

Micro-electro-mechanical systems (MEMS)-based micro-scale direct methanol fuel cell development

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Abstract

This paper describes a high-power density, silicon-based micro-scale direct methanol fuel cell (DMFC), under development at Carnegie Mellon. Major issues in the DMFC design include the water management and energy-efficient micro fluidic sub-systems. The air flow and the methanol circulation are both at a natural draft, while a passive liquid–gas separator removes CO₂ from the methanol chamber. An effective approach for maximizing the DMFC energy density, pumping the excess water back to the anode, is illustrated.

The proposed DMFC contains several unique features: a silicon wafer with arrays of etched holes selectively coated with a non-wetting agent for collecting water at the cathode; a silicon membrane micro pump for pumping the collected water back to the anode; and a passive liquid–gas separator for CO₂ removal. All of these silicon-based components are fabricated using micro-electro-mechanical systems (MEMS)-based processes on the same silicon wafer, so that interconnections are eliminated, and integration efforts as well as post-fabrication costs are both minimized. The resulting fuel cell has an overall size of one cubic inch, produces a net output of 10 mW, and has an energy density three to five times higher than that of current lithium-ion batteries.

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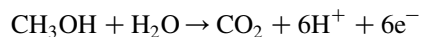
1. Introduction

The search for efficient, reliable, clean and inexpensive power sources has been an important research topic for years. Fuel cells, galvanic devices that convert the chemical energy of the fuels directly into electrical energy, are considered to be the key technology for power generation in stationary, automotive, portable and even microscale systems, and have received considerable research attention in the US and around the world in recent years. Compared to traditional power sources, fuel cell technology is a favorable energy source for a myriad of reasons, including its low environmental impact, high electric conversion efficiency (35–70% for different systems [1–3]), independence of size, reliability and long lasting operation, production of heat that is usable for co-generation cycles, and flexibility of the fuel used. Among all kinds of fuel cells, direct methanol fuel cells (DMFC) have really exhibited the potential to replace current portable power sources and micro power sources in the market, like state-of-the-art lithium-ion batteries.

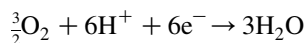
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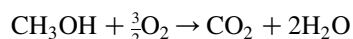
In the direct methanol fuel cell (see Fig. 1), methanol is directly oxidized at the surface of Pt/Ru (platinum/ruthenium) catalytic electrodes on the anode side to generate electricity without the need for any intermediate fuel processing and fuel reforming steps.



Protons, produced at the anode, migrate to the cathode through the proton exchange membrane (PEM) (usually Nafion), accompanied by several water molecules in the methanol solution, with a typical water drag coefficient of 2.5 $\text{H}_2\text{O}/\text{H}^+$ for a Nafion 117 membrane at room temperature (Zawodzinski [4]). On the cathode Pt catalytic layer, water is formed by the reaction between these protons and the oxygen in the air, which flows through the cathodal compartment.



This leads to the overall fuel cell stack electrochemical reaction equation:



DMFC technology is attractive because of its potential for direct utilization of methanol without the need for reforming at ambient temperatures, high energy density and lower ecologically harmless CO_2 emissions. However, it is also attractive because its fuel, methanol, is a low-cost, renewable liquid fuel, and much easier to store and transport without any auxiliary devices for intermediating fuel processing or fuel reforming steps, which are required by hydrogen PEM fuel cells (H_2 -PEMFC). Besides, unlike most rechargeable power sources for portable electronic devices, such as state-of-the-art lithium-ion batteries, the amount of time required to recharge a depleted methanol fuel cell is virtually nothing. In addition, the intrinsic advantages of DMFC include the physical dimensions of the components and the systems migrating from macroscopic to microscopic length scales. Higher surface-to-volume ratios and shorter lengths for reactant diffusion [5] potentially expedite the electrochemical reactions. The diminishing strength of body forces, such as gravitational and buoyant forces, is favorable for gravity-independent systems and is a critical factor in portable applications. Integrated or monolithic design is possible, providing more

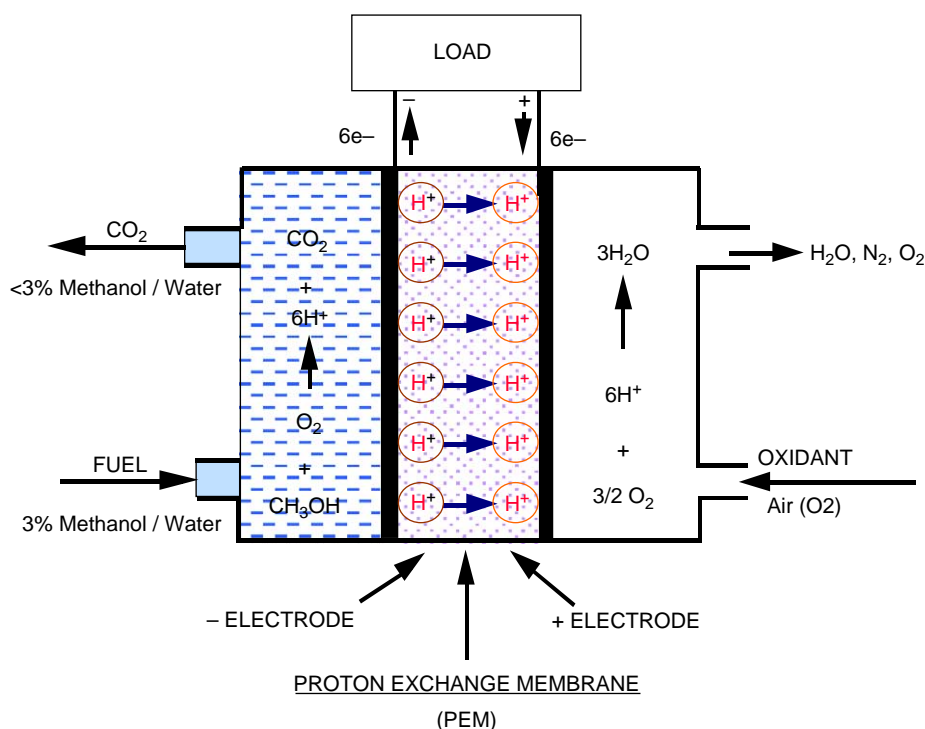


Fig. 1. Schematic of DMFC stack.

efficient operation [6]. Integrated micro systems are also advantageous and cost-effective in terms of batch production characteristics.

