

Development of a 2 W direct methanol fuel cell power source

Chenggang Xie*, Joseph Bostaph, Jeanne Pavio

Microelectronics and Physical Science Labs, Motorola Inc., 2100 E. Elliot Road, Tempe, AZ 85284, USA

Received 1 March 2004; accepted 5 May 2004

Available online 17 July 2004

Abstract

A series of microfuel cell DMFC prototypes in the 1–2 W range has been developed at Motorola Labs. Design criteria, technical issues and the solution to those issues, system and component performance criteria are all discussed in detail with regards to the demonstrated systems. In particular, the industry-wide problem of long-term voltage degradation is explored with the implementation of a successful engineering solution to this issue which resulted in over 1200 h of system lifetime at the average degradation rate of $41 \mu\text{V}/(\text{h per cell})$. With sufficient fuel for 1 week of continuous operation, the system energy density in the 2 W DMFC prototype was 490 Wh/kg and 368 Wh/L, respectively, at an overall system efficiency of 20% (includes both fuel conversion and BOP efficiencies).

© 2004 Elsevier B.V. All rights reserved.

Keywords: Direct methanol fuel cell; Portable power source; Cell voltage degradation; Microfluidic; Low temperature co-fire ceramic; Fuel cell system

1. Introduction

As wireless digital communication and advanced computing technologies merge to combine computing and communication functions, battery technologies, even with considerable improvements in recent years, are limiting the functionality, operating speed, and operating time of those converging devices. Fuel cells potentially offer 5–10× greater energy densities than rechargeable batteries. Most fuel cell research and development targeted the large power systems ranging from 1000 W to 100 kW in the residential, automotive, power station, etc. However, those kilowatt systems cannot simply be scaled down to meet the requirements of portable electronics. Developing fuel cell power sources for portable communication products face a new set of difficult engineering challenges, including miniaturizing reactant delivery systems and developing mass production technologies for fuel cell stacks as well as for fuel cell assemblies [1–4]. In addition to these issues, there are also the basic challenges of commercializing fuel cell technology, such as increasing conversion efficiency, reducing the cost, setting up the delivery infrastructure, codes and standards, etc. Most importantly, fuel cell systems must provide higher energy density than commercial rechargeable batteries in order to enter the mass market.

There are two main choices of fuels for portable power: hydrogen and methanol. Hydrogen in gaseous form occupies relatively large volumes even when compressed, and pressurized hydrogen has potential safety issues in the intended personal use of most portable electronics. One can store hydrogen within metal hydrides or, possibly carbon materials, but compared to the best metal hydride storage densities [5], liquid methanol has greater volumetric and gravimetric energy densities. Depending on the standard free energy number for the reaction and the density of methanol (depending on temperature) the researchers use, the volumetric density and gravimetric density of methanol are reported between 4750 and 4900 Wh/L for volume, and between 6000 and 6200 Wh/kg for weight [4,6]. Based on our estimation, we used 4780 Wh/L and 6000 Wh/kg through the course of the program. Also, methanol is more likely acceptable to consumers and regulatory agencies than hydrogen gas with regards to the safety. We believe methanol currently is the best fuel choice for portable electronics. Direct methanol fuel cell technology uses liquid methanol and air as basic fuel and oxidant feeds and is a relatively simple operating system [7].

One issue that must be addressed in DMFC technology is the problem of methanol crossover. Methanol crossover is the process by which methanol diffuses across the proton-exchange membrane from anode to cathode. This results in lower conversion efficiency, as some of the methanol is directly consumed at the cathode where it releases heat rather than being oxidized solely at the anode to produce electrical current. This effect also lowers the potential at

* Corresponding author.

E-mail address: cxie@motorola.com (C. Xie).

the cathode. The crossover rate is roughly proportional to the excess methanol concentration at the anode, that is, the concentration in excess of the amount needed to ensure adequate methanol diffusion from the flow channels to the anode catalyst layer [8]. One common method to minimize the methanol crossover is to employ lower methanol concentration in the fluid supplied to the anode [9]. However, if we use diluted methanol as fuel, the starting energy density of the overall system is much lower. Typically, 3–5 vol.% methanol concentration is needed to reduce methanol crossover and maintain adequate methanol for conversion at the electrodes. As an example, at 5 vol.% methanol concentration, the energy density of the diluted fuel itself is down to 239 Wh/L, similar to the energy density of the current battery technologies. Therefore, to have a viable product competitive with batteries, it is important to use the fuel with higher methanol concentration. In this paper, we will discuss our approach to develop a 1–2 W direct methanol fuel cell power source for portable electronics. The discussion will include technical issues, such as water recovery, cell voltage degradation and other concerns, as well as our solutions to overcome some of these challenges. Targeted for consumer applications, a low power DMFC system must address the concerns of releasing CO₂ and methanol into the environment. More detailed study on the environmental impact and safety regulation is desired before launching any commercial products.

2. Experimental setup/system criteria

In order to have a high energy density fuel cell system, it requires utilizing a high energy density fuel source, such as pure methanol. The direct methanol fuel cell reaction requires one molecule of water for every molecule of methanol consumed at the anode side ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$) and creates three molecules of water at the cathode side ($6\text{H}^+ + 6\text{e}^- + (3/2)\text{O}_2 \rightarrow 3\text{H}_2\text{O}$). The overall reaction is $\text{CH}_3\text{OH} + \text{H}_2\text{O} + (3/2)\text{O}_2 \rightarrow \text{CO}_2 + 3\text{H}_2\text{O}$.

Since 1 mol of water is required for the electrochemical reaction, the maximum possible concentration of methanol would be 17 mol/L or 69 vol.% (50:50 mol%) without some form of water recovery and recirculation. The energy density of 17 mol/L methanol solution is 3298 Wh/L. Because of the methanol crossover problem in the current commercially available membrane technology (Nafion[®] 117), substantial crossover will occur at this concentration level. Instead, we must use diluted methanol fuel with the concentration ranging typically from 0.5 to 2 mol/L. The direct methanol fuel cell (DMFC) power source developed at Motorola Labs is an active DMFC system using high energy density pure methanol, actively reusing water and feeding in situ diluted fuel to the system. In this way, high energy density is achieved without degrading performance through excessive methanol crossover.

Fig. 1 shows the schematic diagram of our 1–2 W DMFC power source. A typical DMFC system consists of three major parts: fuel stack, fuel tank, and balance of plant (BOP), which includes all the auxiliaries and the electronics. The fuel cell stack is the heart of a fuel cell power source, where the conversion from chemical energy to electrical energy takes place. The current technology for the membrane electrode assembly (MEA) incorporates a commercially available polymer membrane (Nafion[®] 117) coated with electrocatalyst material, also known as a catalyst coated membrane or CCM. The loading level which we have used successfully is 8 mg Pt/cm² for the cathode and 10 mg Pt:Ru(1:1)/cm² for the anode. The detailed description of the fabrication process can be found in the published literature by Fisher and Williams [10].

