Advanced Protonic Conductors

Eric D. Wachsman

Department of Materials Science & Engineering
University of Florida
Gainesville, FL 32611

Start Date = January 2004
Planned Completion = March 2007

Research Goals and Objectives

- The overall objective of this project is to demonstrate the feasibility of producing hydrogen from hydrocarbon based fuels using advanced proton conducting membranes.

- The goal is to develop thin film proton conducting membranes on porous supports, and to demonstrate hydrogen fluxes through these thin supported membranes.

Relevance to Current State-of-the-Art

- The major source of H_2 is steam reformation of natural gas.
- Membrane reactor technology will dramatically improve H_2 production technology from a broad array of conventional (natural gas, coal) and renewable (biomass) fuels.
- Membrane reactors based on ion conducting ceramics provide the technological advance necessary to increase the efficiency and reduce the cost of H_2 production.

Relevance to NASA

- Membrane reactors based on ion conducting ceramics will provide lower cost H_2 for NASA.
- Based on their more compact integrated design, membrane reactors may be applicable to space based H_2 production.

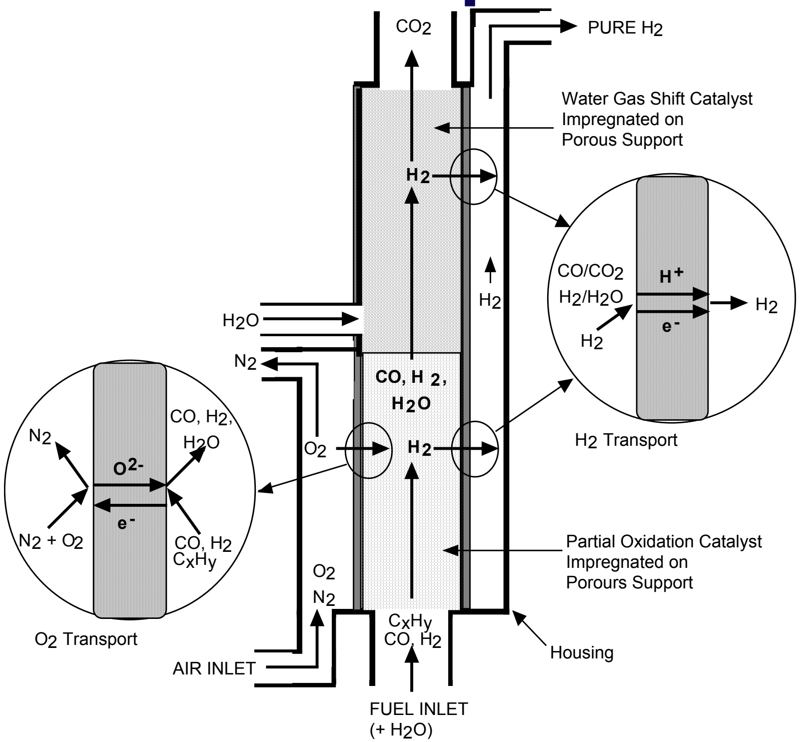
Budget, Schedule and Deliverables

- Budget: $214K + $80K

- Schedule:
- Q1 Fabricate dense thin proton conducting membranes on porous supports that are stable under reducing (H_2) conditions.
- Q2 Scale up size of supported membrane tubes to 15 cm long.
- Q3 Incorporate steam reforming catalysts into porous membrane support.
- Q4 Demonstrate membrane reactor for conversion of hydrocarbon fuel to pure H_2
- Q5 Determine appropriate H_2O/CH_4 for maximum stable H_2 production

- Deliverable: Membrane reactor for conversion of hydrocarbon fuel to pure H_2

Anticipated Technology End Use



Oxygen-ion and proton transport membranes combined in series and integrated with partial oxidation, steam reforming, and water gas shift catalysts, optimize the thermodynamics of hydrogen production.

The oxygen-ion transport membrane separates O_2 from air and reacts any of the hydrocarbons in the feed to form CO and H_2.

The proton transport membrane separates the H_2, providing a pure H_2 gas stream.

