PRAXAIR

Integrated Ceramic Membrane System for Hydrogen Production

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DOE Hydrogen Program

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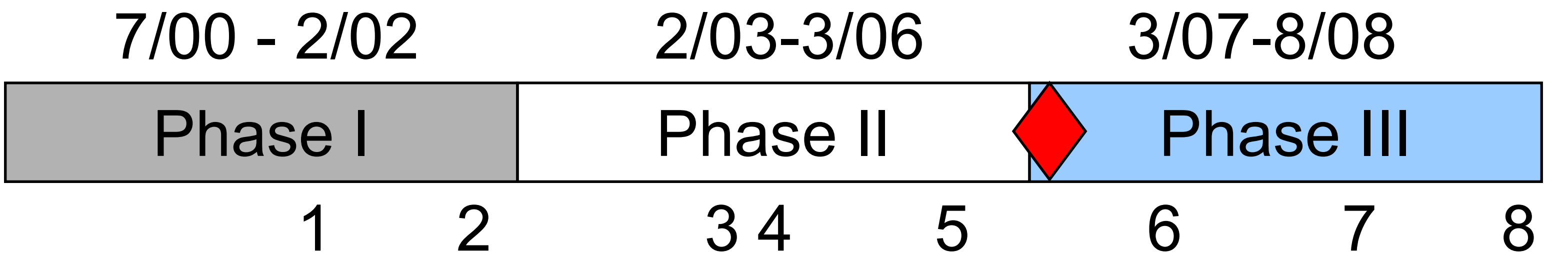
Project ID
PDP-10

Program Timeline



- **Phase I - Feasibility**
  1 Selected Two-Stage Process with Pd Membrane
  2 Assessed Economics vs. Current Options
- **Phase II - Hydrogen Membrane Development**
  3 Select Alloy and Substrate
  4 Membrane Production and Testing
  5 Verify Reactor Performance and Update Process Economics
- **Phase III - System Design and Testing**
  6 Demonstrate Integrated Membrane/Water Gas Shift Performance
  7 Verify System Performance and Update Process Economics
  8 Develop Commercial Offering

FY 2007 Budget

	Committed	Requested	Spent
DOE	$100,000	$313,697	$ 9,369
Praxair	$ 33,333	$104,566	$ 3,123
TOTAL	$133,333	$418,263	$12,492

No funding in FY 2006
No activity in FY 2006

Program restarted in March 2007

Barriers Addressed by HTM

- **A. Reformer Capital Costs**
  - Process intensification (ex. combine WGS and PSA)
  - Reduced capital cost for the entire system
  - Focus on substrates with much lower cost than commercially available porous metals and ceramics
- **B. Reformer Manufacturing**
  - Develop a standard design
  - Take advantage of DFMA and multiple identical units
- **C. Operation and Maintenance**
  - Praxair has an extensive remote operations network
  - Standard design will allow for standard O&M
- **F. Control and Safety**
  - Safety is the top priority and essential to the success of any commercial product

Barriers Addressed by HTM

- **K. Durability**
  - Ceramic substrate eliminates metal/metal interactions
  - Close thermal expansion match allows for thermal cycling
- **L. Impurities**
  - Effects of CO and H_2S are being studied
  - CO is important, but sulfur can be removed upstream
- **M. Membrane Defects**
  - Experience in OTM program has led to a good seal
  - Chemical deposition techniques being improved
- **N. Hydrogen Selectivity**
  - Pd membranes have very high selectivity
  - A good seal and leak-tight membrane ensure selectivity

Barriers Addressed by HTM

PRAXAIR

- **O. Operating Temperature**
  - Pd membrane and WGS operate at similar temperatures
  - WGS temp. is preferred to SMR temp. for maximum yield
- **P. Flux**
  - Consistent improvement in reducing film thickness, increasing porosity, decreasing pore size, and increasing flux
- **Q. Testing and Analysis**
  - Testing targeted to determine cost/performance tradeoffs
  - Lead to real-world commercial membrane unit design
- **R. Cost**
  - Pd cost is fixed by layer thickness
  - Producing low-cost substrate is the key to reducing cost
  - High commercial substrate cost is a significant barrier for HTM

