Integrated Ceramic Membrane System for H_2 Production

Cooperative Agreement: DE-FC36-00GO10534

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Objectives

- **Program - Develop a low-cost reactive membrane based hydrogen production system**
  - Use existing natural gas infrastructure
  - High thermal efficiency
  - Transportation and industrial markets

- **Phase IIA - Develop a cost-effective hydrogen transport membrane (HTM)***
  - Produce Pd-based HTM
  - Low-cost hydrogen separation and purification
  - Demonstrate HTM performance in non-reactive environments

* The OTM is under development outside of this program

Budget

	Phase I	Phase IIA	Total	FY2004
DOE	$224,679	$371,869	$596,548	$116,941
Praxair	$ 74,893	$123,957	$198,850	$38,980
TOTAL	$299,572	$495,826	$795,398	$155,922

FY2004 spending through March 31, 2004

DOE Technical Barriers

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance (O&M)
- C. Feedstock and Water Issues
- E. Control and Safety
- Z. Catalysts
- AA. Oxygen Separation Technology
- AB. Hydrogen Separation and Purification

Palladium Membrane Targets

PRAXAIR

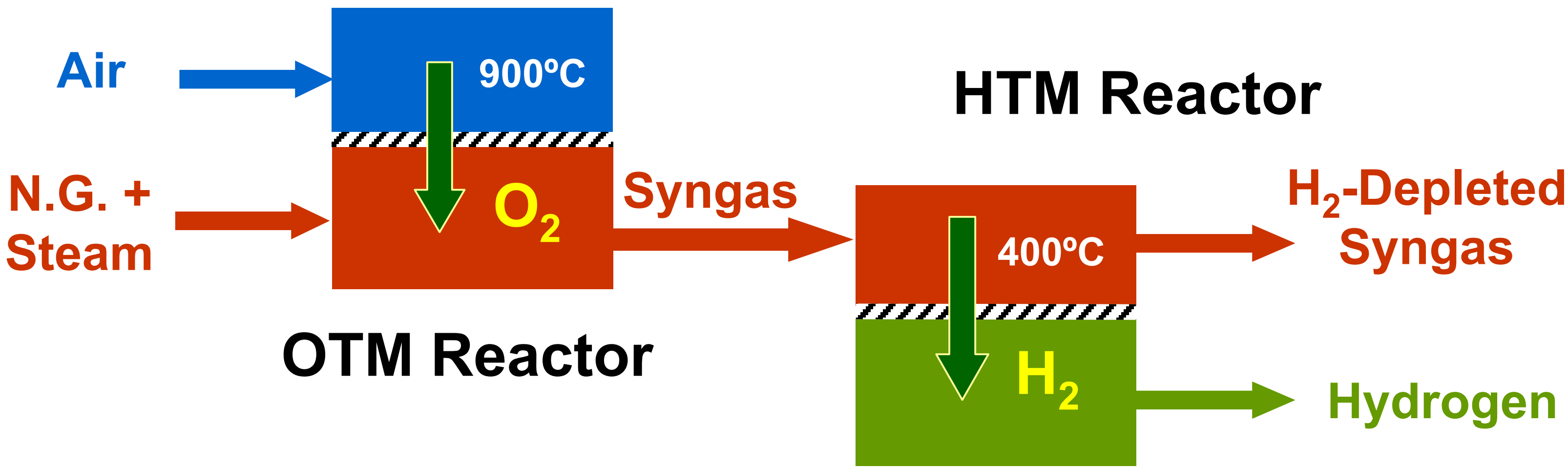
	2003	2005	2010
Flux (scfh/ft^2)	60	100	200
Cost (\$/ft^2)	150-200	100-150	< 100
Durability (hrs)	< 1000	50,000	100,000
Operating Temp (ºC)	300-600	300-600	300-600
Parasitic Power (kWh/1000 scfh)	3.2	3.0	2.8

- Flux based on 20 psid hydrogen pressure at 400ºC
- Parasitic power based on hydrogen compression to 200 psi

