# Distributed Reforming of Renewable Liquids using Oxygen Transport Membranes*


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**Project ID # PD045**


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# Overview

## Timeline

- Project Start Date: FY 08
- Project End Date: 10/2011*
- ≈40% Complete

## Barriers

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

## Budget

- Total Project Funding
  -DOE share: 100%
- Funding received in FY10: $150K
- Funding for FY11: $100K

## Partners

- Directed Technologies, Inc.
- Other Argonne Divisions
- Work is co-sponsored by FE-NETL.
- Project Lead: Argonne National Laboratory

* Project continuation and direction determined annually by DOE

# 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 such as ethanol (EtOH).

- Reactor would use oxygen transport membrane (OTM) to supply pure oxygen for reforming ethanol.

- Objectives during past year were to demonstrate EtOH reforming using OTM to achieve EtOH conversions ≥70% 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. The success of this project will support the DOE objectives by reducing the costs and energy requirements for reforming of EtOH.

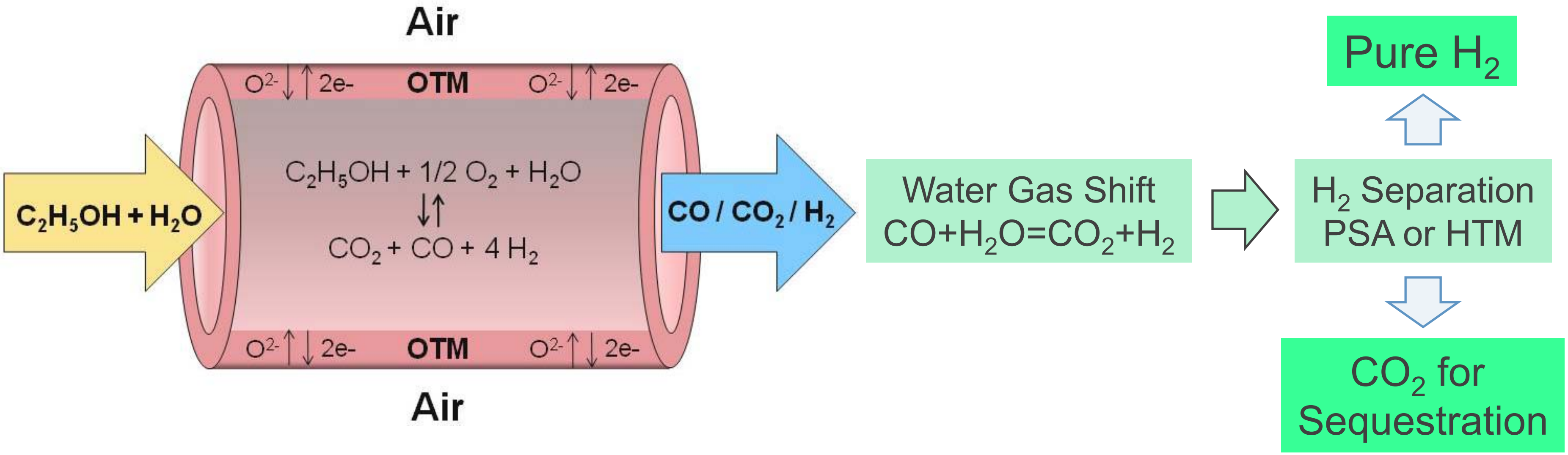
# Relevance to the Overall DOE Objectives

**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,
- O(Operating Temperature) by providing membrane modules that can operate at or near process conditions,
- 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

− Aspen HYSYS® and H2A cost analyses done by DTI shows a production cost of \$3.40/kg $H_2$; system capital cost (installed) of \$1,044K; and overall system efficiency of 61% for a 1500 Kg$H_2$/day system (see slides 10-14)

# Uniqueness of Argonne's Approach

- Pure oxygen is used for reforming rather than air
  - avoids $NO_x$ formation/separation

