2006 DOE Hydrogen Program

Cost-Effective Method for Producing Self-Supporting Pd Alloy Membrane for Use in the Efficient Production of Coal-derived Hydrogen

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Project ID #PD14

Overview

Timeline

- Project start: Sep. 09, 2003
- Project end: Sep. 08, 2006
- Percent complete: ~85%

Budget

- Total project funding (3 year)
  - DOE share: $775,771
  - Contractor share: $194,200
- Funding received in FY05*
  - $258,606
- Funding for FY06*
  - $263,671

Barriers

- Barriers addressed
  - N. Defects (high yield, large area)
  - O. Selectivity (>99.9%)
  - Q. Flux (>100 scth/ft^2)
  - S. Cost (<$1500/ft^2)

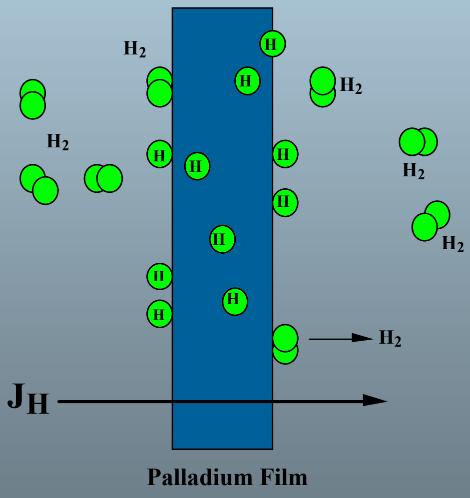
Partners

- Colorado School of Mines (D. Way)
  - H_2 permeation measurements
  - Membrane characterization
- IdaTech (W. Pledger)
  - Large-scale testing
  - Sealing
  - Module demonstration

Project Objectives

Overall DOE Goal: Develop technologies that effectively and economically separate hydrogen from mixed gas streams that would be produced by coal gasification

- **Develop a process methodology for the cost-effective manufacturing of thin, dense, self-supporting palladium (Pd) alloy membranes for hydrogen separation from the mixed gas streams of coal gasification processes,**
- **Reduce Pd membrane thickness by >50% over current state-of-art, and show potential to meet DOE 2010 technical targets.**
- **Demonstrate viability of using large-area vacuum processing to "engineer" a membrane microstructure that optimizes hydrogen permeability, separation efficiency, and lifetime,**
- **Demonstrate efficacy of large-batch and/or continuous roll-to-roll manufacturing of membrane material with performance and yields within pre-defined tolerance limits**
- **Demonstrate separation efficiency of thin palladium membrane in commercial-type fuel processor using mixed gas streams.**

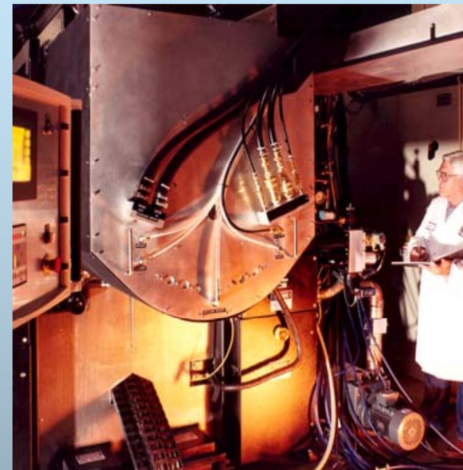


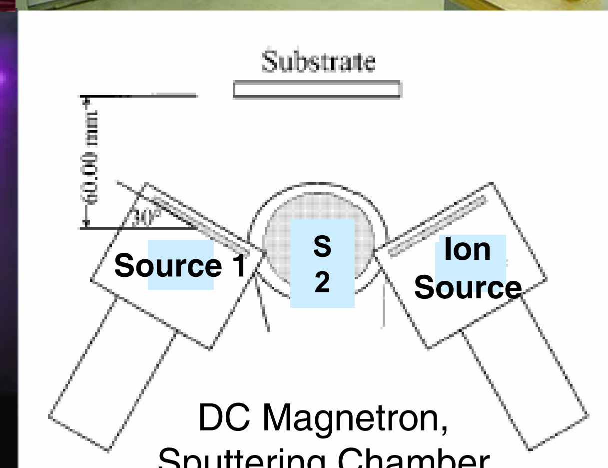
Plan and Approach

- Year 1 (Complete)
  - Task 1: Magnetron Sputter Deposition of Pd-Cu Alloys on Small Samples
  - Task 2: Development of Backing Removal Techniques
  - Task 3: Materials Characterization of Sputtered Pd-alloy Membranes
  - Task 4: Pressure and Purification Testing
  - Task 5: Prototype Module Design
- Year 2 (Complete)
  - Task 1: Fabrication of Larger Area Membranes
  - Task 2: Optimization of Membrane Composition/Microstructure
  - Task 3: Refinement and Down-selection of Backing Removal Methods
  - Task 4: Production of Membranes at least 75 in^2 in Area
  - Task 5: Prototype Module Construction
- Year 3
  - Task 1: Final Optimization/Selection of Membrane Alloy Composition (Complete)
  - Task 2: Pressure and Purification Testing Pilot-Scale Membranes (50% Complete)
  - Task 3: Prototype Module Final Assembly and Testing (50% Complete)
  - Task 4: Develop Cost Estimates for Production of Pd Membranes (25% Complete)

