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-tailed 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.
Results and Current Work

Cordierite honeycomb monolith supports (Applied Ceramics, Inc. 64 cpsi) were coated with successive $\gamma$-alumina support layers in order to cover the large pores (about 50 $\mu$m) 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. 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.

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References