Distributed Reforming of Renewable Liquids using Oxygen Transport Membranes*

U. (Balu) Balachandran

Argonne National Laboratory

Team members: T. H. Lee, C. Y. Park, Y. Lu, J. E. Emerson, J. J. Picciolo, and S. E. Dorris

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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
- ≈20% 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 FY09: $70K
- Funding for FY10: $100K

Partners

- Directed Technologies, Inc.
- 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 renewable liquids. Initial focus (FY05-FY07) on reforming natural gas was changed to ethanol (EtOH) reforming in FY08.

- Objectives during past year were to use OTM to reform EtOH at ≤700°C and generate data for detailed analysis to identify benefits of approach.

- **Relevance:** Membrane technology provides the means to attack barriers (listed on slide #2) to the development of small-scale hydrogen production technology.

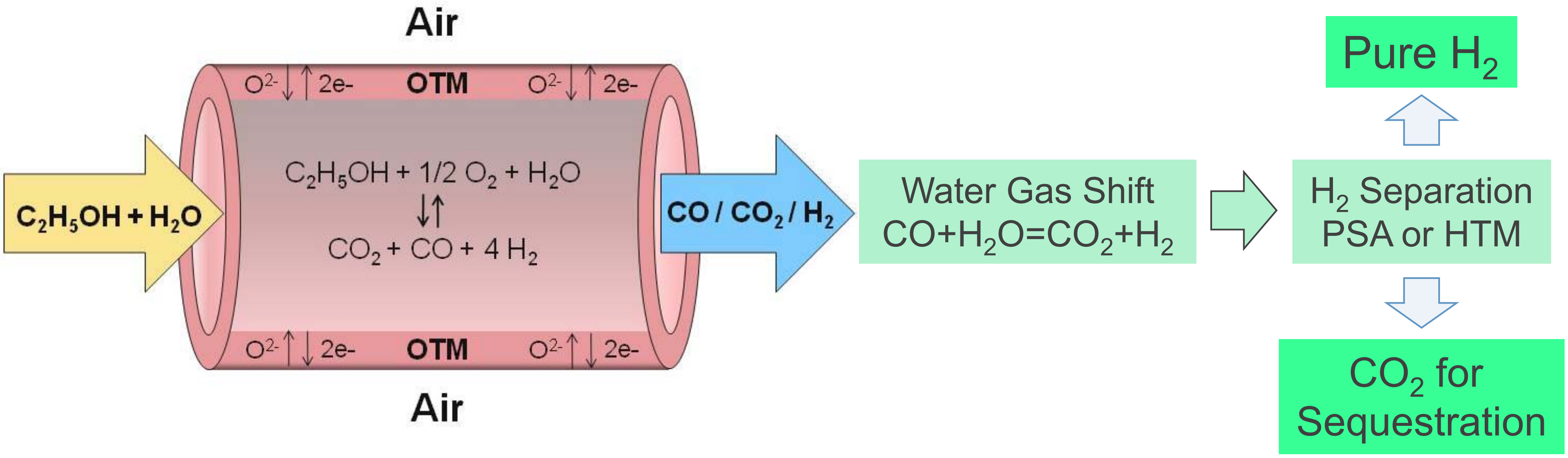
Relevance to the Overall DOE Objectives

This project addresses barriers:

- A(Reformer Capital Costs) by providing low-cost, high-purity oxygen 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 simple, robust membrane systems that require little maintenance,
- N(Selectivity) by transporting pure oxygen for reforming (avoiding formation of NO_x),
- P(Flux) by developing new OTMs with higher flux, and
- R(Cost) by using low-cost membranes to increase H_2 production.

Goal: Reduce capital costs and unit size by developing cost-effective, small-scale reformer technology that increases efficiency, selectivity, and durability.

Approach - Reforming Ethanol with OTM



-OTM enhances ethanol reforming by supplying pure oxygen from air:

- Increases EtOH conversion
- Enhances catalyst performance by preventing coke formation

-Concept proven by industrial consortium: Reforming methane with OTM reduced costs by ≈30-40% and energy consumption by ≈30%.

-A detailed system analysis has been initiated to determine the cost and energy benefits of OTM.

-In this project, we are generating necessary data for the detailed analysis.

Uniqueness of Argonne's Approach

- Pure oxygen is used for reforming rather than air; cost and energy savings from using OTM to reform methane have been proven
  - -avoids NO_x formation/separation

