Novel Hydrogen Purification Device Integrated with PEM Fuel Cells

NETL Hydrogen Separation Project Review - April 29, 2008

Joe Schwartz

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Project Structure

- **Praxair**
  - Substrate development, membrane coating and testing, economic evaluation, prototype design and testing, program management
- **Colorado School of Mines**
  - Membrane coating, testing, and modeling
- Praxair Surface Technologies
  - Substrate manufacturing, alloy deposition
- Boothroyd-Dewhurst
  - Design for Manufacturing and Assembly
- Fuel Cell Manufacturer
  - Consulting role for prototype development and testing

Organizations and Performers – Phase I

- **Prime Contractor – Praxair**
  - Joe Schwartz
  - Hankwon Lim
- **Subcontractor – Colorado School of Mines**
  - Doug Way
  - Sabina Gade
  - Mark Lusk
  - Amanda Lewis
  - Paul Thoen
- **DOE**
  - Dan Cicero
  - Patricia Rawls
  - Bonnie Dowdell

Project Budget

	DOE	Praxair	TOTAL
Year 1	$ 366,011	$ 91,503	$ 457,514
Year 2	$ 439,066	$ 109,766	$ 548,832
Year 3	$ 432,402	$ 108,101	$ 540,503
TOTAL	$ 1,237,479	$ 309,370	$ 1,546,848

Start Date – June 14, 2007
CSM Subcontract Signed – October 17, 2007
End Date – September 30, 2010

Project Objective

- Develop a hydrogen purification device that can reduce the cost of supplying sufficiently high purity hydrogen to PEM fuel cells
- Integrate the device with the fuel cell to minimize total cost and provide maximum benefit

Work Breakdown Structure

- Membrane Development
- Substrate Development
- Computer Modeling
- Membrane Performance Testing
- Economic Evaluation
- Prototype Design and Testing

Project Schedule

Critical Path	2007	2008				2009				2010		
Task	4Q	1Q	2Q	3Q	4Q	1Q	2Q	3Q	4Q	1Q	2Q	3Q
4.1 - Design membrane test unit												
4.3 - Conduct membrane flux tests												
4.4 - Conduct membrane durability tests												
M1 - Demonstrate membrane flux and cyclability					M							
M2 - Demonstrate economic potential					M							
6.1 - Develop preliminary purifier design												
M3 - Develop conceptual design								M				
M4 - Demonstrate conceptual design economics								M				
6.6 - Develop detailed design												
6.7 - Construct prototype												
M5 - Construct prototype										M		
6.8 - Prototype testing												
M6 - Demonstrate prototype performance												M

Project Background

- PEM fuel cells need hydrogen at higher purity than is typically supplied
- Praxair has substantial hydrogen supply and expertise in hydrogen purification
- Palladium membranes produce hydrogen with sufficient purity

Hydrogen Purity Specifications (ppm)

Impurity	Industrial	ISO WG 12
Water	34	5
Hydrocarbons	10	2
Oxygen	10	5
He, Ar, N_2	100	100
CO_2	10	2
CO	10	0.2
Sulfur		0.004
HCHO		0.01
HCOOH		0.2
NH_3		0.1
Halogens		0.05

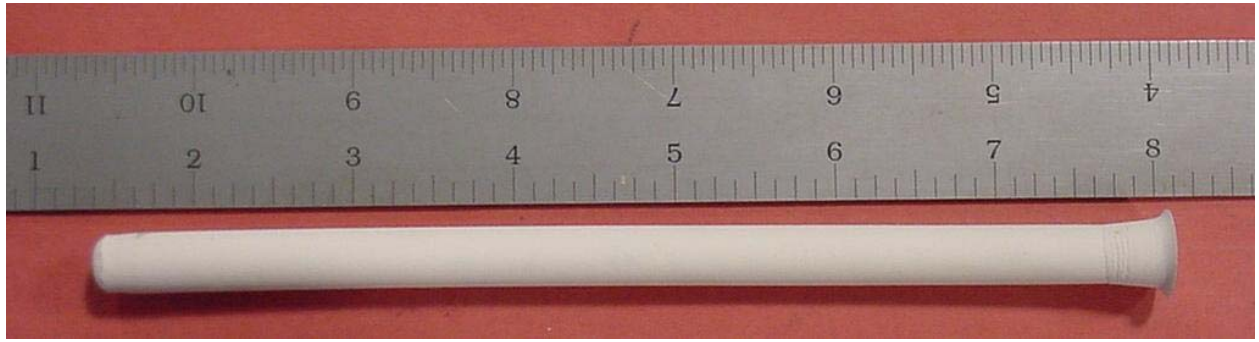
Yield increases as purity decreases

Cost decreases as yield increases

Technology Description

- Supply industrial purity (or preferably much lower) hydrogen to PEM fuel cells
  - Reduce cost of hydrogen supply
  - Increase hydrogen yield from production unit
- Palladium membrane cleans up impurities introduced anywhere in the supply chain
  - Pd membranes used in laboratory purifiers today

