

## 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

# Reaction Chemistry & Engineering Group Members

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# Overview

## Timeline

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

## Budget

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

## Barriers<sup>(1)</sup>

- (G) H<sub>2</sub> Embrittlement
- (H) Thermal cycling
- (I) Poisoning of catalytic surface
- (J) Loss of structural integrity and performance

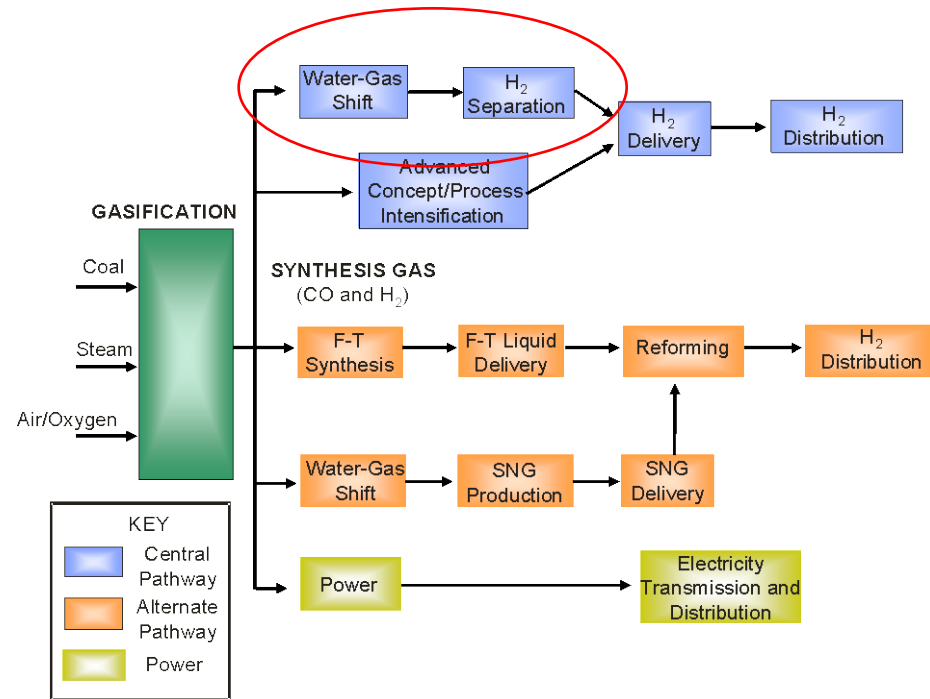
## Partners

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

# Background

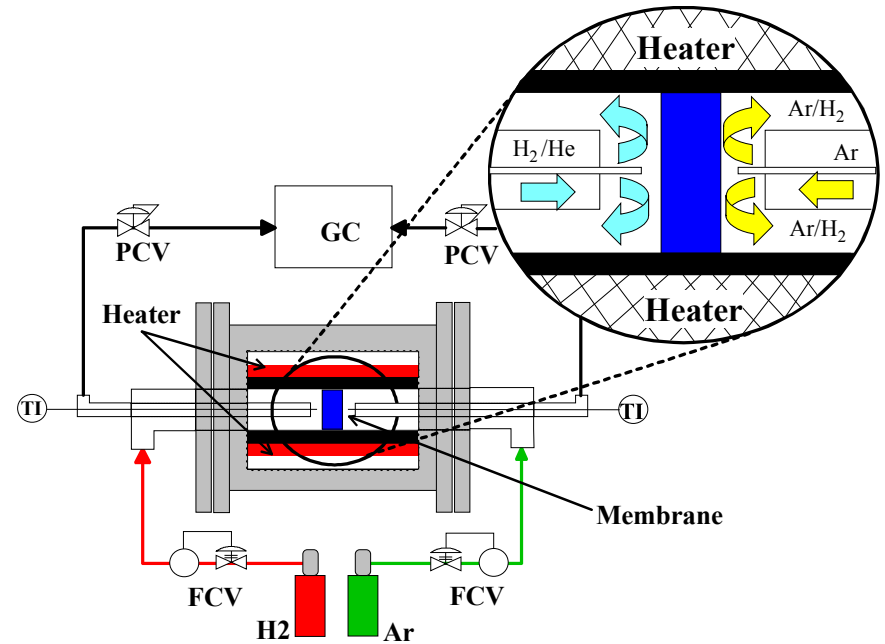
(Relevance)

- **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<sub>2</sub>S
  - 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<sub>2</sub> Membrane Test Protocol”**