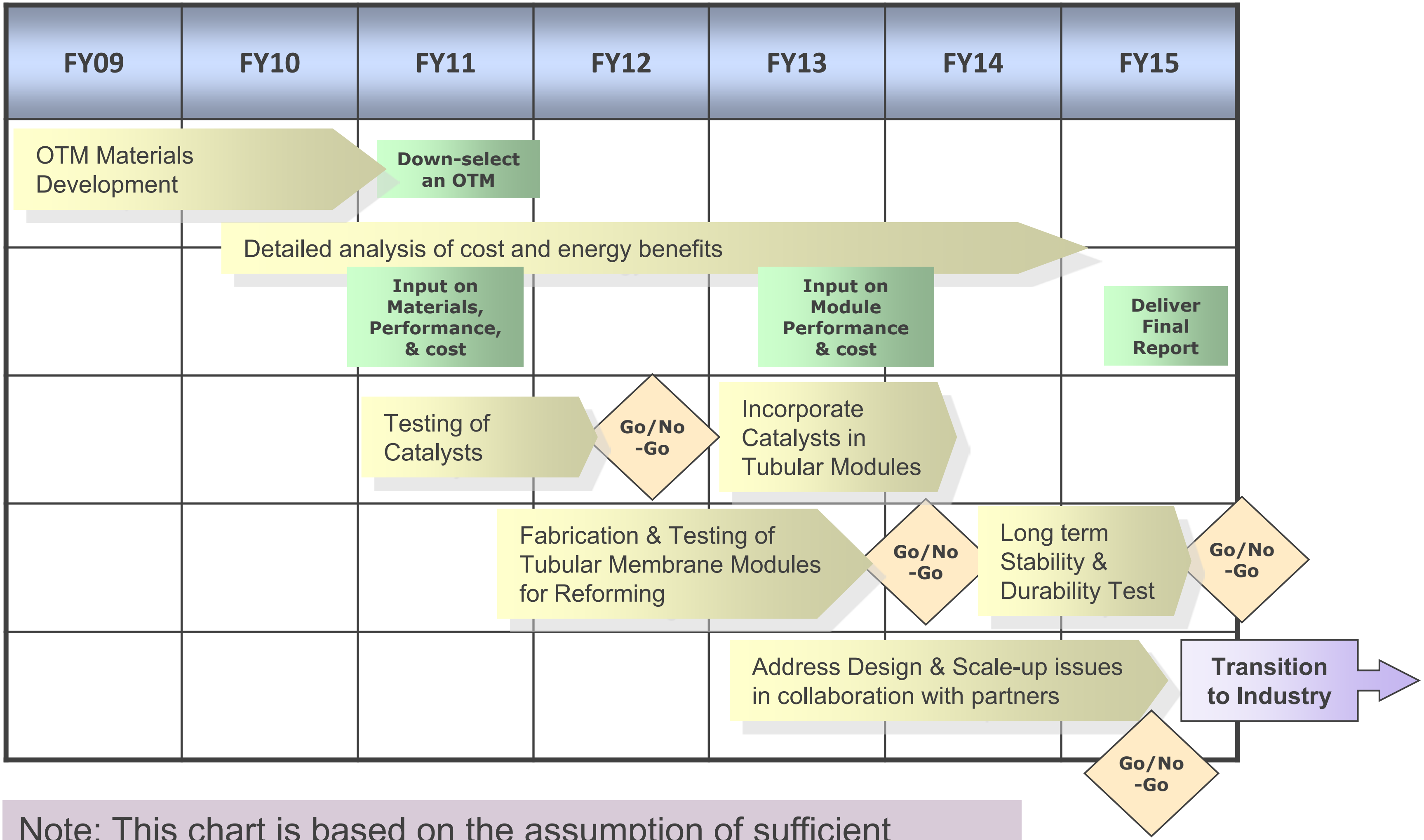
Potential Benefits:

- Incorporates breakthrough membrane separation technology
- Increase EtOH conversion
- Enhance catalyst performance by preventing coke formation
- Reduce 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 simple, robust membrane systems that require little maintenance

Approach - Milestones

Project Milestones	% Comp.	Progress Notes
Perform ethanol reforming studies at temperatures ≤700°C and generate data for detailed analysis.	20%	Did EtOH reforming study (without steam addition) at 500-700°C.
Have third party (Directed Technologies, Inc.) perform detailed system analysis.	5%	A subcontract has been established with DTI.
Reform ethanol using OTM in presence of catalyst.	5%	Investigation of catalyst candidates has begun.
Evaluate chemical stability of OTM during reforming of bio-ethanol.	5%	OTM was stable for ≈100 h during EtOH reforming at ≤700°C with ≈7% EtOH in carrier gas.

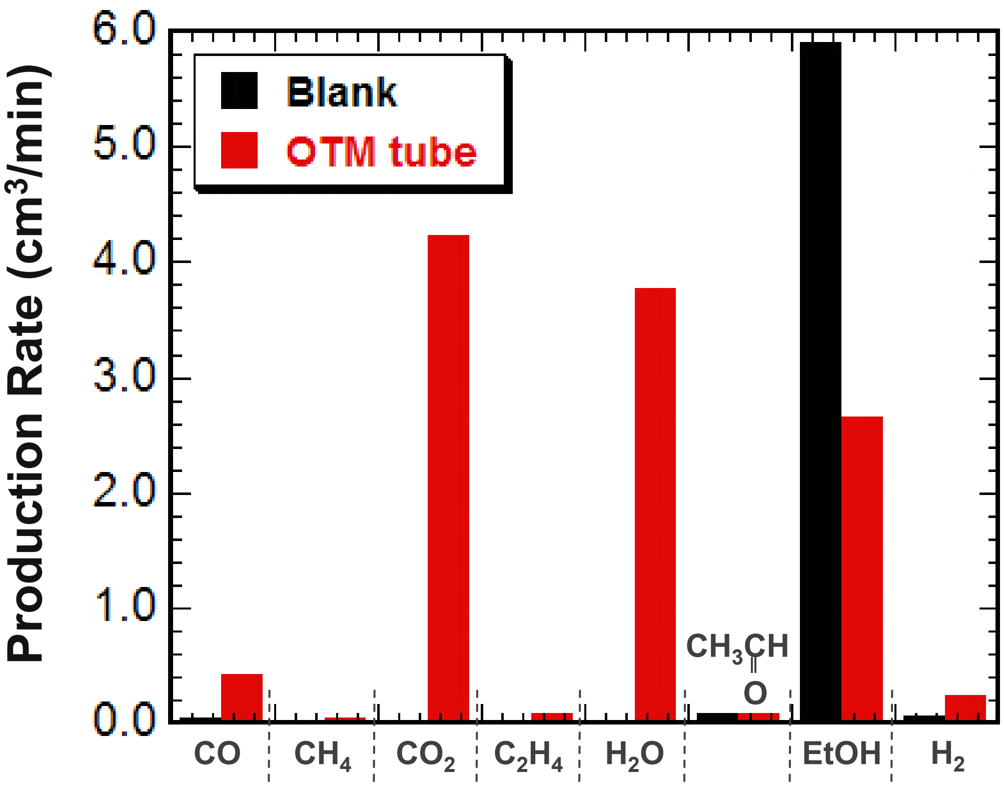
Timeline for Reforming Ethanol using OTM