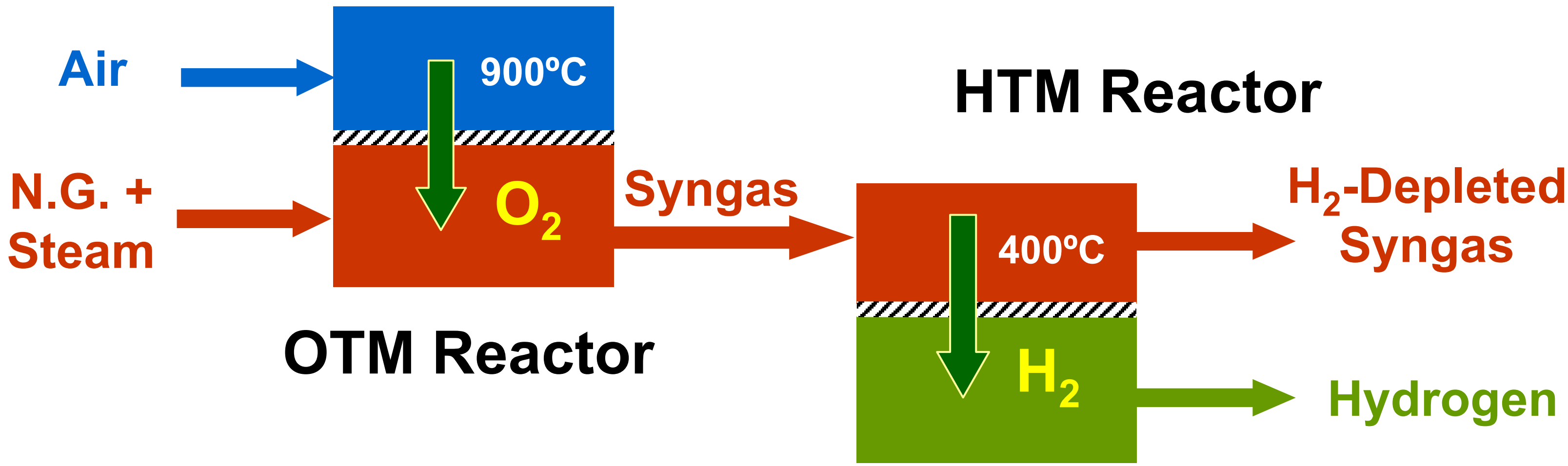
Partners

- **Praxair**
  - Leader in hydrogen purification, production, and distribution
  - Leader in electroceramic materials - dielectrics, superconductors, ...
  - Overall program lead
  - Substrate development
  - Reactor design
  - Membrane testing
  - Process development and economics
- **Research Triangle Institute**
  - Palladium coating
  - Membrane testing
- **Joint**
  - Membrane Production
    - Unique opportunity to integrate substrate and alloy development
    - Iterative process

Objectives

- **Program - Develop a low-cost reactive membrane based hydrogen production system**
  - Use existing natural gas infrastructure
  - High thermal efficiency
  - Serve both the transportation and industrial markets
    - Industrial market provides immediate opportunities
    - Gain valuable operating experience before fuel cells arrive
- **Phase III – Integrate HTM with WGS**
  - Low-cost hydrogen production, separation, and purification
  - Demonstrate HTM performance in reactive environments
  - Develop versatile system that can be combined with any syngas generation method for improving hydrogen production, especially at distributed scale