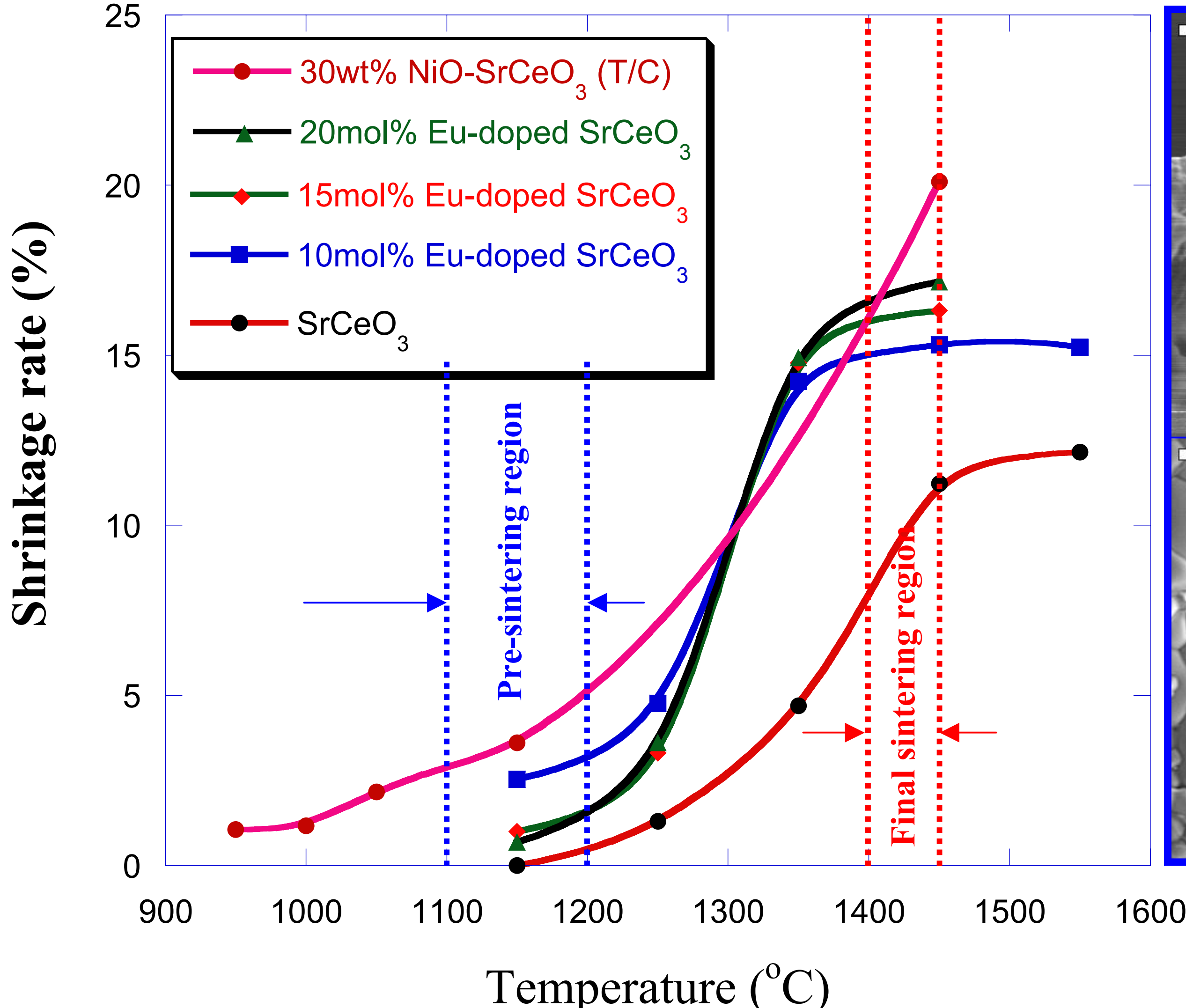
•Membrane reactors for H_2 production from a broad array of conventional (natural gas, coal) and renewable (biomass) fuels has tremendous commercial/civilian applications.