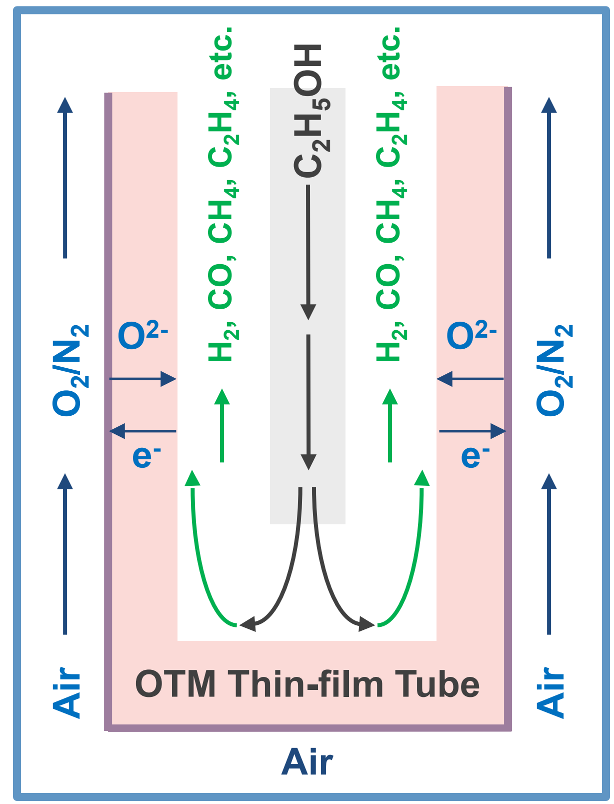
Note: This chart is based on the assumption of sufficient funding. Reduced funding will extend the timeline.

Technical Accomplishments/Progress/Results

Reforming Ethanol with La-Sr-Cu-Fe-O (LSCF) Tube (Without Catalyst)



OTM: LSCF Tube (30 μm)
Fuel: 7% EtOH/balance N_2
O_2 Source: Air
Temperature: 550°C

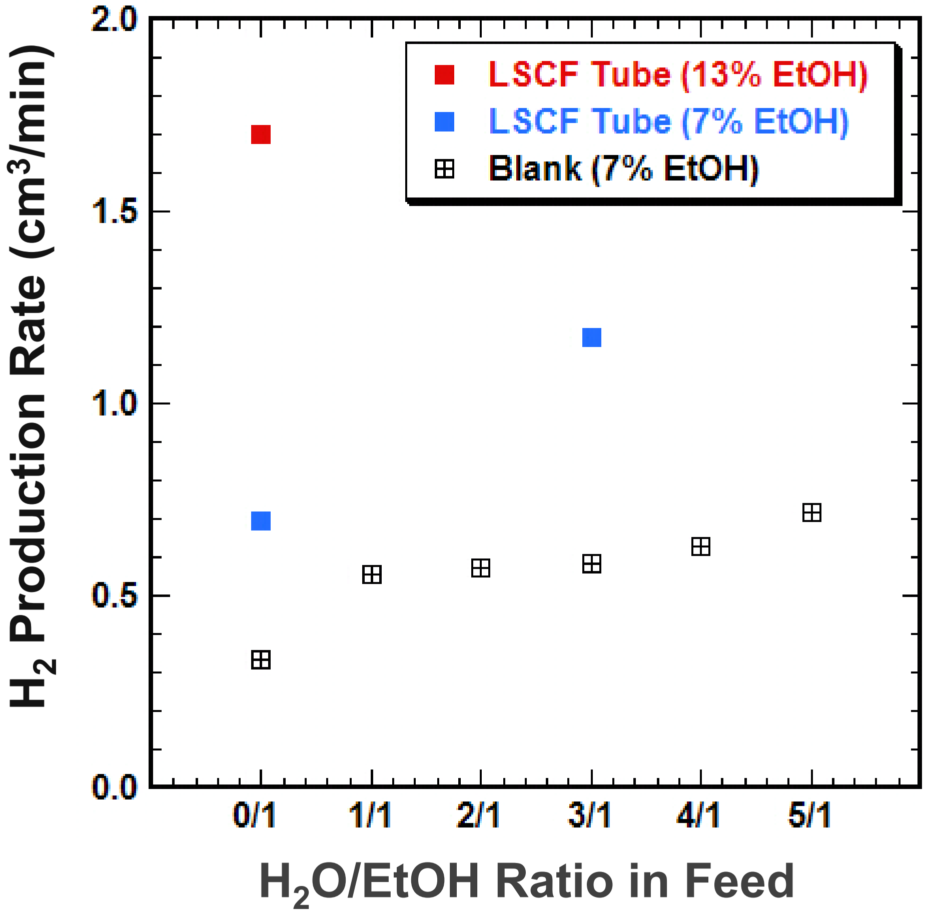


$$\text{EtOH Conversion} = \frac{(\text{EtOH})_{in} - (\text{EtOH})_{out}}{(\text{EtOH})_{in}} = 63\% \ (\text{FY09: } 47\%)$$