DMFC technology has been studied since the mid-1960s. However, only after the acidic solid proton exchange membrane (PEM, also known as polymer electrolyte membrane) had been implemented in the cell stack were remarkable breakthroughs in the electrical characteristics achieved, making the system technically and economically competitive. Since the late 1990s, numerous research interests have been directed towards the development of miniature or microscale DMFCs for powering portable electronics like cellular phones, laptop computers, wearable electronics, camcorders, microsensors and micro-electro-mechanical systems (MEMS) devices [5–21]. Recent efforts at JPL on small size DMFCs operating at ambient temperatures have shown that power densities of over 20 mW/cm^2 can be achieved with a 3% (3 v/v %) methanol solution [22]. Higher operating temperatures yield even higher power densities. With a higher anode methanol solution flow rate and a combination of 20 cells, studies at Penn State University [23] have demonstrated that $0.5 \sim 1 \text{ W}$ of power can be achieved. Their proposed micro DMFC system design, driven by capillary force and natural convection, is pump-less and self-activated by electrochemical reactions. Bostaph et al. [10] have successfully demonstrated a prototype of a 100-mW miniature DMFC based on a multilayer ceramic technology. The stack consisting of four cells consumes 1 M of methanol and oxygen from ambient air at a temperature of 21°C . A microfabricated silicon-based DMFC was built by Sim et al. [13] as an implantable micro power source for medical devices. An equal amount of methanol and water was supplied to the unit cell by capillary forces, with free flow ambient air serving as the oxygen source. The maximum achievable output voltage is only 100 mV due to the poor catalyst material. Kelley et al. [14] fabricated their mini-DMFCs with a working volume of 12 mm^3 on silicon substrates. The cells were able to deliver power densities of about 15 mW/cm^2 at room temperature. Lu et al. [21] introduced a modified anode backing structure to enhance the performance of the microfabricated fuel cells, and reported maximum power densities of about 16 mW/cm^2 , with both 2 M and 4 M methanol supply while operating at room temperature. Most recently, a conceptual design of an integrated fluidic system for microscale DMFCs, including water management at the cathode, a micropump for water recycling, and a gas separation system, was proposed by Yao et al. [20]. Based on their calculations, the microfabricated DMFC with energy efficiency of 35% will be able to provide 650 mW continuously with a total volume of about one cubic inch for a period of 20 h.

Despite its promising potential, microscale DMFCs are not currently ready for a complete commercial application because of low efficiency, high costs, limited durability and other crucial practical application issues. In order to realize commercialization, the power outputs of DMFCs, determined by the power density and total area of membrane electrode assembly (MEA), have to fulfill the power requirement of the system. Since the total area of MEA is limited by the physical dimension of DMFC, power density of MEA becomes the primary concern of development of DMFCs. A severe degradation of MEA power density may occur due to the methanol oxidation. This process is caused by the methanol crossover from the anode to the cathode through the permeable PEM, usually Nafion[®] and driven by concentration gradient [16]. Methanol crossover has been one of the challenging problems affecting the performance of DMFCs and has been investigated extensively [24–27]. Factors affecting the level of methanol crossover include the methanol concentration, PEM material, PEM thickness, operating current density, and operating temperature and pressure. In general, 1 M of methanol is preferable in the presence of an air-breathing PEM DMFC [28,29].

Another crucial practical issue in the development of DMFCs is the length of time they can provide power, which actually is dependent upon the amount of fuel a DMFC can store. However, in reality, the space for methanol storage is quite limited. Therefore, pure methanol instead of diluted methanol needs to be stored within the fuel cell and packaged together, thus increasing the energy density by a factor of two orders of magnitude. The reaction products of the overall electrochemical process are carbon dioxide and water. While it is being produced at the cathode, water is also being consumed at the anode by methanol oxidation and through the water crossover caused by the electro-osmotic drag of proton migration in the PEM. In order to maintain the reaction and reduce methanol loss, water in the anode stream has to be replenished. In addition, the excess water accumulation leads to cathode flooding, which blocks oxygen access to the cathode electrode. An attractive and promising approach is to pump the product water back to the anode compartment [6]. Hence, an auxiliary water management system has to be incorporated so that only pure methanol is stored to extend the working life of DMFCs for a given volume.

Currently, most research on DMFCs has revolved around fundamental issues, such as enhanced electrochemical reaction rate [22,30–33] and superior membrane materials [34–38], and focused little on fluidic issues. Consideration

of the fuel cell stack alone might not be sufficient to ensure that the DMFC technology has a viable competitor to the existing portable power technologies. As pointed out by Ren et al. [39], cell performance can be significantly improved with proper cell design along with novel membrane and catalyst technologies. For a microscale DMFC operating at atmospheric conditions, improved design of fluidic systems for methanol and air circulation, CO₂ separation, water recycle and fuel storage are desired for compactness and efficiency.

This work describes major challenges and solutions in developing a micro power generation (MPG) device, which utilizes ambient temperature direct methanol fuel cells (DMFC) to produce a net output of 10 mW for continuous power generation. With the energy efficiency of 35% and an overall size of one cubic inch, continuous operation time of at least five weeks is anticipated. It has a life span three to five times longer than the state-of-the-art lithium–manganese dioxide batteries, and on a weight basis, it achieves a five-fold advantage. This results in an equivalent system energy density corresponding to 1540 Wh/l. The pure methanol consuming rate, CO₂ generation rate and H₂O loss rate in the methanol chamber are 2.7×10^{-4} , 0.15 and 1.2×10^{-4} cm³/min, respectively. Compared to state-of-the-art lithium-ion batteries, the proposed DMFC will (i) provide a four-fold operating life span, (ii) exhibit a five-fold advantage on a weight basis, and (iii) lessen the environmental impact of battery disposal. This work focuses on the conceptual design of the system together with the design and development of water management at the cathode, micro pumps and valves, CO₂ gas separators, and other fluidic devices conducted at Carnegie Mellon University.

2. System schematic

A schematic of the micro DMFC system is shown in Fig. 2. Besides the fuel cell stack, the micro DMFC system includes components for fuel delivery, fluid pumping, gas–liquid separation, water collection, and air delivery.