OTM/HTM Concept
Preferred Process - Sequential Reactors



OTM Reactor

Synthesis gas generation

$CH_4 + ½ O_2 \rightarrow 2 H_2 + CO$

$CH_4 + H_2O \rightarrow 3 H_2 + CO$

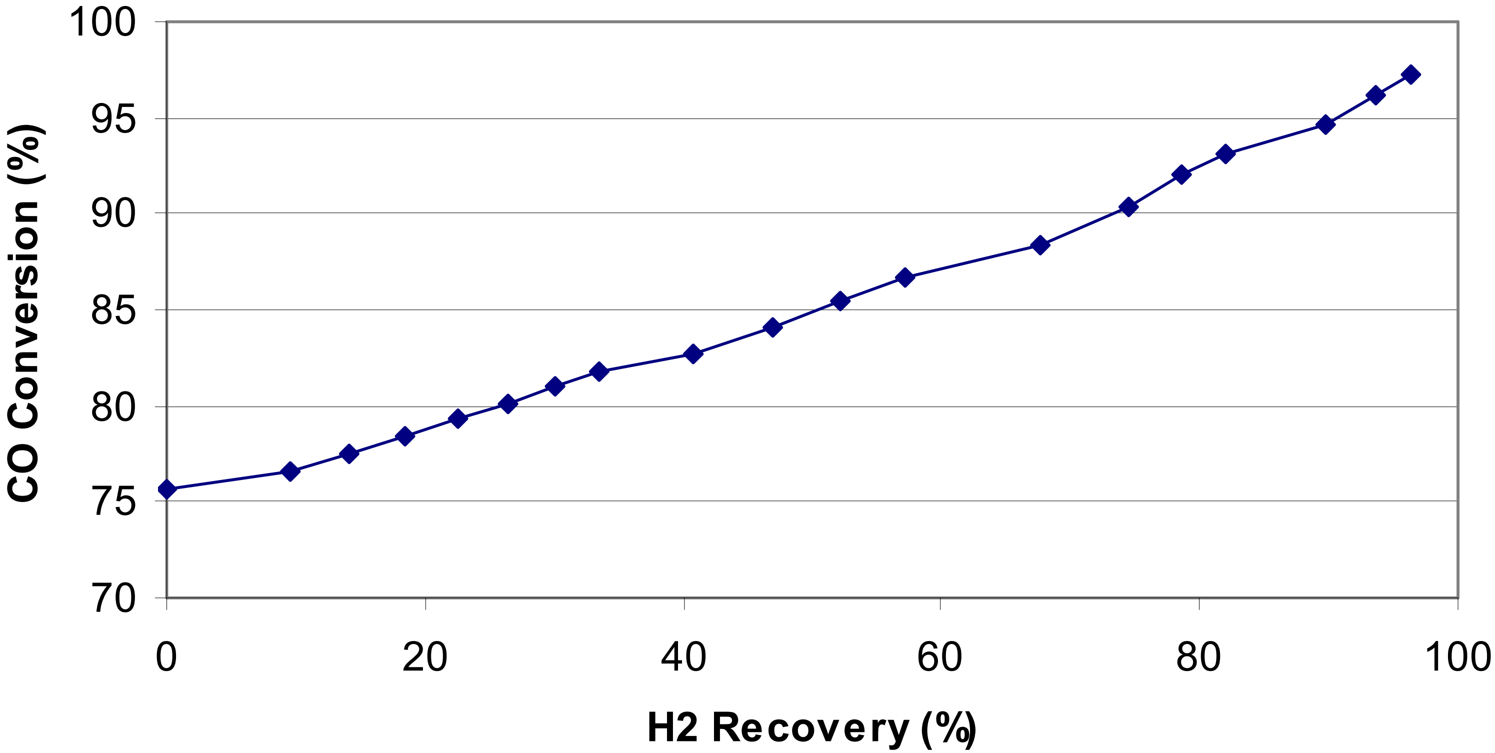
HTM Reactor

Water-gas shift reaction

$CO + H_2O \rightarrow H_2 + CO_2$

Hydrogen Separation

Enhanced CO Conversion



- **Simulation results show enhanced CO conversion is possible using a hydrogen membrane**

HTM/WGS at 400ºC, 150 psig, syngas composition from OTM module

Program Approach

- Phase I - Define Concepts
  - Techno-Economic Feasibility Study
  - Define Development Program
- Phase II - Bench-Scale HTM Development
  - Develop and Test HTM Alloy and Substrate
- **Phase III – System Design and Testing**
  - **Integrate HTM and WGS in Single Tube Tests**
  - **Define Mass Production Methods**
  - **Define Commercial System**

Phase III Plan

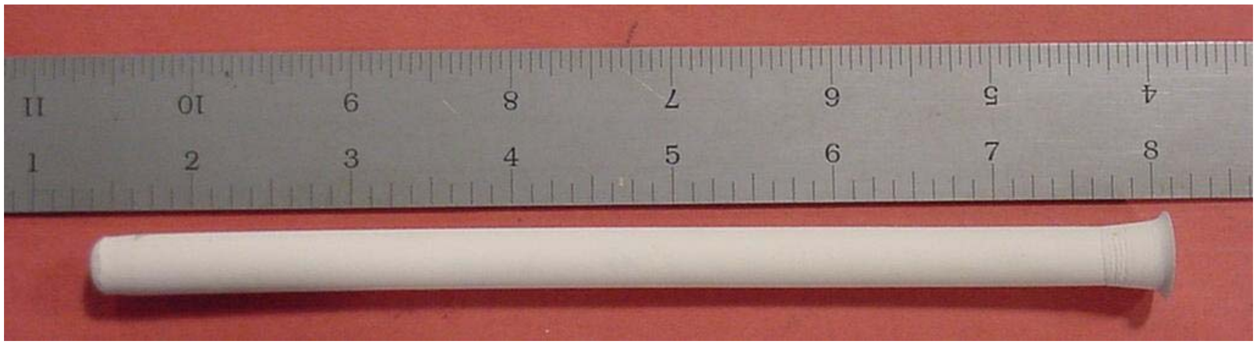
- **Process Development**
  - Demonstrate HTM performance in membrane reactor
    - Integrate HTM with water gas shift
  - Develop conceptual design for full-scale unit
  - Define manufacturing process for producing reactors
- **Process Economics**
  - Confirm membrane and process are cost-effective
  - Assess alternative technologies
  - Go/No Go decision based on technoeconomic viability

Palladium Membrane Targets

	2006	2010	2015
Flux (scfh/ft^2)	> 200	250	300
Cost (\$/ft^2)	1500	1000	< 500
Durability (yrs)	< 1	3	> 5
ΔP Operating Capability	200	400	400-600
Hydrogen Recovery	60	> 80	> 90
Hydrogen Quality	99.98	99.99	> 99.99

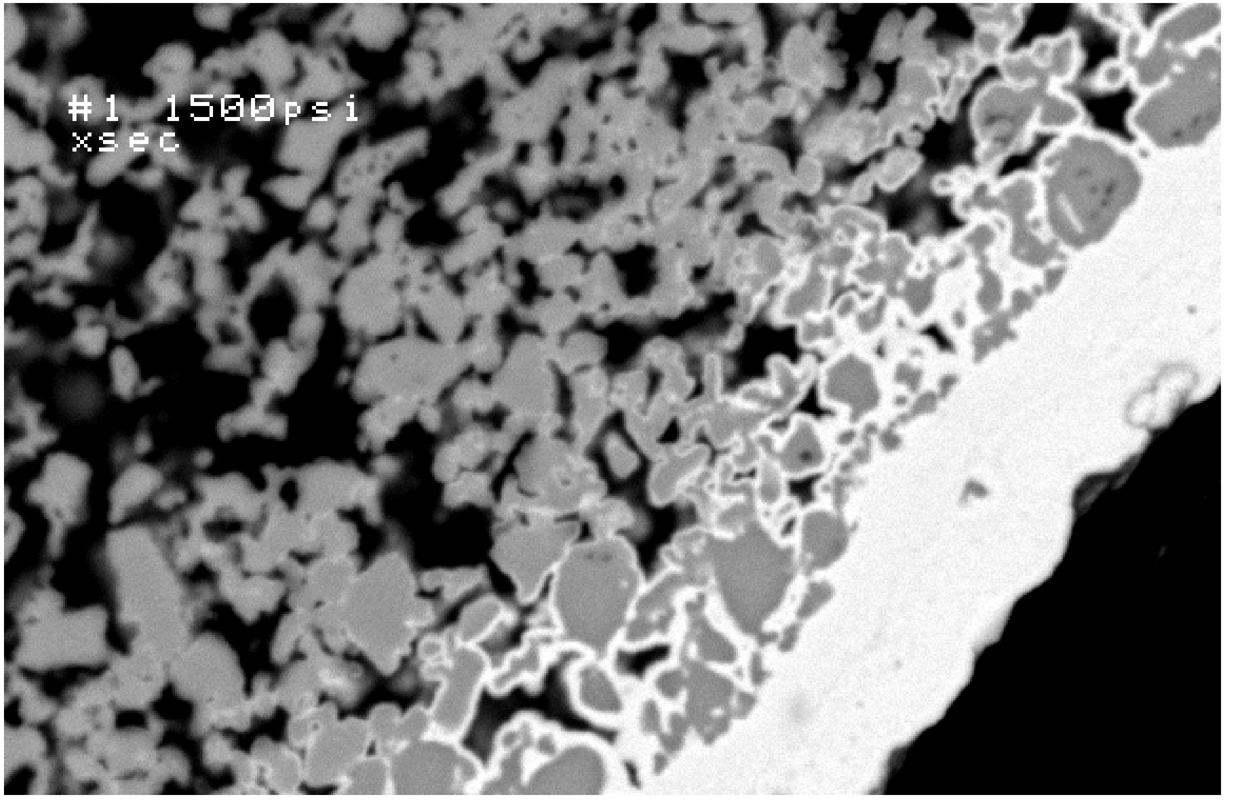
- Flux based on 20 psid hydrogen pressure at 400ºC
- $/scfh is our most important consideration - $4/scfh in 2010