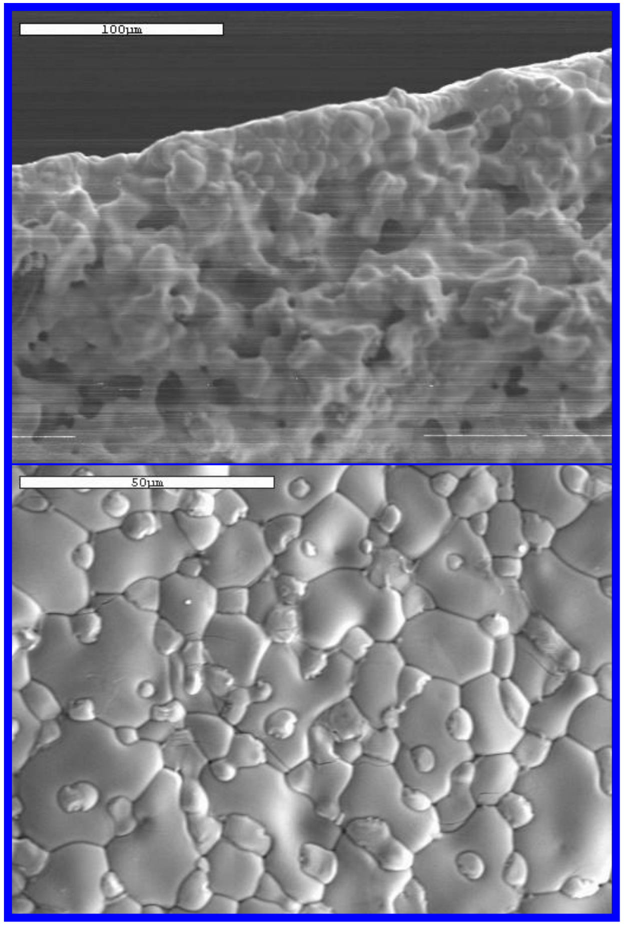
•Compact integrated membrane reactors have many defense applications and may be applicable to space based H_2 production.

Accomplishments and Results

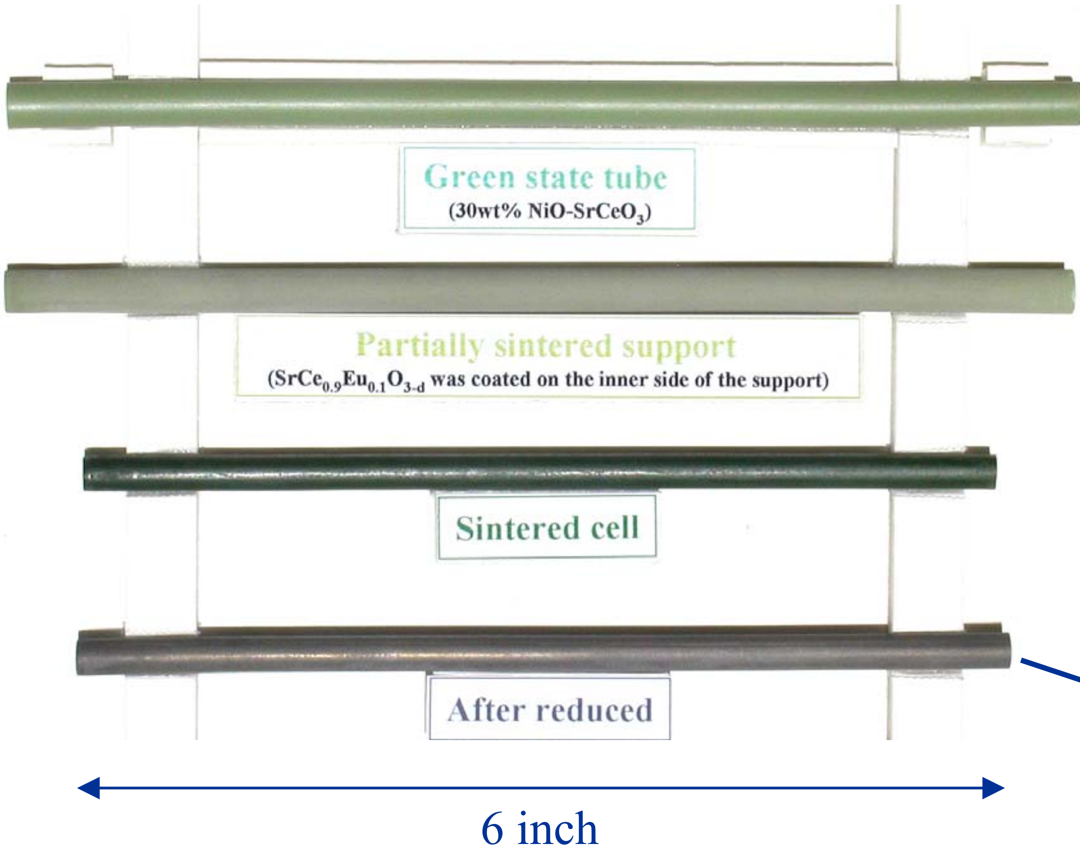
- Developed 10 mol% Eu-doped $SrCeO_3$ membrane supported by Ni-$SrCeO_3$ tubular support
- Fabricated hydrogen permeation reactor
- Demonstrated 5 cc/min hydrogen flux from H_2/He mixture
- Demonstrated membrane reactor will directly produce pure hydrogen from internally steam reformed hydrocarbon gases (CH_4)
- Acheived >3 cc/min hydrogen flux from CH_4/H_2O mixture

