Integrated Ceramic Membrane System for H_2 Production

Cooperative Agreement: DE-FC36-00GO10534

Joe Schwartz
Ray Drnevich
Prasad Apte
Praxair - Tonawanda, NY

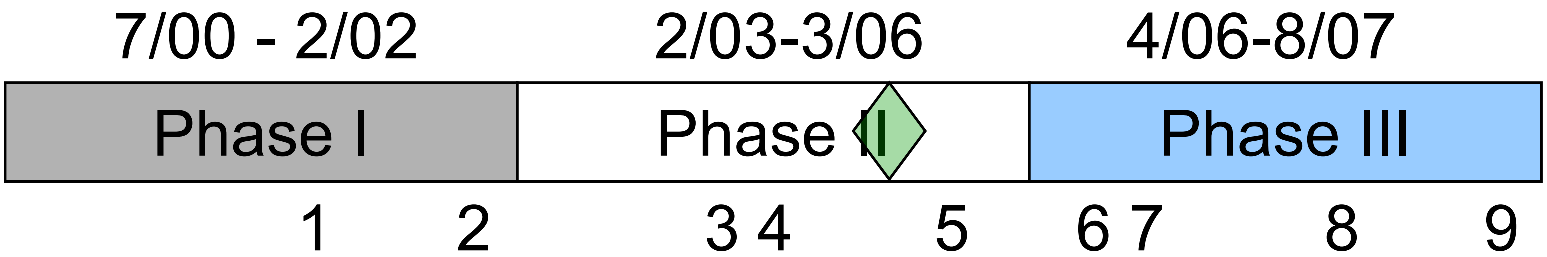
Ashok Damle
Research Triangle Institute
Research Triangle Park, NC

DOE Annual Merit Review Meeting
May 24, 2005

Project PDP3

This paper was written with support of the U.S. Department of Energy under Contract No. DE-FC36-00GO10534.

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 Design (DFMA Focus) and Fabricate Multi-Tube Pilot Unit
  7 Operate Pilot Unit
  8 Verify System Performance and Update Process Economics
  9 Develop Commercial Offering

Budget

	Phase IIB	Spent	FY2005
DOE	$633,697	$101,063	$419,297
Praxair	$211,232	$33,688	$139,766
TOTAL	$844,930	$134,751	$559,063

FY2005 spending through March 31, 2005
Full amount for FY2005 has not been committed

Barriers Addressed

- **A. Fuel Processor Capital Costs**
  - Process intensification (ex. combine WGS and PSA)
  - Focus on substrates with much lower cost than commercially available porous metals and ceramics
- **B. Fuel Processor Manufacturing**
  - Develop a standard design
  - Take advantage of DFMA and multiple identical units
- **C. Operation and Maintenance**
  - Existing remote operations network can monitor all units
  - 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

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

Barriers Addressed

- **P. Operating Temperature**
  - Pd membrane and WGS operate at similar temperatures
  - WGS temp. is preferred to SMR temp. for maximum yield
- **Q. Flux**
  - Consistent improvement in reducing film thickness, increasing porosity, decreasing pore size, and increasing flux
- **S. 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
- **T. Oxygen Separation Technology**
  - Significant work has been done to develop OTM
  - OTM offers a revolutionary breakthrough technology
  - OTM work not funded under this program

Partners

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

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 IIB – 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

Program Approach

PRAXAIR

- Phase I - Define Concepts
  - Technoeconomic Feasibility Study
  - Define Development Program
- **Phase II - Bench-Scale HTM Development**
  - A Develop and Test HTM Alloy and Substrate
  - **B Integrate HTM and WGS in Single Tube Tests**
- Phase III - Multi-Tube Reactor Development
  - Pilot-Scale Demonstration
  - Define Mass Production Methods