**Potential Benefits:**

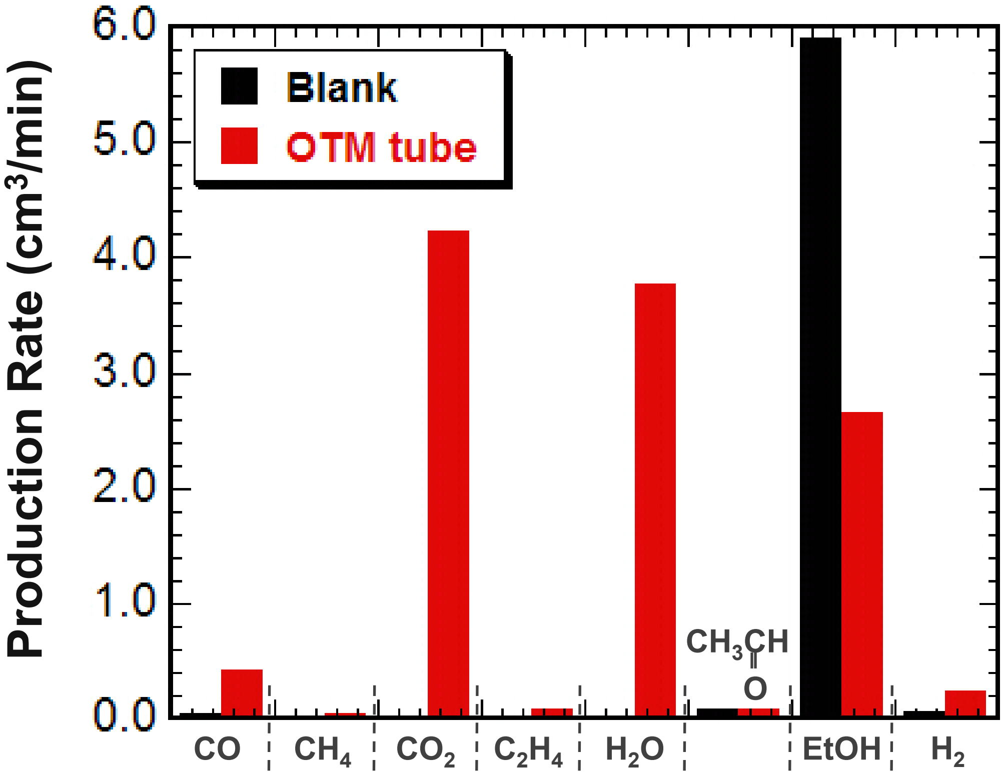
- Incorporate breakthrough membrane separation technology
- Increase EtOH conversion
- Enhance catalyst performance by preventing coke formation
- Reduce foot-print area for the reformer
- Skid-mounted units can be produced using currently available, low-cost, high-throughput manufacturing methods
- Compact design reduces construction costs
- Uses simple, robust membrane systems that require little maintenance

# Approach - Milestones

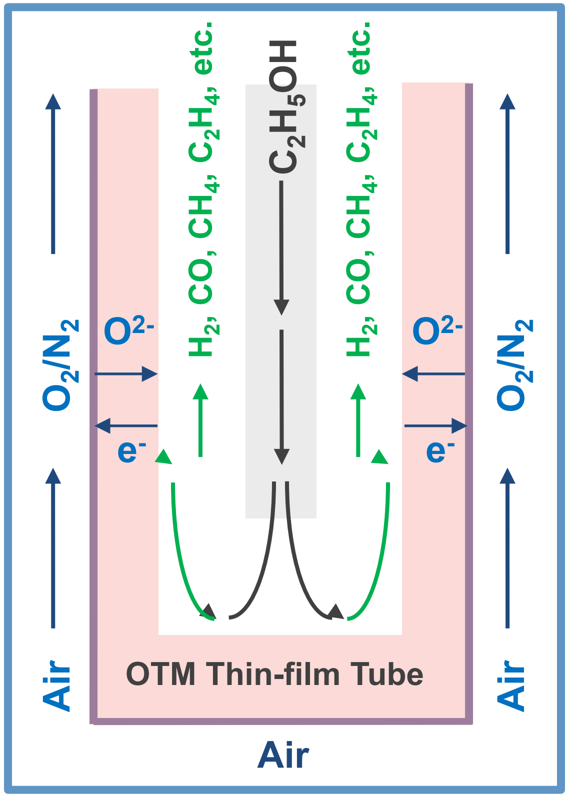
| Project Milestones | % Comp. | Progress Notes |
|---|---|---|
| Demonstrate reforming of ethanol using the OTM membrane in the presence of catalyst(s) to achieve ethanol conversions ≥70%. | 40% | Results show that Rh-based catalyst on an OTM disk shifts ethanol conversion toward more hydrogen production (slide 9); next, the catalyst will be used with a tubular membrane (larger surface area) to achieve ethanol conversion ≥70% in FY11. |
| Perform Aspen HYSYS® analysis to assess the process equipment and heat flow and a cost analysis to estimate the capital costs of the plant design. Feed the results into the H2A cost model to determine the final levelized cost of hydrogen (to be performed by Directed Technologies, Inc.). | 80% | DTI performed the analyses for a 1500 kg $H_2$/day plant. Analyses show a production cost of \$3.40/kg $H_2$; system capital cost of \$1,044K (installed); and overall system efficiency of 61% |

# Technical Accomplishments/Progress/Results

## Reforming Ethanol with OTM Tube (Without Catalyst)




OTM: LSCF Tube (30 μm)
Fuel: 7% EtOH/balance $N_2$
Flow Rate: 150 $cm^3$/min
$O_2$ Source: Air
Temperature: 550°C

