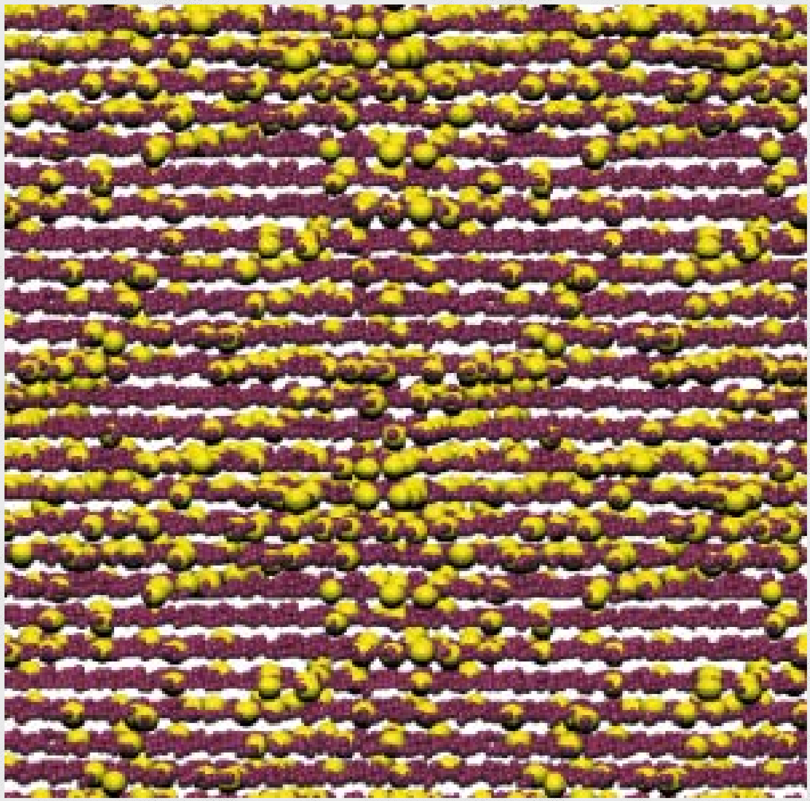
Hydrogen Separating Membranes for Coal Gas Reforming

Stephen N. Paglieri & Stephen A. Birdsell
Los Alamos National Laboratory
Los Alamos, New Mexico, U.S.A.

Overview

- Background
  - Hydrogen separating membranes
- Coal-gas reforming in a PMR
  - Where membranes fit into Vision 21
- Fabrication and testing of palladium composite membranes

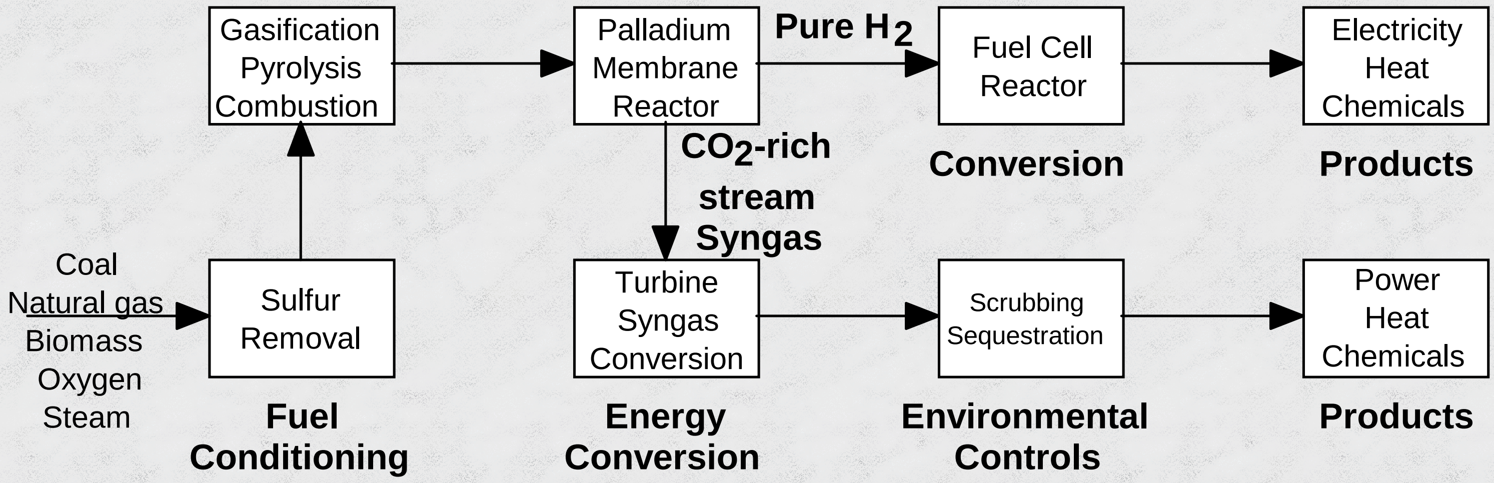
What’s so special about palladium?