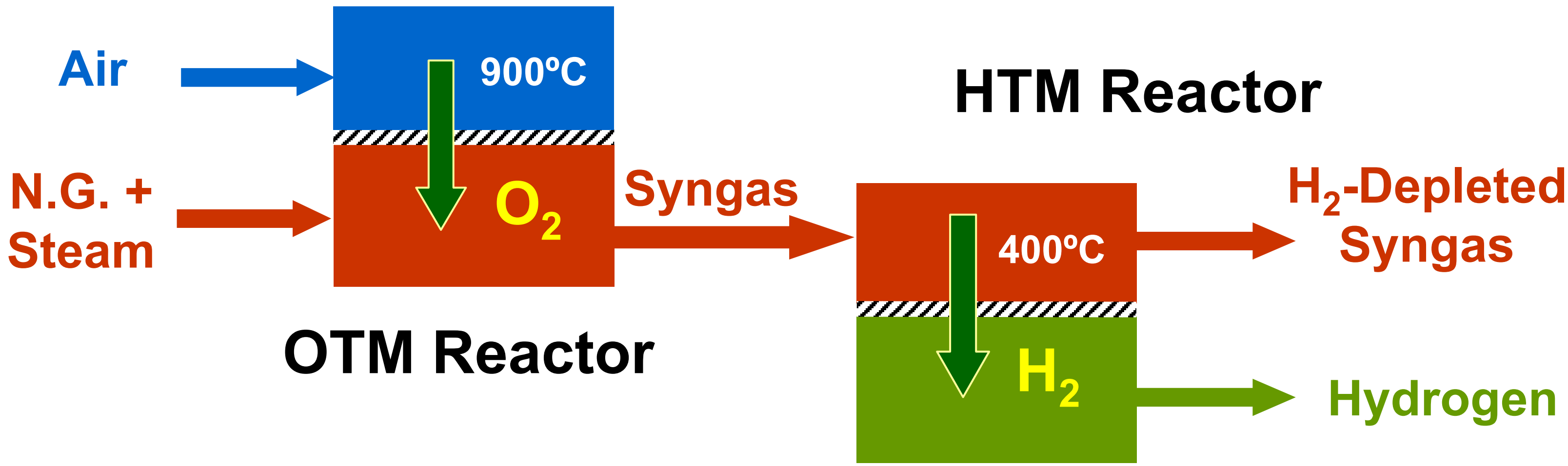
Phase IIB Plan

- **HTM Development**
  - Thin Pd-alloy layer on low-cost ceramic substrate
  - Demonstrate sufficient flux, life, and cycling
  - Demonstrate resistance to contamination
  - Produce commercial-scale membranes
  - Develop manufacturing process for low-cost HTM
- **Process Development**
  - Demonstrate HTM performance in membrane reactor
  - Develop conceptual design for full-scale unit
  - Define manufacturing process for producing reactors

Phase IIB Plan cont.

- **Process Economics**
  - Confirm membrane and process are cost-effective
  - Assess alternative technologies
  - Go/No Go decision based on technoeconomic viability
  - HTM must have the potential to be the preferred method, or others should be pursued instead
- **Phase III Plan**

