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A Microfluidic Hydrogen Generator for Fuel Cell Applications

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ABSTRACT

A study of the reaction rates, heat and mass transfer and flow, in and from a methanol reforming catalytic micro-reactor fabricated on a silicon wafer is presented. Comparison of computed and measured conversion efficiencies are shown to be favorable.

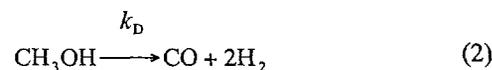
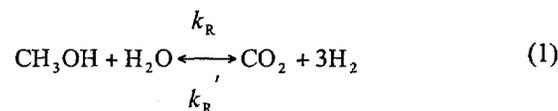
INTRODUCTION

Over the past two decades, there has been increased research in small fuel cells and in miniaturized systems for providing them fuel on demand. Applications include consumer electronics such as cell phones, laptop computers, video camcorders, and radios, as well as military systems such as micro-scale field energy sources for various sensors and remote communication devices.¹

Several fuel candidates for the on-demand generation of hydrogen rich gas have been investigated;^{2,3} methanol steam reforming has been preferred due to the lack of inter carbon bonds in methanol, to the limited carbon monoxide production, and to a higher hydrogen fraction in the reformat than that of

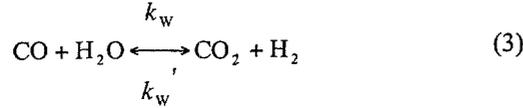
partial oxidation. A MEMS based micro reformer has the advantages of small features, of integrating many components in a coherent way, of obtaining microfluidic stability due to small Reynolds number, and of requiring relatively low heating energy owing to its small size. Because of these advantages, it is reasonable to expect that micro reformers will be developed for eventual integration into micro fuel cell systems.

According to Amphlett *et al.*,⁴ methanol experiences two overall reactions in a reformer in the presence of Cu/ZnO/Al₂O₃ catalyst:



Reaction (1), called reforming, is a primary reaction in the methanol steam reforming process. Some portion of the methanol decomposes to produce carbon monoxide via reaction

(2). In the presence of water, the three products adjust their compositions via the water-gas shift reaction:



For many applications, the reformer working temperature varies from 200 to 300°C, where the dry product composition is such that the proportions of H₂/CO₂/CO are approximately 74/24/2 by volume.⁴

One of the essential issues for reforming for fuel cells is CO contamination. However small, CO always exists in the reformat due to reaction (2), which will poison and ultimately deactivate the Pt catalyzed anode of some fuel cells. Since the poisoning amount of CO is a few tens of ppm, it is very important to estimate accurately the small amount of CO produced.

Since a micro reformer operates at a few hundred degrees Celsius, thermal management is also important. Efficient heat integration as well as thermal isolation is a primary consideration in a miniature fuel cell for portable applications.

THEORY

Kinetics

The chemical kinetics of Amphlett *et al.*⁴ was used:

$$\dot{r}_R''' = k_R C_1, \quad \dot{r}_D''' = k_D \quad (4)$$

$$k_R = \bar{k}_R w_{\text{cat}}''', \quad k_D = \bar{k}_D w_{\text{cat}}''' \quad (5)$$

$$\bar{k}_R = [A_R + B_R \ln(\text{SMR})] \exp\left[-\frac{E_R}{RT}\right] \quad (6)$$

$$\bar{k}_D = A_D \exp\left[-\frac{E_D}{RT}\right] \quad (7)$$

Governing equations

The governing equations for a three dimensional analysis of the reacting flow inside a reforming bed are:

- mass conservation

$$\nabla \cdot (\rho \mathbf{u}) = 0 \quad (8)$$

- momentum conservation

$$\nabla \cdot (\rho \mathbf{u} \mathbf{u}) = \nabla \cdot \mu(\mathbf{r}) \nabla \mathbf{u} - \nabla p + \mathbf{S}_{\text{mm}}, \quad (9)$$

where the momentum source is an additional pressure drop caused by the flow resistance due to the packed catalyst bed. The Ergun equation⁵ neglecting the inertial resistance contribution was employed to represent the pressure drop.