**Task 2: Robust Metal Membrane Development**

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

# Task 1: H<sub>2</sub> Membrane Test Protocol

## •Objective

- Define a H<sub>2</sub>-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 <sup>(a)</sup>	sccm/cm <sup>2</sup>	51	102	152.4
Temperature	°C	400–700	300–600	250–500
S Tolerance	ppmv	----	20	>100
Cost	\$/ft <sup>2</sup>	150	100	<100
WGS Activity	-	Yes	Yes	Yes
ΔP Operating Capability <sup>(b)</sup>	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

<sup>a</sup> For 100 psi ΔP (hydrogen partial pressure basis)

<sup>b</sup> ΔP = total pressure differential across the membrane reactor

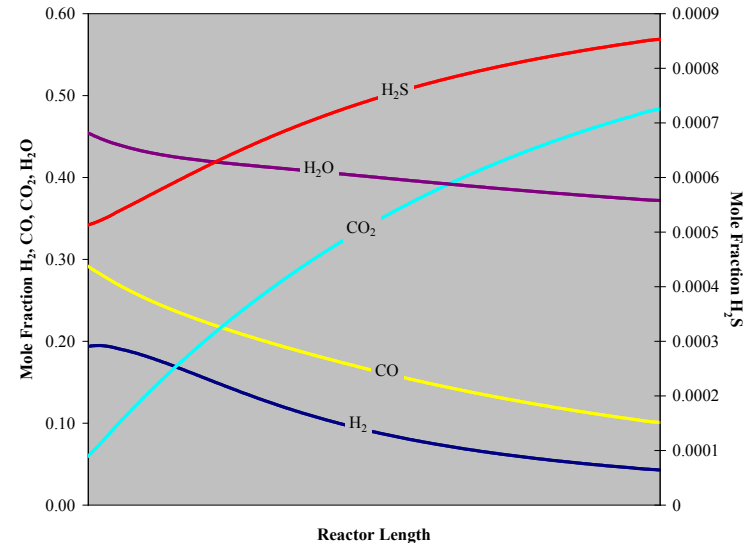


# Task 1: H<sub>2</sub> Membrane Test Protocol

## (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<sub>2</sub> 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<sub>2</sub>S
- Test 2b: Shifted syngas with ~50% H<sub>2</sub> removal
- Test 2c: Shifted syngas with ~90% H<sub>2</sub> removal



	Test 1	Test 2a	Test 2b	Test 2c
H <sub>2</sub>	50%	50%	33%	5%
CO	1%	1%	1%	2%
CO <sub>2</sub>	30%	30%	40%	57%
H <sub>2</sub> O	19%	19%	25%	36%
H <sub>2</sub> S	0.0%	0.2%	0.3%	0.4%
Temp	300-600oC			
P <sub>Ret</sub>	200 psi			
P <sub>Per</sub>	atm			



# Task 1: H<sub>2</sub> Membrane Test Protocol

## *(Technical Accomplishments)*

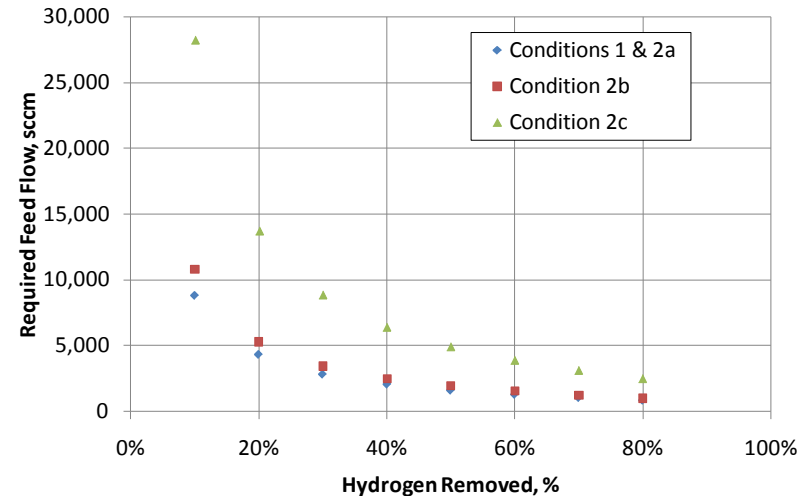
- **Infrastructure**

- Moved the membrane test units to new location
- Modified membrane units to accommodate the “test protocol”

