# MEMS-Based Reformed Methanol Fuel Cell for Portable Power

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## Abstract

A reformed methanol fuel cell system is described. The use of a microfluidic fuel processor enables component scaling and integration sufficient to achieve power sources in the 2-10 W regime that are competitive in size and energy density in comparison to alternative power sources. While carbon monoxide tolerance of proton conducting membranes has typically limited the performance of reformed methanol fuel cells, phosphoric acid doped polybenzimidizole membranes have been tested that exhibit no degradation for carbon monoxide >2% mole fraction. Further benefits of the PBI membrane include operating temperature of 150-200°C, and no need for water to assist protonic conduction. As a result, a chemically and thermally robust fuel cell power source is realized. Results of methanol steam reforming, catalytic combustor heating elements, and PBI membrane performance will be discussed.

*Keywords: MEMS, microfluidic, reformer, combustor, fuel cell, methanol*

## 1 - INTRODUCTION

At present, scaling of fuel cells for portable power sources in the 2-10 W regime requires new methodologies and design schemes to compete with primary and rechargeable battery technologies. A key focus for fuel cells has been the use of hydrocarbon fuels as a result of the high volumetric energy density. Methanol has gained the most attention since it can be easily stored in liquid form, with catalytic reactions releasing the hydrogen occurring at relatively low temperatures. While the prospect of utilizing methanol directly at the fuel cell anode is encouraging, direct methanol fuel cells (DMFCs) are limited to low concentrations of methanol (1-2 M) delivered to the anode in order to reduce the effects of methanol crossover of the Nafion membrane[1]. This necessitates a complex water management system for DMFCs that effectively reduces the energy density of the fuel cell power source. Furthermore, the low activity of the methanol-water kinetics at the anode limits the power density that can be achieved for these systems. Reformed methanol fuel cells (RMFCs) provide an option for micro-fuel cell power sources whereby high concentration methanol-water fuel mixtures can be utilized, providing a higher energy and power density system. Limitations for RMFC systems include thermal management of high temperature components, and tolerance of fuel cell anode catalyst to residual carbon monoxide (CO) in the reformate fuel feed. Nafion based membranes are limited to low temperature (<100°C) operation due to the membrane drying out, which effectively degrades the proton conductivity of the membrane. At these temperatures, CO adsorbs to the anode catalyst, resulting in a long term poisoning effect that is difficult to reverse.

## 2 - REFORMED METHANOL FUEL CELL

Steam reforming of methanol is an endothermic catalytic process described by the reaction;

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad \Delta H = 126 \text{ KJ/mol} \quad (1)$$

From (1), $\Delta H$ is the higher heating value of the reactants. For a $CuZnO/Al_2O_3$ catalyst[2], reaction (1) occurs in the 250-300°C range producing a hydrogen rich fuel feed to the fuel cell anode with an approximate composition of 75% $H_2$, 24% $CO_2$, and <1% CO. A RMFC system diagram is illustrated in Fig 1. The heat needed for the steam reforming is supplied by either a resistive or catalytic heater, with the latter being more convenient since the fuel supply and any unutilized fuel from the fuel cell anode will drive the catalytic reactions described by;

$$CH_3OH + 3/2 \, O_2 \rightarrow 2H_2O + CO_2 \quad (2)$$

and

$$H_2 + \frac{1}{2} \, O_2 \rightarrow H_2O \quad (3)$$
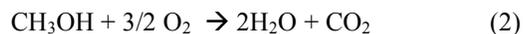
From (3) above, $\Delta H = -243$ KJ/mol is the exothermic energy produced by the reaction. Theoretically, 1 mole of methanol generates 3 moles of hydrogen and the combustion of 0.5 mole of hydrogen (17% of generated hydrogen) can provide the higher heating value (i.e. lower heating value plus latent heat) of the methanol steam reforming process. Due to both the thermal loss to ambient through an insulated package and

