Pd Alloy Membranes for Hydrogen Separation from Coal-Derived Syngas

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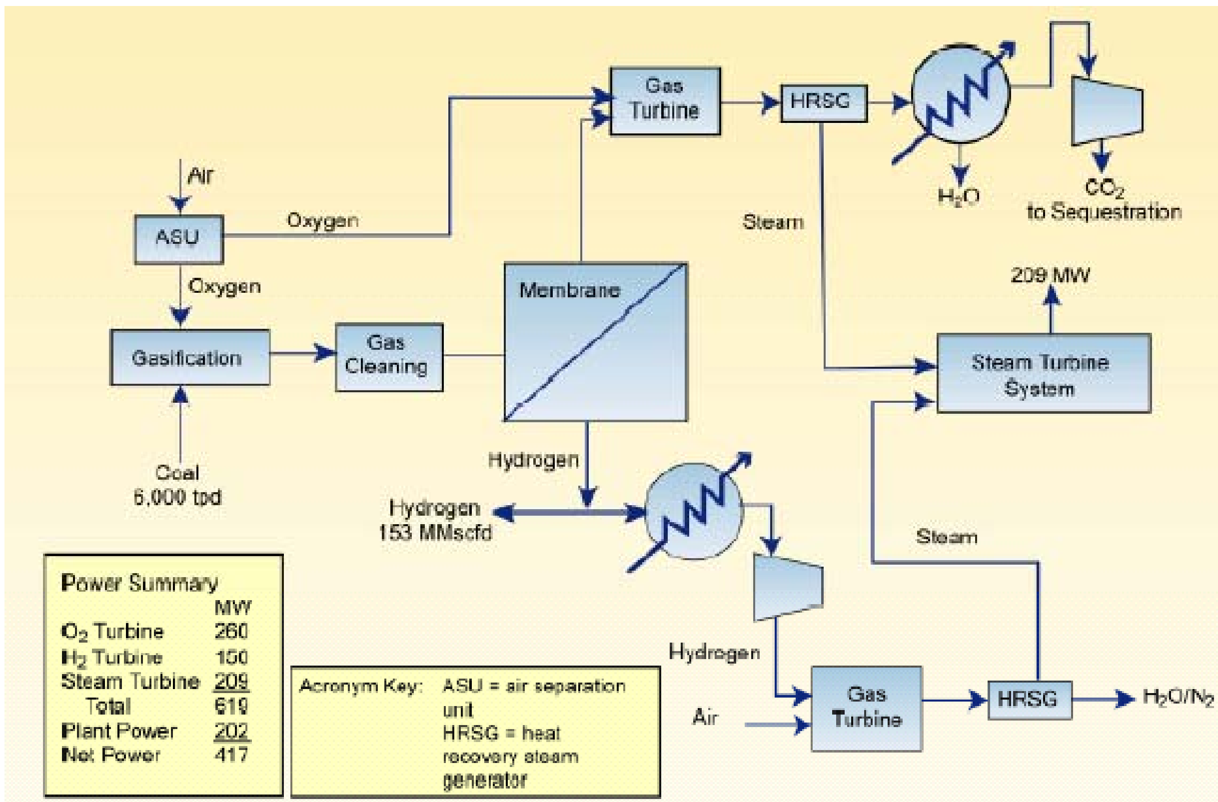
Introduction

- **Advanced coal-to-hydrogen plants have the potential of co-generating power and a hydrogen in volumes sufficient to fuel the fuel cell-powered vehicles**
- **System studies show enhanced efficiency for coal-to-hydrogen plants if the WGS and H_2 separation were combined into a single step**
  - **H_2 can be produced at $3.98/MMBtu ($0.54/kg) in IGCC-based co-generation plant**
  - **Further cost reduction to $3.0/MMBtu if SOFCs were used to generate electricity**



Source: Mitretek Report to NETL, Gray and Tomlinson, 2003.

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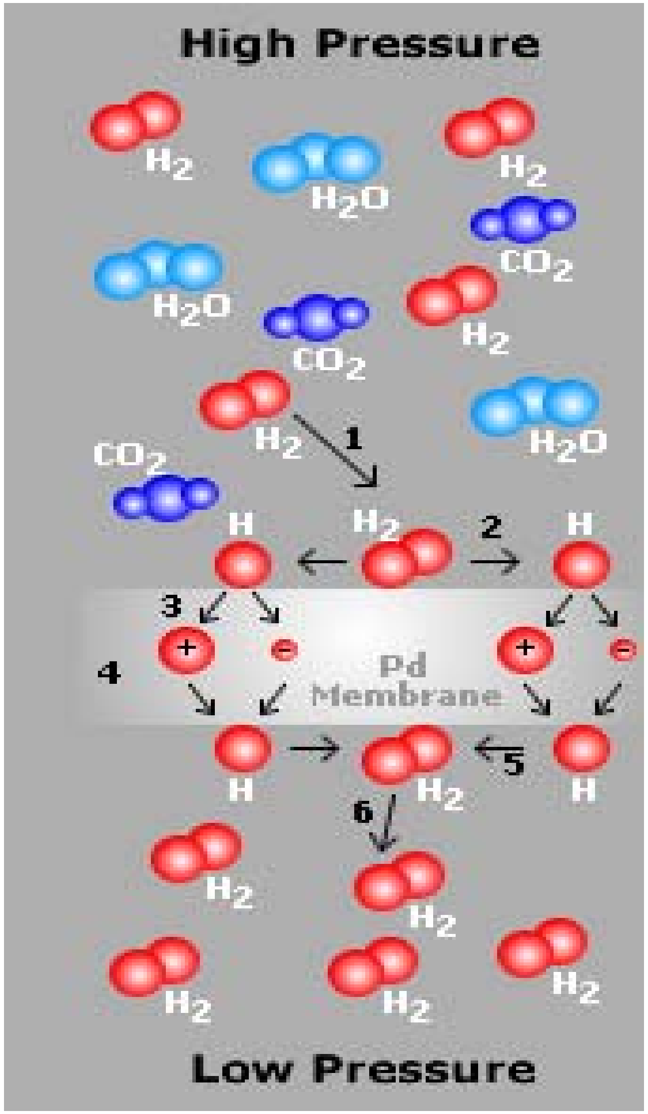
Membrane Requirements

- **Requirements**
  - High H_2 flux
  - High H_2 purity
  - Robustness and resistance to degradation by thermal cycling
  - Operation at the right temperature range (260-450^{o}C)
    - Above the dew point of the syngas but low enough to achieve effective contaminant control
  - Tolerance to all components of coal-derived synthesis gas
    - Particularly to sulfur
- **Potential Technologies for H_2 Separation**
  - Pressure Swing Adsorption (PSA)
  - Ceramic membranes
  - Dense ceramic membranes
- **Our approach is composite Pd alloy membranes**
  - CSM carries out film deposition and characterization
  - TDA carries out support development, membrane testing and module development

Why Pd Membranes?

