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

DE-FC26 03NT41849

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Southwest Research Institute®
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Project ID # PD40

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Overview

Timeline

- Project start: Sep. 09, 2003
- Project end: March 31, 2008
- Percent complete: 100%

Budget

- Total project funding (3 year)
  - DOE share: $775,771
  - Contractor share: $194,200
- Funding received in FY07
  - $0
- Funding for FY08
  - $0

Barriers

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

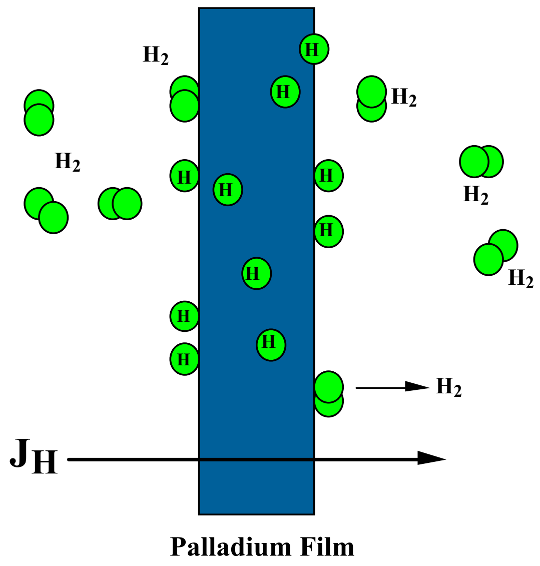
Partners

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

Objectives

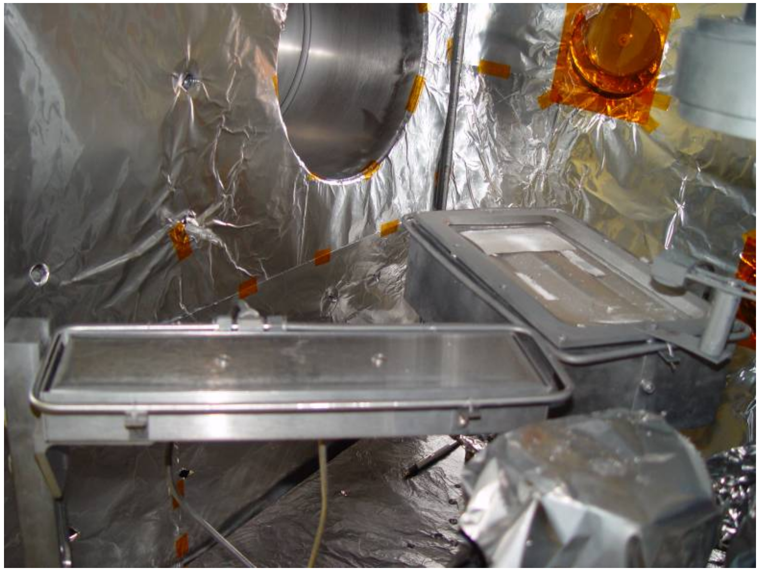
Overall DOE Goal: Develop technologies that effectively and economically separate hydrogen from mixed gas streams that would be produced by coal gasification

- 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.

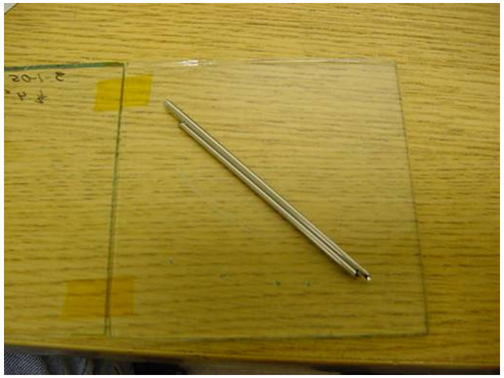


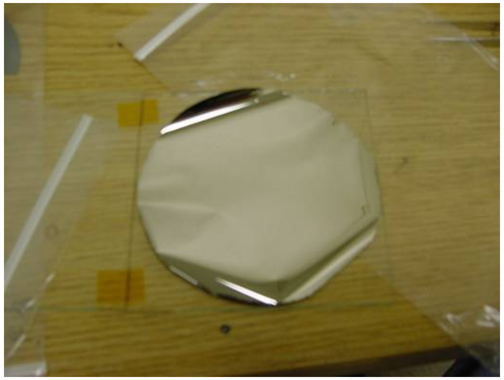
Deposition

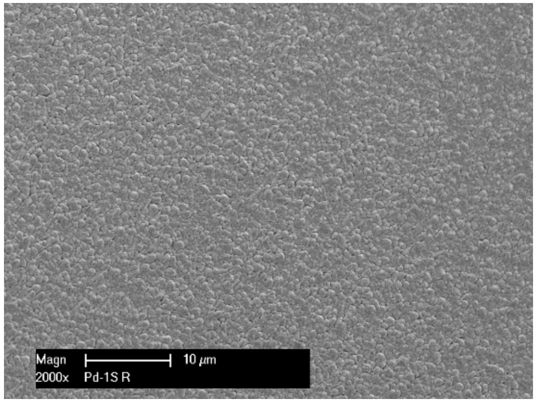
Sample Number	Date	Maker Pd %	EDAX Pd %	Max Flux @ 400C & 20psi [$cm^3/cm^2 \cdot min$]	CSM Thickness [microns]	Source	Maker Thickness	Permeance @ 400C [$cm^3(STP)/cm^2 \cdot s \cdot cmHg^{0.5}$]	Permeability @ 400C [$cm^3(STP) \cdot cm/cm^2 \cdot s \cdot cmHg^{0.5}$]
051206#1	7/25/2002	---	57.00	17.9	8.80	SEM	---	5.98E-02	5.26E-05
051206#1	7/25/2002	---	57.00	30	8.80	SEM	---	1.00E-01	8.83E-05
072806#1	8/6/2002	62.00	---	N/A	---	SwRI	4.40	N/A	N/A
072806#1	8/27/2002	62.00	---	22.21	4.40	SwRI	4.40	5.14E-02	2.26E-05
073106#1	8/6/2002	62.00	---	N/A	---	SwRI	4.40	N/A	N/A
073106#1	8/7/2002	62.00	---	N/A	---	SwRI	4.40	N/A	N/A
073106#1	8/7/2002	62.00	---	N/A	---	SwRI	4.40	N/A	N/A
073106#1	9/10/2002	62.00	---	19.3	4.40	SwRI	4.40	6.46E-02	2.84E-05

