Distributed Reforming of Renewable Liquids using Gas Transport Membranes*

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Overview

Timeline

- Project Start Date: May 2005; on-hold in FY 06
- Project End Date: Project continuation and direction determined annually by DOE
- 35% Complete

Barriers

- (A) Reformer Capital Cost
- (B) Reformer Manufacturing
- (C) Operation/Maintenance
- Membranes also address various cross-cutting barriers. (Barriers N, P, R).

Budget

- Total Project Funding
  - -DOE share: 100%
- Funding received in FY08: $400K
- Funding for FY09: To Be Determined

Partners

- Other Argonne divisions
- Work is co-sponsored by FE-NETL.
- Project Lead: Argonne National Laboratory

Relevance - Objectives

- Overall objective is to develop a compact, dense, ceramic membrane reactor that meets the DOE 2017 cost target of <$3.00/gge for producing hydrogen by reforming renewable liquids.
- Reactor would use oxygen transport membrane (OTM) to supply pure oxygen for reforming and hydrogen transport membrane (HTM) for water gas shift (WGS) & H_2-separation. Focus was initially on reforming natural gas (FY05-FY07), but was changed to ethanol (EtOH) reforming in FY08.
- Objectives over the past year were to optimize the performance of the OTM and show feasibility of using OTM to reform EtOH.
- **Relevance:** Membrane technology provides the means to attack barriers (listed on slide #2) to the development of small-scale hydrogen production technology.

Relevance to the Overall DOE Objectives

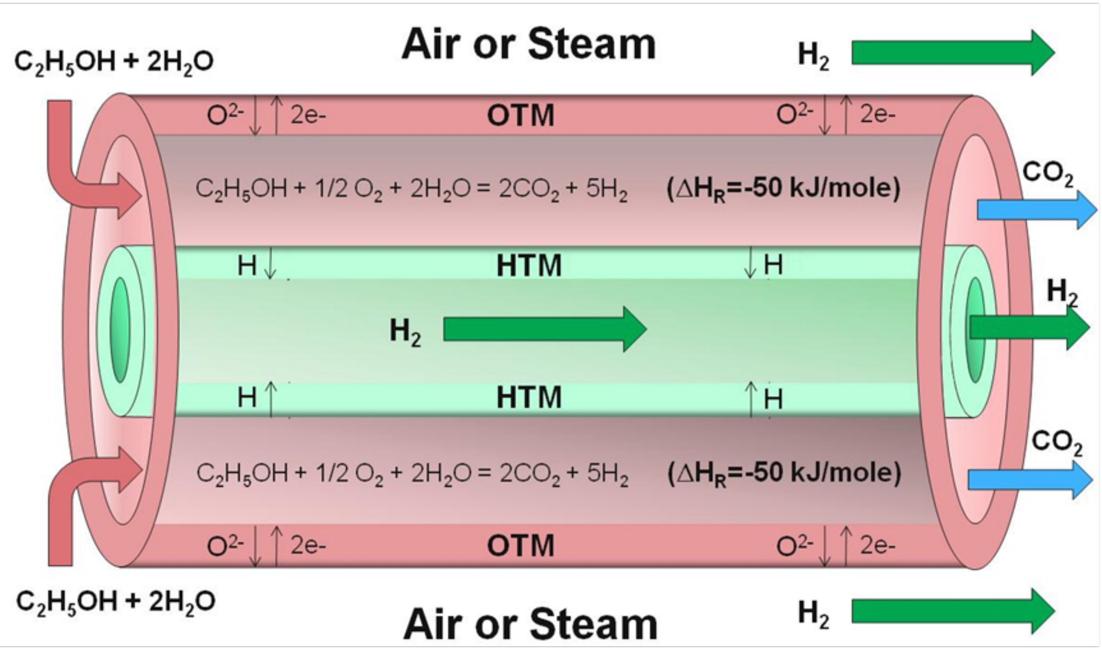
This project addresses barriers:

- A(Reformer Capital Costs) by combining oxygen separation and reforming with shift and hydrogen purification in a compact, appliance-type, membrane reactor,
- B(Reformer Manufacturing) by developing compact membrane units that can be made using low-cost manufacturing methods,
- C(Operation and Maintenance) by providing robust membrane systems that require little maintenance,
- N(Selectivity) by transporting pure oxygen for reforming (avoiding formation of NO_x) and separating pure H_2,
- P(Flux) by developing new OTMs with higher flux, and
- R(Cost) by providing high purity hydrogen using low-cost membranes.

