NATIONAL ENERGY TECHNOLOGY LABORATORY

Development of Robust Hydrogen Separation Membranes

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Reaction Chemistry & Engineering Research Group Leader

NETL Office of Research & Development

2010 DOE Hydrogen Program Review

Project ID# PD008

U.S. DEPARTMENT OF ENERGY

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Overview

Timeline
- Project start date: 10/1/2009
- Project end date: 9/30/2010
- Percent complete: 58%

Barriers[1]
- (G) H_2 Embrittlement
- (H) Thermal cycling
- (I) Poisoning of catalytic surface
- (J) Loss of structural integrity and performance

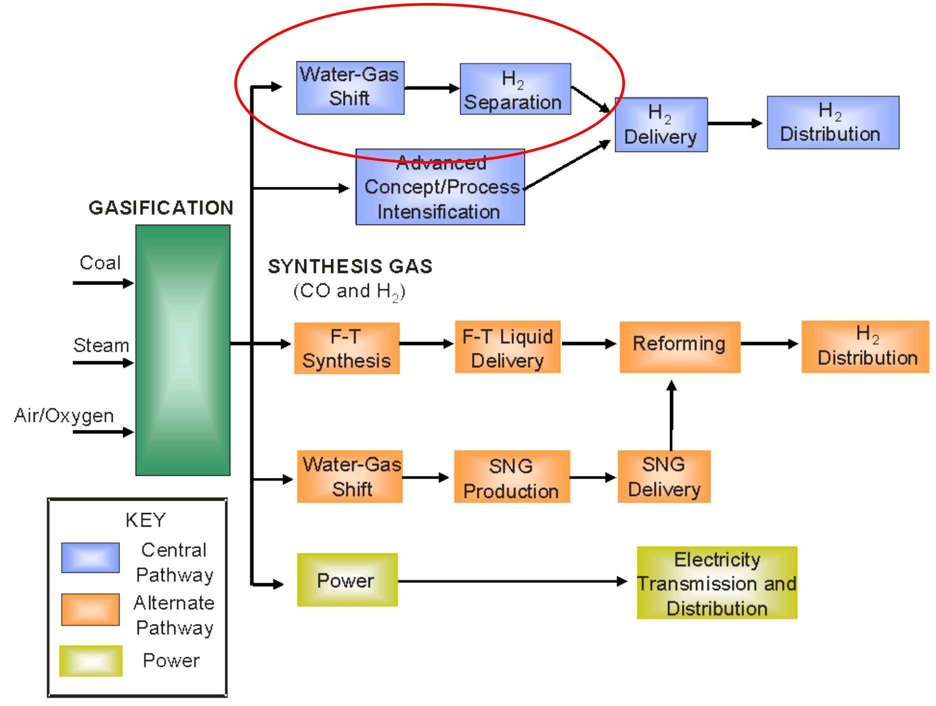
Budget
- FY10 Funding: $681
- FY09 Funding: $746k
- FY08 Funding: $1,000k
- FY07 Funding: $1,230k

Partners
- Carnegie Mellon University
- University of Pittsburgh
- Gas Technology Institute
- Los Alamos National Lab.
- NETL Computational Chemistry

[1] *2008 Hydrogen from Coal Program: Research, Development and Demonstration Plan*

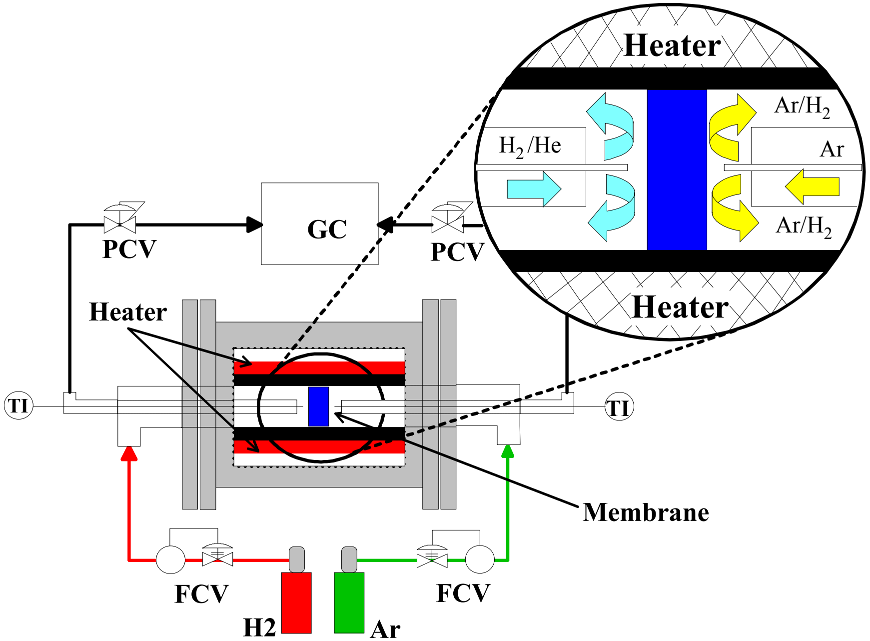
Background
(Relevance)

