Integrated Ceramic Membrane System for H_2 Production

Cooperative Agreement: DE-FC36-00GO10534

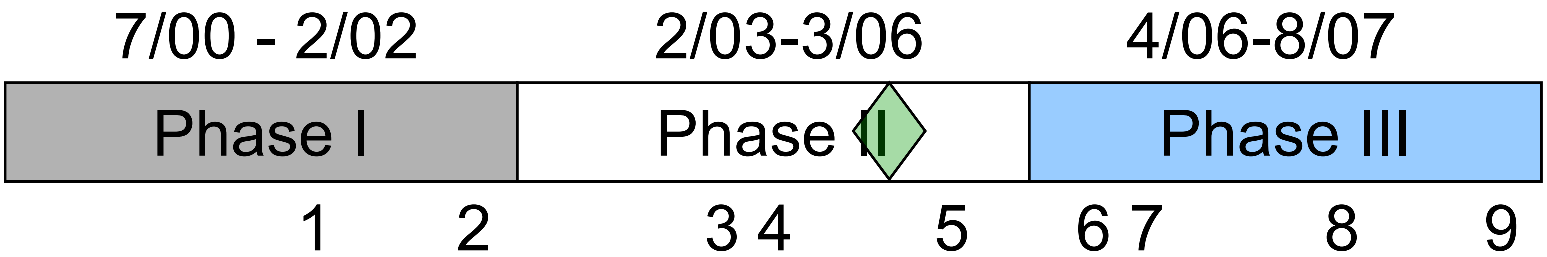
Joe Schwartz
Ray Drnevich
Prasad Apte
Praxair - Tonawanda, NY