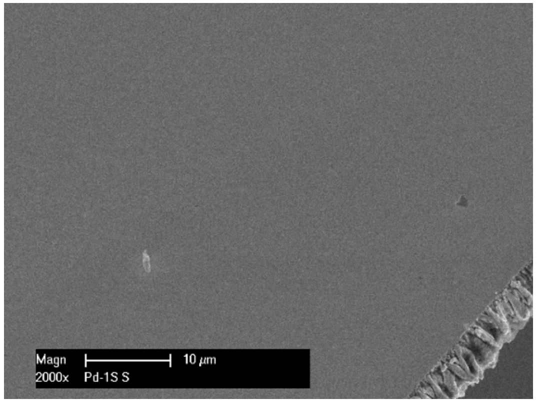


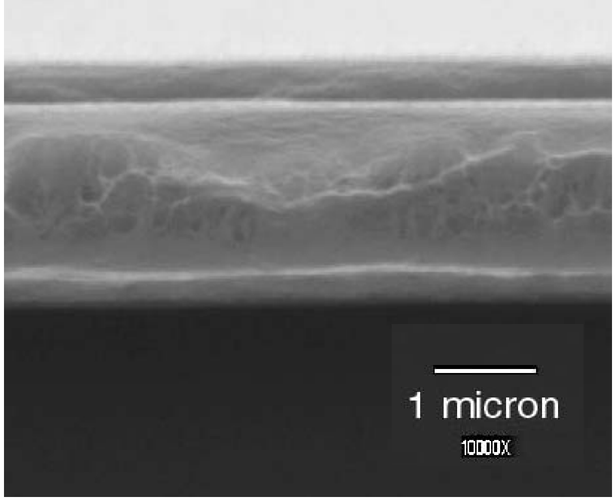
Membranes

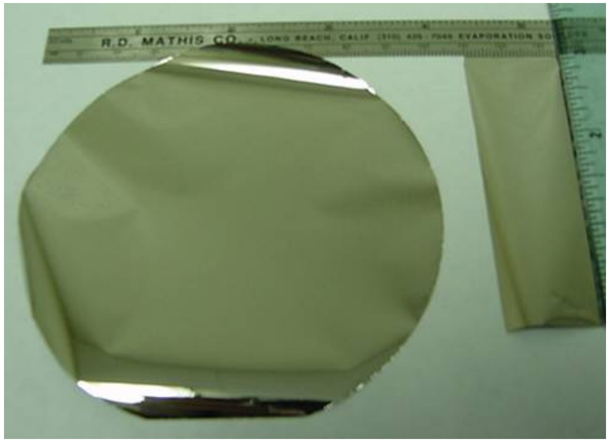





Magn
10 μm
2000x Pd-1S R


Magn
10 μm
2000x Pd-1S S


1 micron
10000X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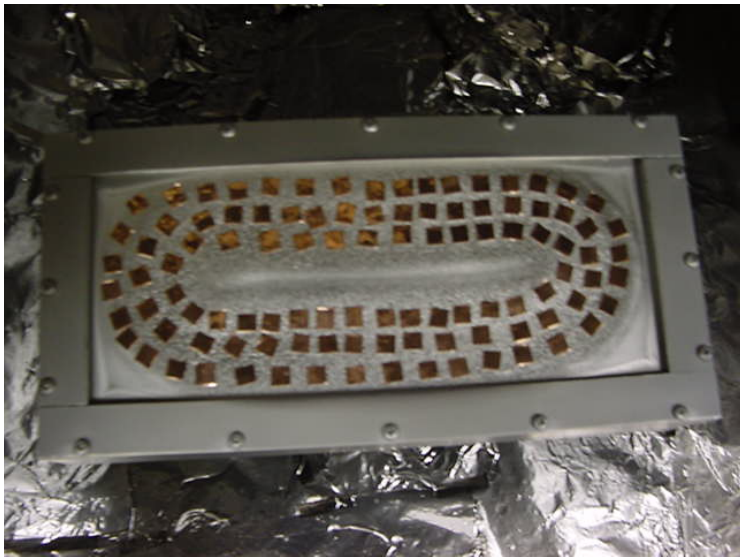
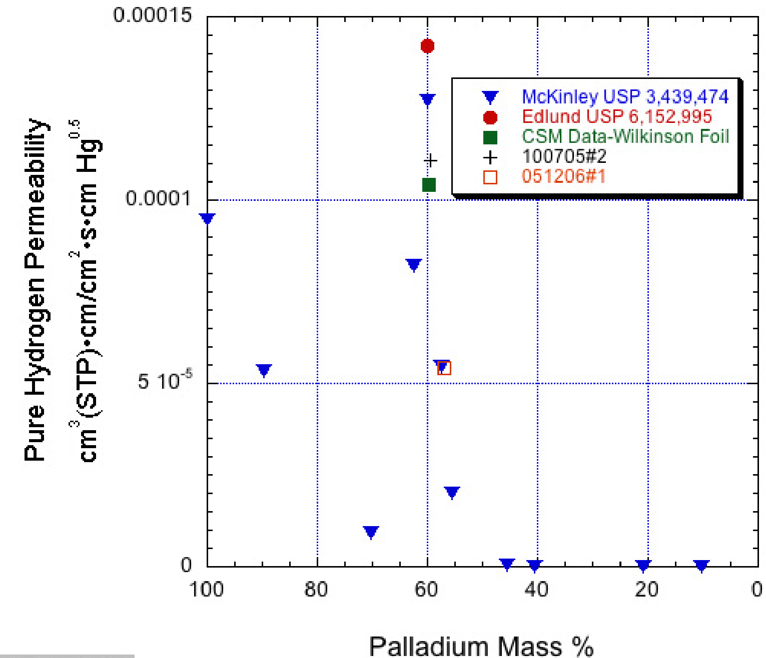
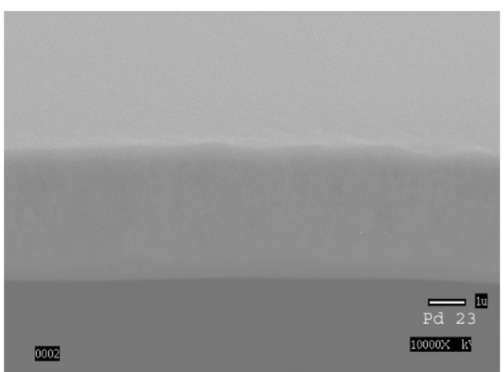
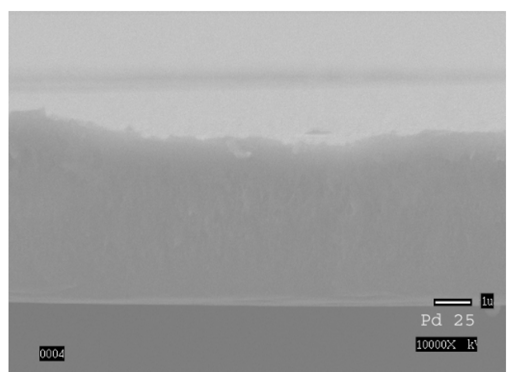
Membrane Composition