$$\mathbf{S}_{\text{mm}} = -\frac{150\mu(1-\epsilon)^2}{\epsilon^3 D_p^2} \mathbf{u} \quad (10)$$

- energy transport

$$\nabla \cdot (\rho \mathbf{u} c_p T) = \nabla \cdot \Gamma(\mathbf{r}) \nabla T + \mathbf{S}_{\text{cr}}, \quad (11)$$

where the thermal conductivity is a volume weighted average of the catalyst bed material (Cu/ZnO/Al₂O₃) and the gas mixture.

$$\Gamma = \varepsilon \Gamma_f + (1 - \varepsilon) \Gamma_s \quad (12)$$

Endothermic reactions in the reformer result in an energy sink that can be represented as

$$S_{CR} = -\Delta H_R \dot{r}_R^m - \Delta H_D \dot{r}_D^m \quad (13)$$

- *species transport*

$$\nabla \cdot (\rho \mathbf{u} m_i) = \frac{\dot{r}_i^m}{M_i} \quad (14)$$

Properties such as density, molecular viscosity, and thermal conductivity were calculated assuming an ideal gas mixture. Thus the density was calculated from

$$\rho = \frac{P}{RT} M = \frac{P}{RT} \sum_i x_i M_i \quad (15)$$

Wilke's formula⁶ was employed to calculate the molecular viscosity and thermal conductivity of an ideal gas mixture.

Boundary conditions

At the inlet, values of all the variables are assigned:

$$\rho \mathbf{u} = \rho_{in} \mathbf{u}_{in}, \quad m_i = m_{i,in}, \quad T = T_{in} \quad (16)$$

The reactor wall is regarded as no-slip and an impermeable surface:

$$\mathbf{u}|_w = 0, \quad \frac{\partial T}{\partial r}|_w = 0, \quad \frac{\partial m_i}{\partial r}|_w = 0 \quad (17)$$

At the axis of the flow channel, symmetry

was applied. Finally, at the outlet, a traction free or pressure boundary condition was applied with zero gauge pressure.

SERPENTINE MICRO REACTOR

The micro reformer considered is a serpentine shaped reactor designed to provide enough residence time for the reacting species. A 1mm wide mesoscale channel is etched in a silicon substrate (Fig. 1) to 400µm depth to provide a catalytic reaction zone. Cu/ZnO/Al₂O₃ catalyst fills the channel, and electric heaters on the opposite side of the substrate supply the required amount of heat into the channel across the silicon substrate. A Pyrex glass covers the packed bed channel and the rest of the substrate surface. Liquid methanol-water solution (approximately 48 mole% methanol) at room temperature enters the channel inlet to travel through an evaporator zone equipped with a heater. The vaporized methanol-water gas mixture flows into a packed-bed catalytic reaction zone at about 250-300°C where hydrogen, carbon dioxide and carbon monoxide are formed.

The reformer was fabricated and tested with the mesoscale channel etched in a 2.54cm×2.54cm×500µm silicon substrate and a 1mm thick Pyrex glass cover. In the model (to save computing time), the glass cover was replaced by a one-dimensional thermal resistance boundary condition. Thus the

geometry considered as the computational domain in this study includes only the channel and a silicon substrate. The domain was divided into triangular cells: 33,000 fluid cells for the channel and 135,000 solid cells for the substrate.

Conjugate heat transfer at the interface of the fluid channel and the solid substrate is obtained by equating the heat fluxes from both the fluid and solid sides.