- Potential for perfect H_2 selectivity
  - The transport mechanism is unique to hydrogen
  - Palladium catalyzes the dissociation of molecular H_2 into atomic H
  - H atom is soluble in Pd metal and transports through a solution-diffusion mechanism
  - H atoms recombine at the low pressure side and desorb from the surface
- Potential for high flux
  - Flux and permeability a function of solubility and diffusion rate



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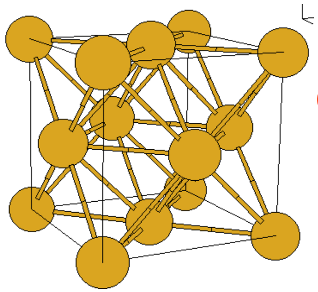
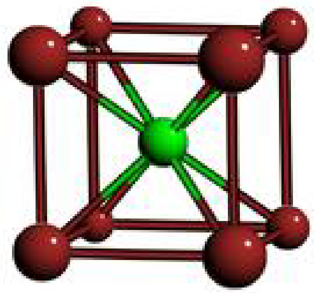
Why Pd Alloy Membranes?

- **Membranes based on *pure* Pd suffer from embrittlement and cracking due to the α→β Pd hydride phase transition (at ~300°C)**
  - FCC to BCC phase change causes structural deformations in the film



α phase is FCC

- **Pd alloys avoids the α→β phase transition in pure Pd**
  - Alloying eliminates swelling, warping, cracking due to phase transitions
  - Eliminates the problems associated with thermal cycles



β phase is BCC

- **Some Pd alloys shows higher permeability than the pure Pd**
  - 27% Ag, 6% Ru, 40% Cu, 5% Au alloys have shown to have much higher fluxes than pure Pd films
- **Additional benefits of alloying**
  - Reduced cost (depending on the selected component)
  - Resistant to H_2S
  - Dimensional stability (small degree of swelling)

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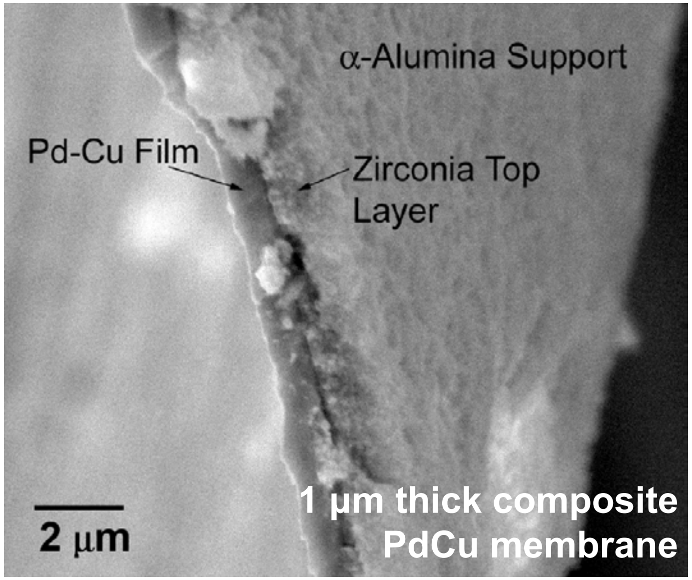
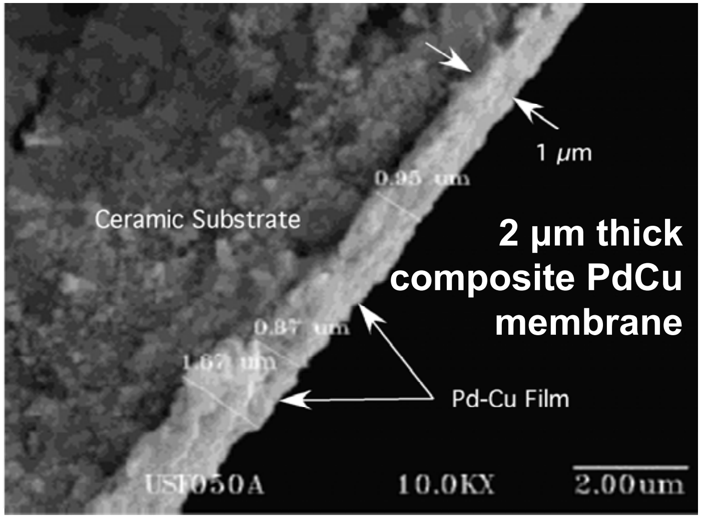
Why Pd Composite Membranes?

- Pd alloys can be prepared into self supporting structures or can be prepared on porous supports (i.e., composite membranes) as thin films
- Thin films increases the H_2 flux at a given pressure
- Flux equation in Pd membranes (Way, 1996)

$$J_H = \frac{P_H}{l_m}\left(\sqrt{p_{H_2,feed}} - \sqrt{p_{H_2,permeate}}\right)$$

- Low cost when the alloys made into thin alloy films
  - 5 µm PdCu (60/40) film
    - Pd cost = $20/ft^2 Cu Cost = 0.70/ft^2
- 25 µm PdCu alloy will cost 5 times higher material cost and its flux will be much lower
- The original idea is from the work of Uemiya and Kikuchi, *Chem. Lett.*, 1687, 1988
- The challenge is how to make them and operate them at high pressures





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Why Electroless Plating?

- **Advantages**
  - No expensive, complex equipment needed
  - Scale-up feasible
  - Simple technique with easy parameters to control
  - Can plate complex geometries
  - Consecutive plating followed by annealing to produce alloys
  - Produces high flux membranes
- **Disadvantages**
  - Possible contamination from carbon
  - Pd membrane thickness related to support surface roughness

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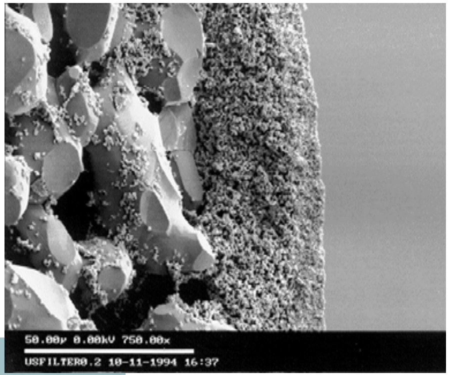
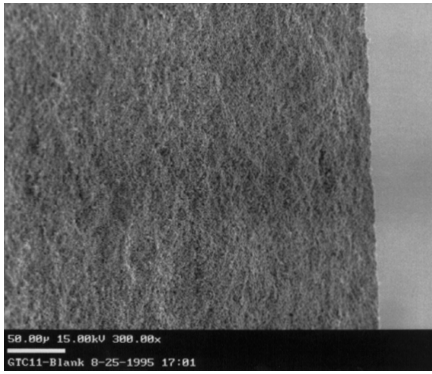
Porous Supports for Deposition of Pd Films