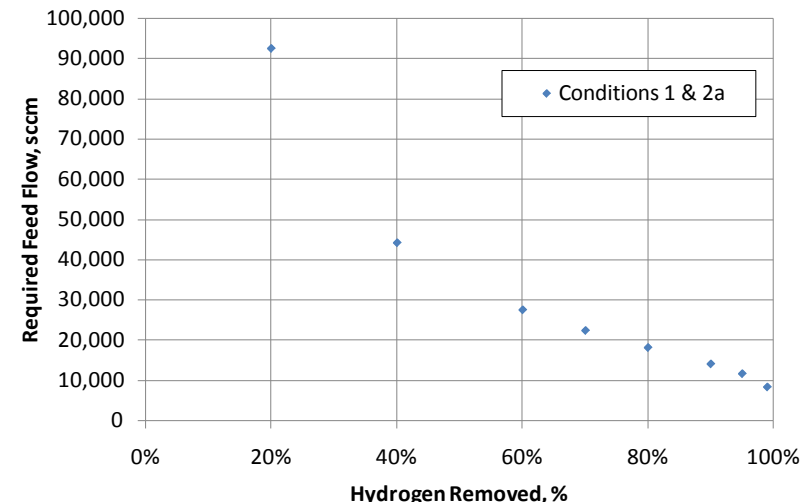
- **Flow ranges and membranes to test**

- Conducted detailed analysis of the flow requirements to test a variety of membranes being developed
  - Disks, tubes
  - Performing at 2015 targets

Feed Flow Required for 3/4" Disk



Feed Flow Required for 6" L x 1/2" D Tube



# Task 1: H<sub>2</sub> 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<sub>2</sub> Separation Projects**
  - Provide unbiased performance verification testing
    - REB Research
    - ORNL
    - Eltron Research
    - WRI

# Task 1: H<sub>2</sub> 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<sub>2</sub>S
    - For example, Cl<sup>-</sup> 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<sub>2</sub> 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
Flux <sup>(a)</sup>	sccm/cm <sup>2</sup>	51	102	152.4
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<sup>a</sup> For 100 psi  $\Delta$ P (hydrogen partial pressure basis)

<sup>b</sup>  $\Delta$ P = total pressure differential across the membrane reactor

# Task 2: Robust Metal Membrane Development

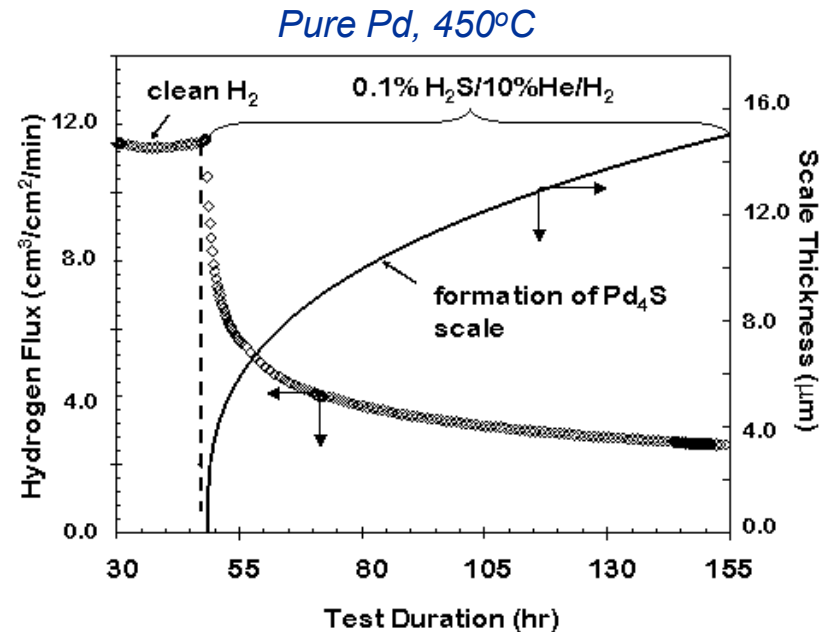
## (Background)

### Corrosive decay

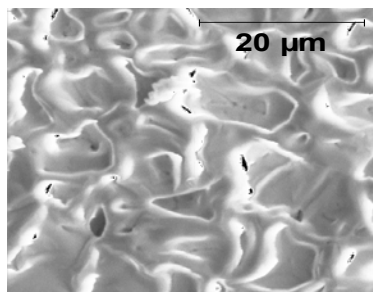
- “turns on” slowly
- Associated with formation of  $\text{Pd}_4\text{S}$  scale