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 of Pd followed by Au

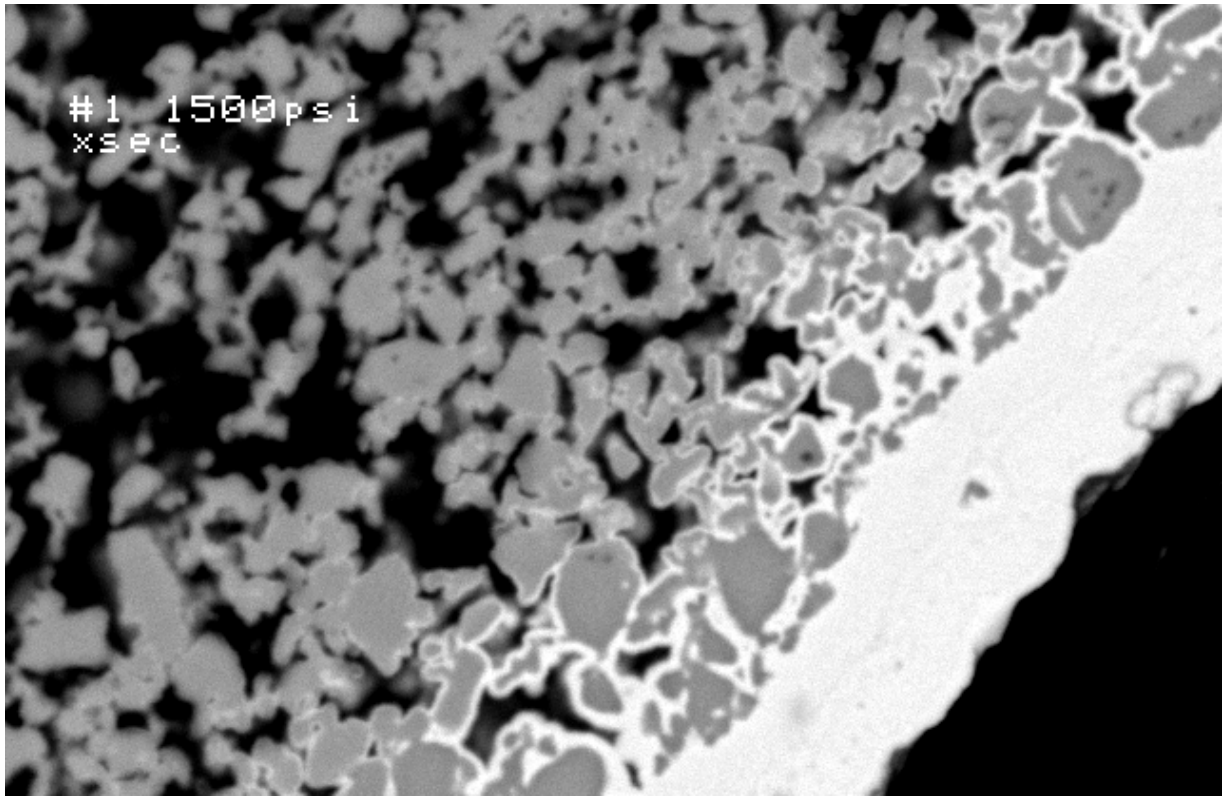
Metal Deposition by Electroless Plating

- Support is seeded with Pd nanocrystallites to catalyze electroless plating reaction:

$$2Pd(NH_3)_4^{++} + N_2H_4 + 4OH^- \longrightarrow$$
$$2Pd^0 + 8NH_3 + N_2 + 4H_2O$$