enthalpy retained in the outflow, the required hydrogen flow in the micro-combustor will be higher.
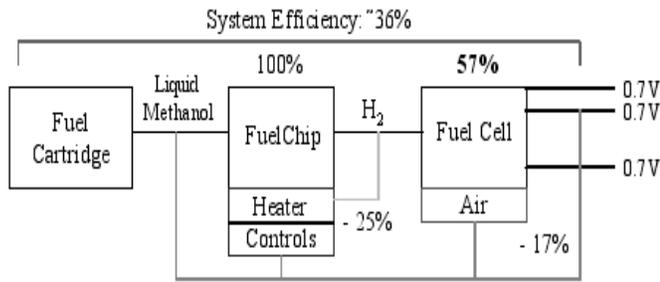


**Figure 1** - Schematic diagram of RMFC

Therefore, the above exothermic reactions will provide heat to drive the endothermic steam reforming process. RMFC systems enable the use of high concentration methanol fuel that only has to be diluted to approximately 1:1 steam-to-methanol ratio for effective reforming. This provides a hydrogen rich fuel feed for the fuel cell, and high power density PEM fuel cells can be used to justify the added complexity of the thermal components for fuel processing. A key issue with this approach is the small quantity of CO present in the fuel feed from the reaction described by (1) is sufficient to poison the anode catalyst at typical operating temperatures for Nafion based fuel cells (25-80°C). To address this issue, various approaches have been investigated including preferential oxidation, water-gas shift reactors or absorbers to remove the CO from the fuel feed[3]. These approaches have had limited success for low temperature (<100°C) PEM fuel cells as CO concentrations present in the fuel feed at the 50-100 parts per million range are sufficient to degrade anode catalyst performance.

In order to optimize RMFC system operation, a membrane electrode assembly (MEA) that operates at >150°C is desired such that any CO present in the fuel feed will rapidly desorb from the anode catalyst, resulting in limited degradation. The use of phosphoric acid doped polybenzimidizole (PBI) membranes[4] enables an MEA technology that performs at >150°C, has sufficient proton conductivity to be competitive with Nafion, and has the benefit of not requiring any humidification for efficient operation. The drawback is the membranes do not operate well at temperatures <140C, so startup requires that the MEA and fuel cell stack be brought up to temperature before significant power is delivered. To provide thermal integration, rapid startup, and microminiaturization of the RMFC fuel cell power source, a MEMS-based fuel processor and catalytic combustor has been developed[5]. The design and performance of a microfluidic steam reformer is described, along with the nominal performance of the RMFC system for a 3-5 W power source.

## 3 - MICROFLUIDIC FUEL PROCESSOR

MEMS fabrication techniques provide the means to integrate a steam reformer and catalytic combustor in a single monolithic design. The fuel processor design utilizes deep reactive ion etching (DRIE) to form high aspect ratio microchannel arrays as illustrated in Figure 2. This specific design incorporates a wraparound reformer surrounding the catalytic microcombustor. The catalyst bed for both reformer and combustor are formed using DRIE to etch microchannels
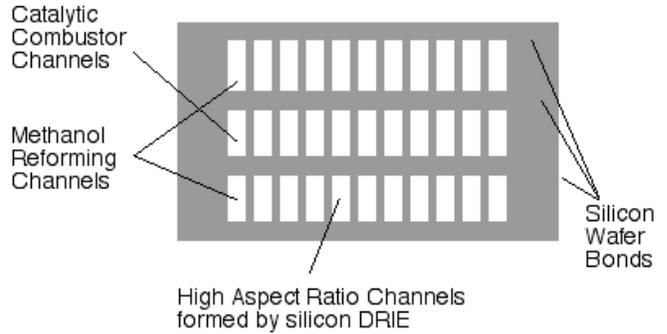