- Palladium (Pd) can absorb many times its volume in hydrogen
- Pd is catalytically active for hydrogen dissociation
- Alloys of Pd are durable

*http://www.psc.edu/MetaCenter/MetaScience/Articles/Wolf/Wolf.html

Vision 21



Gasification Pyrolysis Combustion

Palladium Membrane Reactor

Pure H_2

Fuel Cell Reactor

Electricity Heat Chemicals

CO_2-rich stream Syngas

Conversion

Products

Coal
Natural gas
Biomass
Oxygen
Steam

Sulfur Removal

Turbine Syngas Conversion

Scrubbing Sequestration

Power Heat Chemicals

Fuel Conditioning

Energy Conversion

Environmental Controls

Products

- Part of Vision 21 entails coal gasification to recover both H_2 for fuel cell use and CO_2 for sequestration
  - http://www.netl.doe.gov
- A PMR accomplishes this in a single unit operation

Scale-up issues for Pd membranes

- Cost
  - price of Pd is ~$150/ounce (April, 2003)
  - thickness of Pd film will be $< 2\ \mu m$ for $\$50\text{-}100/ft^2$
- Poisoning by process stream impurities
  - unsaturated hydrocarbons, H_2S, carbon monoxide (CO)
  - should be regeneratable in steam or air
- Embrittlement
  - resistance to thermal cycling
  - $\alpha \rightarrow \beta$ (α’) phase transition
- Leak-free sealing

How do we address these problems?

- Cost
  - thin films of Pd on hydrogen-porous supports
  - minimize Pd film thickness
- Poisoning
  - remove most H_2S up front
  - $PdCu_{40}$ is sulfur resistant
- Embrittlement
  - Pd alloys reduce distortion upon hydriding/dehydriding

Types of composite configurations

- Refractory metals have high hydrogen permeabilities
  - surfaces readily poisoned
  - must coat with Pd on both sides of metal foil or tube
  - ion-cleaning in-situ followed by sputter deposition of Pd
- Pd on a porous support
  - porous metal supports
    - easier to weld into a module
    - available pore sizes take thick Pd coatings (>20 μm) to plug
  - porous ceramics
    - possess high temperature stability
    - commercially available tubes with well-defined pore sizes
    - α and γ-alumina, titania, zirconia

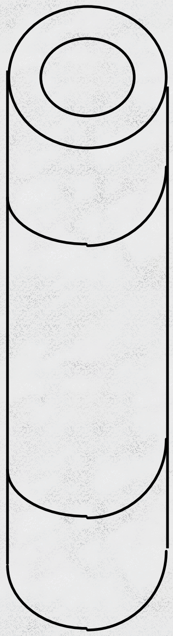
Palladium alloys

- Increased hydrogen permeability and durability
- $PdAg_{23}$ (weight %)
  - tubes (100 μm thick) commonly used to purify hydrogen for semiconductor industry and hydrogen isotope recovery
  - grain coarsening during operation at higher temperatures
- $PdRu_6$
  - higher melting point metal imparts high-temperature stability and strength
- $PdCu_{40}$
  - sulfur resistance
  - D.L. McKinley, U.S. 3,439,474 (1969)
  - D.J. Edlund

