Distributed Reforming of Renewable Liquids via Water Splitting using Oxygen Transport Membrane (OTM)*

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U.S. Department of Energy

UChicago Argonne LLC

Office of Science U.S. DEPARTMENT OF ENERGY

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Overview

Timeline

Project Start Date: May 2005

Project End Date: Project continuation and direction determined annually by DOE

15% Complete

Barriers

- (A) Reformer Capital Cost
  Target: $1.0 M by 2012
- (C) Operation and Maintenance
  Efficiency Target:
  72.0% (LHV) by 2012
- (R) Cost
  Target: $3.80 gge by 2012

Budget

Total Project Funding
-DOE share: 100%

Funding received in FY07: $350K

Funding for FY08: $400K

Partners

Interactions: Membranes being developed also address various cross-cutting barriers.

Work is co-sponsored by FE-NETL.

Project Lead: Argonne National Laboratory

Objectives

- Overall objective is to develop a compact, dense, ceramic membrane reactor that enables efficient and cost-effective production of hydrogen by reforming bio-derived liquid fuels using pure oxygen formed by water splitting and transported by the membrane. (During FY05 – FY07, the objective was to reform natural gas. In FY 08, the focus was changed to bio-derived liquids).

- Objectives for FY08 were to optimize the performance of the oxygen transport membrane (OTM) and demonstrate reforming of ethanol (EtOH).

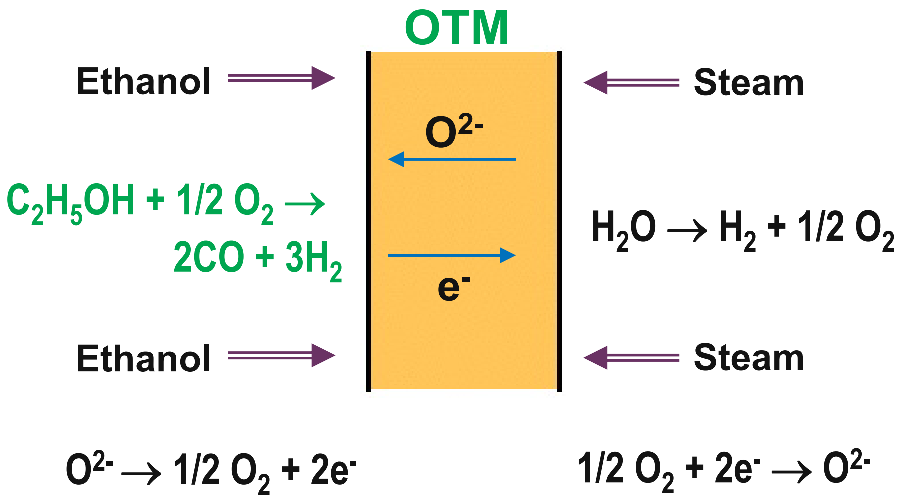
- **Relevance:** Membrane technology provides the means to attack barriers to the development of small-scale hydrogen production technology.

Milestones

Expected Date of Completion	Milestone
March 2007	Optimize OTM performance by doping and controlling microstructure, and measure H_2 production rate.
June 2007	Fabricate thinner membranes to enhance H_2 production rate.
September 2007	Refine system analysis using measured OTM performance to determine requirements of cost-effective reactor.
December 2007	Enhance performance of thin (<0.1 mm) OTMs by controlling surface microstructure.
March 2008	Evaluate chemical stability of OTMs in short-term (≤100 h) exposure to reaction conditions.
September 2008	Reform liquid fuels (EtOH) using OTM.

Approach

Reforming of Fuels via Water Splitting using OTM



-Fuel is reformed using oxygen formed by water splitting and transported by the OTM.

-H_2 is produced on both sides of the OTM.

-Predominant products of ethanol reforming: H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, H_2O

-Non-Galvanic

-No electrical circuitry or power supply

-Single material, i.e., no electrodes needed

$$H_2O \Leftrightarrow H_2 + 1/2\ O_2$$

- Very low H_2 and O_2 concentrations are generated even at relatively high temperatures (0.1% H_2 and 0.042% O_2 at 1600°C).
- Significant amounts of H_2 & O_2 can be generated at moderate temperatures if the reaction is shifted toward dissociation by removing either O_2, H_2, or both.