- **Overall goal**
  - Development of robust hydrogen separation membranes for integration into coal conversion processes, including integrated WGSMR
- **Studies suggest that incorporating separation membranes into coal conversion processes can reduce costs by 8%**



Facilities & Capabilities

- **3 Membrane Test Rigs**
  - Continuous, bench-scale units
  - T to 1000°C, P to 1000 psi
- **2 Laboratory Membrane Screening Rigs**
  - Continuous, lab-scale units
  - T to 1000°C, P to 30 psi
- **Materials Lab**
  - Depositions chamber
  - Vacuum arc-melter
  - Micro-welder
  - High-T box and annealing ovens
  - XRD w/hot-stage
  - SEM w/EDS
  - TGA for use with H_2S
  - UHV analysis capabilities
- **High Throughput Materials Science**
  - Deposition tools
  - Spatially resolved characterization
- **Computation**
  - DFT, Kinetic Monte-Carlo, COMSOL CFD



Outline

Task 1: Performance testing of external membranes and the "NETL H_2 Membrane Test Protocol"

Task 2: Robust Metal Membrane Development

- Objective
- Approach
- Technical Accomplishments
- Collaborations
- Proposed Future Work

Task 1: H_2 Membrane Test Protocol

- **Objective**
  - Define a H_2-membrane test protocol that
    - will advance the technology towards application to coal conversion processes
    - is consistent with overall FE program metrics, and
    - yields a basis for an "apples-to-apples" comparison
- **Approach**
  - Apply understanding of engineering principles, membrane technology and coal conversion processes to define a sequential protocol

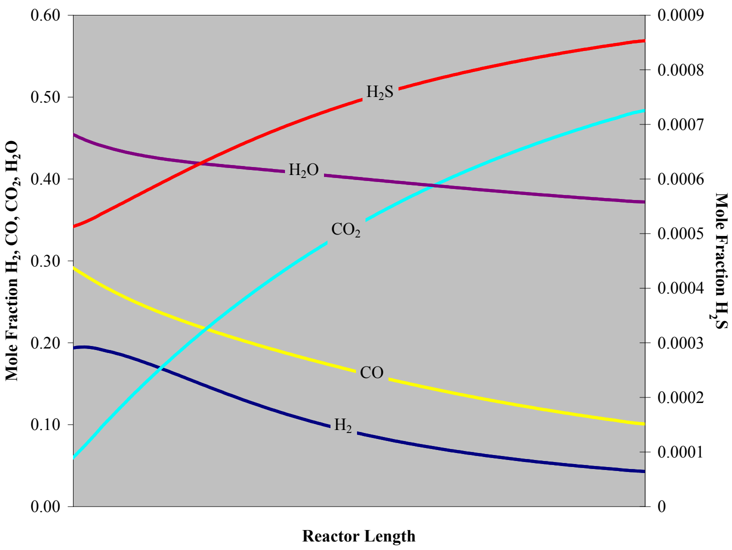
Performance Criteria	Units	2007 Target	2010 Target	2015 Target
Flux [a]	$sccm/cm^2$	51	102	152.4
Temperature	ºC	400–700	300–600	250–500
S Tolerance	ppmv	----	20	>100
Cost	$\$/ft^2$	150	100	<100
WGS Activity	-	Yes	Yes	Yes
ΔP Operating Capability [b]	psi	100	Up to 400	Up to 800 to 1,000
Carbon Monoxide Tolerance	-	Yes	Yes	Yes
Hydrogen Purity	%	95%	99.5%	99.99%
Stability/Durability	years	1	3	5

[a] For 100 psi ΔP (hydrogen partial pressure basis)
[b] ΔP = total pressure differential across the membrane reactor

Task 1: H_2 Membrane Test Protocol

(Background)

- Completed a survey to determine the effluent composition of a WGS unit
- Developed COMSOL model to predict the influence of WGS reaction and/or H_2 removal on overall gas composition
- Identified the test conditions and gas compositions that are relevant to syngas conversion flowsheet options:
  - Test 1: Shifted syngas, with no sulfur
  - Test 2a: Shifted syngas with 20ppm H_2S
  - Test 2b: Shifted syngas with ~50% H_2 removal
  - Test 2c: Shifted syngas with ~90% H_2 removal