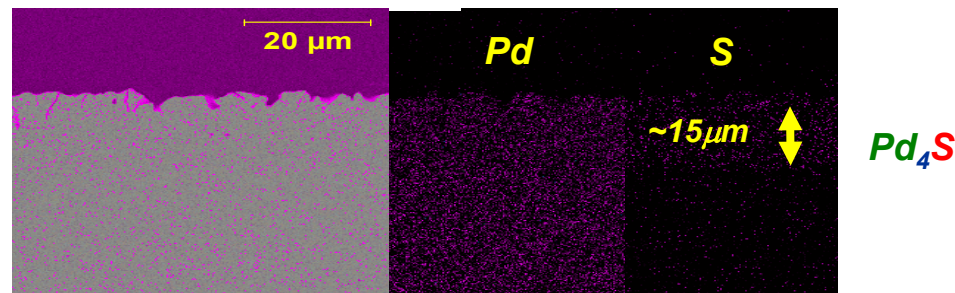
- Flux never = 0



Membrane Surface



Membrane Cross Section

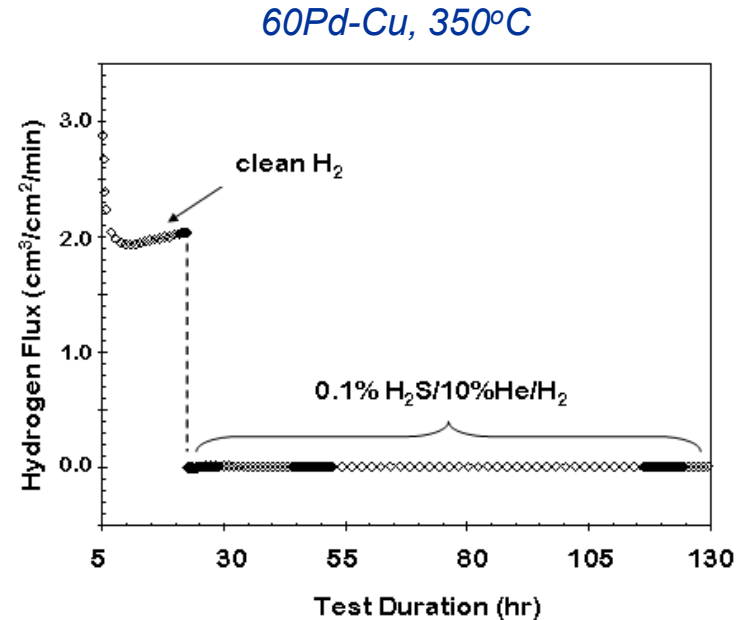


# Task 2: Robust Metal Membrane Development

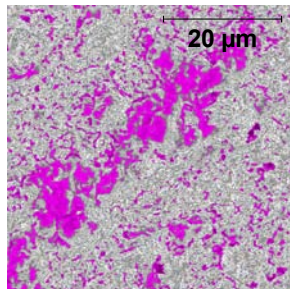
## (Background)

### Catalytic poisoning

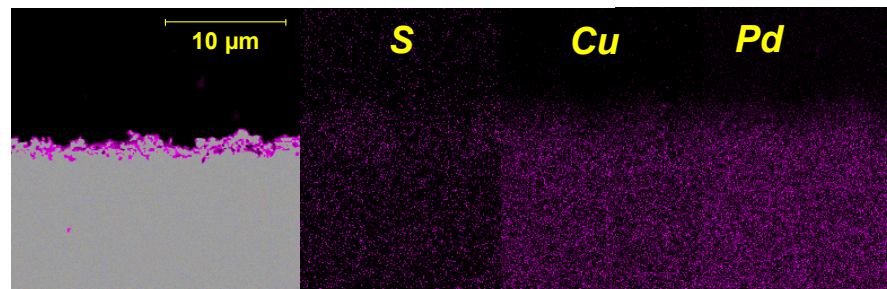
- Immediate
- Usually partially reversible
- No bulk Pd-S compound formation
- Characteristic of alloy at low temperatures