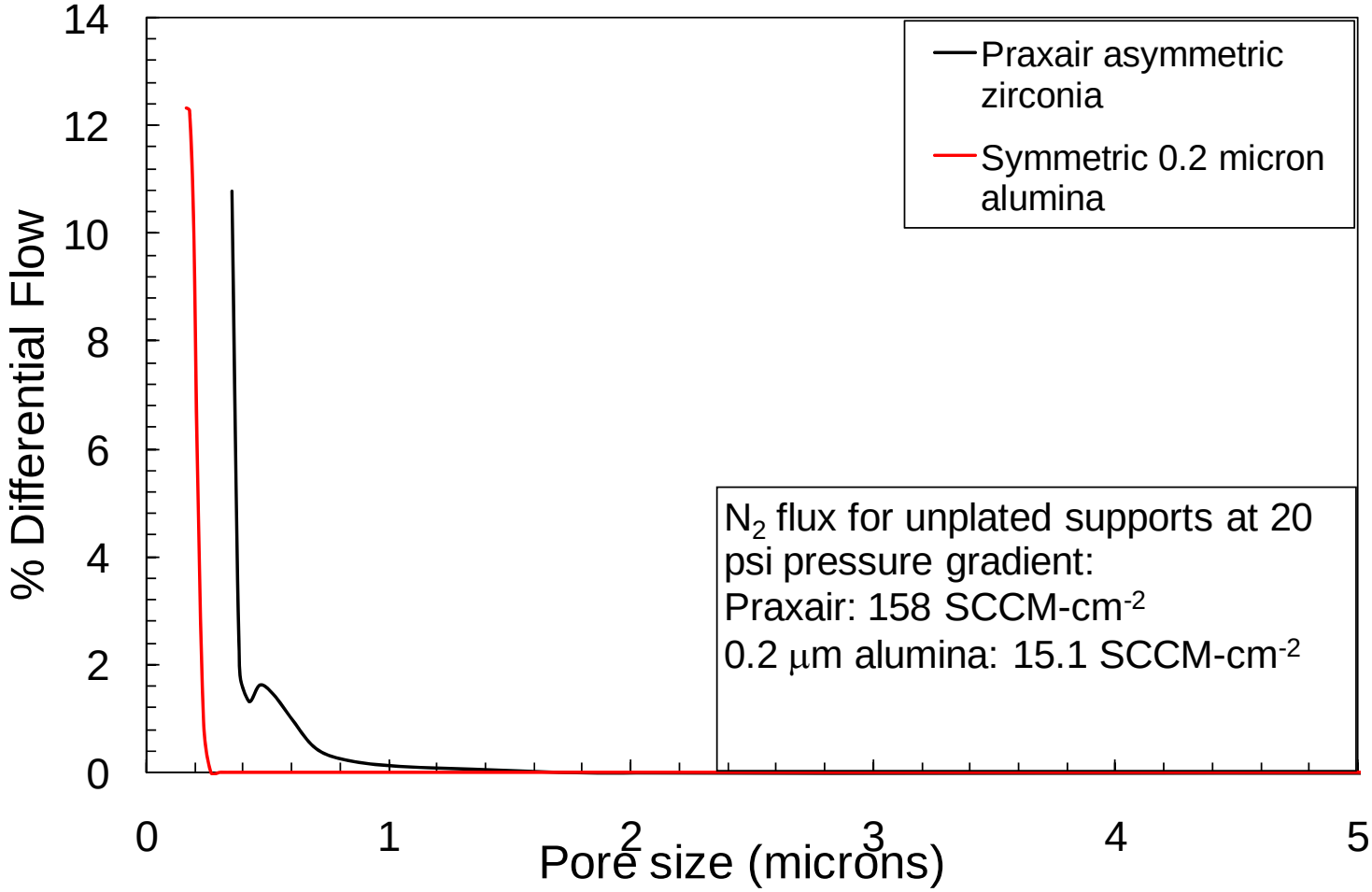
- Flowing plating solution over support minimizes bubble aggregation on surface and improves film quality