Fabrication of a Pd-Cu Composite Membrane

- Sequentially deposit Pd and then Cu
- Anneal to promote metallic interdiffusion
  - > 350°C
- Characterization
  - hydrogen flux and permselectivity
  - thickness: SEM, EPMA
  - composition: EDX, XRD
  - depth profiling: XPS, AES, Rutherford backscattering

Preparation of Pd/Ceramic Membrane



clean ceramic membrane

↓

seal ends of ceramic membrane with high temp. glaze

↓

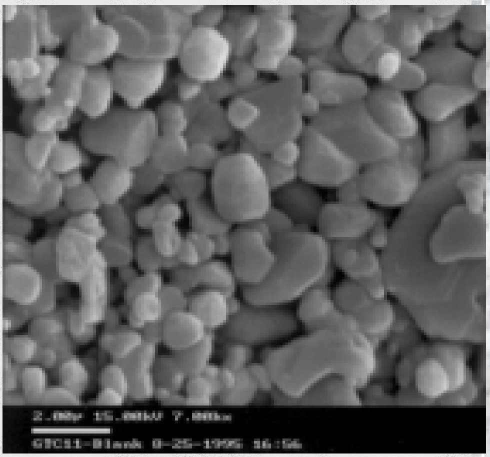
Sensitize surface w/$SnCl_2$ solution

↓

activate or seed surface with Pd crystallites

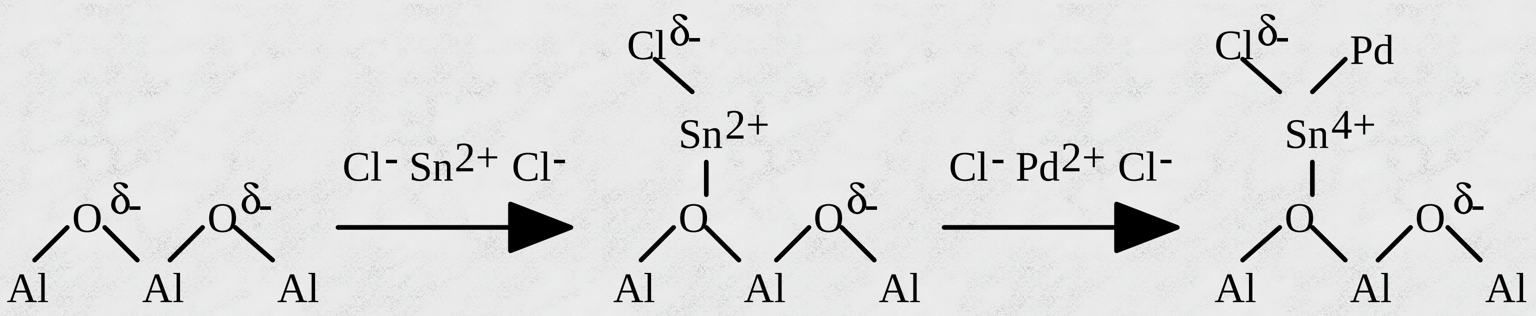
↓

plate in aqueous solution of Pd-amine complex and reducing agent (N_2H_4)



- Surface of GTC 998 0.2 µm symmetric Al_2O_3 Tube
  - »Scalebar is 2 µm

Sensitizing/Activating



M. Charbonnier et al. *J. Electrochem. Soc.* **143**(2) 472 (1996).

- Must catalyze surface of non-conductor to initiate deposition
- Sensitization w/$SnCl_2$
- Activation w/$PdCl_2$
- Water rinse

Membrane Preparation

- Ends of porous tube are glazed to prevent gas bypass of selective layer
- Electroless plating set-up enables solution circulation while membrane is immersed in sucrose solution