Low-Cost Ceramic Substrate



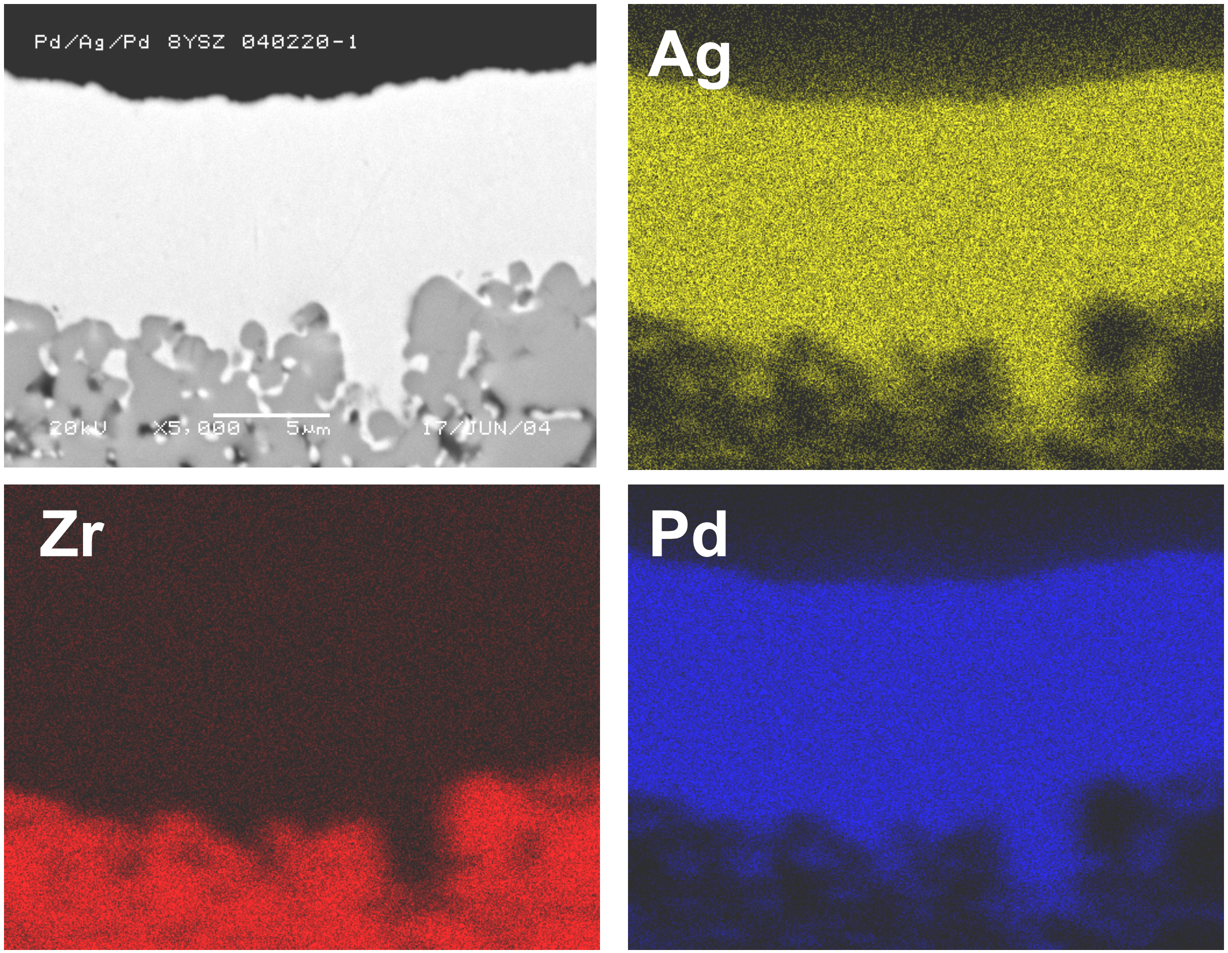
- Modified zirconia designed to match thermal expansion of palladium alloy and to have high strength and stability
- Layered structure produced using Praxair's patented isopressing technique for producing porous ceramics
- Layer adjacent to membrane has smallest pore size
- Closed-end tube allows for expansion and simplifies sealing
- Substrate is coated using electroless plating