Ashok Damle
Research Triangle Institute
Research Triangle Park, NC

DOE Annual Merit Review Meeting
May 24, 2005

Project PDP3

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

PRAXAIR

- **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

- 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

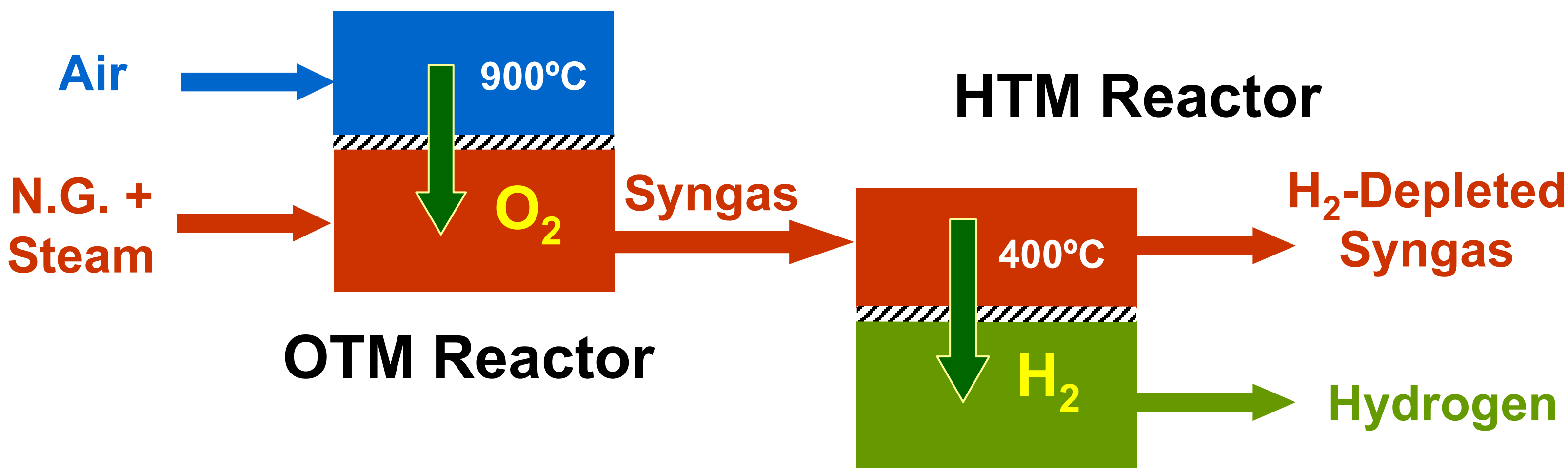
Phase IIB Plan

- **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



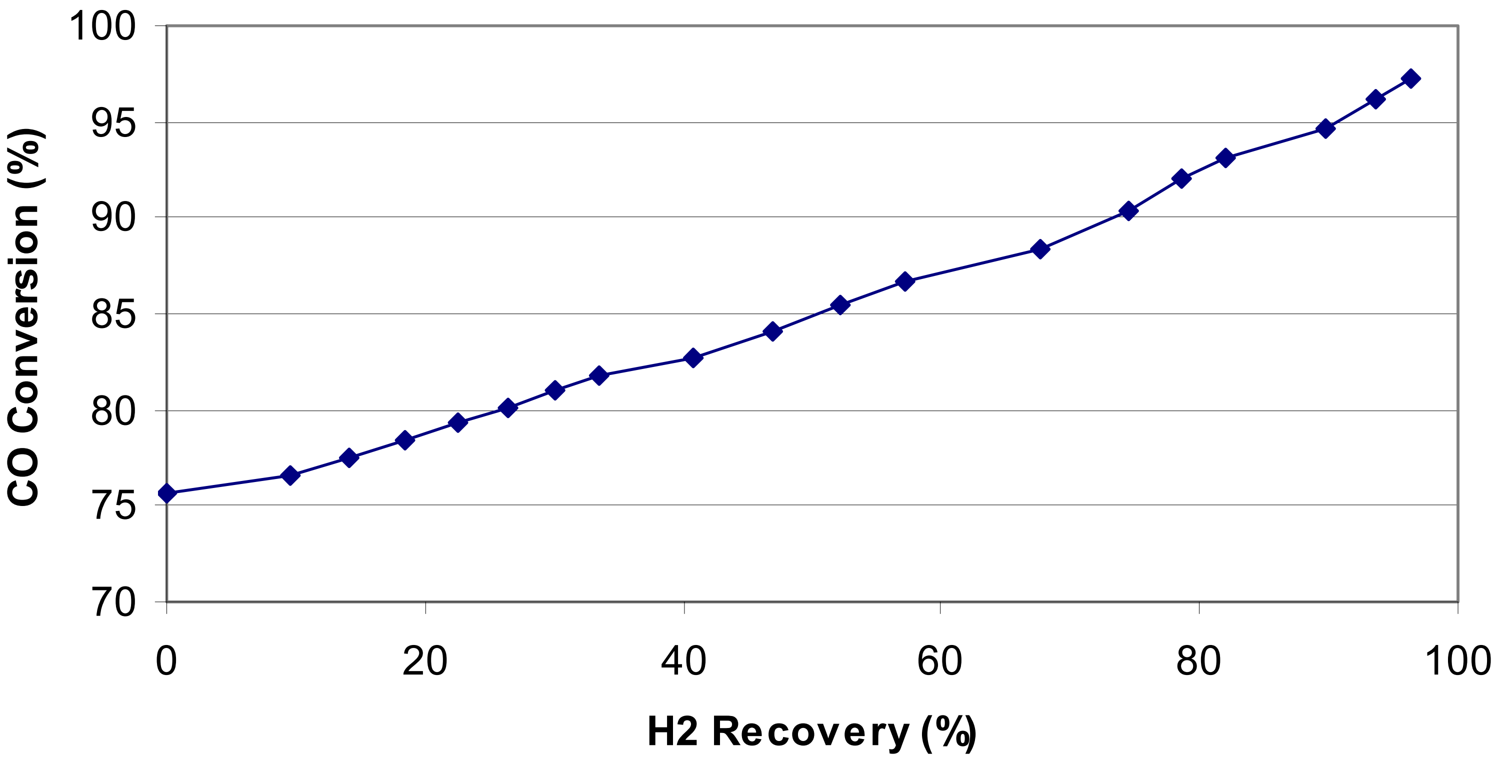
OTM Reactor

- Synthesis gas generation
- $CH_4 + ½\ O_2 \rightarrow 2\ H_2 + CO$
- $CH_4 + H_2O \rightarrow 3\ H_2 + CO$

