

Feedstock for Micro Fuel Cells: Efficient Hydrogen Production in the Reverse-Flow Autothermal Catalytic Microreactors with Fractal Structuring of the Catalytically Active Surface

Timo Kikas¹, Huiping Zhang¹, Ilya Bardenshteyn¹, Cornelius Ejimofor¹, Pushpinder Puri², Cynthia Phillips¹
and Andrei G. Fedorov^{1,✉}

¹ George Woodruff School of Mechanical Engineering, Georgia Tech, Atlanta, Georgia 30332-0405, USA

² Air Products & Chemicals, Inc., Corporate Science and Tech Center, Allentown, PA 18195-1501

Electrochemical fuel cells have clear potential to revolutionize energy conversion technologies of the nearest future for both military and civil applications. However, this potential cannot be realized unless simple, cheap and energy efficient means for hydrogen production become available. Recent advances in microfabrication have led to development of compact chemical microreactors in the USA, Europe, and Japan for various applications, especially where on-demand, small-scale production of chemicals is of interest. The chemical processing rates in heterogeneous microreactors increase significantly due to a decrease in the resistance to the species transport caused by a drastic reduction in the thickness of the boundary layer. Ideally, with a decrease in the channel size (diameter), one hopes to achieve reaction kinetics at its intrinsic rate and to maintain sufficiently large reactor throughput by using the parallel chemical processing in many small channels comprising the reactor. In addition to rapid heat and mass transport, the miniaturization of chemical reactors results in high productivity rates due to fast non-equilibrium surface chemistry as well as in opportunities for energy and chemical conversion at the optimal locations. However, these advantages of the microscale can be exploited to the full extent if and only if the innovative MEMS-reactor designs are developed and the underlying physical/chemical processes and their interactions are fundamentally understood. This yet remains to be a significant research challenge from both theoretical and experimental viewpoints.

In addition to benefits associated with microscale, enormous opportunities arise to increase performance of catalytic processes using forced unsteady-state operation (FUSO) (e.g., reverse-flow operation) by exploiting and controlling the dynamic interactions between the catalyst properties (i.e., state, structure, and composition) and the multiscale heat and mass transfer processes in the catalytic microreactor. The FUSO approach makes it possible to generate and control the spatio-temporal patterns of temperature, concentrations and catalyst states that cannot be attained under the steady-state operation. The transient operation provides thermodynamically favorable conditions for reversible reactions (i.e., declining temperature profiles for exothermal reactions and increasing temperature profiles for endothermic ones) to achieve maximum reaction conversion and selectivity. It also offers opportunities for exploiting catalyst dynamic properties, and results in lower average operating temperatures, thereby reducing pressure drop and heat losses.

Among various alternatives, production of the hydrogen rich synthesis gas (H₂/CO mixture with some CO₂, H₂O, and N₂) followed by the hydrogen separation from the stream via composite metal (Pd-Cu or Pd-Ag) is one of the most economically plausible processes for hydrogen generation. Conversion of various hydrocarbon fuels (e.g., methane) into synthesis gas can be accomplished via different techniques, and we suggest that autothermal reverse-flow operation of the reactor appears to be most promising from the productivity, energy efficiency and selectivity viewpoints. It combines strongly exothermic partial oxidation of the fuel with endothermic heterogeneous steam/CO₂ reforming followed by the slightly exothermic water-gas shift reaction, and, in the case of methane, it is described by the following reaction kinetics:



Since the overall partial catalytic oxidation process is slightly exothermic, it can be effectively executed in the reverse-flow catalytic reactor. In this transient regime, the reactor is first preheated to a uniform temperature of 800 to 1000°C, and then it continuously operates via autothermal heat regeneration accomplished by periodic flow reversal. In other words, as the up-stream part of the reactor is progressively cooled down by the cold reactants, the methane partial oxidation takes off and the temperature wave propagates through the reactor in the direction of the flow. The flow is reversed before the reaction zone reaches the exit of the reactor, and this causes the high temperature wave front to move in the opposite direction. Thereby, the heat is effectively retained inside the catalytic monolith, and no additional external reheating is needed. Fine-tuning of the temperature profiles in the reactor can be accomplished via controlling the degree of reduction of the steam reforming catalyst (e.g., Ni/Al₂O₃). In addition to favorable autothermal operation, the oscillatory motion of the high