The goal is to develop cost-effective, small-scale reformer technology that increases efficiency, selectivity, and durability and integrates process steps to minimize capital costs, and unit size.

Approach

Reforming of Ethanol using OTM/HTM



-Ethanol is reformed using OTM to supply pure oxygen and HTM for WGS/H_2-separation.

-Benefits of O_2 during reforming: Increases EtOH conversion and enhances catalyst performance by preventing coke formation.

-Sources of oxygen: Air or Steam

-H_2 is produced on both sides of the OTM if steam is source of oxygen.

-Proven concept: Reforming methane with OTM reduced costs by ≈30-40% and energy consumption by ≈30%.

- Air or steam can be used as source of oxygen.
  - Water splitting requires heat input, but there is a potential payoff.
  - A detailed system analysis must be done to determine the most cost- and energy-effective oxygen source.
- In this project, we are generating necessary data for the analysis.

Uniqueness of Argonne's Approach

- Pure oxygen is used for reforming rather than air; cost advantages of using OTM to reform methane has been proven
  - -avoids NO_x formation/separation

Potential Benefits:

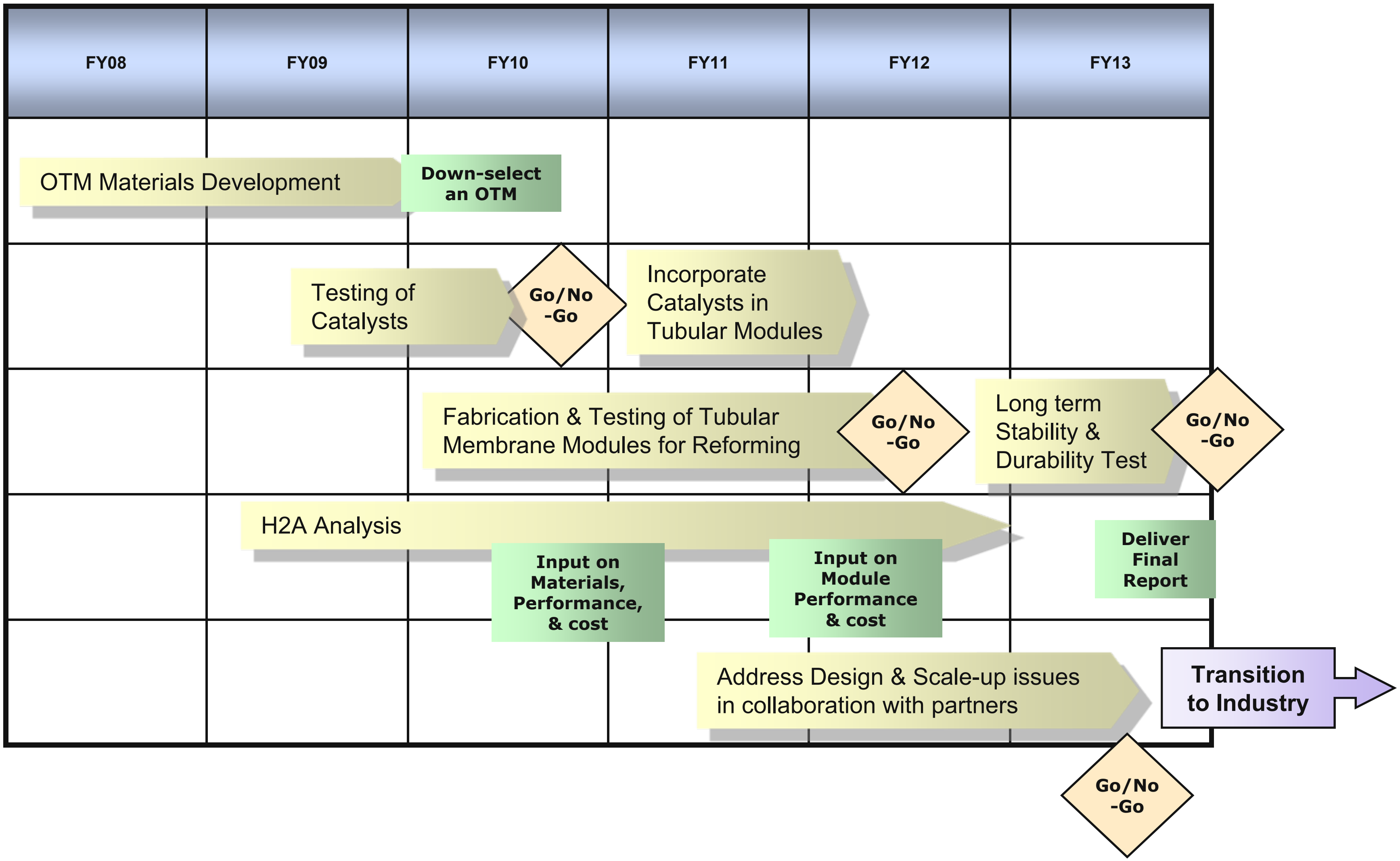
- Incorporates breakthrough membrane separation technology
- Intensifies reforming process by combining oxygen separation, shift and hydrogen separation operations (using OTM & HTM)
  - - offers potential for high energy efficiency
- Reduces foot-print area for the reformer
- Skid-mounted units can be produced using currently available, low-cost, high-throughput manufacturing methods
- Compact design reduces construction costs
- Uses robust membrane systems that require little maintenance