Thin Film Activities at SwRI

- Six large chambers utilize a variety of vacuum based coatings and surface treatments.
- Recent DOE projects in:
  - Boiler tube coatings
  - SOFC interconnects
  - PEMFC catalysts



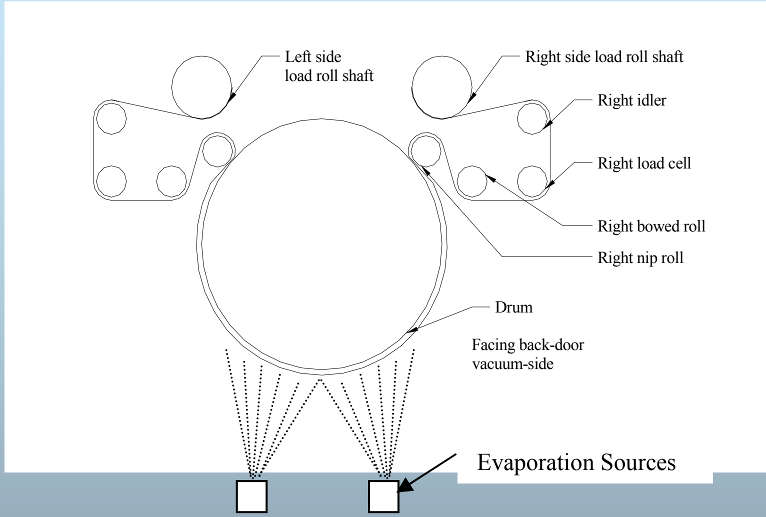



Membrane Fabrication – Flexible Substrates

- Concurrent and sequential e-beam evaporation
  - Utilized DOE approach to screen variables (dep/feed rates, drum temperature, etc)
  - Established level of significance with EIES (optical) control
  - Typical deposition rates between 0.8-1.2 nm/sec at feed rate of 0.12 m/sec

	Co-Evap	Sequential
Pros	Simple, Fast (High Rate)	Compositional Control over large areas, Fast
Cons	Compositional control over large areas	Multiple Steps Post Treatment

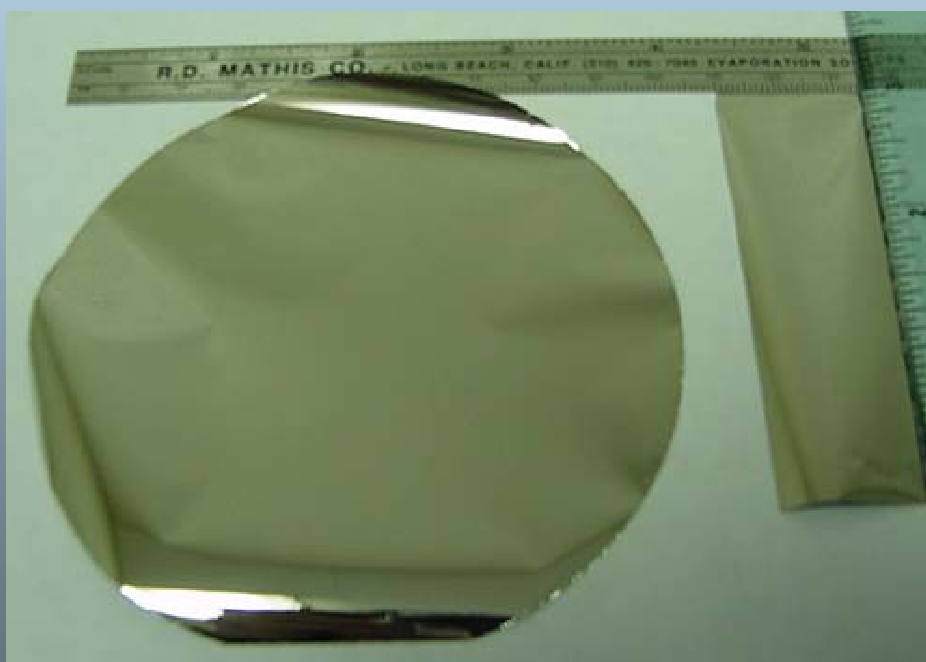
- Magnetron Sputtering (60/40 alloy target)
  - Good composition (tiling) /strain control
  - Control of density
- **Successful deposition on PS, PI, PVA, PE, and PET**
  - Over 200 linear feet of material produced
  - Demonstration over large areas (75 in2)
  - Issues with defects and stress control at thicknesses less than 12 um