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

OTM/HTM Concept
Preferred Process - Sequential Reactors



OTM Reactor

Synthesis gas generation

$CH_4 + \frac{1}{2} O_2 \rightarrow 2 H_2 + CO$

$CH_4 + H_2O \rightarrow 3 H_2 + CO$

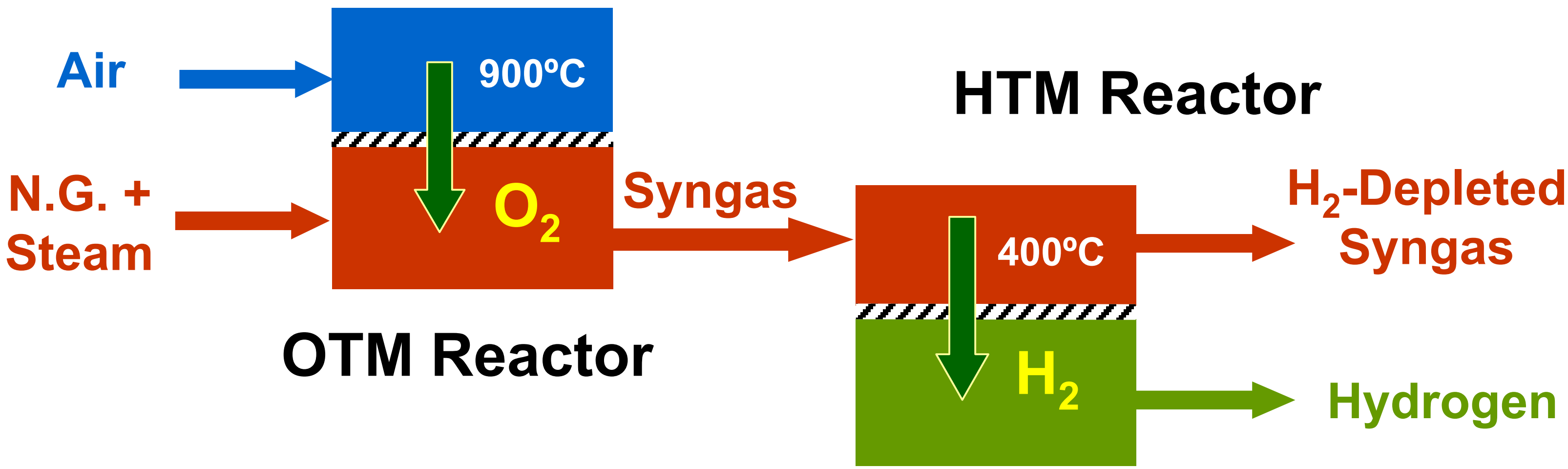
HTM Reactor

Water-gas shift reaction

$CO + H_2O \rightarrow H_2 + CO_2$

Hydrogen Separation

OTM/HTM Concept
Preferred Process - Sequential Reactors



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HTM Reactor

Water-gas shift reaction

$CO + H_2O \rightarrow H_2 + CO_2$

Hydrogen Separation

Phase IIA Plan

- **Select Substrate**
  - Strength, Thermal Expansion Match
  - Metal or Ceramic
- **Select Alloy**
  - Flux, Life, Cycling, Contaminant Resistance (S, CO, …)
- **Membrane Testing**
  - Confirm Performance in Simulated Syngas Environment
- **Process Economics**
  - Confirm Membrane is Cost-Effective
- **Phase IIB and Phase III Plan**

Project Safety

- Safety reviews conducted for all equipment
- All applicable external and internal standards followed
- Potential safety issues will be identified as testing progresses
  - Incorporate safety information in component design
- FMEA or HAZOP to be performed after detailed PFD is defined