Pd-Ag Film Structure



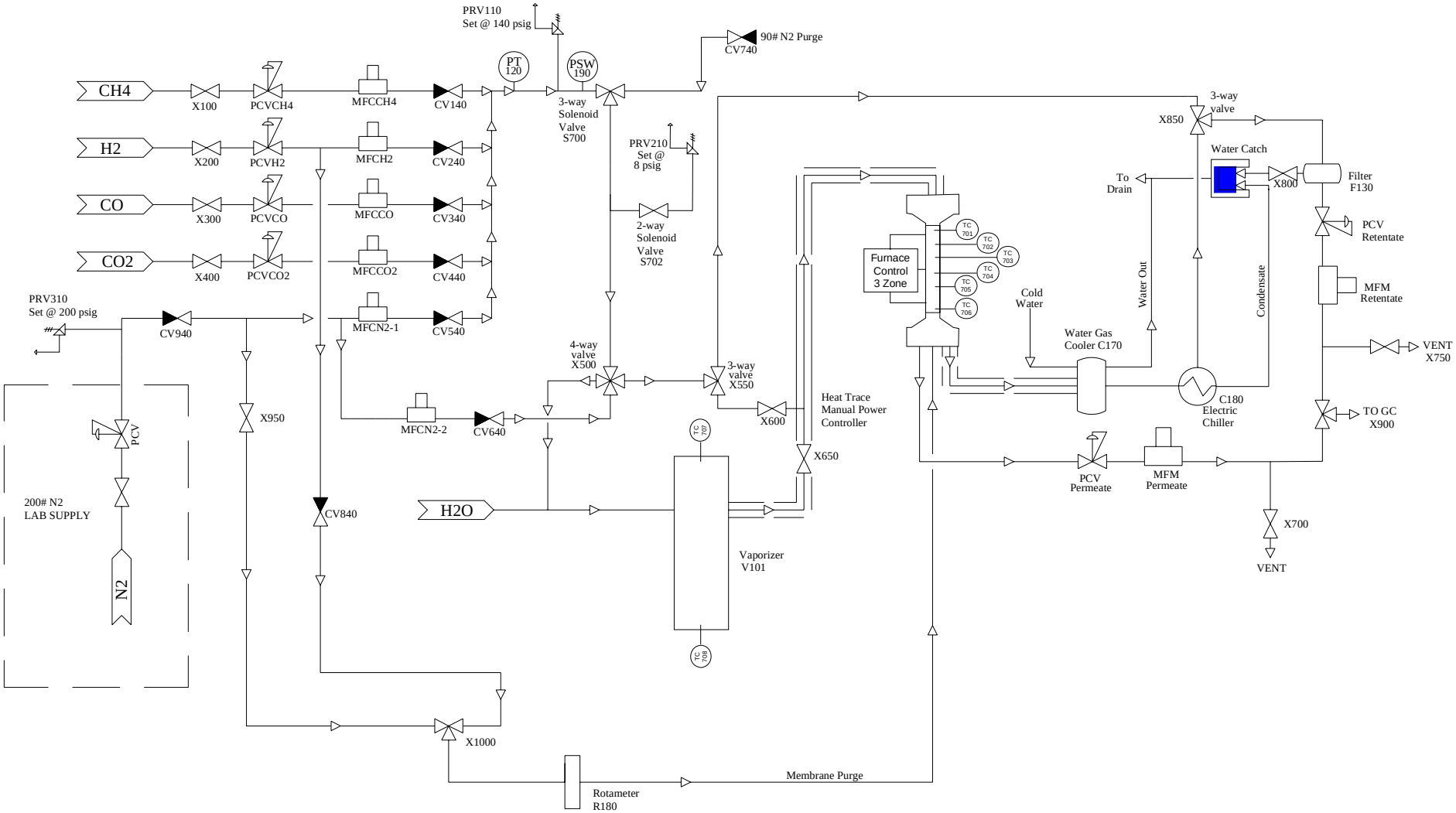
- Surface treatments produced very small surface pores compared to larger pores in the bulk layer