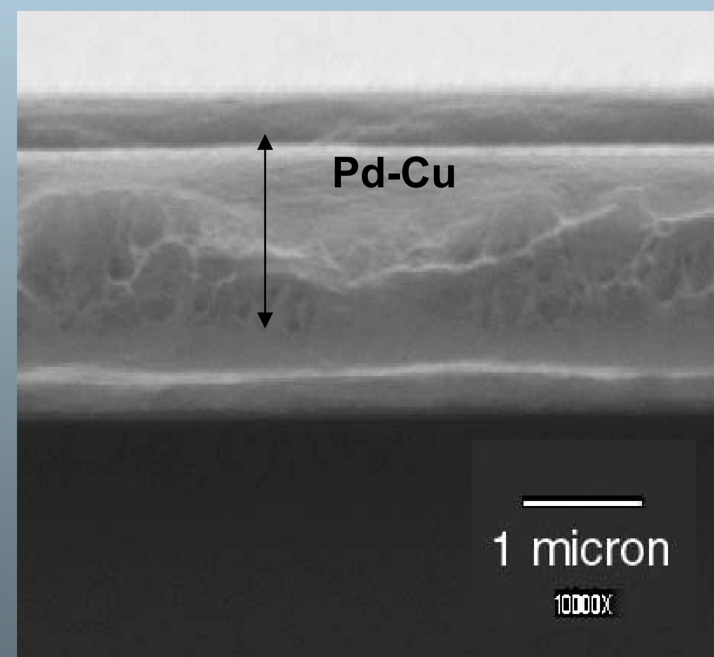


Web roll coater with evaporation sources

Membrane Fabrication – Rigid Substrates

- Formation of free-standing, gas impermeable Pd-Cu membranes up to 110 in^2 in area and less than 5 μm thick, using rigid backing materials such as glass and silicon.
- Formation of free-standing, Pd-Cu membranes as thin as 1 μm with minimal defects.



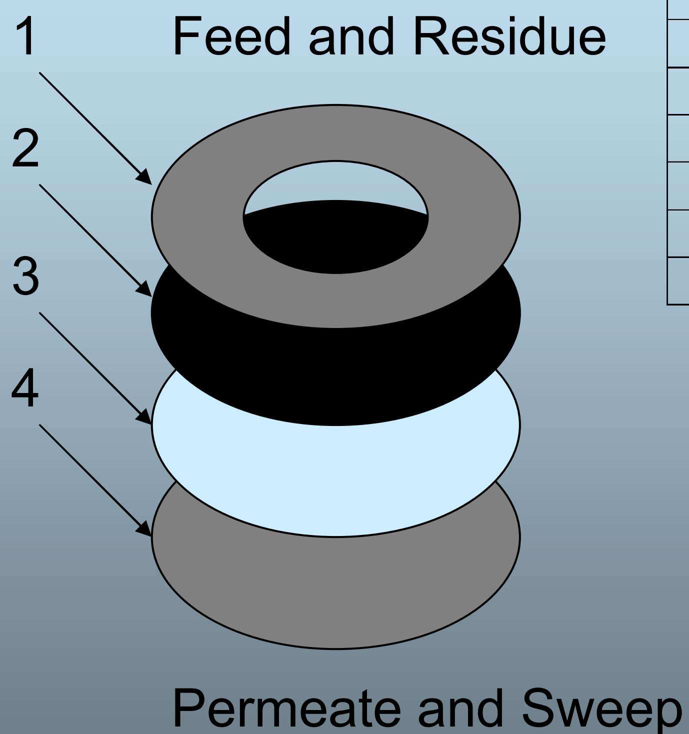


Process Optimization

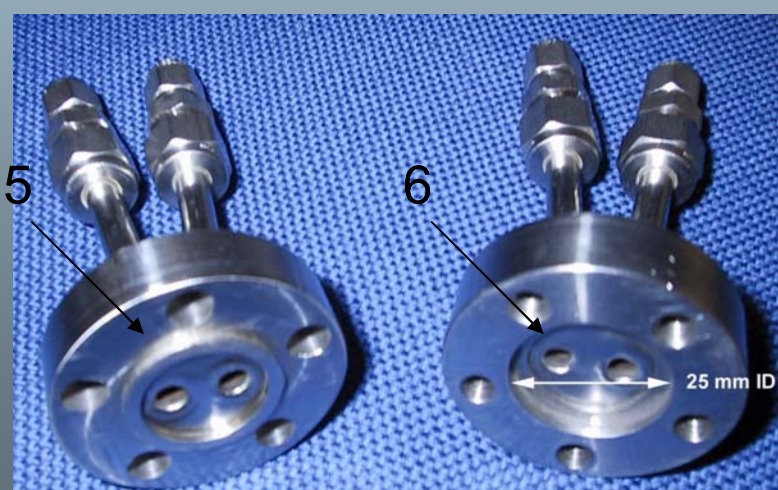
- Conducted statistical DOE to identify conditions for production of defect–free films on silicon wafers with easy release (neutral film stress)