Pd-Ag Film Structure



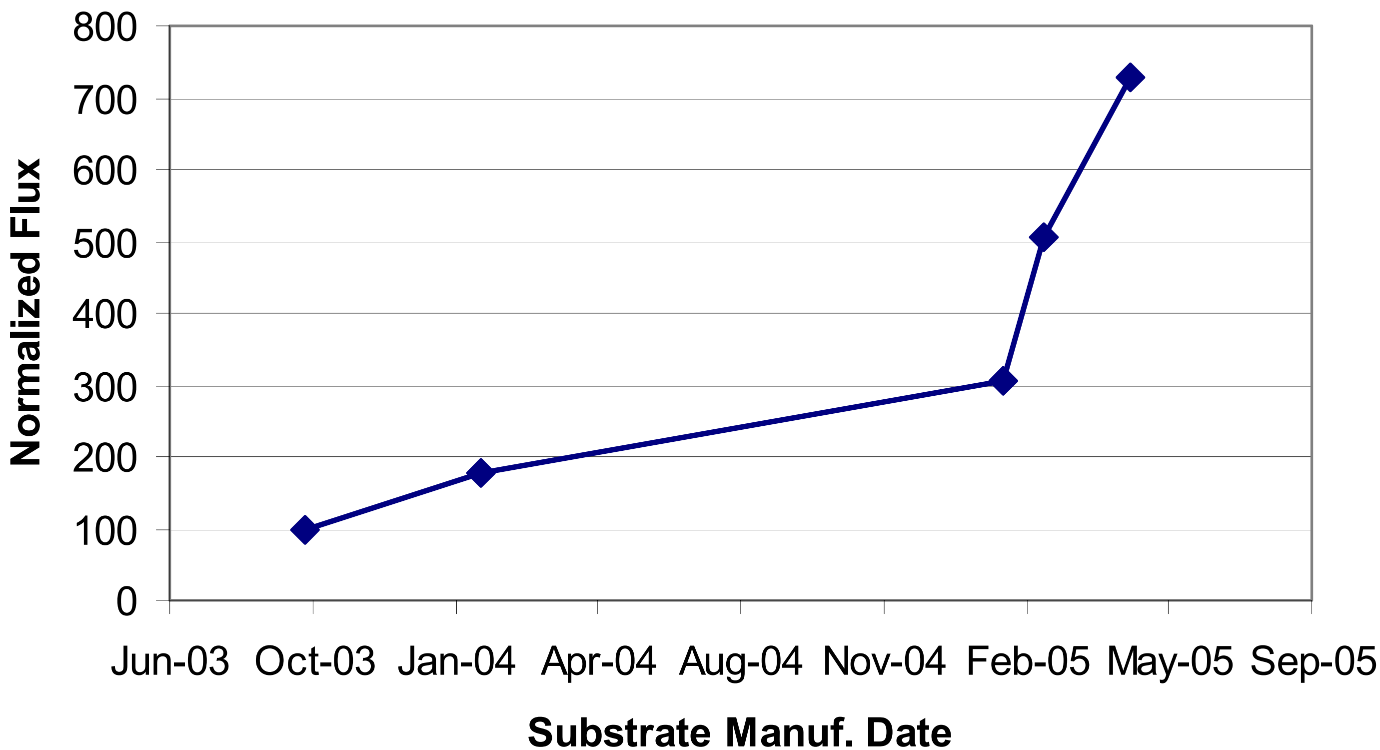
- Surface treatments produced very small surface pores and larger pores in the bulk layer