- **Previous work at CSM focused on preparing thin Pd or Pd alloy films on ceramic supports**
  - Pd alloy film thickness ~1-5 µm
  - Supports are commercially available by CoorsTek, and Pall originally developed for gas filtration
- **The substrates can be symmetric (constant pore size) or asymmetric (gradient in pore size)**
- **Symmetric ceramic supports**
  - Low cost
    - Symmetric Supports ~ $25/ft^2
    - Asymmetric Supports > $500/ft^2
  - Higher strength, less defects



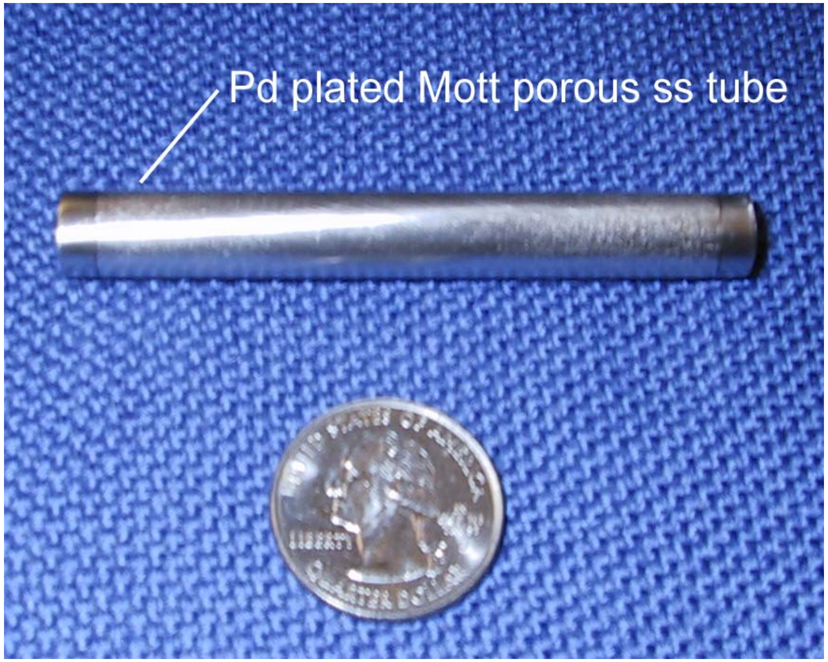
Asymmetric Support



Symmetric Support

- **Membrane film is deposited either on the inside or outside diameter of the porous supports**

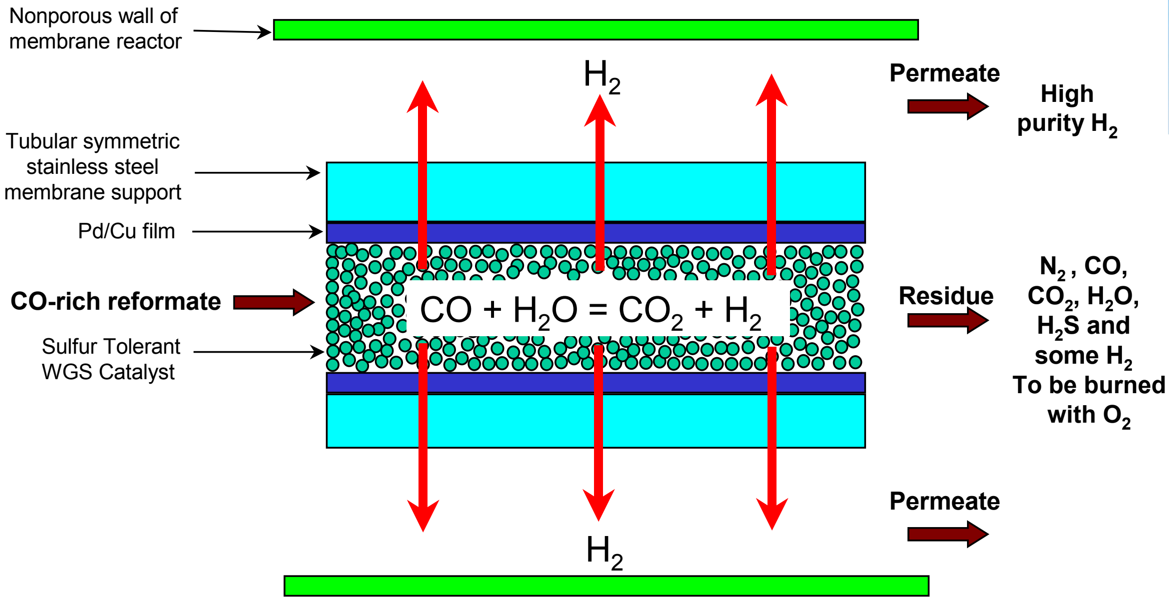
Preparation of Pd Alloy Films on Steel Supports

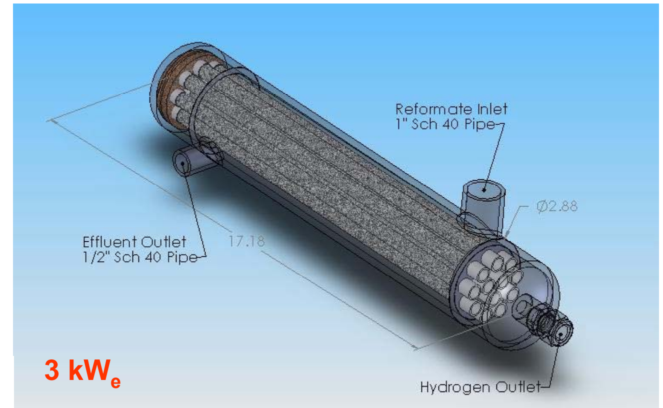


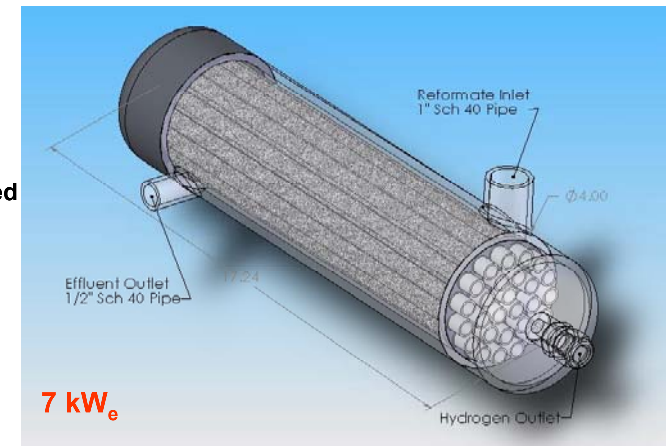
- **Porous steel supports increases the robustness over the ceramic supports**
- **It is much easier to incorporate the metal supported membranes into modules**
  - Welding or brazing
- **Elimination of ceramic/metal joints minimize leaks**
- **Issues need to be addressed:**
  - Surface roughness
    - Thicker films are required
  - Inter-metallic diffusion
    - Cause formation of an undesired alloy
- **A diffusion barrier addresses all these problems:**
  - An oxide layer diffusion barrier deposited on steel support prior to plating prevent diffusion of Pd membrane and support
  - If the oxide layer diffusion barrier can be applied is in the form of small particles, surface roughness may be reduced