Power (kW)	*Flow (sccm)*	*Press (mtorr)*	*Angle (deg)*	*Ion*
0.27	21.3	0.3	0	
0.28	24	0.24	10	Assist Clean
0.28	27	0.3	10	Clean

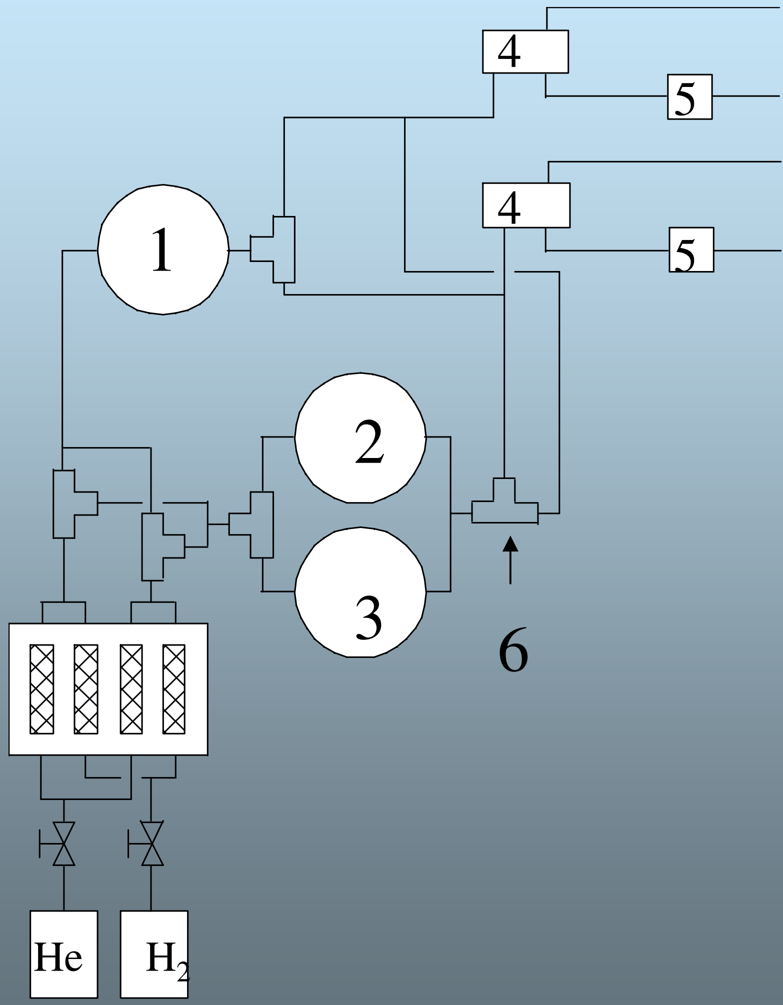
CSM Membrane Test Cell



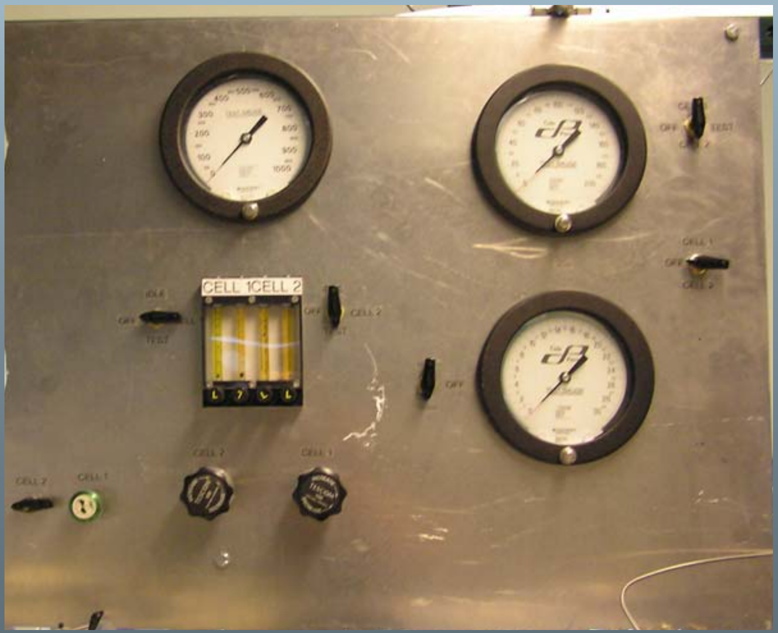
Part Number	Description
1	Graphite Gasket for Sealing
2	Membrane
3	Ceramic Paper (Diffusion barrier)
4	Porous Stainless Steel Support
5	Feed and Residue attachment
6	Permeate and Sweep attachment