Unlike with previous prototypes where ceramic anode and cathode plates were used [11], we utilized bipolar graphite stacks with six cells for our latest prototypes. The DMFC operates at 20 mW/cm² at approximately 0.5 V, per cell with the total cell voltage under full load (2 W net output) at approximately 3.0 V. Fuel and air are fed to the cells in parallel. The air flow rate is approximately 320 ml/min and the

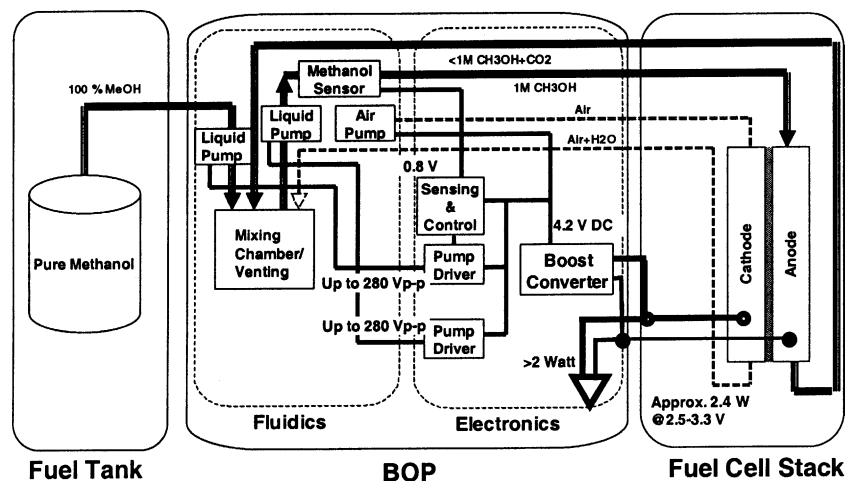


Fig. 1. The schematic diagram of our low power direct methanol fuel cell (DMFC) power source.

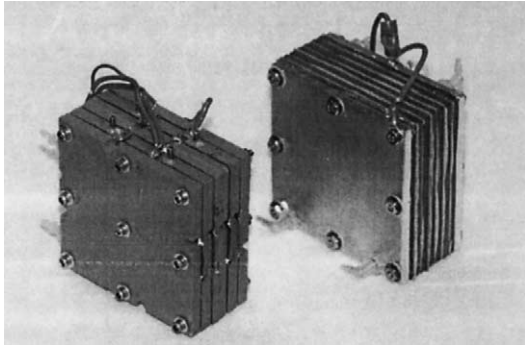


Fig. 2. The picture of the ceramic and graphite stacks.

diluted fuel flow rate is approximately 100 ml/h. The flow rates for the system are not optimized for DMFC stack performance. They were designed around a system with one set flow rate for each anode and cathode, therefore the performance at the maximum power out was not optimized. At peak power, the cathode air flow stoic was approximately 4.2, and the anode 1 M flow stoic was approximately 3.7. Although we have noticed some performance differences between individual cells in the stack, we could not statistically correlate the difference to the manifold design. The footprint of the plates is 55 mm × 55 mm. The total stack thickness is 30 mm. The stack has an active area of 110 cm² and is insulated with Zircar[®] alumina blanket. Under normal operation condition, stack temperature can reach 50–60 °C. The graphite plates and MEAs are stacked, and are held together by eight long screws, as shown in Fig. 2.

The BOP is the part of the system that supports the power generation process. As mentioned previously, because of high crossover rates of methanol through Nafion[®] 117, pure methanol is diluted to approximately 4 vol.% prior to reacting at the MEA. The dilution takes place in an approximately 10 ml size container, referred to as the mixing chamber. The mixing chamber collects the water/air mix from the cathode as well as the fuel/CO₂ mix from the anode. The air and CO₂ are vented into the ambient air. A methanol concentration sensor monitors the concentration of methanol in the fuel coming out of the mixing chamber, and when methanol is below a preset value, the sensor triggers a liquid pump to add more methanol to the mixing chamber. A second pump continuously feeds the fuel (approximately 4 vol.% in water) to the fuel cell stack in a recirculation loop. On the cathode side of the fuel cell, air is used as the source of O₂. An air pump and water recovery system supplies the required O₂ from air, removes the water from the cathode and pumps both the air and water back to the mixing chamber. The liquid pumps used in the system are piezo-driven liquid pumps manufactured by PAR Technology Inc. The piezo-driven pumps are low profile and low power consumption. Potentially, they can be integrated with other components, such as sensors, mixing chamber, and fuel cell stacks. The piezo-pumps are driven by 200–400 V peak-to-peak AC waveform. A low power pump driving circuitry was developed to convert low

DC voltage (3–5 V) up to 280 V p-p AC using an electro-luminescent lamp driving IC from Durel Inc. [12]. Under zero backpressure, the pump can deliver the fuel at a rate up to 8 ml/min. The block pressure of the pumps, at which the pump stops pumping any fluid, is around $(1.72\text{--}2.41) \times 10^4$ Pa. Therefore, the stack geometry including the manifold must be optimized to minimize the pressure drop across the system. The air pump used is a diaphragm air pump (diaphragm pump model 3D) purchased from Gast Manufacturing Inc. It satisfies some system requirements, but this off-the shelf diaphragm air pump is bulky, noisy and has short life in this application.

The performance of the fuel cell is very sensitive to the methanol concentration in the fuel. Either too high or too low of a concentration could affect the cell performance a great deal. It is very critical to have an accurate, low power and fast response methanol sensor in order to control the methanol concentration in the fuel. The sensor we used in the system was initially developed by Los Alamos National Laboratories (LANL), and its brief description is given as follows [13]. Pt catalyst is used for both methanol electro-oxidation and hydrogen evolution. Our methanol sensors are prepared by direct application of ink composed of 90% Johnson–Matthey Pt black (unsupported Pt) and 10% soluble Nafion[®] ionomer, dispersed in DI-H₂O, on two sides of a Nafion[®] 112 (0.05 mm thick) film. The Nafion[®] film was conditioned prior to use, similar to the procedure for MEAs. The area of the electrodes is 0.635 cm × 0.635 cm with a loading level of 7 mg/cm². The MEA is sandwiched by the backings and the anode and cathode collectors. Once assembled, the methanol sensor is placed inline with the fuel to the anode. The sensor is a standalone device, physically separated from the stack. For all different power levels, the same type of sensor is used. An 0.8 V DC potential is applied across the sensor, which generates a diffusion current proportional to the methanol concentration. This current is monitored to determine methanol concentration compared to a predetermined value. The typical current is about 1 mA at 1 mol methanol concentration, varying from sensor to sensor. Each sensor is calibrated before use in the system. Periodically, the methanol concentration in the solution is checked using a density meter.