**Figure 2** - Cross section of integrated fuel processor formed in silicon by DRIE and wafer bonding.

of 200 μm diameter, 850 μm deep, and 250 μm center to center spacing. The integrated fuel processor is created by first aligning, then fusion bonding the silicon layers, after which the catalyst is applied to each chamber using a wash coating process. For the reformer, a $CuZnO/Al_2O_3$ (30 wt.% Cu) composition is used, and for the catalytic combustor a $Pt/Al_2O_3$ (5.% Pt) composition is applied. Figure 3 illustrates an integrated fuel processor chip.
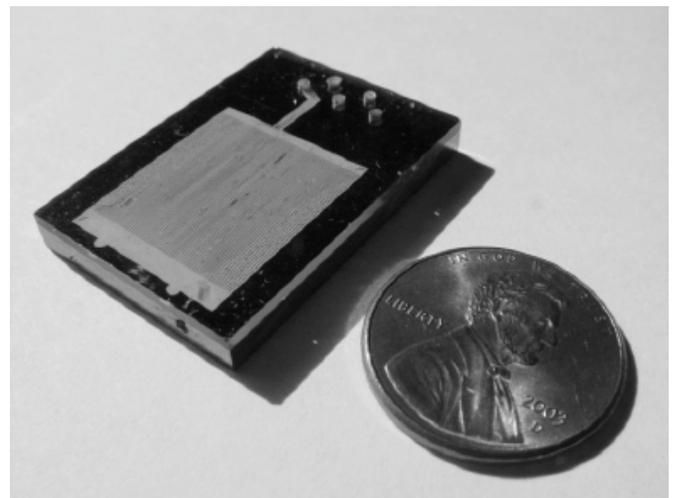


**Figure 3** – Integrated fuel processor chip .

Typical quantities for each catalyst bed are 78 mg of the $CuZnO/Al_2O_3$ in the steam reforming section, and 38 mg of the $Pt/Al_2O_3$ in the combustor section.

The fuel processor was characterized using a $CH_3OH:H_2O$ (1:1.1) inlet flow controlled by a syringe pump. Fluidic connection to the fuel processor was achieved using 0.04" internal diameter stainless steel tubing using a compression fitting with high temperature silicone o-rings. Initial testing to characterize catalyst performance was conducted using resistive heaters attached to one surface of the integrated silicon fuel processor. The fuel processor chip was thermally insulated using a 0.5" thick layer of Kapton foam that was wrapped around the chip and held using Kapton tape. A type-K thermocouple was attached to the surface of the silicon fuel processor to accurately monitor the temperature of the reformer. This temperature is assumed to be within 5 °C of the catalyst bed temperature due to the high thermal conductivity of silicon and the high surface to volume ratio of the fuel processor. The reformer catalyst was characterized as a function of temperature and different flow rates. The results are illustrated in Figure 4 below.
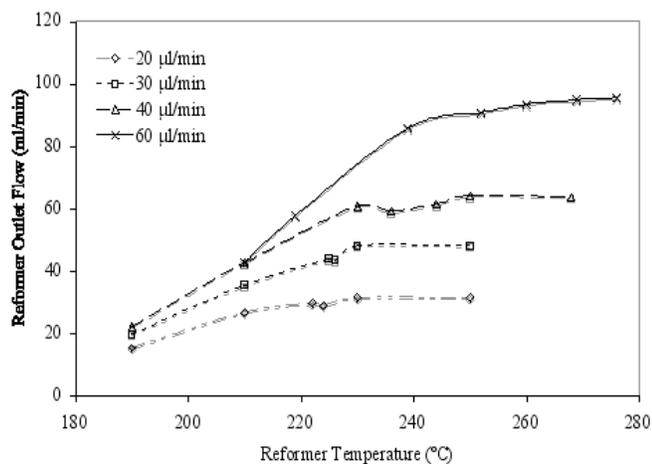


**Figure 4 -** Reformate output flow rate as a function of temperature for several methanol-water inlet flow rates.

From these results in Figure 4, it can be seen that conversion of the fuel inlet streams approaches 100% in the 240-260°C range. Higher inlet fuel flow would shift the curves to the left. Thus, for specific system designs, the appropriate operating temperature and flow rates can be chosen.