CSM Permeation Apparatus



Part Number	Description
1	Idle Pressure Gauge
2	High Pressure Test Gauge
3	Low Pressure Test Gauge
4	Membrane Housing
5	Back Pressure Regulator
6	3-way valves

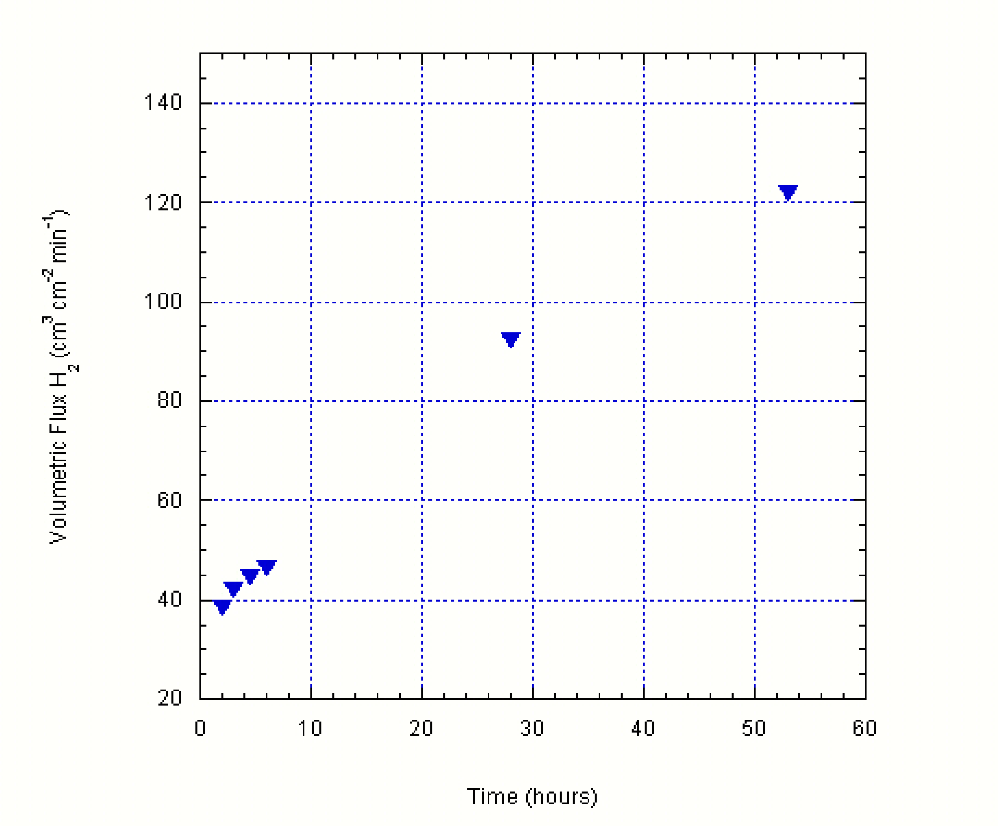


Test Conditions

- Feed Conditions
  - Pure hydrogen at 20 psig or pure helium at 20 psig
- Permeate Conditions
  - Gauge pressure of 0 for all runs
  - Atmospheric pressure in Golden, CO = 12 psia
- Temperatures
  - Most permeation measurements are taken at 400^{o}C
  - Membranes are run at temperatures ranging from 250^{o}C to 550^{o}C