Approach - Milestones

Project Milestones	% Comp.	Progress Notes
Enhance performance of thin OTMs by controlling their surface microstructure.	100%	Nearly tripled the hydrogen production rate by optimizing the processing conditions.
Check feasibility of reforming ethanol using OTM.	50%	Showed reforming of N_2/EtOH at 900°C using ≈9 cm long, thin-film OTM tube.*
Test performance of OTMs at low temperatures (550-800°C) compatible with ethanol reforming.	30%	Hydrogen production rates of three types of OTMs have been measured at 700°C.*
Evaluate chemical stability of OTM during reforming of bio-ethanol for up to ≈1000 h at temperatures in range 550-800°C.	15%	OTM was stable for ≈900 h during ethanol reforming at 900°C with ≈6% EtOH in carrier gas.*
As input for H2A analysis, generate data using air and steam as oxygen source.	20%	Samples are prepared for hydrogen production rate measurements.*
Reform ethanol using OTM in presence of catalyst.	5%	Investigation of catalyst candidates has begun.*

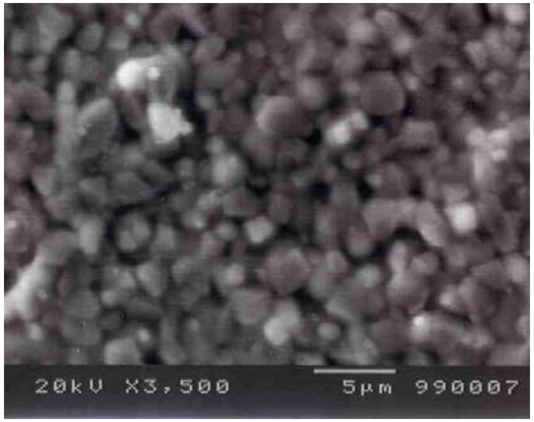
*Completion date depends upon the allocation of future funds.