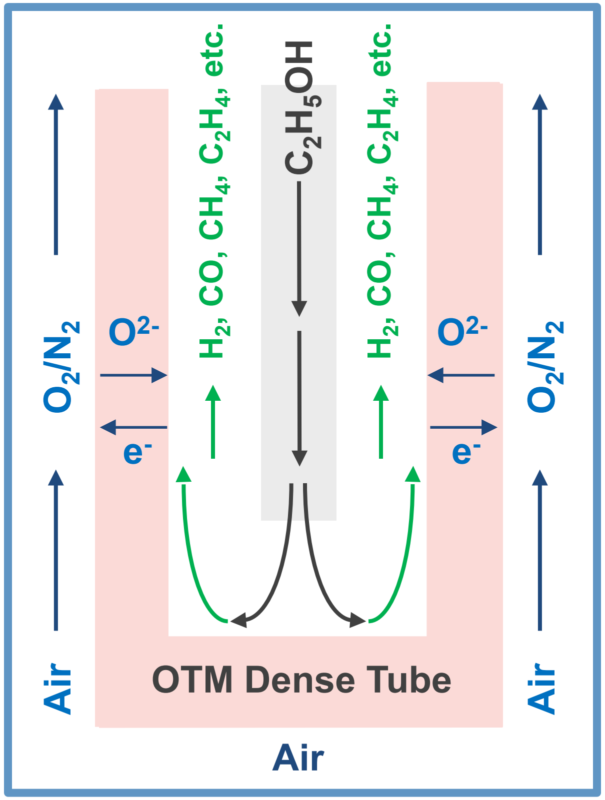
- OTM significantly enhanced EtOH conversion at low T (≤700°C). Higher O_2 flux should further enhance conversion.

Technical Accomplishments/Progress/Results (Cont.)

Ethanol Reforming (Effects of EtOH Conc., H_2O in Feed)



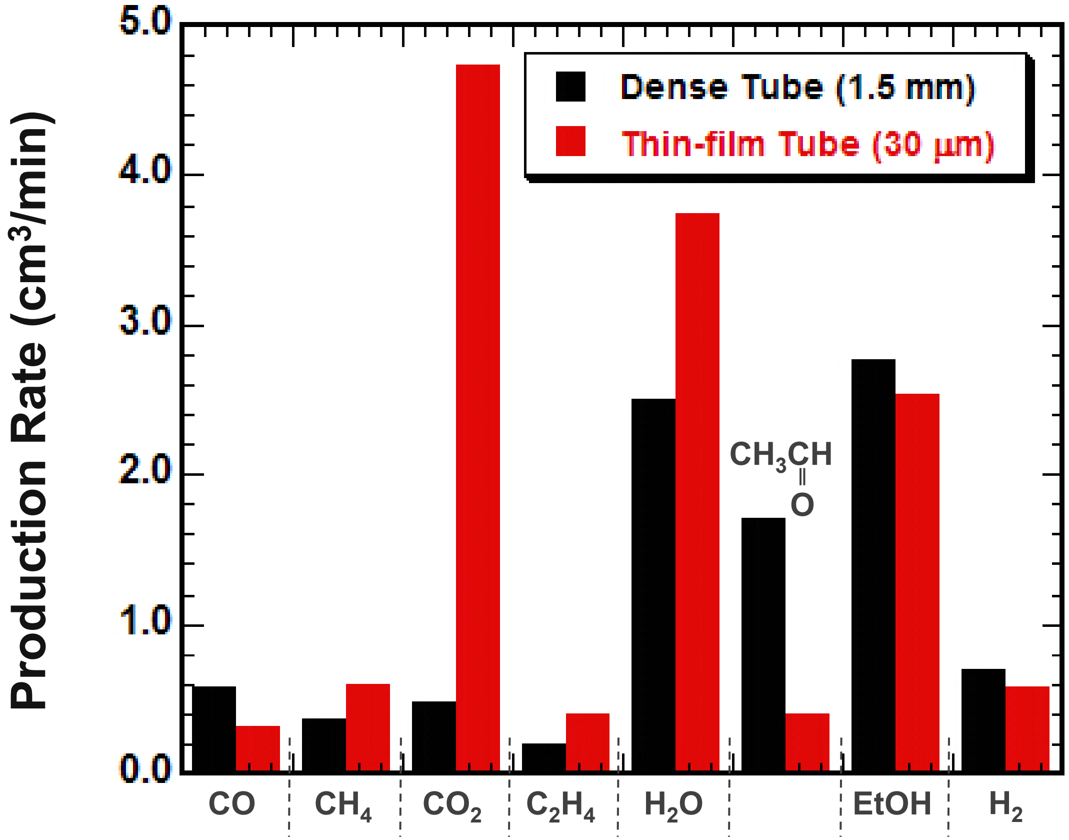
OTM Thickness: 1.5 mm
Fuel: 7-13% EtOH in N_2
O_2 Source: Air
Temperature: 700°C