Membrane Surface



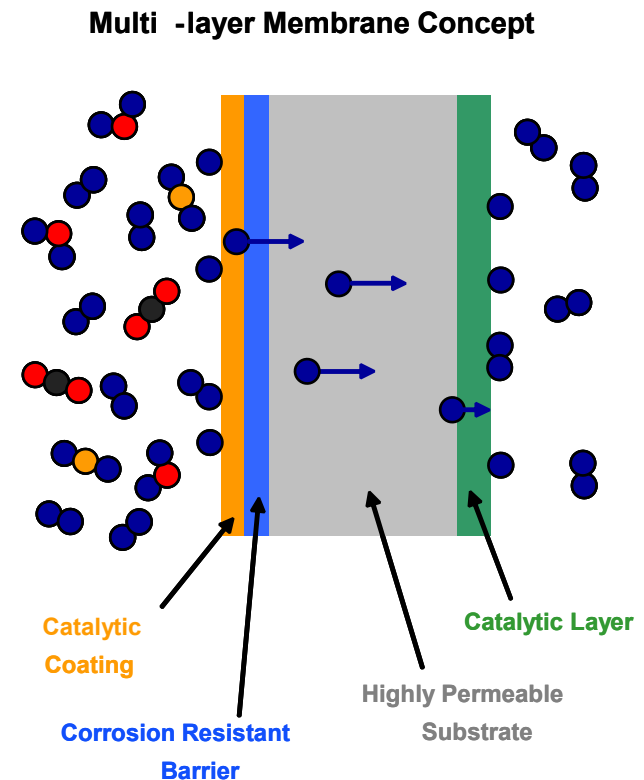
Membrane Cross Section



# Task 2: Robust Metal Membrane Development

## (Approach)

- Develop a multi-layered membrane system that utilizes the catalytic activity shown with  $\text{Pd}_4\text{S}$  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





# Task 2: Robust Metal Membrane Development

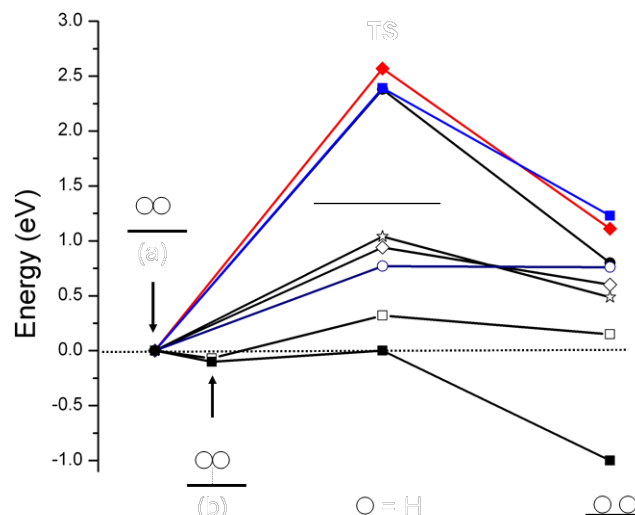
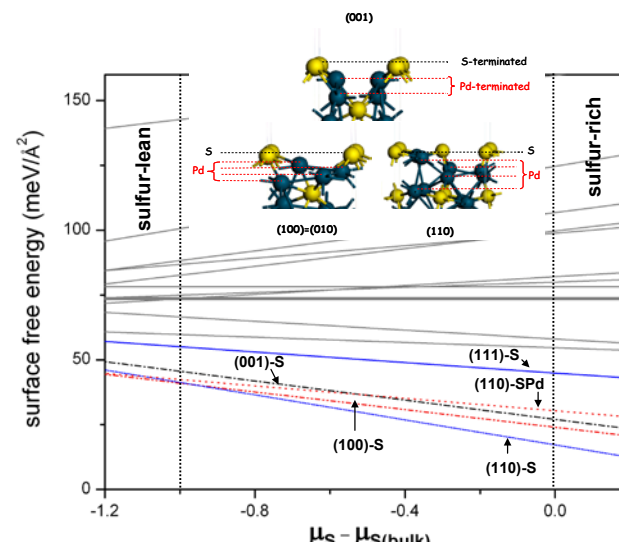
*(Technical Accomplishments – Catalytic Activity, Gas-Scale Interface)*