The catalytic combustor design provides efficient conversion of unutilized fuel from the fuel cell anode to heat through the exothermic reactions described by (2) and (3). Directly coupling the combustion chamber to the reformer chamber through the integrated MEMS design enables rapid heat transfer and spreading to the high surface area reformer catalyst bed. Additionally, for the fuel cell operation, it is easier to design flow fields that utilize 75-80% of the anode fuel feed, compared to 90-100% utilization. The catalytic combustor was tested using both hydrogen and pure methanol as fuel. By volume, a fuel/oxygen ratio between 1-1.2 is used for optimal reactions. In the case of methanol fuel, the air feed flows over the methanol inlet causing the fuel to

evaporate and flow into the combustor chamber in vapor phase. Figure 5 shows the combustor thermal ramp-up from room temperature.
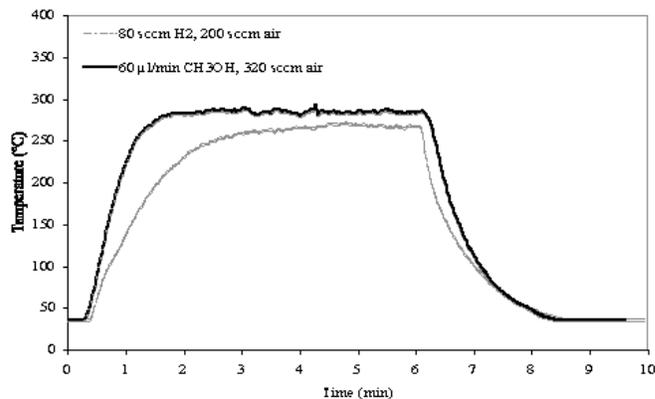


**Figure 5 -** **Microchannel combustor temperature as a function of time for both methanol and hydrogen fuel.**

In operation, the fuel processor would be ramped up to temperature prior to any fuel flow into the steam reforming catalyst bed. Similarly in turning off the fuel processor, the preferred method would be to stop the methanol-water mixture flow to the steam reforming chamber enabling the catalyst to dry out, then ramping down the combustor temperature by decreasing the fuel flow.

## 4 - FUEL CELL PERFORMANCE

As discussed previously, CO poisoning of the fuel cell anode catalyst is of key concern for reformate fed fuel cells. Previous performance with Nafion PEM fuel cells has exhibited limited performance and long term stability using reformate feeds having CO in the 100-6000 ppm range. Recent improvements in phosphoric acid doped PBI membranes make this a viable candidate for RMFC systems. Figure 6 below illustrates the performance of a phosphoric acid doped, PBI membrane fuel cell utilizing reformate fuel produced from a microfluidic fuel processor. The fuel cell electrode area is 5 cm x 5 cm, with a flow field formed in graphite plates. The fuel flow into the fuel processor is 60 µl/min, providing a nominal reformate feed to the fuel cell of ~190 ml/min. The cathode air flow was maintained at 900 sccm, with an estimated volumetric oxygen to fuel ratio of 2.5 for optimal fuel cell performance. The fuel cell was operated at 180°C, and in this case a hot plate and thermocouple feedback loop was used to maintain the temperature. The catalytic combustor was heated using a separate methanol feed of 60 ml/min controlled by a syringe pump, mixed with 320 sccm air. Overall, the fuel cell operation was stable for the several hours over which testing occurred. The PBI membrane exhibited a nominal power density of 230 mW/cm$^2$ at a cell potential of 0.6 V (57% efficient), with the possibility of further improvements through optimization of membrane electrode assembly compression by the graphite plates.
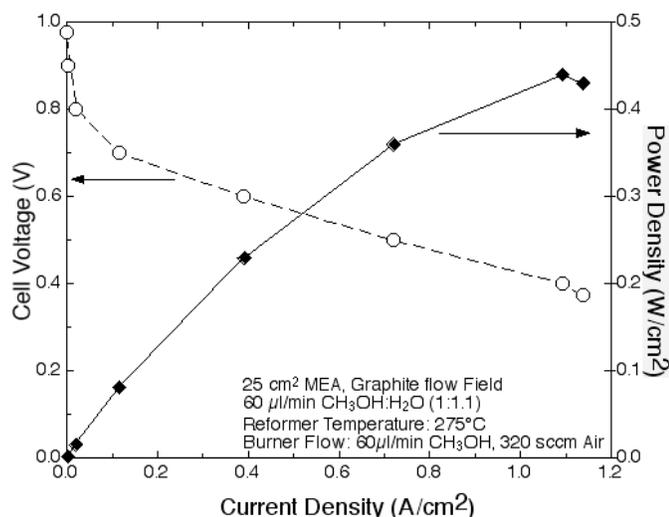
**Figure 6** - Performance of PBI membrane fuel cell using reformate fuel.