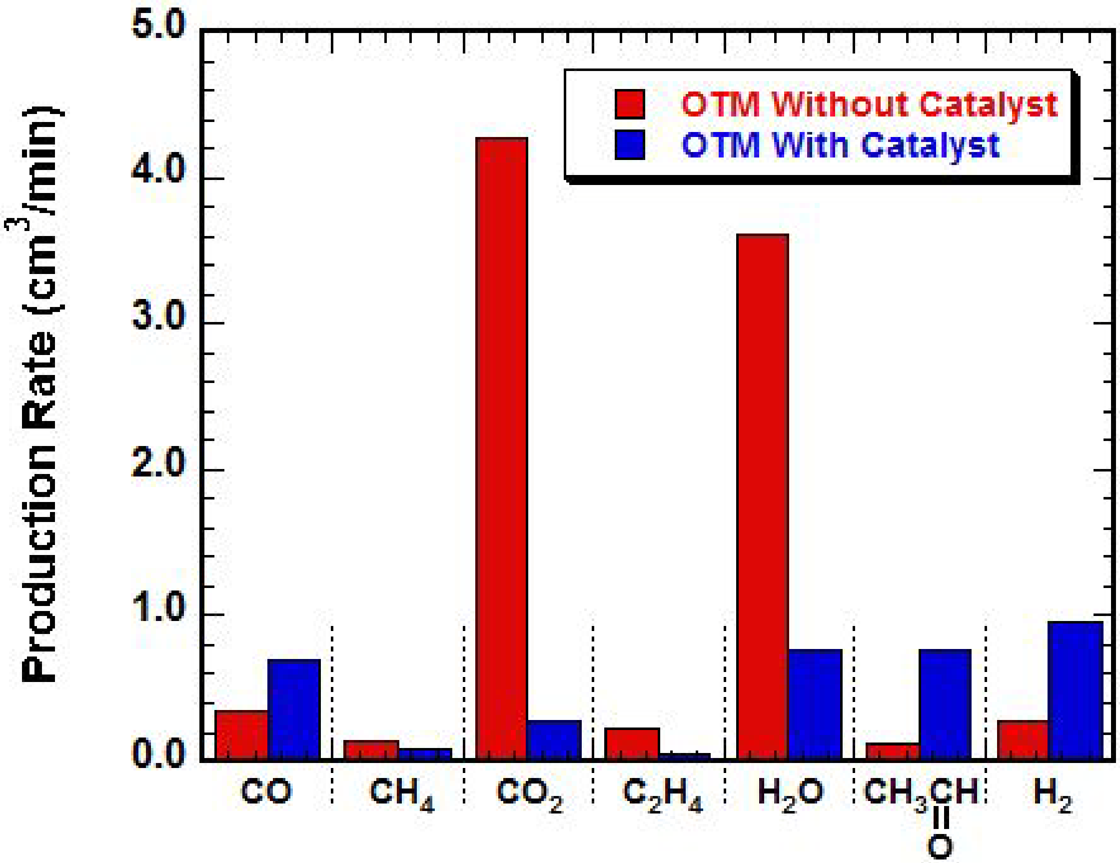



$$\text{EtOH Conversion} = \frac{(\text{EtOH})_{in} - (\text{EtOH})_{out}}{(\text{EtOH})_{in}} = 63\%$$

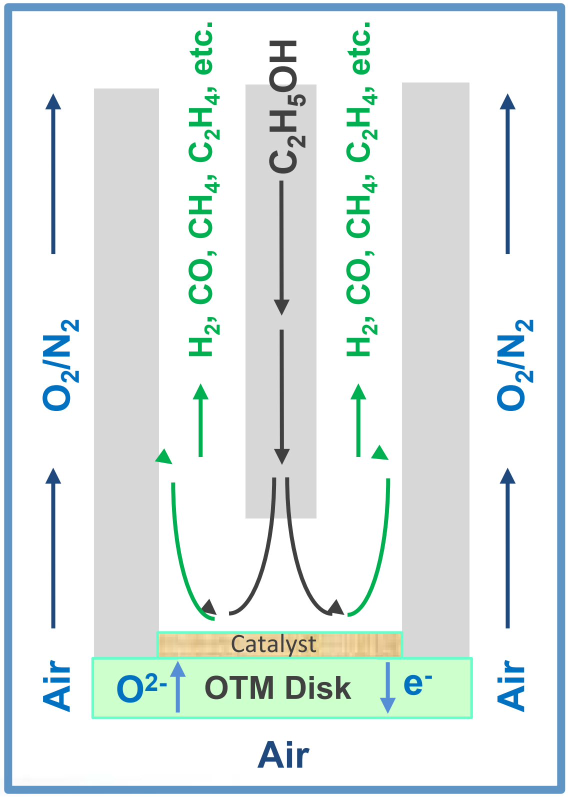
- OTM significantly enhanced EtOH conversion at low T(≤700°C). Catalyst will shift conversion toward more hydrogen production.