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**

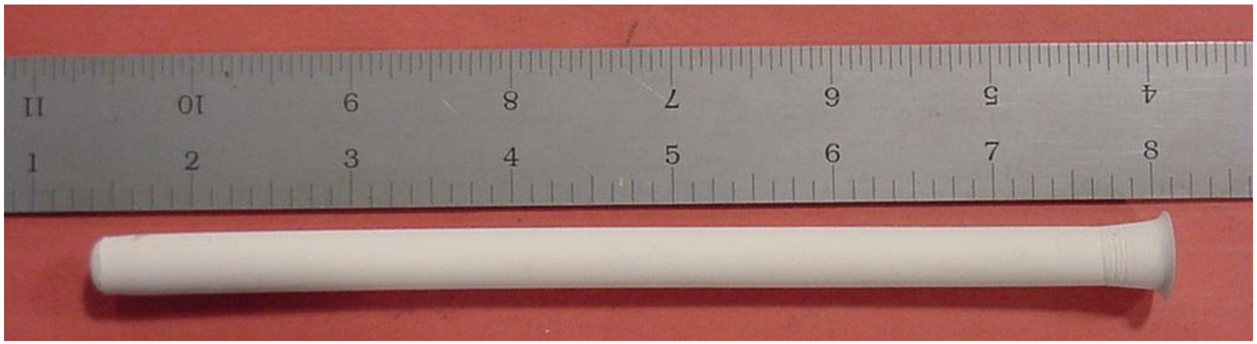
  HTM/WGS at 400ºC, 150 psig, syngas composition from OTM module

Palladium Membrane Targets

	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

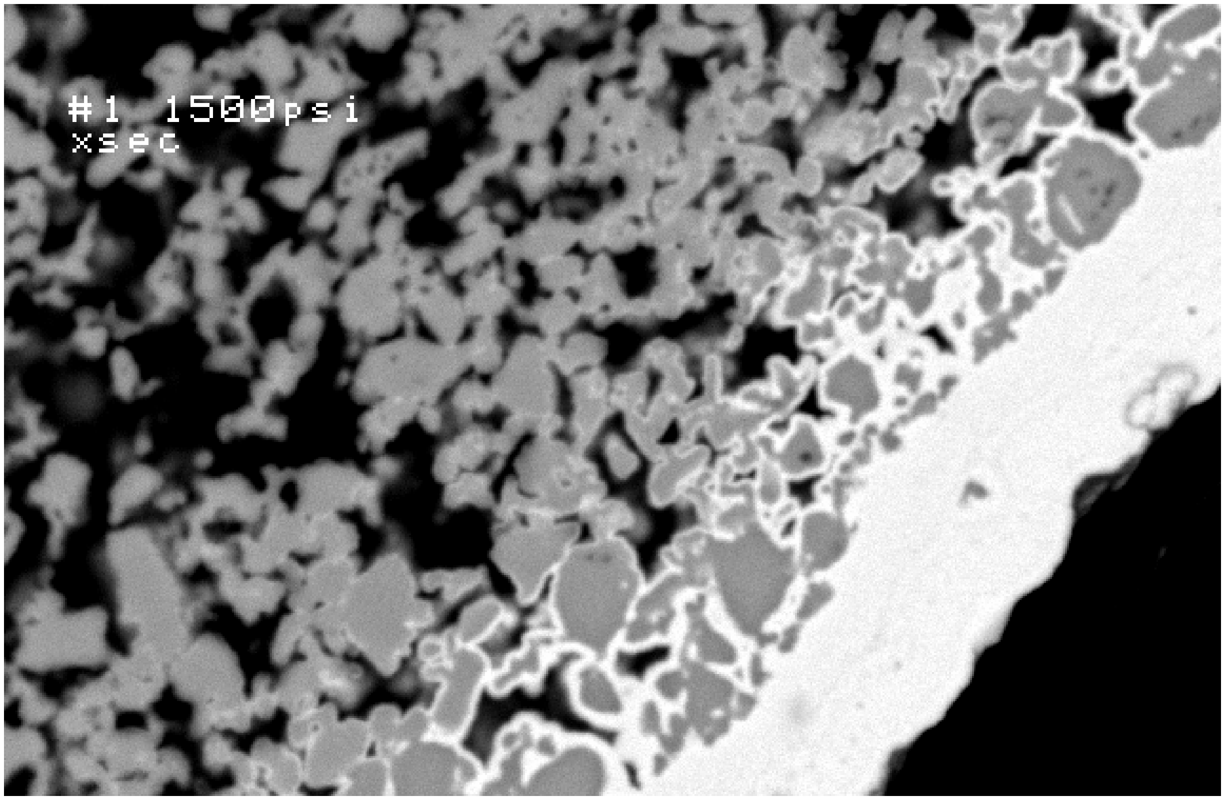
- **Flux based on 20 psid hydrogen pressure at 400ºC**
- **$/scfh is our most important consideration - $5/scfh in 2010**