Measured H_2 Flux Has Surpassed Program Goals

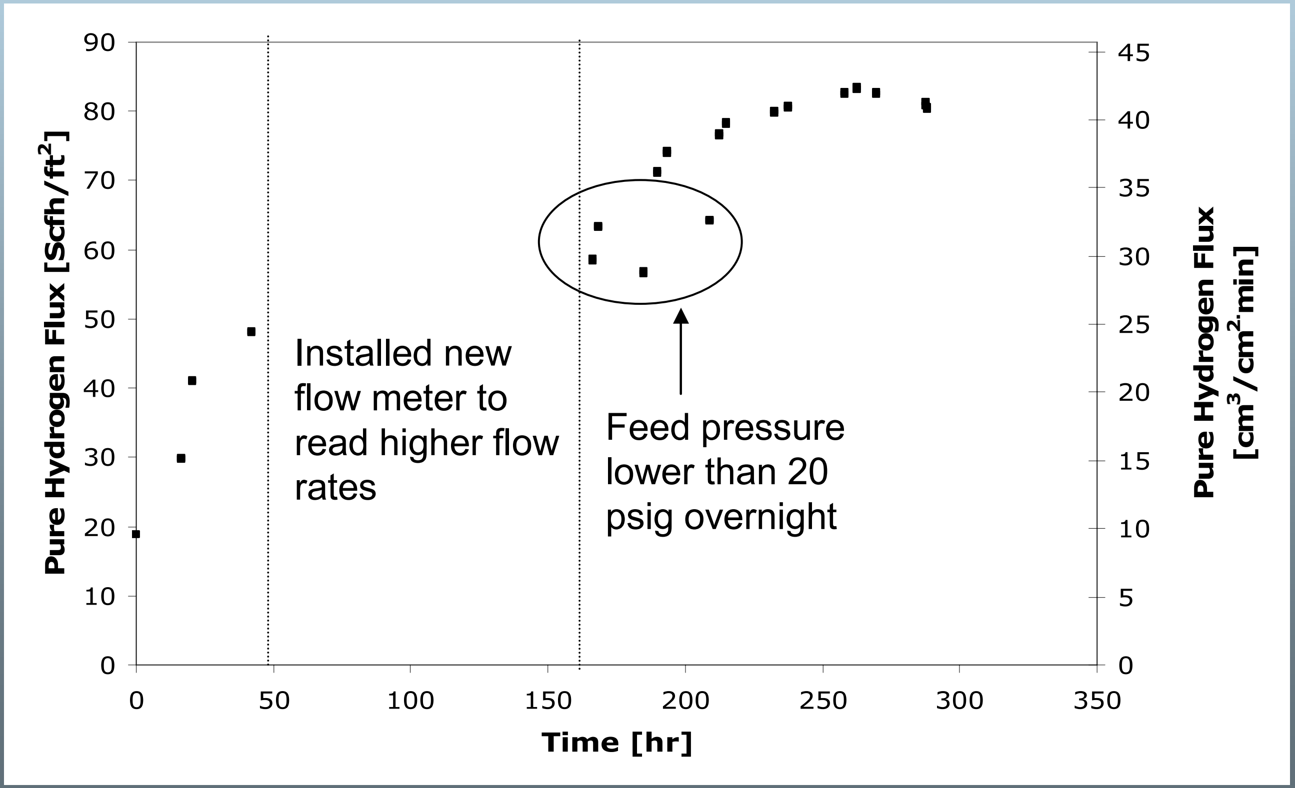
- Best performance data @ 400 °C shown for a 2.5 µm Pd-Cu alloy foil, area = 2.6 cm^2
  - *Pure H_2 permeability =* **8 •10^{-5} cm^3•cm/cm^2•s•$cmHg^{0.5}$**
  - *H_2 Flux = 124 cm^3/cm^2•min =* **242 scfh/ft^2**
  - *Feed pressure =* **20 psig**
- Exceeds DOE Hydrogen Program and 2010 DOE Fossil Energy targets



Performance Criteria	SwRI Membrane	2007 Target	2010 Target	2015 Target
Flux scfh/ft^2 @ 100 psi DP H_2 partial pressure & 50 psid	564	100	200	300