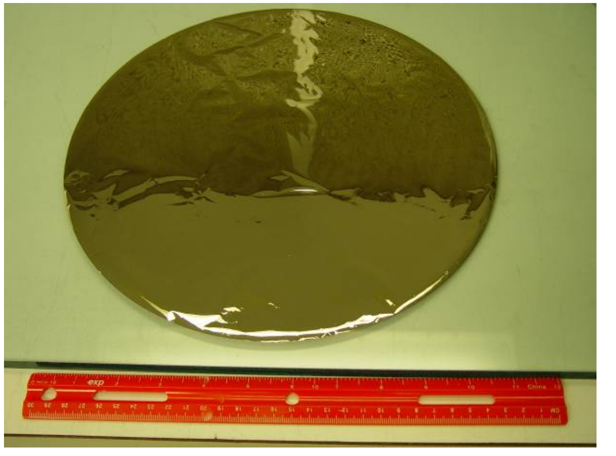






Foil Samples Provided

- CSM & IdaTech - Program partners
- Steve Paglieri – Los Alamos National Lab
  - No data
- Joe Schwartz – Praxair
  - No data
- Rob Hui – NRC, Canada
  - No data



- Gohkan Alptekin – TDA Research
  - 8.83 x 10-5 cm3(STP)cm/cm2.s,cmHg0.5 @ 400ºC and 50 psig H2
- Dave Edlund – Protonex
  - 100 SCFH/ft2 @ 400ºC and 50 psig H2

Measured H_2 Flux Has Surpassed Program Goals

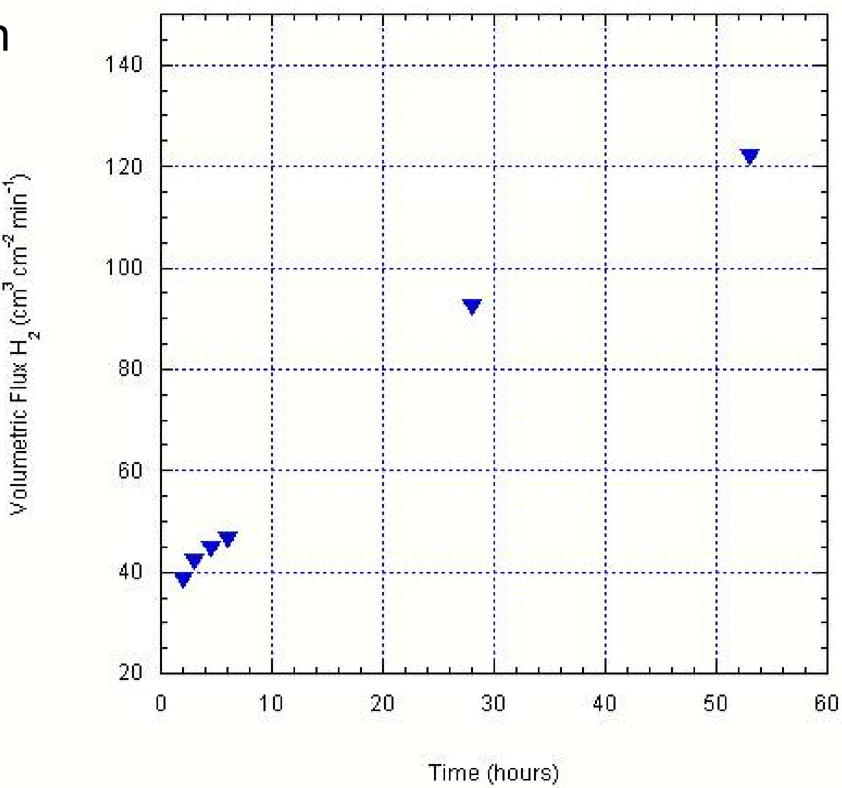
Best performance data @ 400°C shown for a 2.5 μm Pd-Cu alloy foil, area = 2.6 cm2

- *Pure H2 permeability =*

8 •10^{-5} cm^3•cm/cm^2•s•$cmHg^{0.5}$

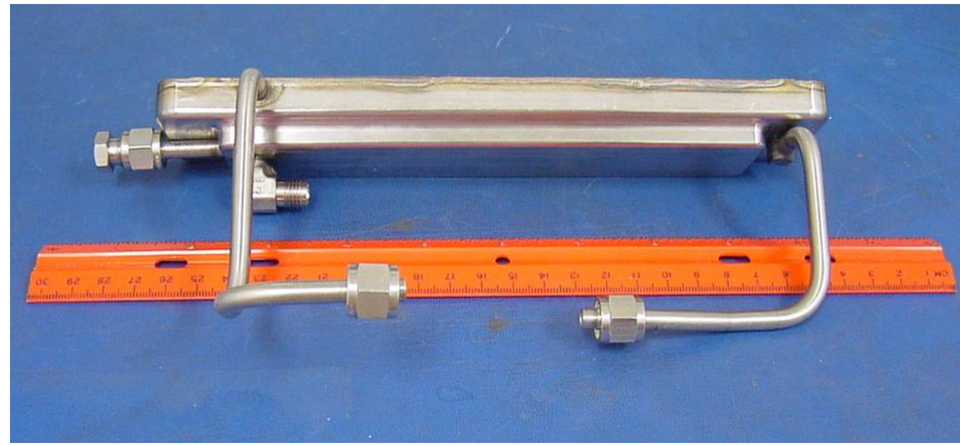
- *H_2 Flux = 124 cm^3/cm^2•min =*
  242 SCFH/ft^2
- *Feed pressure =* **20 psig**

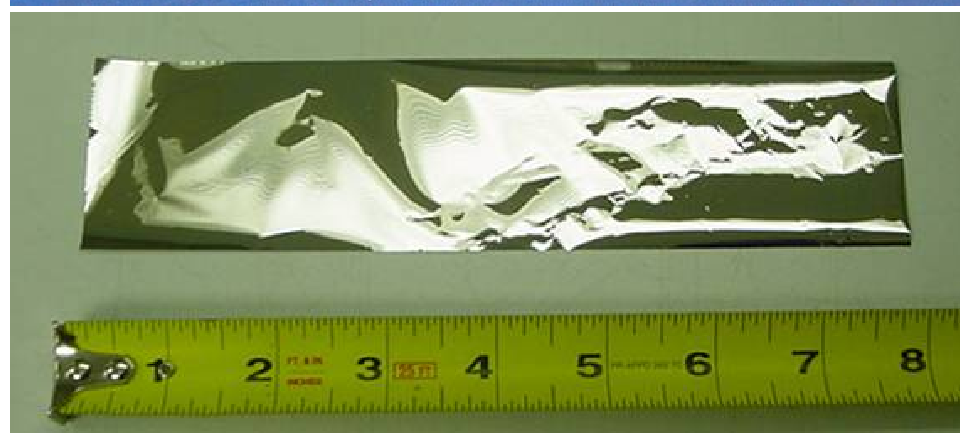
Exceeds DOE Hydrogen Program and 2010 DOE Fossil Energy targets