This micro DMFC is simple in design, operates at an ambient temperature, and is capable of operating with any orientation. The air flow at the cathode side and the methanol circulation at the anode side are all at a natural draft. A passive gas bubble separator removes CO₂ from the methanol chamber at the anode side. The membrane-electrode-assembly is mainly silicon based. The back planes of both electrodes are made of silicon wafers with an array of etched micro-sized holes. Nano-tube catalysts are fabricated on the planes. The nanotube catalysts have an orientation in the [111] crystallographic direction so that the power density and the efficiency of the fuel cell are both maximized.

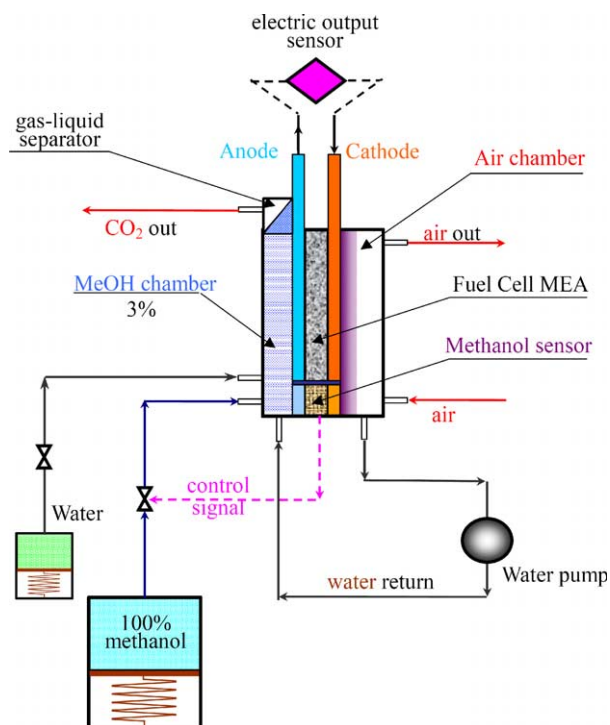


Fig. 2. Schematic of micro DMFC system.

The 3% methanol solution at the anode and the air at the cathode are driven by natural convection instead of being pumped. Since water management is critical to the DMFC because it competes with the present lithium-ion battery, a water management system (as shown in a later section), enhanced with surface wettability control on silicon, is exploited to guide and collect at the cathode. A micro pump sends water back to the anode side. The water is recycled from the cathode to the anode by a micro pump so that a minimal supply of water is needed. Most of the storage space is, therefore, devoted to the 100% pure methanol storage reservoir, as shown in Fig. 3. Furthermore, putting a small water tank in the system renders the fuel cell more robust during start up after a long period of storage. The storage reservoirs are slightly pressurized and valved, rather than pumped. The fuel cell will be compact with the support of the MEA formed by thin silicon walls. The CO₂ gas separation at the anode side is passive. The design is further simplified by putting the CO₂ gas separator, flow channels, micro pumps/valves and their control circuit on the same silicon wafer, which yields a miniaturized, integrated and unified system that promises to be highly efficient. The 3% concentration of methanol solution in the fuel cell chamber is monitored with a methanol concentration sensor. Feedback is provided to the control valve of the pre-pressurized methanol and water reservoirs. When the concentration is below 3%, the valve is opened, and the pure methanol is injected from the reservoir into the methanol chamber. A uniform concentration of methanol in the fuel cell chamber is maintained by the high diffusivity of methanol and by the mixing driven by the buoyant CO₂ bubbles.

As shown in Figs. 3 and 4, the whole micro DMFC system is divided into two major parts. On the right hand side is a thin methanol solution chamber, which links to the fuel cell stack and the integrated micro-fluidic components. The supply reservoirs on the left hand side are for fuel and water storage, which can be replaced or refueled when methanol is used up, providing a cost effective DMFC system.

This micro DMFC system, designed for microsensor applications, needs to maximize power generation efficiency and the use of consumable resources. With a 25 mW/cm² power density, the total MEA area around 1 cm² can provide enough power to a 10 mW microsensor along with the extra power needed for internal use, such as water pumping, electronic controls, and process conditioning. In the present design of this system, the nominal flow rates of air, pure methanol, and water–methanol solution are 1.1, 2.7×10^{-4} and 0.2 cm³/min, respectively. Accordingly, the reaction rates of other species in the DMFC stack can be derived as shown in Table 1. The theoretic energy density

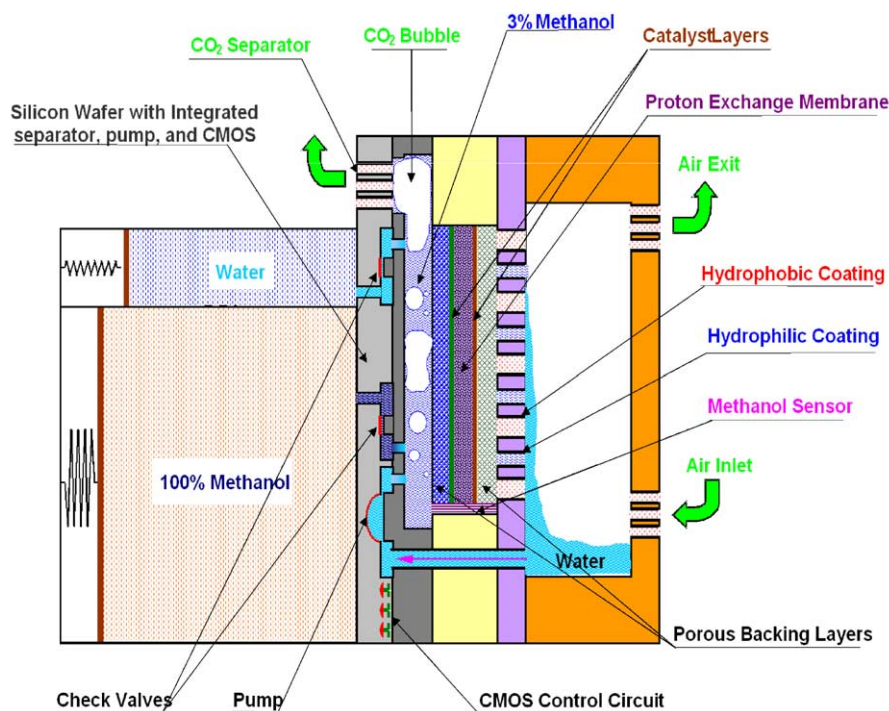


Fig. 3. Cut view of micro DMFC system.

