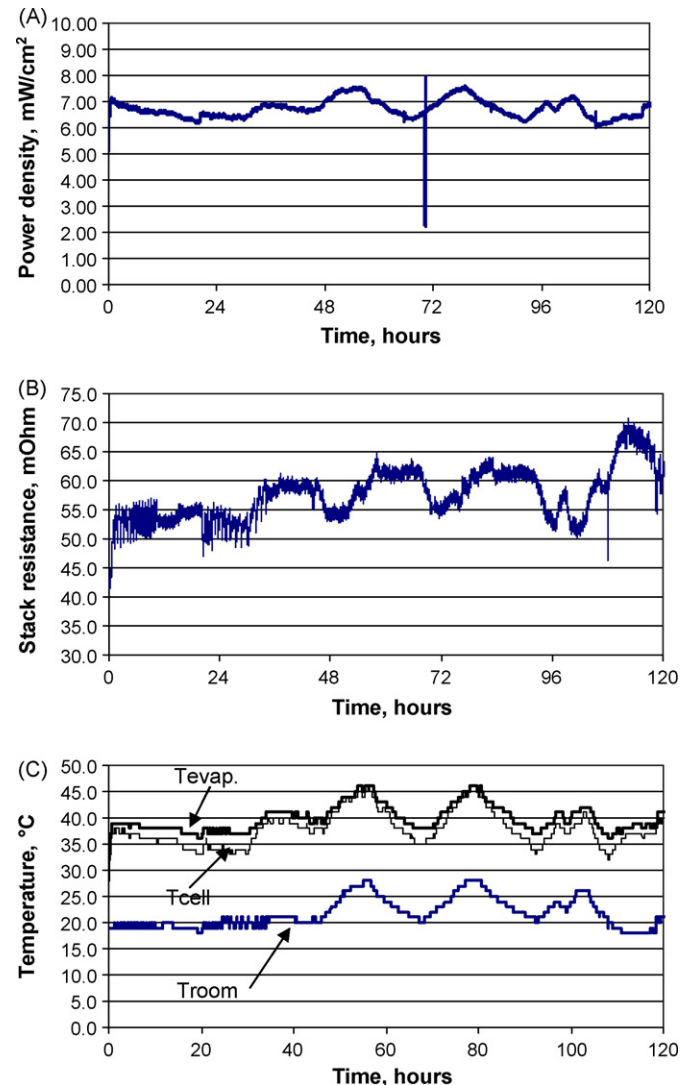


Fig. 9. The vapor feed DMFC system performance plots. (A) Power density vs. time, (B) stack resistance vs. time, and (C) operational temperatures vs. time.

An additional embodiment of passive water delivery is shown in Fig. 8. This system was found to be helpful in improving the system's operational reliability. Specifically, water is transferred from a water reservoir through a water wick to the anode. The water wick can be a hydrophilic porous material. A DC power supply, which was set at a constant voltage of 1.5 V, was used to provide electricity to the heater. Three thermocouples were used to measure the temperatures of the cell, the room and the evaporation pad. The test started with filling the methanol and water tanks. It was found that the cell could not start up without prime, so a small amount of methanol (about 0.2 g) was dropped on the evaporation pad. The cell voltage increased immediately. After the cell voltage reached the maximum value of about 0.6 V, the load was added to the fuel cell, which was a constant current of 0.2 A in this case. As shown in Fig. 9, the cell was capable of reaching a power density over 7.0 mW cm^{-2} . The power density curve oscillates with variations of room temperature. The cell experienced moderate temperature rises ($35\text{--}45^\circ\text{C}$), the temperature of evaporation pad was $1\text{--}3^\circ\text{C}$ higher than the cell. The stack resistance oscillated between 50 and $70 \text{ m}\Omega$, which is about $15 \text{ m}\Omega$ higher than the same parameter measured in the dilute methanol solution supply tests. In the longer time scale the stack resistance increased slightly when the fuel cell was operated with a vapor feed system, a phenomenon that was not observed in the dilute methanol solution. A reasonable conclusion is that the membrane of the fuel cell with a passive fuel supply system was not as well hydrated as the dilute methanol solution supply. In the 120 h of operation, the total methanol and water consumption was 25.5 and 12.4 g, respectively.

In the previous experiment, the system demonstrated stable operation at “normal” position (liquid feed fuel cell systems can only work properly at this position) as shown in Fig. 8. The same

fuel cell system was operated in an “upside down” position. The system demonstrated stable operation and similar performance (e.g., power density, operation temperature and internal resistance) with both of these positions. The system was also operated in other positions; it appears that physical orientation has negligible effect on the fuel cell's performance. Vapor fuel feed provides a mechanism for efficient operation and high stability in various physical orientations. This is an obvious advantage over liquid feed systems.