Low-Cost Ceramic Substrate



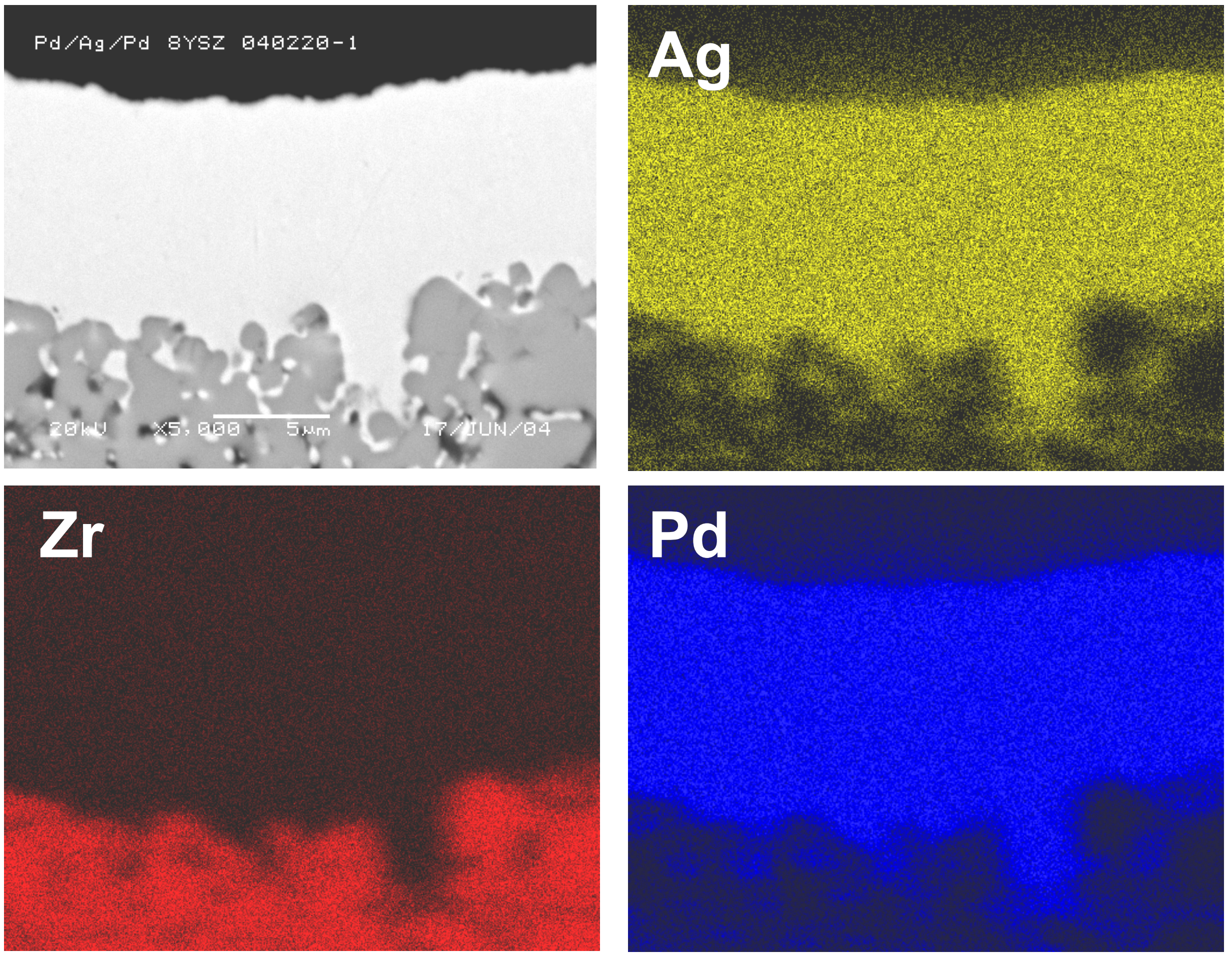
- Modified zirconia designed to match thermal expansion of palladium alloy and to have high strength and stability
- Layered structure produced using Praxair's patented isopressing technique for producing porous ceramics
- Layer adjacent to membrane has smallest pore size
- Closed-end tube allows for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