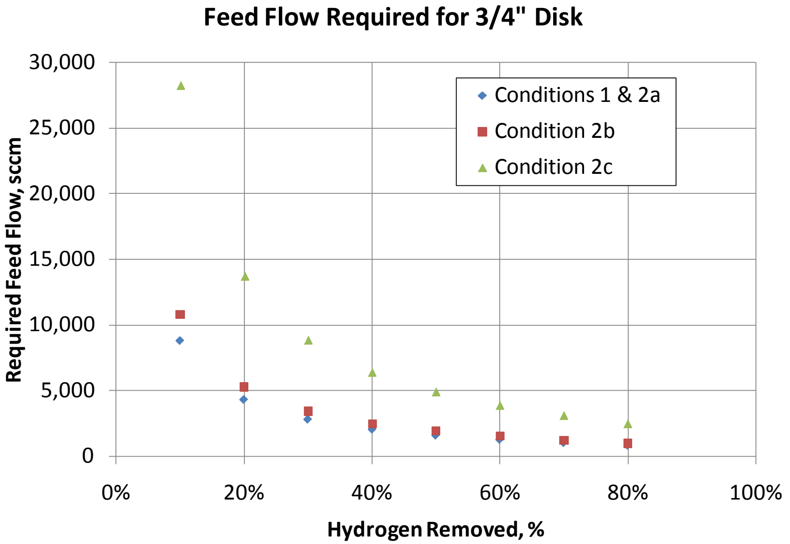
	Test 1	Test 2a	Test 2b	Test 2c
H2	50%	50%	33%	5%
CO	1%	1%	1%	2%
CO2	30%	30%	40%	57%
H2O	19%	19%	25%	36%
H2S	0.0%	0.2%	0.3%	0.4%

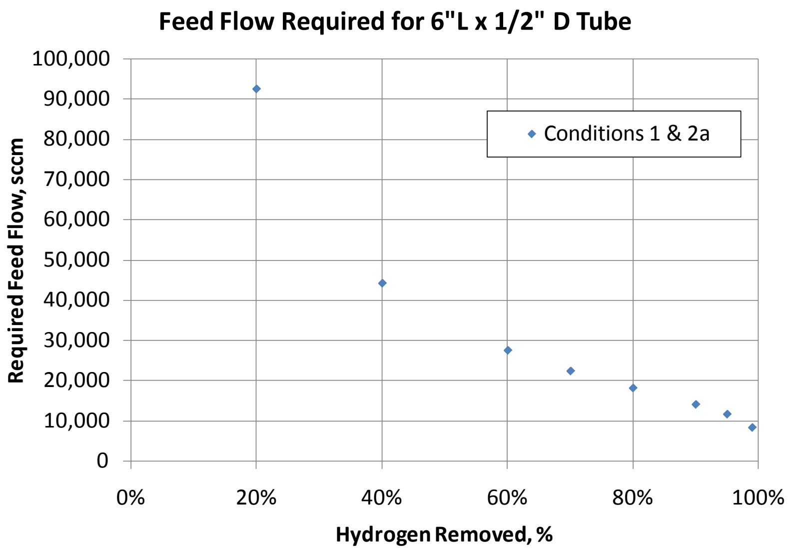
Temp	300-600oC
P_{Ret}	200 psi
P_{Per}	atm

Task 1: H_2 Membrane Test Protocol

(Technical Accomplishments)

- **Infrastructure**
  - Moved the membrane test units to new location
  - Modified membrane units to accommodate the “test protocol”
- **Flow ranges and membranes to test**
  - Conducted detailed analysis of the flow requirements to test a variety of membranes being developed
    - Disks, tubes
    - Performing at 2015 targets





Task 1: H_2 Membrane Test Protocol

(Collaborations)

- **NETL Technology Manager and Technology Team**
  - The development of the test protocol was a team effort consisting of several participants of the Technology Team
- **NETL funded H_2 Separation Projects**
  - Provide unbiased performance verification testing
    - REB Research
    - ORNL
    - Eltron Research
    - WRI

Task 1: H_2 Membrane Test Protocol

(Proposed Future Work)

- **Continue to support the development of test protocols to include more "commercially relevant" conditions**
  - Higher transmembrane pressure differentials
  - Contaminants other than H_2S
    - For example, Cl- and N-compounds for biomass co-feed
  - Integration of WGS reactor and Membrane separator

Task 2: Robust Metal Membrane Development

Identify membrane compositions and configurations that meet the criteria outlined in FE H_2 from Coal RD&D plan per the NETL Membrane Test Protocol

Provide design guidance to collaborators who will fabricate membranes at commercial scales and thicknesses

Performance Criteria	Units	2007 Target	2010 Target	2015 Target
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[a] For 100 psi ΔP (hydrogen partial pressure basis)
[b] ΔP = total pressure differential across the membrane reactor

Task 2: Robust Metal Membrane Development

(Background)