Membrane Composition



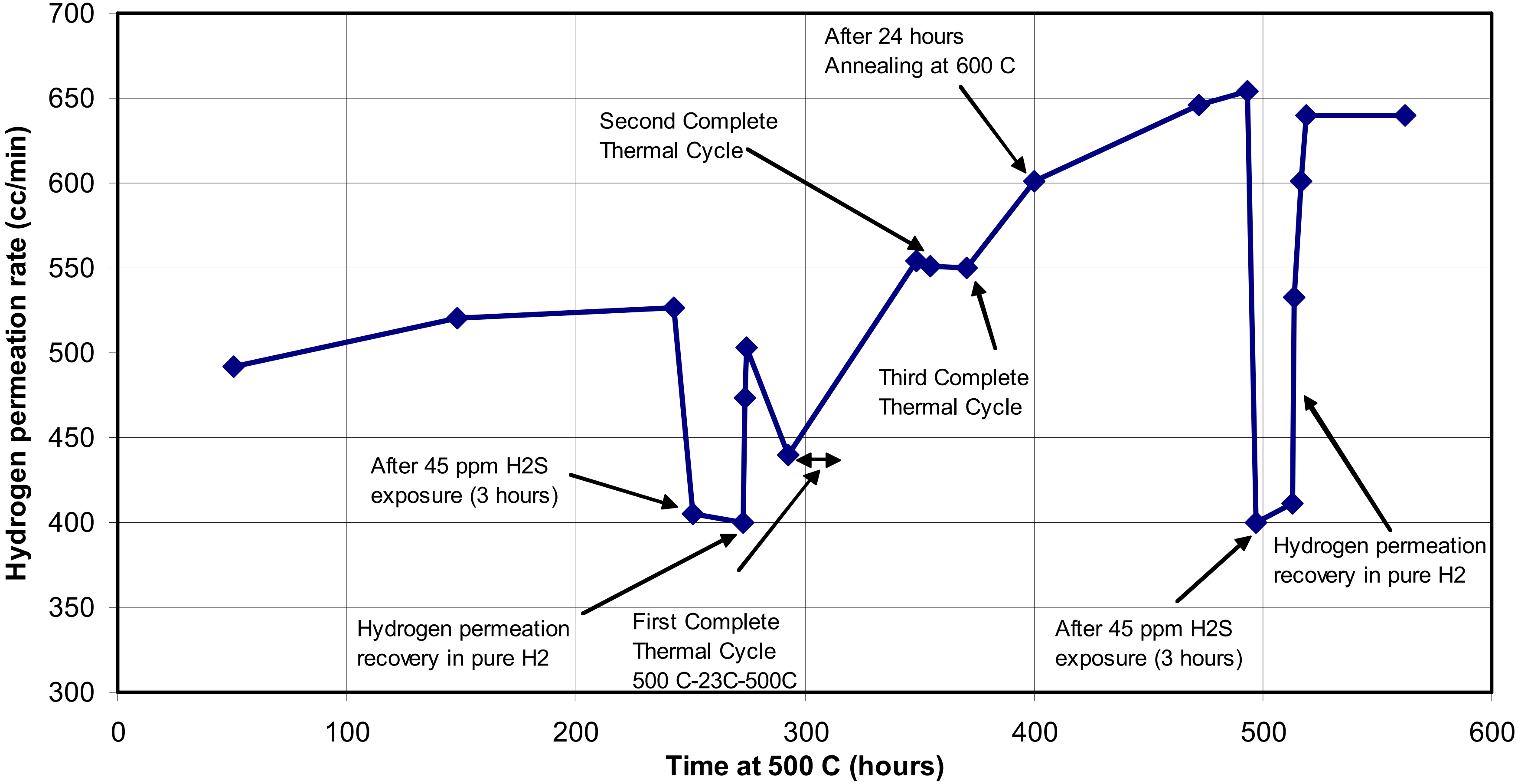
- Ag and Pd mixed well and penetrated deep enough to adhere

Pd-Ag Membrane Flux



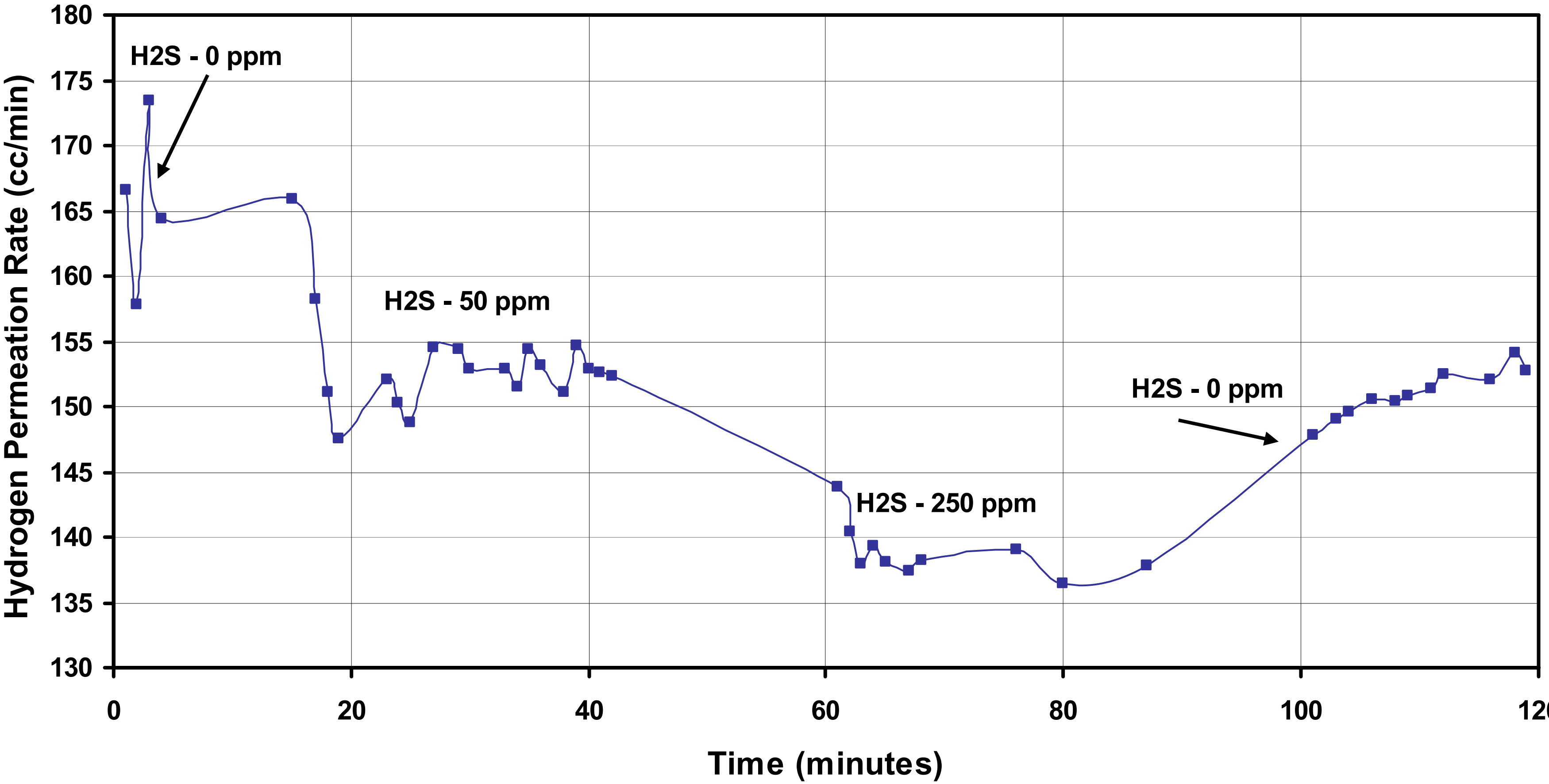
- **Continuous improvement in membrane performance while maintaining or reducing cost**
- **Significant step-change improvement in early 2005**