Pd-Ag Film Structure



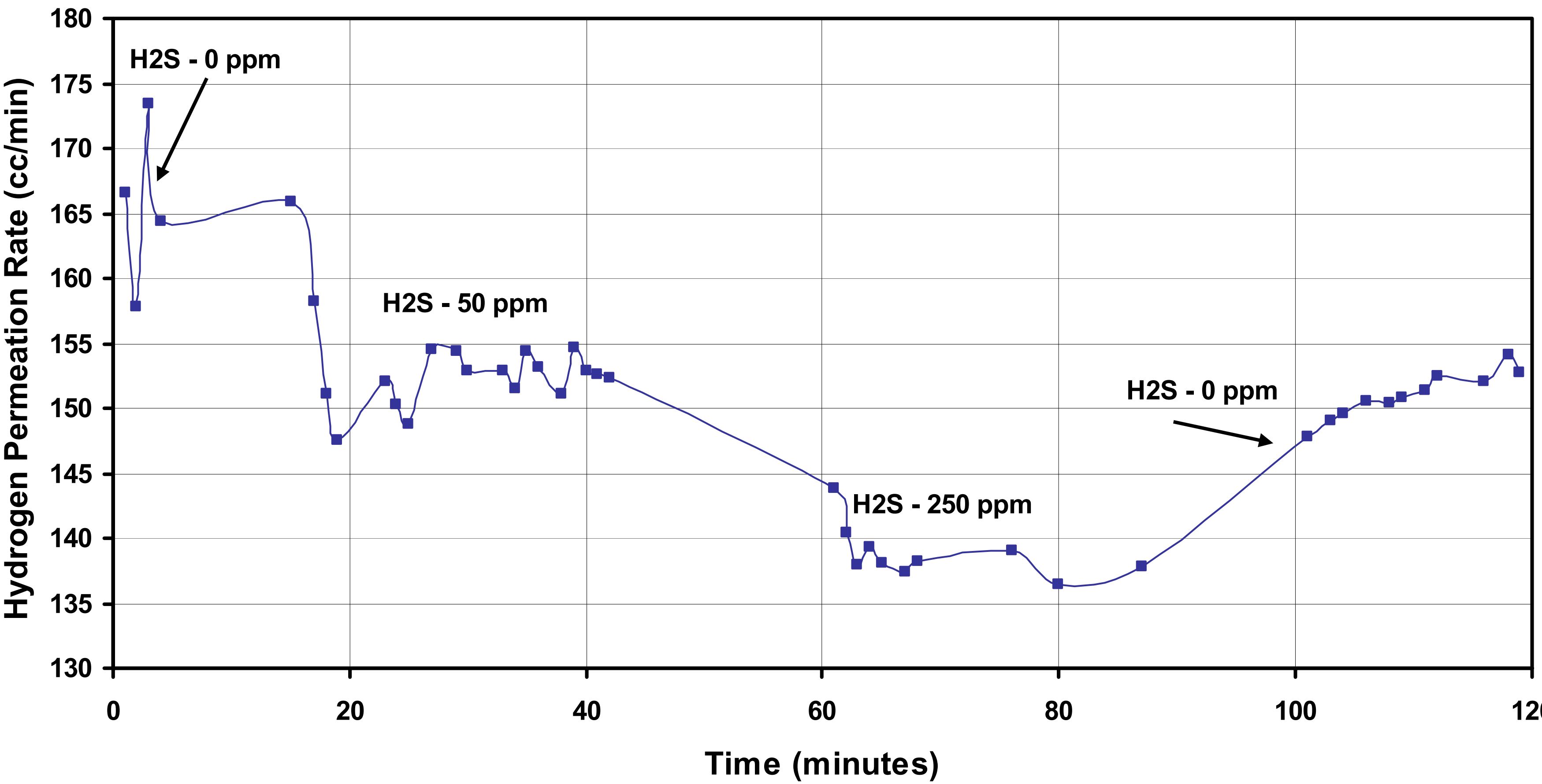
- Surface treatments produced very small surface pores and larger pores in the bulk layer