Substrate Pore Size Distribution

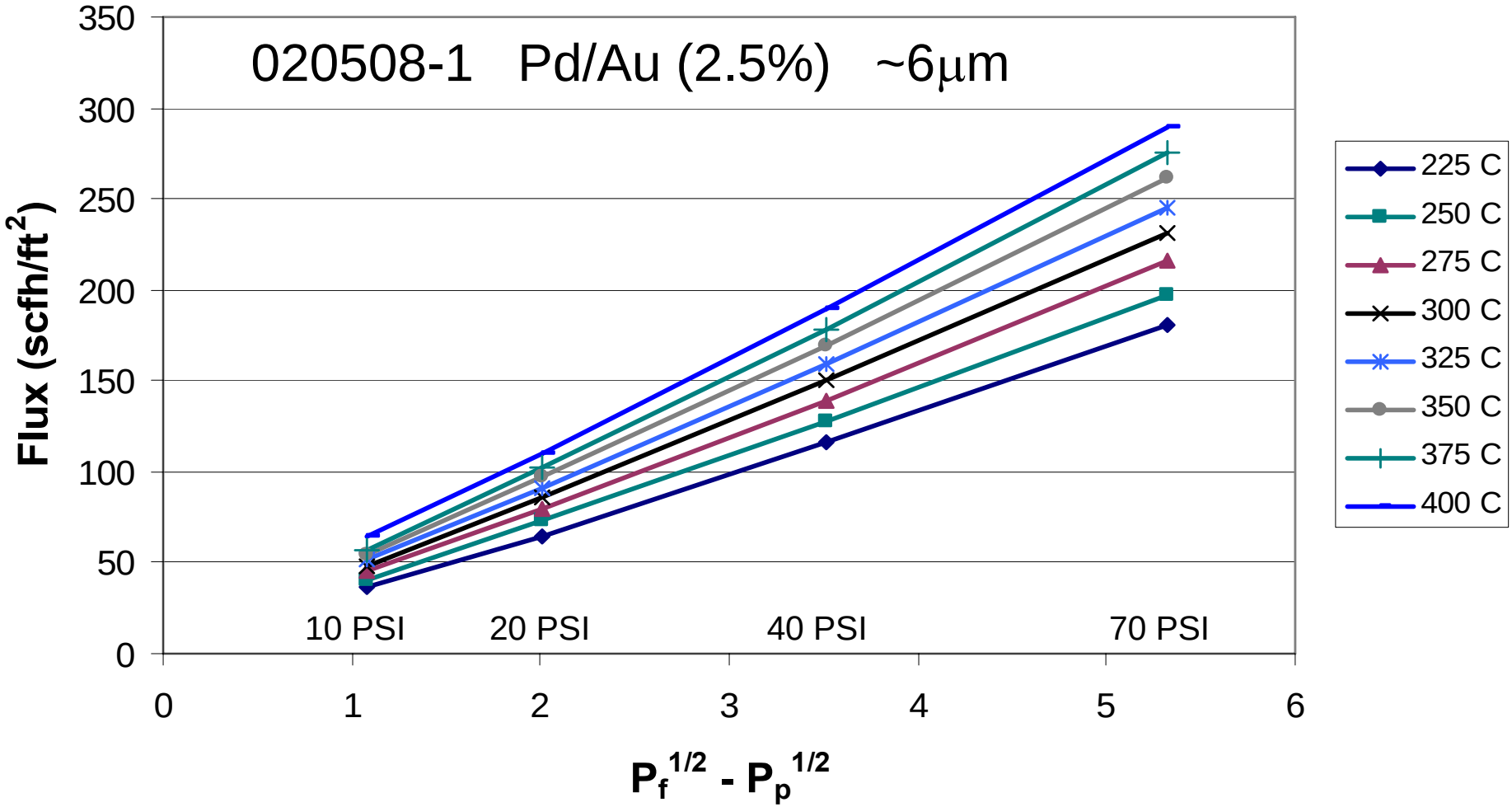


- Substrate must have small pores to enable a thin alloy membrane to cover the pores without leaks

