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 #PD16

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Overview

Timeline

- Project start: Sep. 09, 2003
- Project end: Oct. 31, 2007
- Percent complete: ~95%

Budget

- Total project funding (3 year)
  - DOE share: $775,771
  - Contractor share: $194,200
- Funding received in FY06
  - $263,671
- Funding for FY07
  - $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)

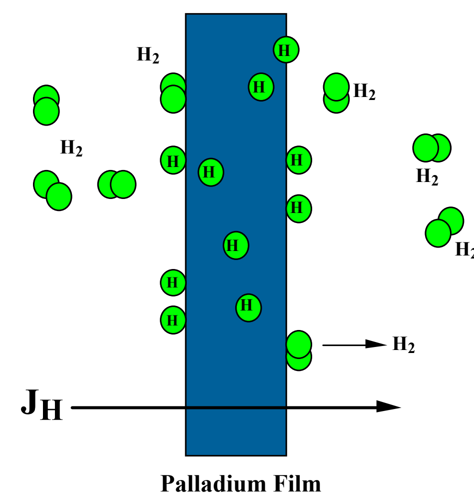
Partners

- 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.**



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 (Complete)
  - Task 3: Prototype Module Final Assembly and Testing (75% Complete)
  - Task 4: Develop Cost Estimates for Production of Pd Membranes (Complete)

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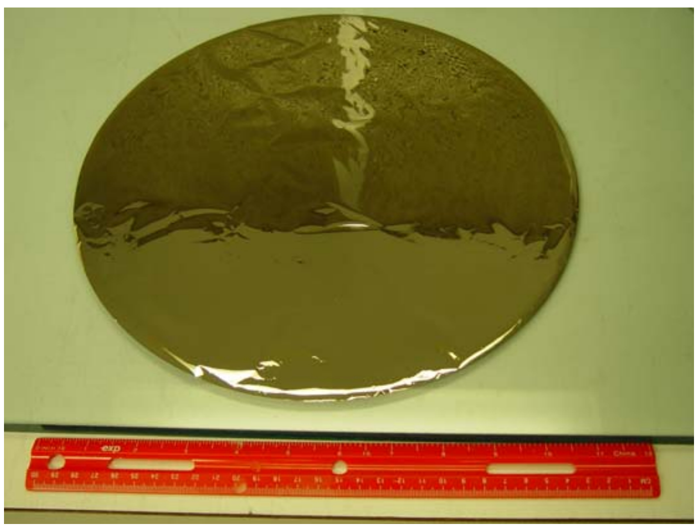
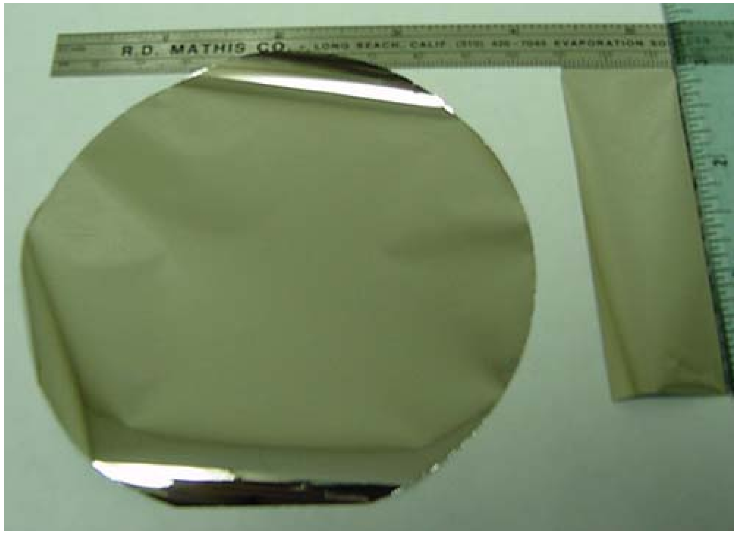
Deposition