Timeline for Reforming Renewable Liquids using OTM

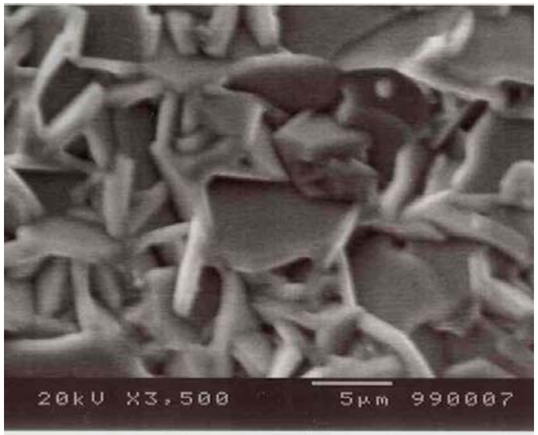


Technical Accomplishments/Progress/Results

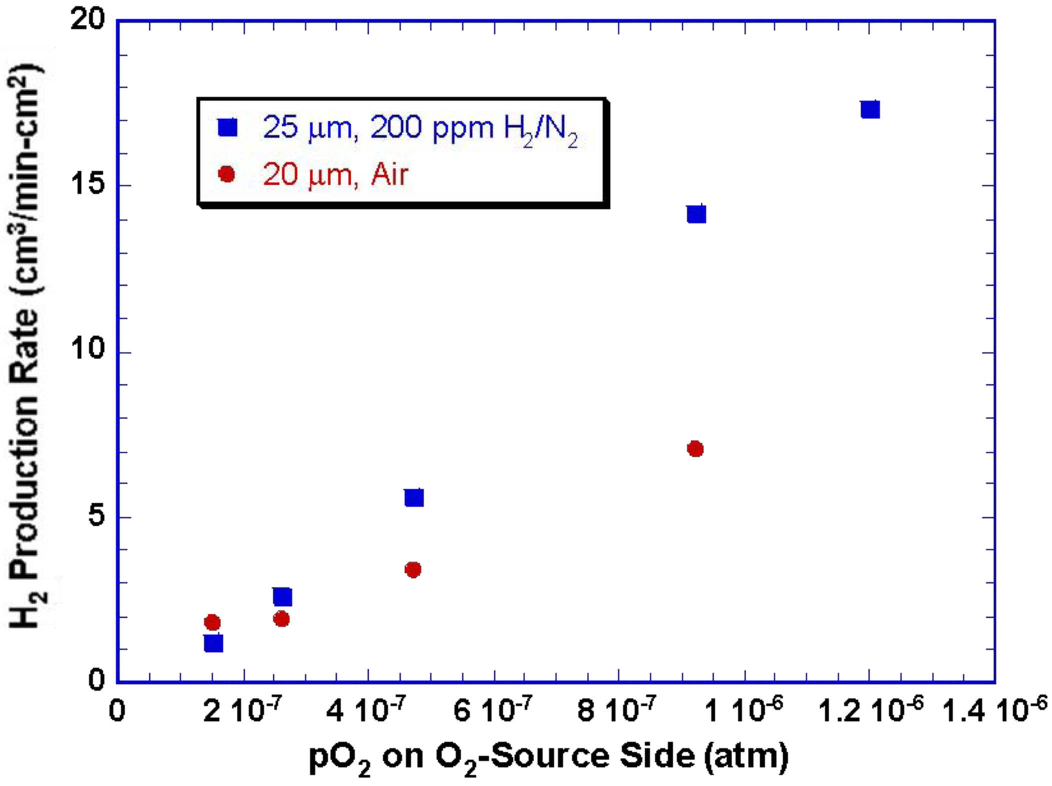
Optimizing OTM Performance by Controlling Microstructure