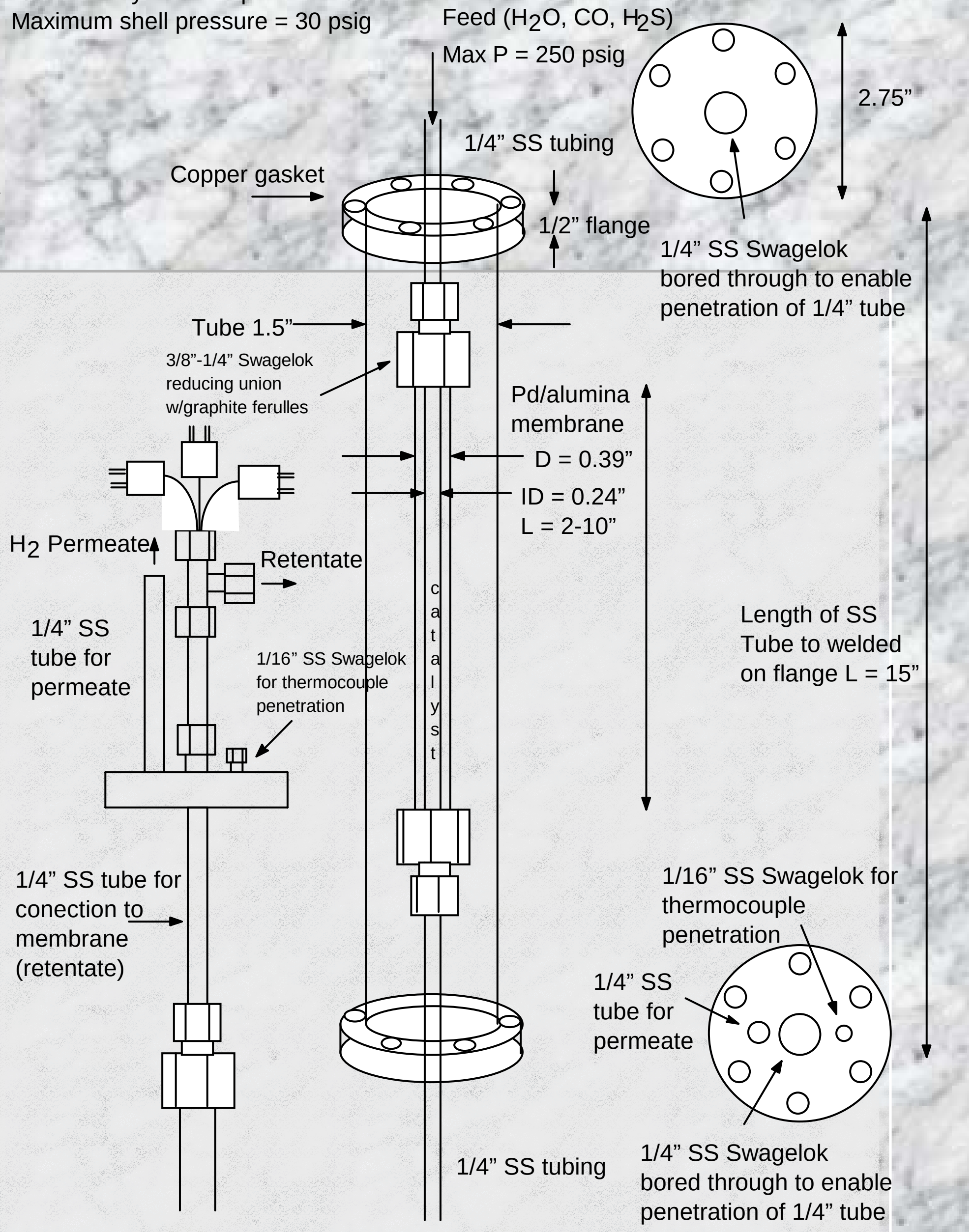
Pd-Cu/Alumina Composite Membrane

- Image of a broken membrane showing copper layer
- Membrane is sealed into the module using compression fittings with graphite ferrules