The power generated from the fuel cell is highly unregulated. The stack voltage varies significantly depending on the load. To provide stable operation, a DC–DC converter is used to supply the regulated power to all the auxiliaries. The output voltage to the auxiliaries is regulated at 3.3 or 4.2 V, depending on the requirements. A 1682 high efficiency step-up converter from Maxim Inc. is used, which can give more than 90% conversion efficiency. Since most portable electronics have their own voltage regulator, sometimes, we use the fuel cell output to directly power the device. For use as a battery charger, a battery charging IC is connected between the DMFC power source and the battery. Techtium Inc. provides the battery charger used in this system.

3. Results and discussion

3.1. Stack design

Our initial stack design is based on the planar ceramic stack design developed at Motorola Labs [14]. The ceramic stack is fabricated using low temperature co-fired ceramic (LTCC) technology. For 1 W net output, assuming 75% of balance of plant efficiency, the gross output power from the fuel cell is about 1.33 W. The balance of plant efficiency is defined as the ratio of the net output power to the gross output power from the fuel cell. A certain amount of the power generated from the fuel cell is used to support the fuel cell system operation. Assuming that the fuel cell operates at 25 mW/cm² under load, the active area is 53 cm². For a 1 W DMFC, the ceramic stack contains four layers with four fuel cells per layer. The total number of cells is 16 and the total active area is 56 cm². It can generate a peak power of 2.1 W at the power density of 38 mW/cm². Fig. 3 shows the stack polarization curve and power density. The typical operating voltage for 1 W net output is around 6 V. To obtain the required voltage of 8.4 V for charging a two-cell Li-ion battery, a step-up DC–DC converter was required.

Although the planar design is suitable for sub-watt applications [13], we have found that the planar LTCC stack design had at least three shortcomings: low surface utilization, high backpressure and high resistance. In the planar design, because of its need to have a few millimeter gap between the cells to avoid cross-talk, the ratio of active surface area to total surface area in our initial design was about 46%. Although further optimization could reduce the dead surface significantly, the surface utilization rate of the planar design will likely be lower than that of the conventional stack [15]. Also, the depth and width of the channels are limited, to avoid mechanical failure due to structural fragility. In our current design, the depth and width of the channels are 0.43 mm in the anode, and 0.89 mm and 0.43 mm in the

cathode. Because of the small cross-sectional area of the channels, the LTCC planar/stack design generates undesirably high backpressure, 1.93×10^4 Pa in the anode and 3.31×10^4 Pa for the cathode for the 1 W stack at the required flow rates. Consequently, this adds more load on the liquid and air pumps, which in turn, requires more energy from the fuel cell. Secondly, the interconnect resistance of the planar stack design is higher because of its surface conduction. Because of these issues, the ceramic stack is not an ideal candidate for applications above 1 W. The assembled stack has a total volume of 81.5 cm³ with a weight of 225 g. The stack was self-heating in the system to a temperature of about 45 °C while the peak power density at that temperature was 38 mW/cm². Using these values, the fuel cell stack has a specific power of 9.3 W/kg and a power density of 26.1 W/L.

To overcome the shortfalls of the ceramic planar/stack design, we have designed and built a more conventional composite graphite stack with parallel flow on both the anode and cathode. The stack consisted of six cells electrically connected in series. The footprint of this stack is very similar to the LTCC design, but greater surface area is available for active catalyst area in the design. The active area encompasses 62% of total surface area, 16% improvement over the ceramic planar/stack design. Since the graphite plates are thinner, a smaller pitch (cell thickness) can be obtained. In approximately the same stack volume, the graphite stack has almost twice the active area compared to the LTCC stack (1.9 times), with a total active area of 110 cm². Table 1 shows the comparison between the graphite stack and the ceramic stack using similar MEAs. At the same operating temperature, the graphite stack has double the power compared to the ceramic stack with little stack volume increase. However, because the direct methanol fuel cell typically operates in a self-heating mode and the graphite stack generates more power and more heat in the same volume, under the steady state operation, the temperature inside the graphite stack rises much higher,

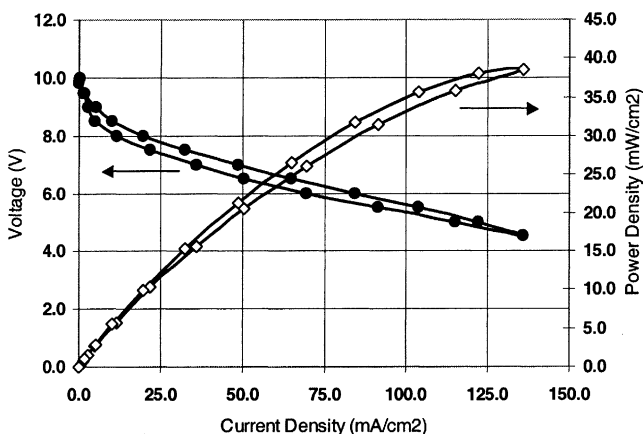


Fig. 3. The polarization curve of the ceramic stack with four layers each layer having four cells. The measurement was done under the conditions: methanol concentration in fuel is 1 M, fuel flow rate is 100 ml/h, air flow rate is 250 sccm, and temperature is 43 °C.

Table 1

The performance comparison between the graphite and ceramic stacks

Stack plate material	Ceramic	Graphite
Volume	81.5 cm ³	86.7 cm ³
Active area	56 cm ²	110 cm ²
Peak power density (self-heat)	38 mW/cm ²	60 mW/cm ²
Peak power (self-heat)	2.1 W	6.7 W
Stack peak power density (self-heat)	26.1 W/L 9.3 W/kg	77 W/L 37 W/kg
Weight	225 g	180 g
Anode backpressure (standard design at 1 W net)	19.3 kPa	3.45 kPa
Cathode backpressure (standard design at 1 W net)	33.1 kPa	5.5 kPa
Typical operating voltage for 1 W net stack (number of cells)	6 V (16 cells at 0.375 V each)	3 V (6 cells at 0.5 V each)