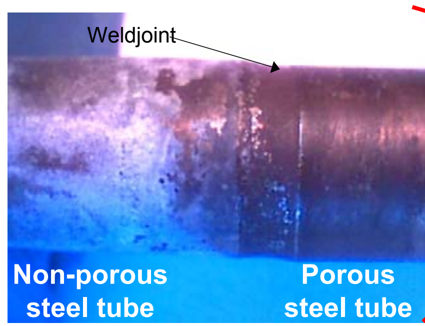
Module Construction

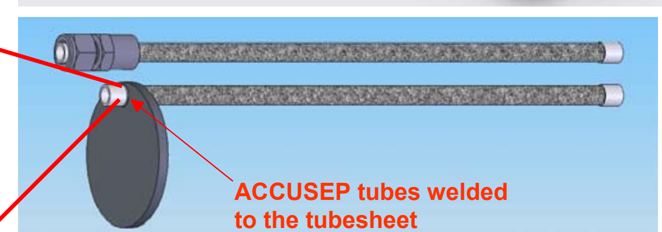
- **The final membrane module or the membrane-WGS reactor will be similar to a shell-and-tube type heat exchanger**











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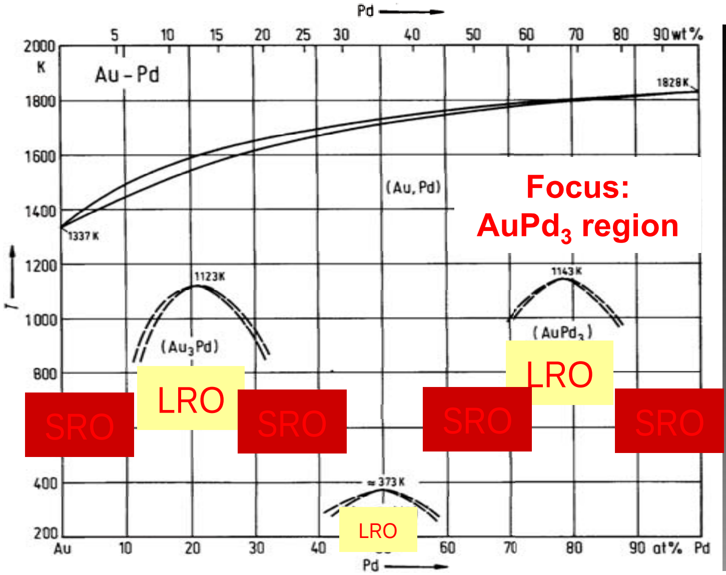
Outline

- **Introduction**
- **Background on Composite Pd Alloy Membranes**
- **Results**
  - Sulfur Tolerant Composite PdAu Membranes
  - Metal Supported PdAu Membrane
- **Future Work**

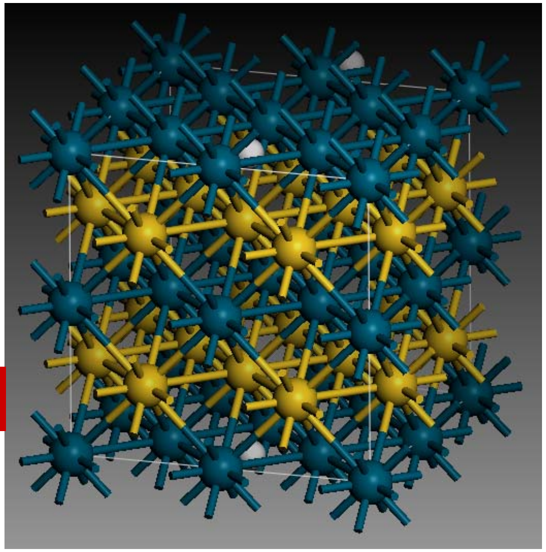
Molecular Modeling

- **Molecular Dynamics Simulation is used to identify a promising Pd alloy composition that provides high flux and sulfur resistance**
- **PdCu and PdAu alloys were selected for initial considerations**
  - Pd-rich alloys were examined both because of their lower cost and higher performance

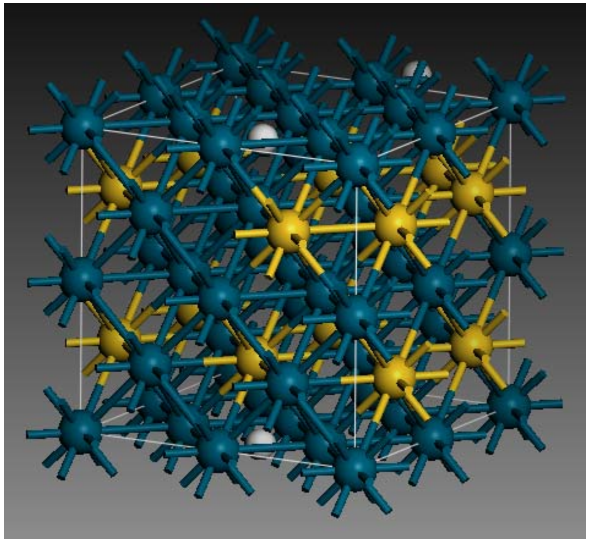
Polycrystalline arrangements



All crystal structure in diagram are FCC



$Au_{50}Pd_{50}$



$Au_{25}Pd_{75}$

- **Atomistic studies were performed to measure rate of H atom diffusion through Au-Pd_3 lattice at 300-400^{o}C range**