# Technical Accomplishments/Progress/Results

## Reforming Ethanol with OTM Disk (With Catalyst)



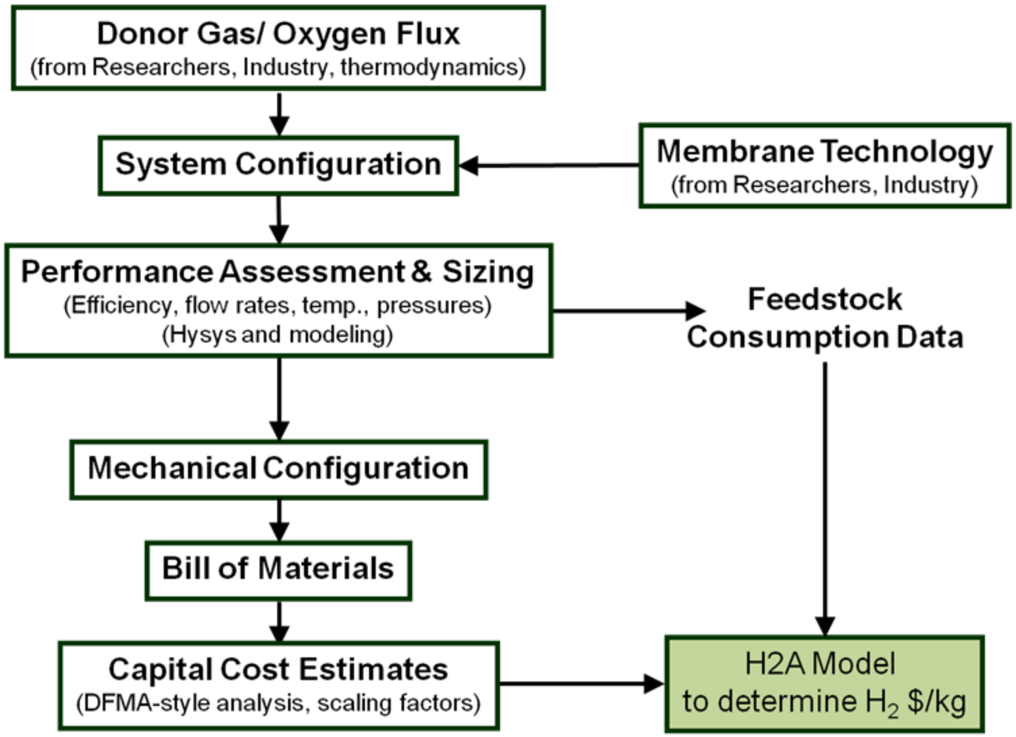

OTM Thickness: 1000 μm
Fuel: 7% EtOH/balance $N_2$
Flow Rate: 150 $cm^3$/min
$O_2$ Source: Air
Temperature: 600°C




- Use of OTM with catalyst increased production of $H_2$ and reduced production of $H_2O$ and $CO_2$.

# Accomplishments/Progress/Results (Cont'd.)

## Preliminary Analysis of Reforming of Ethanol using OTM
## General Approach Implemented in this analysis (done by DTI)




- Aspen HYSYS® was used to assess the process equipment and heat flows.
- A cost analysis was performed to estimate the capital costs of the plant design.
- The results of both analyses were fed into the H2A cost model to determine the final levelized hydrogen cost.

# Accomplishments/Progress/Results (Cont'd.)

## Key Assumptions used in the Analysis by DTI

- **Basic Parameters**
  - 65% EtOH efficiency
  - $H_2$ outlet = 300 psi
  - No $H_2$ Compressor req'd.
  - PSA gas cleanup at 75% $H_2$ recovery
  - Reactor: Tube-in-Shell construction with ceramic OTM tubes operating at ~700°C
  - 300 psi pressure on both oxidant and reformate sides
- **Economic**
  - 20 yr analysis period and plant life
  - 1500 kg/day forecourt unit
  - $1.07/gallon Ethanol
  - 85.2% Op Cap Factor
  - 5-yr life on OTM (entire unit replaced)
  - Yearly O&M = 0.5% Cap