OTM sintered in 200 ppm H_2/N_2



OTM sintered in Air

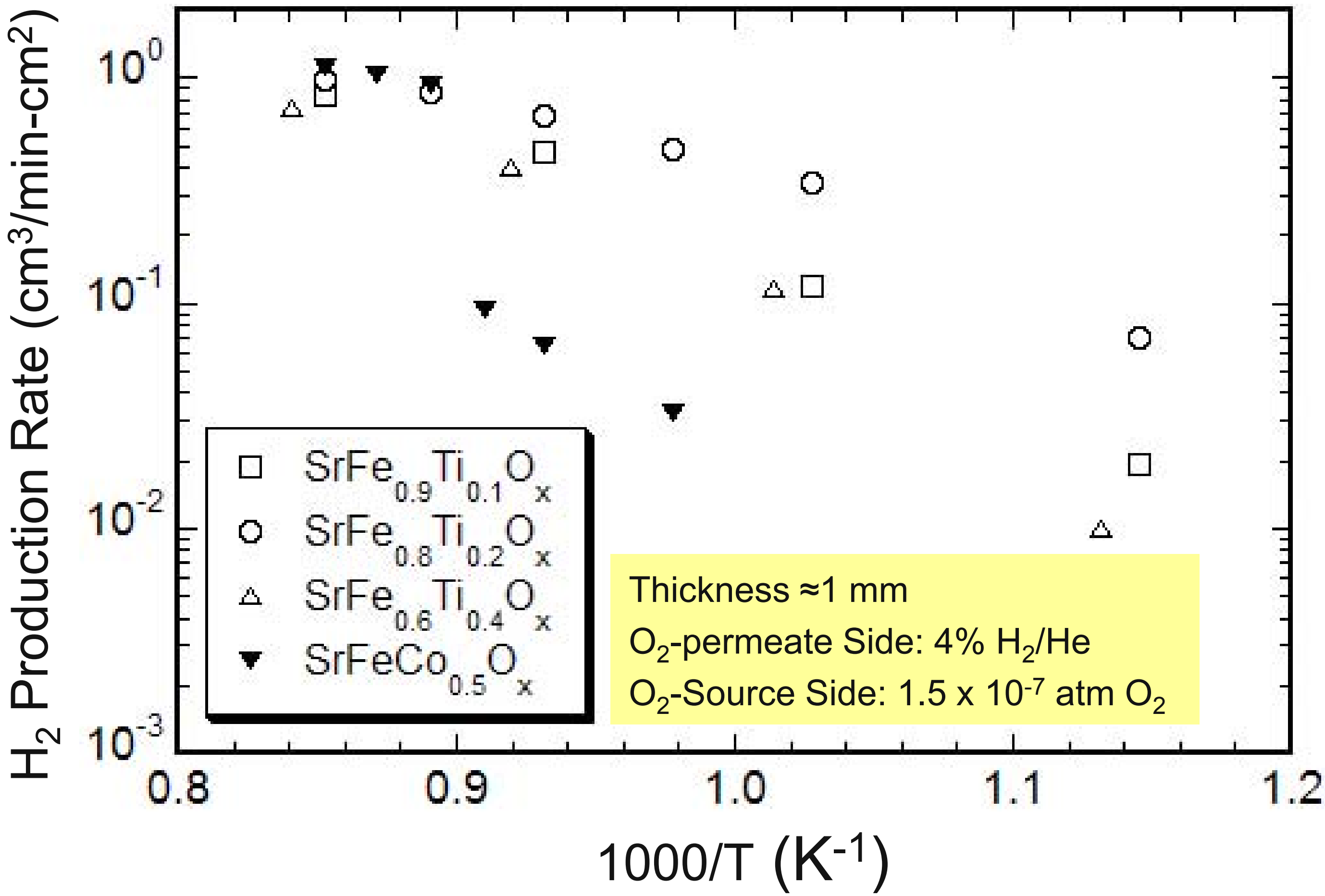


■ Sintering atmosphere profoundly affects OTM's microstructure.

■ OTMs with a fine, equiaxed microstructure give a much higher hydrogen production rate.

Technical Accomplishments/Progress/Results (Cont.)

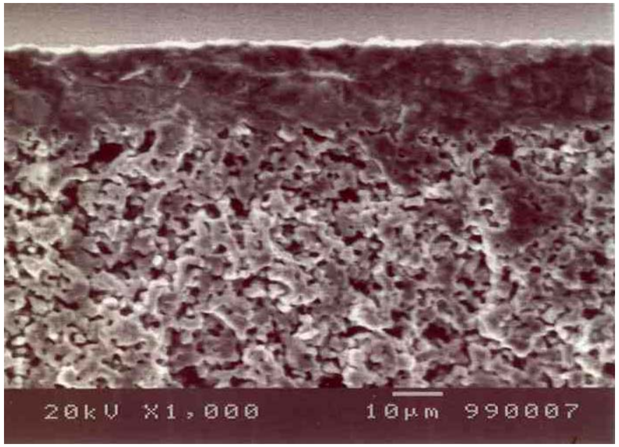
Optimizing OTM Performance by Doping



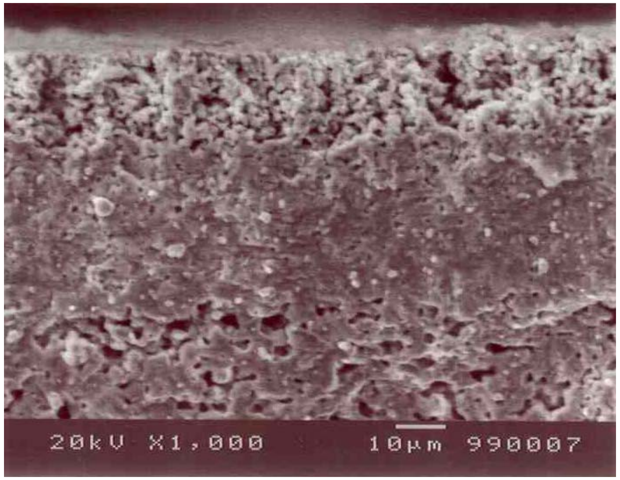
- **Proper doping eliminates phase transition and gives high hydrogen production rate at low temperatures (<825°C).**

Technical Accomplishments/Progress/Results (Cont.)

