2005 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 # PDP16

Overview

Timeline

- Project start: Sep. 09, 2003
- Project end: Sep. 08, 2006
- Percent complete: ~50%

Budget

- Total project funding (3 year)
  - DOE share: $875,771
  - Contractor share: $194,200
- Funding received in FY04*
  - $253,494
- Funding for FY05*
  - $258,606

Barriers

- Barriers addressed
  - 75% feedstock utilization efficiency (LHV) when producing fuels such as H_2 or liquid transportation fuels alone from coal
  - Efficient separation of hydrogen from the reaction zone of water-gas-shift or reforming reactions
  - "Low" temperature (350 – 450 C) separation technology to compliment existing high temperature ceramic membranes

Partners

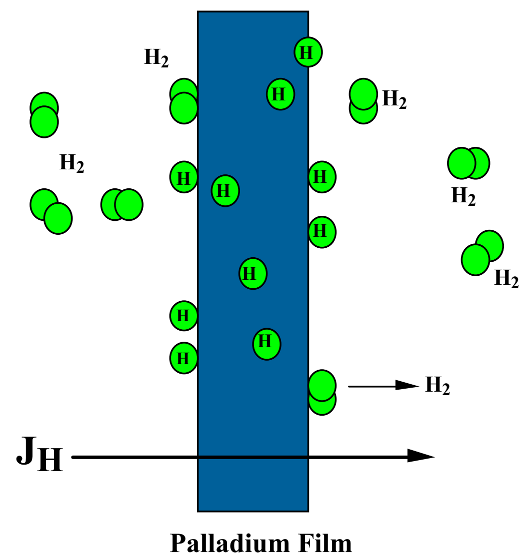
- Interactions/ collaborations
  - Colorado School of Mines (D. Way)
  - IdaTech (D. Edlund)

***Note: Contractual funding profile as program is incrementally funded**

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 (<5 μm thick), 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,**
- **Demonstrate viability of using ion-assisted, vacuum processing to "engineer" a membrane microstructure and surface that optimizes hydrogen permeability, separation efficiency, and lifetime,**
- **Demonstrate efficacy of continuous roll-to-roll manufacturing of membrane material with performance and yields within pre-defined tolerance limits**
- **Establish "scale-independent" correlations between membrane properties and processing parameters**

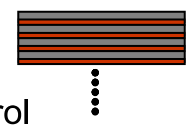


Technical Approach

- Formation of dense Pd alloy films on supporting substrates using ion/plasma-based vacuum processing
  - Deposition of membrane onto sacrificial polymeric membrane such as polystyrene or polyvinyl (PVA)
  - Deposition onto a substrate pretreated with a thin release coating
- Optimization of “release” processes (membrane/substrate)
- Characterization/Testing
  - Nitrogen leak test, SEM/EDX. and XRD
  - H_2/N_2 permeation rates (5-50 psig feed pressure, 200 – 600^{o}C)
  - Determine pressure dependence of H_2 flux
- Membrane Optimization- Microstructural Engineering
  - Surface pre-treatment (restructuring)
  - Micro-alloy additions

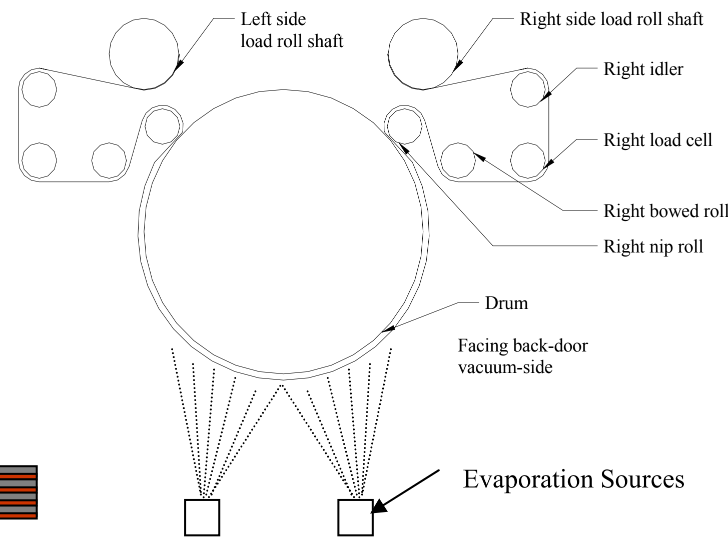
Membrane Fabrication – Flexible Substrates