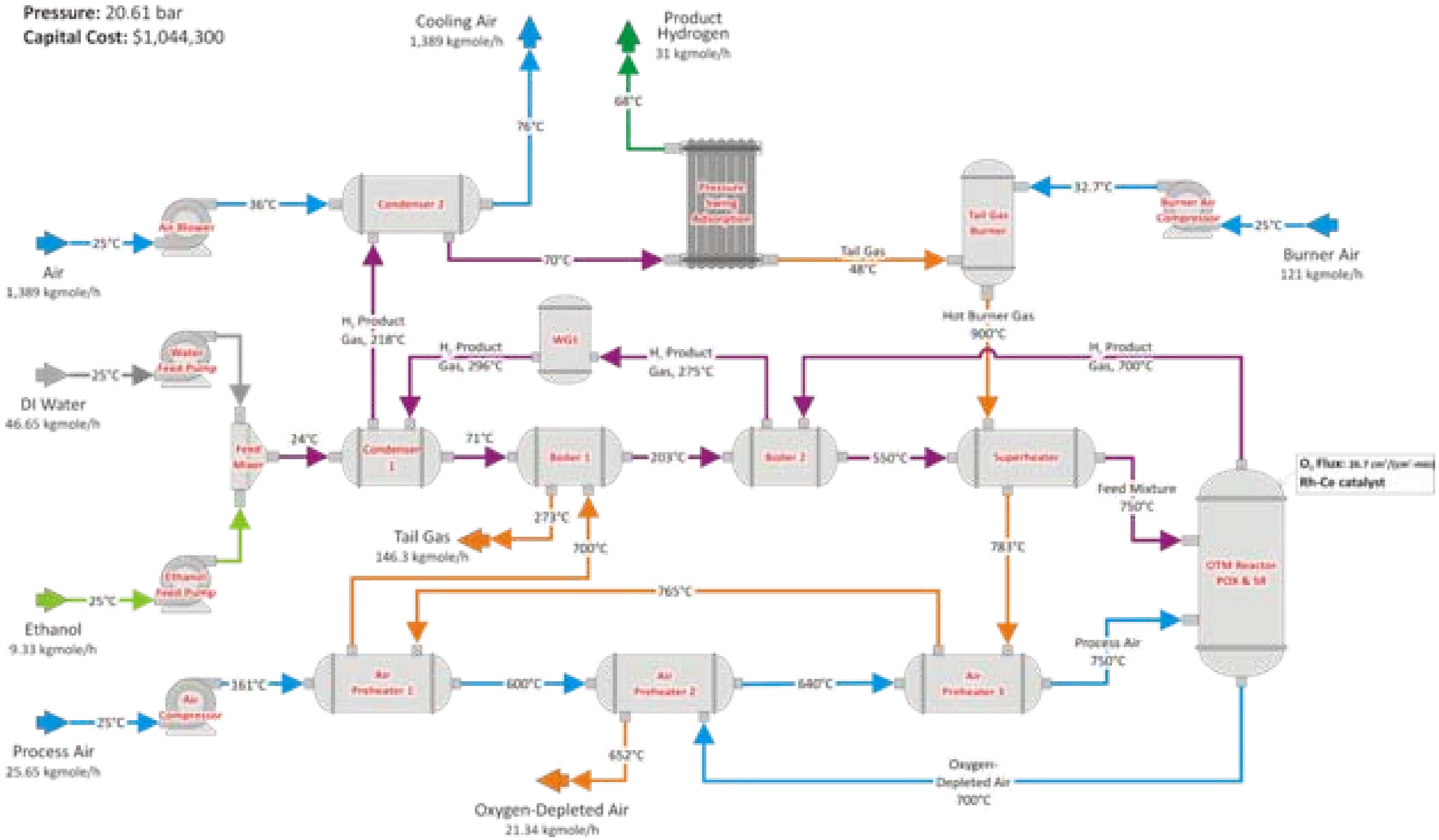
# Accomplishments/Progress/Results (Cont'd.)
## Key Assumptions used in the Analysis by DTI

- **Oxygen Transfer Membrane:**
  - 30 μm OTM layer
  - 1 cm diameter, 1 mm thick, porous zirconia support tube
  - 300 psi air pressure
  - 300 psi reformate pressure
  - 700°C
  - Average $O_2$ flux: 33 $cm^3/(cm^2\text{-min})$
  - Flux is high enough that layer thickness can be used to tailor the flux as a function of axial location and thereby attain isothermal operation
- **Partial Oxidation Reactor:**
  - Rh-Ce catalyst
  - 100 μm layer thickness applied via wash-coating
  - 100,000/hr space velocity assumed
  - Steam-Carbon ratio of 2.5
  - Modeled reactions;
    - POX: $C_2H_5OH + 3O_2 => 2CO_2 + 3H_2O$
    - SR: $C_2H_5OH + 2.55H_2O => 0.27CH_4 + 0.29\ CO + 1.45CO_2 + 5.02\ H_2 + 0.19O_2$