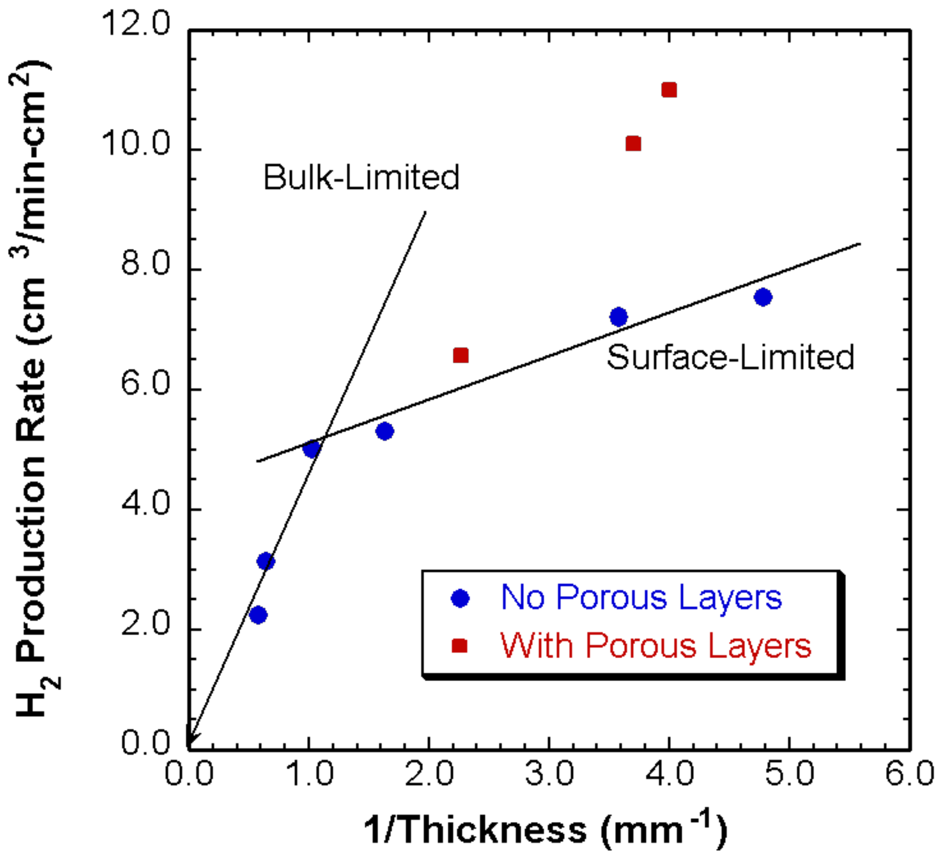
Fabricating Thinner OTMs to Enhance Hydrogen Production Rate