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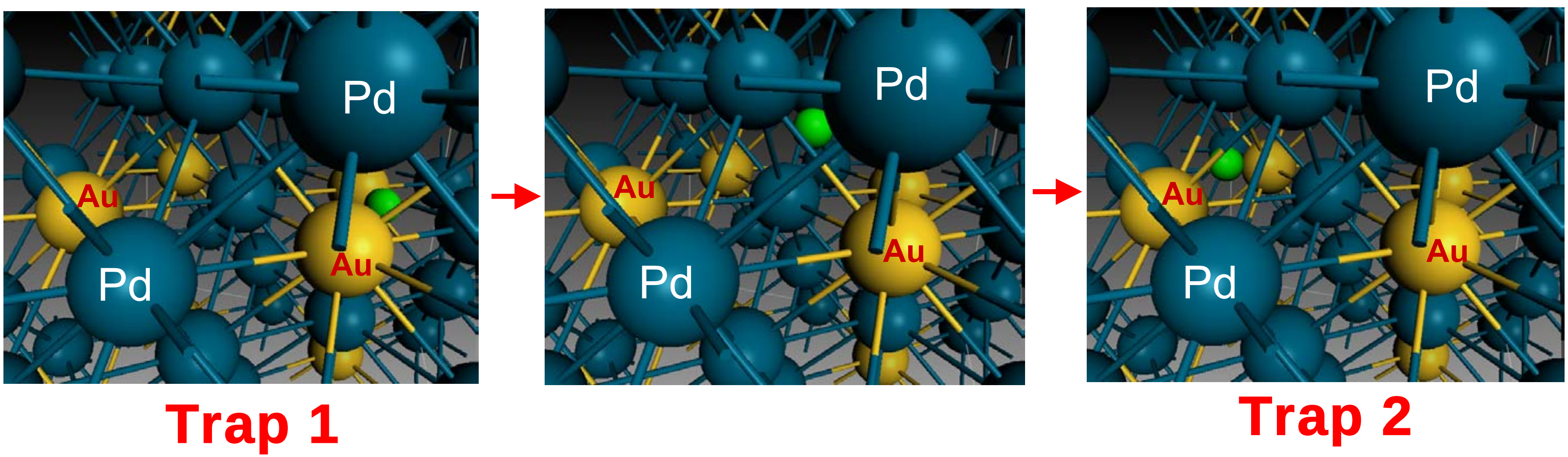
Diffusion of H through PdAu Alloy

- **Molecular simulation results showed that H atom transport in the $Pd_{75}Au_{25}$ matrix is slower than it is in the $Pd_{60}Cu_{40}$ at 400°C**
  - Both lattices are dilated to the same extent lattice to increase diffusivity



- **Au atoms act as effective trap sites for H atom and slow the diffusion rate**
  - Slower transport rates are correlated to higher activation energy for H diffusion

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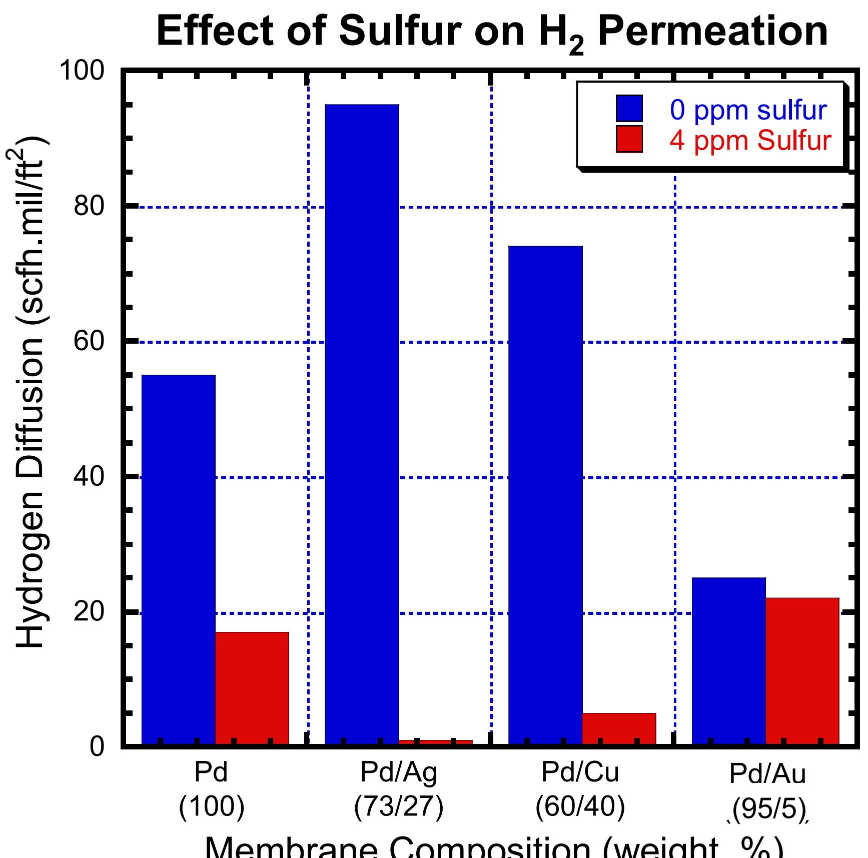
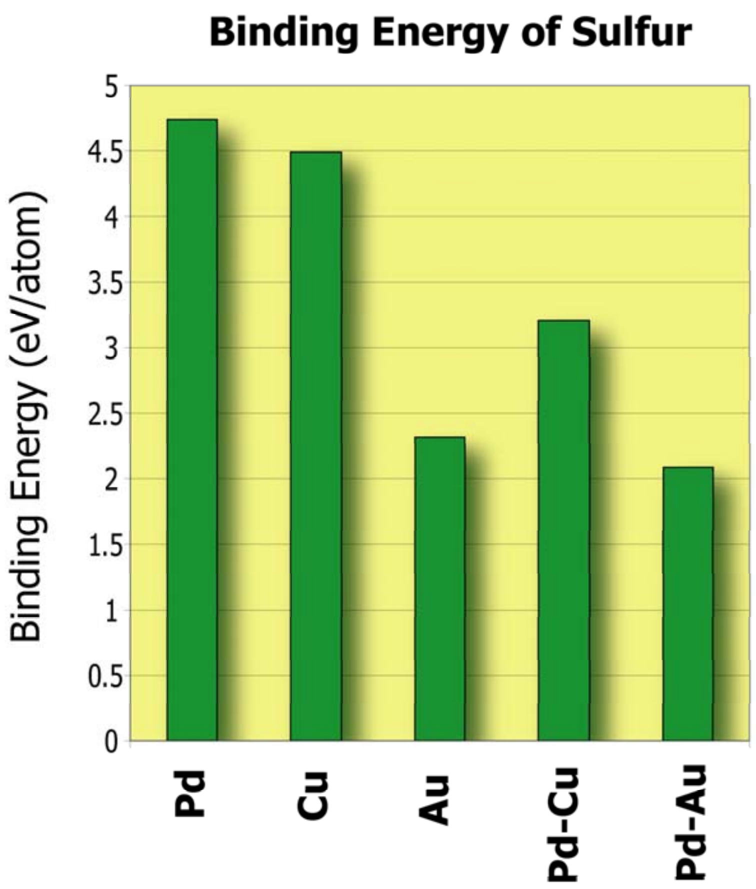
Impact of Sulfur on Pd Alloys



Int. Conf. On Membranes (Way and Alptekin, 2006)



- Experimental evidence also confirms our model predictions
- In the presence of sulfur PdAu alloys show much higher stability
- PdAu alloy shows the a low binding energy for sulfur atom