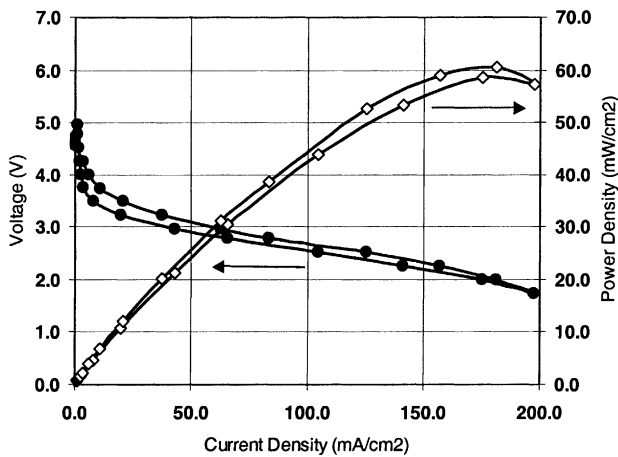


Fig. 4. The polarization curve and power density–current density curve of a graphite stack with six cells. The measurement was done under the conditions: methanol concentration in fuel is 1 M, fuel flow rate is 100 ml/h, air flow rate is 320 sccm, and temperature is 55 °C. The stack was wrapped with thermally insulating material.

55 °C in the graphite stack versus 43 °C in the ceramic stack. Under the steady state operation, the graphite stack wrapped with thermally insulating material can generate a peak power of 6.7 W, comparing to 2.1 W from the ceramic stack. The increase in power is largely due to an increase in active area as well as an increase in operating temperature of the fuel cell. Fig. 4 shows the power–voltage curve of a graphite stack with six cells. Another significant improvement of the graphite stack over the ceramic stack is the significant reduction of backpressure in both anode and cathode plates. This significantly eases the requirements for the piezo-driven liquid pump and diaphragm air pump used in the system. Backpressure was reduced down to 3.45×10^3 Pa in the anode and 5.51×10^3 Pa in the cathode during normal operation compared to the ceramic stack. The piezo-driven pump is low power and low profile, but very sensitive to pressure in the system. Reducing the backpressure can significantly reduce the pump power consumption at the desired flow rate. Since there are only six cells in the graphite stack, the typical stack operating voltage is about 3 V, 0.5 V for each cell. The power conditioning circuitry was modified to accommodate the change in the stack output. With a few minor changes including wrapping the graphite stack with thermally insulating material, the system, which previously generated 1 W net power, now is able to produce 2 W net power. The assembled stack has a total volume of 86.7 cm³, and a weight of 180 g. Calculating specific power and power density of this stack gives us 37 W/kg and 77 W/L, respectively. Improvements of the graphite stack over the ceramic stack are summarized in Table 1.

3.2. Methanol concentration control

Pure methanol is mixed in the mixing chamber with the returned fuel from the anode, and water collected from the

cathode. Due to the inherent methanol crossover problem in the current DMFC technology, it is absolutely essential to have good control over the methanol concentration in the fuel. Too high or too low of methanol concentration could cause unstable operation or even result in failure due to insufficient stack voltage to support the power conditioning circuit. We have found that the methanol concentration in the fuel must be kept within the range of 0.5–2 mol/L for our system; otherwise the system would quickly go into failure. It is noted that the power output requirement in the system is more difficult to meet than in the lab test. In the fuel cell stack test, a constant current mode is commonly used, i.e. drawing constant current from fuel cell and measuring stack voltage. When the stack deteriorates, the stack voltage drops and the stack generates less power. However, in the system, constant power is drawn. As the system deteriorates, the stack voltage drops and, to compensate for the power loss, more current is drawn, which forces the stack voltage go lower. Even worse, the conversion efficiency of the DC/DC step-up converter drops as the input voltage drops. To output the same amount of power, the system then demands more power from the stack as the stack voltage is dropping. Another system constraint is the size of the mixing chamber, which needs to be as small as possible to minimize system volume and weight. To address the issue, we have developed a simple mixing scheme combining the mixing chamber design and controlling procedures.

The methanol sensor described previously is basically a current drain. The current it provides depends on the methanol concentration of the fuel passing through it. A simple current sensing circuit converts the current to DC voltage output. When the voltage output is below the preset value, the controlling circuitry turns on the pump connected to a fuel cartridge containing pure methanol to add more fuel into the mixing chamber until the methanol level goes above the preset level. However, the time for methanol to naturally dissolve into the diluted fuel in the mixing chamber without external force is too long for a micro-DMFC system. It took more than a minute for the sensor to sense the change in the concentration after the pump added pure methanol into the chamber. Very large concentration variations were observed in a passive mixing design without using any external force for mixing. As a result, the system usually failed just after a few hours of operation. There are other mixing techniques, such as piezo-mixer, chaotic mixer or mechanical mixing, which may be applicable to the fuel cell applications but all need extra components and power. Therefore, they probably are not suitable to the micro-DMFC system we are developing for portable power applications due to the power and space constraints. In order to be able to do rapid mixing, we use the returned air from the cathode to create bubbles and turbulence in a small mixing chamber. The bubbles and turbulence in the fuel accelerate the mixing process. From the experimental results, we have no measurable performance degradation in the system before and after bubbling under our normal testing conditions. It is noted that the returned

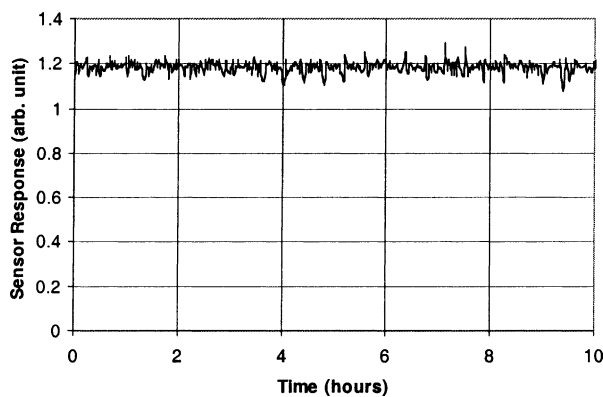


Fig. 5. The methanol concentration in fuel.

fluid from the anode is already saturated with CO_2 . Compared to other mixing techniques, this method does not require any extra components and consumes very little power. It significantly reduces the time for mixing.

To further improve the mixing process, we have also developed a pulsed fuel injection method. Instead of continuously pumping pure methanol into the mixing chamber, the system injects pure methanol into the mixing chamber for a very short period when the methanol concentration is below the preset value. Then, there is a time delay of 10–45 s for pure methanol to fully disperse into the fuel inside the chamber and for the sensor to respond. If the methanol concentration is still low, more pure methanol will be added to the chamber. The ratio of pumping time and delay time can be adjusted to meet the requirements of a specific design. The controlling electronics is very simple and cost effective. With a mixing chamber of less than 10 mm^3 volume, we observe a significant improvement in methanol concentration control compared to the simple passive mixing method, as shown in Fig. 5. In Fig. 5, the y-axis shows the sensor current response in arbitrary unit. The methanol concentration in the fuel is controlled within $\pm 3\text{--}6\%$ of the desired value in the short term. Results from our long-term experiment show that we have good control over the methanol concentration, which has proven to be adequate for extended, long-term operation. In this case, the methanol concentration was directly measured periodically using a density meter (Anton Parr DMA4500). The variation was in the range of $\pm 10\%$ of 0.9 mol/L .