[✉] **Corresponding author:** MITf-Lab, School Mechanical Engineering, Georgia Tech, Atlanta, Georgia 30332-0405, 404-385-1356 (ph), 404-894-8496 (fax), andrei.fedorov@me.gatech.edu (email), <http://www.me.gatech.edu/MITf-Lab> (web).

Acknowledgements: Financial support of Air Products & Chemicals for the microreactor work, Alcoa Graduate Fellowship for Ms. Cynthia Phillips, and Georgia Tech Research Corporation.

temperature wave in the reactor leads to gasification and removal of the carbon/soot, which is potentially deposited on the catalyst due to endothermic methane cracking and exothermic Boudouard reaction.

During last two years, we have been focusing our efforts on developing and proving new design concepts and quantifying the advantages of the catalytic microreactors operated in the autothermal reverse-flow regime. In this presentation, we will present several innovative designs of the reactor, including our patented nearly zero dead volume sliding integrated microreactor-valve, and discuss the experimental results on the efficiency and selectivity of hydrogen production by the reverse-flow microreactors. Major emphasis will be placed on example-based highlighting of the urgent need to develop simple, yet unconventional designs of the chemical microreactors that are compatible with MEMS planar fabrication technology in order to indeed be able to exploit potentially enormous benefits of the chemical processing on the small scale. Figure 1 shows a schematic and the photograph of the test rig for experimental studies of catalytic microreactors. Two microreactors that we have developed and tested are shown in Figs. 2 and 3. The first reactor (Fig. 1) is based on a ceramic pipe with four 500 μm ID holes and the Pt/Rh wire (100 μm OD) is used as a catalyst. The second reactor (Fig. 3) features an integrated design concept that includes the reagent mixing chamber, reaction chamber, and a zero-dead-volume valve for flow reversal in a single device, which is inherently suitable for further miniaturization using conventional planar MEMS fabrication techniques.

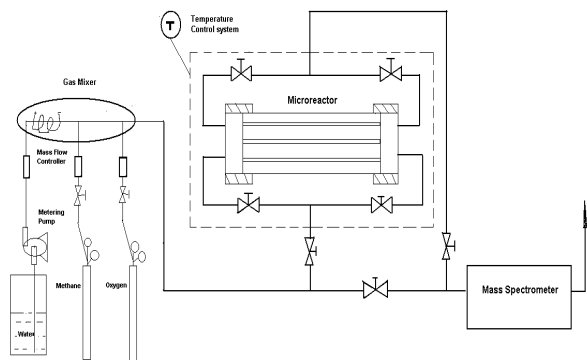
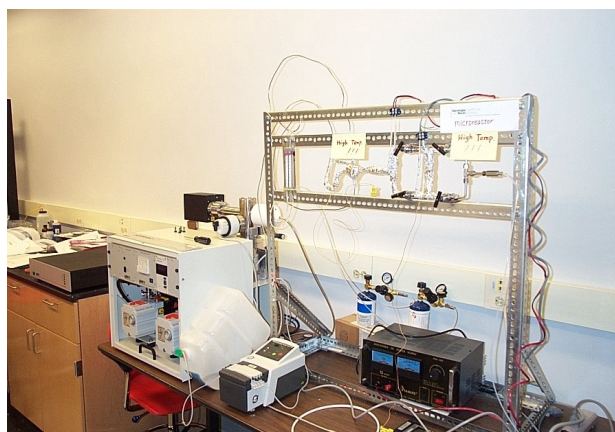