## 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

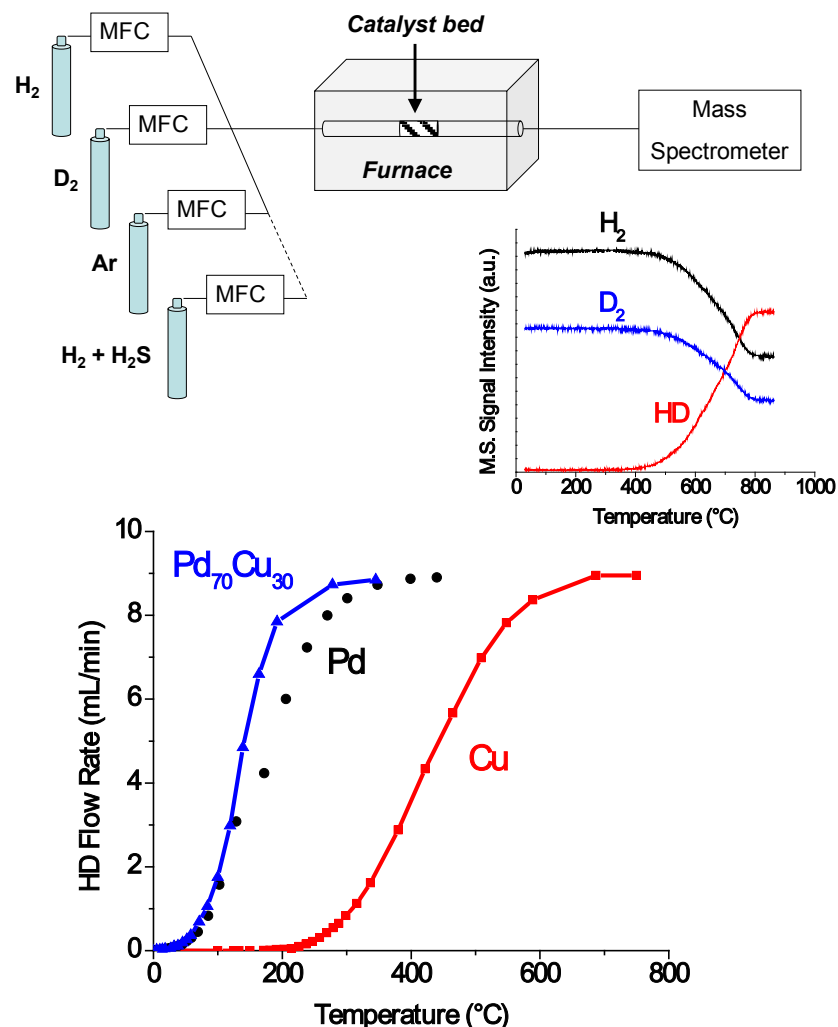


# Task 2: Robust Metal Membrane Development

*(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<sub>2</sub>

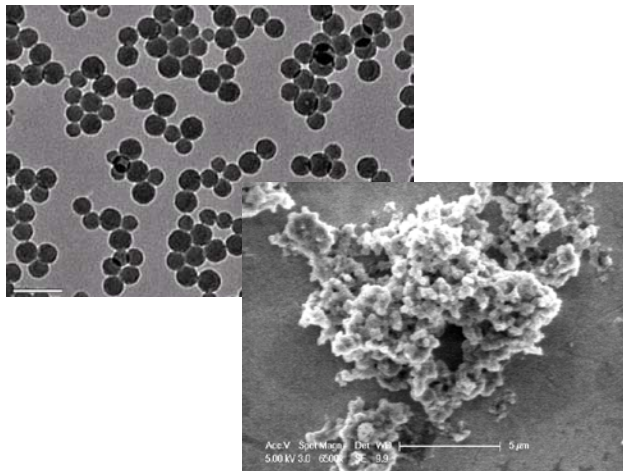


# Task 2: Robust Metal Membrane Development

*(Technical Accomplishments – Stability, Scale Growth & Transport)*

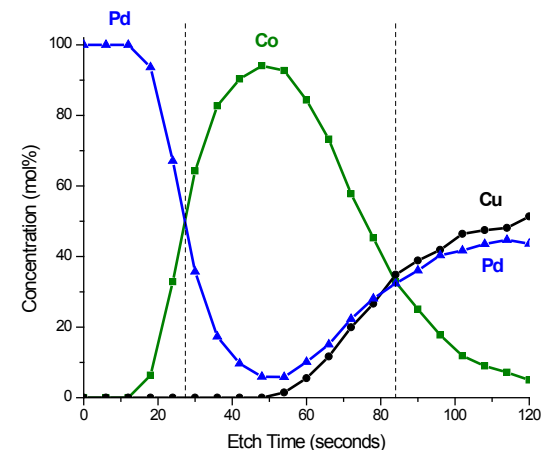
## Synthesized multi-layered membranes

- Continuous and dispersed overlayers
- 25 $\mu$ m PdCu substrate (corrosion resistance)