OTM/HTM Concept
Preferred Process - Sequential Reactors



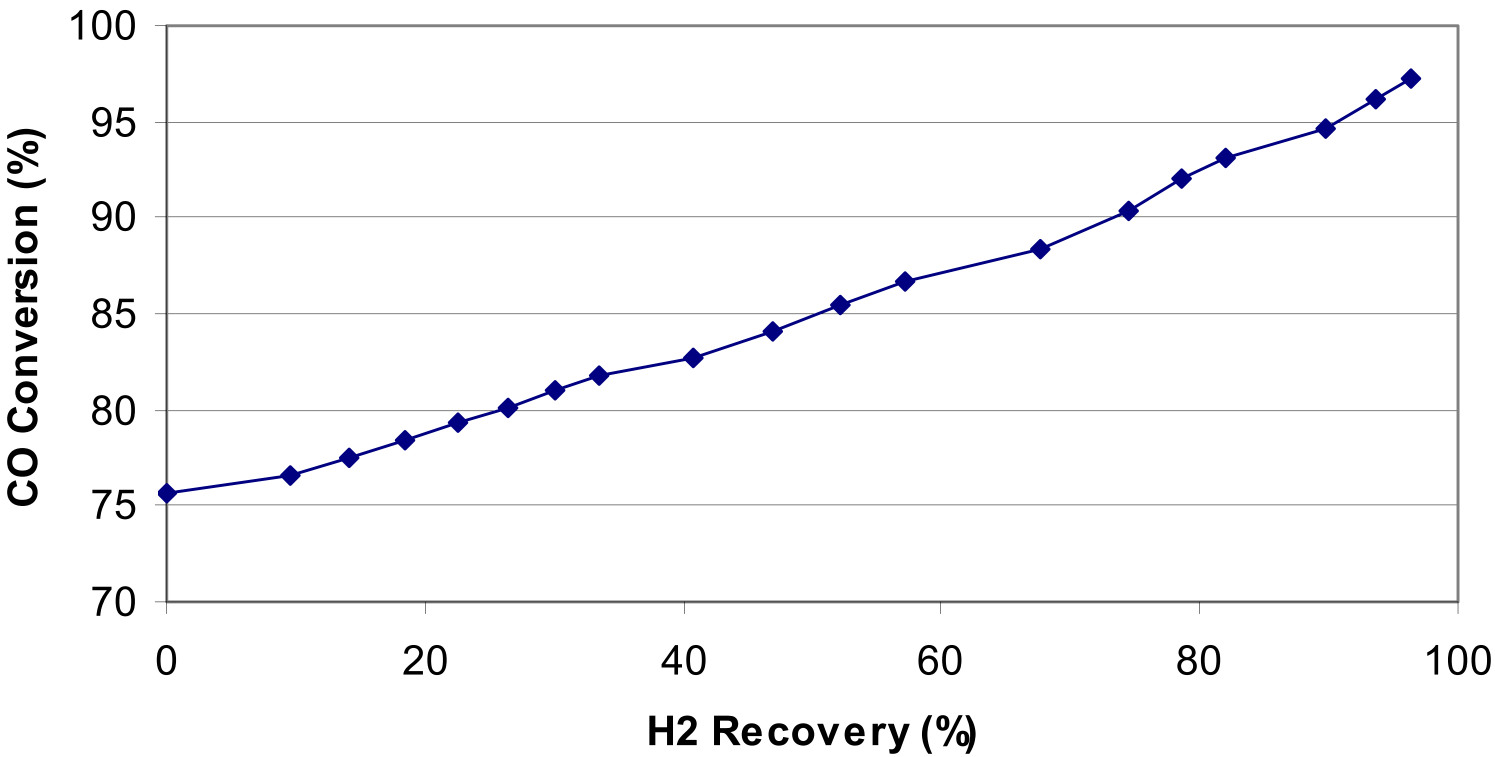
OTM Reactor

- Synthesis gas generation
- $CH_4 + \frac{1}{2} O_2 \rightarrow 2 H_2 + CO$
- $CH_4 + H_2O \rightarrow 3 H_2 + CO$

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

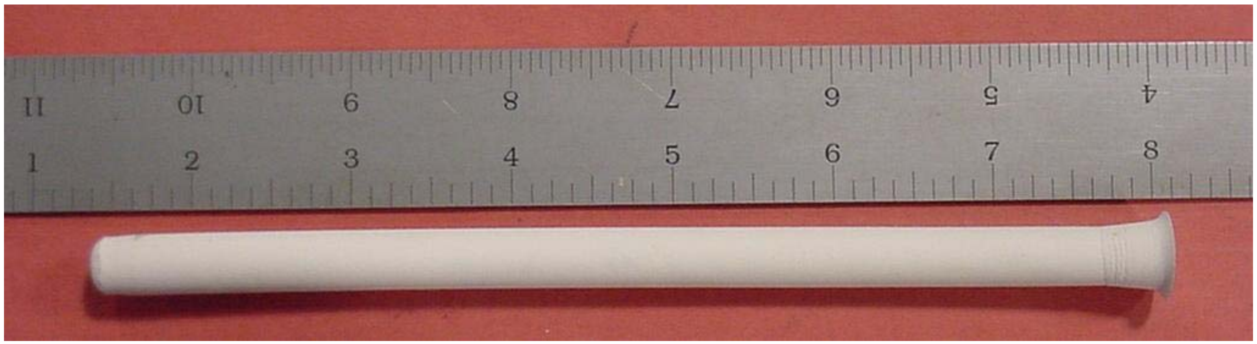
Palladium Membrane Targets

PRAXAIR

	2003	2005	2010
Flux (scfh/ft^2)	60	100	200
Cost ($/ft^2)	2000	1500	1000
Durability (yrs)	< 1	1	3
ΔP Operating Capability	100	200	400
Hydrogen Recovery	60	> 70	> 80
Hydrogen Quality	99.9	99.9	99.95