3.3. Performance degradation

Although performance degradation is a major issue for many micro-DMFC developers, to the best of our knowledge, there has been no published report on performance degradation of a completed micro-DMFC system. There are very limited references on performance degradation of polymer electrolyte membrane fuel cells (PEMFC) [16,17]. Many potential causes or mechanisms, which could attribute to cell voltage degradation in PEMFC, are discussed in M. Fowler's papers. These include: degradation of the

electrode material, electrode and membrane contamination from various components, poor water management, loss of catalytic material, resistive increase in the membrane or other components, etc. Compared to large size stationary systems, a micro-DMFC system has little space available to add extra components, such as filters and water treatment to remove the contaminants. Cost and system complexity also serve as the constraints limiting the use of additional components. At this time, we have not been able to precisely and conclusively identify the specific mechanisms causing performance degradation observed in our prototype. We have instead concentrated, for the near term, on developing an operating procedure to extend the life of the fuel cell.

The performance degradation is mainly reflected in the cell voltage degradation over time. Without any improvement, the measured rate of the cell voltage degradation in the DMFC system was $1\text{--}10 \text{ mV/h}$ per cell under constant power load. This degradation rate is unacceptable for any portable energy source for electronics applications. In some cases, it only takes 24–48 h for the stack voltage to drop below the minimum input voltage required for the DC/DC converter. It is noted that the environment under which the prototype is operated is not well controlled. The temperature varies from day time to night time and from weekday to weekend. We have not used any filter for air or liquid. We believe those factors could also contribute to the large cell voltage degradation. Experimentally, we have found that the performance degradation of the DMFC system can be partially recovered. Simply stopping the operation completely for a short period of time, under a specific set of conditions, can regenerate the fuel cell and recover some parts of the cell voltage decreases. A series of experiments were performed to understand the phenomena and how it can be utilized in a real system. The initial experiments were done on the ceramic quad cells measured by a fuel cell tester developed by Fuel Cell Technology Inc. The fuel cell was tested by forcing current and measuring voltage under the constant power mode. Under the constant power mode, the current drawn from the fuel cell is constantly adjusted to meet the power requirement. As the cell voltage degrades, more current is drawn from the fuel cell. Due to the limitation of the resolution of the instrument, sometimes, small steps occur in the measured voltage–time curves, as shown in Fig. 6, when the current steps up or down. Strictly speaking, the fuel cell was tested at a quasi-constant power mode. Typically, each quad cell (planar four-cell array) can generate 0.5 W power at maximum. For all experiments, the power was set at 200 mW , the airflow rate at 250 ml/h , and the fuel flow rate at 41 ml/h unless indicated otherwise. The methanol concentration in the fuel was 1 mol/L . The test was done at ambient temperature. Because of self-heating, the temperature inside the cell rose roughly to $40\text{--}43 \text{ }^\circ\text{C}$.

First, by alternating running the fuel cell at high and low load, we wished to determine whether running at lighter load could regenerate the fuel cell voltage. A quad cell was alternately run at 200 mW for 20 h, and then at 75 mW for

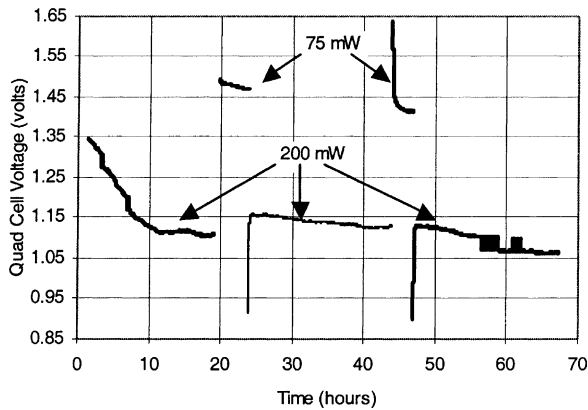


Fig. 6. The cell voltage changes over time as the loads were alternated between high and low loads.

4 h. The average degradation rate for the first 20 h was about 4 mV/h/cell. As seen from Fig. 6, the quad cell recovered some after operating at lower power level. The quad cell voltage at 200 mW load was slightly higher after 4 h at 75 mW operation. However, the quad cell still showed noticeable performance degradation over time. But it was found that by simply cycling off the system for a time, almost all of the voltage degradation could be recovered. Fig. 7 shows the quad cell voltage change at 200 mW load, with a cycle of 17 h on, then off for 7 h.

During the 7 h interrupt period, there was no air or fuel flowing to the fuel cell. During the 17 h operation, the quad cell voltage dropped from 1.55 V down to 1.25 V. After the 7 h interrupt time, the quad cell voltage was back to 1.55 V, actually a bit higher in this case. It seems that the fuel cell was completely regenerated by stopping air and fuel flow. The regeneration does not solve the degradation problem completely but it provides a potential engineering solution to the performance degradation of DMFC systems. As long as we continue to regenerate the fuel cell, the total voltage of the fuel cell can be kept above the minimum input voltage requirement of the electronics. Based on the experimental results, turning off the fuel cell for 1 or 2 min was sufficient time to regenerate the fuel cell.