Porous layer on one surface



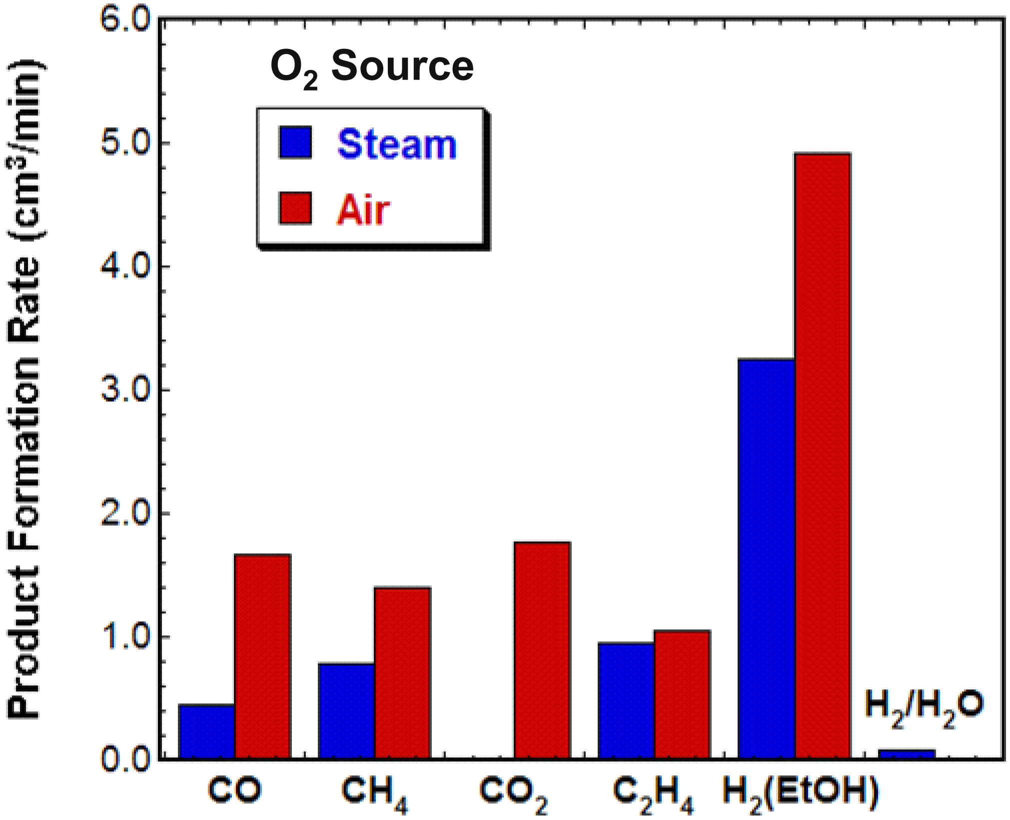
Porous layer on both surfaces



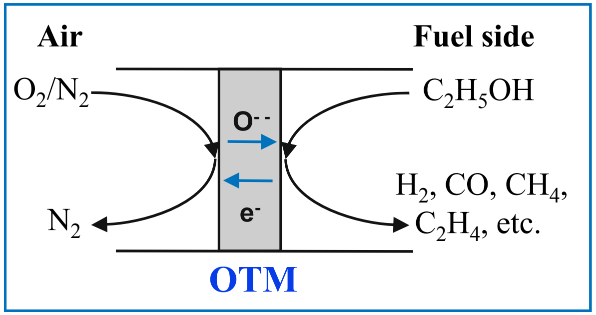
- Reducing OTM thickness increases hydrogen production rate, but porous layers are needed to overcome limitations from surface reaction kinetics.

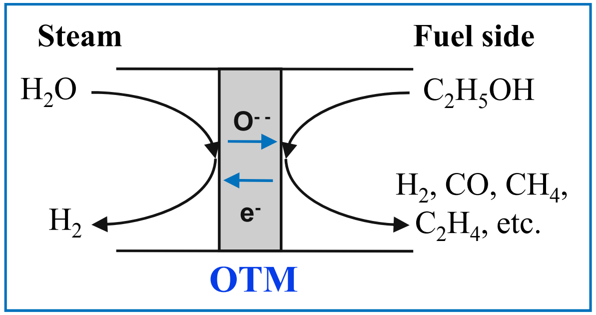
Technical Accomplishments/Progress/Results (Cont.)

Reforming of Ethanol using OTM (Without Catalyst)



OTM Thickness: 15 μm
Fuel: N_2 (0.076 atm EtOH)
O_2: Air or He(0.49 atm H_2O)
Temperature: 700°C