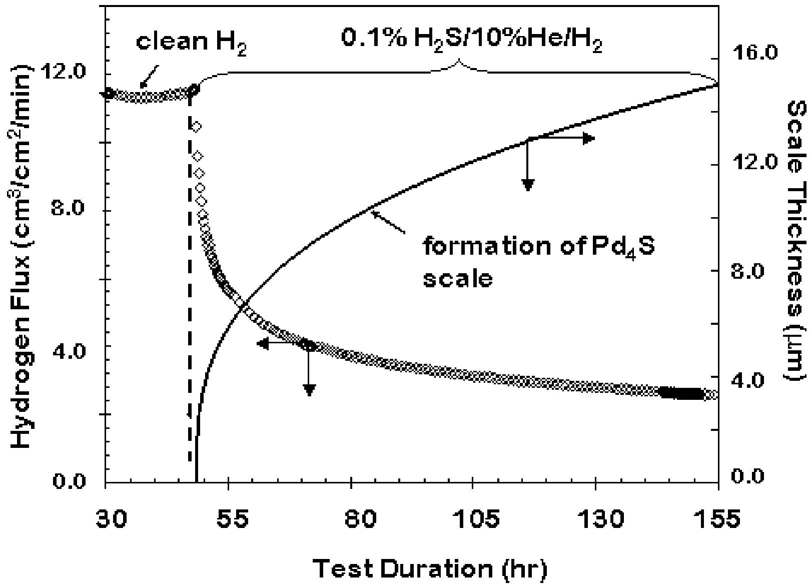
Corrosive decay

- "turns on" slowly
- Associated with formation of Pd_4S scale

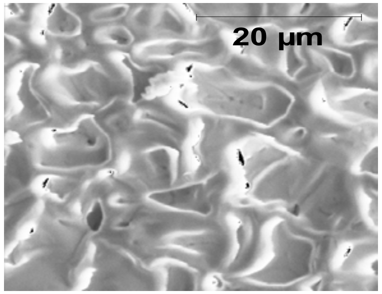
$4Pd + H_2S \rightarrow Pd_4S + H_2$

- Flux never = 0

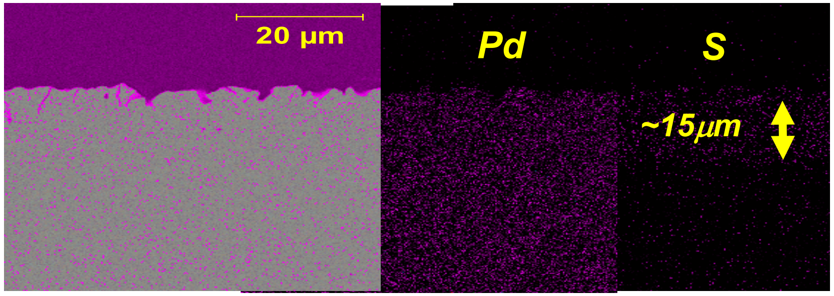
Pure Pd, 450°C



Membrane Surface



Membrane Cross Section



Pd_4S

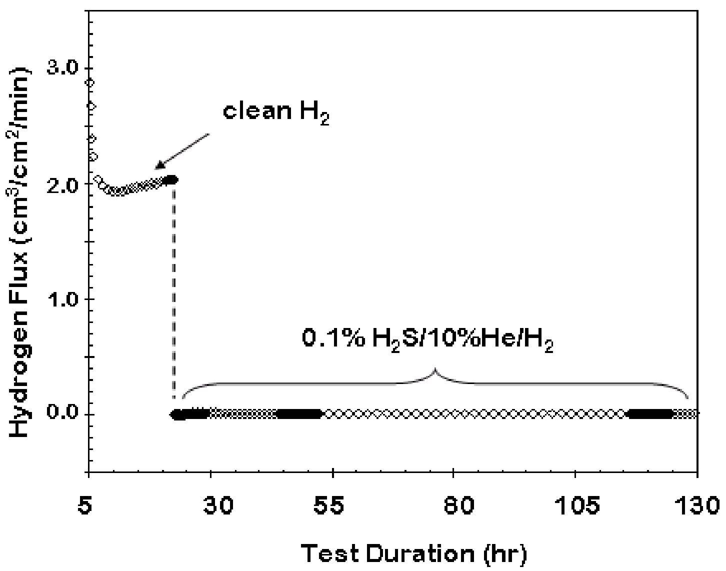
Task 2: Robust Metal Membrane Development

(Background)

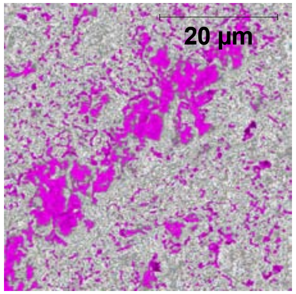
Catalytic poisoning

- Immediate
- Usually partially reversible
- No bulk Pd-S compound formation
- Characteristic of alloy at low temperatures