A key remaining issue is the inability of the PBI membrane to operate at room temperature, therefore some fraction of system energy must be utilized to heat up and maintain the fuel cell stack temperature during operation. By appropriate stack and system design, the steady state operating temperature can be maintained by the fuel cell losses, i.e; for a 57% efficient fuel cell, 43% of the power goes to waste heat. To address startup operation, the catalytic combustor provides sufficient means of generating the necessary heat, as well as the ability for a cold start, so long as the thermal mass of the fuel cell component remains small enough. One method that has been explored is the use of MEMS-based fuel cells whereby the typical components of a fuel cell are formed in a silicon substrate via micromachining approaches. The benefit of this approach includes reduction of size and mass, good thermal conductivity through the silicon, and omponents that can be integrated in a monolithic fashion. The latter includes formation of flow fields, gas diffusion layer, electrodes, and even MEAs through a continuous fabrication process flow. Figure 7 below illustrates an example of a MEMS-based fuel cell platform. In this example, the flow field, gas diffusion layer, and current collector electrode have been formed on a silicon chip using DRIE and thin film sputtering processes. From the figure, the flow field channels are evident. The channel widths are 400 μm, and 400 μm deep. The flow field is laid out to provide a constant pressure drop from inlet to outlet.

The GDL consists of arrays of pores etched in the silicon connecting the bottom of the flow field channels to the electrode layer. The pores are 4 μm diameter and 80 μm deep, thereby providing both high surface area and mechanical support for compression of the MEA to give good electrical contact. The opposite side of the silicon flow-field is coated with 1 μm of gold or other corrosion resistant metal to act as a current collector contact to the fuel cell electrode.

Fuel cells have been formed by either attachment of an existing MEA to the surface having the current collector electrode, or by coating the various layers of the MEA in thin film form to create a monolithic MEA. Efforts are ongoing and moving toward accomplishing this with PBI membranes, with the limiting factors being the approach to attaching the MEA to the electrode formed on the silicon GDL.
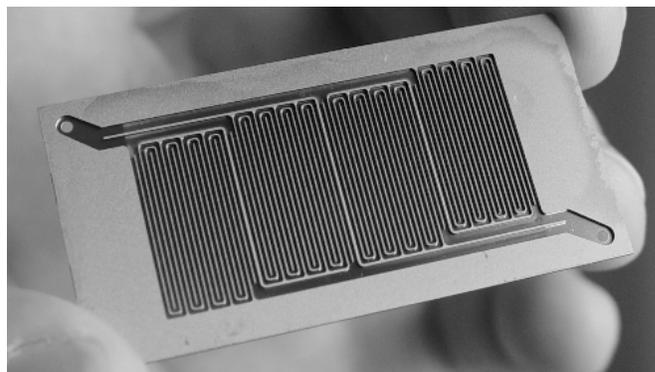


**Figure 7** - Flow-field formed in silicon substrate using DRIE.

## 5 – CONCLUSION
A MEMS based reformed methanol fuel cell system has been described. The performance of the key components has demonstrated both thermal and chemical compatibility for stable and efficient fuel cell operation. Further improvements and scaling of fuel cell stack design will enable both rapid startup operation and higher volumetric energy density for the system.

## 6 - ACKNOWLEDGEMENT

## 7 - REFERENCES
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