- **Target:** <12 μm-thick, alloy film (40w/o Cu/60w/o Pd with less than 0.1% variance)
- 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 (Hi 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

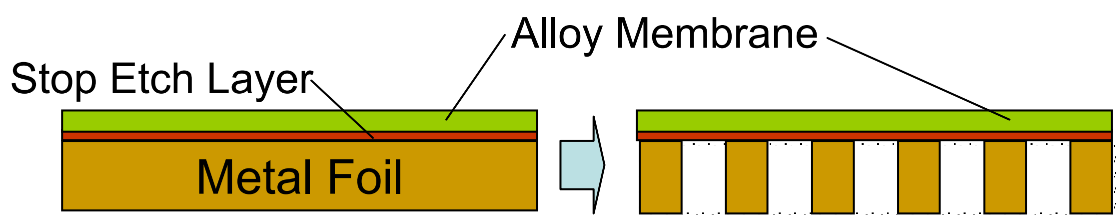


Web roll coater with evaporation sources

Polymer/Flexible Backing Materials

- Successful deposition on PS, PI, PVA, PE, and PET with silicone/non-silicone release liner (CP Films) over large areas (10.5” wide); over 200 feet of material produced
  - Demonstration over large areas (75 in^2)
  - Issues with defects at less than 12 μ-thick

- Deposition on thin (smooth) metal foils (Al, Cu)
  - Selective etch-back of metal backing foil with stop etch layer(structural support)



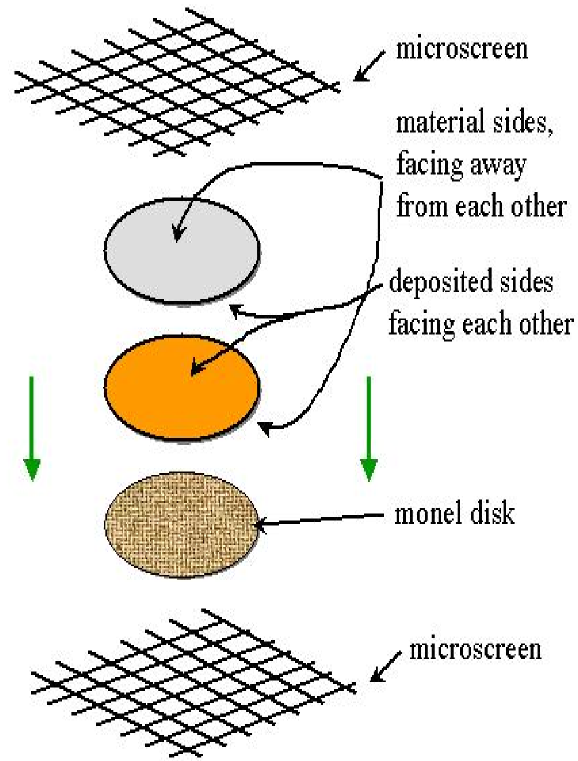
  - Use of inorganic (oxide/salt) release layer for complete removal

Backing Removal Results

•Established procedures for backing removal (solvent) from polymer films

Sacrificial

- Single layer versus sandwich configuration
- Dissolution of backing material as f(time, temperature)
  - 30 seconds in H_2O for PVA (solublon)
  - 600 seconds in chloroform (toluene) for PS
- Air dried
- Permeable supports: Monel mesh, Ag screen, AAO foil, Zircar cloth, ceramic-coated Ag screen