$$K = \frac{P_{H_2} P_{O_2}^{\frac{1}{2}}}{P_{H_2O}}$$

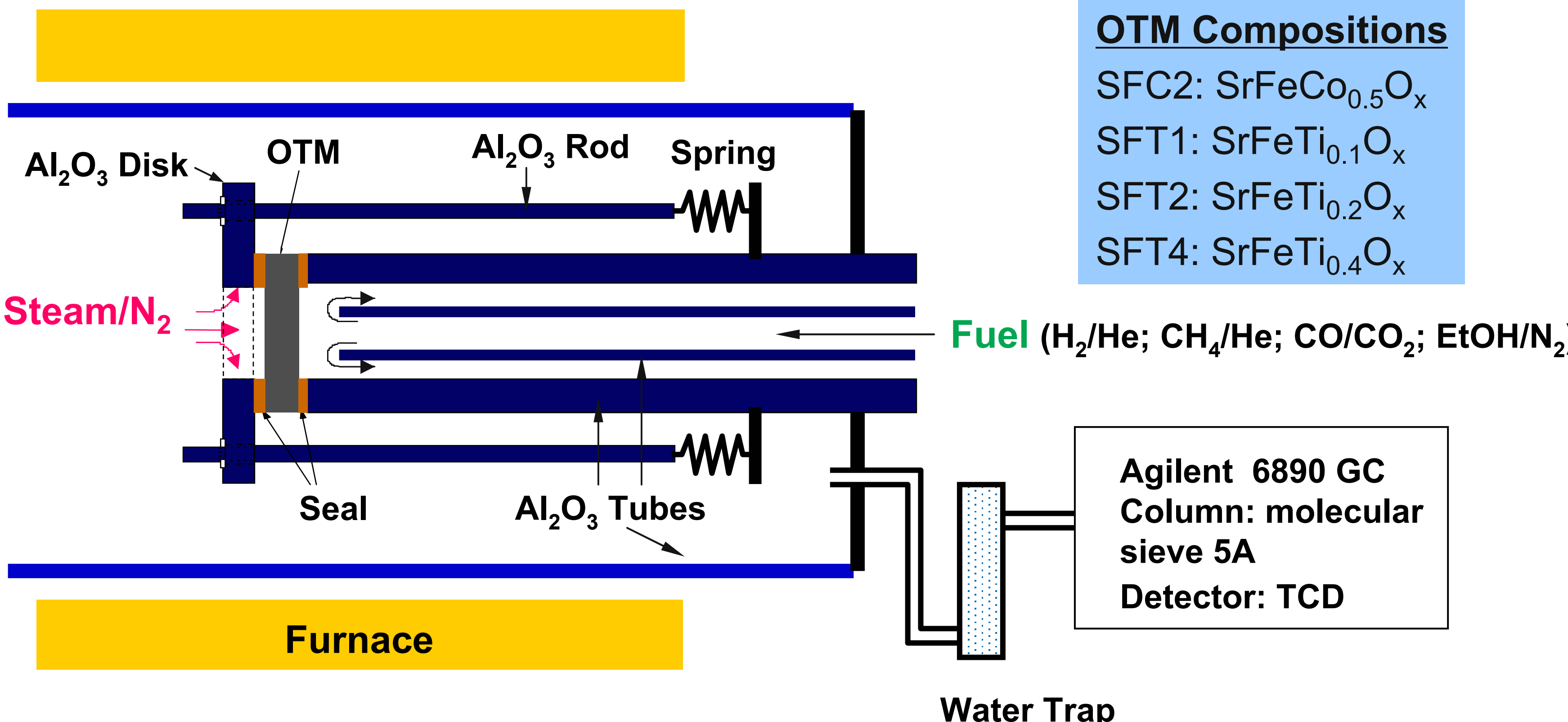
Uniqueness of Argonne's Approach

- Pure oxygen (produced by steam dissociation & transported by OTM) is used for reforming rather than air
  - avoids NO_x formation/separation
- Heat is generated where it is needed
  - simplifies heat exchanger issues
- Incorporates breakthrough separation technology
- Reforming process is intensified by combining unit operations
  - offers 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

Specific Tasks for FY08

- Optimize performance of dense oxygen transport membrane (OTM) by doping and controlling OTM's microstructure.
- Fabricate thinner (≤25 μm) OTM to enhance its hydrogen production rate.
- Fabricate/test small (≈3 in. long) tubular OTM.
- Demonstrate reforming of EtOH using OTM.

Schematic of Experimental Setup – Disk-Type Membrane



OTM Compositions

SFC2: $SrFeCo_{0.5}O_x$

SFT1: $SrFeTi_{0.1}O_x$

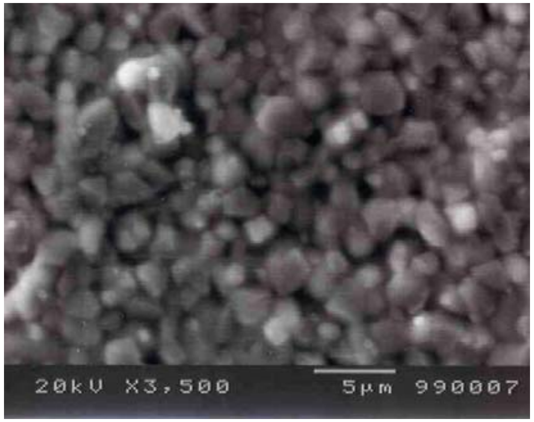
SFT2: $SrFeTi_{0.2}O_x$

SFT4: $SrFeTi_{0.4}O_x$

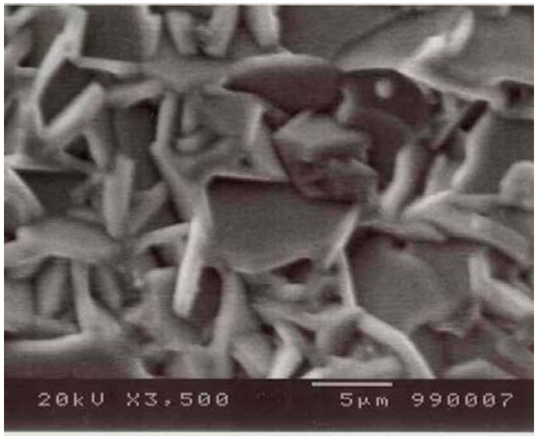
- Flow rates: ≈200 cc/min
- OTM sample size: ≈20 mm dia.
- Feed concentration: H_2/He; 5% CH_4/He; 10% CO/CO_2; ≈5% EtOH/N_2(or He)
- H_2 production rate: ≈18 cc/min/cm^2
- Temperature: 500-900°C