Effect of H_2S on Pd-Ag



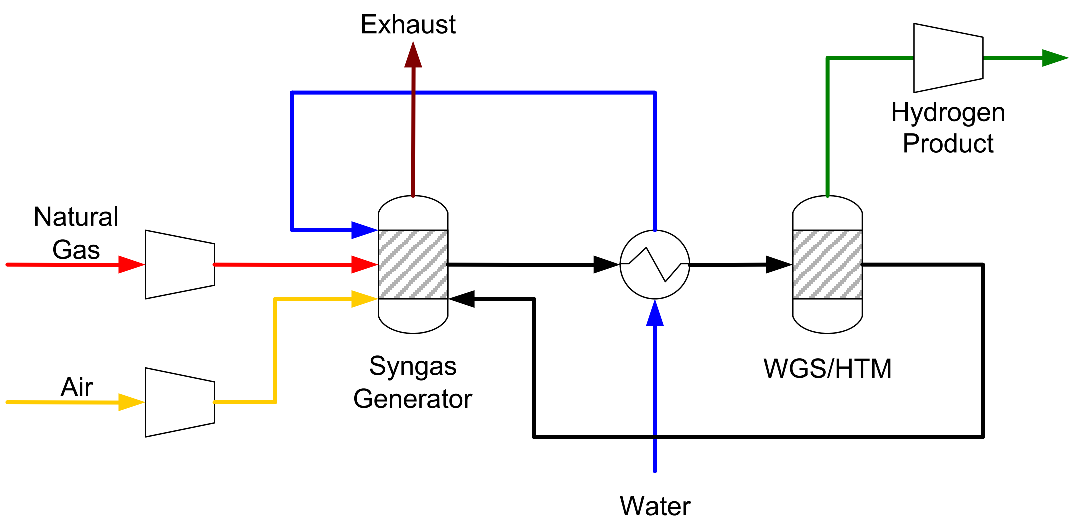
- **Excellent response to thermal cycling**

Effect of H_2S on Pd-Cu

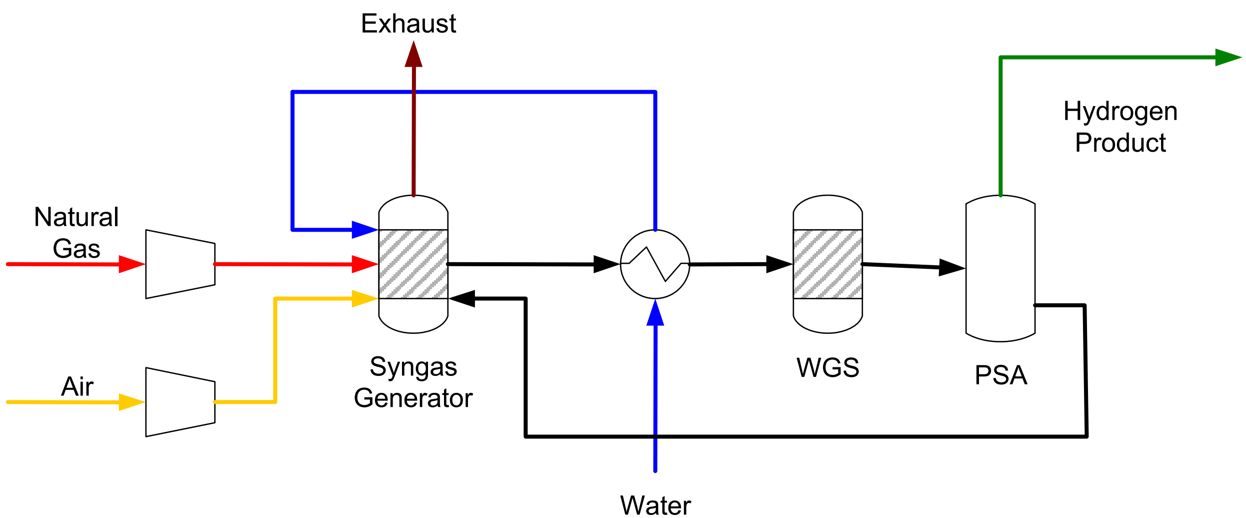


- H_2S reduced flux within minutes
- Most of lost performance was recovered when H_2S was removed