# Accomplishments/Progress/Results (Cont'd.)
## Process Diagram for Ethanol Reforming using OTM)

**Oxygen Transport Membrane with Air as Donor Gas**

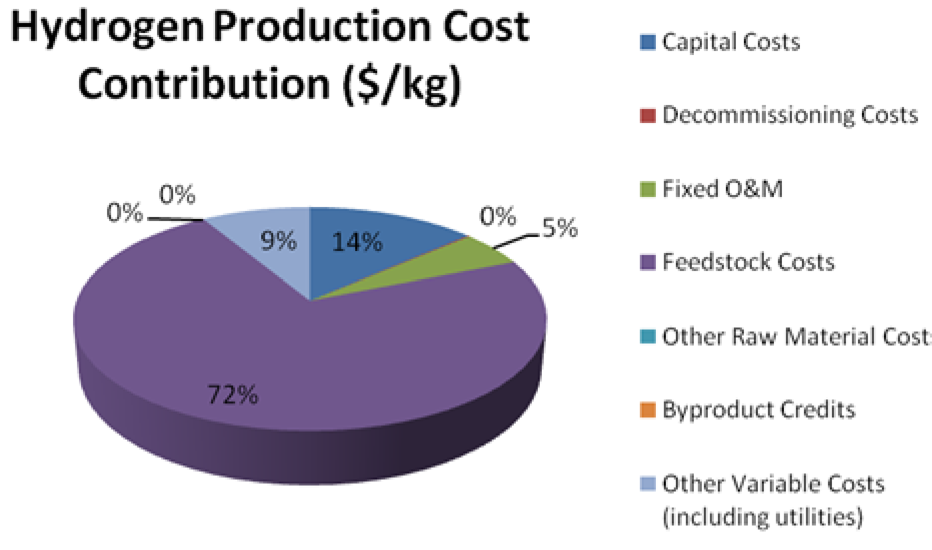
**Capacity:** 1500 kg/day
**Ethanol Efficiency:** 65.03%
**Overall Efficiency:** 60.75%
**Elec. Load:** 3.611 kWh/kg $H_2$
**Steam to Carbon Ratio:** 2.5
**PSA Recovery:** 75%
**Pressure:** 20.61 bar
**Capital Cost:** $1,044,300



# Accomplishments/Progress/Results (Cont'd.)

## Hydrogen Production Cost for Station Size of 1500 kg/day (Reforming of Ethanol using OTM)

| Hydrogen Production Cost Contribution ($/kg) | |
|---|---|
| **Cost Component** | **Air OTM System** |
| **Capital Costs** | $0.46 |
| **Decommissioning Costs** | $0.00 |
| **Fixed O&M** | $0.18 |
| **Feedstock Costs** | $2.46 |
| **Other Raw Material Costs** | $0.00 |
| **Byproduct Credits** | $0.00 |
| **Other Variable Costs (including utilities)** | $0.30 |
| **Total ($/kg$H_2$)** | **$3.40** |




- Cost of $H_2$ is dominated by the feedstock cost
- OTM is not the most costly component in the system but rather the necessary peripheral equipment make a much greater contribution to the overall capital cost

| | **Air OTM System** |
|---|---|
| **$H_2$ Production Rating** | 1500kg$H_2$/day |
| **System Ethanol Efficiency** | 65.03% |
| **Electrical Consumption** | 3.611 kWh/kg$H_2$ |
| **Overall System Efficiency** | 60.75% |
| **Hydrogen Projected Cost** | $3.40/kg$H_2$ |
| **System Capital Cost (Installed)** | $1,044,300 |

# Collaborations

- Directed Technologies, Inc. (Mr. B. James and Ms. J. Perez)
  - DFMA (Design for Manufacturing and Assembly) cost assessment and H2A analysis
- Chemical Science & Engineering Division, Argonne (Dr. S. Ahmed)
  - Catalysts, reactor design, and ethanol reaction chemistry
- Georgia Tech (Prof. M. Liu)
  - Graduate students' Ph.D. thesis research on mixed-conductors
- University of Maryland (Prof. E. Wachsman, formerly at University of Florida)
  - 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)
  - 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*

- Small (1.3 $cm^2$) OTM disk with a Rh catalyst significantly enhanced the production of hydrogen (slide 9). To achieve ethanol conversion >70%, we will increase the OTM's active area by using a tubular membrane; enhance oxygen transport by reducing OTM's thickness to ≤10 μm; and fabricate the OTM with a material whose oxygen transport properties are intrinsically superior (examples of materials shown in slide 19).
- If the Rh-based catalyst proves ineffective, we will identify an alternative catalyst (in collaboration with commercial catalyst providers) and test its effectiveness.
- Modify the experimental set-up and inject ethanol vapor into the membrane reactor to minimize decomposition of the ethanol before it contacts the OTM.
- Evaluate chemical stability of OTM during reforming of ethanol.