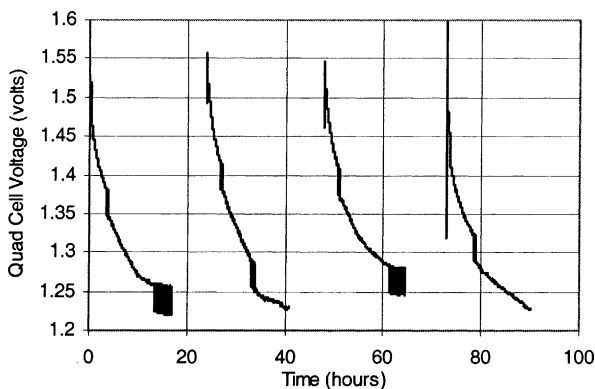
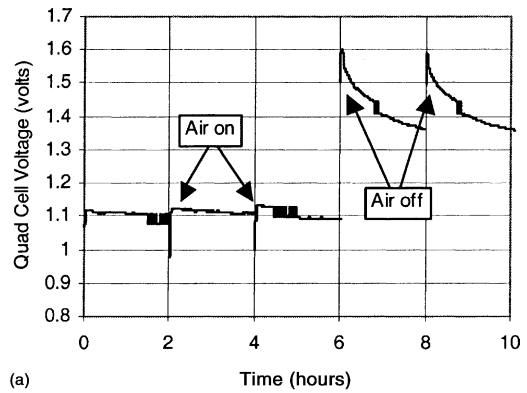
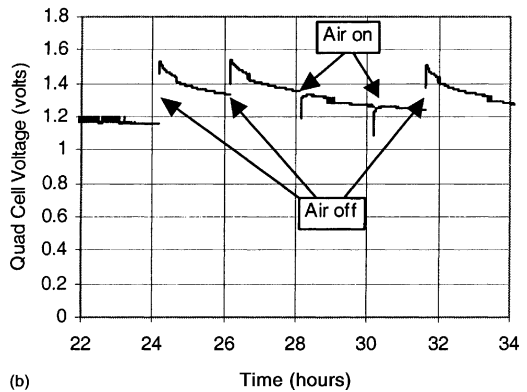


Fig. 7. The quad cell voltage changes over time as every 17 h, the air supply to the cathode was turned off for 7 h.



(a)



(b)

Fig. 8. The voltage change over time under 200 mW load with (a) 1 min interrupt; (b) 5 min interrupt.

More importantly, we have also found that cutting off the air supply to the cathode had a very significant impact on the recovery of the cell voltage degradation. First, the quad cell was run at 200 mW for 24 h. Then it was electrically disconnected from the test station for 1 min while air and fuel were continuously pumped into the cathode and anode. Afterwards, the cell was re-connected to the test station. Again, the cell was generating 200 mW power for another 2 h. The procedure was repeated for several times. In later cycles, the air flow was cut off during the 1 min period while the fuel was continuously flowing to the anode. As seen from Fig. 8a, the cell voltage increased only slightly and then continuously decreased when the air supply was on during the interrupt period. But, when the air supply to the cathode was turned off completely during the interrupt period, the cell voltage returned back nearly to the original level, 1.6 V in Fig. 8a. Afterwards the cell voltage degraded quickly at the rate of around 5 mV/(h cell). Fig. 8b shows another set of the data with 5 min interrupt in the second day of the experiment. Turning off the air supply to the cathode for a short time has significant impact on the cell voltage. Again, we have noticed little recovery when the air supply is on. Due to the nature of the experimental setup, the cell voltage was not monitored during the interrupt. We also found that whether the fuel was flowing or not during the interrupt period had no impact on the recovery of cell voltage degradation. Although we do not fully understand the mechanism(s) for this

regeneration phenomenon at this time, this finding provides us with an acceptable engineering solution to the cell voltage degradation problem of DMFC, which greatly extends the life of a DMFC system. Future experimentation could focus on a number of potential causes such as interactions occurring at the cathode, which may induce this temporary voltage degradation. To simplify the procedure and reduce the power consumed by the pumps, in most cases, we have chosen to turn off both air and fuel flows to the cell during the interrupt time. We have experimented with various interrupt times from a few hours down to 10 s and have found that cutting off the air for at least 1 min is sufficient for the fuel cell to recover. The 10–30 s seemed not long enough for full recovery. The ability to recover also depends on the cell voltage during the interrupt time. As air and fuel are turned off, the cell voltage starts to discharge slowly. For the quad cell in the test, it took about 1 min to completely discharge. For 10–30 s interrupt time, the quad cell voltage (the anode potential relative to the cathode) was still above 0 V. In a separate experiment, we have intentionally biased the cathode above the anode during the interrupt time (air and fuel off). The recovery seems much smaller than when the fuel cell voltage drops to near zero. It strongly suggests that the recovery process depends on the relative potential of the cathode to the anode.

Turning off air to the cathode is found to be very effective to regenerate the fuel cell and recover some of the cell voltage degradation. However, without air, the fuel cell stops generating power. In practice, a second power source, such as rechargeable battery or super capacitor, may be needed to provide the backup power to the device when the fuel cell is being regenerated. To implement this into the prototype, a regeneration scheme is used with 27 min on and 2 min 25 s off. The reasons for choosing that particular scheme are two-fold: to further extend the operating life, and to minimize the power loss during the interrupt period.

A fuel cell is an unregulated power source. The output voltage varies with change of the load. Typically, a DC/DC converter is used in the system to regulate the output voltage at a fixed level, 3.3 or 4.2 V in some cases. There is a minimum voltage requirement for a DC/DC converter. If the input voltage to the DC/DC converter falls below the minimum input voltage requirement for the converter, the converter will stop working. The minimum voltage of the DC/DC converter used in the system was 2.5 V for 1 W or above. It is much lower, around 1.2 V, for lower power (100–200 mW). In a 1 W prototype, a total of six cells without thermal insulation can generate 1.5 W gross power. The typical stack voltage is around 3 V. When the stack voltage falls below 2.5 V, the whole system becomes unstable and eventually stops working. Hence, the key is to keep the stack voltage above the minimum input voltage. If the time between the interrupts is too long, the system may fail before it is regenerated. Typically, the degradation rate without regeneration was about 1–10 mV/h/cell. For a six-cell stack, the overall degradation rate, six times the degradation rate for each cell, was 6–60 mV/h. For the stack voltage to drop from 3

to 2.5 V would take approximately 16 h. In the worst case, it takes less than 8.5 h. Furthermore, the conversion efficiency of the fuel cell depends on the cell voltage. The higher the cell voltage, the better the efficiency. Therefore, we decided to use a regeneration scheme of 24 min on/2.5 min off. This means that for every 27 min of operation, the system turns off air and fuel flow to the fuel cell for 2 min 25 s, and the load is disconnected from the system during the time that the fuel cell does not produce power. The overall duty cycle, the percentage of time the fuel cell generates power, is 91.8%, which is acceptable for battery charging applications. For other applications, we are in the process of implementing the necessary circuitry with a secondary power source, such as a rechargeable battery, to provide seamless power output for electronics devices. The current DMFC system using the regeneration scheme has run continuously over more than 1200 h, as shown in Fig. 9. The average rate of cell voltage degradation was 41 μ V/h per cell, at least 100 times improvement compared to the prototype without the regeneration process. Fig. 10 gives the dynamic change rate (the slope of the degradation curve) of cell voltage. The data indicates that the degradation slows down over time. The oscillation in the rate is partly due to the temperature change in the lab. The test was terminated at 1200 h because of the failure of other system components (broken tubes and pumps).