Process Flow Diagrams for Cost Comparison

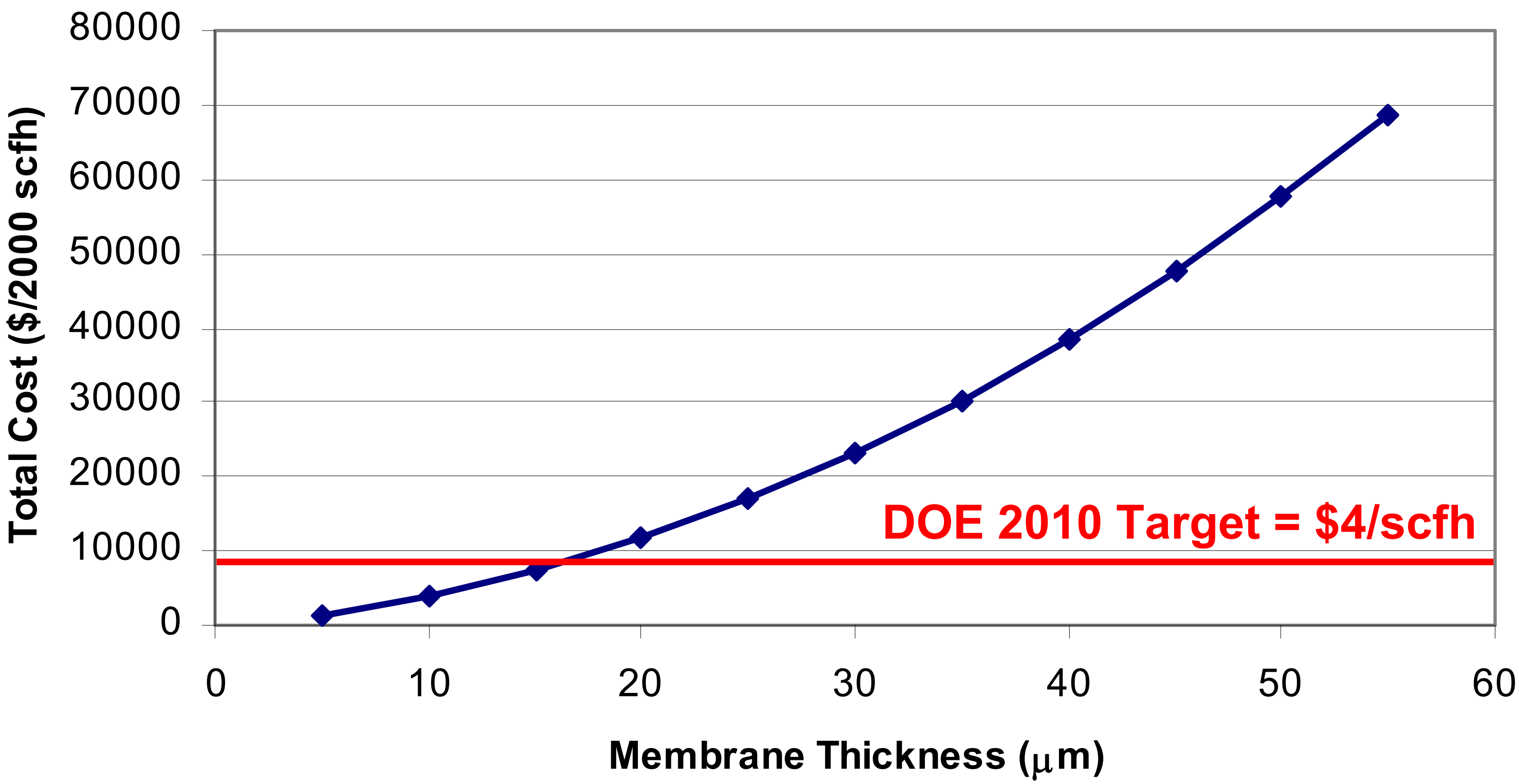


Hydrogen Membrane Process



Shift Reactor/PSA Process

Membrane Module Cost



- **Assumes an average flux of 100 scfh/ft^2 for a 10-μm HTM**
- **Assumes flux is inversely proportional to thickness**
- **Assumes substrate, coating, and other module costs of $100/ft^2**
- **Pd cost of $360/oz and silver cost of $14/oz (prices as of 4/10/07)**

Hydrogen Cost Reduction by HTM Reactor

Parameter	HTM Reactor	PSA/WGS
Capital Cost	$8,000	$50,000
Cost ($/kg H_2)	$0.081	$0.508

- **Assumes:**
  - 2000 scfh, 70% utilization
  - 30% annual capital cost recovery factor
  - DOE 2010 target is met
- **HTM reactor enables possible capital cost savings**
  - Capital cost savings becomes more significant as utilization decreases
- **The cost of hydrogen compression is an important factor**
  - HTM is likely to provide a lower compressor suction pressure at sufficient recovery
  - HTM has potentially higher purity
  - HTM has an advantage if product pressure is not important

Future Work

- Continue performance improvement
- Demonstrate performance in integrated WGS/HTM reactor
- Design low-cost reactor and membrane toward meeting hydrogen cost goal of $4/scfh in 2010
- Confirm that HTM has the potential to be the lowest-cost option, or pursue other technology instead

Conclusions

- Pd-based membrane tubes can be produced at a relatively low cost using Praxair's substrates and manufacturing techniques
- Membrane and substrate properties have continuously and significantly improved
- 2010 cost goal of $4/scfh will be difficult to achieve and probably cannot be done with current high-cost substrates
- HTM must provide advantages by integration with WGS to beat low-cost PSA for hydrogen purification and production