**Our plan is to increase hydrogen production by improving the performance of OTMs and by incorporating an appropriate catalyst to enhance ethanol conversion (>70%) and hydrogen selectivity.**

*** Dependent on availability of sufficient funding**

# SUMMARY

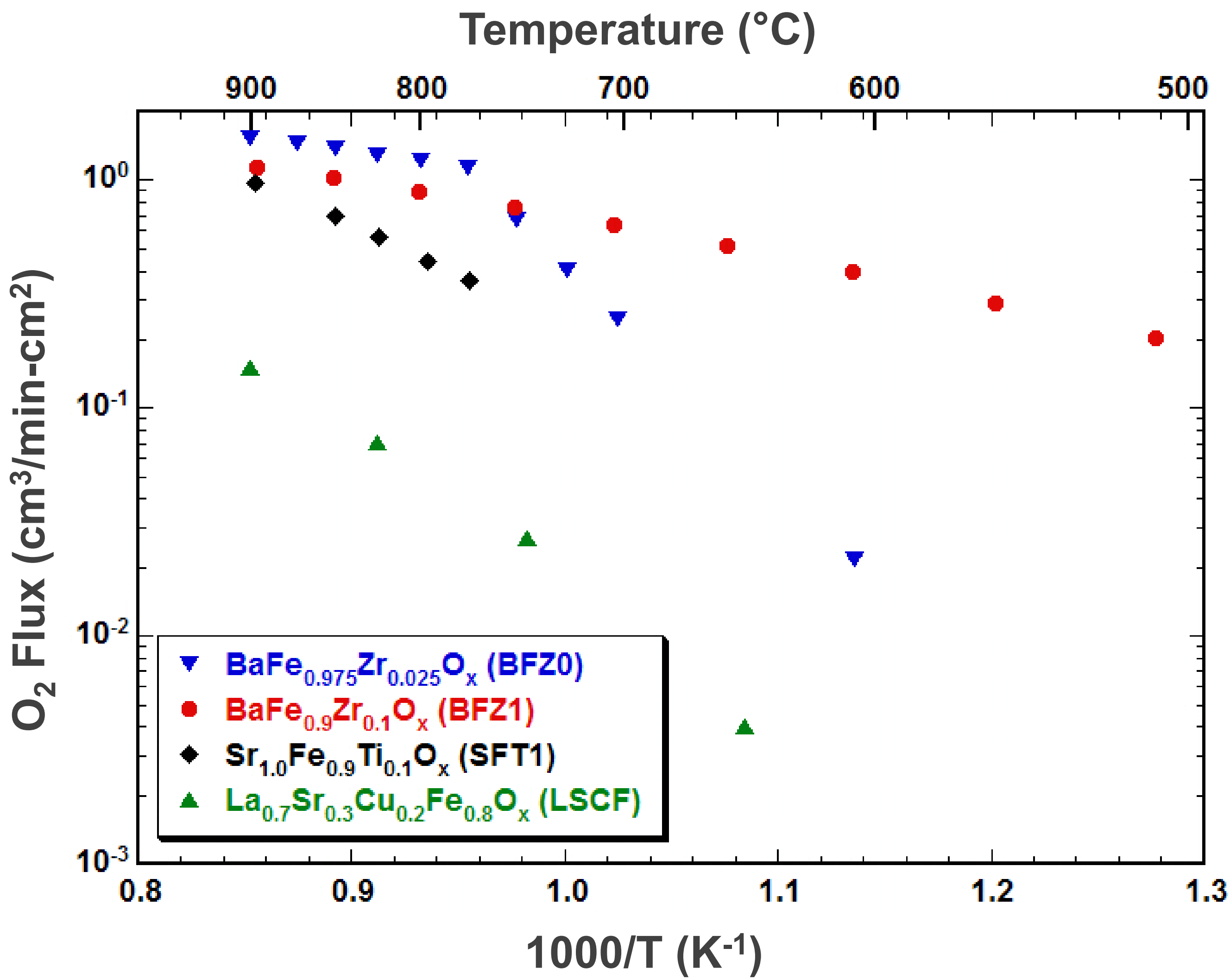
- A dense ceramic membrane reactor is being developed to cost-effectively produce hydrogen by reforming ethanol. Reactor would use an OTM to supply pure $O_2$ for reforming.
- DFMA cost assessment and H2A analysis (done by DTI) show a hydrogen production cost of \$3.40/kg $H_2$ and system capital cost (installed) of \$1,044K for a 1500 kg $H_2$/day unit. DTI's report concludes that this method of producing hydrogen has several merits, primarily the low cost and simplicity of the OTM reactor.
- 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.