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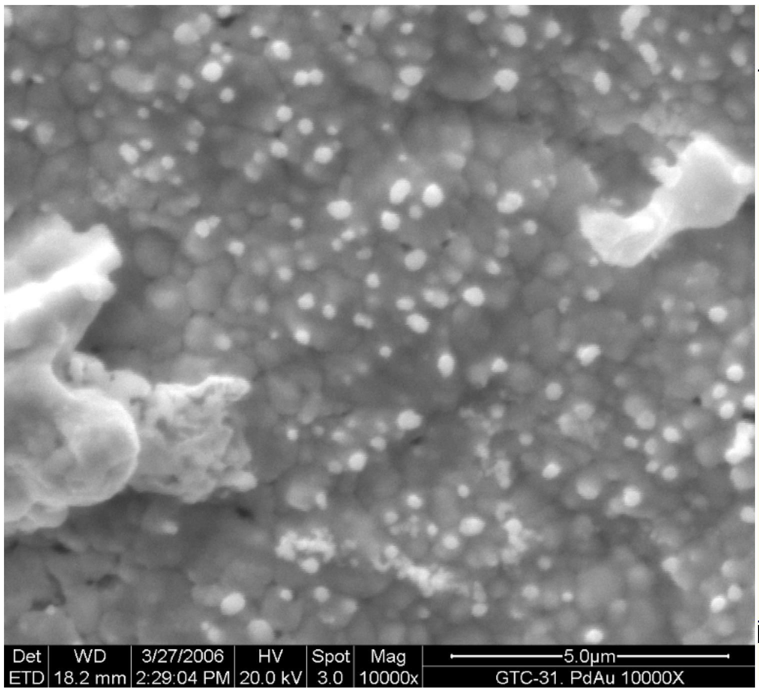
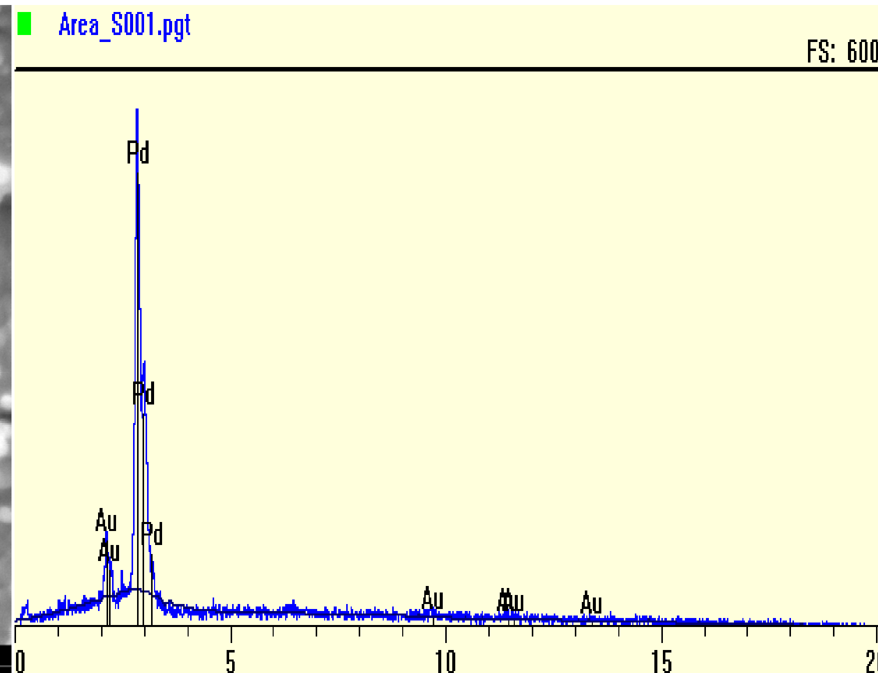
Membrane Preparation

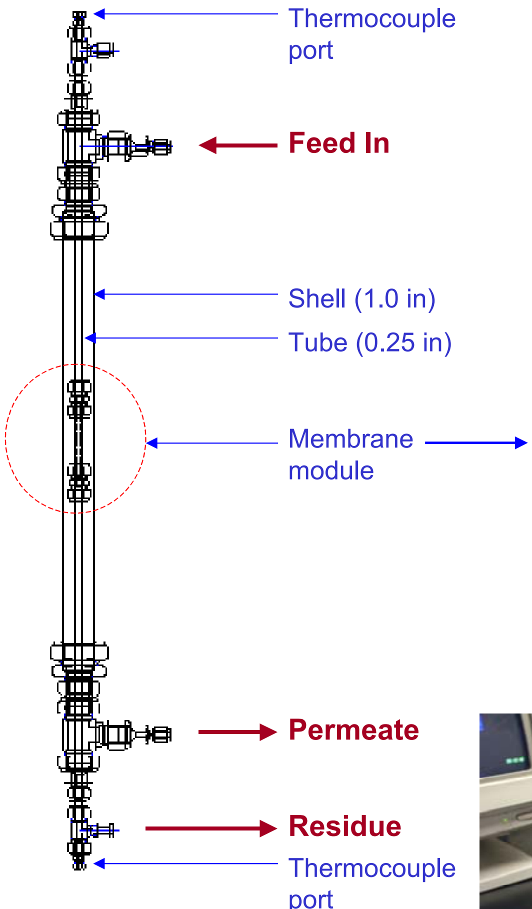
- **Several PdCu and PdAu composite membranes were developed for testing**





- **EDX analysis indicates that membrane consists of 87% Pd and 13% Au**
- **Small number of spots or defects in the surface of the membrane**
  - **Nitrogen leak rate measurements show that the surface defects do not penetrate the entire thickness of the membrane**