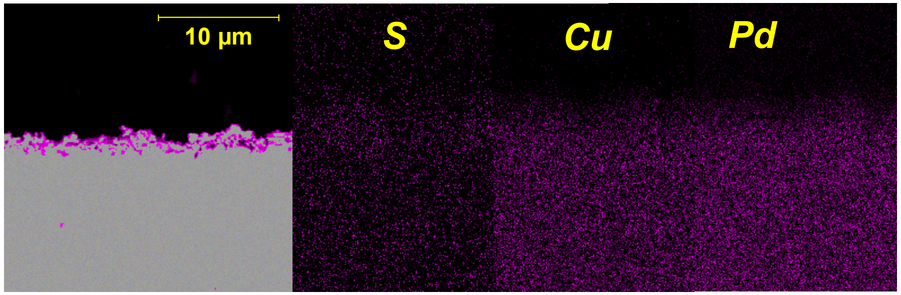
60Pd-Cu, 350°C



Membrane Surface



Membrane Cross Section



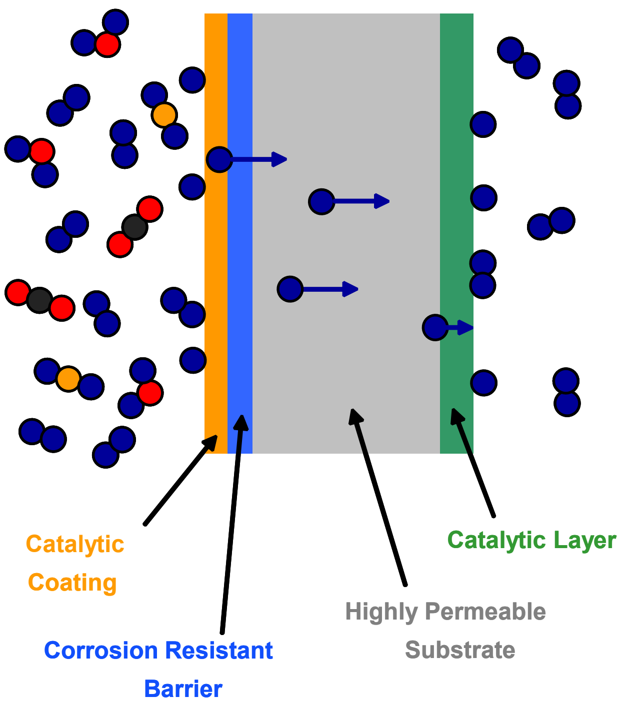
Task 2: Robust Metal Membrane Development

(Approach)

- **Develop a multi-layered membrane system that utilizes the catalytic activity shown with Pd_4S and the corrosion resistance of select PdCu alloys**

- **Use computational and experimental techniques to understand the**
  - catalytic activity at the gas-scale interface
    - Pd, Cu, Mo, Fe, Ni, Co, etc.
  - Hydrogen transport properties of the layers and interfaces
  - stability and growth scale

Multi -layer Membrane Concept



Task 2: Robust Metal Membrane Development

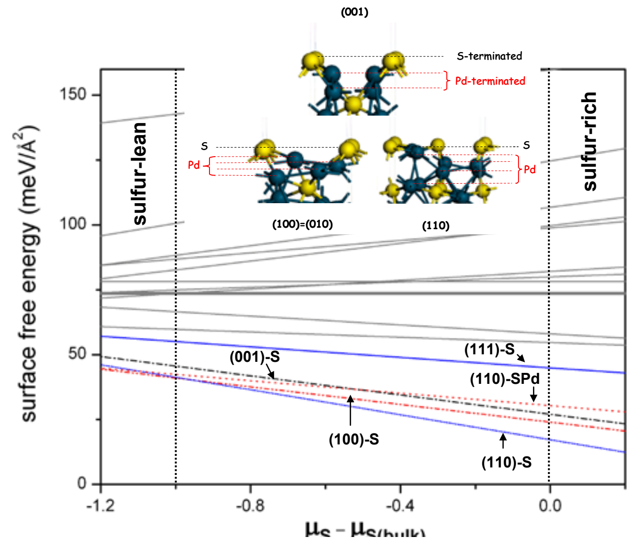
(Technical Accomplishments – Catalytic Activity, Gas-Scale Interface)

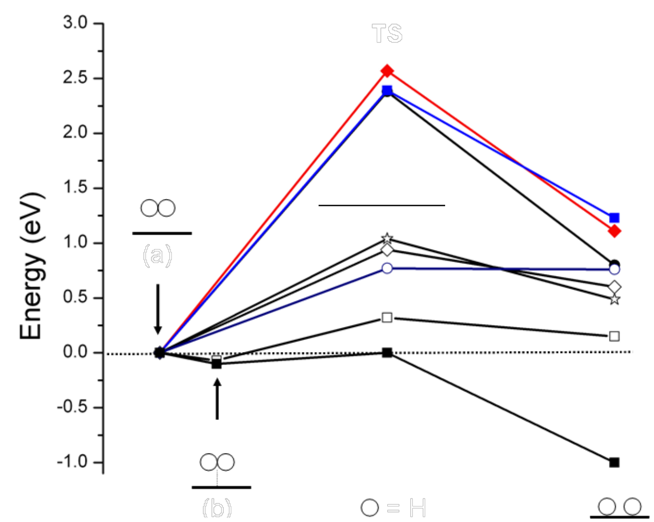
Surface Stability

- **Pd-terminated surfaces are least stable**
- **S-Pd-terminated surfaces are most stable**

Catalytic Activity

- **Incorporation of S into the Pd system decreases catalytic activity**
- **Pd-participation in the surface reaction allows rates high enough to meet DOE targets**
  - Pd-terminated
  - Sub-surface Pd