Accomplishments/Progress/Results

Optimizing OTM Performance by Controlling Microstructure

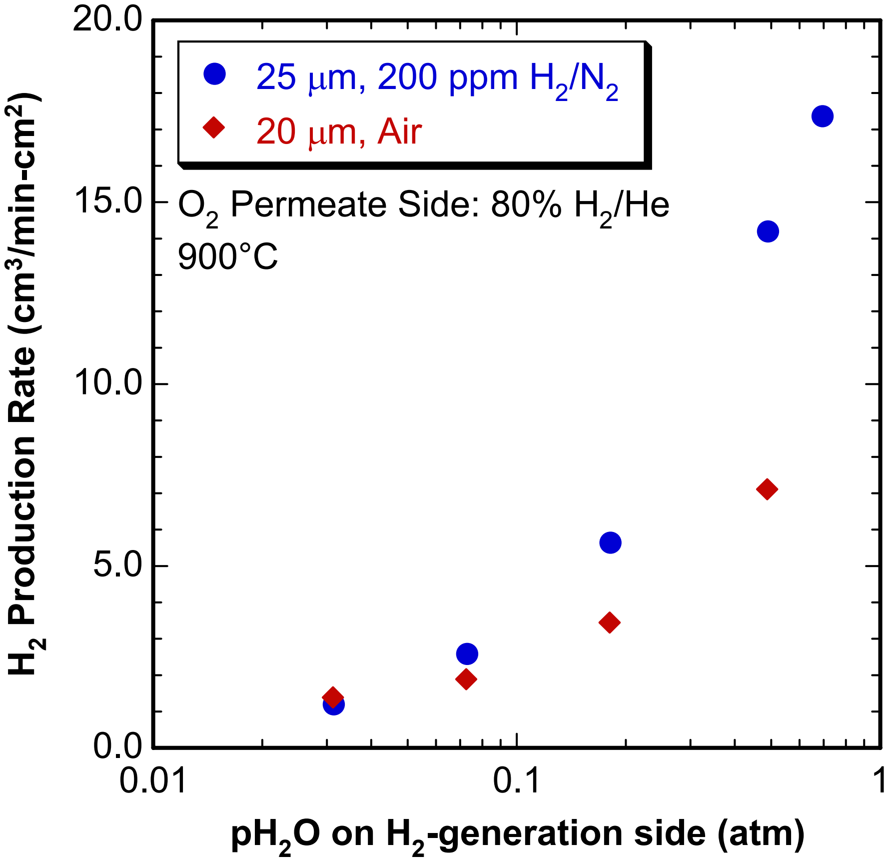


SFC2 sintered in 200 ppm H_2/N_2



SFC2 sintered in Air

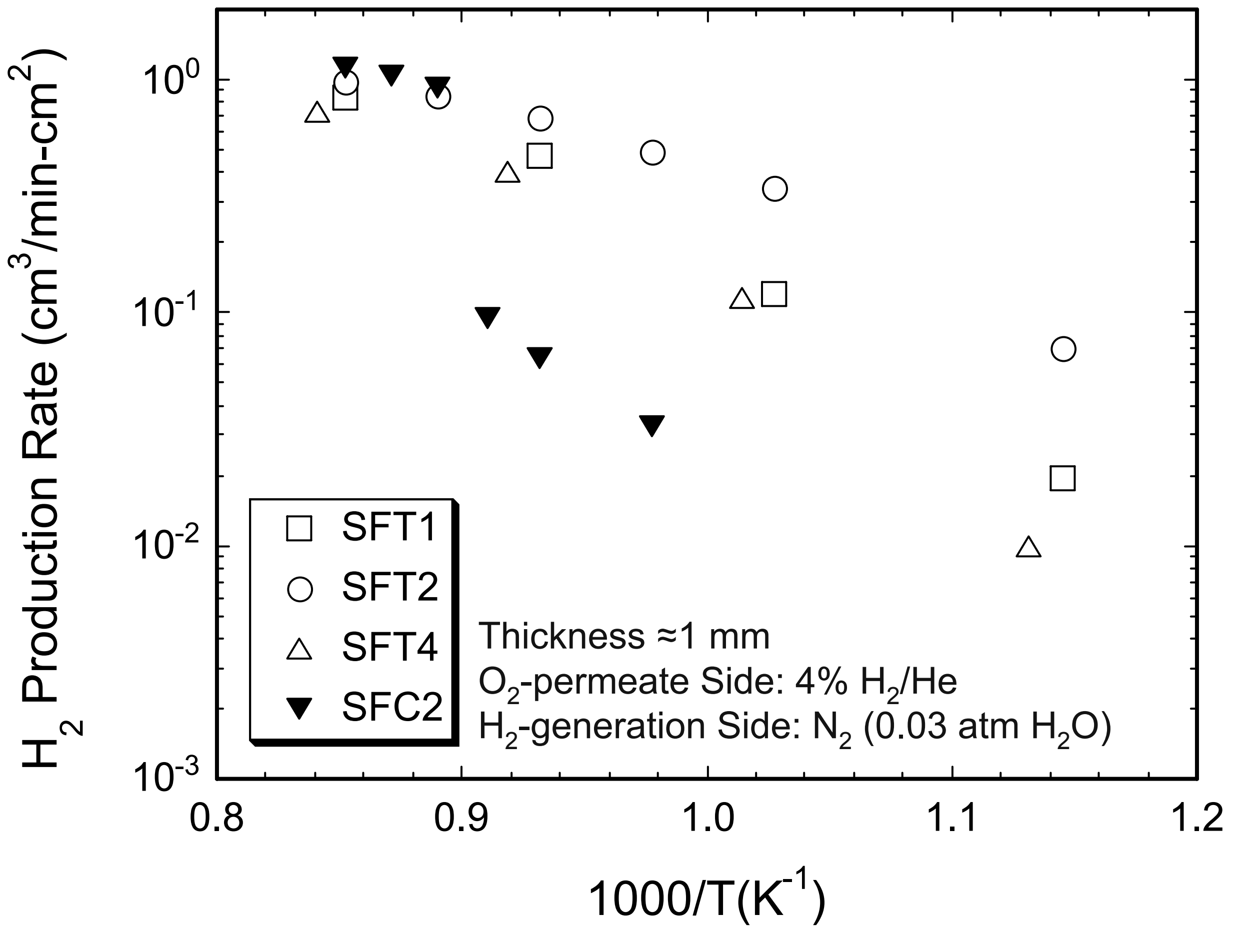
- **Sintering atmosphere profoundly affects OTM's microstructure.**



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

Accomplishments/Progress/Results (Cont'd.)