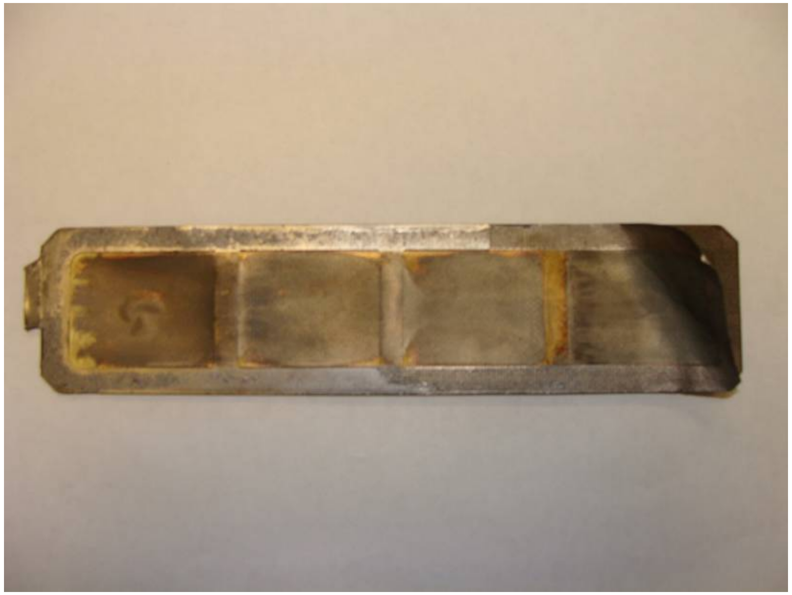
Module Development and Testing at IdaTech

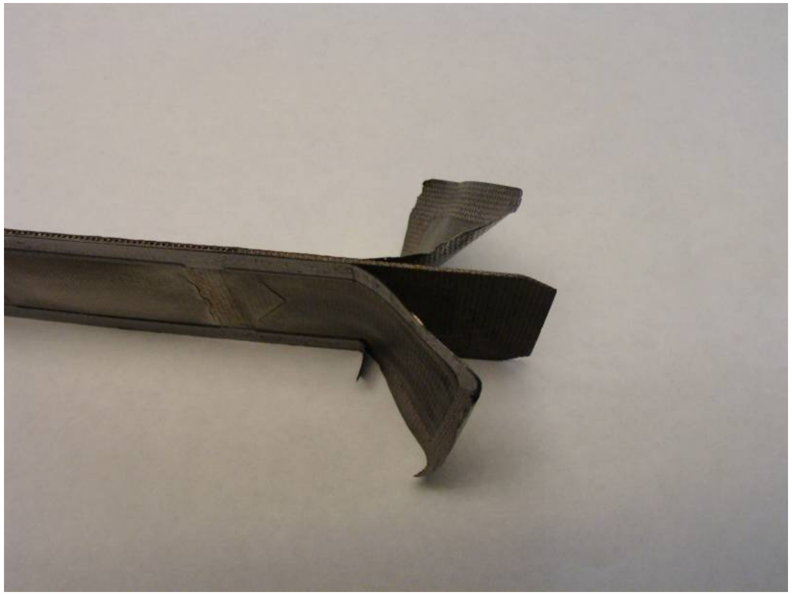
- Measured H_2 flux of 420 SCFH/ft^2 (400°C and 100 psig) on smaller samples provided by SwRI.
- Investigating gasketing arrangements to reliably seal thin membranes.
- Full-scale module test delayed
- More than a dozen full-size prototype membranes have been delivered to IdaTech





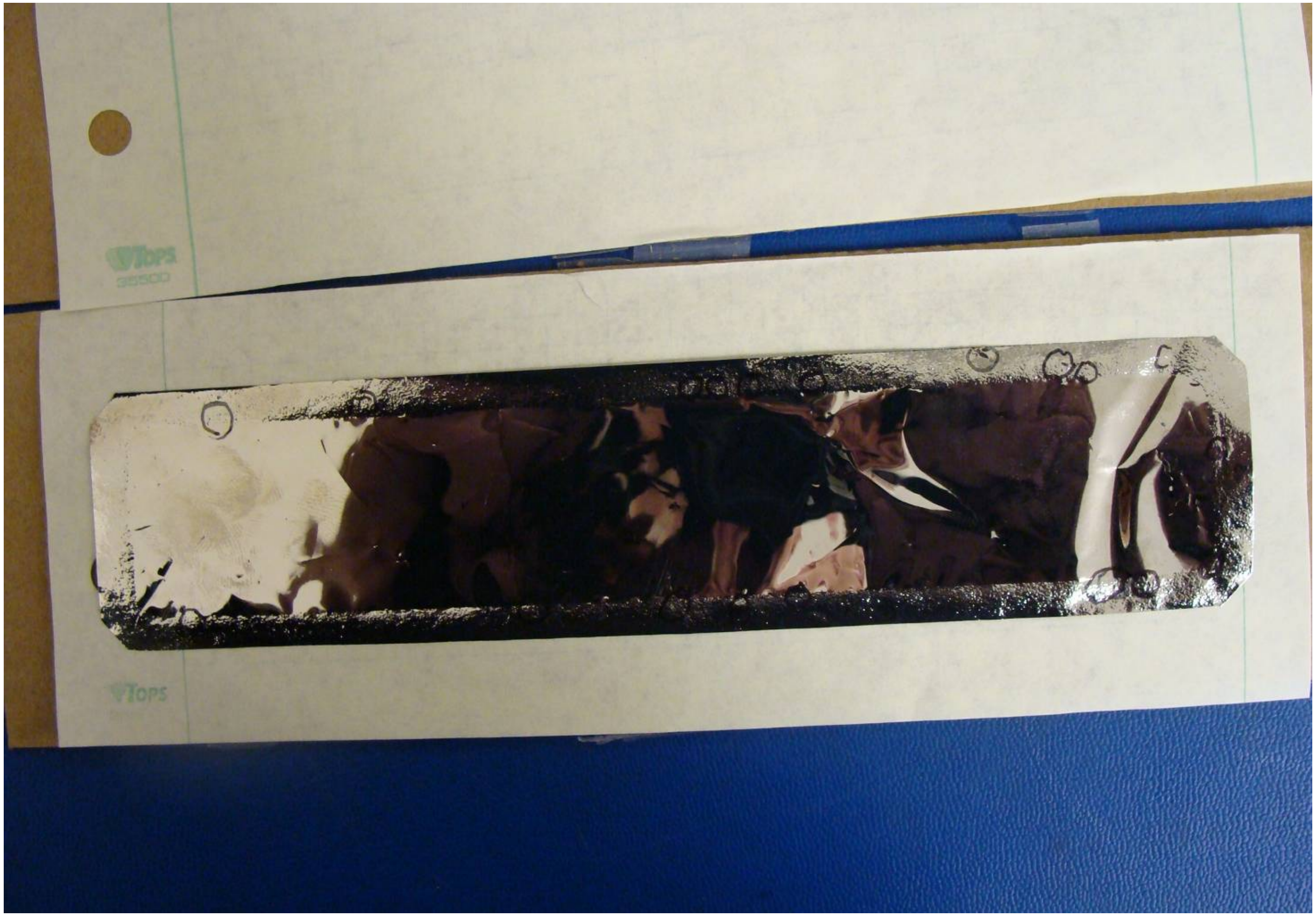
Membrane Assembly





- Membrane performance confirmed
- Issues
  - Membrane stress
  - Brittleness
  - Flatness
  - Pinholes
- Annealing reduces stress and brittleness but may cause pinhole formation
- Attempts to fabricate a membrane module failed due to membrane mechanical failure during assembly