Membrane Composition



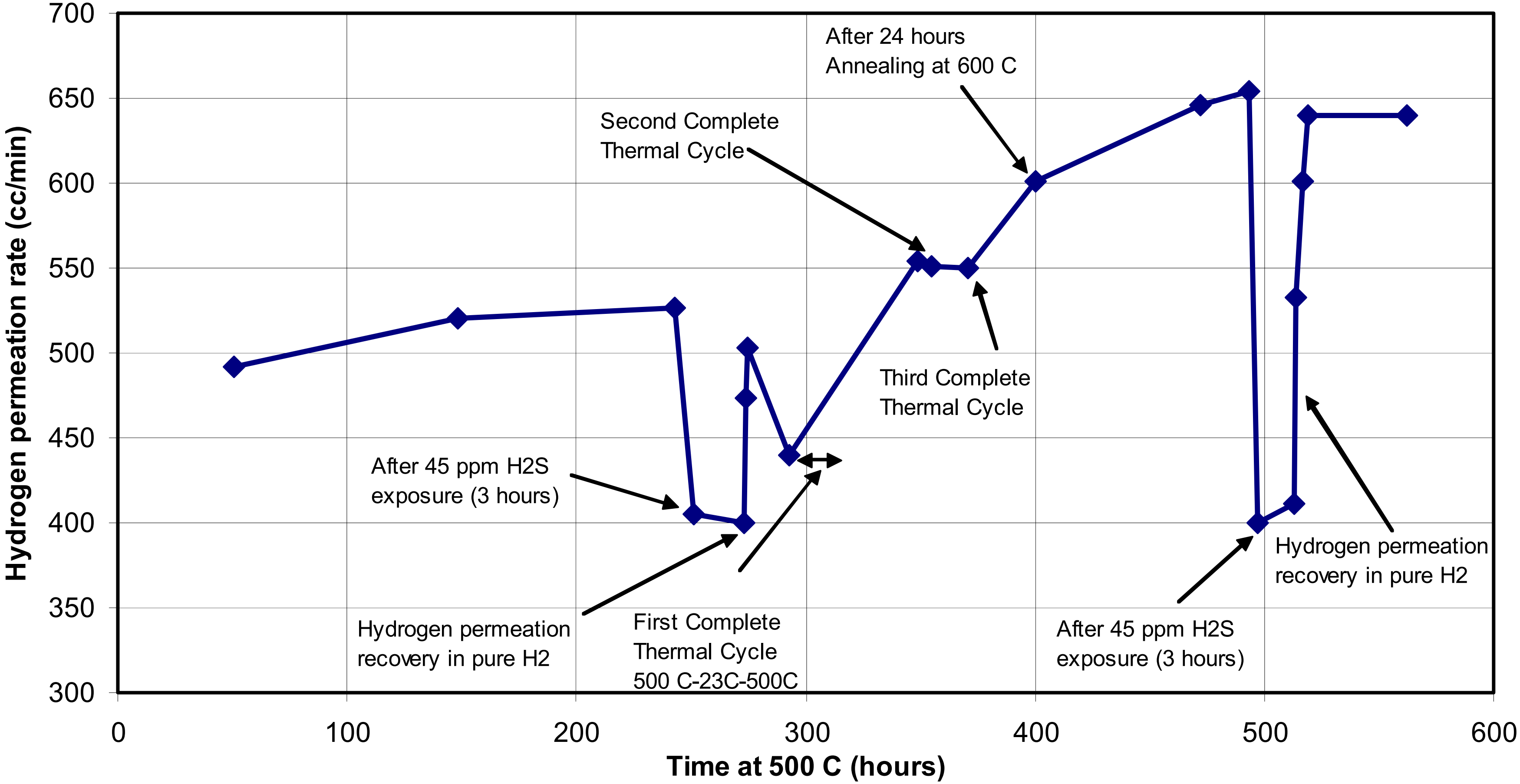
- Ag and Pd mixed well and penetrated enough to adhere