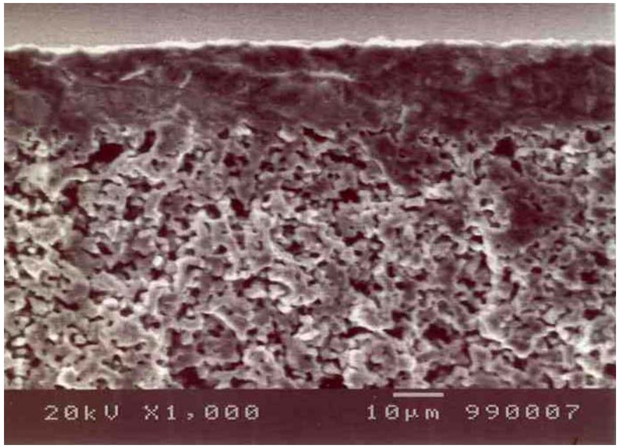
Optimizing OTM Performance by Doping



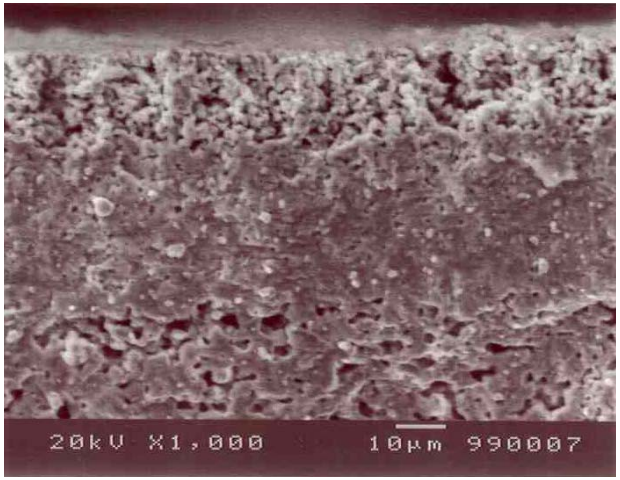
- **Proper doping eliminates phase transition and gives high hydrogen production rate at low temperatures (<825°C).**

Accomplishments/Progress/Results (Cont'd.)

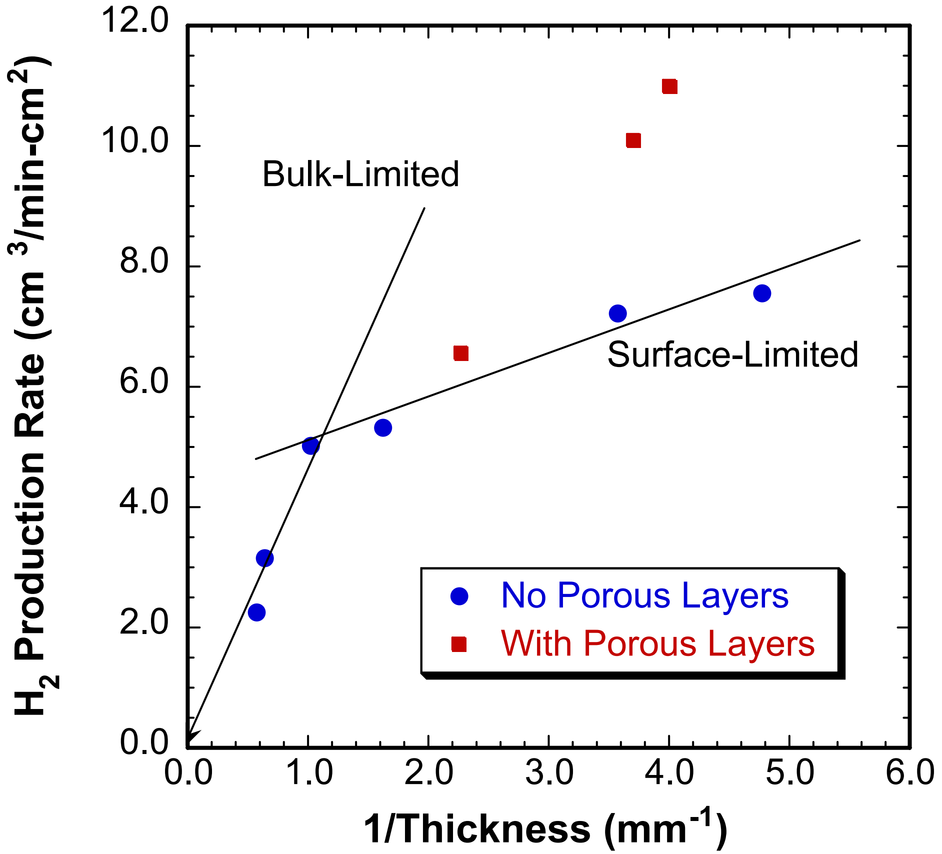
Fabricating Thinner OTMs to Enhance Hydrogen Production Rate