Test Module

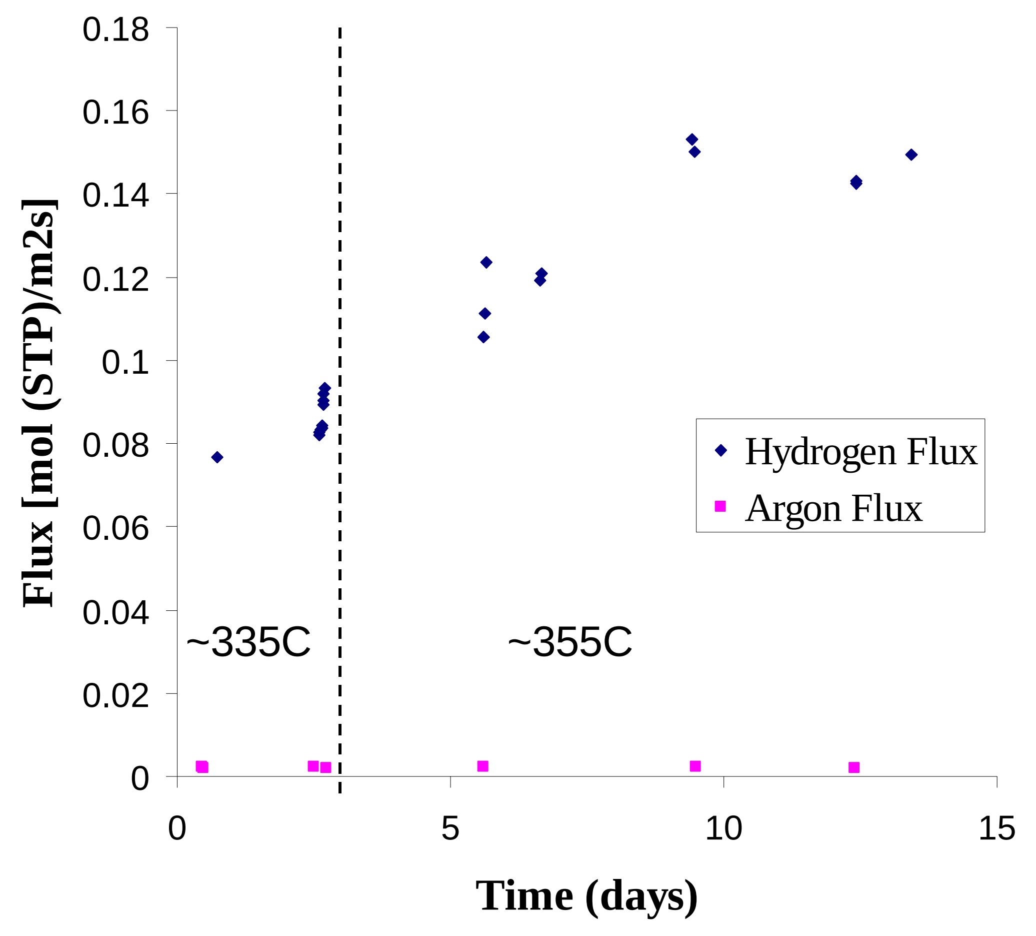
- 3 thermocouples on both the inside and outside of membrane
- Catalyst packed inside the Pd-composite membrane
- Max T = 550°C
- Max P = 250 psig