3.3. Two-cell stack development and performance evaluation

Two cells were attached to a fuel cell frame and connected in series as shown in Fig. 10. The evaporation pad was made of SPCTM Oil Sorbents, which was connected with the fuel tank through a fuel wick. Water was transferred from the water tank to the anode through a cotton wick. A capton heater (14.4Ω) with a surface size of $1.25 \text{ cm} \times 1.25 \text{ cm}$ was used to heat the evaporation pad. The heater was powered by a DC supplier that was set up in a constant voltage mode. A series of experiments were carried out to test the system stability and reliability.

In the first experiment, a ceramic fiber wick was used for fuel delivery. As shown in Fig. 11, the fuel cell ran 99.1 h with stable power output under a constant current of 0.2 A. The stack resistance was around $140 \text{ m}\Omega$ during the whole operation period indicating that the water wick worked well. The room temperature fluctuated greatly due to the weather throughout the first 20 h of operation and the cell temperature fluctuated accordingly. The total methanol usage was 24.75 g. The total power output was 7.58 Wh resulting in an energy efficiency of 5.02% based on the lower heating value.

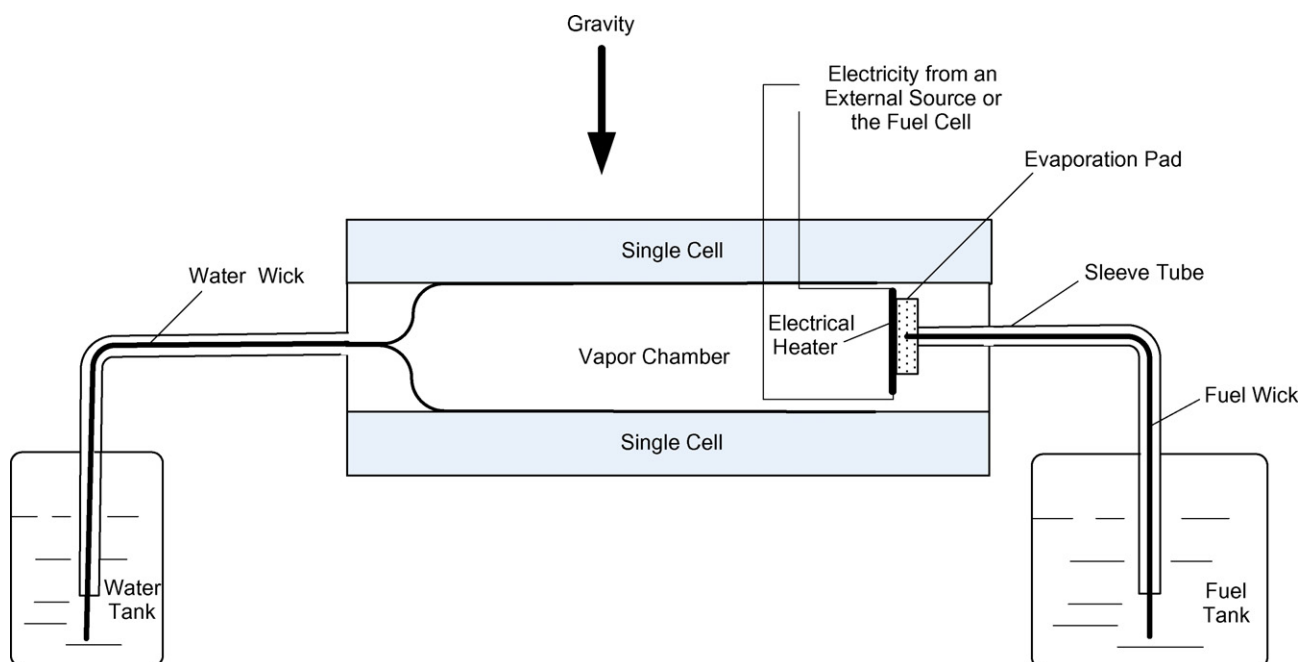


Fig. 10. Vapor fuel delivery system with an evaporation pad heated by an electric heater. Two cells were used in this arrangement.