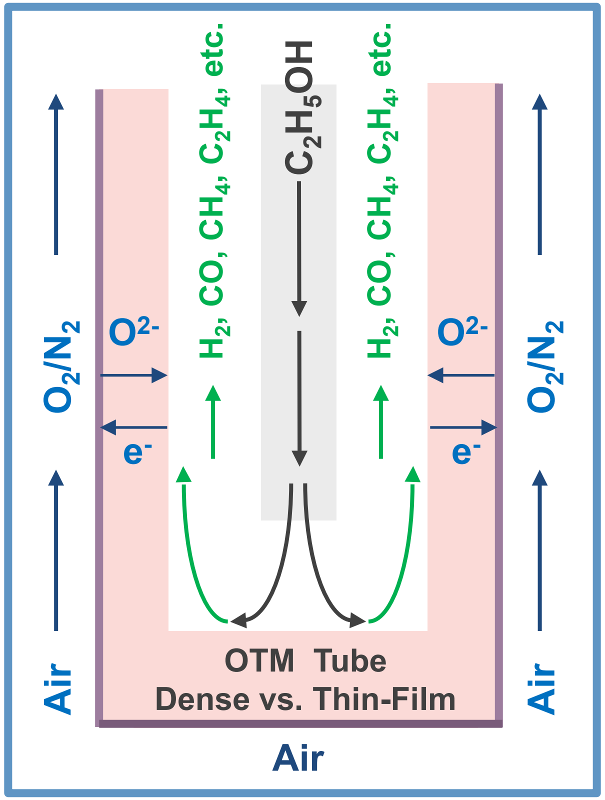
- Higher H_2 production rate can be achieved with higher EtOH concentration and H_2O/EtOH in feed.

Technical Accomplishments/Progress/Results (Cont.)

Ethanol Reforming (Effect of Oxygen Flux)



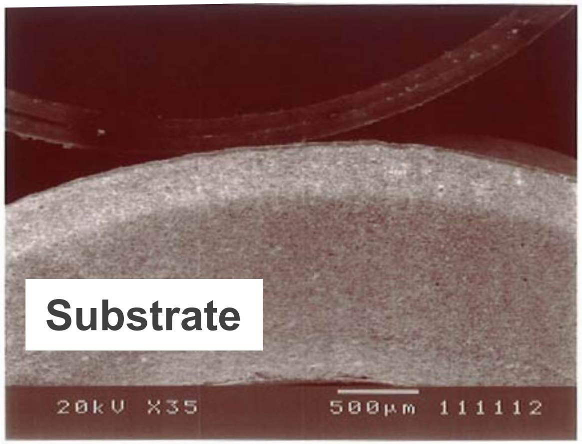
OTM: LSCF Tubes
Fuel: 7% EtOH/balance N_2
O_2 Source: Air
Temperature: 700°C

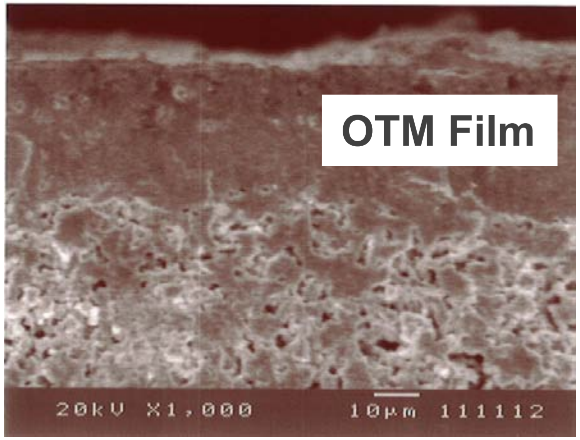


- Higher O_2 flux with thin-film tube is evident in much higher production rates for CO_2 and H_2O. Slightly lower H_2 production rate for thin-film tube, despite its higher EtOH conversion, indicates importance of catalyst.

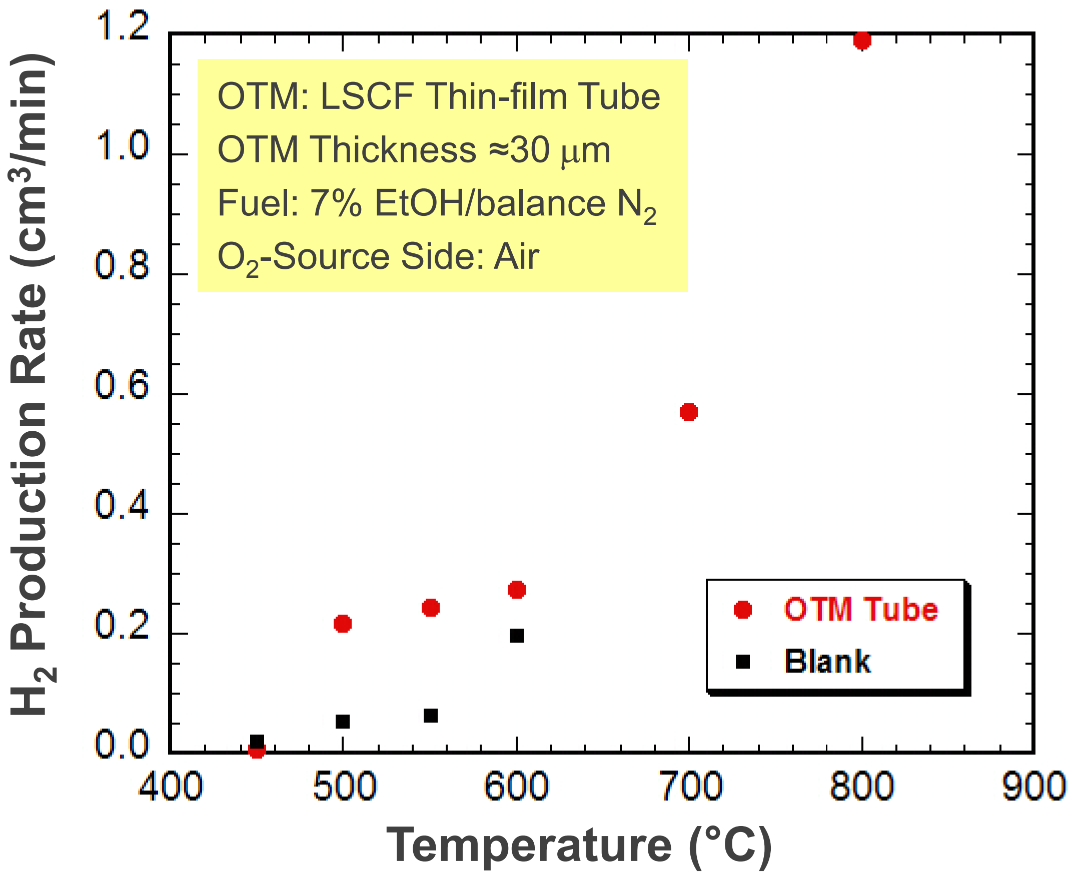
Technical Accomplishments/Progress/Results (Cont.)