Effect of H_2S on Pd-Cu



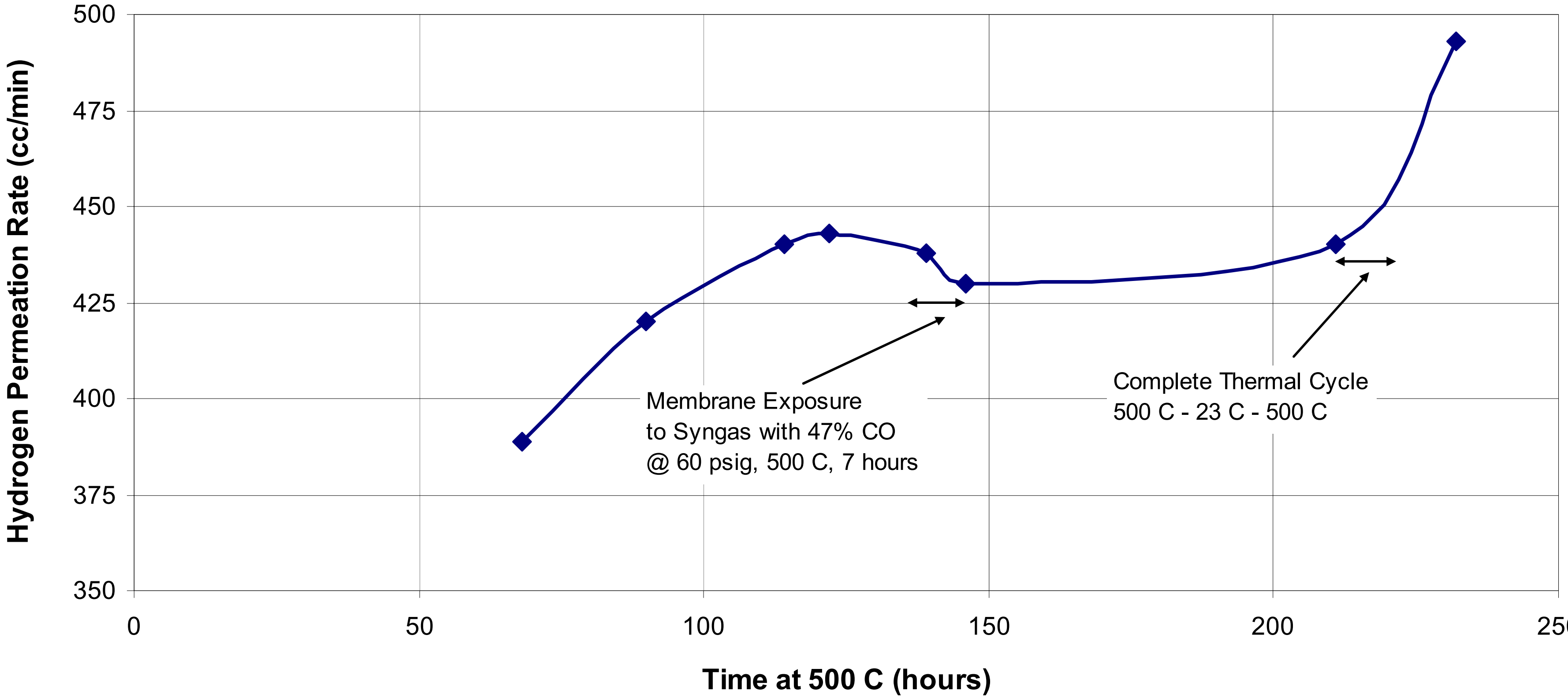
- H_2S reduced flux within minutes
- Most of lost performance was recovered when H_2S was removed