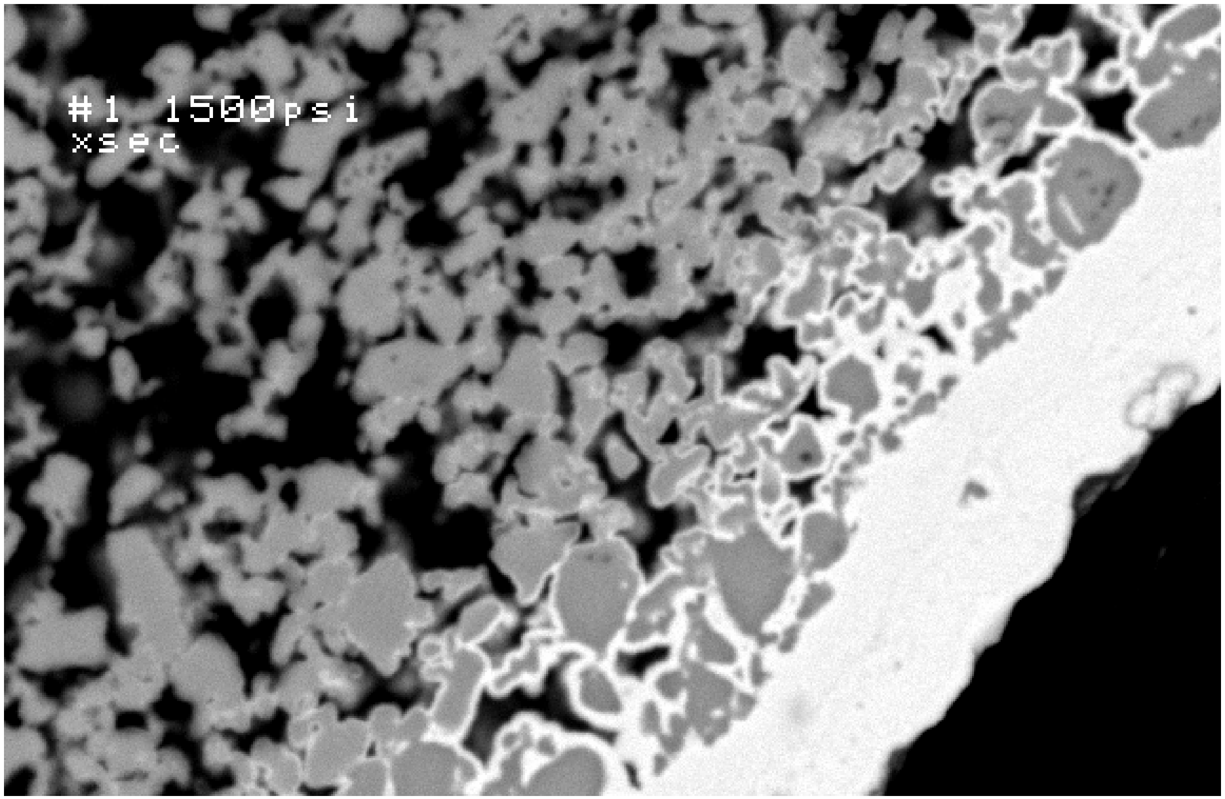
- **Flux based on 20 psid hydrogen pressure at 400ºC**
- **$/scfh is our most important consideration - $5/scfh in 2010**

Low-Cost Ceramic Substrate



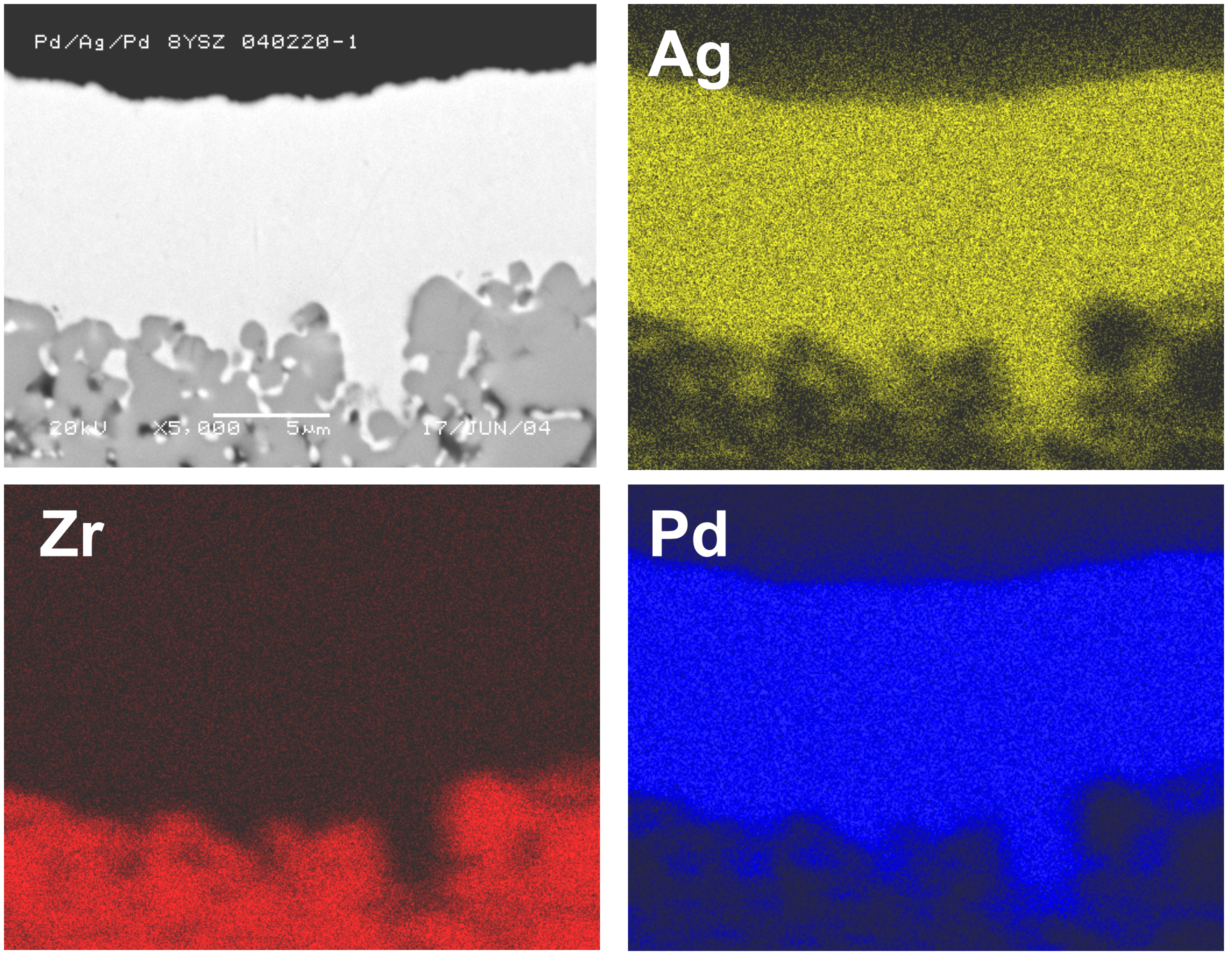
- Modified zirconia designed to match thermal expansion of palladium alloy and to have high strength and stability
- Layered structure produced using Praxair's patented isopressing technique for producing porous ceramics
- Layer adjacent to membrane has smallest pore size
- Closed-end tube allows for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