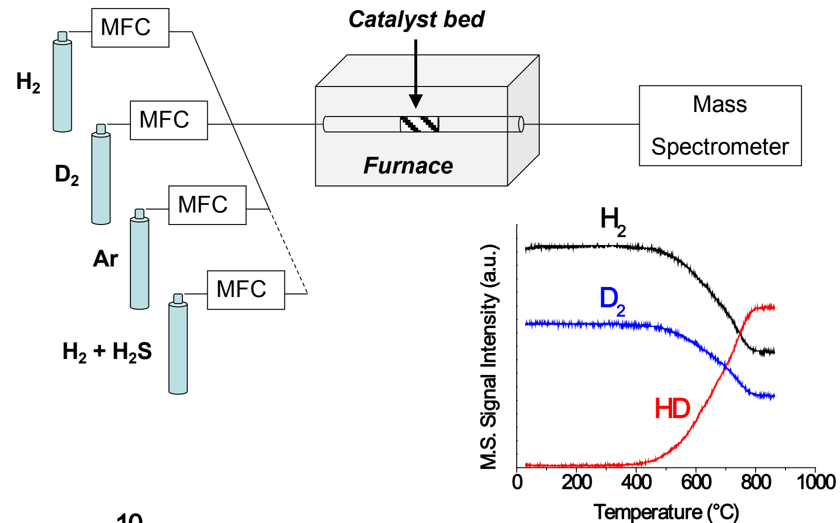


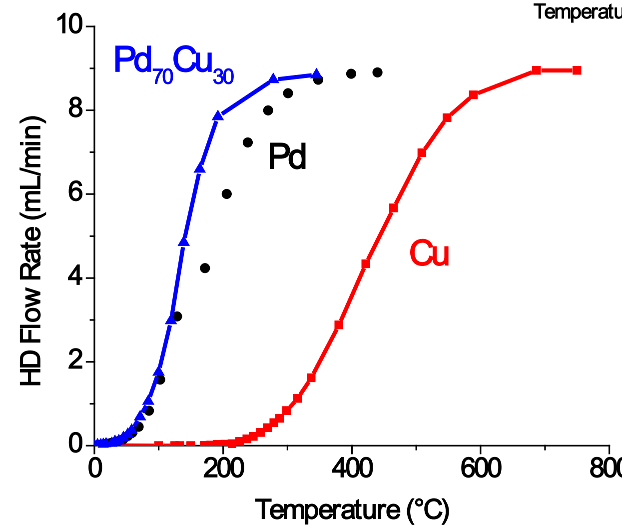
Task 2: Robust Metal Membrane Development

(Technical Accomplishments – Catalytic Activity, Gas-Scale Interface)

HD-Exchange Experiments

- Modified quartz reactor system
- Developed kinetic model
- Initiated experimentation on Pd, Cu and 80Pd-Cu
  - The 80Pd-Cu system is “more catalytic” than pure Pd in H_2





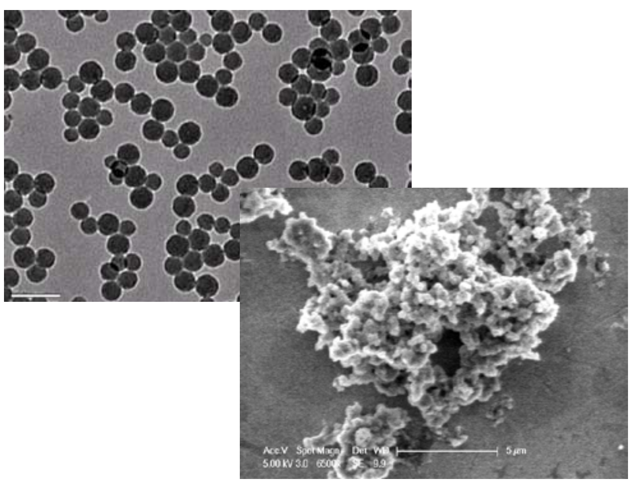
Task 2: Robust Metal Membrane Development

(Technical Accomplishments – Stability, Scale Growth & Transport)

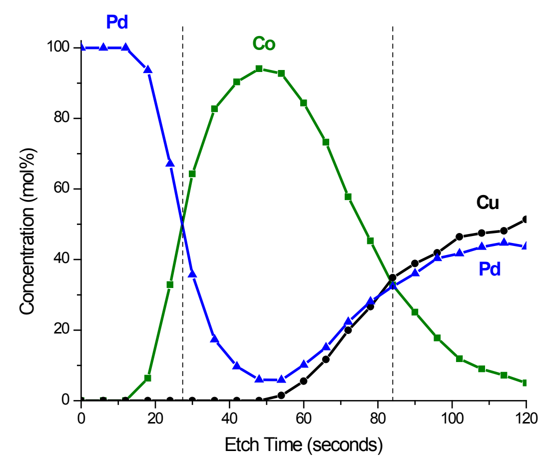
Synthesized multi-layered membranes

- Continuous and dispersed overlayers
- 25µm PdCu substrate (corrosion resistance)