Thinner OTM Enhances Hydrogen Production Rate





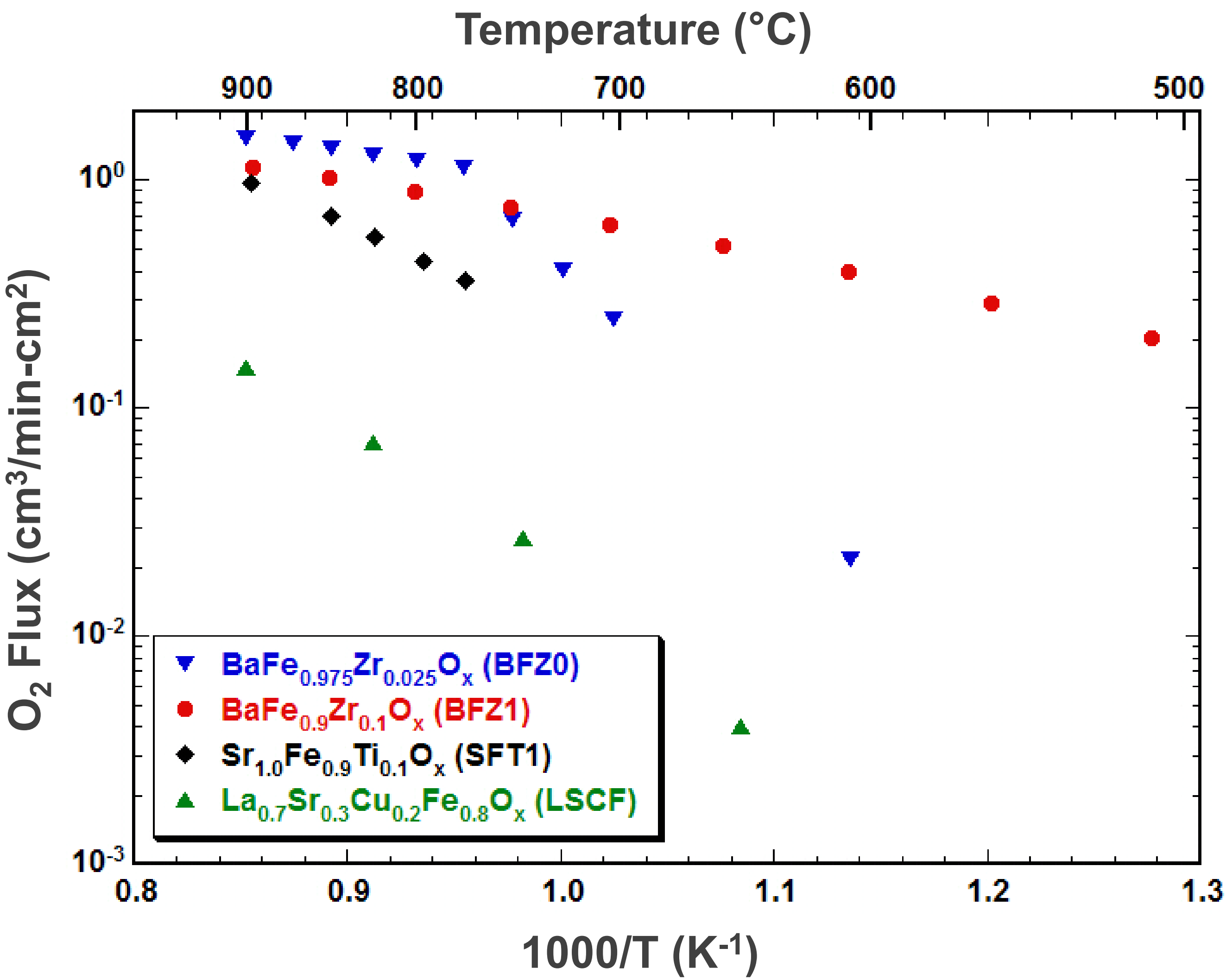
LSCF Thin-film OTM Tube
$La_{0.7}Sr_{0.3}Fe_{0.2}Cu_{0.8}O_x$



- OTM increased H_2 production at low T (≤700°C) and could increase it significantly more by using new OTM composition (BFZ1) and/or adding catalyst.