Pd-Ag Film Structure



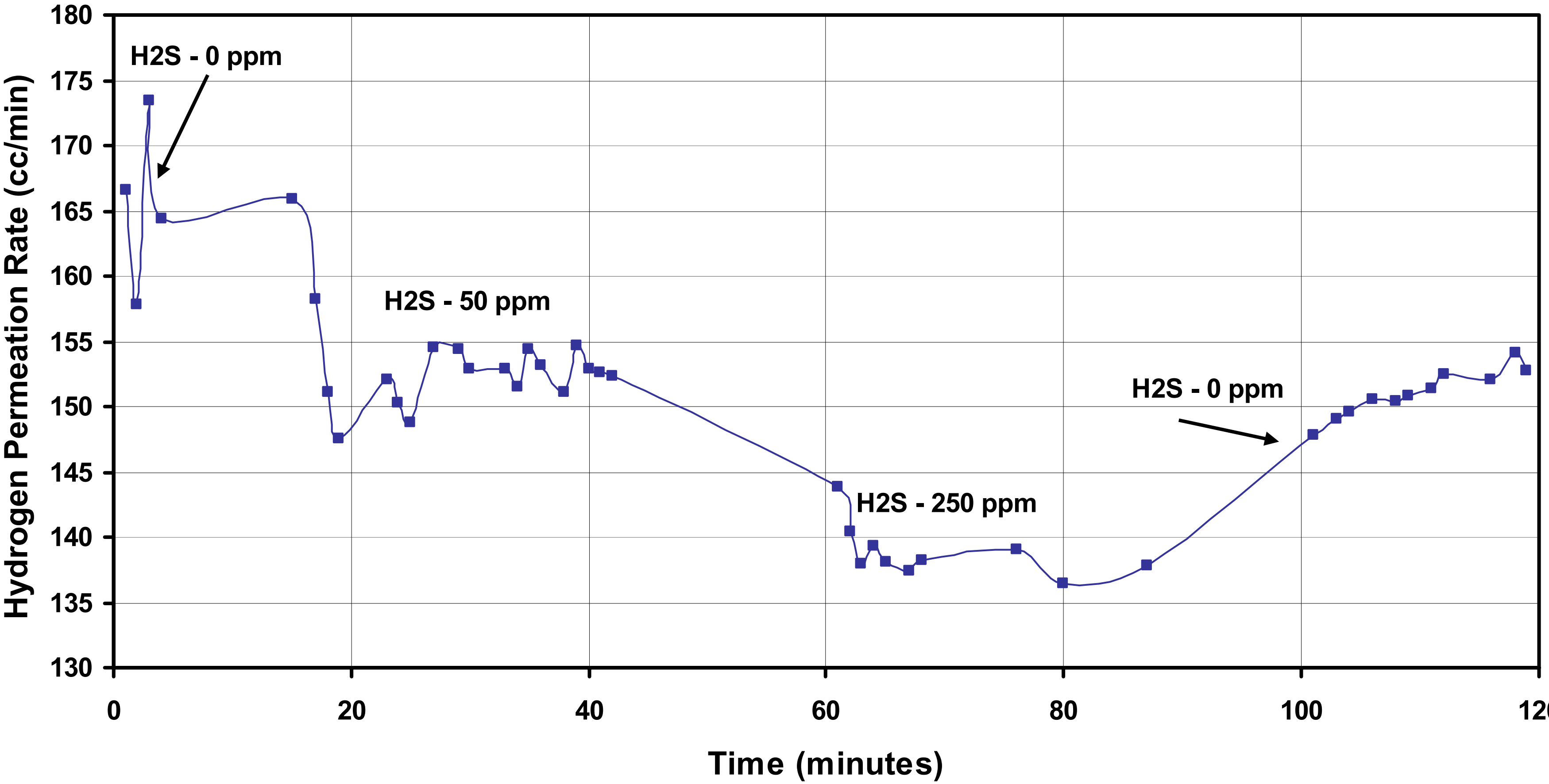
- **Surface treatments produced very small surface pores and larger pores in the bulk layer**