Membrane Fabrication

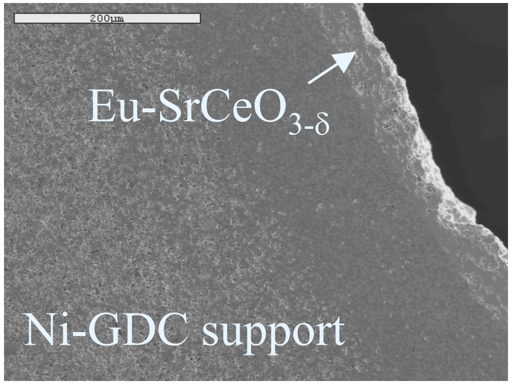




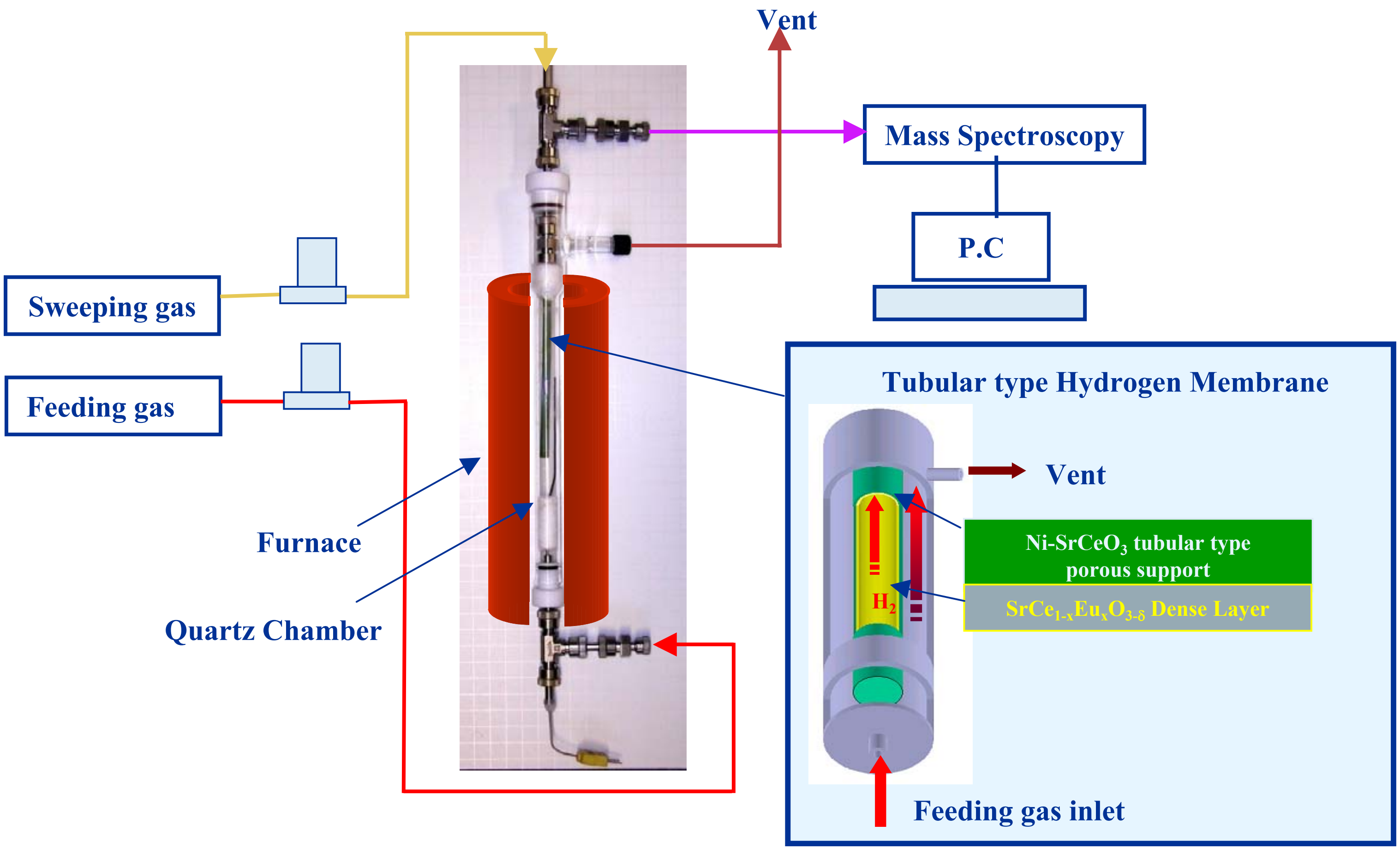
1450°C 5hrs



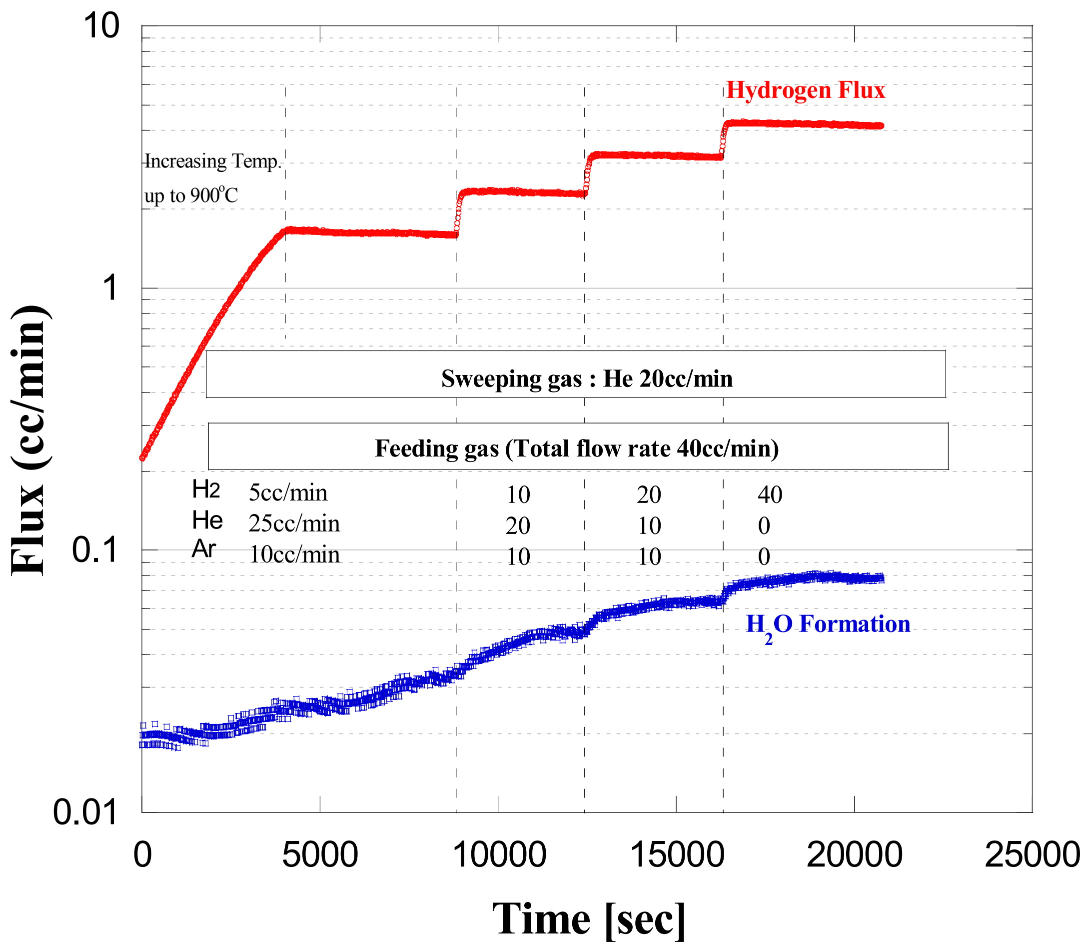
- Successfully fabricated supported 10 μm thin-film membrane tubes
- Matched thermal expansion for stable H_2 production