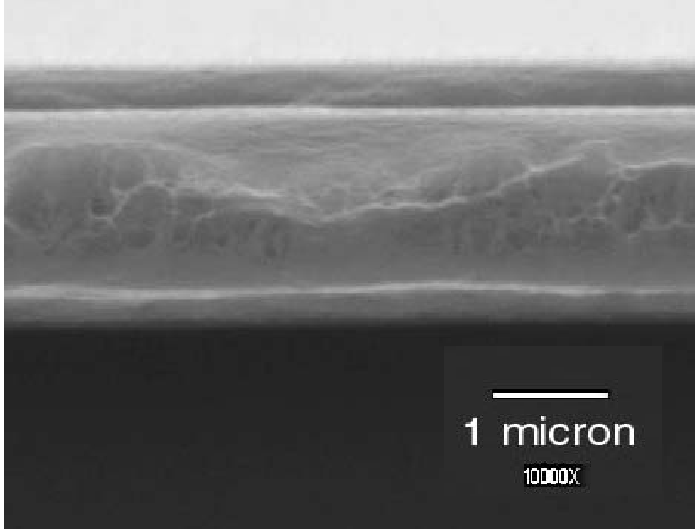
	Plasma Clean	Compliant Layer	Deposition
Power (Watts)	18	500	500
Pressure (mTorr)	0.2	18.0	0.15
Deposition rate (A/s)	-	3.6	3.6
Duration (min)	15	2	245



Membranes

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



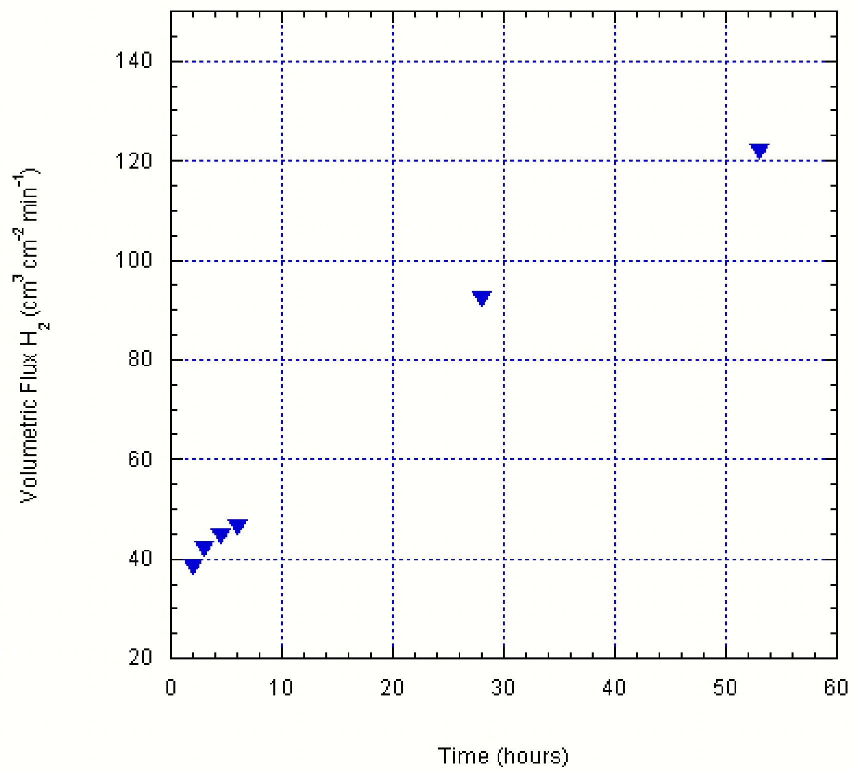


Measured H_2 Flux Has Surpassed Program Goals

- Best performance data @ 400 °C shown for a 2.5 μm Pd-Cu alloy foil, area = 2.6 cm2
  - *Pure H2 permeability =*