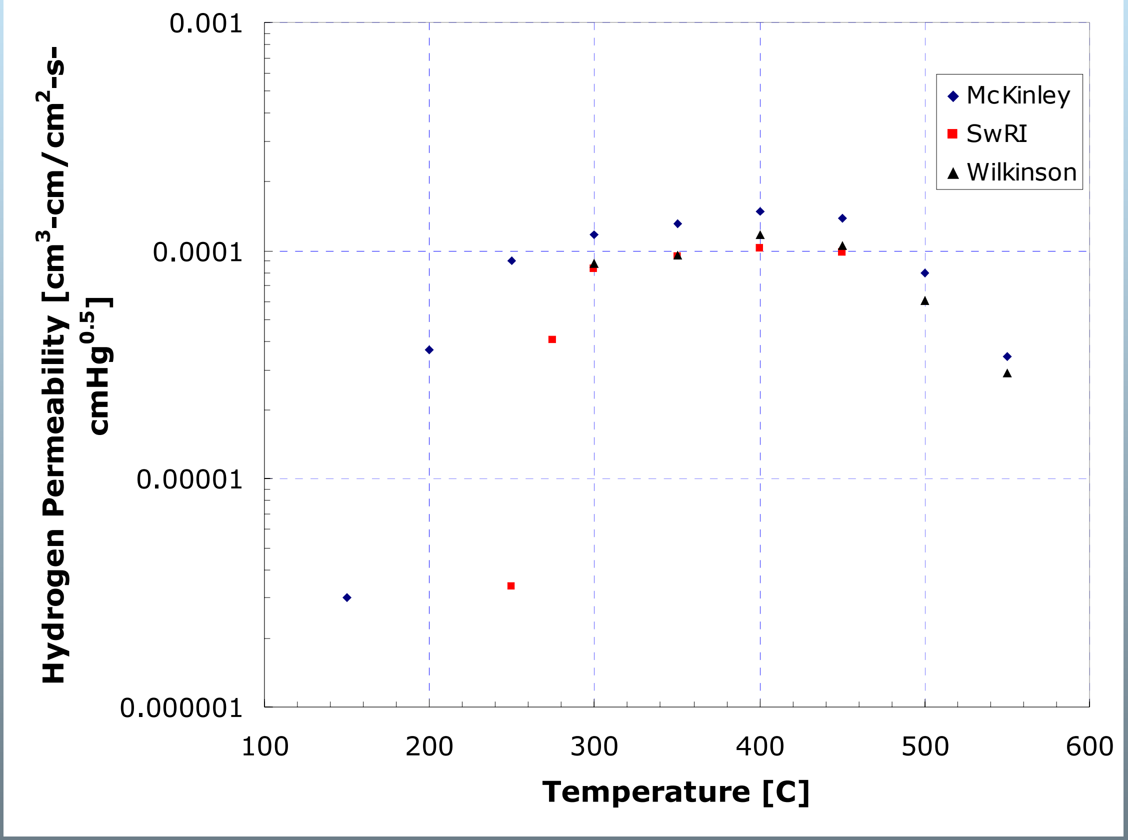
Extended Testing of SwRI Membrane

- Demonstrated separation of >99.95% pure hydrogen from helium
- Perfect H_2 selectivity measured throughout the test (i.e. no pinholes or other defects)
- Short term testing at 50 psig differential pressure without rupture
- Hydrogen permeability = 1.09E-4 $cm^3(STP) \cdot cm/cm^2 \cdot s \cdot cmHg^{1/2}$



Influence of Temperature on Permeability of 60 wt% Pd Foil

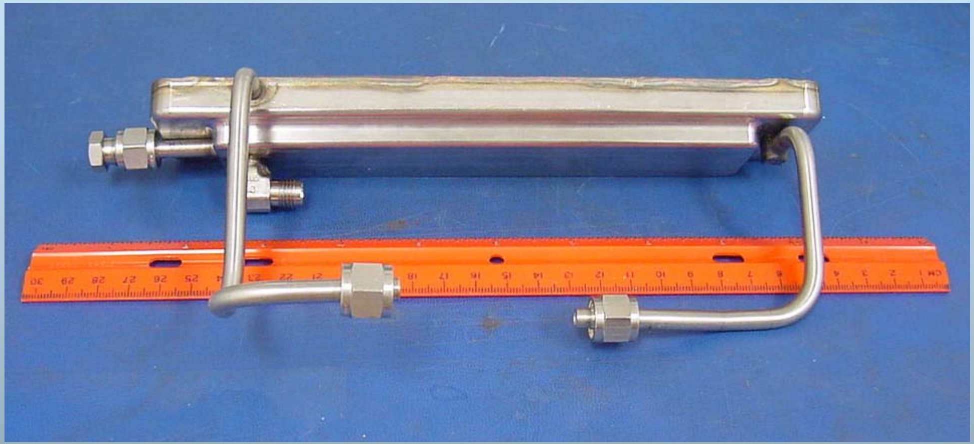
- Demonstrated maximum permeability at 400 C
- SwRI membranes match the Wilkinson and McKinley data both in permeability and composition
- 60-40wt% PdCu composition has been verified by EDX