Porous layer on one surface



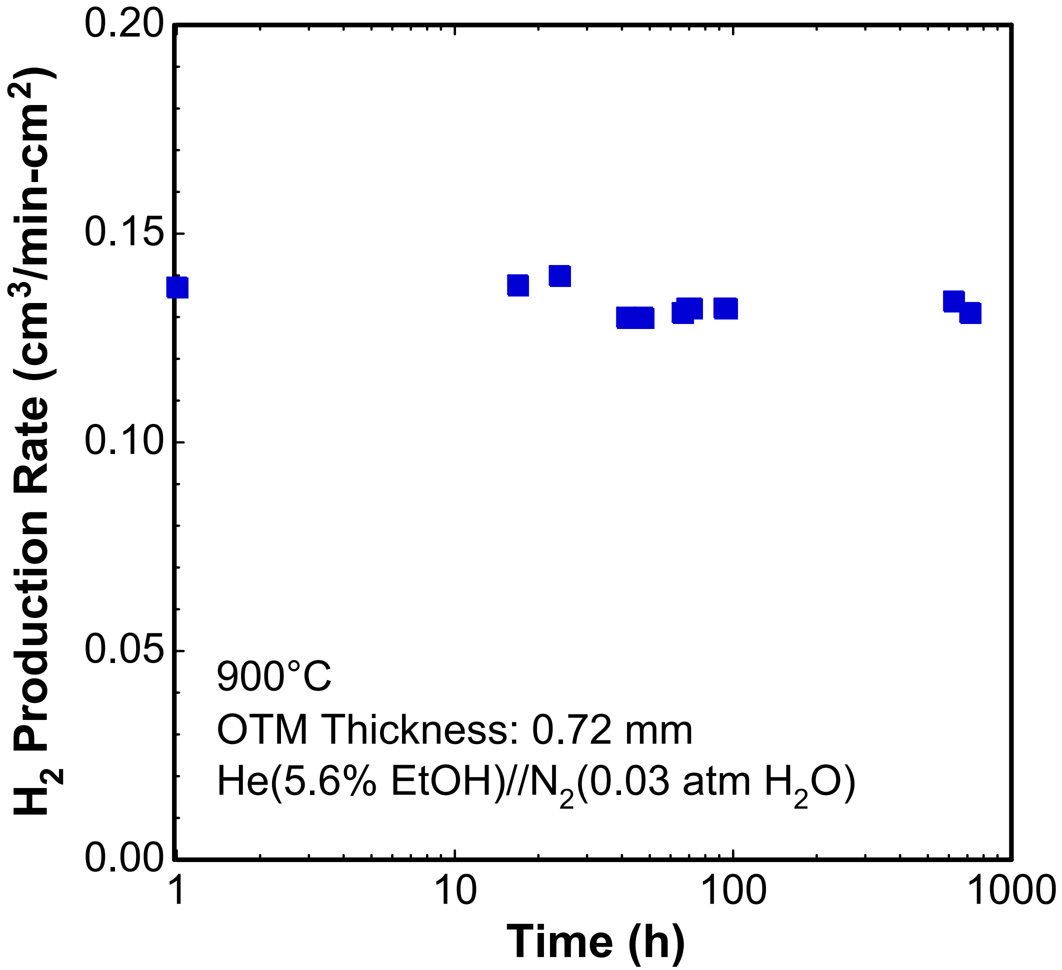
Porous layer on both surfaces



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

Accomplishments/Progress/Results (Cont'd.)

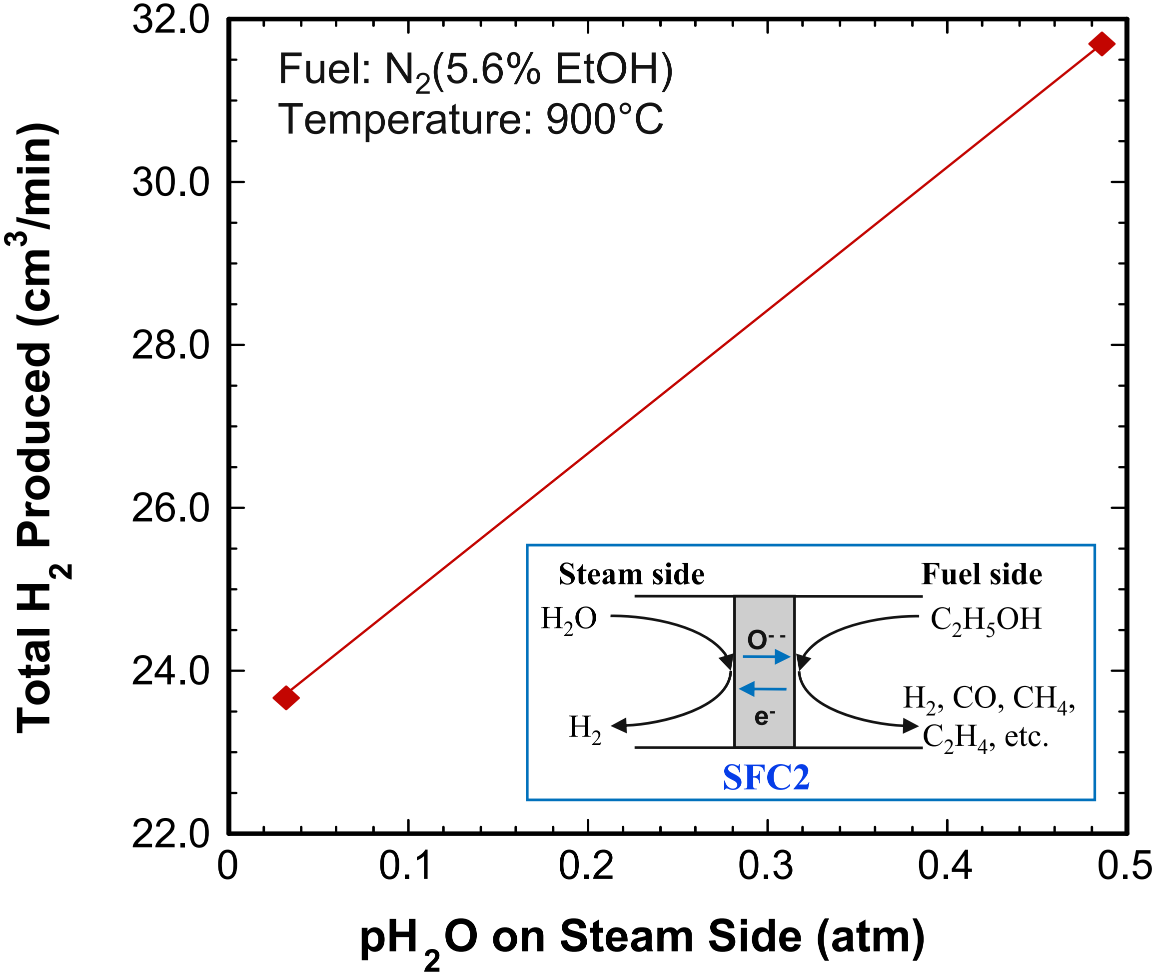
Short-Term Chemical Stability of Tubular Membrane



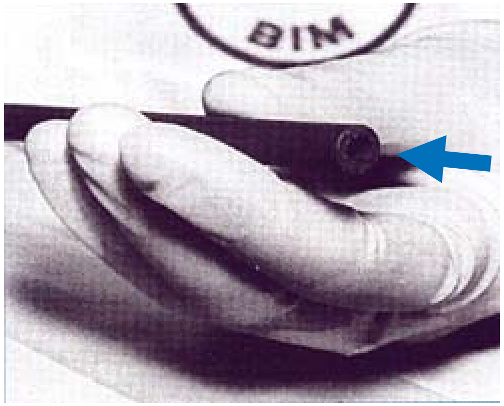
- **OTM is stable during short-term (≈900 h) ethanol reforming test.**

Accomplishments/Progress/Results (Cont'd.)