Program Timeline

7/00 - 2/02	2/03-8/05	9/05-12/06
Phase I	Phase II	Phase III

1 2 3 4 5 6 7 89

- **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

Accomplishments and Progress

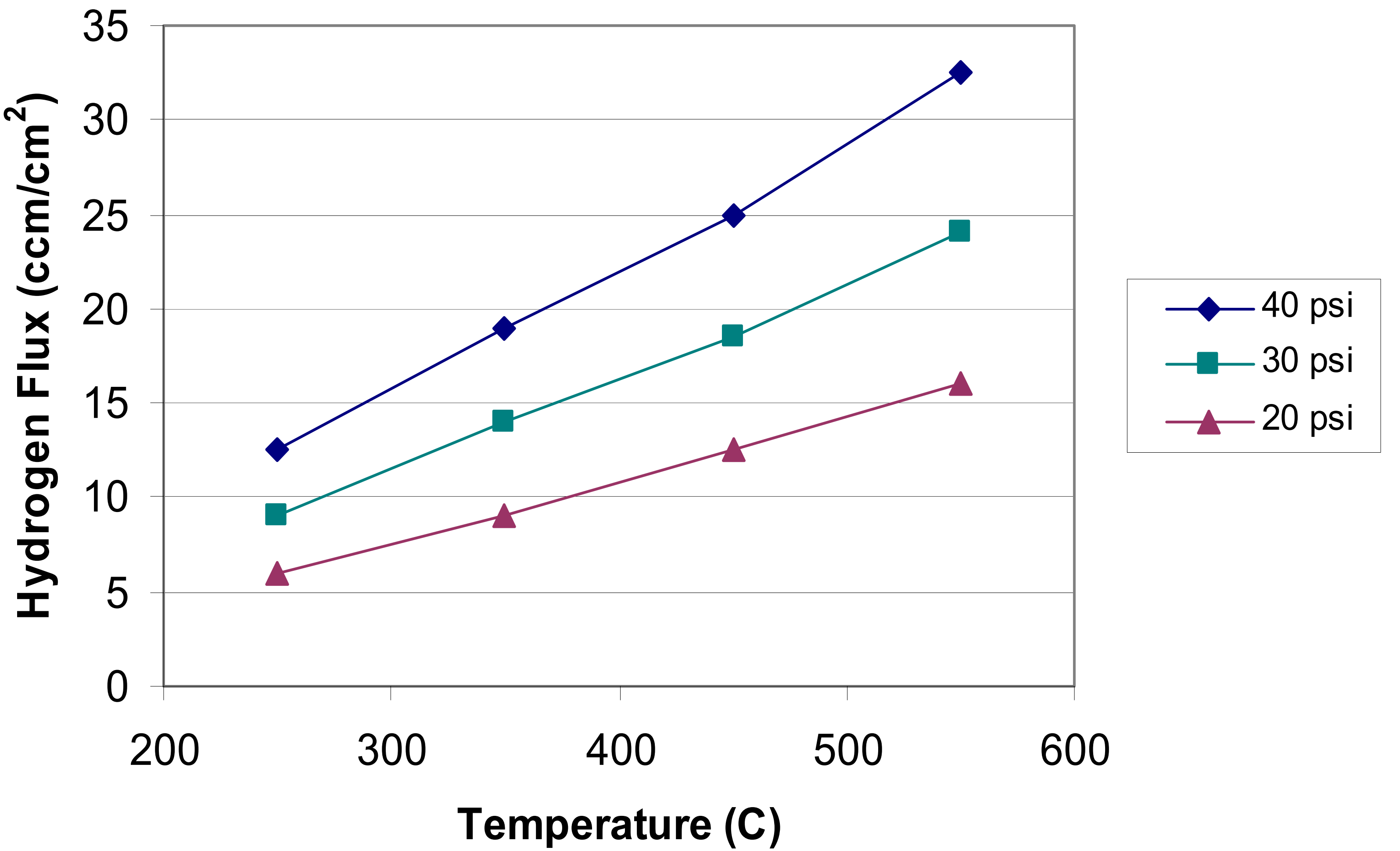
- **Pd-Ag alloy composite membrane tubes produced that are leak tight with reasonable flux**
- **First successful test in September**
- **Flux has almost doubled in the last 5 months**
- **Pore size decreased from > 50 μm to < 5 μm**
- **Alloy and substrate optimization in progress**
- **Initial economic analysis looks promising**
  - Pd/Ag cost for 2000 scfh H_2 production is under $2500 for 10-$\mu$m film