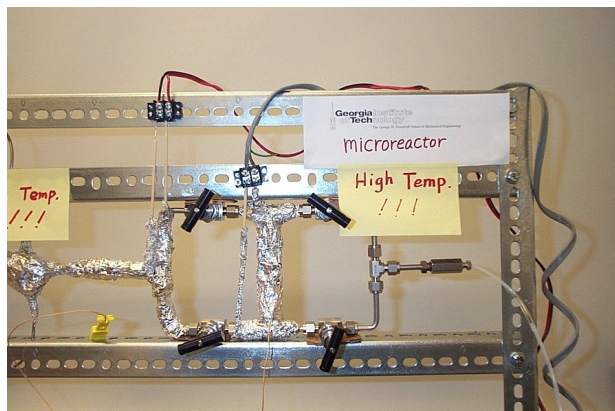
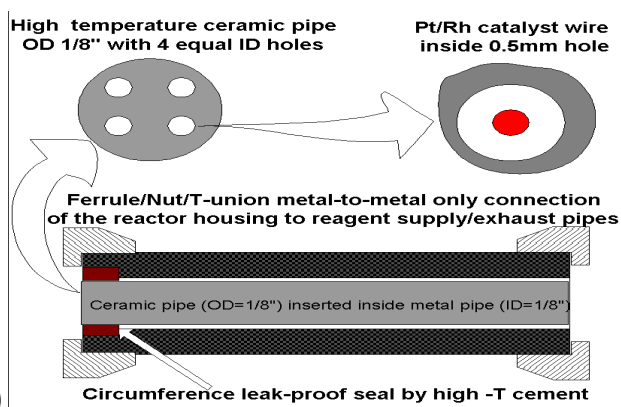
Fig. 3 Diagram of methane partial oxidation with steam reforming in a reverse flow catalytic microreactor



(a)

(b)

Fig. 1: (a) Flow diagram of experimental rig; (b) Photograph of assembled experimental setup



(a)

(b)

Fig. 2: Tubular ceramic microreactor (patent pending): (a) schematic of reactor design; (b) photograph of the actual reactor

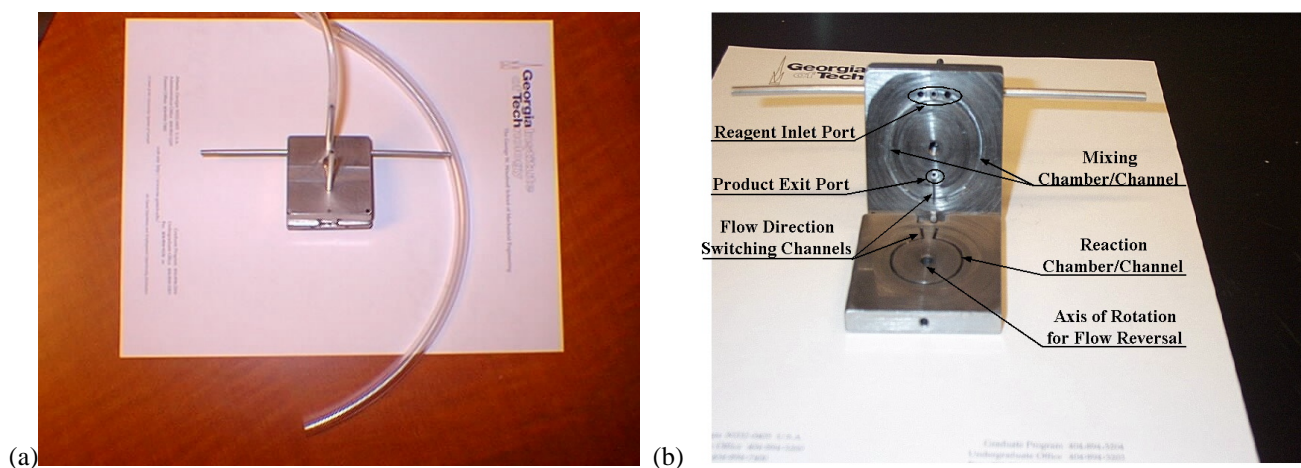


Fig. 3: Reverse-flow microreactor with zero dead-volume valve (patent pending): (a) assembled; (b) disassembled

Currently, we are obtaining the detailed experimental data on the methane conversion and selectivity toward hydrogen for the partial oxidation, steam reforming, and combined partial oxidation/steam reforming reaction in the catalytic microreactors for a wide range of operating conditions (i.e., feed composition, total flow rate and the reagent/catalyst contact time, and reaction temperature) under conditions of the uni-directional and reverse-flow operation.