Fabricated Hydrogen Permeation Reactor



Hydrogen Flux from He/Ar/H_2 Mixture

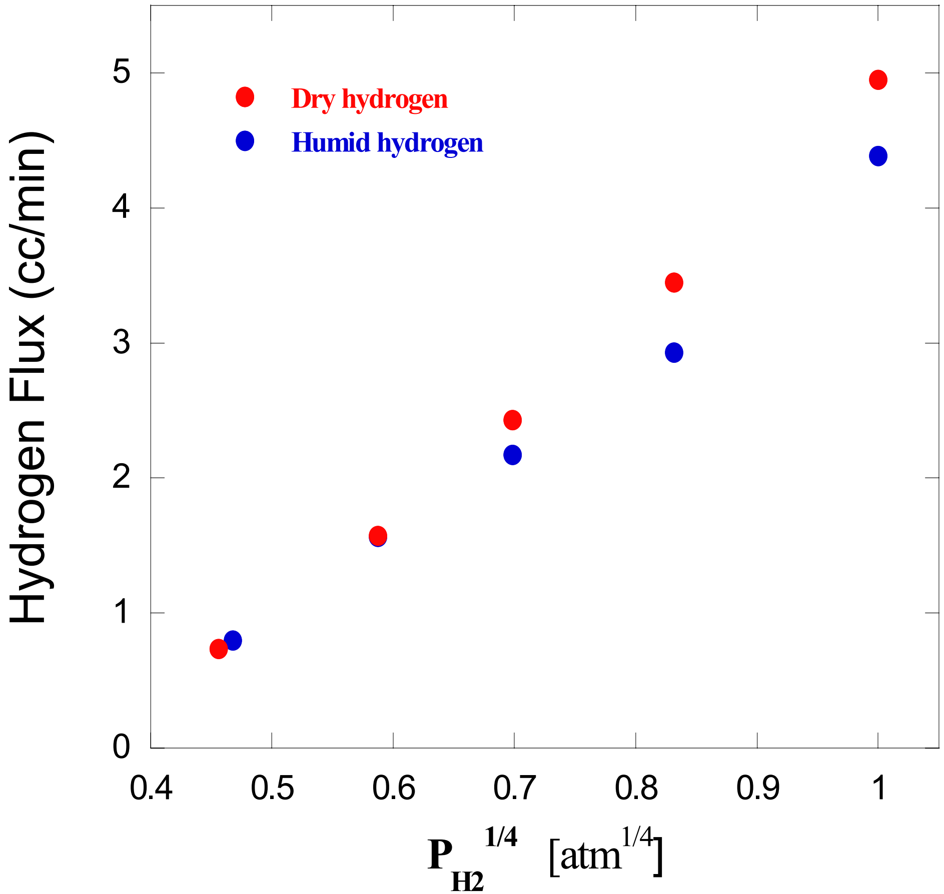


Cell length 15 cm
(effective area <15 cm^2)

Temperature: 900 °C

Sweep: He (20ccm)
Feed: He/Ar/H_2 (total 40ccm)