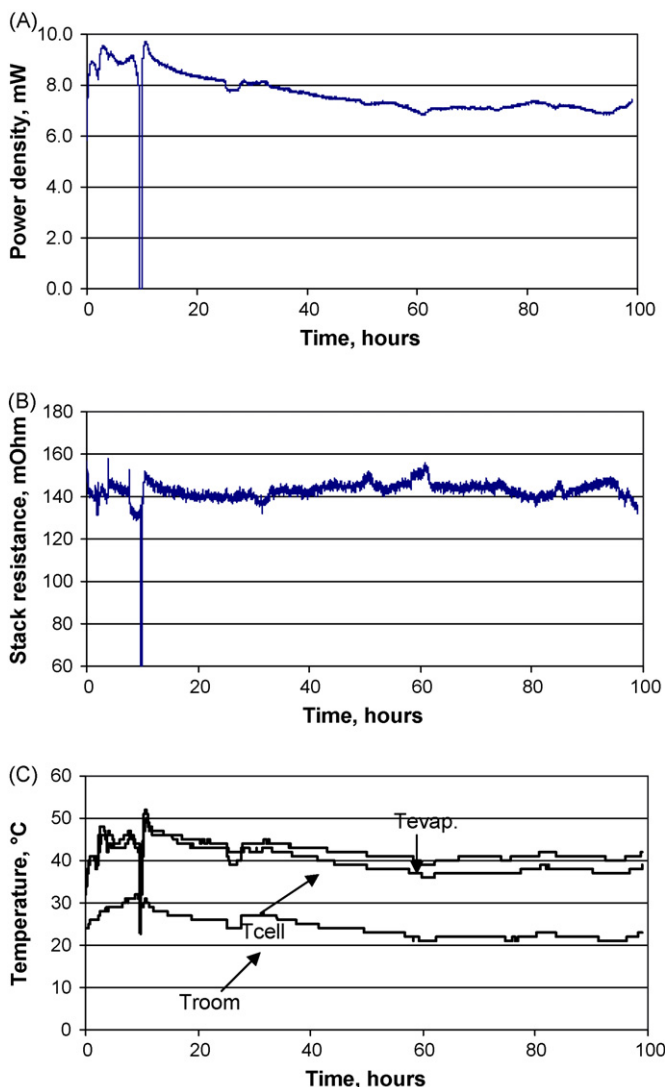


Fig. 11. The vapor feed DMFC system performance plots at constant current of 0.2 A. (A) Power density vs. time, (B) stack resistance vs. time, and (C) operational temperatures vs. time.

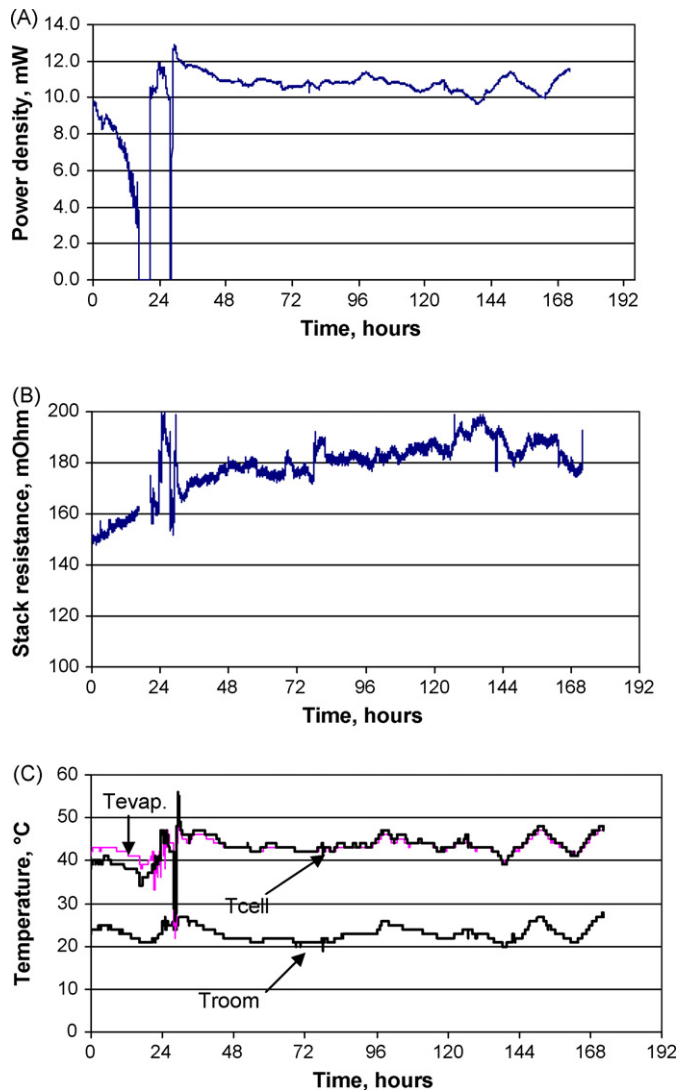


Fig. 12. The vapor feed DMFC system performance plots at constant current of 0.30 A. (A) Power density vs. time, (B) stack resistance vs. time, and (C) operational temperatures vs. time.