The catalyst loading was ~65mg into the packed bed volume of $5.0 \times 10^{-8} \text{ m}^3$ for a catalyst density, w_{cat}'' , of 1,300 $\text{kg}_{\text{cat}}/\text{m}^3$. At the inlet the mass flow rate is $1.43 \times 10^{-7} \text{ kg/s}$, temperature is 100°C , and the steam-to-methanol molar ratio is 1.1. The inlet mass flow rate corresponds to the liquid input of $10 \mu\text{L}/\text{min}$ at 20°C . The boundary condition at the portion of the bottom substrate wall contacting the main heater is a constant heat flux, corresponding to 2 to 4 W of Joule heating. The portion of the bottom wall contacting the evaporator heater was set to 18mW (corresponding to the latent heat of the convecting liquid mixture). The other wall surfaces are assigned natural convection boundary conditions with an ambient temperature of 20°C .

RESULTS AND DISCUSSION

The velocity variation along the channel (Fig. 2) shows a local maximum inside each corner turn. As the fluid flow passes through the curved part of the channel, the inner particles accelerate to acquire the same pressure drop in a relatively shorter path. When the flow emerges from the corner region and

is driven into the straight channel part, inertia makes it sustain the non-uniform profile for a certain length depending on the flow rate. The mole fractions of methanol and hydrogen are given in Fig. 3 and 4.

Due to the high thermal conductivity of silicon, the micro reformer temperature field is largely uniform (Fig. 5). For 3.3W supplied to the main heater, the average temperature is ~512K and variation is ~15K across the 2.54cm square device.

The temperature variations of both the methanol conversion efficiency and the CO mole fraction are shown in Fig. 6. The conversion efficiency has a typical stretched S shape approaching 100% conversion. CO mole fraction increases exponentially as a function of the reformer temperature. Therefore, when we consider the reformer as the fuel processor for some types of fuel cells, the production of carbon monoxide may restrict operating temperature. Alternatively, another reactor containing a preferential oxidation catalyst may be employed to reduce the CO to acceptable levels.

CONCLUSION

Testing and analyses were used to study the reacting flow in a catalytic micro reformer. Modeling indicates that reactor temperature is nearly constant in the reformer due to the high thermal conductivity of silicon. This is a positive effect as one seeks to have a reactor operating at uniform optimal conditions but is a negative effect as one seeks to insulate the smallest possible hot zone to minimize heat loss to the surroundings.

ACKNOWLEDGMENTS

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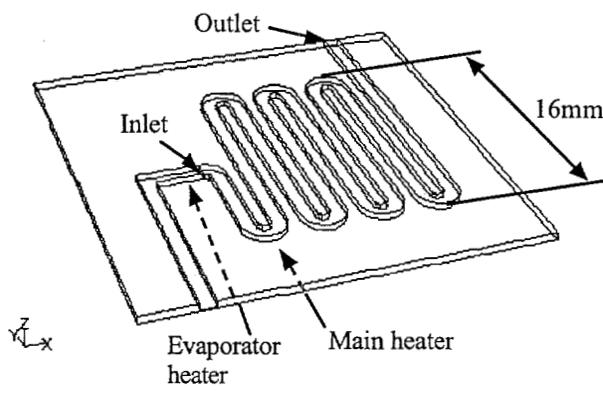


Fig. 1 A serpentine micro catalytic reformer channel, 1mm wide, 400 μ m deep, and 15cm long; the main heater follows the channel shape.