Effect of H_2S on Pd-Ag



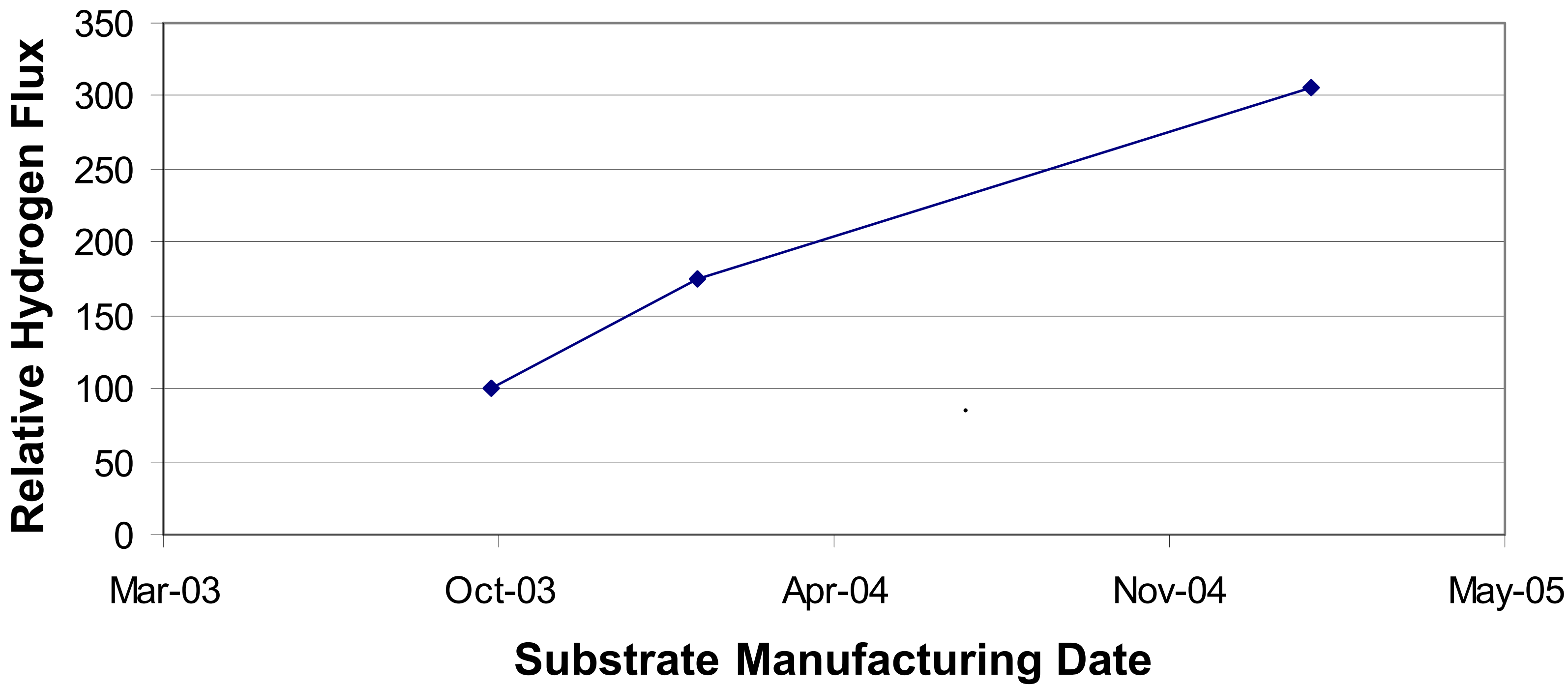
- **Excellent response to thermal and compositional cycling**

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

- **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

PRAXAIR

- 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**