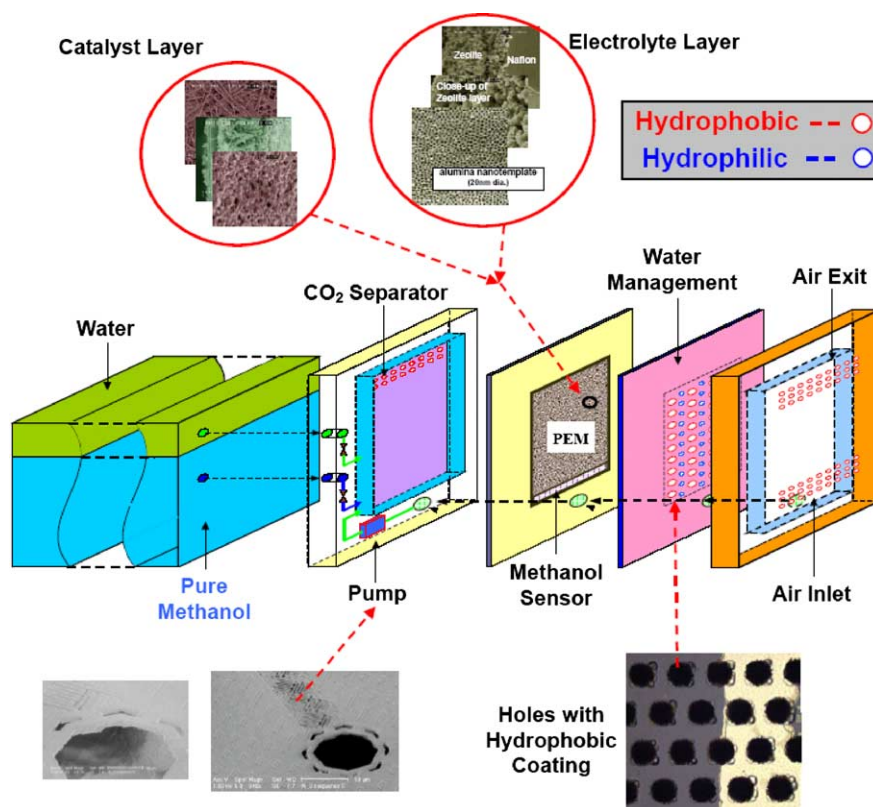


Fig. 4. Component assembling view of micro DMFC system.

of pure methanol is around 4800 Wh/l. With an available cell level energy efficiency of 35% and $2.7 \times 10^{-4} \text{ cm}^3/\text{min}$ methanol consuming rate, 14 cm^3 of pure methanol storage can easily support a continuous operation of this 10 mW microsensor for at least five weeks. After incorporating the fuel cell stack, microfluidics and extra water storage into the system, the overall size of the micro DMFC can be controlled within one cubic inch and the system energy can reach 1540 Wh/l.

3. Water management at the cathode

The concentration of methanol solution in the fuel cell chamber is 3%, which is stoichiometric within the process to compensate for the water loss due to the reaction at the anode and leakage through the membrane during proton transport. The ability to collect water at the cathode, while pumping it back to the anode, allows the water, by being recycled, to avoid sizable water storage. This allows large storage space for pure methanol in the system, resulting in a high energy density for the DMFC system. The cost of portable power could also

Table 1
Reaction rates of all the reactants in the DMFC stack

Species	Reaction rate
CH ₃ OH (μl/min)	0.27
CO ₂ (ml/min)	0.15
H ₂ O(A) (μl/min)	0.12
H ₂ O(T) (μl/min)	1.80
H ₂ O(C) (μl/min)	0.36
O ₂ (ml/min)	0.23
Air (Q _{ST}) (ml/min)	1.10

be reduced due to the lower cost of methanol fuel. Because the water level in a fuel cell strongly affects membrane properties, reactant transport, and electrode reaction kinetics, maintaining an optimal water balance between the anode and cathode is important in achieving good cell performance. During the operation of a DMFC, water transport in the polymer electrolyte membrane in a fuel cell can occur by several modes, namely, by diffusion when there is a water activity gradient across the membrane and by electro-osmotic drag of proton migration when the cell is under current. As the fuel is directly fed to the anode, reaction occurs in the oxidation of the methanol. Without water, the proton will resist permeating through the membrane, resulting in lower performance. Each hydrogen proton should accompany 2.5 water molecules in order to drift through the membrane. At the cathode, the reaction occurs in oxygen reduction and as a result, more water is generated. Therefore, too much water content at the cathode side may result in flooding. When flooding takes place, the surface of the cathode catalyst may be covered with water and reduce the electrochemical reaction rate. In addition, water will obstruct the oxygen reactant approaching the catalyst.

This issue can be resolved by using a silicon back plane at the cathode and applying a localized hydrophobic coating to passively guide the water to flow to the desirable collecting point. This process would also ensure that the cathode will not be seriously blocked by water. This arrangement will not only assure the success of the present goal but will also support technological advancement in other types of proton exchange membrane fuel cell (PEMFC) development.

4. Concept of the approach

On the back plane of the cathode is a silicon wafer, typically 300 μm in thickness. The *skin* of the silicon surface is a thin layer of oxide which reacts hydrophilically to water. The silicon wafer is etched with a number of small holes, in the order of 20–60 μm in diameter, using the deep reactive ion etching (DRIE) process. Strips of protective coating will then be applied on the wafer and the covered areas preserve the surface of the silicon. The silicon wafer, which has been produced, can be installed in DMFC at the cathode with the strips oriented with gravity. During operation, water is rejected from the cathode through the hydrophilic holes and forms larger drops. The drops eventually fall along the strip, while coalescing with other drops along their paths. The water will also be channeled to the collecting point of the micro-pump. At the same time, the liquid forms a meniscus at the mouth of the opening, without flowing into the small hole because of surface tension forces and the silane coating, which allows the air to feed into the hole and contact with the catalyst. Even in a humid air environment, the supply of oxygen to the cathode will be assured through the hydrophobic holes.

A schematic of the process is shown in Fig. 5. Fig. 5(a), (b), and (c) show the top cut-view, with the evolution of water management processing during the formation of drops. Fig. 5(d) shows the drops formed at the front view of the cathode surface and their downward slide, as the force of gravity overcomes surface tension force.