*Mo nano particles, spin coated*

	1 ML	1 nm	10 nm	100 nm	1 $\mu$ m
<b>Co</b>	Pd <sub>13</sub> Cu <sub>3</sub> S <sub>7</sub> + Cu <sub>2</sub> S	Pd <sub>13</sub> Cu <sub>3</sub> S <sub>7</sub> + Cu <sub>2</sub> S		Co <sub>9</sub> S <sub>8</sub>	
<b>Cr</b>	Pd <sub>13</sub> Cu <sub>3</sub> S <sub>7</sub> + Cu <sub>2</sub> S		no "thick" sulfides	no "thick" sulfides	
<b>Fe</b>	Pd <sub>13</sub> Cu <sub>3</sub> S <sub>7</sub> + Cu <sub>2</sub> S			Fe-sulfide (spalled)	
<b>Mo</b>	Pd <sub>13</sub> Cu <sub>3</sub> S <sub>7</sub> + Cu <sub>2</sub> S	Pd <sub>13</sub> Cu <sub>3</sub> S <sub>7</sub> + Cu <sub>2</sub> S			
<b>Ni</b>	Pd <sub>13</sub> Cu <sub>3</sub> S <sub>7</sub> + Cu <sub>2</sub> S			Ni-sulfide	
<b>Pd</b>		Pd <sub>13</sub> Cu <sub>3</sub> S <sub>7</sub> + Cu <sub>2</sub> S	Pd <sub>13</sub> Cu <sub>3</sub> S <sub>7</sub> + Cu <sub>2</sub> S	Pd <sub>13</sub> Cu <sub>3</sub> S <sub>7</sub> + Cu <sub>2</sub> S	Pd <sub>4</sub> S
<b>Pt</b>	Pd <sub>13</sub> Cu <sub>3</sub> S <sub>7</sub> + Cu <sub>2</sub> S				

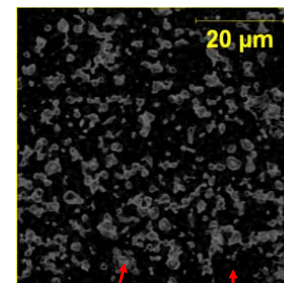
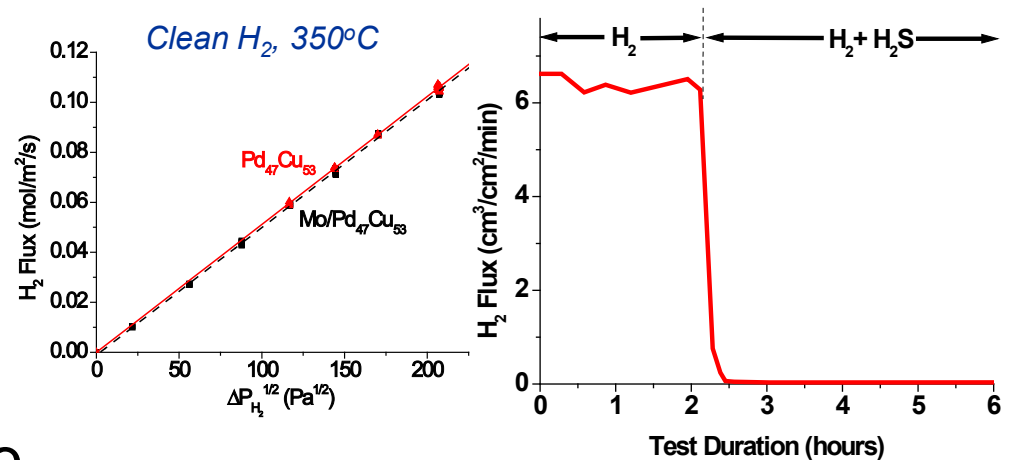


# Task 2: Robust Metal Membrane Development

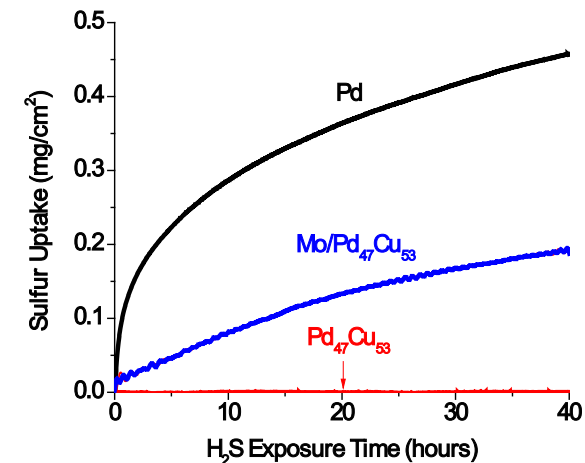
*(Technical Accomplishments – Stability, Scale Growth & Transport)*