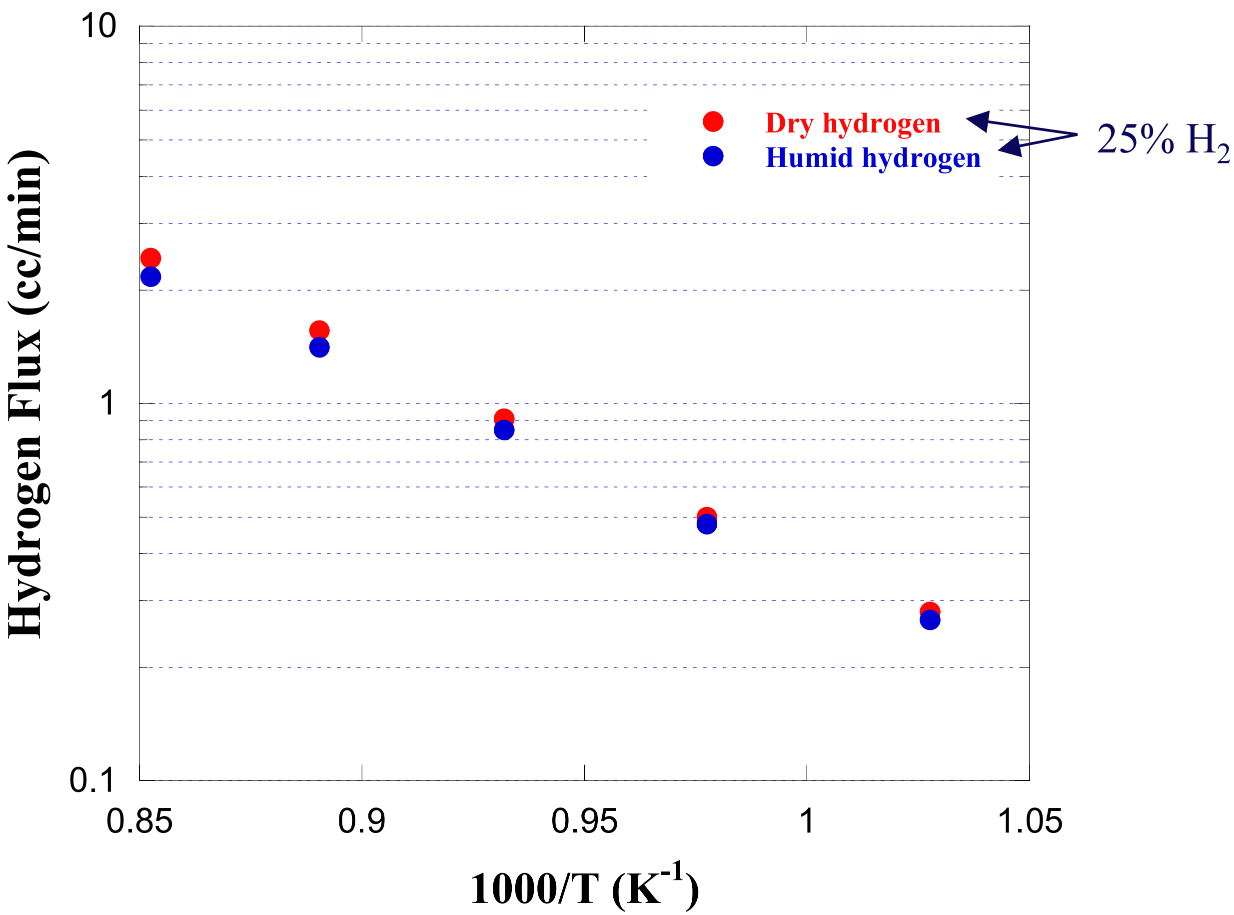
Hydrogen Flux vs. $P_{H2}^{1/4}$



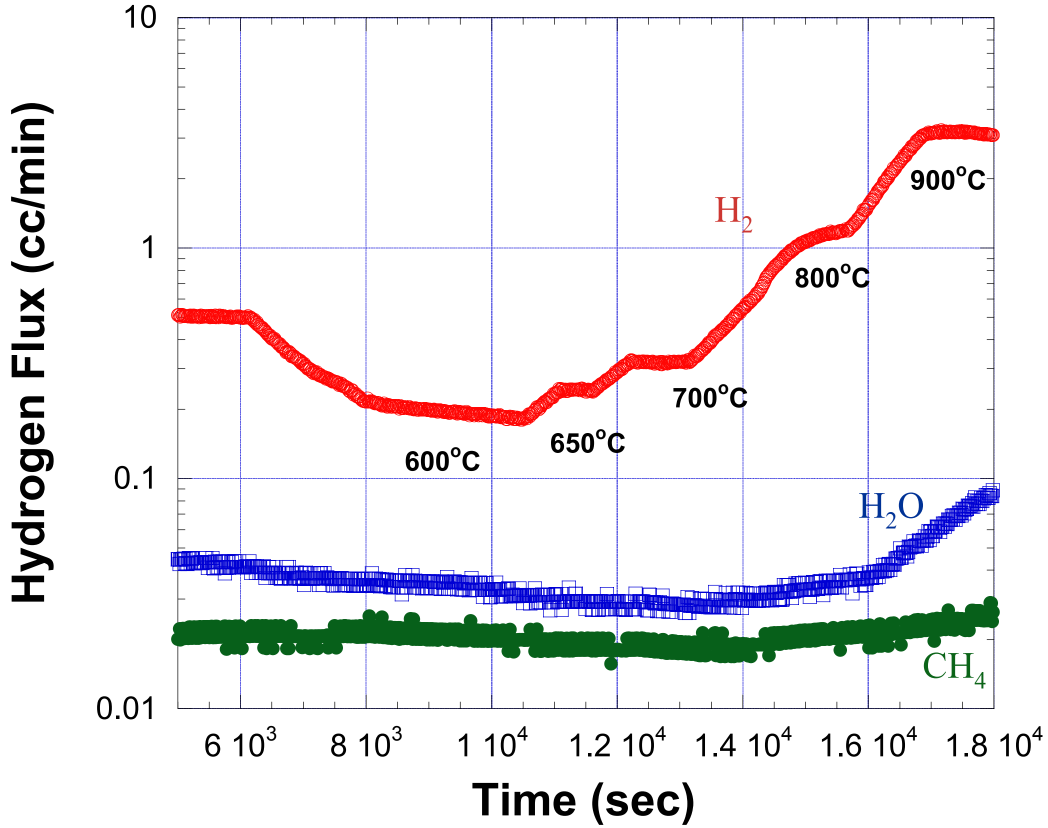
5 cc/min H_2 flux achieved at 900 °C

Protons and electrons are dominant defects. Under this condition the hydrogen flux is proportional to $[P_{H2}]^{1/4}$.