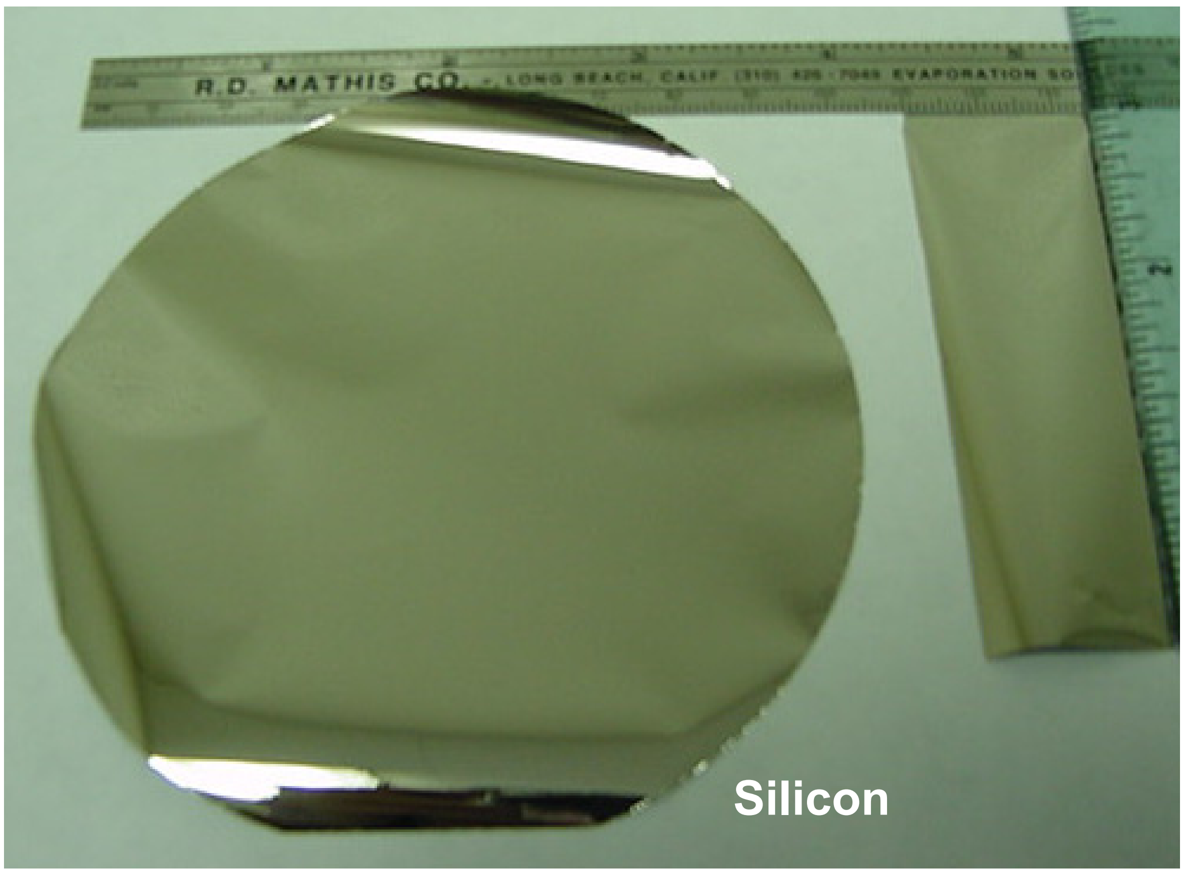
Schematic of sandwich configuration

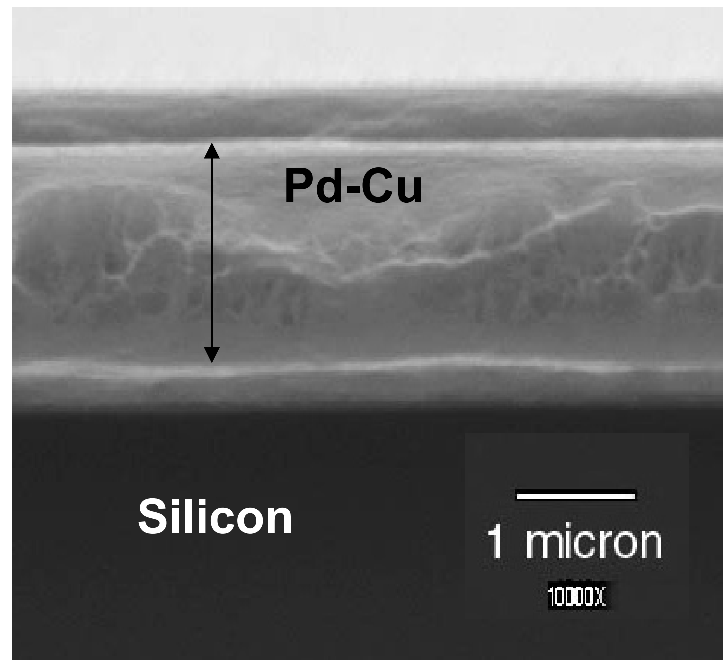
Release

- Coated glass and plastic samples with precursor salt layer (i.e., $MgCl_2$)