Substrate Progress

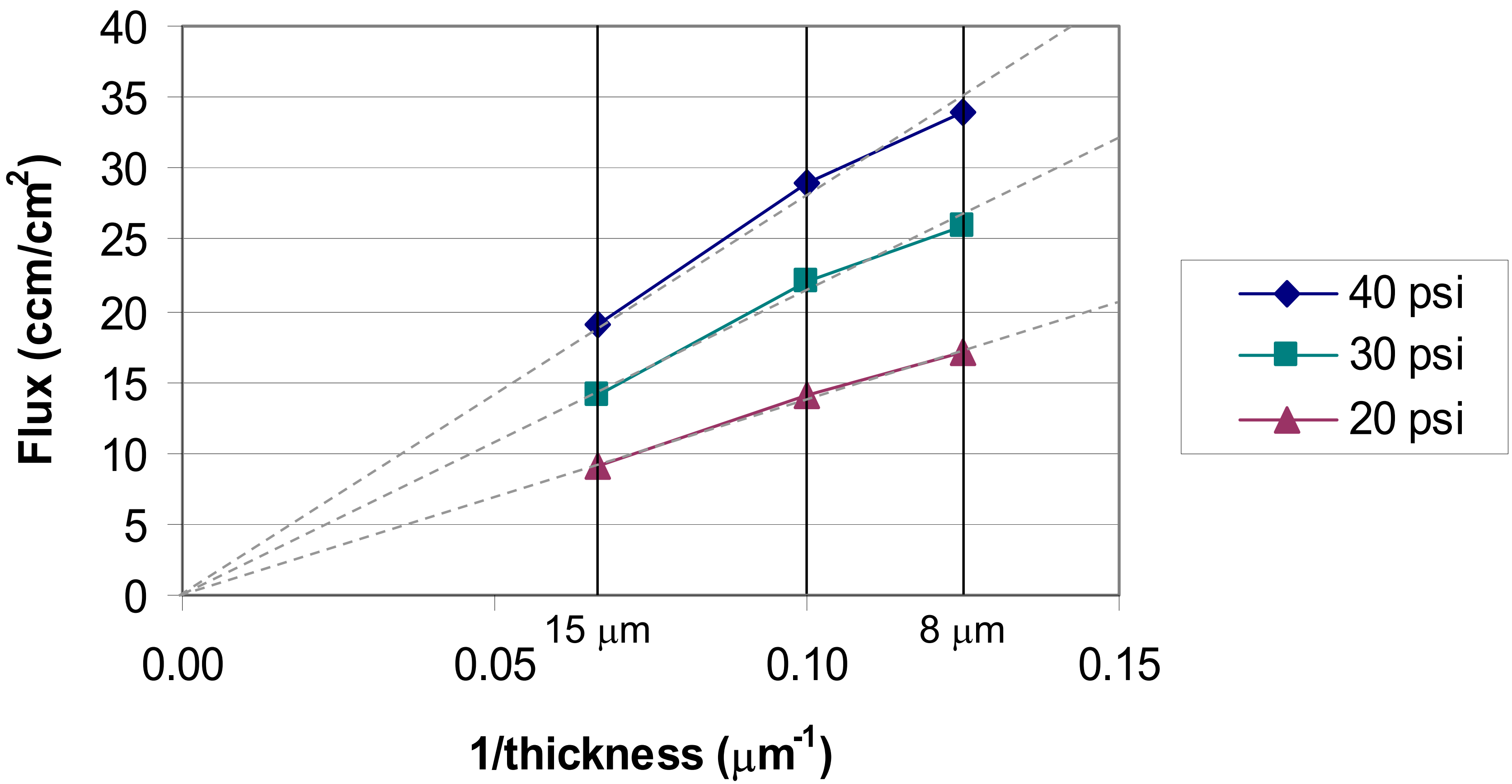
Substrate Fabrication Date	Pore Size (μm)	Nitrogen Leak Rate, 25ºC (ccm/cm^2)	Hydrogen Flux 40 psi 550ºC (ccm/cm^2)
Feb 2003	> 50		N/A
Mar-Apr	50		N/A
Apr-Jun	20	20 at 10 psid	N/A
Jun-Aug		3 at 5 psid	N/A
Sep-Nov	5-10	1 at 30 psid	18.8
Dec-Mar	< 5	< 1 at 30 psid	33

- **Progressive changes in pore former and fabrication method have enabled significant reduction in pore size, and corresponding film thickness**

Palladium Membrane Flux



Palladium Membrane Flux



- **Further substrate improvement is necessary**
  - Film needs to be less than 2 μm to meet target flux

Accomplishments vs. Targets

	Current	2005	Next Step
Flux (scfh/ft^2)	22	100	Improve substrate and coating
Cost (\$/ft^2)	150	100-150	Decrease substrate and coating costs
Durability (hrs)	> 200	50,000	Conduct life test
Operating Temp (ºC)	300-600	300-600	none
Parasitic Power (kWh/1000 scfh)	3.2	3.0	H_2 compression outside current program

- Flux based on 20 psid hydrogen pressure at 400ºC

Future Work (2004-05)

- **Complete Phase IIA**
  - Demonstrate Pd membrane performance in non-reactive environment
  - Confirm that the OTM/HTM system can produce hydrogen at low cost

- **Start Phase IIB**
  - Demonstrate Pd membrane performance in single tubes integrated with water gas shift reaction
  - Confirm that the OTM/HTM system can produce hydrogen at low cost

Interactions and Collaborations

- **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

2003 Questions

- **Main weakness sited was lack of hard data**
  - Testing has now begun and data were presented
- **2003 Recommendation - Add partners to help with pretreatment and reforming**
  - Phase II focuses on HTM development
  - We are considering adding a partner to help with WGS catalyst

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Questions?

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