$8 \cdot 10^{-5}$ cm³•cm/cm²•s•cmHg$^{0.5}$

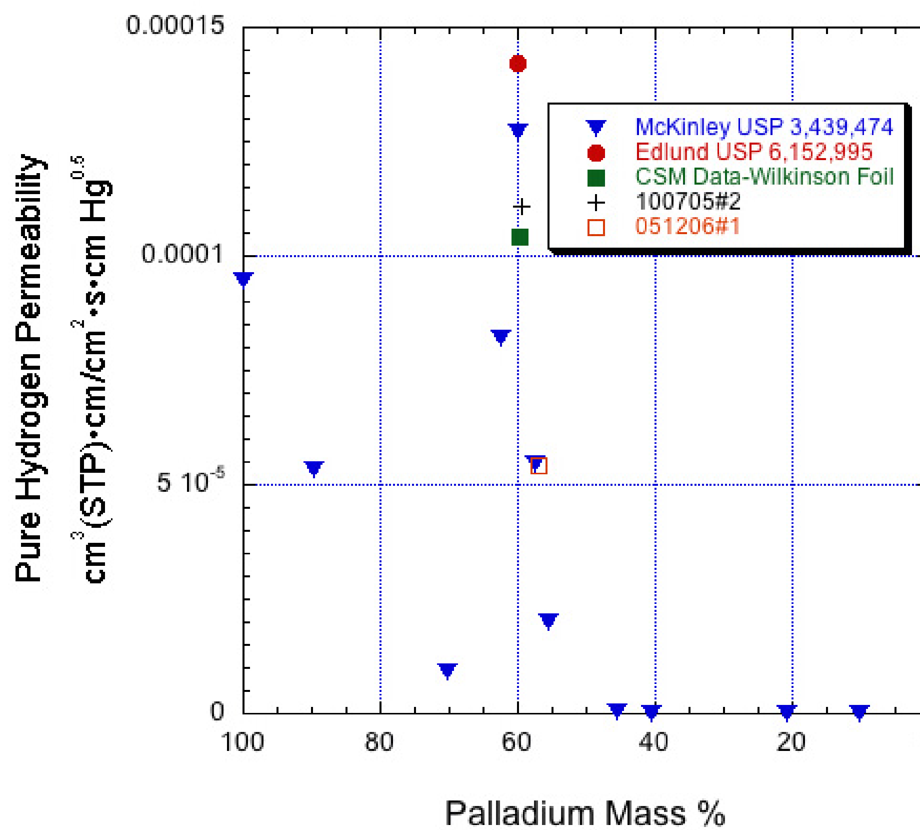
  - *H_2 Flux = 124 cm³/cm²•min =* **242 scfh/ft²**
  - *Feed pressure =* **20 psig**
- Exceeds DOE Hydrogen Program and 2010 DOE Fossil Energy targets



	SwRI Membrane	2007 Target	2010 Target	2015 Target
Flux scfh/ft² @ 100 psi DP H_2 partial pressure & 50 psid	564	100	200	300