Membrane Fabrication – Rigid Substrates

- Formation of free-standing, gas impermeable Pd-Cu membranes, <5 μ-thick, using rigid silicon backing
- Formation of free-standing, Pd-Cu membranes <1 μ-thick with minimal defects

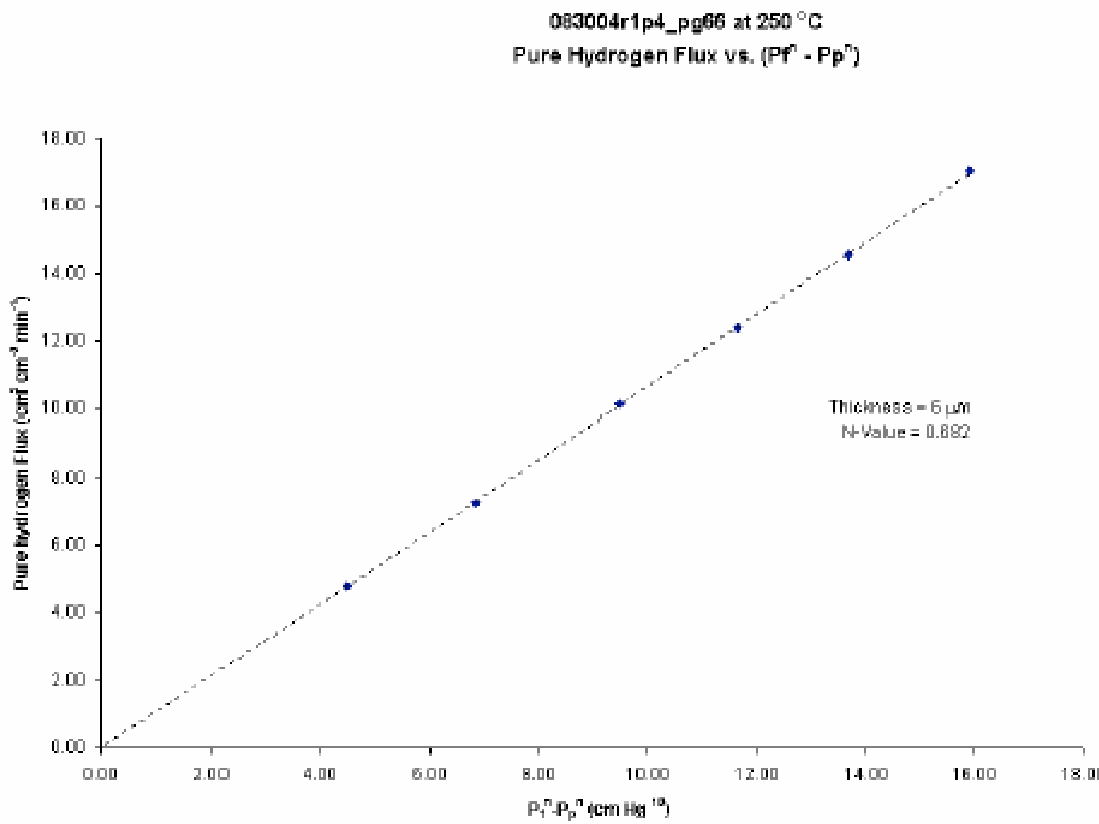




Pure Hydrogen Permeation

- **Demonstrated separation of >99.95% pure hydrogen**