Reforming of Ethanol using OTM via Water Splitting



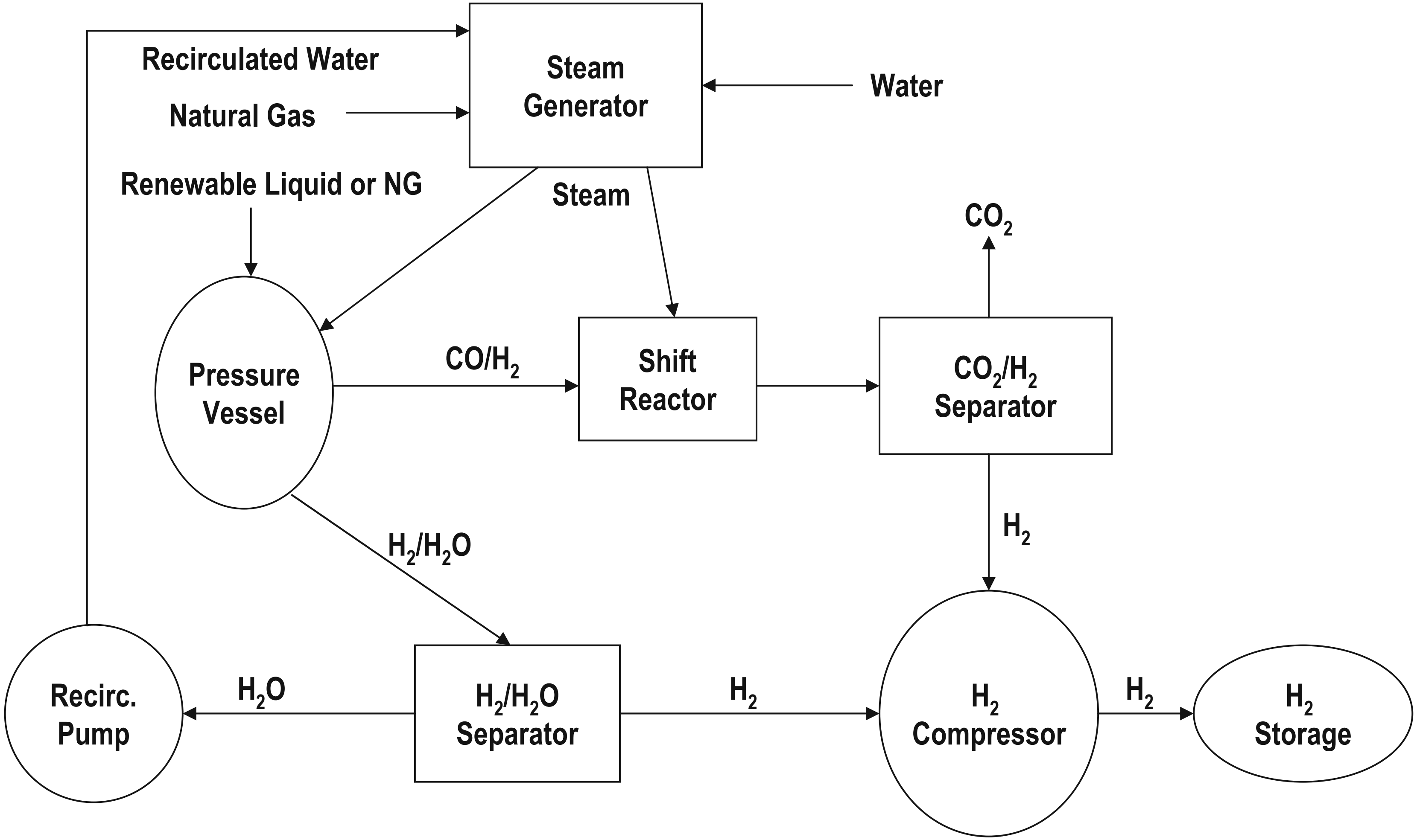
OTM Tube length ≈7 cm
OD ≈1.3 cm
Wall thickness ≈0.72 mm



- **Total H_2 produced increased as partial pressure of steam increased.**

Accomplishments/Progress/Results (Cont'd.)

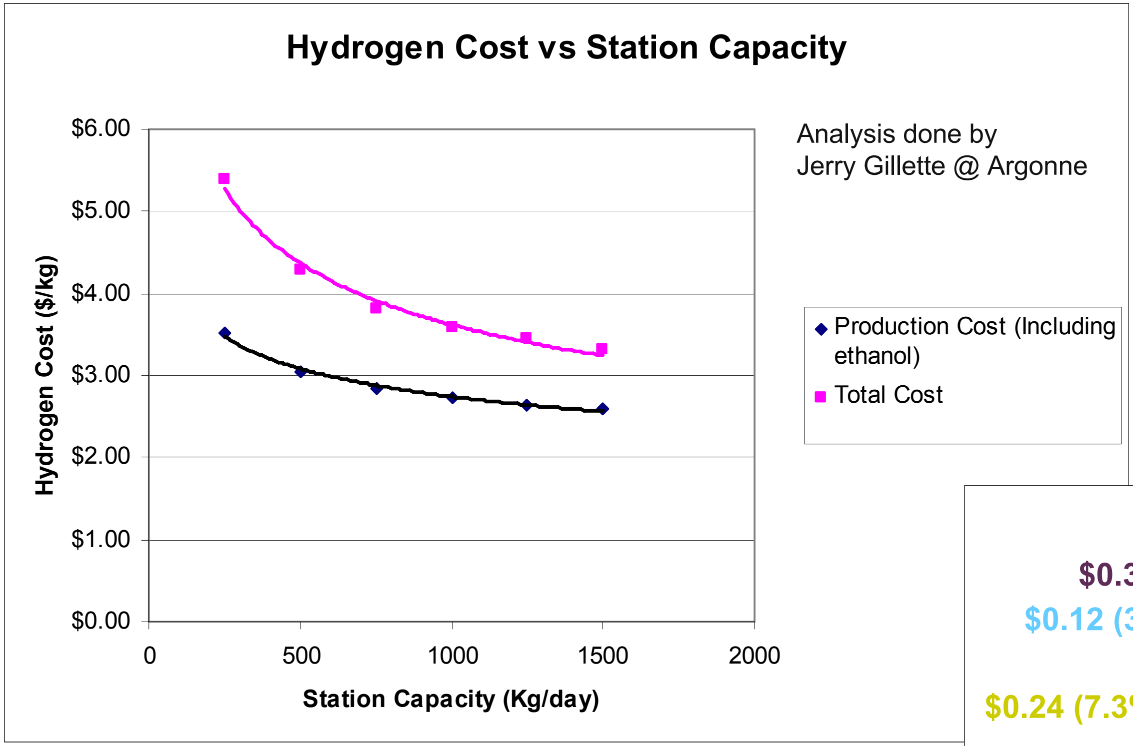
Flow Diagram for Hydrogen Production by Reforming Methane/Renewable Liquids Using OTM Membrane via Water Splitting