3.4. The 2 W system performance analysis

Whether or not fuel cell technology will become a mainstream energy source for portable electronics largely depends on its ability to compete with battery technology in performance. A fuel cell must provide better energy density and lower cost advantage compared to comparable battery or charger technology. The size of the previous 1 W prototype for 48 h of operation (with 100 ml of fuel) is 0.605 kg and 0.812 L. During the long-term test with 100 ml of fuel delivering 48 Wh of energy, we calculated the system energy density at 79 Wh/kg and 59 Wh/L. With improvements in BOP and system miniaturization, the total weight and volume of the system (not including fuel tank) of our latest 2 W prototype are 0.334 kg and 0.5 L. Table 2 lists the volume and weight of three major parts of the 2 W net system. The fuel cell stack is heavier than the BOP, but the BOP (including dead space, electronics and insulation) takes up 42% of the total volume. In BOP, dead space is the major constituent. The fuel tank in Table 2 includes sufficient fuel for running the system for 168 h.

Table 2
Volume and weight of the three major components

	Volume (cm ³)	Weight (kg)
Fuel cell stack	87	0.18
Fuel tank	413	0.351
BOP	416	0.155

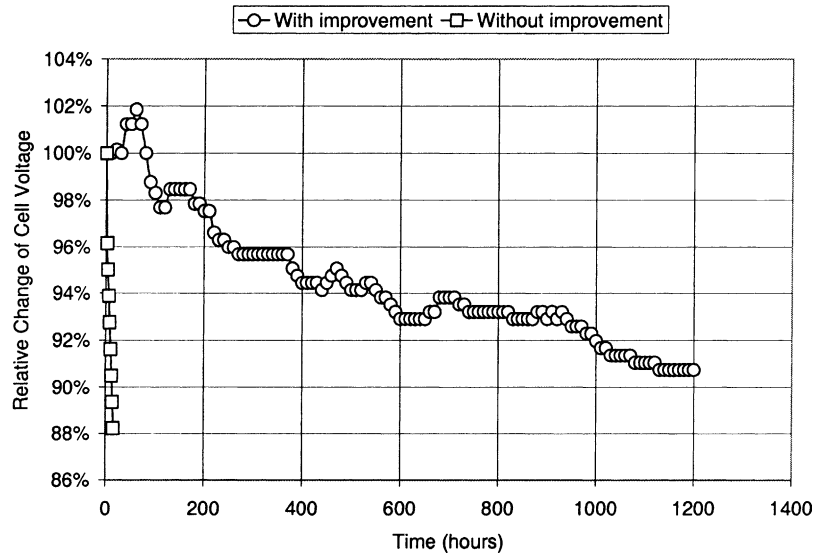


Fig. 9. The change of the cell voltage with respect to the initial voltage over time.

The BOP efficiency is defined as the ratio of net power output to gross power from the fuel cell. First, the power from the fuel cell must be conditioned to the desired voltage before the load device and any auxiliaries in the system, such as pumps, sensors, etc. can use. Part of the conditioned power is provided to the system auxiliaries to support fuel cell system operation. The BOP efficiency, η_{BOP} is equal to

$$\eta_{BOP} = \eta_{DC/DC} \frac{1}{1 + r_{au}}$$

where $\eta_{DC/DC}$ is the efficiency of the DC–DC converter and r_{au} the ratio of auxiliary power to net power. The auxiliary power includes all power consumption by the system except the DC/DC converter for user’s device. In the 2 W design using commercially available components, liquid and air pumps, DC/DC converter, sensors, timers, lights, etc. use a total of 375 mW. The ratio (r_{au})

of auxiliary power to net power is about 18.75%. If power conditioning circuitry is used inside the electronic device (almost all devices have some kind of power conditioning circuitry), the device can be powered directly from the fuel cell without conditioning (DC/DC converter) and achieve the BOP efficiency (η_{BOP}) of 84%. Providing the regulated power to the device by a DC/DC converter with 90% DC/DC conversion efficiency, the system has BOP efficiency (η_{BOP}) of 76%. It means that 24% of the power generated by the fuel cell is used to support the system operation.

Another very important parameter to characterize the system performance is the total efficiency of the system. The total efficiency is defined as the ratio of the electrical energy available for use to the chemical energy consumed. The total efficiency of our 2 W system was measured directly as described below. During output of 2 W net to an

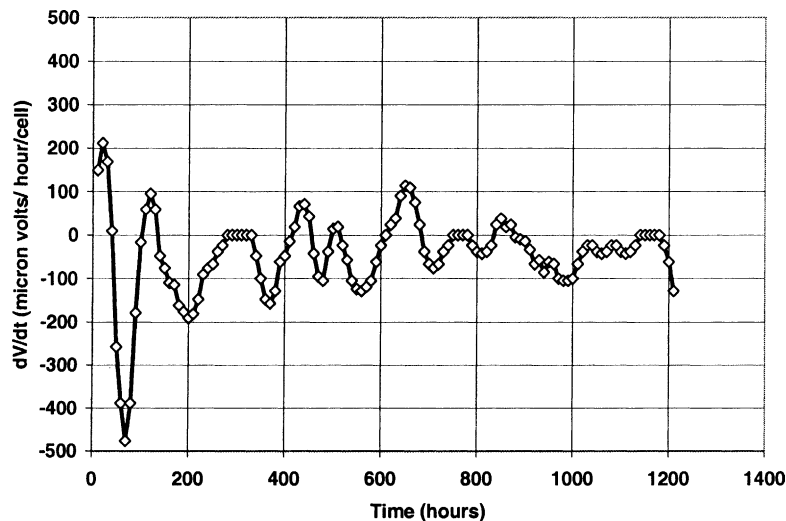


Fig. 10. The dynamic change rate (the slope of the degradation curve) of cell voltage.

external source, the BOP requires 0.375 W to support the fuel cell operation including running three pumps, methanol sensing, etc. A 3 Ω resistor load was applied directly to the fuel cell output, and the current and voltage of the fuel cell were monitored. The stack voltage, the current passing the resistor and the time were recorded at regular intervals. The interrupt cycle occurs every 27 min. Total system off time was 2 min and 25 s while the overall duty cycle was approximately 91.8% for this 2 W system. The test ran for a total of 5 h and 15 min (315 min) with 10 “off” cycles (2 min 25 s each) during that period for a total “off” time of 1450 s (24 min 10 s). The actual run time the fuel cell provided power output was 4.85 h. The average net power output from the fuel cell was 2.08 W and total energy produced was 4.85 h \times 2.08 W = 10.09 Wh. The system used up 10.5 ml of pure methanol fuel during this test. In the 10.5 ml of fuel there is 50.19 Wh available energy (0.0105 L \times 4780 Wh/L). Determining for overall total system efficiency, we have 10.09/50.19 Wh = 20% efficiency. It is much lower than the voltage efficiency.