Membrane Composition



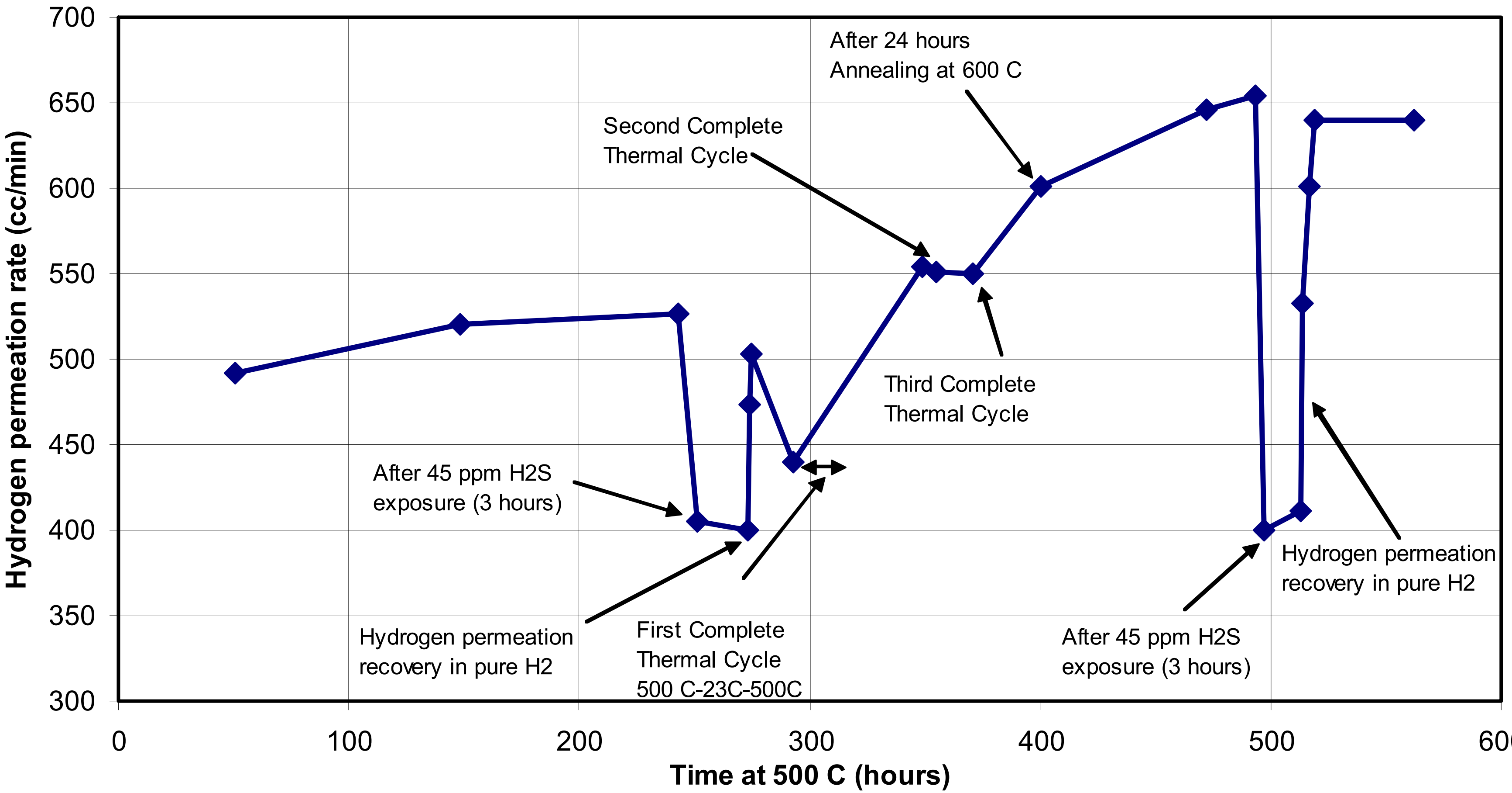
- **Ag and Pd mixed well and penetrated enough to adhere**