- **A conceptual flow diagram was established for performing H2A analysis.**

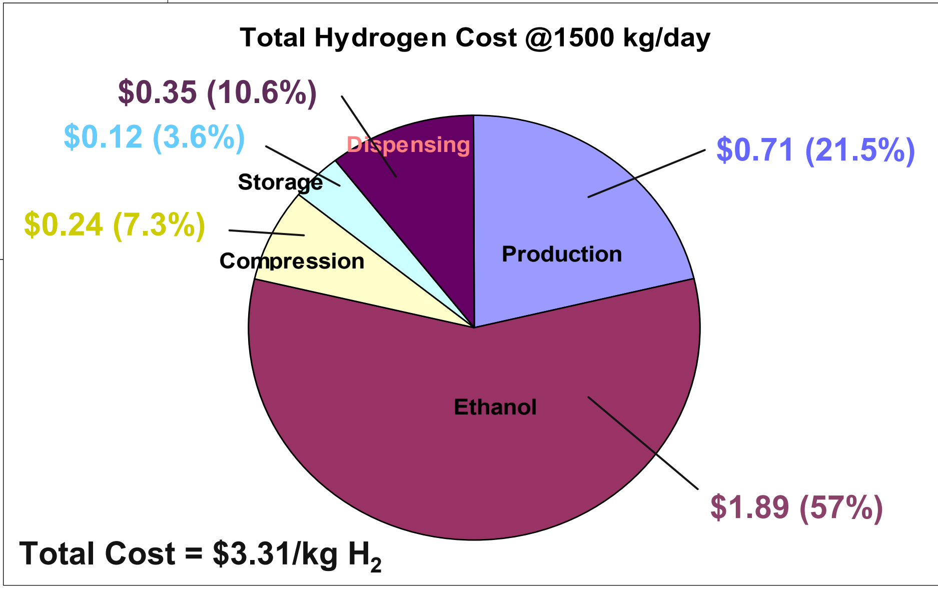
Accomplishments/Progress/Results (Cont'd.)

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



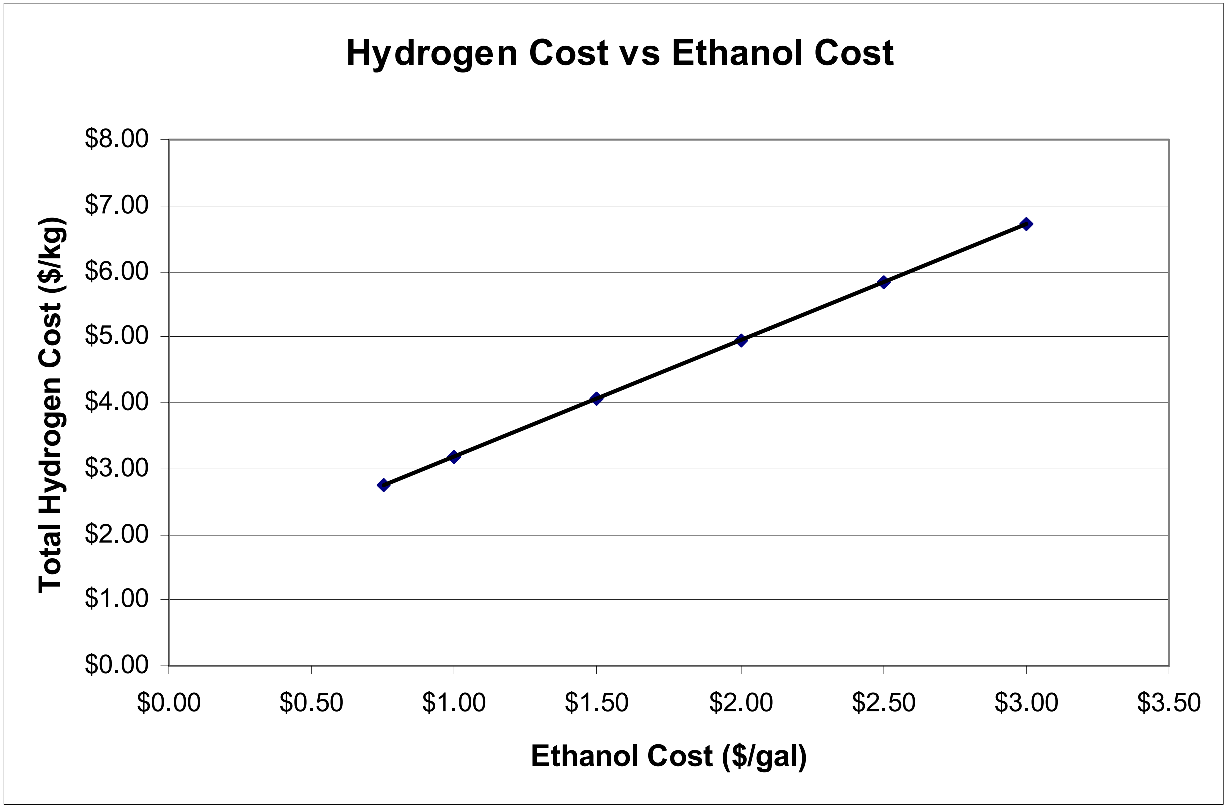
Station Size (kg/day)	Production Cost Incl. Ethanol ($/kg)	Total Cost ($/kg)
250	3.52	5.39
500	3.04	4.29
750	2.84	3.81
1000	2.73	3.59
1250	2.65	3.44
1500	2.60	3.31