Hydrogen Flux vs. Temperature



Hydrogen Flux from Steam Reformed CH_4

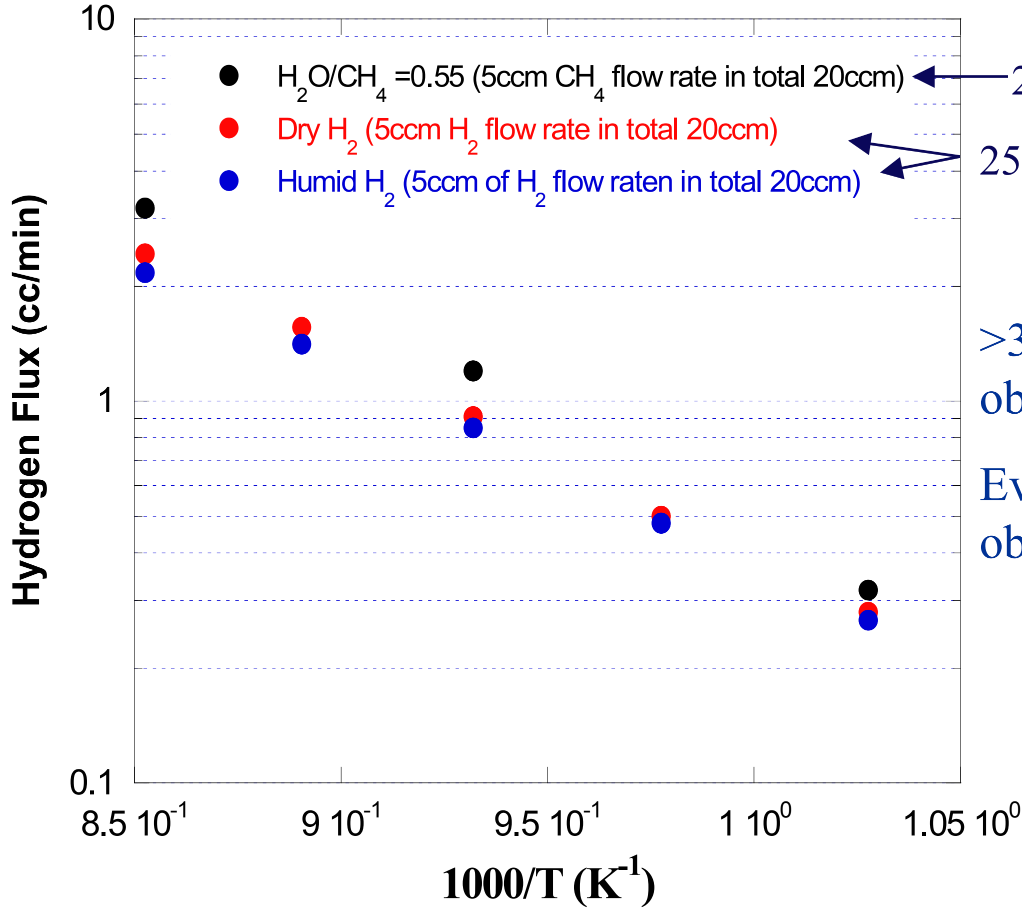


Cell length 16.5 cm
(effective area <16 cm^2)

Sweep: He (20 ccm)

Feed: CH_4 in He/Ar
(total flow rate 20 ccm)
with 55% H_2O

Hydrogen Flux vs. Temperature



25% CH_4

25% H_2

>3 cc/min H_2 flux obtained from CH_4/H_2O

Even higher than flux obtained from H_2

Issues

- Membrane thermodynamic stability limited at low P_{O2} (decomposition) and low H_2O/CH_4 (coking)
- Need effective membrane area to calculate effect of scaling up reactor size

Future Plans

- Optimize the performance (maximize flux and membrane stability) of the hydrogen permeation reactor in terms of:
  - Window of operation (Temp. and H_2O/CH_4 concentration)
  - Membrane composition
- Quantify flux vs. membrane area by masking part of tube length
- Produce higher hydrogen fluxes by scaling up reactor size