Effect of H_2S on Pd-Cu



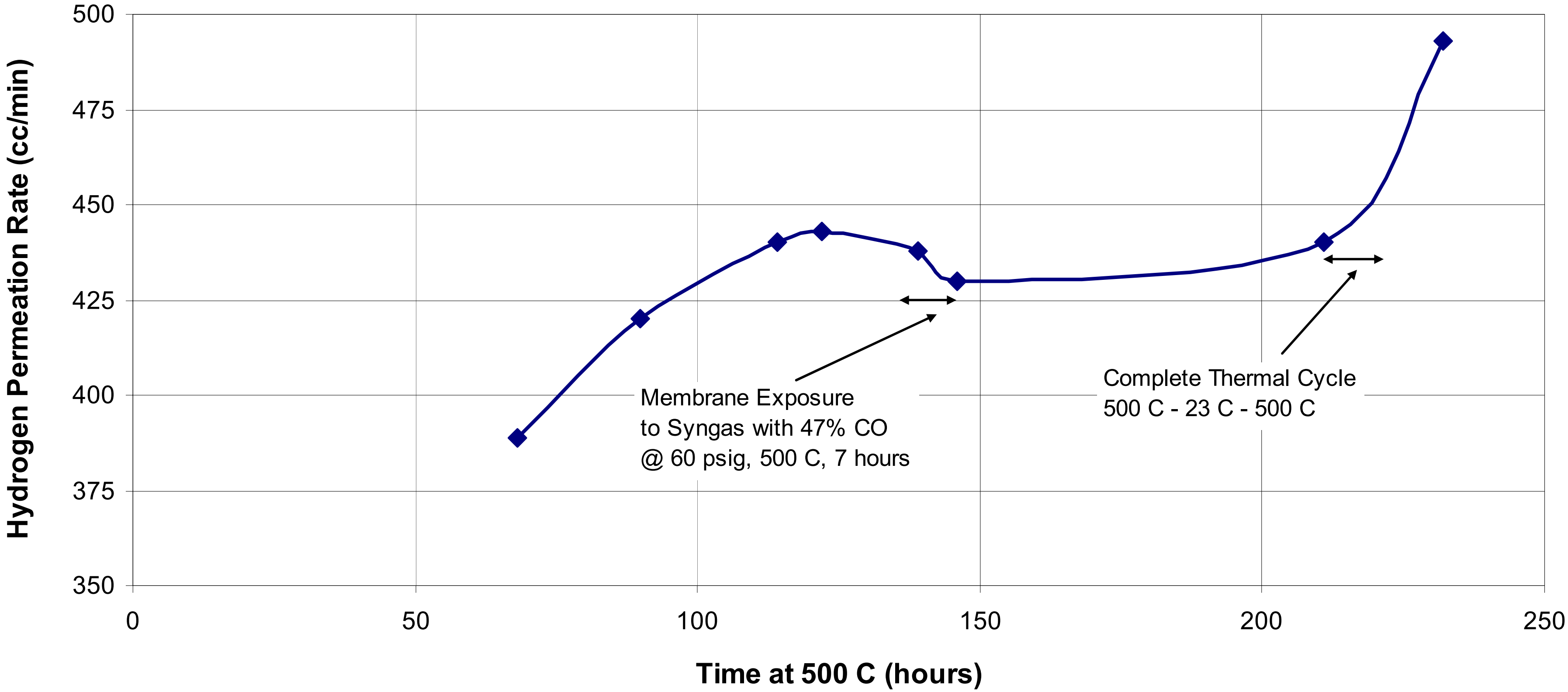
- H_2S reduced flux within minutes
- Most of lost performance was recovered when H_2S was removed