	1 ML	1 nm	10 nm	100 nm	1 µm
Co	$Pd_{13}Cu_3S_7$ + Cu_2S	$Pd_{13}Cu_3S_7$ + Cu_2S		Co_9S_8	
Cr	$Pd_{13}Cu_3S_7$ + Cu_2S		no "thick" sulfides	no "thick" sulfides	
Fe	$Pd_{13}Cu_3S_7$ + Cu_2S			Fe-sulfide (spalled)	
Mo	$Pd_{13}Cu_3S_7$ + Cu_2S	$Pd_{13}Cu_3S_7$ + Cu_2S			
Ni	$Pd_{13}Cu_3S_7$ + Cu_2S			Ni-sulfide	
Pd		$Pd_{13}Cu_3S_7$ + Cu_2S	$Pd_{13}Cu_3S_7$ + Cu_2S	$Pd_{13}Cu_3S_7$ + Cu_2S	Pd_4S
Pt	$Pd_{13}Cu_3S_7$ + Cu_2S				



Mo nano particles, spin coated

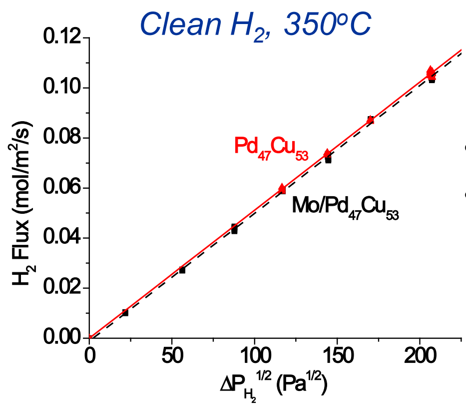


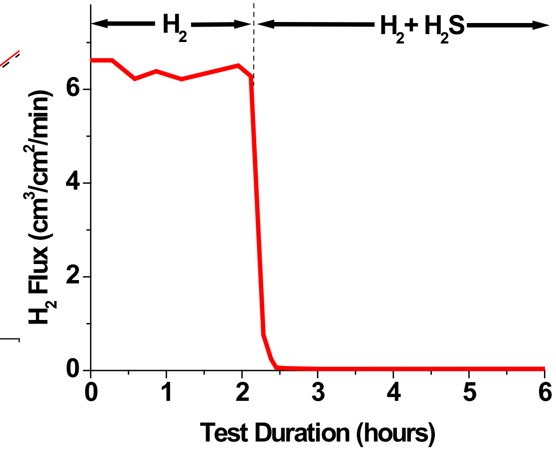
Task 2: Robust Metal Membrane Development

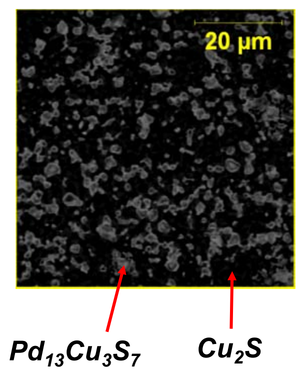
(Technical Accomplishments – Stability, Scale Growth & Transport)

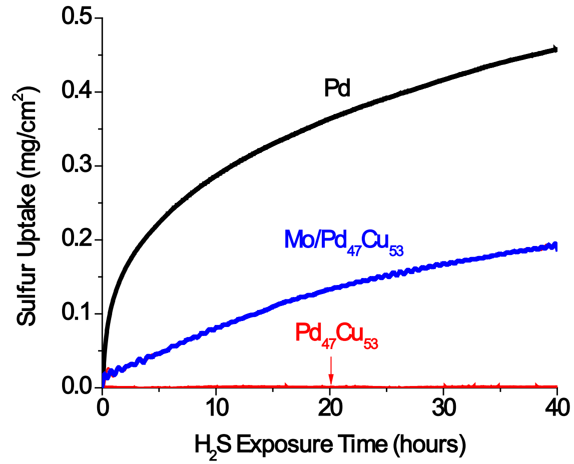
Synthesized multi-layered membranes

- Mono-layer Mo film
- Expected performance in H_2
- H_2S catalyzed the corrosion of PdCu substrate