5. Results

The final look of silicon wafer after the fabrication process is shown in Fig. 6. The silicon wafer is mounted inside the experimental test. The syringe pump is supplied with water at a flow rate of 0.261 cc/h. It is provided through the different layers of thin stainless steel perforated carbon paper and the silicon wafer. In Fig. 7(a), a photo of the two patterns of opening holes is shown: the small ones were coated with a non-wetting agent while the big ones were non-coated. The water is allowed to exit slowly through the big opening holes only, and not through the small ones. After several hours of running the test, the water continued spreading along the surface of silicon wafer as strips (Fig. 7(b)). The water accumulated as a large droplet that covered the big opening holes (Fig. 7(c)). The boundary of the droplet does not cover the zone of small holes (Fig. 7(d)), which proves that the hydrophobic coating is working successfully.

The fuel cell is working vertically, and the droplets will drop down due to the gravity force, be able to collect the water, and then pump it back by using a micro-pump. So, the flooding problem in the fuel cell can then be solved by the hydrophobic–hydrophilic silicon wafer which improves the efficiency of the fuel cell.

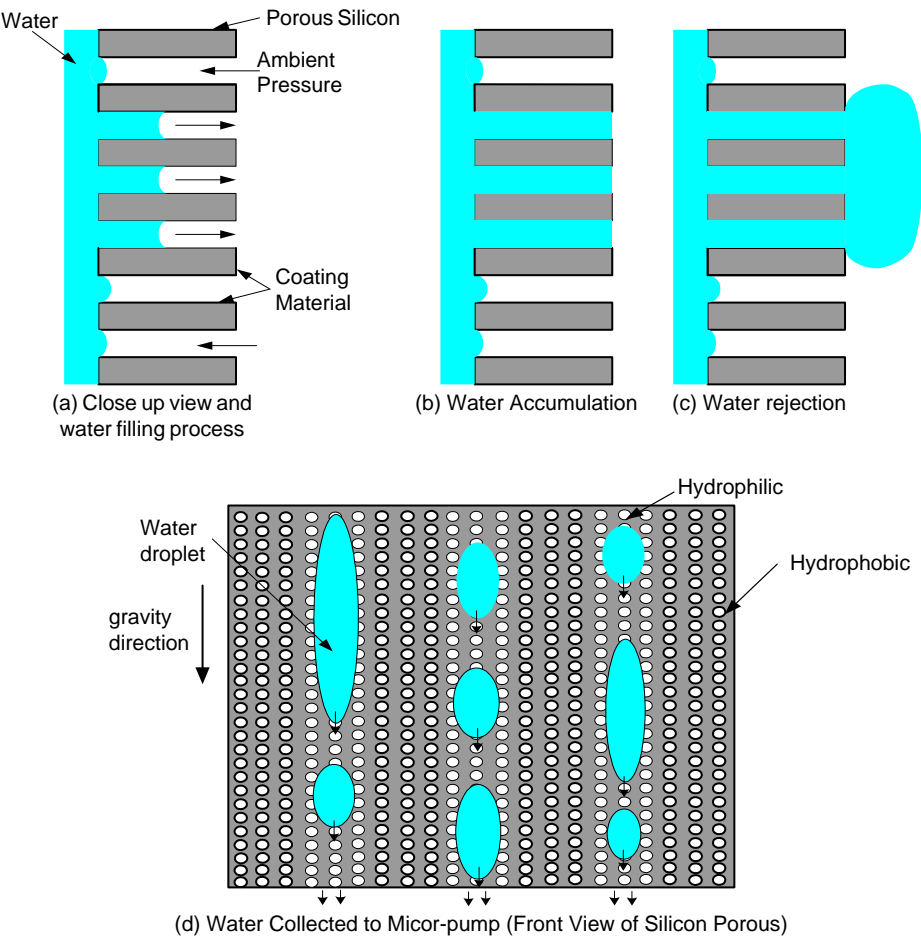


Fig. 5. Evolution of water management processing PEM fuel cell (cathode side).

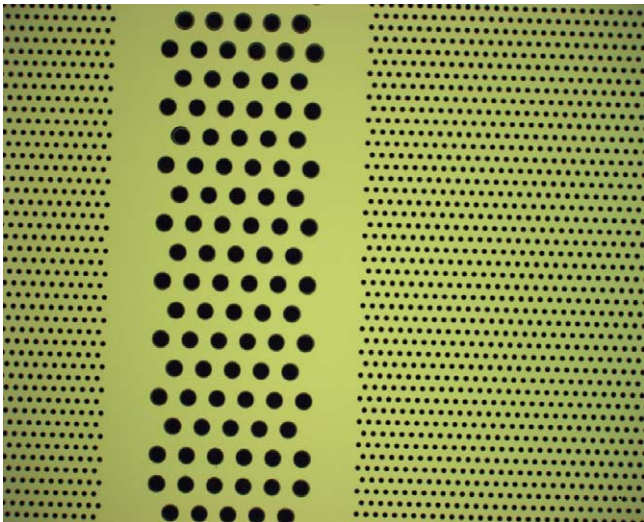


Fig. 6. Different strips of holes, with big holes for water and small holes for air.