Test Apparatus

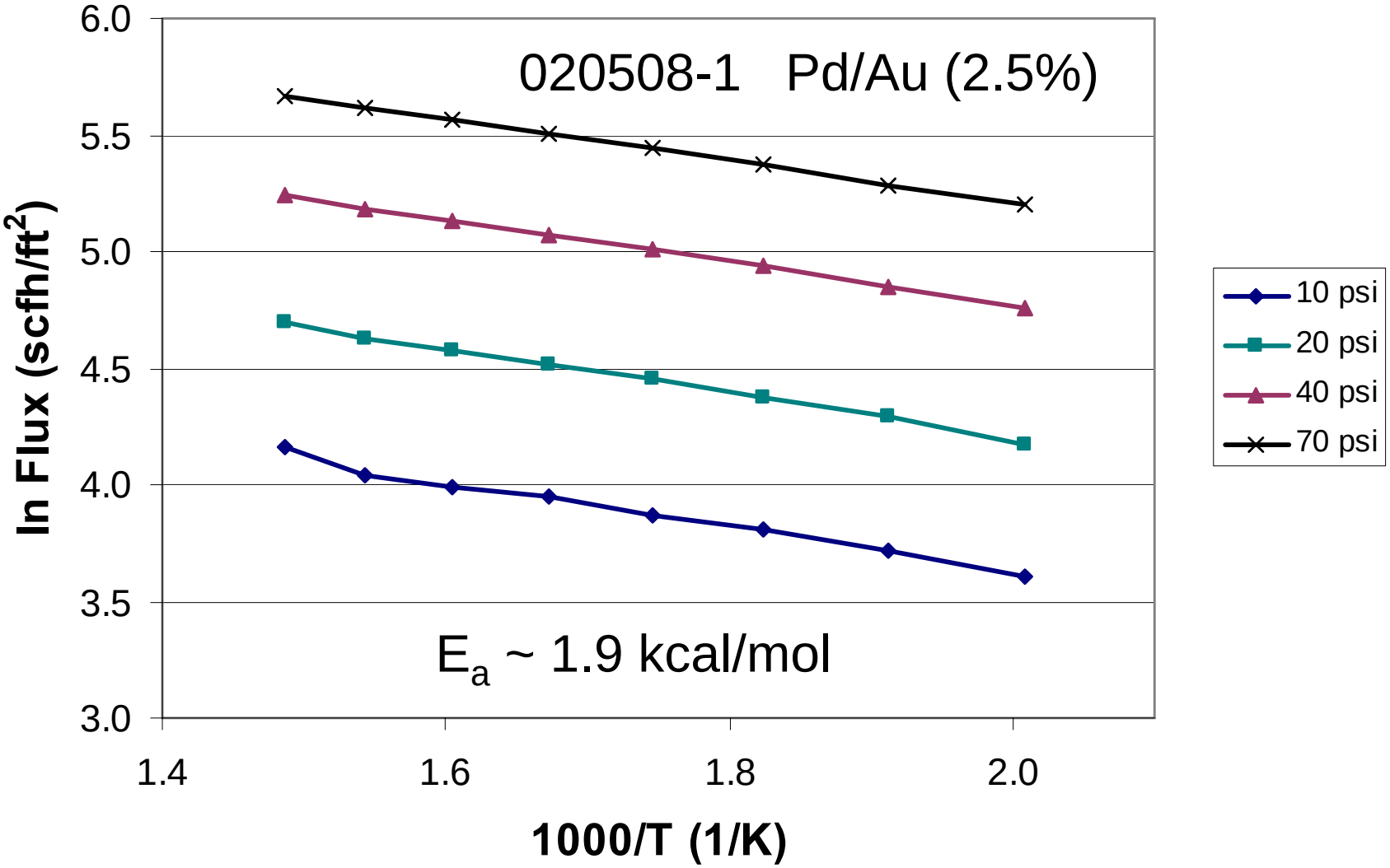


Hydrogen Flux

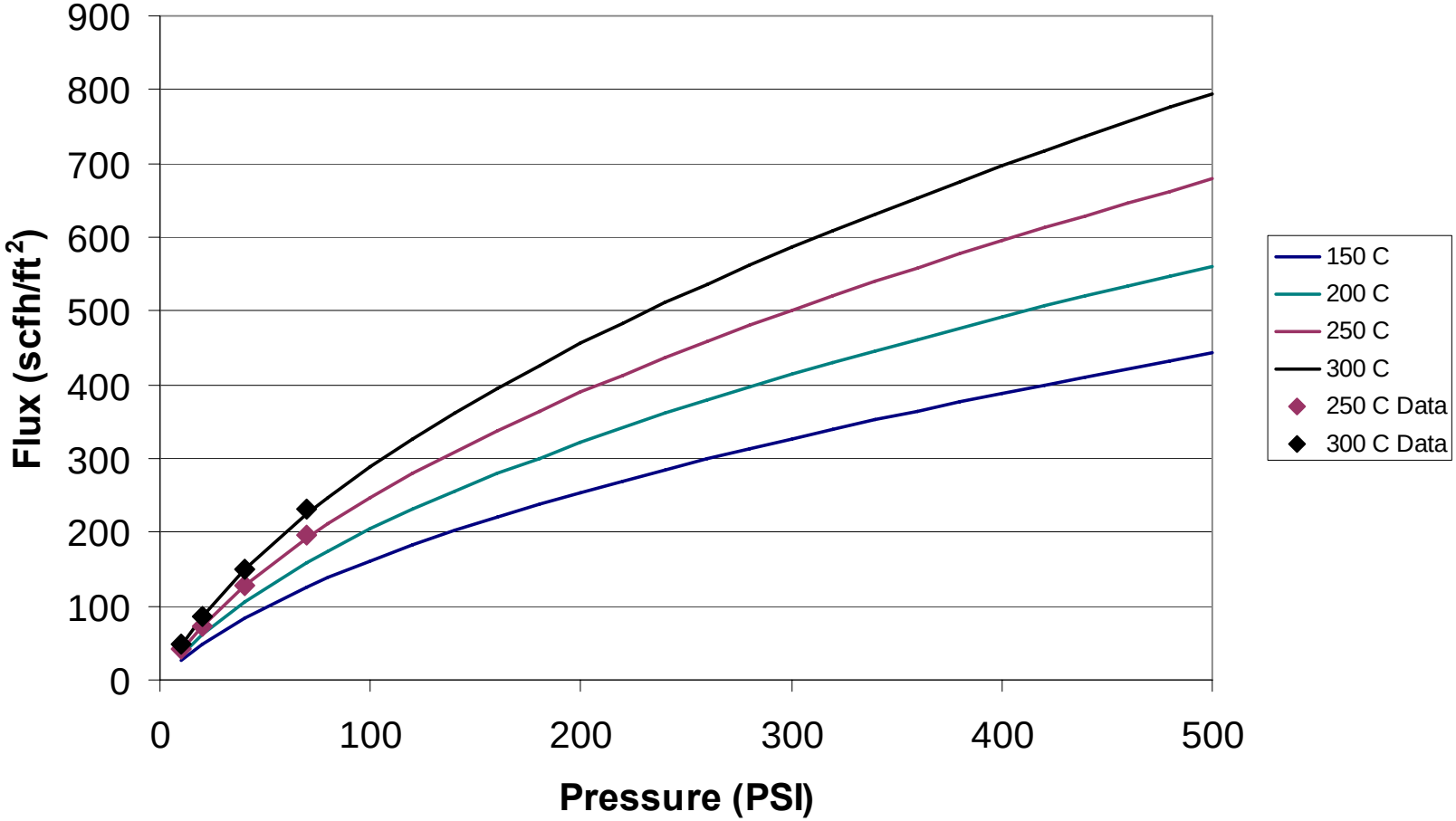


- System could operate at 200 PSID or higher

Hydrogen Flux

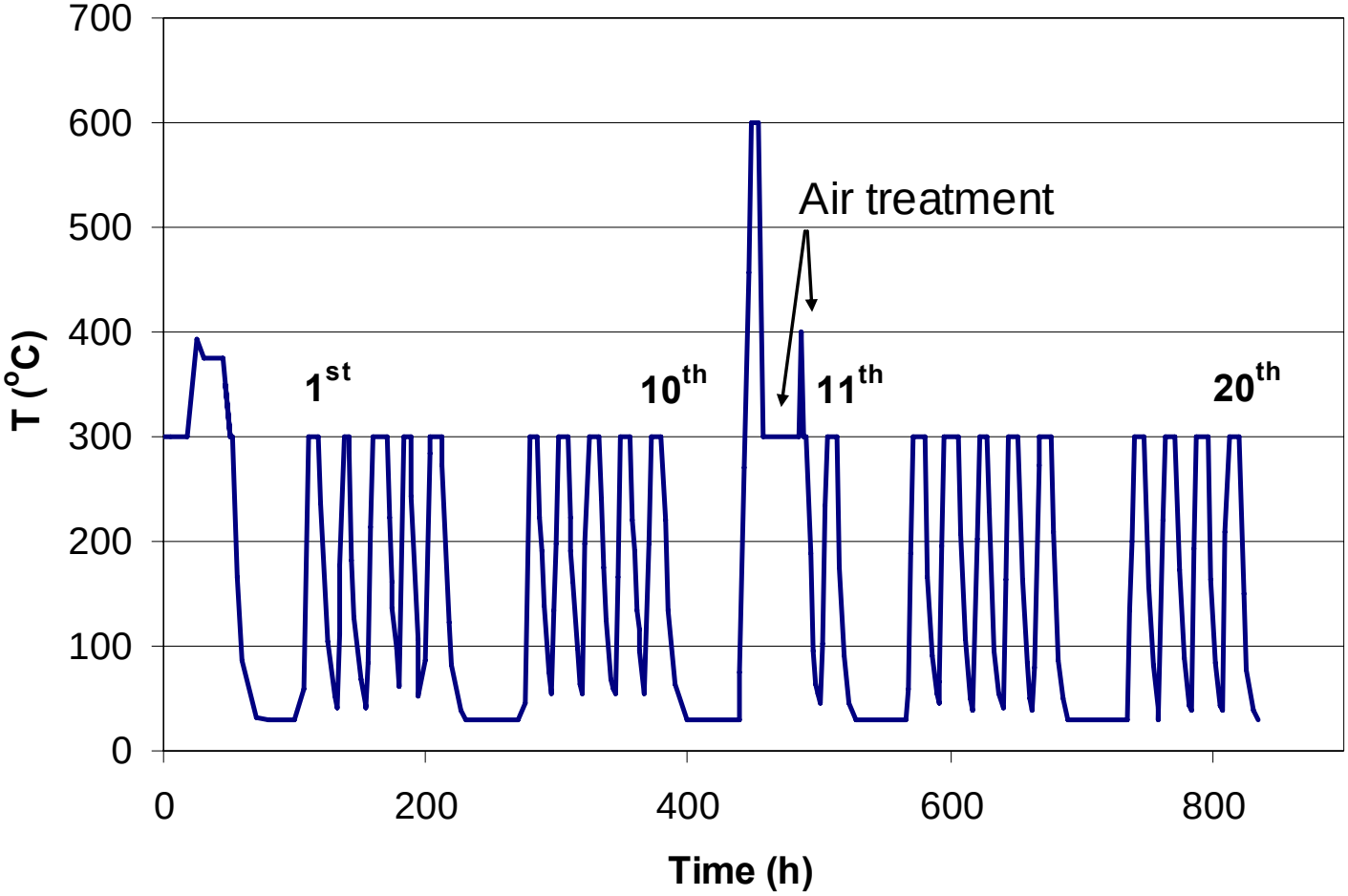


Hydrogen Flux – Extrapolated Modeling Results



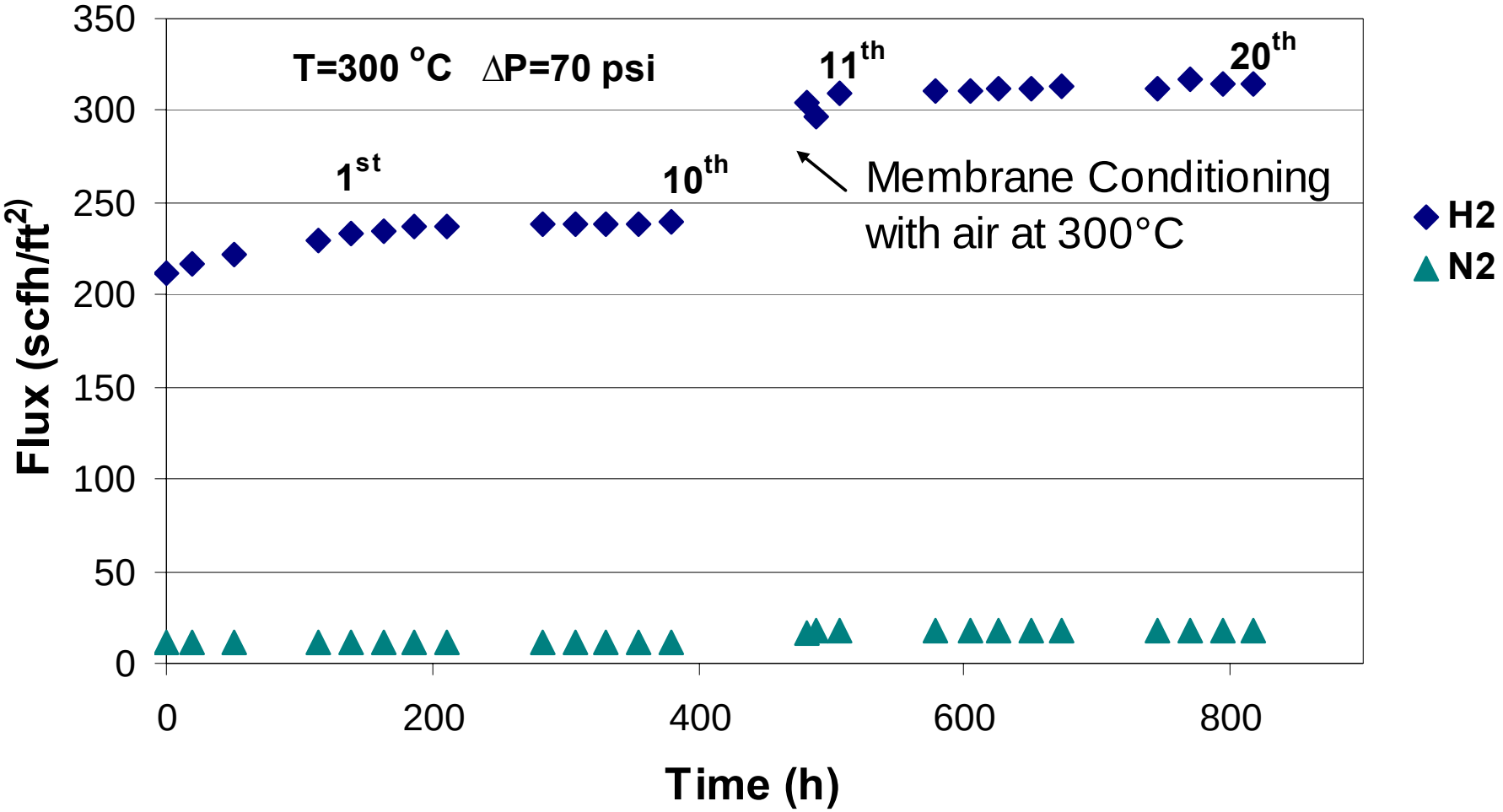
- System could operate at 200 PSID or higher
- Need to upgrade test unit for higher pressure

Thermal Cycling Test – Pd/Au (7%)



- 20 thermal cycles completed without failure
- Thermal cycling done in nitrogen
- Tried to repair original pinhole leak after 10 cycles using ceramic glaze

Thermal Cycling Test – Pd/Au (7%)



- Air treatment increased hydrogen flux by about 30%

Hydrogen Transport Modeling

Transport of H_2 to Membrane

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Dissociative Adsorption of H_2

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Surface-to-Bulk Transition of H

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Bulk Diffusion of H

↓

Bulk-to-Surface Transition of H

↓

Recombinative Desorption of H_2 ← Alloying may be particularly helpful here.

↓

Transport of H_2 from Membrane

- Examine the entire hydrogen transport process
- Membrane performance at low T might be different than expected

Membrane Composition Modeling

- Density Functional Theory
  - Used to obtain activation energies for small clusters of metal alloys
  - Provides input building block structures to Cluster Expansion code
- Cluster Expansion
  - Automated testing of a large number of atomic configurations to estimate rate constants in alloys
  - Provides rate data to continuum model

Technical Accomplishments

- 20 thermal cycles completed
- Stronger zirconia support material developed

Future Work

- Upgrade test unit to higher pressure
  - Confirm that membrane and seal can work at higher ΔP or improve the seal
- Use modeling to suggest alloy with better low-temperature flux
- Find alloy that can be heated and cooled to ambient temperature in hydrogen
  - Pd-Au membrane failed at 200°C
- Develop coating process for the new alloy and make and test tubes