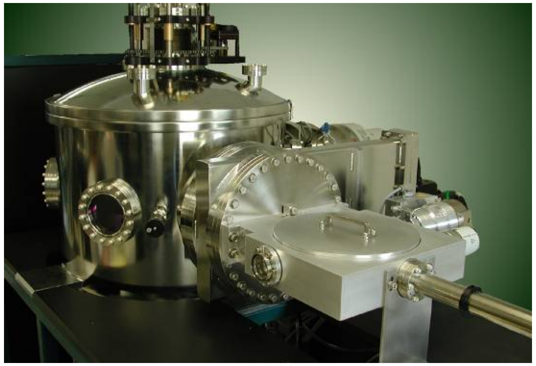
Foil After Gasket Compression

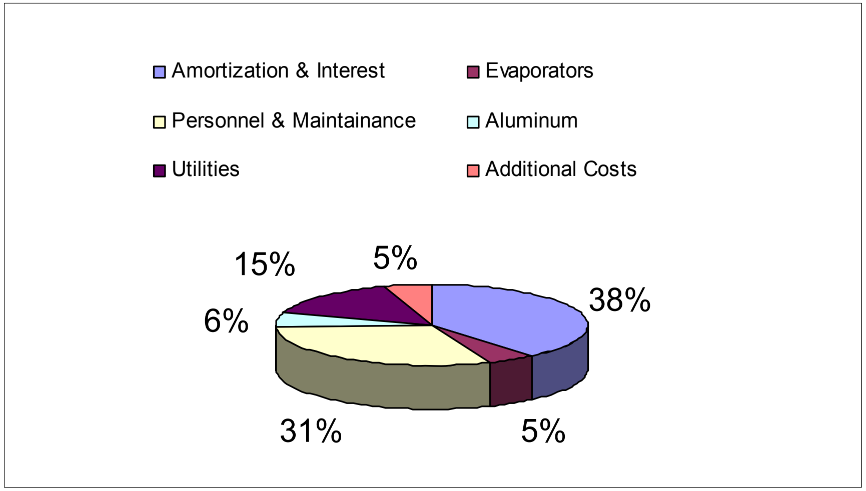


Cost Projections

Total Cost/ft^2 = (F + L + E) / (P*S*1.75 x10^5) + R

- F is the equipment depreciation,
- L is the fully burdened labor costs
- E is the cost of utilities and maintenance,
- P is the throughput per minute,
- S is the # of 8 hour shifts per day
- R is the raw material cost





- $35/ft2 of Pd
- Total final cost - $45.50/ft2

Areas for Future Work

- **Membrane fabrication**
  - Fine tune annealing process
  - Eliminate surface defects
  - Increase membrane area
  - Study optimum thickness with respect to durability – grain growth and impact on durability
- **Modularization**
  - Sealing; Gasket, Welding, Brazing, Hybrid
  - Wetted component material selection
  - Optimize footprint
  - Membrane support
  - Cost analysis on module – not just membrane
  - Design for cascading modules together
- **Long term testing**

Summary

Year 1

- 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

- 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
- Task 2: Pressure and Purification Testing Pilot-Scale Membranes
- *Task 3: Prototype Module Final Assembly and Testing*
- Task 4: Develop Cost Estimates for Production of Pd Membranes

High Permeability Ternary Palladium Alloy Membranes with Improved Sulfur and Halide Tolerance:

DE-FC26-07NT43056

Objective: To utilize a iterative modeling, rapid fabrication, and testing approach to develop and demonstrate an ultra-thin (<5 micron) durable ternary Pd-alloy membrane with excellent resistance to sulfur and halogen attack.

Overview

Timeline

- Project start: May 02, 2007
- Project end: May 01, 2010
- Percent complete: 30%

Budget

- Total project funding
  - DOE share: $1,199,049
  - Contractor share: $299,763
- Year 1(2008)
  - DOE share: $354,490
  - Contractor share: $88,623

Barriers

- Barriers addressed

  G. Hydrogen Embrittlement

  I. Poisoning of Surfaces

  Q. Impurities in Hydrogen

Scope of Work

1) Materials modelling and composition selection:
2) Fabrication of ternary alloy membranes:
3) Membrane testing and evaluation:

Collaborators

Craig Engel, **Miguel Esquivel**, ***Roger Wiseman,*** Surface Engineering

David Sholl, Professor, Chemical Engineering and Materials Science

J. Douglas Way, Professor, Chemical Engineering Department,

Bill Pledger, P.E., Senior Vice President, Chief Engineer, IdaTech

Gohkan Alptekin, Principal Engineer

Rick Dunst

Milestones

Phase I (Year 1)

- *Milestone 1.1*: Use DFT methods to predict H_2 flux through $Pd_{96}M_4$ for M = Ni, Rh, Pt, Nb, Ta, V, Mg and Y. Use same methods to predict H_2 flux $Pd_{74}Cu_{22}M_4$ for at least 3 of the same M.
- *Milestone 1.2*: Screening of initial set (≤ 6) of ternary alloys by pure gas (H_2 and N_2) permeation experiments.

Phase II (Year 2)

- *Milestone 2.1*: Fabricate a minimum of 20 membrane specimens with different copper concentrations based on CMU hydrogen transport predictions for the 2-3 most promising ternary element additions.
- *Milestone 2.6*: Complete 4-5 preliminary tests membrane samples at TDA and IdaTech with clean Syngas and single impurity additions of H_2S and COS.

Phase III (Year 3)

- *Milestone 3.1*: Produce a minimum of 5 sq. ft. of optimized membrane material for use at CSM and TDA and for independent third-party evaluation by IdaTech.
- *Milestone 3.2*: CSM will complete mixture permeation testing with H_2/CO and H_2/H_2S binary mixtures with best three samples from the final optimization study.

Theory to Model Metal Membranes

Given: Alloy phase diagram

→

Understand and predict intrinsic membrane properties

Hierarchial Approach

Use **quantum chemical methods** (Density Functional Theory) to calculate atomic level information: i.e. hydrogen binding energies, energy barriers, etc.