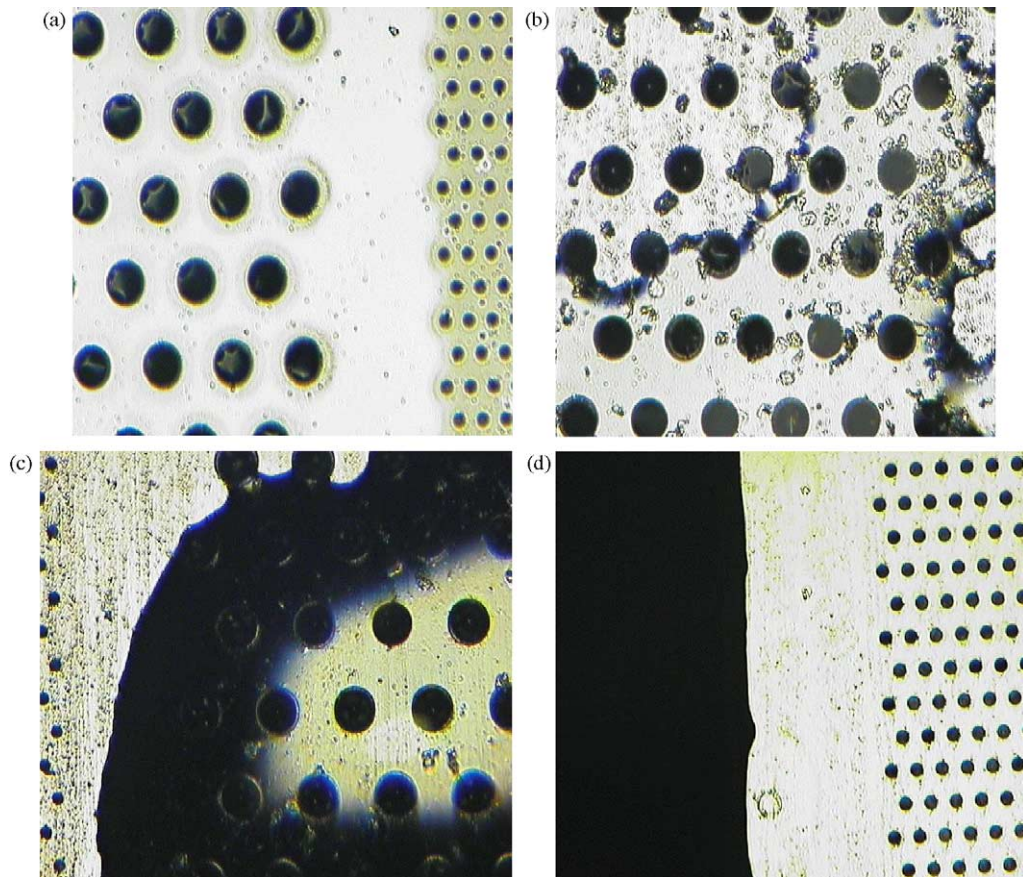


Fig. 7. Microscope pictures with magnification $5\times$ of silicon water with hydrophobic–hydrophilic strips. (a) Water is coming out from the big holes. (b) Water has just exited one of the holes. (c) Water is spreading on the hydrophilic surface. (d) Clear boundary of the droplet without cross covering the small holes.

6. Development of micro pumps

A MEMS fluidic pump will be implemented based on a polymer membrane with an embedded metal mesh. The purpose of the pump is to feed water from the cathode back to the anode. To achieve the desired output power, the constraints have a pressure of 0.5 PSI (3.44 kPa) across the pump and a maximum flow rate of 0.1 cc/min.

In prior work, CMU has fabricated working acoustic speakers based on similar electrostatically actuated membranes [40,41] (see Fig. 8). The membrane is made by first fabricating a fine mesh of aluminum and silicon oxide micro-beams and then by coating this mesh with a polymer to seal the membrane. The membrane is suspended over a cavity etched into the silicon substrate prior to the polymer deposition [42]. An applied voltage between the embedded metal mesh and the substrate causes the mesh to pull down into the cavity.

The membrane technology is being expanded upon to act as a liquid valve. For the conversion to a valve, the membrane is ‘capped’ by sealing the top with another wafer. The system fluid will be drawn into the gap between the membrane and the capping wafer as the membrane is electrostatically pulled down. When the voltage is removed, the membrane, elastically returns to its original position, expelling the system fluid. Three of these valves in peristaltic motion will form a pump. The membranes exhibit experimentally proven deflections of over 20 μm , which provide the pump with a large stroke. Electrostatic pumps are efficient, as the energy stored in the capacitance is only dissipated during switching, and no DC power is dissipated in the device.

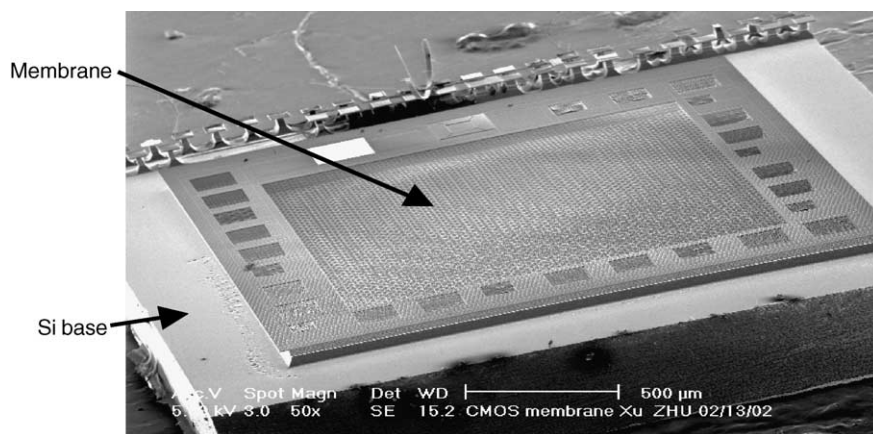


Fig. 8. SEM of MEMS membrane made in foundry CMOS, followed by micromachining.

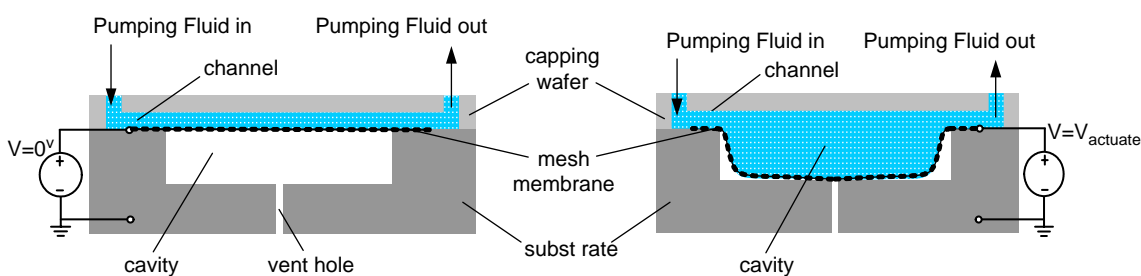


Fig. 9. Cross section of basic valve. On the left, valve is in the un-actuated state; 0 V applied between the membrane and substrate. On the right, a voltage, V_{actuate} , is applied between membrane and substrate causing the membrane to pull down and draw in the system fluid.

For the conversion to a valve, the membrane will be ‘capped’ by sealing the top of the membrane with another wafer (see Fig. 9). The fluid will be drawn into the valve as the membrane is electrostatically pulled down and will be forced out as the membrane elastically returns to its original position. Three of these valves with coordinated peristaltic action form a pump.