In the second experiment the two-cell stack was operated at a constant current of 0.3 A. The test started up with a ceramic fiber wick for fuel delivery. As shown in Fig. 12, the fuel cell could produce a power density of 10.0 mW cm^{-2} , however, the power density decreased to zero in the first 16 h. The evaporation pad temperature was higher than the cathode temperature; a situation where water usually could not condense on the evaporation pad. The evaporation chamber was opened to inspect the evaporation pad, and the evaporation pad was found almost dry. It was concluded that the ceramic fiber wick could not provide sufficient fuel to the evaporation pad. After a cotton wick was used to replace the ceramic fiber wick, the power density was improved to 11.0 mW cm^{-2} . The stack performance became stable and the stack resistance increased from 140 to 190 mΩ during the entire operation period, which demonstrated that the water wick could not provide sufficient water for the stack. The room temperature fluctuated greatly due to the weather in the last 2 days. The cell temperature also fluctuated accordingly. Overall

the fuel cell's performance was stable with the cotton fuel wick. The total methanol usage was 55.0 g. The total power output was 31.6 Wh resulting in an energy efficiency of 9.3%, a 100% increase from the last experiment.

In the third experiment the two-cell stack was operated at a constant current of 0.4 A with DC supply voltage of 1.3 V. Stack performance was stable and the average power density was improved to 13.1 mW cm^{-2} (see Fig. 13). The evaporation pad's temperature was about 1°C lower than the cathode temperature. Stack resistance fluctuated around 190 mΩ during the operation period. The total methanol usage was 24.53 g and total power output was 36.1 Wh.

In the fourth experiment the two-cell stack was operated at a constant current of 0.54 A and the results are shown in Fig. 14. The power density was found to be 16.5 mW cm^{-2} which was stable with DC supply voltage of 1.2 V. As DC supply voltage was reduced to 1.0 V at the 10th hour, the evaporation pad temperature decreased from 49 to 46°C in 1 h. The cell temperature

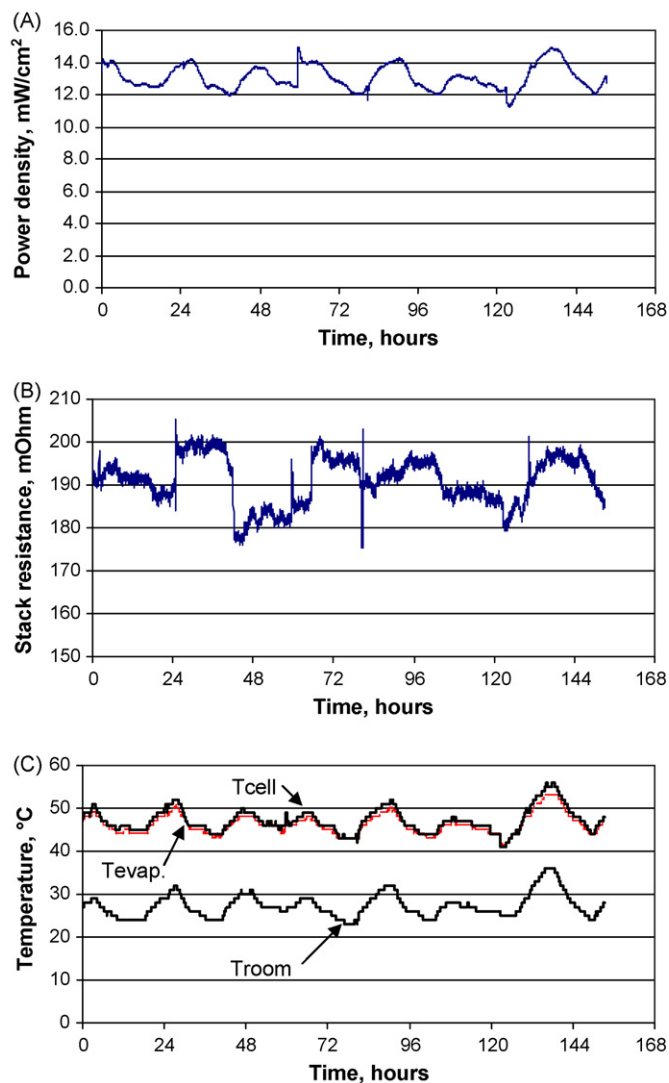


Fig. 13. The vapor feed DMFC system performance plots at constant current of 0.40 A. (A) Power density vs. time, (B) stack resistance vs. time, and (C) operational temperatures vs. time.