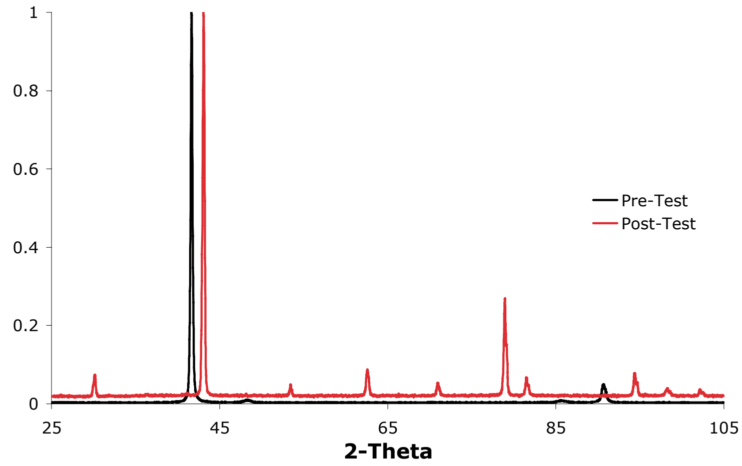
Membrane Composition

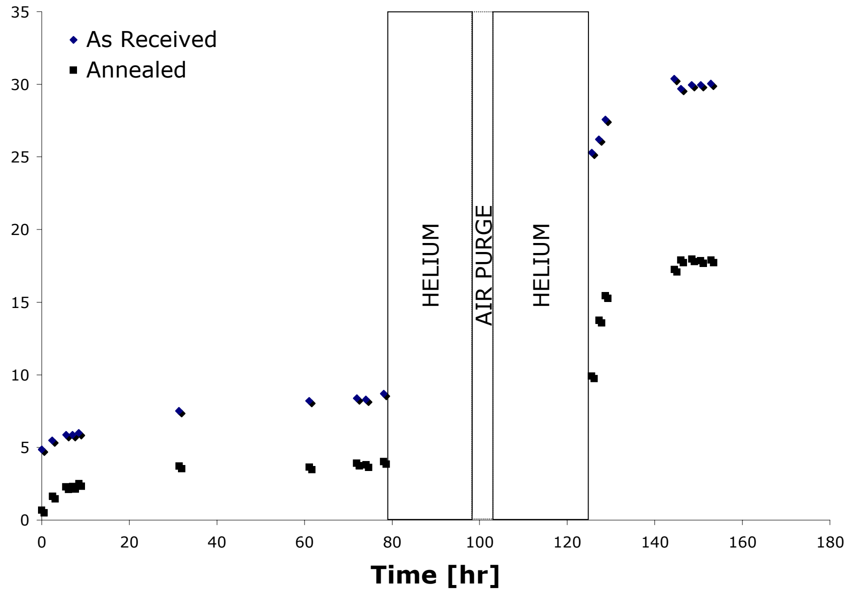
- Permeability correlation with composition consistent with literature
- Wilkinson Foil as a standard
- Test Cycle
  - Forming gas, 8hrs 400°C
  - He, 24 hrs, 400°C (no flux)
  - H_2, 250hrs, 400°C
  - Air Purge, 400°C
  - H_2, 400°C



Annealing

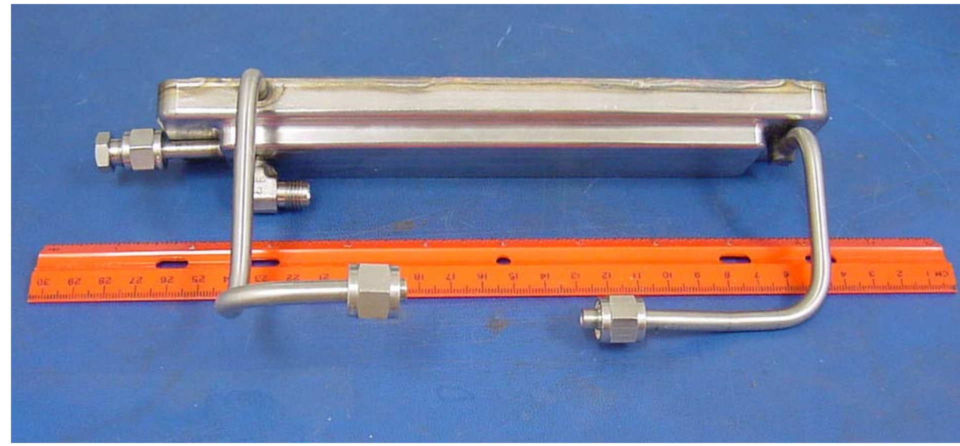
- As prepared
  - 8.83x10^{-5} cm^3(STP)cm/cm^2.s,cmHg$^{0.5}$
- Annealed 450°C
  - 5.26x10^{-5} cm^3(STP)cm/cm^2.s,cmHg$^{0.5}$
- Stress relieved following annealing
- Phase change from alpha to beta