↓

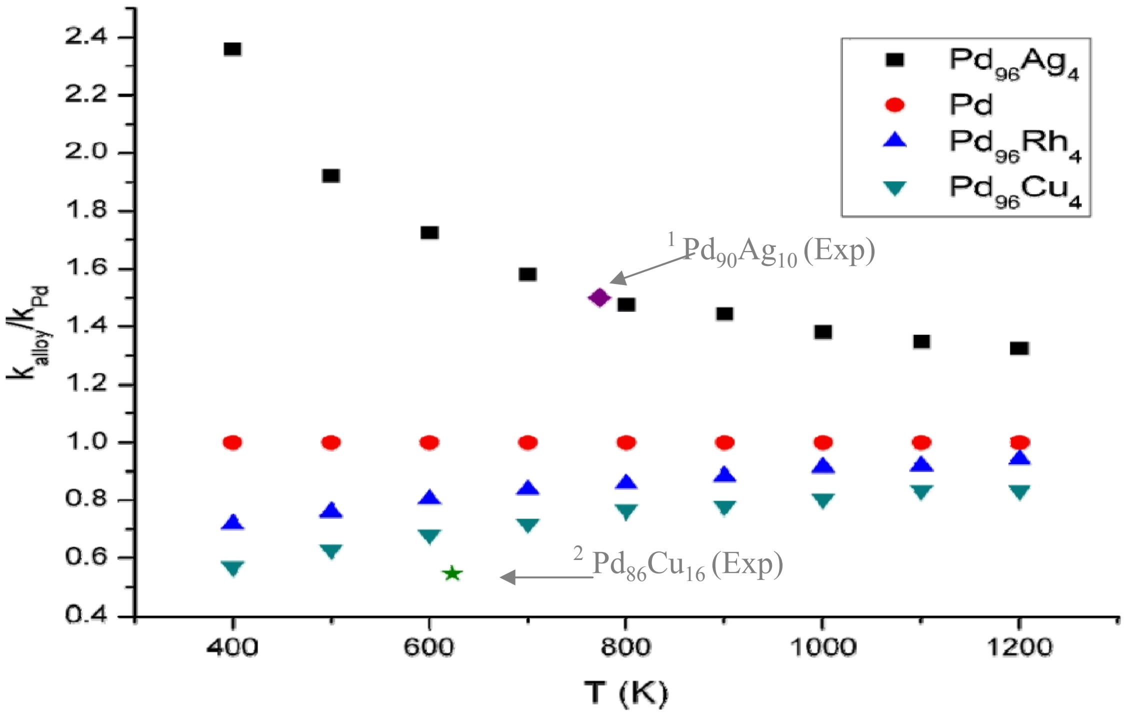
Input for **coarse grained lattice gas models** to calculate long-range transport properties

↓

Predict **macroscopic properties** that can be directly compared with experimental data

Permeability: Binary Alloys

Semidey-Flecha and Sholl, J. Chem. Phys., in press

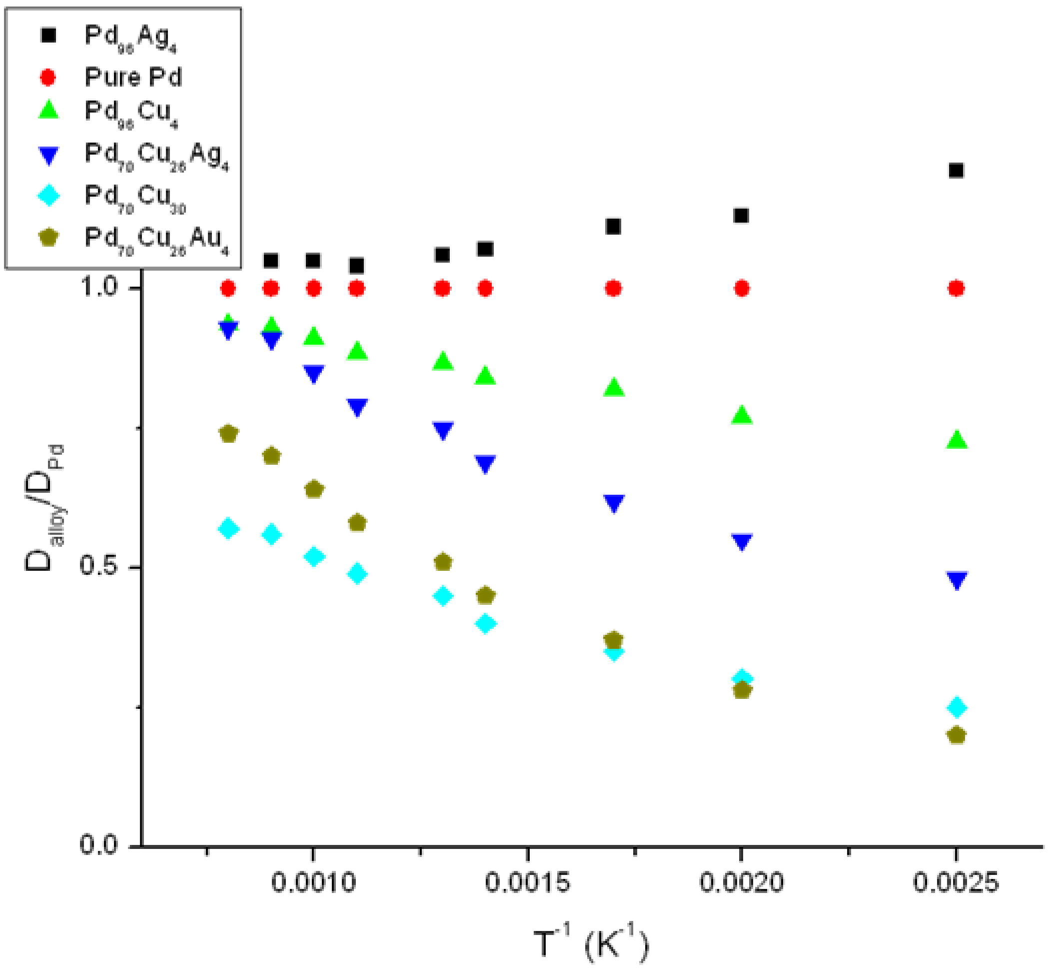


All results are normalized with respect to pure Pd

1. Gryaznov, V., *Sep. Purif. Methods*, **2000**, 29(2), 171.
2. McKinley, D., *US Patent 3439474*. **1969**

H Diffusivity in Alloys

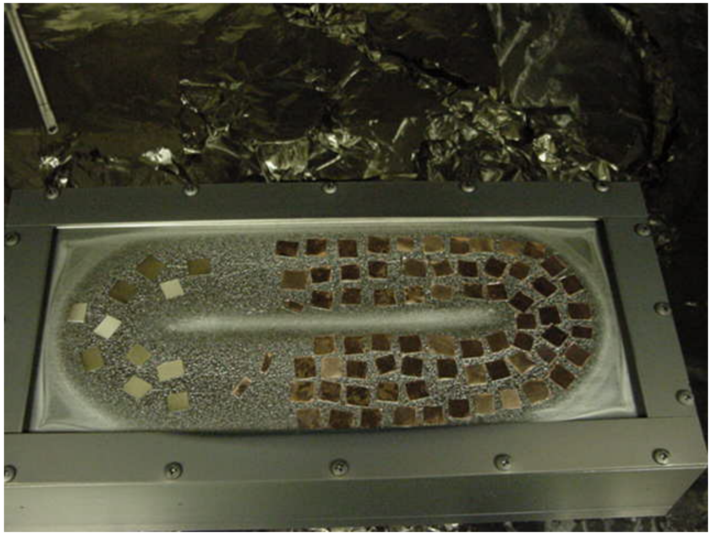
All results are normalized with respect to pure Pd