In addition, to minimize the cost of heterogeneous catalytic systems, which is primarily determined by the amount of the chemically active catalyst, usually highly expensive noble metals or alloys, that needs to be loaded to achieve desired rate of chemical conversion, we have developed an alternative approach for significant reduction of the catalyst loading by optimal structuring of active catalyst surfaces in the heterogeneous chemical reactors and fuel cells. Intuition tells us that any decrease in the active (i.e., loaded with catalyst) surface area should result in an equivalent decrease in the reaction yield and efficiency. However, our theoretical analysis shows that the active surface and hence the catalyst loading can be reduced drastically in the diffusion-limited heterogeneous reaction systems, while the conversion rate remains essentially unchanged by using fractals for spatial distribution of the catalyst load. The simulation results indicate (Fig. 4) that introduction of periodic singularities into the boundary conditions through fractal structuring of the active surface allows a 76% reduction in the catalyst loading while losing only 2.25% of the original rate of chemical conversion. The effect of fractal structuring of the active surface is the most profound to the design of micro/nano scale systems, for which the Peclet and Rayleigh numbers are intrinsically small due to the small characteristic length scale and body forces. Thus, introduction of periodic singularities into the mass transfer boundary condition is ideally suited for drastically lowering the cost of MEMS devices for chemical and biological processing as well as micro/nanoporous electrodes for fuel cells, and it can be exploited to its fullest extent by utilizing the advances in our abilities to manipulate matter on the micro/nano scale.

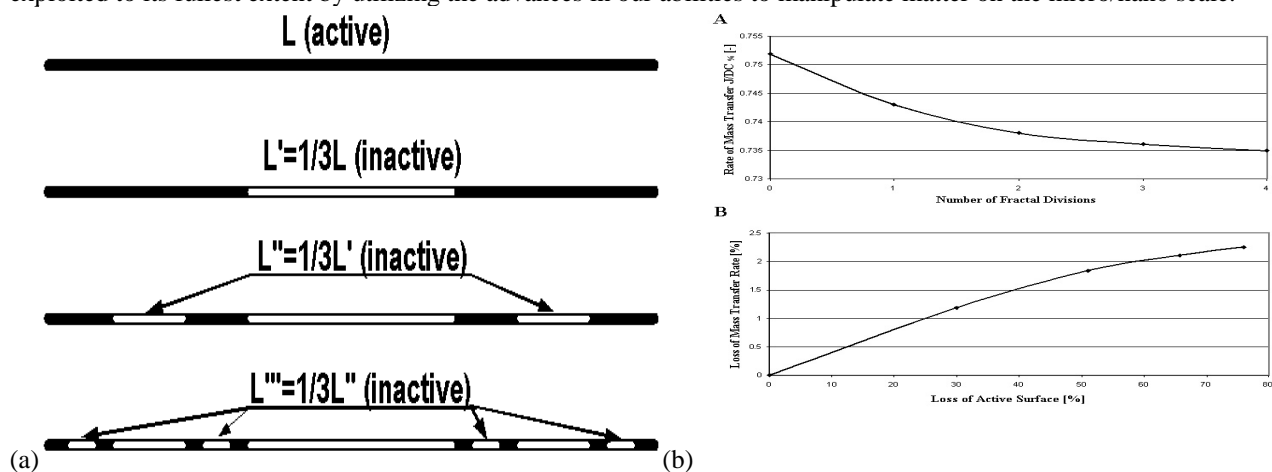


Fig. 4: (a) Schematic of fractal structuring of the catalytically active surface. (b) Effect of the fractal-based reduction of the catalyst loading on the rate of mass transfer (top panel) and its relative-to-nominal loss in percents (bottom panel).