Technical Accomplishments/Progress/Results (Cont.)

Optimizing OTM Performance by Doping

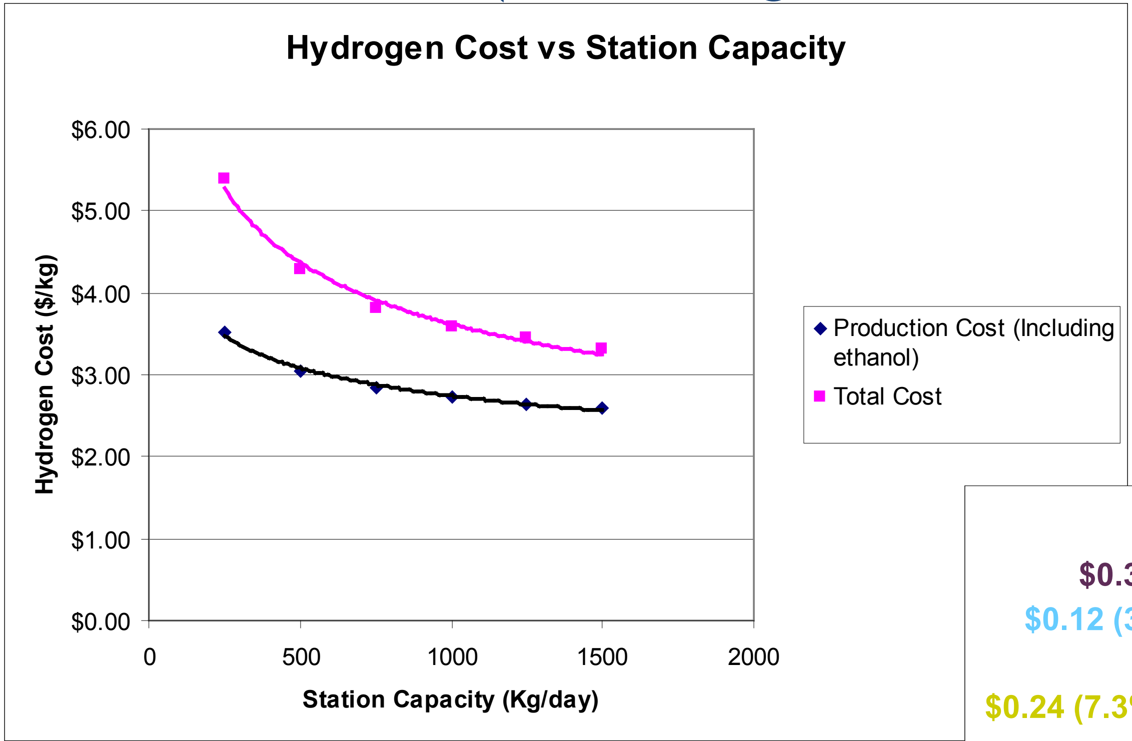


Thickness ≈1 mm
O_2-permeate Side: He
O_2-Source Side: Air

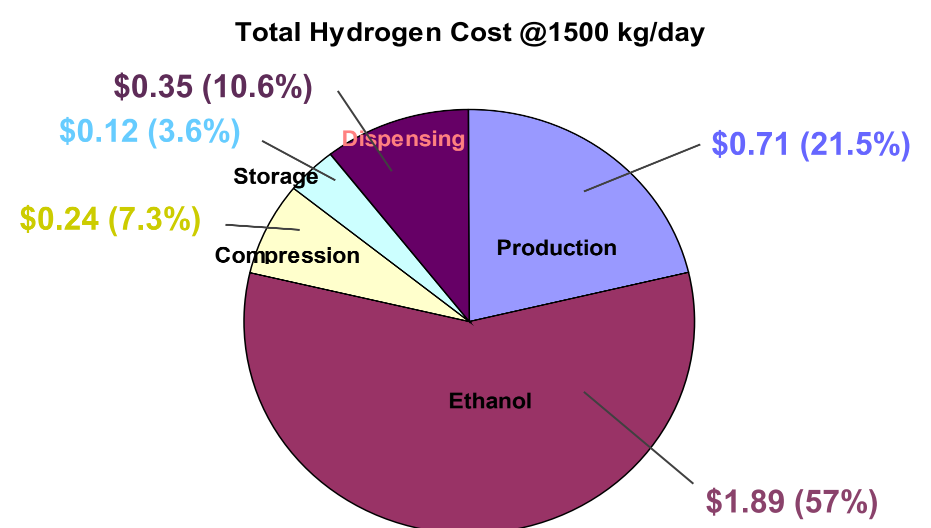
- **Proper doping suppresses phase transition, significantly increasing oxygen flux at temperatures ≤700°C. New OTM (BFZ1) could significantly enhance EtOH conversion at lower temperatures.**

Accomplishments/Progress/Results (Cont'd.)