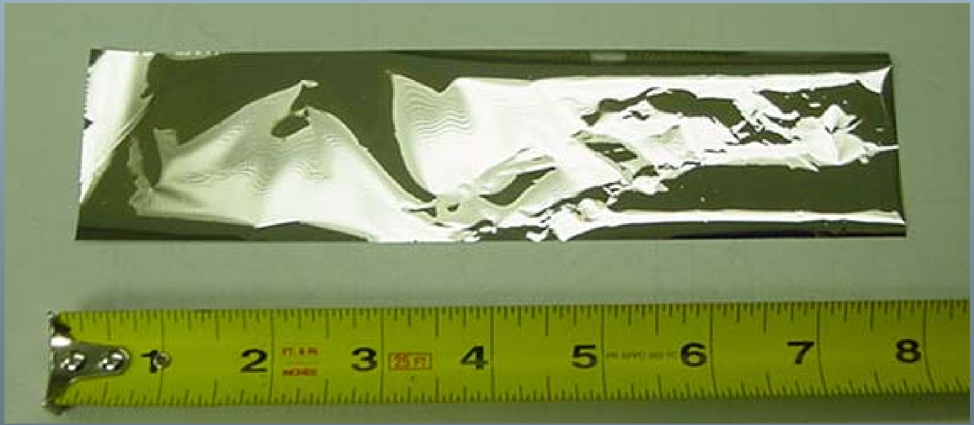


IDATECH
An IDACORP Company

Module Development and Testing at Idatech

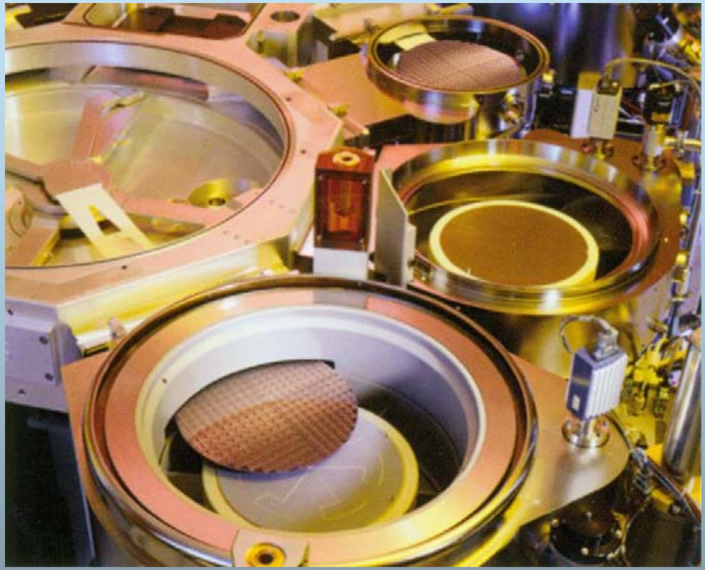
- Measured H_2 flux of 420 SCFH/ft^2 (400°C and 100 psig) on smaller samples provided by SwRI.
- Investigating gasketing arrangements to reliably seal thin membranes.
- First full-scale module test expected in coming weeks
- More than a dozen full-size prototype membranes have been delivered to Idatech





Cost Projections

- Off-the-shelf semiconductor equipment should be adaptable for large-scale membrane production
  - Estimated throughput of ~25 ft^2/hr with a single cluster tool
- Currently costs SwRI ~$1500/$ft^2$ to produce Pd alloy membranes in small quantities (few ft^2 per day)
- Raw materials cost is not the most significant factor
  - 3μm thick 60wt% membrane, has ~$21/$ft^2$ of Pd (assuming $350/oz)



Novellus INOVA xT

Future Work

- Continue efforts to establish reliable sealing methods for ultra-thin membranes
- Ternary alloy development (Pd-Cu-X)
  - Early-stage collaborations with LANL (Steve Paglieri) and CMU (David Sholl)
- Full-Scale Prototype Module Demonstration
  - Target production rate of 50 cm^3/cm^2-min of 99.95% pure hydrogen
- Prepare a more detailed cost analysis of membrane production process

Project Summary

- Relevance
  - Robust, high efficiency methods to extract pure hydrogen from coal gas and other sources is critical to the development of a hydrogen economy
- Approach
  - Use a novel, scalable vacuum deposition method to fabricate free standing Pd alloy hydrogen separation membranes and evaluate their performance
- Accomplishments
  - Produced some of the thinnest (3 um), largest area (110 in^2), highest performance separation membranes ever reported

Summary (Cont'd)

	2005 DOE Target	2010 DOE Target	SwRI
Flux (scfh/ft^2)	100	200	242
Cost (\$/ft^2)	1500	1000	1500
Hydrogen Quality	99.9	99.95	99.95
DP Operating Capability	200	400	100

- Collaborations
  - Strong commercial partner in Idatech, long track record testing hydrogen membranes at CSM, new interactions with LANL and CMU
- Future R&D
  - Test under more aggressive conditions, develop new ternary alloy formulations with increased durability, demonstrate low-cost pilot production

Backup Slides

Reviewer's Comments

- Future work should include some lifetime tests to evaluate the stability of the membrane over time.
  - Membranes have been tested up to 300 hours at 400^{o}C
  - A lot of bottled hydrogen is needed for these tests
- With better matrix experiment design, approach should lead to significant results
  - Statistic DOE has been implemented in optimization of membrane stress, release, and defect density.
- Hydrogen purity levels derived in recent tests (99.95%) would be insufficient for direct use in fuel cell vehicles
  - Further increases in purity are possible, Idatech has demonstrated membrane purification to <1 ppm CO and <5 ppm CO_2.

Publications and Presentations

- Fabrication of Self-Supported Pd Alloy Membranes Using Vacuum Deposition Methods, International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, May, 2005
- Ultra-thin Palladium Alloy Membrane for Hydrogen Gas Separation, J. Arps, B. Lanning, G. Dearnaley, *Technology Today*, April 2006
- Development of Ultra-Thin, Large-Area, Self-Supported Palladium Alloy Membranes for use in Efficient Production of Coal Derived Hydrogen, 9th International Conference on Inorganic Membranes, Lillehammer, Norway, June, 2006

Critical Assumptions and Issues

- Performance and durability in more realistic syngas environments
  - bcc Pd alloys are known to be sensitive to sulfur
- Demonstrate ability of vacuum deposition method to produce membranes at low cost and in large quantity
  - Several industrial examples prove such methods can be cost effective
- Pressure and sealing issues for thin membranes can be overcome with advanced designs