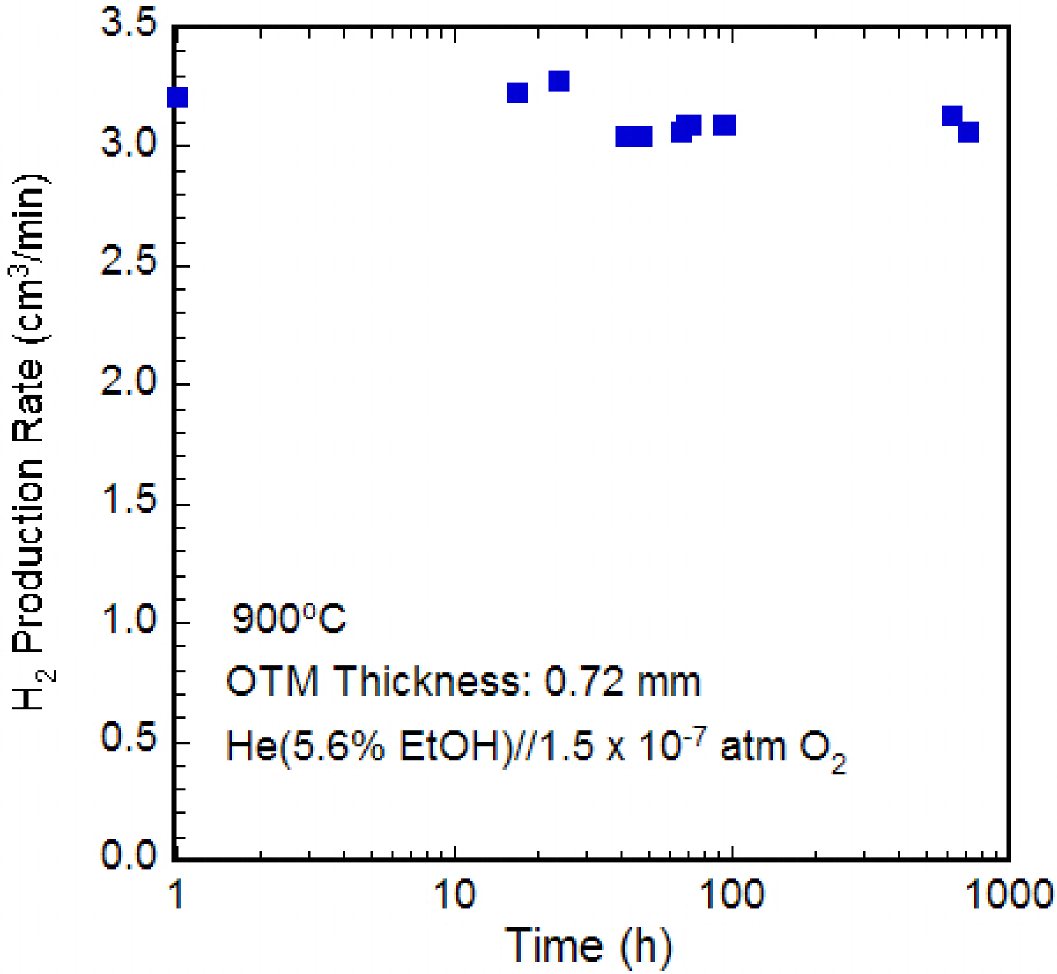


$$EtOH\ Conversion = \frac{(EtOH)_{in} - (EtOH)_{out}}{(EtOH)_{in}} = 47\%$$

$$H_2\ Selectivity = \frac{H_2}{H_2 + 2CH_4 + 2C_2H_4 + 3C_2H_6 + 2CH_3CHO + H_2O} = 28\%$$

Technical Accomplishments/Progress/Results (Cont.)

Chemical Stability of Tubular OTM Membrane



- **OTM is stable during ≈900 h of reforming at 900°C with ≈6% EtOH in carrier gas.**

Collaborations

- Chemical Science & Engineering Division, Argonne (Dr. S. Ahmed) "Pressurized Steam Reforming of Bio-Derived Liquids for Distributed Hydrogen Production (PDP-16, Tuesday, May 19, 6-9 pm).
  - Catalysts, reactor design, and ethanol reaction chemistry
- Georgia Tech (Prof. M. Liu)
  - Graduate students' Ph.D. thesis research on mixed-conductors
- University of Florida (Prof. E. Wachsman)
  - Graduate student's Ph.D. thesis research on modeling of solid-state defects in mixed-conductors
- University of Houston (Prof. K. Salama)
  - Mechanical property measurement
- National Energy Technology Laboratory (Dr. D. Cicero & Dr. B. Morreale)
  - Co-sponsor of the project; development of gas transport membranes for hydrogen production from coal

- Professors' expertise is transferred using graduate students and post-docs as conduit.

Future Work

- Test OTMs for hydrogen production at temperatures compatible with ethanol reforming.
  - Study effects of EtOH concentration, gas flow rates, OTM thickness.
- Reform ethanol using OTM in presence of catalyst(s).
  - Employ catalysts to enhance the reforming of ethanol & oxygen transport.
- Generate necessary data for H2A analysis using air and steam as oxygen source.
  - Have a third party (e.g., DTI) perform detailed cost analysis to judge which is more cost- and energy-effective.
- Evaluate chemical stability of OTM for up to ≈1000 h during reforming of ethanol at temperatures in range 550-800°C.
  - Select OTM composition(s) and reaction conditions.
- Perform ethanol reforming with longer tubular membranes.
  - Increase surface area of the membranes, define suitable reforming conditions.

SUMMARY

- Dense ceramic membrane reactor is being developed to cost-effectively produce hydrogen by reforming renewable liquids.
- Reactor would use OTM to supply pure O_2 for reforming and HTM for water-gas shift and H_2-separation (HTM work is funded by DOE-FE).
- Data are being generated for a detailed system analysis to determine the most cost- and energy-effective oxygen source.
- **Benefits of OTM** [Frusteri et al., Intl. J. Hyd. Energy, 31, 2193-2199 (2006)]:
  - Injection of oxygen increases EtOH conversion and enhances catalyst performance by reducing coke formation.
- **Benefits of HTM** [Gallucci et al., Intl. J. Hyd. Energy, 33, 644-651 (2008)]: Comparing conventional EtOH steam reforming (ESR) to HTM-assisted ESR showed that HTM increases EtOH conversion and H_2 yield.
  - In particular, at 8 bar, conversion with the membrane was 95.3%, as compared to 44.5% in the conventional reactor.
  - Moreover, a CO_x-free H_2 stream can be directly produced with membrane.
- **This project aims to capitalize on benefits from both OTM and HTM.**