- Total 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 Reforming of Ethanol using OTM via Water Splitting (@1500 Kg/day)



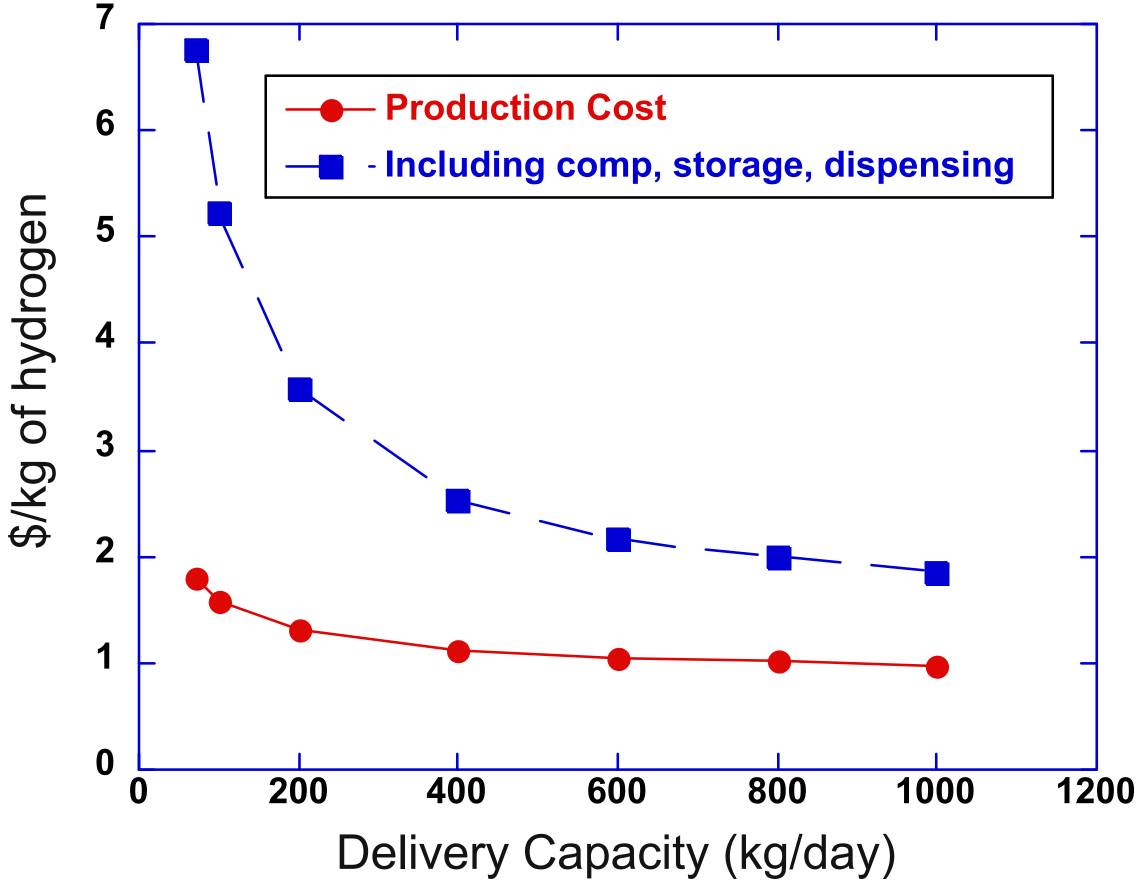
H2A Analysis done by Jerry Gillette @ Argonne

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.**

Accomplishments/Progress/Results (Cont'd.)

Preliminary Analysis of Hydrogen Cost vs. Station Capacity (Reforming of natural gas using OTM via Water Splitting)



Station Size (kg/day)	Production Cost ($/kg)	Total Cost ($/kg)
70	1.79	6.76
100	1.58	5.23
200	1.31	3.58
400	1.13	2.54
600	1.05	2.16
800	1.01	2.00
1000	0.98	1.85

Analysis done by
Jerry Gillette @ Argonne

- **Total cost of H_2 by reforming NG using OTM via water splitting is $1.85/kg.**

Future Work

- Reform ethanol using OTM……………………………………………09/2008
  - -Study effects of EtOH concentration, gas flow rates, OTM thickness
- Evaluate long-term (200-1000 h) stability of membranes……….03/2009
  - -Select OTM composition(s) and reaction conditions
- Measure H_2 production rates of newly developed membranes….09/2009
  - -Rank performance relative to existing OTMs
- Revise H2A analysis using updated OTM performance…………09/2009

SUMMARY

- Oxygen transport membrane (OTM) materials are being developed for distributed reforming of renewable liquids via water splitting.
- Hydrogen production rate of ≈18 cm^3 (STP)/min-cm^2 was measured at 900°C (using 25 μm thick membrane).
- Production rate increased with increasing steam pressure, increasing pO_2 gradient, and with decreasing membrane thickness.
- Preliminary H2A analysis showed the following results for a station capacity of 1500 kg/day of H_2:
  - H_2 production cost including cost of ethanol (@ $1.07/gal) = $2.60/kg
  - Total cost of H_2 (including costs of production, ethanol, compression, storage, & dispensing) = $3.31/kg
  - Total cost of H_2 increased from $3.19 to $4.96/kg when cost of ethanol increased from $1 to $2/gal
  - Total capital investment per station = $3.2 M
  - Annual operating cost of $1.8 M of which $1 M is for ethanol @ $1.07/gal