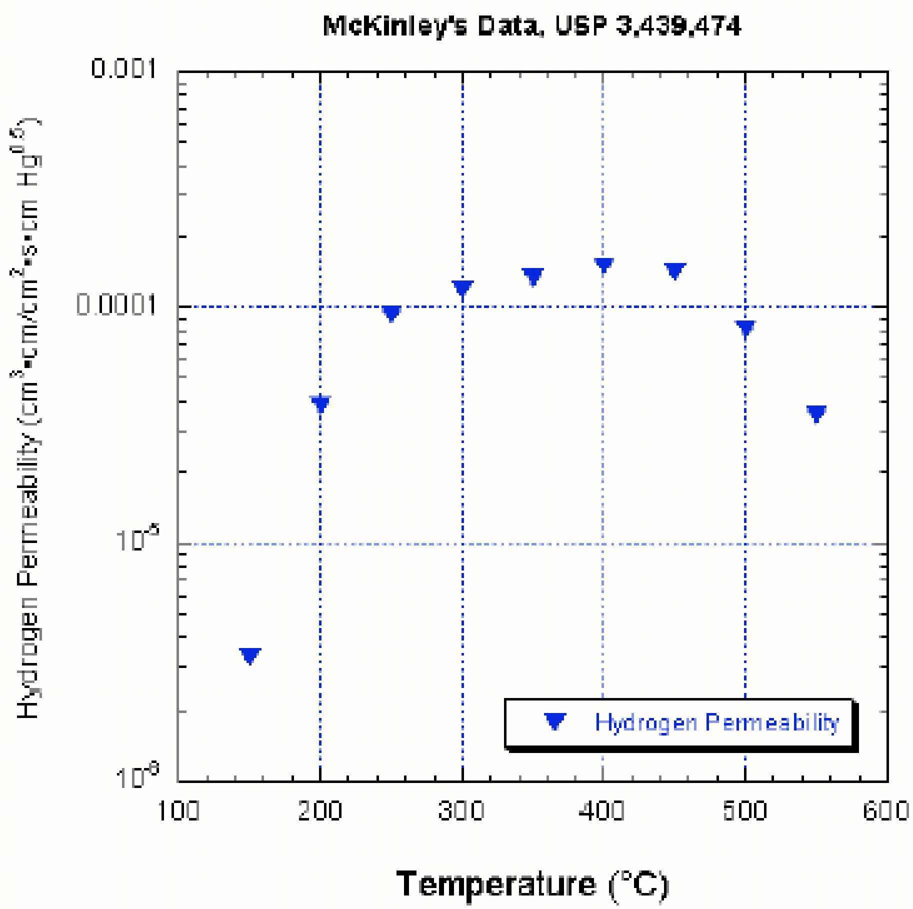
- Thickness = 6 µm
- Composition: 63 wt. % Pd
- Ideal H_2/He selectivity = 9.6
- N-Value = 0.682
  - Flux likely has contributions from solution diffusion as well as Knudsen flow
- Pure H_2 permeability at 250 °C = $2.9 \cdot 10^{-5}$ cm^3 cm / cm^2 s cm $Hg^{0.5}$