## Synthesized multi-layered membranes

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



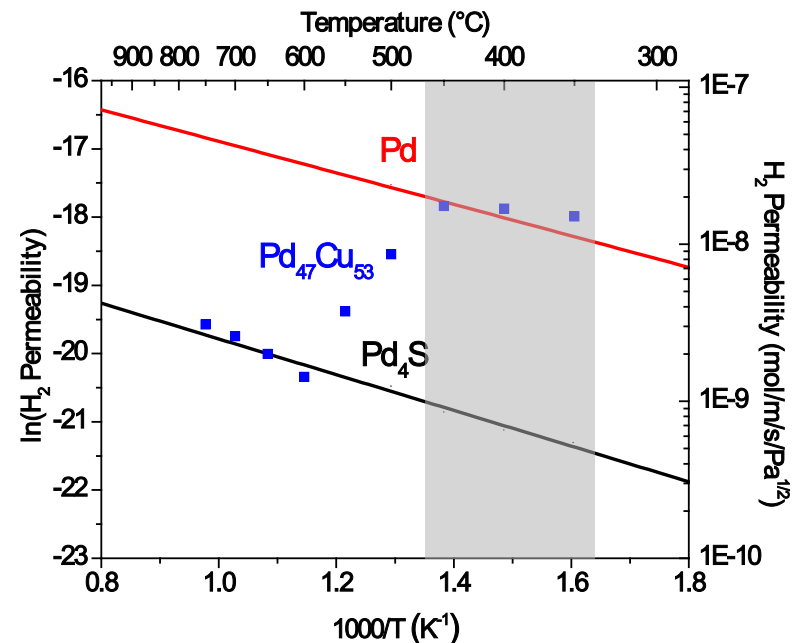
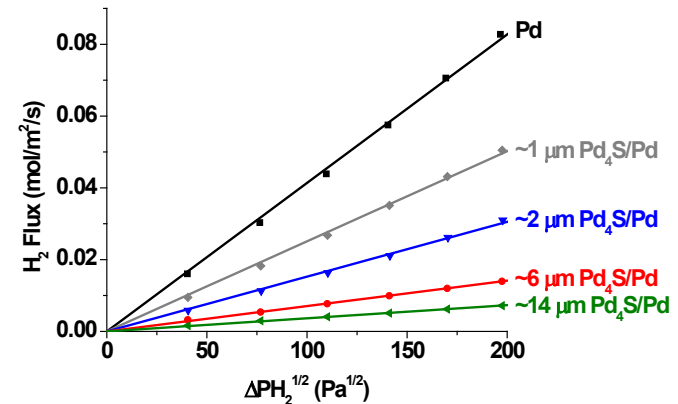
$Pd_{13}Cu_3S_7$   $Cu_2S$



# Task 2: Robust Metal Membrane Development

*(Technical Accomplishments – Stability, Scale Growth & Transport)*

- **Directly measured the permeability of Pd<sub>4</sub>S**
  - In the presence of H<sub>2</sub>, appears to follow Sievert's law
  - Permeability of Pd<sub>4</sub>S is ~10x less than Pd
  - and consistent with fcc-phase 60Pd-Cu



# Task 2: Robust Metal Membrane Development

*(Collaborations)*

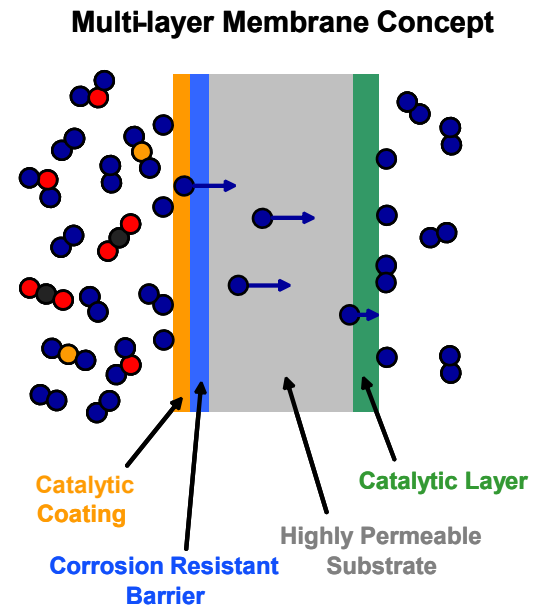
- **The research team conducting the work on the task consisted of participants from**
  - Carnegie Mellon University
  - NETL Reaction Chemistry & Engineering Group
  - NETL Computational Research Group
    - Dominic Alfonso

# Task 2: Robust Metal Membrane Development

## *(Proposed Future Work)*

Identify membrane compositions and configurations that meet the criteria outlined in FE H<sub>2</sub> from Coal RD&D plan per the NETL Membrane Test Protocol

- **Catalytic activity**
  - Utilize computational and experimental approaches to screen the H<sub>2</sub>-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





# 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 Monte Carlo and H<sub>2</sub>-D<sub>2</sub> exchange**
  - In the presence of H<sub>2</sub>, 80Pd-Cu appears more catalytic than Pd
  - Pd<sub>4</sub>S shows catalytic properties for H<sub>2</sub> 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.**
  - Pd<sub>4</sub>S is approximately 10x lower than pure Pd.