Preliminary Analysis of Hydrogen Cost vs. Station Capacity (Reforming of Ethanol using OTM)



Station Size (kg/day)	Production Cost Incl. Ethanol ($/kg)	Total Cost ($/kg)
250	3.52	5.39
500	3.04	4.29
750	2.84	3.81
1000	2.73	3.59
1250	2.65	3.44
1500	2.60	3.31

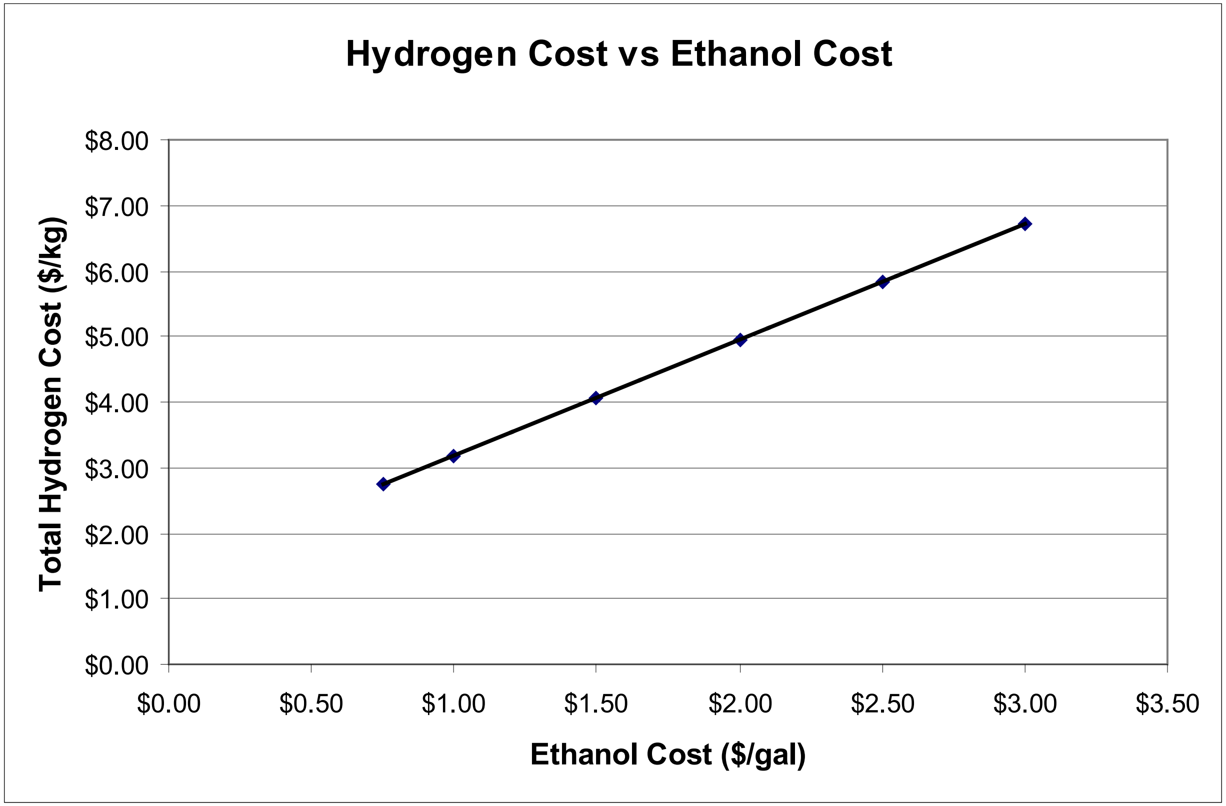


Total Cost = $3.31/kg H_2

- Total capital investment per station: $3.2 M (1500 kg H_2/day)
- Annual operating cost of $1.8 M of which $1 M is for ethanol (@$1.07/gal)
- Energy Efficiency (not including electricity): Energy out in the form of H_2/Energy in Ethanol + Energy in NG to produce steam = 68%

Accomplishments/Progress/Results (Cont'd.)

Preliminary Analysis of Total Hydrogen Cost vs. Ethanol Cost Using OTM to Reform Ethanol (@1500 Kg/day)



H2A Analysis done by Jerry Gillette @ Argonne

Ethanol Cost ($)	Total H_2 Cost ($/kg)
0.75	2.75
1.00	3.19
1.50	4.07
2.00	4.96
2.50	5.84
3.00	6.72

- **Total cost of H_2 increases from $3.19 to $4.96/kg when cost of ethanol is increased from $1 to $2/gal.**

Collaborations

- Directed Technologies, Inc. (Dr. B. James)
  - DFMA (Design for Manufacturing and Assembly) cost assessment and H2A analysis
- Chemical Science & Engineering Division, Argonne (Dr. S. Ahmed) “Pressurized Steam Reforming of Bio-Derived Liquids for Distributed Hydrogen Production (PD-003, Tuesday, June 8, 9:30 am).
  - 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, presently at University of Maryland)
  - 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. Driscoll & 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.

Proposed Future Work

- Demonstrate proof-of-concept and generate key data for performing detailed economic analysis.
- Test performance of OTM materials during ethanol reforming at lower temperatures (T ≤ 700°C).
  - Study effect of EtOH concentration, gas flow rates, OTM thickness.
- Reform ethanol using OTM in presence of catalyst(s).
- Evaluate chemical stability of OTM during reforming of ethanol.
- Have Directed Technologies, Inc. (DTI) perform detailed cost and energy analysis to judge the merits of using OTM to enhance H_2 production by ethanol reforming.

SUMMARY

- Dense ceramic membrane reactor is being developed to cost-effectively produce hydrogen by reforming renewable liquids.
- Data are being generated for a detailed system analysis to determine the most cost and energy benefits.
- Reactor would use OTM to supply pure O_2 for reforming.
- **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.
- Results show that catalyst development will be critical to fully capitalize on benefits of OTM during ethanol reforming.