The overall energy density of the system depends on the amount of net energy output without refuel. In order to calculate energy densities, it is necessary to understand the volume and weight of the fuel cartridge with the system. For 48 h of operation, 200 ml of fuel would be required and the system will total 0.489 kg and 0.694 L. Delivering 96 Wh of energy (48 h at 2 W), we calculated the 2 W system would have an energy density of 221 Wh/kg and 155 Wh/L (system efficiency of 20%, fuel cartridge delivery of 85%). The system size remains the same for longer operation time; only the fuel supply gets larger. The 2 W system for 1 week (168 h) of operation (540 ml fuel) will total 0.685 kg and 0.913 L. Delivering 336 Wh of energy (1 week at 2 W), we calculate that the 2 W system has an energy density of 490 Wh/kg and 368 Wh/L (system efficiency of 20%, fuel cartridge delivery of 85%), while the fuel cartridge energy density is 812 Wh/L. The system approaches an upper limit of 956 Wh/L and 1200 Wh/kg during extended operation when the volume/weight of fuel far exceeds the system. This limit is determined by the system efficiency (20%). The refueling methanol cartridge has the effective energy density of 860 Wh/L and 1080 Wh/kg assuming 90% fuel cartridge delivery.

4. Summary

A discussion of direct methanol fuel cell prototypes has been presented with detailed design criteria and their relationships to overall performance. For small, portable energy systems to be used in electronic applications, direct methanol fuel cells are a good technology choice and can provide competitive viability when compared to battery systems. With sufficient fuel for 1 week of operation, we have achieved the overall system energy density of 490 Wh/kg

and 368 Wh/L in the 2 W DMFC system at an overall system efficiency of 20%. The fuel cartridge energy density is 812 Wh/L with 85% packaging efficiency. We also found that periodically cutting off air supply to the system could extend the life of the fuel cell significantly. As a result, the completed DMFC system has achieved over 1200 h of operation. The in situ mixing method for a micro-DMFC system was described and has demonstrated good control over methanol concentration in the fuel with 3–6% variation. Although several improvements have been made during the course of the development, there are still significant technical challenges, such as lifetime, cost, ease of use, etc. to overcome before any DMFC product is introduced into the mainstream consumer market.

Acknowledgements

The authors would like to thank Jerry Hallmark and members of the fuel cell team, especially Alison Fisher and Billy Mylan, without whose help we could not have undertaken this effort. Also, this work has been partially supported through funding from the Army Research Laboratory Collaborative Technology Alliance in Power and Energy, Cooperative Agreement No. DAAD 19-01-2-0010.

References

- [1] H.L. Maynard, J.P. Meyers, Miniature fuel cells for portable power: design considerations and challenges, *J. Vac. Sci. Technol. B* 20 (2002) 1287–1297.
- [2] M.M. Mench, Z.H. Wang, K. Bhatia, C.Y. Wang, Design of a micro-direct methanol fuel cell, in: *Proceedings of the International Mechanical Engineering Congress and Exposition (IMEC'01)*, New York, November 11–16, 2001.
- [3] J. Bostaph, C.G. Xie, J. Pavio, A.M. Fisher, B. Mylan, J. Hallmark, Design of a 1-W direct methanol fuel cell system, in: *Direct Methanol Fuel Cell Proceedings of the 40th Power Sources Conference*, 2002, pp. 211–214.
- [4] C. Dyer, Replacing the battery in portable electronics, *Sci. Am.* (1999) 88–93.
- [5] W. Pyle, Hydrogen storage, *Home Power Mag.* (59) (1997) 14–20.
- [6] W. Vielstich, Electrochemical energy conversion-methanol fuel cell as example, *J. Braz. Chem. Soc.* 14 (4) (2003) 503–509.
- [7] K.R. Williams, O.P. Gregory, P. Jones, Hydrocarbon fuel cell technology, in: B.S. Baker (Ed.), *Proceedings of the Symposium of the American Chemical Society*, American Chemical Society, Washington, DC, 1965, pp. 143–149.
- [8] X. Ren, T.E. Springer, S. Gottesfeld, Water and methanol uptakes in Nafion membranes and membrane effects on direct methanol cell performance, *J. Electrochem. Soc.* 147 (1) (2000) 92–98.
- [9] B. Pivovar, M. Hickner, T.A. Zawodzinski Jr., X. Ren, S. Gottesfeld, System issues for Nafion-based portable direct methanol fuel cells, in: *Direct Methanol Fuel Cell Proceedings of the 199th Electrochemical Society Meeting*, March 25–29, 2001, pp. 221–230.
- [10] A. Fisher, R. Williams, Effect of catalyst loading on the performance of air-breathing direct methanol fuel cells at ambient temperature, in: *Proceedings of the ACS Spring 2002 Meeting*, April 7–11, 2002.
- [11] J. Bostaph, C.G. Xie, J. Pavio, A. Fisher, B. Mylan, J. Hallmark, 1 W direct methanol fuel cell system as a desktop charger, in: *Proceedings*

- of the 2002 Fuel Cell Seminar Abstracts, November 18–21, 2002, pp. 996–999.
- [12] C. Xie, J. Boggs, A low power and low cost driving circuit for piezoelectrically actuated pump, in: *Proceedings of the 2001 Microelectromechanical Systems Conference*, Berkeley, CA, August 24–26, 2002, pp. 80–82.
- [13] X. Ren, S. Gottesfeld, US Patent 6,488,837 (2002).
- [14] J. Bostaph, R. Koripella, A. Fisher, D. Zindel, J. Hallmark, J. Neutzler, L. Bai, Microfluidic fuel delivery system for 100 mW DMFC, in: *Direct Methanol Fuel Cell Proceedings of the 199th Electrochemical Society Meeting*, March 25–29, 2001, pp. 274–285.
- [15] H. Dohle, J. Mergel, H. Scharmann, H. Schmitz, Development of an air-breathing 50 W direct methanol fuel cell stack, *Electrochem. Soc. Proc.* 2001–2004 (2001) 209.
- [16] M. Fowler, J.C. Amphlett, R.F. Mann, B.A. Peppley, P.R. Roberge, Issues associated with voltage degradation in a PEMFC, *J. New Mater. Electrochem. Syst.* 5 (2002) 1–7.
- [17] M. Fowler, R.F. Mann, J.C. Amphlett, B.A. Peppley, P.R. Roberge, Incorporation of voltage degradation into a generalized steady state electrochemical model for a PEM fuel cell, *J. Power Sour.* 106 (2002) 274–283.