Membrane Testing System



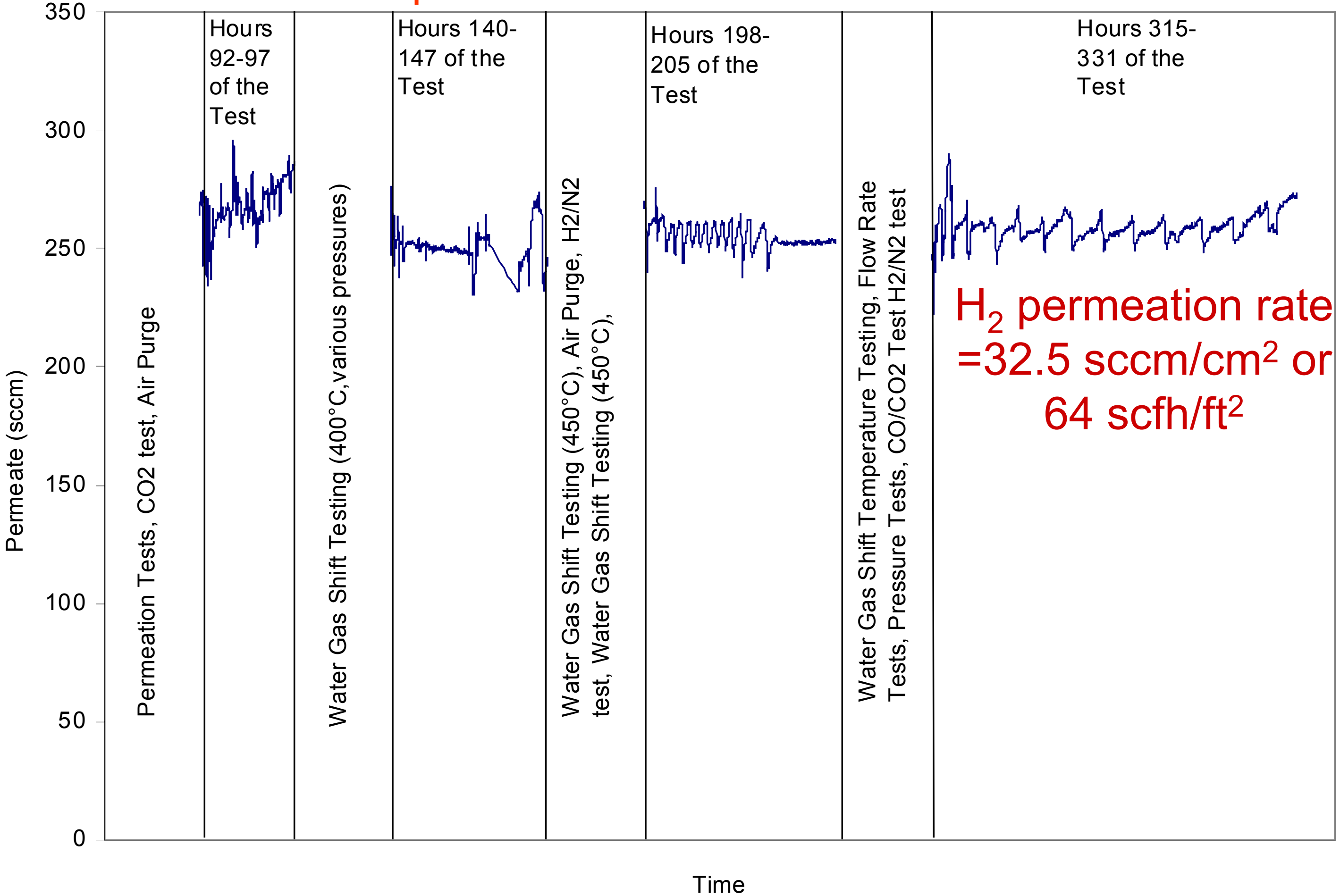
Membrane module

Test apparatus

Sub-ppm level sulfur detection capability with Sievers Chemiluminescence Detector

Baseline Performance of PdAu Membrane

T=400°C, P_{feed}= 100 psig, P_{perm}= 2 psig, Feed $H_2/H_2O/CO/CO_2$ Conc. = 51/21/26/2



- A stable membrane performance (i.e., H_2 permeation and selectivity) was observed for over 300 hrs in the presence of CO, CO_2, H_2O and H_2 mix

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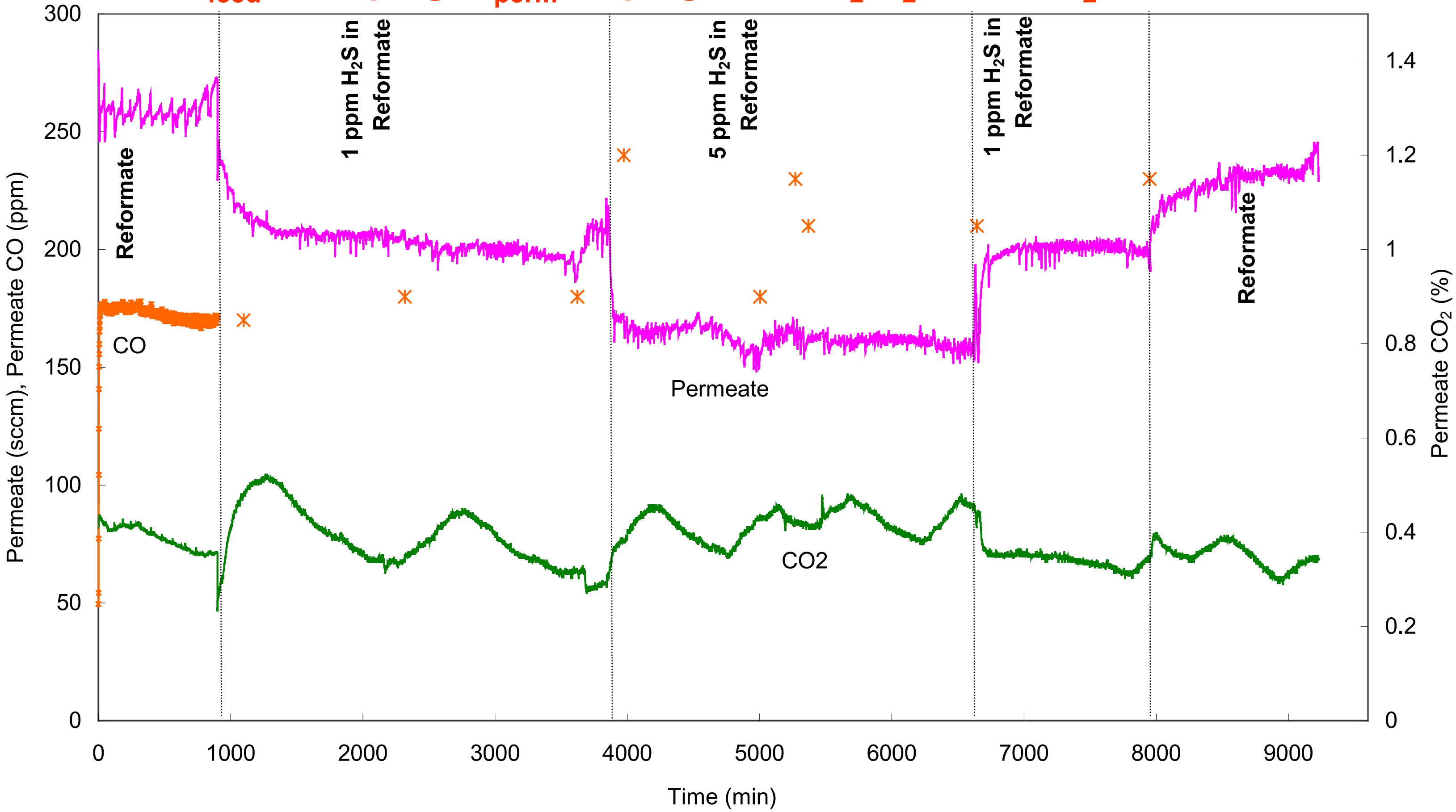
Effect of H_2S on PdAu Membrane