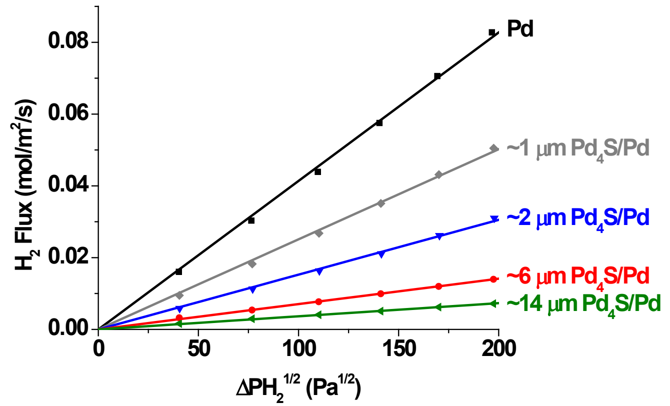


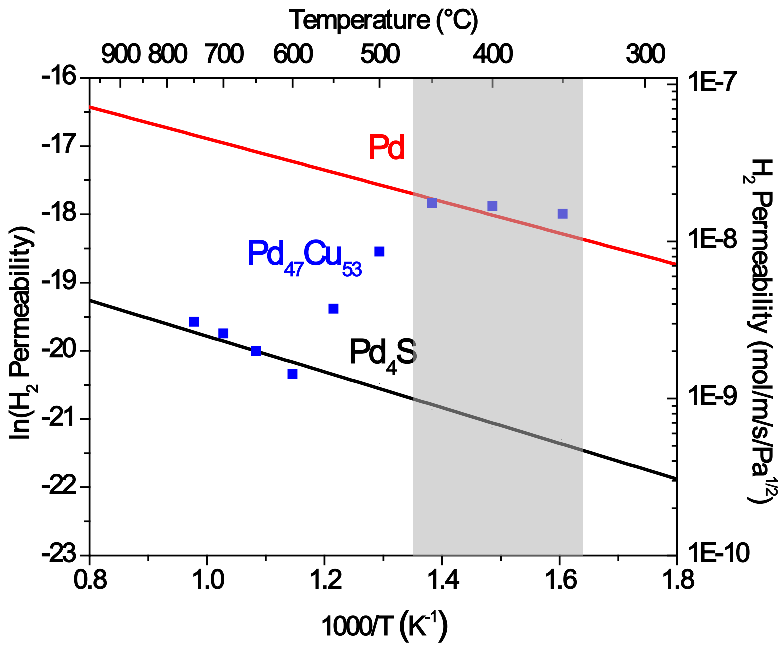


Task 2: Robust Metal Membrane Development

(Technical Accomplishments – Stability, Scale Growth & Transport)

- **Directly measured the permeability of Pd_4S**
  - In the presence of H_2, appears to follow Sievert's law
  - Permeability of Pd_4S is ~10x less than Pd
  - and consistent with fcc-phase 60Pd-Cu





Task 2: Robust Metal Membrane Development

(Collaborations)

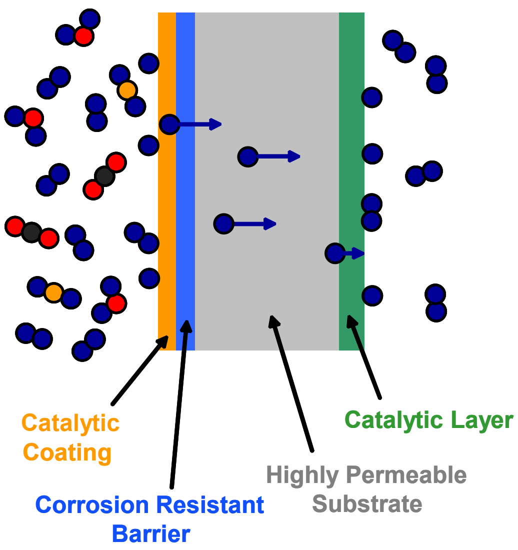
- **The research team conducting the work on the task consisted of participants from**
  - Carnegie Mellon University
  - NETL Reaction Chemistry & Engineering Group
  - NETL Computational Research Group
    - Dominic Alfonso

Task 2: Robust Metal Membrane Development
(Proposed Future Work)

Identify membrane compositions and configurations that meet the criteria outlined in FE H_2 from Coal RD&D plan per the NETL Membrane Test Protocol

- **Catalytic activity**
  - Utilize computational and experimental approaches to screen the H_2-dissociation properties of potential membrane surfaces (metals, oxides, sulfides, carbides, glasses)
    - High-activity, thermally stable and corrosion resistant
  - High-throughput methodologies that can measure properties over the entire composition spectrum of up to 4-components
- **Hydrogen transport properties**
  - Utilize computational and experimental approaches to quantify the permeability of base materials and scales that form during operation
    - High permeability, high mechanical strength
- **Scale growth and stability**
  - Quantify the scale growth of corrosion products, and stability of membrane overlayers at relevant conditions
- **Membrane fabrication**
  - Utilize the observations above to synthesize membranes for characterization per the NETL Test Protocol

Multi-layer Membrane Concept



Summary

- **A test protocol has been developed and NETL's test systems have been modified to allow testing of various membrane geometries and performance levels**
- **Evaluation of the catalytic activity of potential membrane catalyst layers has been initiated utilizing DFT, kinetic Monet Carlo and H_2-D_2 exchange**
  - In the presence of H_2, 80Pd-Cu appears more catalytic than Pd
  - Pd_4S shows catalytic properties for H_2 dissociation
- **Several multi-layered membrane systems have been fabricated using both continuous and dispersed catalysts**
  - Thin catalyst layers appear to catalyze the corrosion of a corrosion resistance PdCu alloy
- **The characterization of sulfide permeability has been initiated.**
  - Pd4S is approximately 10x lower than pure Pd.