Influence of Temperature on Permeability of 60w/o Pd Foil

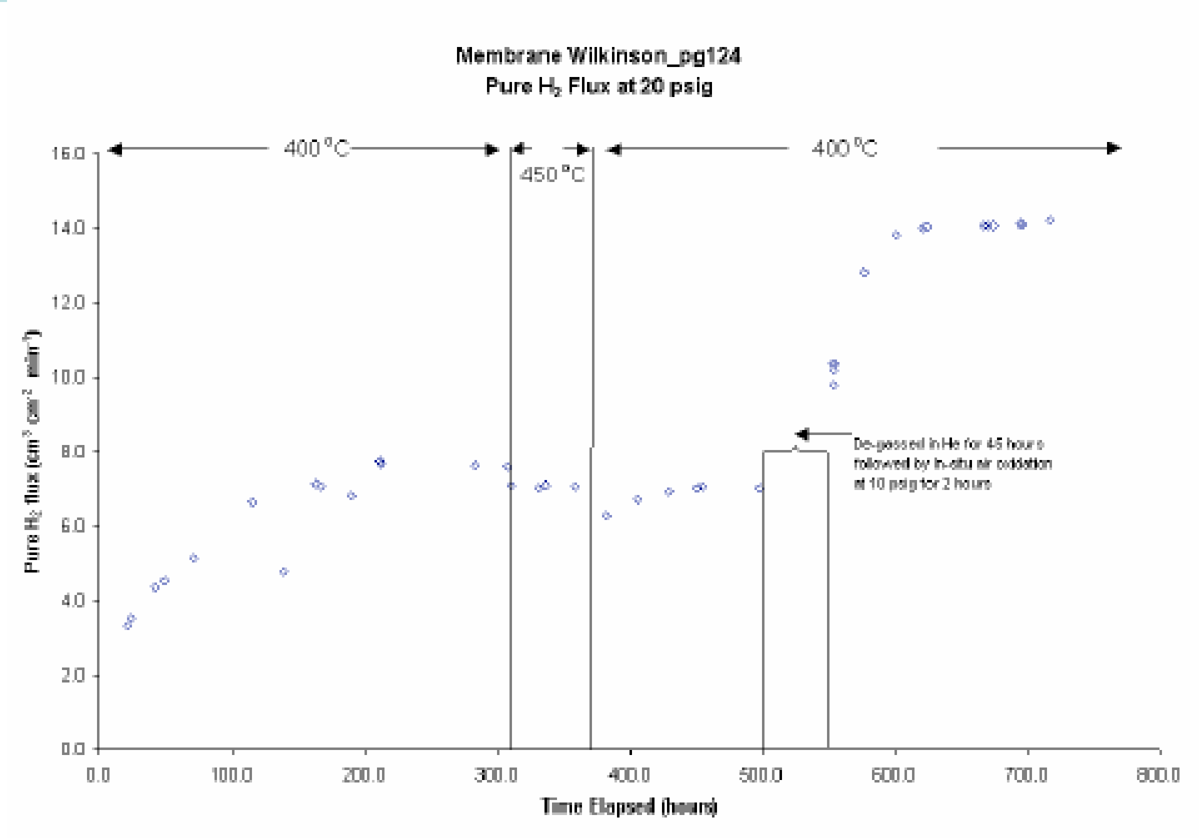
- **Demonstrated maximum permeability at 400 C with sub-optimal composition/structure (transformation from pure β to α plus β structure)**

- Maximum permeability at 400 °C
  - Pure β to mixed phase
- Can predict permeability of 62.5 wt.% foil assuming a constant activation energy
  - At 250 °C, predicted pure H_2 Permeability is $5.2 \cdot 10^{-5}$ cm^3 cm / cm^2 s $cmHg^{0.5}$

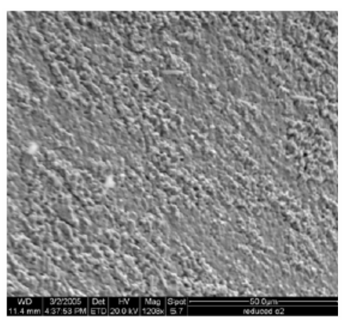


Influence of Surface Pre-treatment (Restructuring)

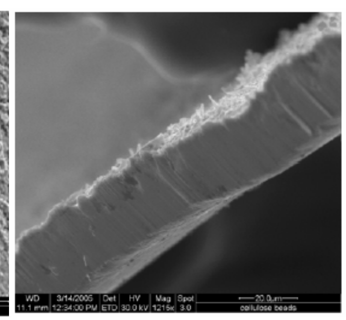
- **Surface pre-treatment prior to operation establishes new steady state performance with increases in hydrogen permeation of up to 100%**
- **Repeatable process with same material**



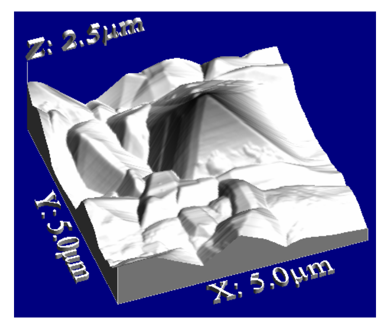
- **SEM characterization confirms surface restructuring**



