# INTEGRATED CERAMIC MICRO-MEMBRANE NETWORKS FOR HYDROGEN PRODUCTION FROM ETHANOL

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*Summary*

This work describes our efforts towards realizing scalable ceramic microreactors for producing high-purity hydrogen from ethanol liquid fuel by coupling catalytic reforming with permselective palladium membranes. This integrated ceramic micro-membrane network will enable production of high-purity hydrogen suitable for feeding PEMFCs as part of an overall energy system. Dense palladium thin films of < $10^{-5}$ m thickness are deposited via electroless-plating on alumina-washcoated cordierite monolith supports (64 cpsi) for hydrogen separations. Catalytic washcoatings for ethanol reforming and water-gas-shift are applied over the palladium film to realize a compact membrane reformer configuration. Results provide the basis for system scale-up and thermal considerations for realizing autothermal operation.

*Keywords*

Hydrogen, Microreactors, Membranes, Palladium

## Introduction

Fuel cells are receiving great interest as an alternative energy source for applications ranging from portable power (e.g., automotive, personal electronics) to large-scale production. At the same time, biofuels such as ethanol and other renewables have emerged as promising alternatives to dwindling fossil resources. By developing technologies capable of extracting high-purity hydrogen from multiple biofuels, a fuels infrastructure based upon a single “energy currency,” of hydrogen for subsequent use by polymer-based proton exchange membrane fuel cells (PEMFCs) may be realized. Our research efforts at the University of Connecticut have focused upon developing cartridge-based, scalable microreactors capable of producing high-purity hydrogen suitable for fuel cell use at either the fixed- or portable-scale.

Ethanol can be reformed to produce hydrogen either via steam reforming, partial oxidation, or autothermal reforming.[1,2] In all three cases, further boosting of hydrogen yield can be achieved via additional water-gas-shift reaction. The resulting hydrogen-rich reformate must then be purified to reduce carbon monoxide levels to below 10 ppm for use in a PEMFC without experiencing performance losses; this can be accomplished using a dense, permselective palladium membrane. Microreactors make possible the integration of all three of these processes within one compact unit, while providing order-of-magnitude improvements in mass and heat transfer rates for greater efficiency while providing portable, lightweight chemical processors.[3]

## Micro-Membrane Networks

At the University of Connecticut, our research team has developed a cost-effective, cartridge-based ceramic microchannel network capable of integrating multiple chemical and/or physical processes within a single integrated processor. This is accomplished by packaging precision-machined fluidic distributors (fashioned from either silicon or brass) to extruded cordierite honeycomb monoliths. This hybridization of two separate technologies overcomes existing limitations of mini- and micro-channel reactors and conventional monolith reactors to demonstrate a new class of highly integrated chemical reactors.[4,5] Extrusion technologies offer a means to fabricate large networks of parallel mini- to microscale flow channels at a minimum cost, while allowing selection from a broad range of substrate materials, including ceramics with custom-tailored porosities. Precision machining allows fabrication of complex two-dimensional patterns, incorporated into distribution caps sealed directly to the monolith face, addressing process flows into and out of each individual channel. By packaging the monolith with these channel-specific distributors, two-dimensional networks of unique, separate process flows in a variety of radial distribution patterns can be realized for efficient heat and mass transfer over a range of materials properties. This presentation details our efforts to-date in utilizing these cordierite microchannel networks for hydrogen extraction via coupled ethanol steam reforming and hydrogen purification using dense palladium membrane microchannels.

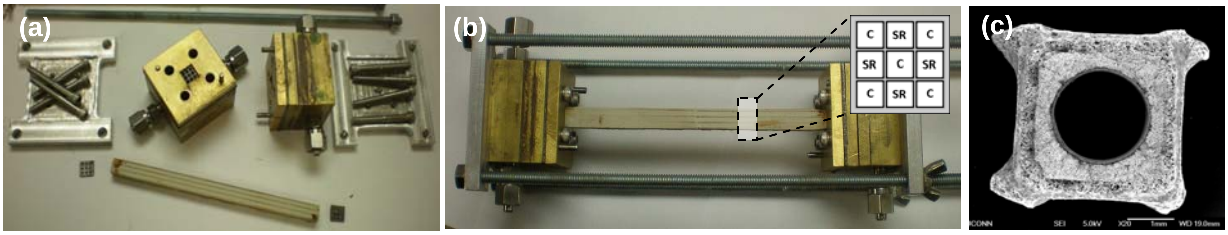

**Figure 1**: Distributor-packaged ceramic microchannel network; (a) unassembled system showing two distributors, ceramic microchannel network (3x3), graphite gaskets and compression chuck; (b) assembled view [Legend: C – combustion; SR – steam reforming]; (c) cross-section of single palladium membrane deposited within cordierite microchannel.

## Results and Current Work

Cordierite honeycomb monolith supports (Applied Ceramics, Inc. 64 cpsi) were coated with successive γ-alumina support layers in order to cover the large pores (about 50 μm) on the cordierite and provide a uniform, crack-free and low-stress mechanical support layer for electroless plating of dense palladium films. First, a thick micropowder alumina layer was applied to the cordierite square channels to create a uniform, crack-free cylindrical surface for subsequent depositions. Secondly, a thin nanopowder alumina layer was applied to provide a low roughness surface for electroless plating of dense defect-free palladium films. The resulting microchannels were electroless-plated with palladium thin films (~8 mm) using a modified recipe based upon that reported by Nair and coworkers.[6] Hydrogen separations were carried out in a smaller, two-channel membrane assembly. Sealing was accomplished using ceramic cement to attach 1/16" stainless steel plumbing to each channel. The entire assembly was maintained at temperature by placement in a tube furnace. Experiments were performed employing helium-hydrogen feed mixtures and nitrogen sweep gas at 350°C to measure permeation rates and hydrogen-helium selectivities in the presence of all species involved in the reforming of ethanol (Figure 8). In all cases, hydrogen selectivities remained in excess of 1000:1.

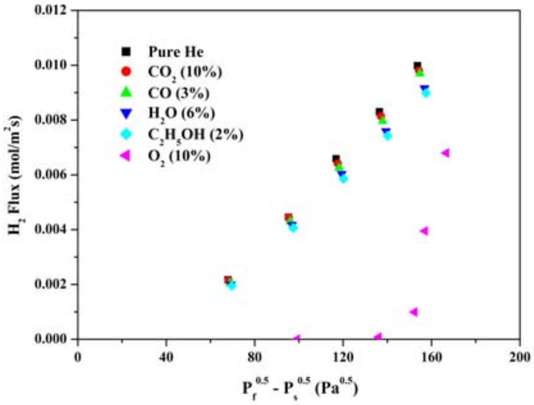

**Figure 2:** $H_2$ Flux of as-deposited palladium membranes within the microchannel network, under different exposure levels of reforming co-reagents. In all cases, selectivities were in excess of 1000:1.

This presentation will detail permeation experiments, materials analysis of resulting membranes both prior to and after long-term gas exposures. Lastly, investigations into coupled ethanol reforming integrated within the ceramic microchannels will be presented. Each micro-channel of the cordierite monolith will be coated with Co/ZnO, Ni/$Al_2O_3$ Rh-Ce catalysts to conduct the ethanol steam reforming, autothermal reforming and partial oxidation reaction, respectively, for producing hydrogen. The optimization of steam/oxygen/ethanol molar ratio and heat supply will be performed to maximize the ethanol conversion to hydrogen within the integrated ceramic micro-reactors. Results provide the necessary basis for designing large-scale micromembrane networks coupling ethanol reforming with water-gas-shift and hydrogen purification.

## Acknowledgement

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