T=400°C, P_{feed}= 100 psig, P_{perm}= 2 psig, Feed $H_2/H_2O/CO/CO_2$ Conc. = 51/21/2/26



- With the introduction of sulfur to the syngas feed H_2 permeation rate decreased (5 ppmv sulfur caused 40% decrease)
- When sulfur flow was stopped, membrane performance recovered

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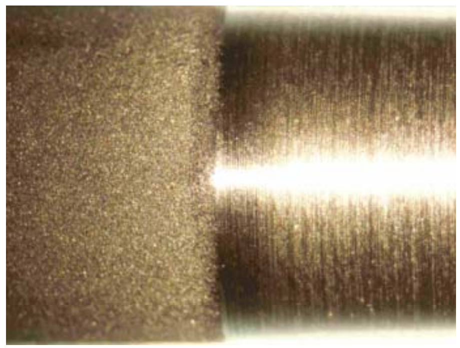
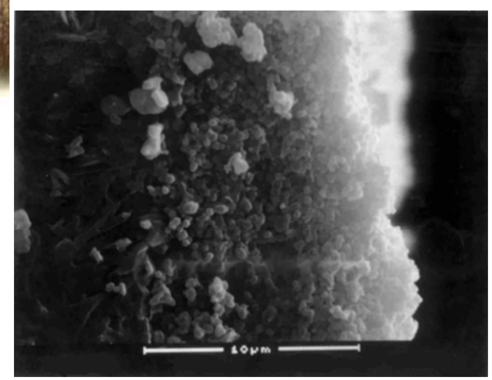
PdAu on Porous Steel Substrates

Treatment of the porous steel tubes (elimination of oils, grease etc for the application of coating)

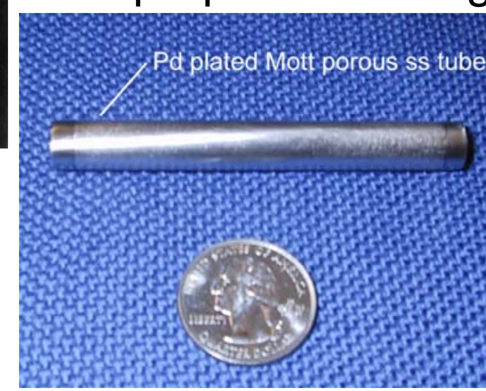


Hermatic sealing of the ends of the porous steel tubes

Application of an oxide diffusion barrier

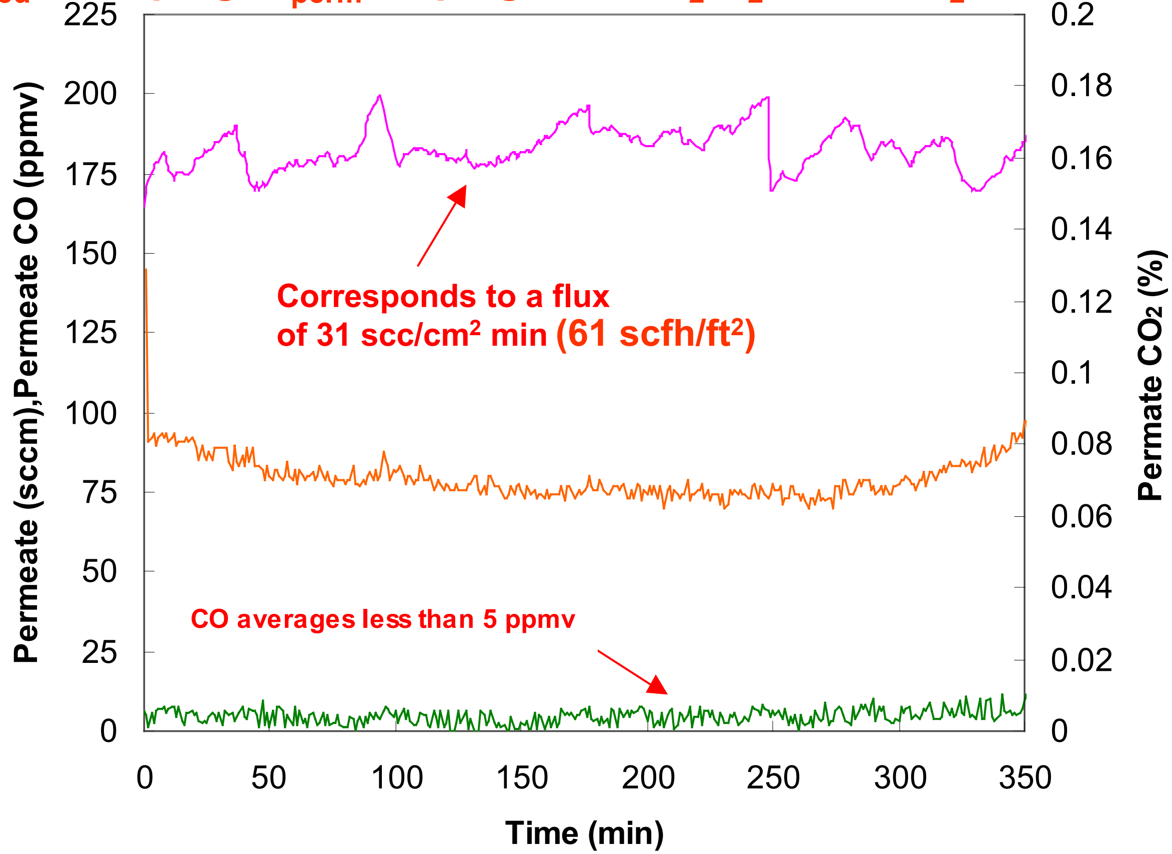


Deposition of Pd film (followed with deposition of gold and proper annealing



Evaluation of PdAu on Porous Steel

T=400°C, P_{feed}= 100 psig, P_{perm}= 2 psig, Feed $H_2/H_2O/CO/CO_2$ Conc. = 51/21/2/26



- The PdAu membrane prepared on porous steel support showed improved selectivity indicating non-selective transport is most likely due to the seals
- Even with a thicker film, H_2 permeation rate of this membrane matched to that prepared on ceramic support

Future Work

- **Work on reducing the thickness of the membrane film over the porous steel supported (PSS) membranes**
- **Evaluate performance of the PSS membranes in the presence of H_2S**
  - At sulfur concentrations up to 100 ppmv
- **Evaluate the potential problems associated with other coal gas contaminants**
  - Arsenic, selenium, HCl …
- **Module design and development**
  - H_2 separation module
  - Membrane Water-Gas-Shift Reactor

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- **DOE SBIR Phase I Project**
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