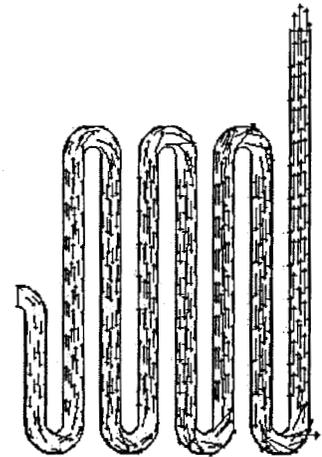


Fig. 2 Apparent velocity in micro catalytic reformer channel

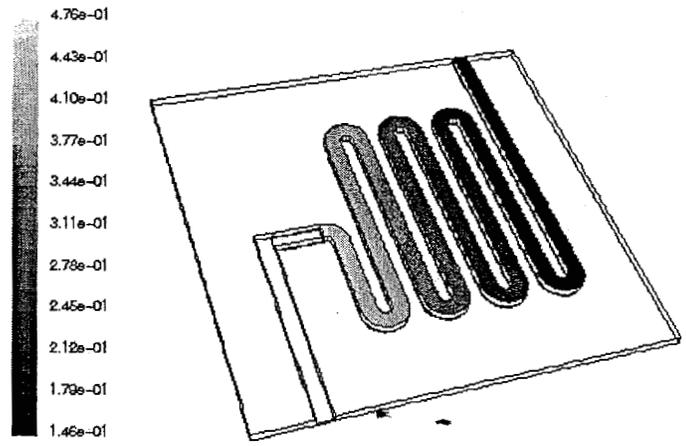


Fig. 3 Mole fraction of methanol

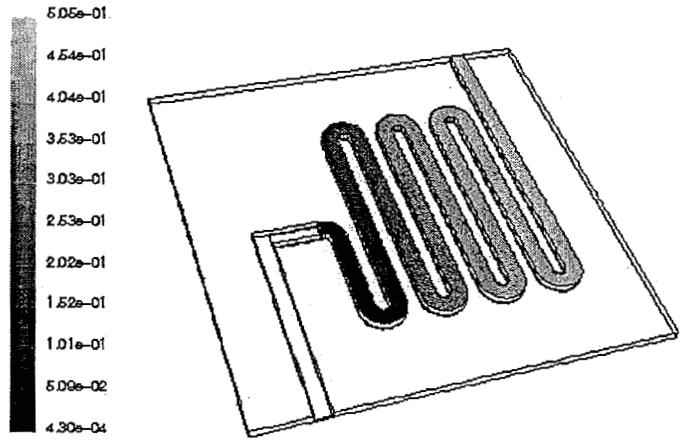


Fig. 4 Mole fraction of hydrogen

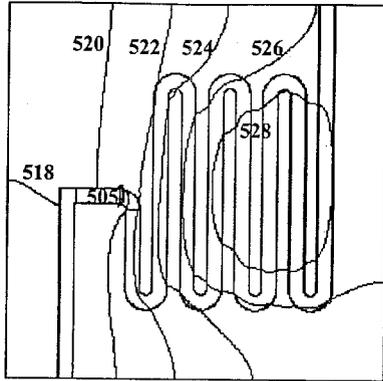


Fig. 5 Temperature profile in Kelvin

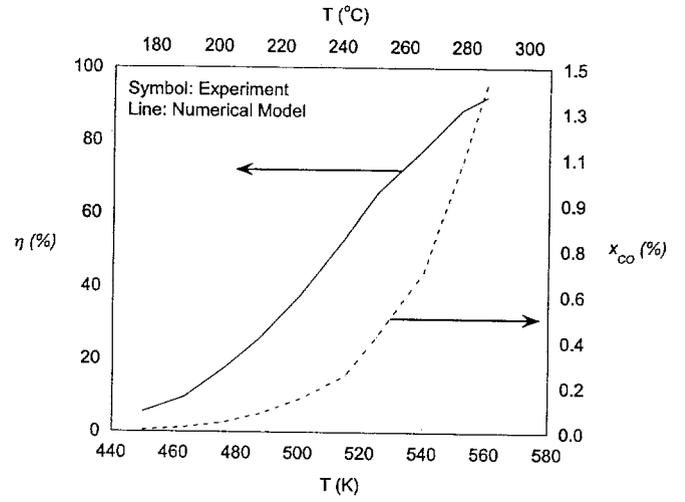


Fig. 6 Variations of conversion efficiency and the CO mole fraction with respect to temperature