Effect of H_2S on Pd-Ag



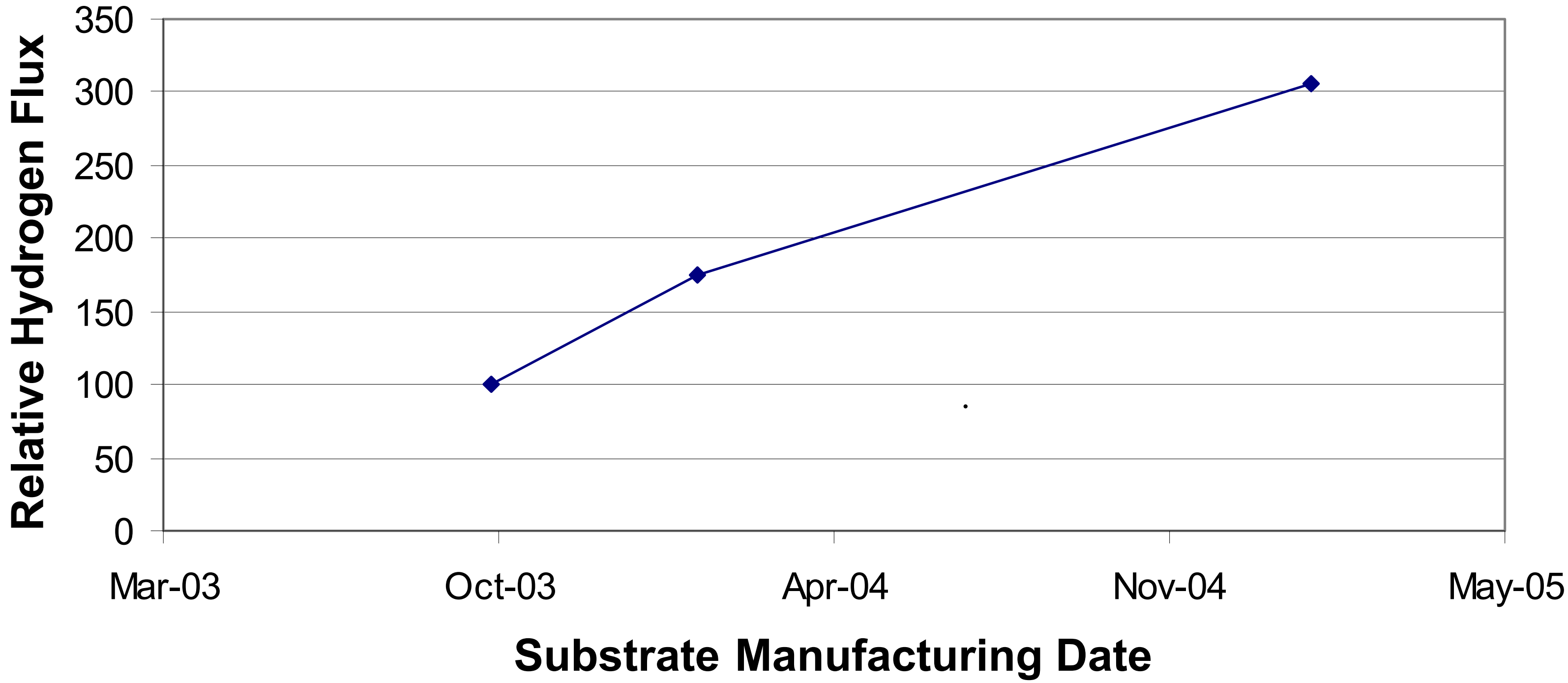
- **Excellent response to thermal and compositional cycling**

Effect of CO on Pd-Ag



- **7 hours of CO exposure had no significant impact on membrane performance**

Pd-Ag Membrane Flux



- **Hydrogen flux has tripled compared to earlier membranes**
- **Continuous improvement in membrane performance while maintaining or reducing cost**

2004 Reviewer Comments

PRAXAIR

- **Need to look at effect of contaminants**
  - Review of effects of H_2S and CO underway
- **Applicable to steam reforming?**
  - HTM can be used downstream of SMR, but Pd membranes would probably not be used in a high-temperature SMR
- **Suggest WGS catalyst partner as a good idea**
  - Large WGS catalyst manufacturer has provided help
- **Need new membrane material**
  - Other materials are being considered, but Pd is the lead candidate
- **Systems approach – focus on entire system**
  - This program is focused on developing the WGS/HTM portion
  - Insufficient resources to develop the OTM portion
- **Consider collaboration with other programs**
  - Additional collaboration will be considered if it can add value

Future Work

- **Continue performance improvement**
  - Improve substrate and coating to increase flux, life, cyclability, and resistance to contaminants
- **Demonstrate performance in integrated WGS/HTM**
  - Multi-tube pre-commercial system
- **Design low-cost reactor and membrane to meet hydrogen cost goal of $5/scfh in 2010**
  - Use performance test results and integrated design to minimize the cost of producing hydrogen
- **Confirm that HTM has the potential to be the lowest-cost option, or pursue other technology instead**
  - Compare HTM to other options based on the cost of producing hydrogen

Conclusions

PRAXAIR

- **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, but do not meet the 2010 DOE goals**
- **2010 cost goal of $5/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**

Additional Required Information

Publications and Presentations

- DOE Review Meeting Presentation
- DOE reports
- "Palladium-Alloy Based Membrane Reactor Process for Hydrogen Generation" abstract submitted to 2005 Fuel Cell Seminar

Hydrogen Safety

- **The most significant hydrogen hazard associated with this project is:**

  Failure to contain flammable and toxic gases, including hydrogen and especially CO

Hydrogen Safety

- **Our approach to deal with this hazard is:**
  - Ensure that the test, pilot, and commercial units are designed properly to prevent leaks and that any accidental leak is properly directed to a safe location
  - Test facilities are equipped with CO and flammable gas detection equipment
  - Tests are done at elevated pressure to ensure that air will not enter the system
  - Conduct safety reviews for all experimental setups
  - Follow all applicable external and internal standards
  - Identify and mitigate potential risks as testing progresses
  - Incorporate safety information in component design
- **FMEA or HAZOP will be performed after detailed PFD for pilot system is defined**