Although the pump is based on the original micro-speaker development, there are improvements that will need to be implemented, especially regarding pull-in voltage. The first major improvement will reduce the electrostatic pull-in voltage by using a cavity with a curved bottom electrode, rather than a flat bottom [43–46]. The curved electrode provides more electrostatic force near the membrane anchors, initiating pull-down (see Fig. 10). The membrane can then pull down with less voltage onto the remaining central part of the bottom electrode.

A key challenge is to etch the silicon in such a way as to fabricate the valves with a sinusoidal profile. To do this, etch lag (also called micro-loading) will be used. When etching silicon for a large exposed area, a deeper etch will be produced for the same amount of etching time. Etch lag, as shown in Fig. 11, is used to produce the varying depths in silicon by varying the spacing in the mesh that masks it. Towards the edges, where the etch is shallow, the gaps are smaller. The gaps in the middle of the mesh are wider to etch deeper into the substrate. Experimental results in Fig. 12 show etch depth versus gap spacing for the same amount of time.

7. Development of the CO₂ gas bubble separator

Carbon dioxide is evolved in the anode stream in the form of gas bubbles due to its limited solubility in the methanol–water solution. The existence of CO₂ bubbles in a DMFC system could be destructive. Therefore, removing CO₂ bubbles from the flow stream is essential in maintaining the cell performance. A possible approach for effective gas–liquid separation in microscale devices is the modification of the surface’s wettability.

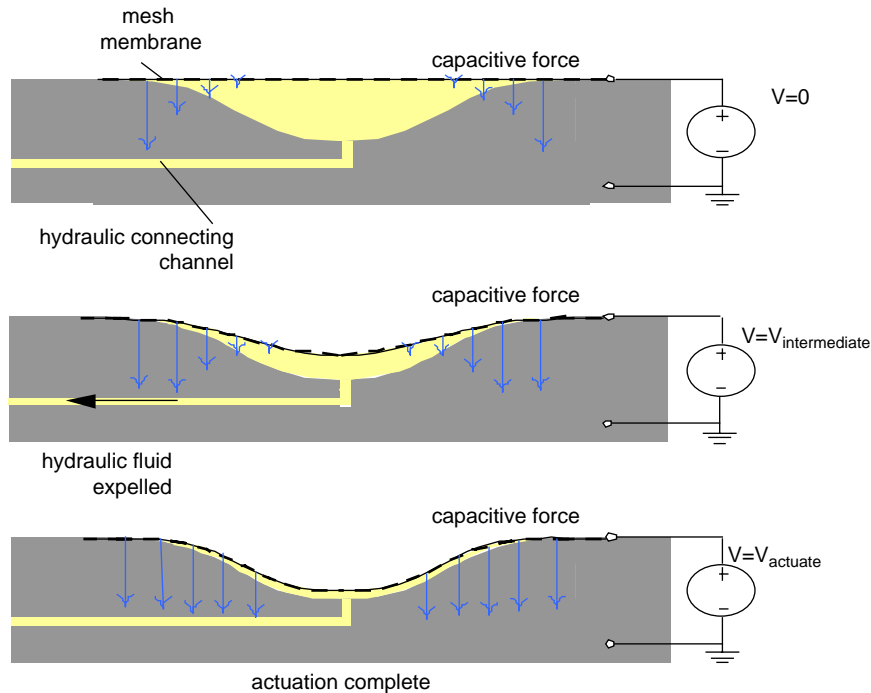


Fig. 10. Demonstration of the ‘zipper effect’: strong force exists at the membrane edges where the gap is small. This strong force pulls down the membrane at the edges causing the force to increase in the rest of the membrane, further pulling it down.

The proposed gas–liquid separation system, shown in Fig. 13, consists of two parallel silicon wafers with an array of etched-through holes. The gas separator is coated with a thin layer of hydrophobic polymer (octafluorocyclobutane (C_4F_8)) to create an effective passage for gas bubbles and to prevent the liquid from getting into these holes. On the other hand, the liquid separator is hydrophilic (silicon or silicon dioxide) to facilitate the liquid removal from the gas–liquid mixture. The two wafers are then bonded together to form a chamber with a narrow gap between them. The two-phase flow is directed to the narrow chamber and the gas–liquid separation takes place passively.

Several successful gas–liquid separation tests have been carried out at Carnegie Mellon. This separation system performs well as long as the limiting pressure is not exceeded [47,48]. The CO_2 slug bubble entered the separation

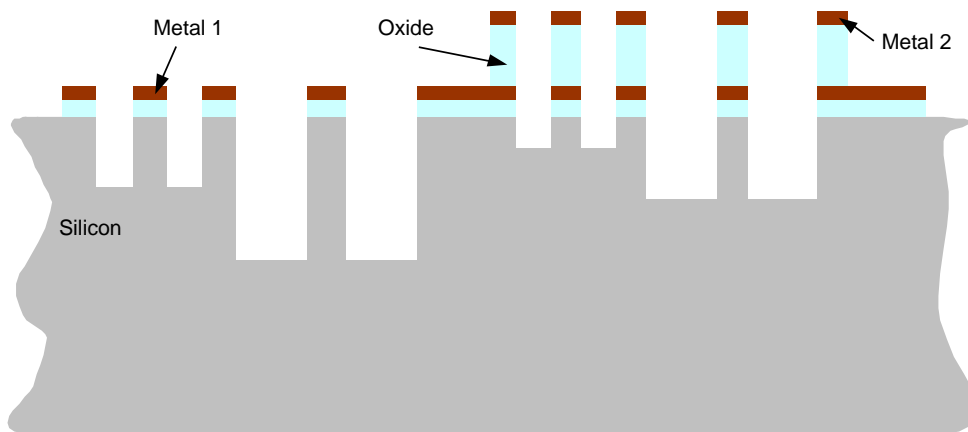


Fig. 11. Demonstration of ‘etch lag’: when etching silicon, the etch depth varies with the gap in the mask. Therefore, a smaller gap leads to a smaller etch depth. This is probably caused by reactive species difficulty in transit through smaller, tighter gaps. Correspondingly, the phenomenon also occurs with higher aspect ratio masks, which occur if Metal 2 is used as a mask instead of just Metal 1.