# Technical Back-Up Slides

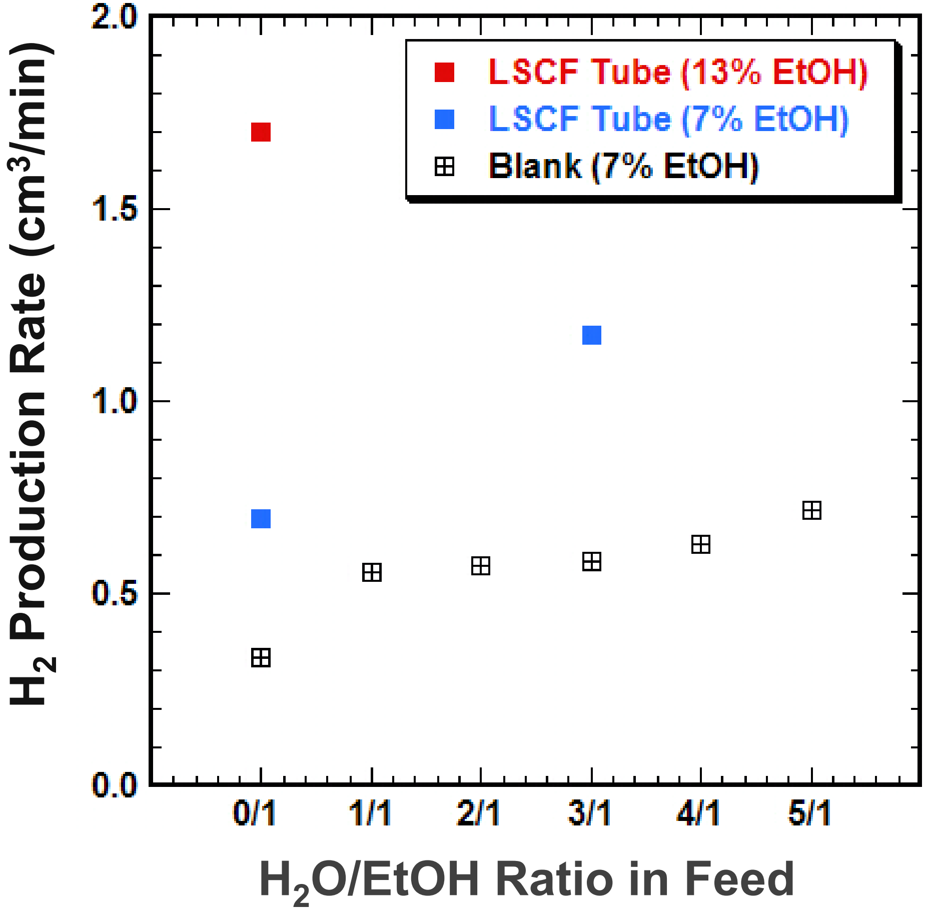
# Optimizing OTM Performance by Doping



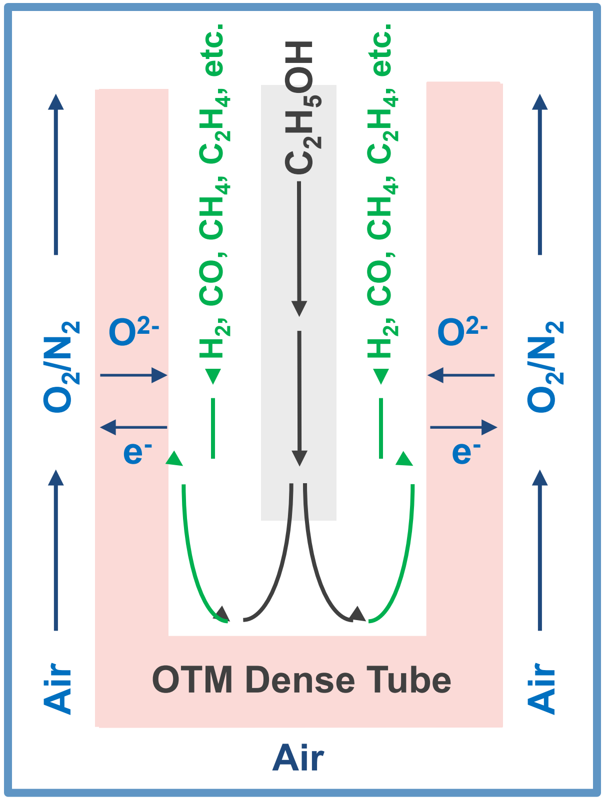

Thickness ≈1 mm
$O_2$-permeate Side: He
$O_2$-Source Side: Air

- **Doping suppresses a flux-limiting phase transition, thereby giving significantly higher oxygen flux at temperatures ≤700°C. A new OTM (BFZ1) could significantly enhance EtOH conversion at lower temperatures.**

# 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.