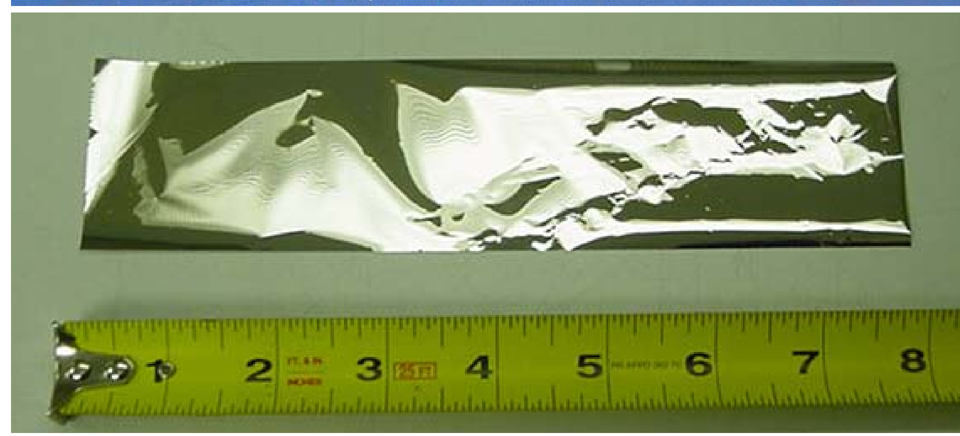




Module Development and Testing at IdaTech

- 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





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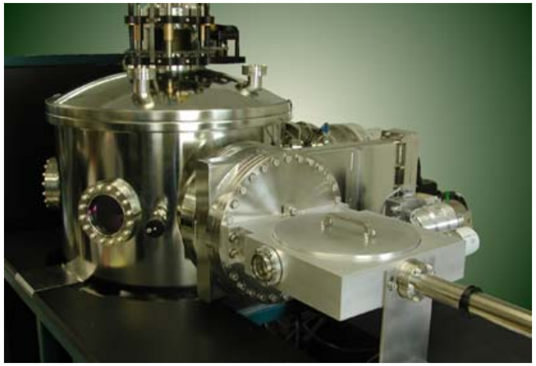
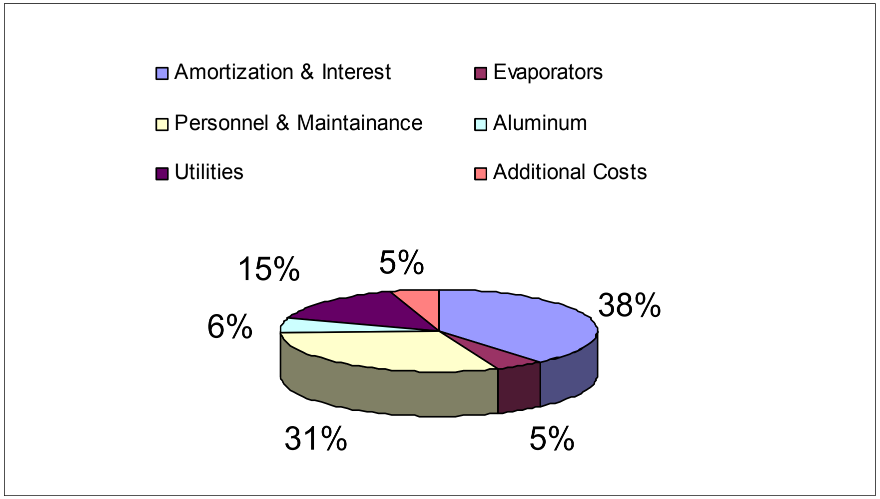
Cost Projections

Total Cost/ft² = (F + L + E) / (P*S*1.75 x10⁵) + 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



Future Work

High Permeability Ternary Palladium Alloy Membranes with improved Sulfur and Halide Tolerance - DE-PS26-06NT42800

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.

Scope of Work

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

Partners

Colorado School of Mines (Way)	TDA Research (Alptekin)
Carnegie Mellon University (Sholl)	IdaTech (Pledger)

Future Work (Continued)

Milestones

Phase I (Year 1)

- *Milestone 1.1*: Use DFT methods to predict H2 flux through Pd96M4 for M = Ni, Rh, Pt, Nb, Ta, V, Mg and Y. Use same methods to predict H_2 flux Pd74Cu22M4 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 H2/CO and H_2/H_2S binary mixtures with best three samples from the final optimization study.

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, new interactions with CMU
- **Future R&D**
  - Test under more aggressive conditions, develop new ternary alloy formulations with increased durability, demonstrate low-cost pilot production