Maximum system temperature = 550 C
Maximum shell pressure = 30 psig

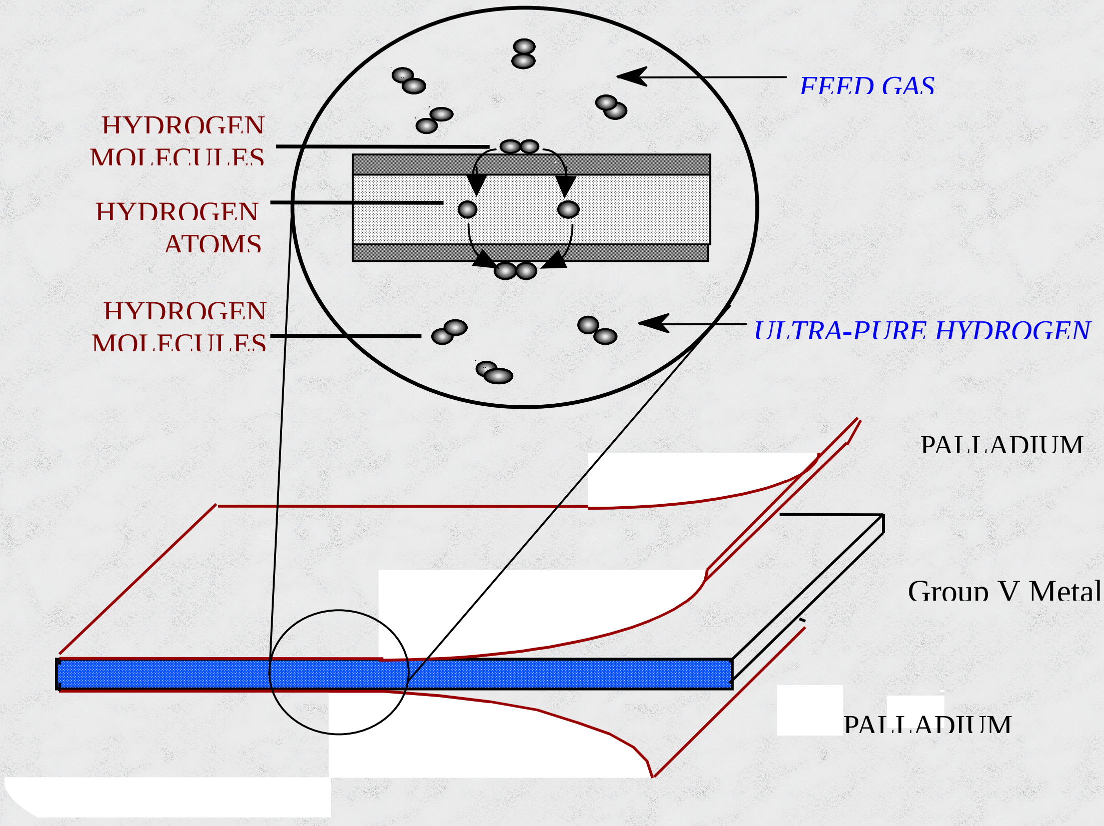


Hydrogen & Argon Flux vs. Time through Pd-Cu/Alumina Membrane

- Hydrogen flux increases as Pd and Cu interdiffuse
- $\Delta P = 100$ psi
- $\alpha_{H_2/Ar} \cong 68$