decreased from 53 to 50 °C during this same time period. Power density decreased steadily due to the reduction of the methanol supply. At the 17th hour the DC supply voltage was increased to 1.2 V, and the power density became stable at 14.0 mW cm⁻². To obtain a higher power density, the DC power supply voltage was increased again to 1.5 V at the 23rd hour. The power density climbed up slowly to 15.5 mW cm⁻². At around 40th hour, the cell experienced a high stack resistance increase due to water depletion. As the water tank was refilled at the 47th hour, the power density increased to 16.0 mW cm⁻² in a very short time period. The stack resistance decreased to 200 mΩ. The DC power supply voltage was reduced from 1.2 to 1.0 V at the 62nd hour, and the power density decreased accordingly. As DC power supply voltage was increased to 1.5 V at the 72nd hour, the power density increased to 16.5 mW cm⁻². The power supply was shut down at the 93rd hour, cell voltage and power density decreased quickly due to the shortage of methanol supply.

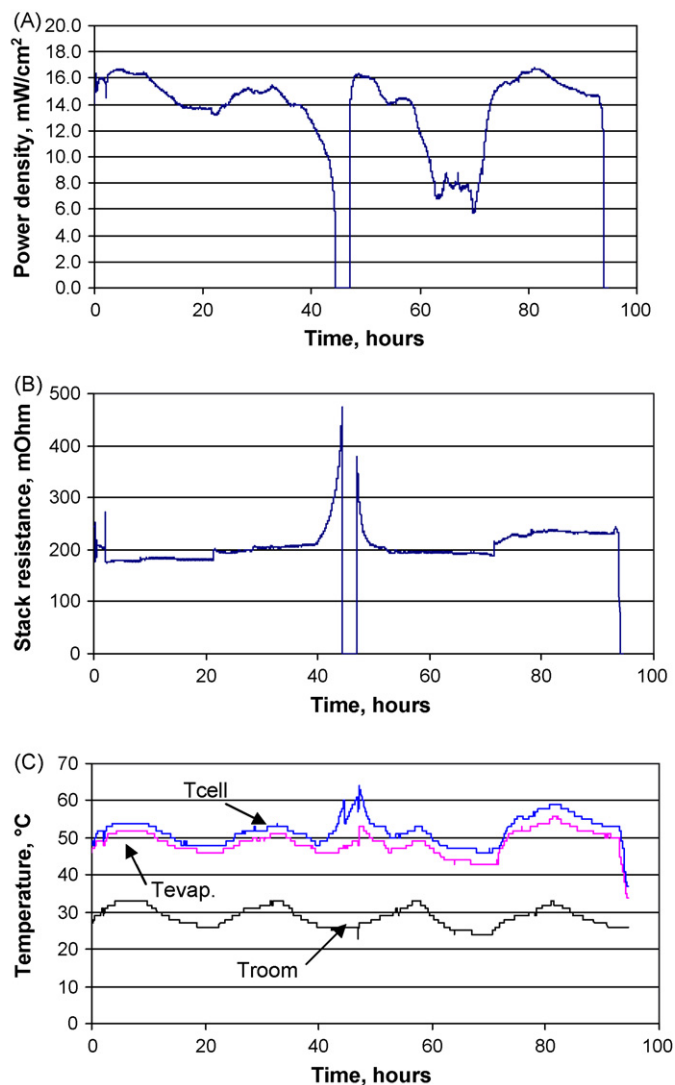


Fig. 14. The vapor feed DMFC system performance plots at constant current of 0.54 A. (A) Power density vs. time, (B) stack resistance vs. time, and (C) operational temperatures vs. time.