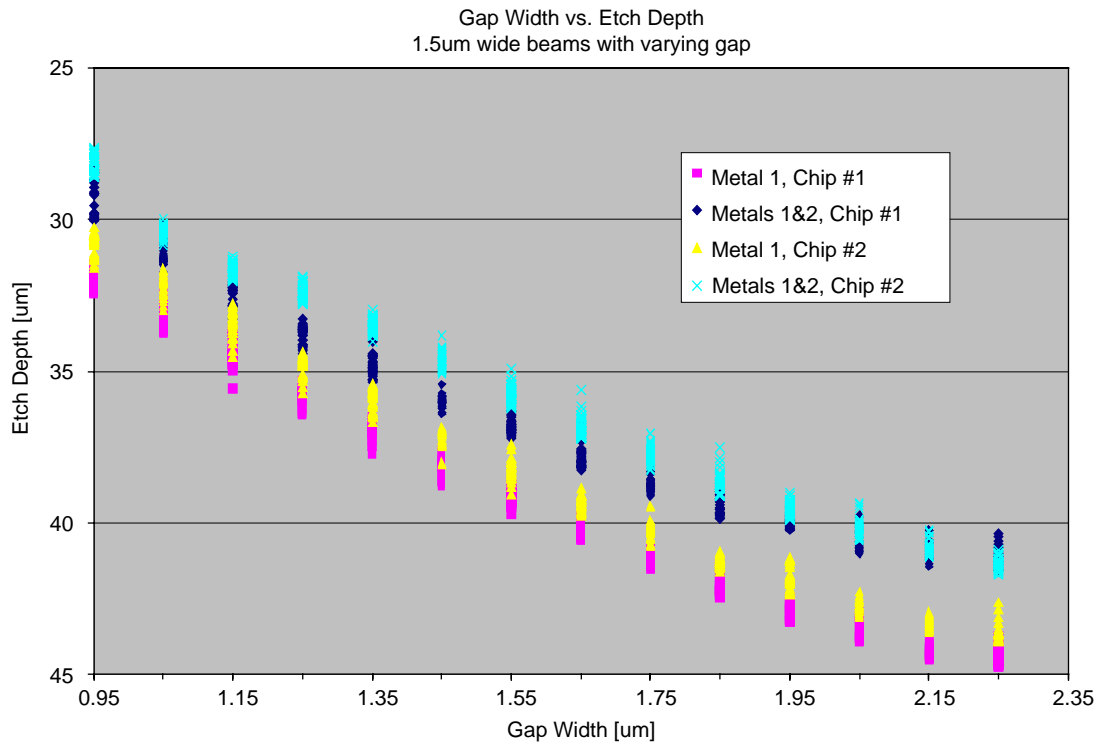


Fig. 12. Experimental results taken from two different chips with two different mask heights: just Metal 1 and Metal 1 & 2. As expected, for smaller gaps and higher aspect ratios, the etch depth decreases. Note that the etch depth is in microns below the silicon surface; hence it is negative.

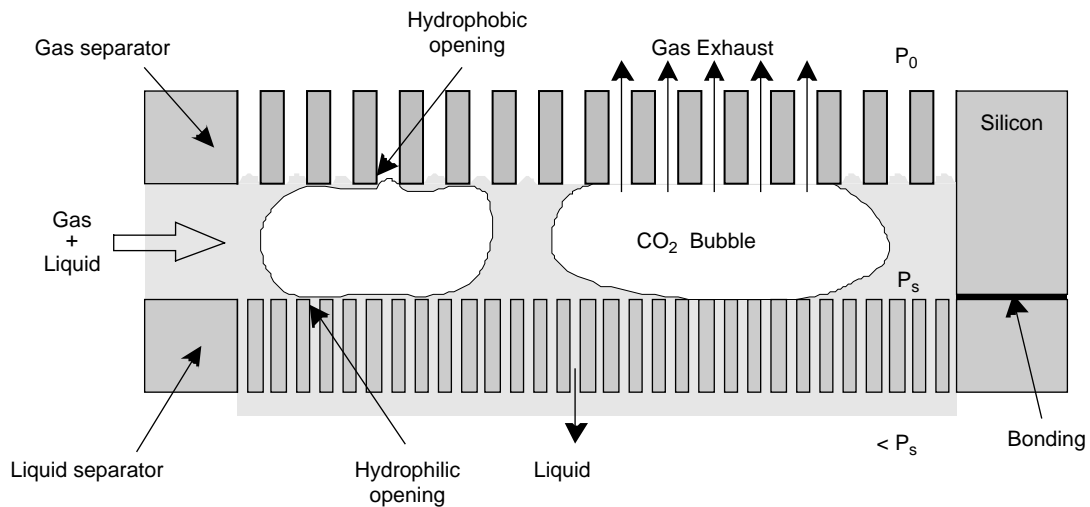


Fig. 13. Gas–liquid separation system with hydrophobic gas separator and hydrophilic liquid.

chamber and escaped through the gas separator, while the water was drained from the liquid separator, and no liquid was found in the gas outlet.

8. Conclusion

This paper demonstrates a silicon-based micro-scale DMFC system, which can replace state-of-the-art lithium-ion batteries used in micro sensor applications, designed to maximize energy density and power efficiency operating

under atmospheric conditions. The ability to collect water at the cathode and pump it back to the anode allows water recycling, to avoid the need for sizable water storage. The water management system that recovers the excess water at the cathode and pumps it back to the anode enables the realization of a high energy density DMFC system which requires mostly storage of pure methanol. Effective water collection at the cathode is feasible with a well-guided, non-wetting coating on arrays of fine holes etched on silicon support planes.

Mesh membrane based micro pumps have been developed with curved electrodes using the etching-lag property of DRIE. Compatible with silicon wafer manufacturing and integration, a passive CO₂ liquid–gas separator has been developed on a pair of silicon wafers, where holes etched on the gas separation side are coated with a non-wetting agent. All of these micro-electro-mechanical systems (MEMS) components are fabricated with a common set of micro manufacturing processes on the same pair of silicon wafers. As a result, the interconnections are eliminated and the cost is minimized.

Acknowledgements

The authors gratefully acknowledge the support of the DARPA MPG program and the Pennsylvania Infrastructure Technology Alliance (PITA), a partnership between Carnegie Mellon University, Lehigh University and the Commonwealth of Pennsylvania's Department of Community and Economic Development.

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