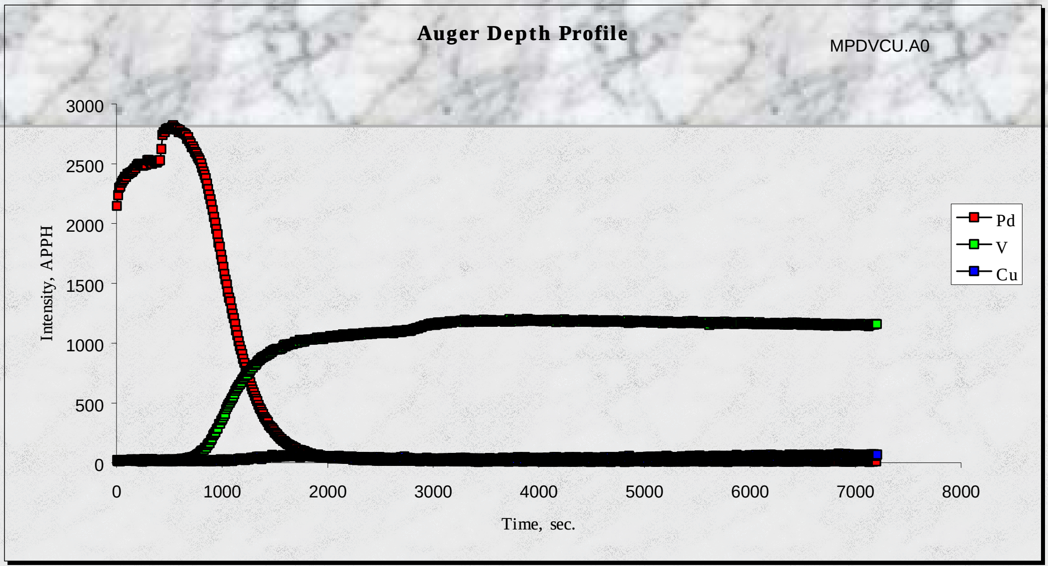
Pd/refractory foil/Pd Composite

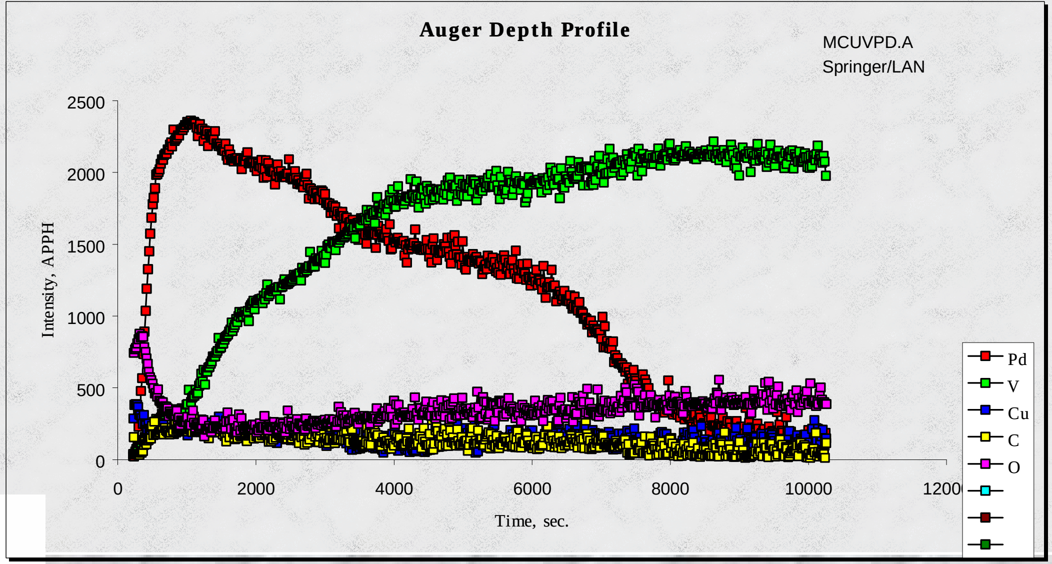


Pd/V-alloy/Pd membrane

- Palladium coating is very thin
  - 1000 Å
- Alloy of vanadium reduces hydrogen embrittlement
- Welded into the shape of a tube
  - SS VCR fittings
  - Flux = 0.4 sccm/cm^2•min @ $\Delta P = 5$ psi

AES Depth Profiles of Pd on V-Cu





Future Work

- Membrane reactor
- Pack catalyst around membrane
- Low, medium, and high temperature water-gas shift
- Fe-Cr-Cu oxide, Cu-ZnO catalysts
- Test sulfur resistance of membrane materials

Acknowledgements

- Membrane development work was funded by the US DOE, Office of Fossil Energy
- Rob Dye, David Pesiri, Bob Springer, Don Gettemy, John Moya, Stan Bennett, Stephen Cole, Jerry Schobert, Mike Brooks, Frank Smith, Ron Snow, Robert Barbero, Felix Garcia, Fino Armijo, John Valdez, Vincent Hesch, and Kevin Hubbard

Fuel Reforming for Fuel Cells

- High efficiency
- High quality electricity
- Backup (UPS)
- Decentralized power system
- Home, business, vehicle
- Liquid or gaseous fuel
  - $C_nH_m + nH_2O \leftrightarrow nCO + [(m+2n)/2]H_2$