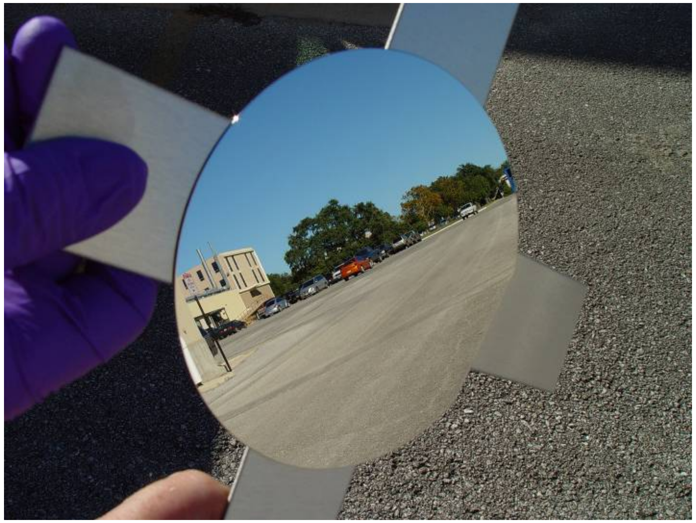


Enhanced diffusivity in PdCuAg relative to PdCu suggests Ag may be a useful “additive” to PdCu

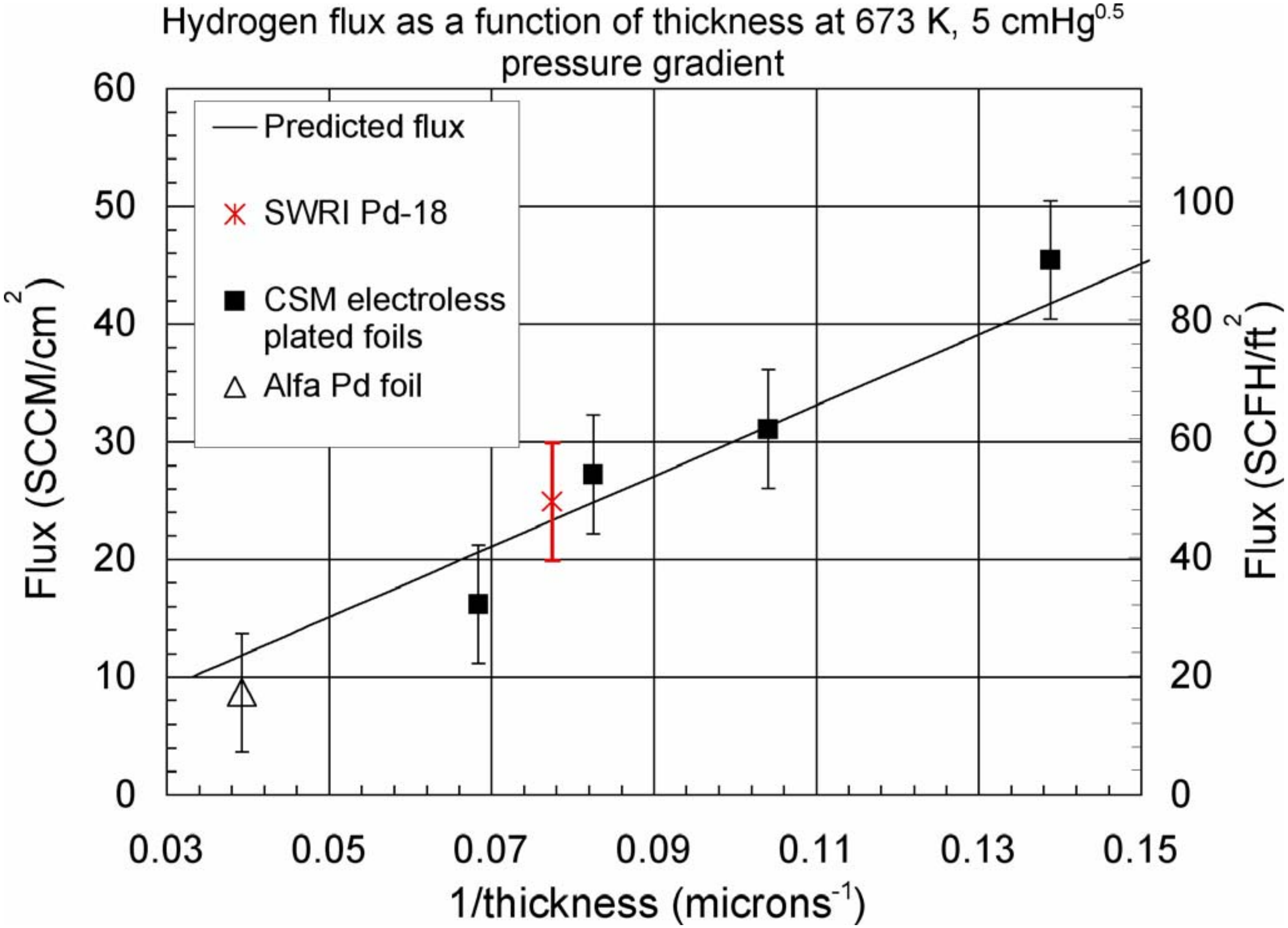
Binary & Ternary Membranes

	Elemental Composition (wt%)			Measured	
Run #	Pd	Cu	Ag	Thickness	Comments
Pd-21	100.0	0.0	0.0	5,201A	tooling run for tk/uniformity
Pd-22	95.3	4.7	0.0	7 um	1st test Pd/Cu 5%, sample sent for EDS, full release mod tens
Pd-23	86.0	14.0	0.0	5.3 um	full release/mildly tensile/4 pinhole. Sample toEDS/thickness
Pd-24	90.8	0.0	9.2	5.6 um	full release/mildly tensile/10+ pinholes. Sample toEDS/thickness
Pd-25	78.3	0.0	21.7	6.2 um	full release/slightly tensile, 1 pinhole, delicate easy to tear
Pd-26	100.0	0.0	0.0	10,000A	test for thickness uniform
Pd-27	100.0	0.0	0.0	na	run to clean target, Cu and Ag chips removed
Pd-28	68.3	27.5	4.2	5.3 um	Pd target with 72 Cu chips/11 Ag chips