3.4. Two-cell stack with catalyst burner

In order to achieve the self-sustained operation of the fuel cell, a methanol catalytic burner, which is schematically shown in Fig. 5, was developed to replace electrical heaters used in previous experiments. The structure of the two-cell stack remained the same as before. The two-cell stack with the catalytic burner has been successfully operated at different constant current modes for 6 months. Fig. 15 shows the recent testing results at a constant current of 0.36 A. Since this experiment was conducted in a lab without an AC system, the room temperature varied with the weather. The room temperature usually reached 20–28 °C during early afternoons and was down to 15–17 °C in the early mornings. Comparing Fig. 15A and C, it is apparent that the power density varied with room temperatures. The two interruptions of the fuel cell operation as shown in the figure, one near the 45th hour and the other near the 220th hour, represent the time periods at which the fuel tank was depleted. After

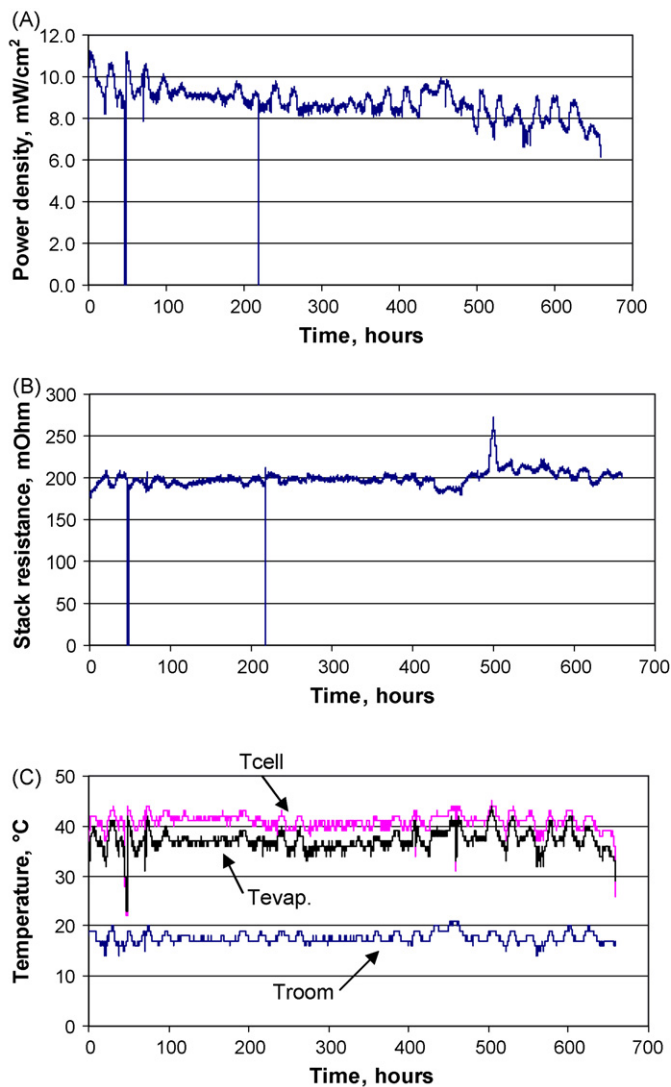


Fig. 15. The vapor feed DMFC system performance plots at constant current of 0.36 A. (A) Power density vs. time, (B) stack resistance vs. time, and (C) operational temperatures vs. time.

recharging the fuel tank the power output was resumed without any manual assistance, which demonstrated that the system can self-start. The stack resistance was stable during the operation. The test stand could not determine the stack resistance when the fuel cell was operated with near zero current density at the 45th hour and the 220th hour due to the lack of fuel. One higher spike of the cell resistance at about the 500th hour in Fig. 15B was due to membrane dehydration; the water tank was empty at that moment. After refilling the water tank, the resistance of the fuel cell stack decreased steadily to 200 mΩ. Even though the water consumption rate was very low, a water supply mechanism provided in this study was needed to keep the membrane well hydrated. The evaporation pad temperature was 2–5 °C higher than the cell temperature during the entire course of the test, which guaranteed there was no water condensing on the evaporation pad. Therefore, steady methanol vapor evaporation was ensured. After 6 months of continuous operation, the degradation of the fuel cell was negligible.

4. Conclusions

This study provides a vapor feed method in a miniature DMFC, with the following features: (i) simple fuel delivery system design; (ii) simple fuel flow rate control; (iii) versatile portable fuel cell platform, suitable for various volatile organic fuels feed fuel cells. The study also provides a complete ancillary system, namely a thermal-fluids management system, for small DMFCs. The thermal-fluids system includes fuel management, water management, air management and thermal management. The prototypes have demonstrated efficient operation and high stability in various physical orientations and environmental conditions. The two-cell stack with the catalytic burner has been successfully operated at different constant current modes for 6 months.

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