Top View



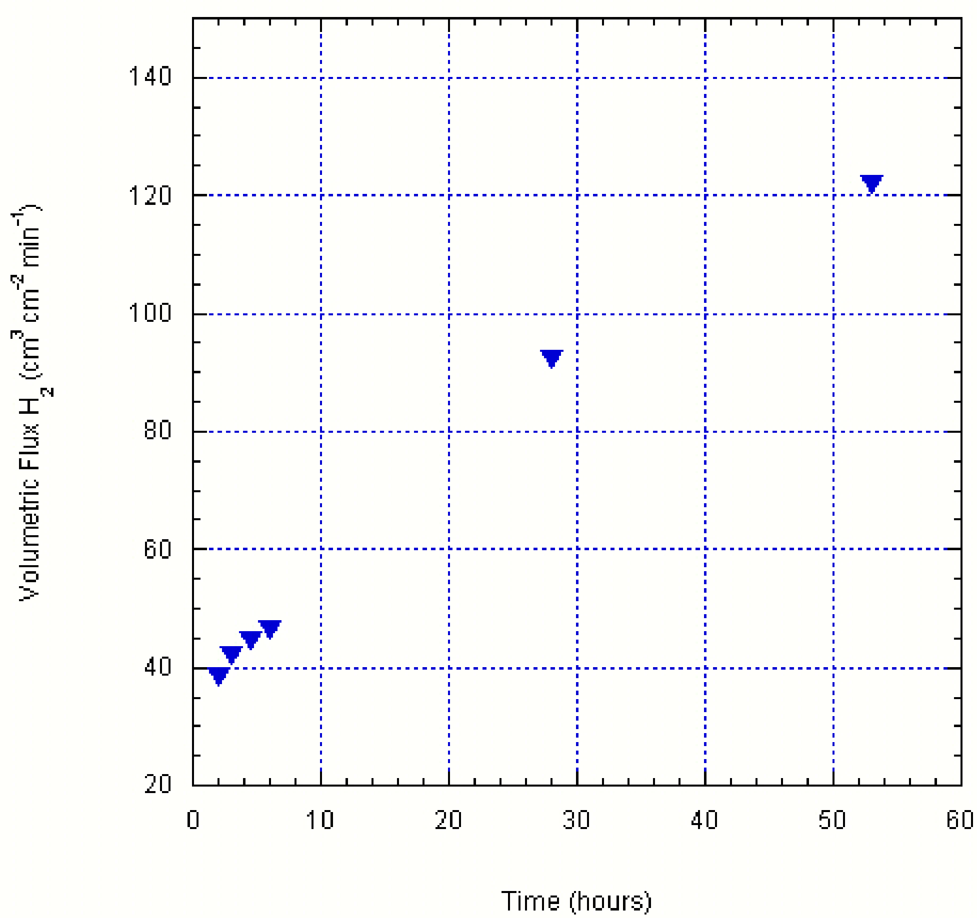
Cross Section



Representative AFM Image

Measured H2 Permeability Surpassing Program Goals

- Best performance data @ 400 °C shown for a 5 µm Pd-Cu alloy foil, area = 2.6 cm^2
  - *Pure H_2 permeability* = **$2 \cdot 10^{-4}$ $cm^3 \cdot cm/cm^2 \cdot s \cdot cmHg^{0.5}$**
  - *H_2 Flux = 124 $cm^3/cm^2 \cdot min$* = **242 $SCF/ft^2 \cdot h$**
  - *Feed pressure =* **20 psig**
- Exceeds DOE Hydrogen Program and 2010 DOE Fossil Energy targets!



Future Work

Remainder of FY05

- Enhanced H_2 permeation (Pd alloy system)
  - Alloy (Ag, Sn, V, Y, other)/Structure Optimization
  - Minimization of defects
- Module Demonstration (Complete performance and characterization studies @ 75 in^2)
  - Develop procedures for handling and alternative designs for sealing
  - Develop pre-treatment protocols for optimum performance

FY06

- Prototype Module Demonstration

  (50 cm^3/cm^2-min of 99.95% pure hydrogen)

Supplemental Slides

The following three slides are for the purposes of the reviewers only – they are not to be presented as part of your oral or poster presentation. They will be included in the hardcopies of your presentation that might be made for review purposes.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Explosion during hydrogen permeation testing

Hydrogen Safety

Our approach to deal with this hazard is:

- Pressure testing of all metal system with helium (smaller, “slippery” gas) prior to hydrogen testing
- Full implementation of gas detection system that automatically shuts down system in the event of a leak
- Small volume testing under hood where dilution effect is enormous