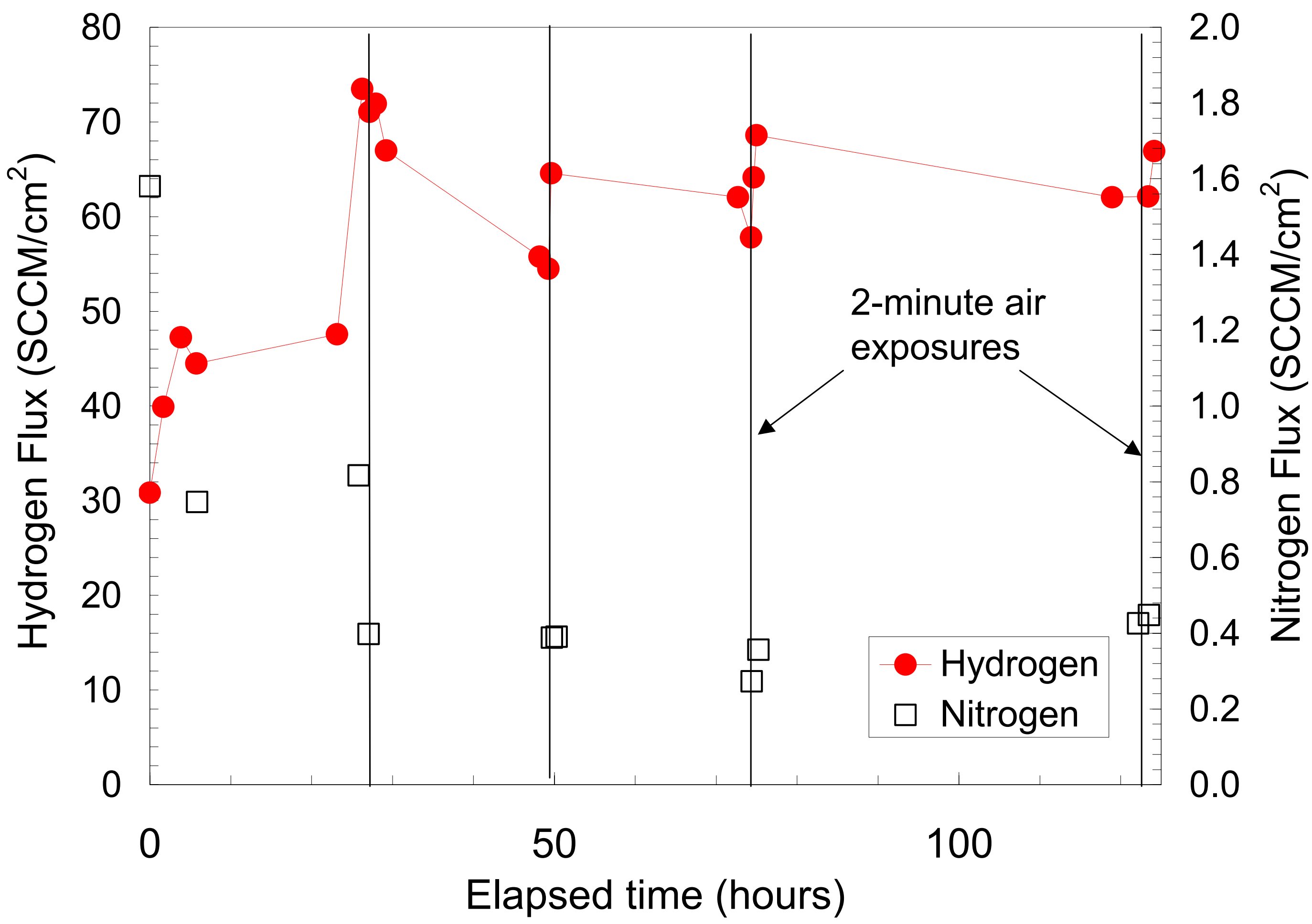




The influence of reciprocal thickness on the pure hydrogen flux at 400°C and 32 psia hydrogen feed pressure



The development of flux as a function of time at 400°C and 20 psi feed pressure



Comparing Ternary and Binary Films

Two foils tested under identical conditions
$Pd_{80}Cu_{17}Ag_4$ and $Pd_{86}Cu_{14}$ (wt.%)

T (^oC)	H_2/N_2 Selectivity		Permeability Ratio
	Binary	Ternary	
250	45	> 640	1.24
350	74	>1320	1.22
400	134	>1790	1.21

Adding a small amount of Ag appears to improve permeability of binary alloy, although observed increase is less dramatic than predicted by theory for similar compositions

Theory suggests that permeability ratio will increase as T is lowered – this is not observed in the current experiments

Future Work

The following milestones will be addressed.

- A minimum of 20 membrane specimens with different copper concentrations based on GT hydrogen transport predictions for the 2-3 most promising ternary elements will be fabricated.
- Four to five preliminary membrane samples will be tested at TDA and IdaTech with clean Syngas and single impurity additions of H_2S and COs.

Specifics

- Calculations in progress: Pd-Cu-Ni and Pd-Cu-Pt
  - planned: Pd-Ag-Au and Pd-Ag-Pt
- Further experimental testing with thicker foils (10-15 mm) will be used to characterize ternary foils

Summary (Year 1)

- A rigorous strategy for predicting H permeability through ternary alloys using first-principles calculations has been developed for
  - Pd-Cu-Ag and Pd-Cu-Au
  - Calculations in progress: Pd-Cu-Ni and Pd-Cu-Pt
- Thin (5-10 micron) membranes of Pd60/Cu40, Pd96M4 and Pd74Cu22Ag4 have been coated and these samples provided to CSM for structural and composition measurements and permeation testing
- Pure gas hydrogen and nitrogen permeation rates have been determined at CSM for a range of pressure differentials (5 to 150 psig feed pressure) and temperatures ranging from 200 to 500°C.
- Freestanding alloy films of Pd, Pd-Cu, and Pd-Cu-Ag show
  - Pure Pd and Pd-Cu alloys give permeabilities in reasonable agreement with prior literature
  - Preliminary tests indicate that adding ~4 wt.% Ag improves permeability of Pd-Cu by ~20-25%.
- Program is on-schedule and on budget.

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 in2), highest performance separation membranes 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**
  - Commercial partner in IdaTech, long track record testing hydrogen membranes at CSM, modeling with Georgia Tech
- **Future R&D**
  - Test under more aggressive conditions, develop new ternary alloy formulations with increased durability