NATIONAL ENERGY TECHNOLOGY LABORATORY

Development of Robust Metal Membranes for Hydrogen Separation

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2009 DOE Hydrogen Program Review

U.S. DEPARTMENT OF ENERGY

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Overview

Timeline

- Project start date: 10/1/2008
- Project end date: 9/30/2009
- Percent complete: 67%

Barriers[1]

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

Budget

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

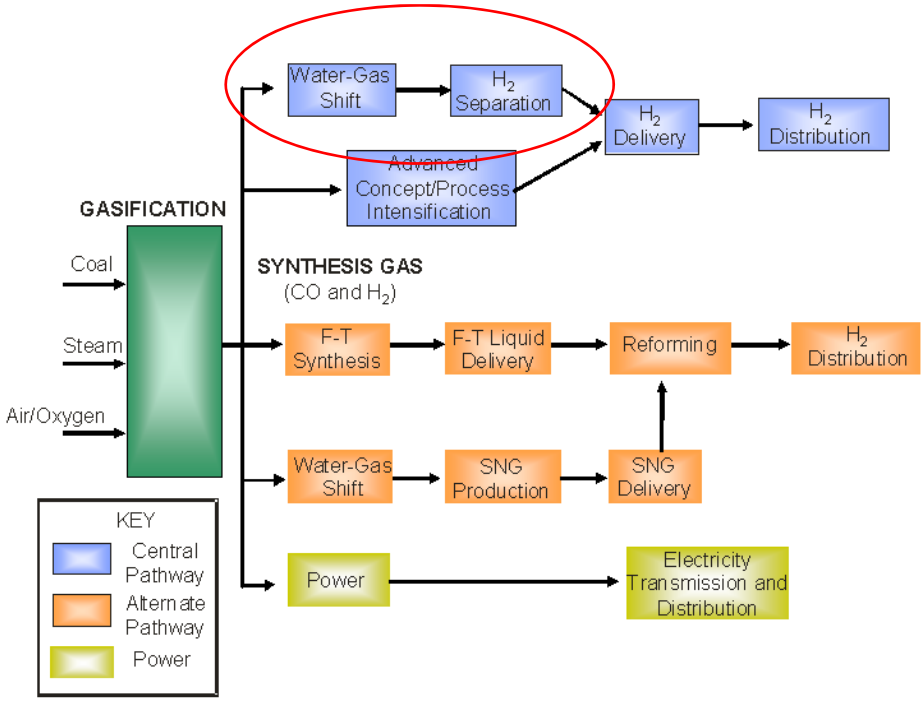
Partners

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

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

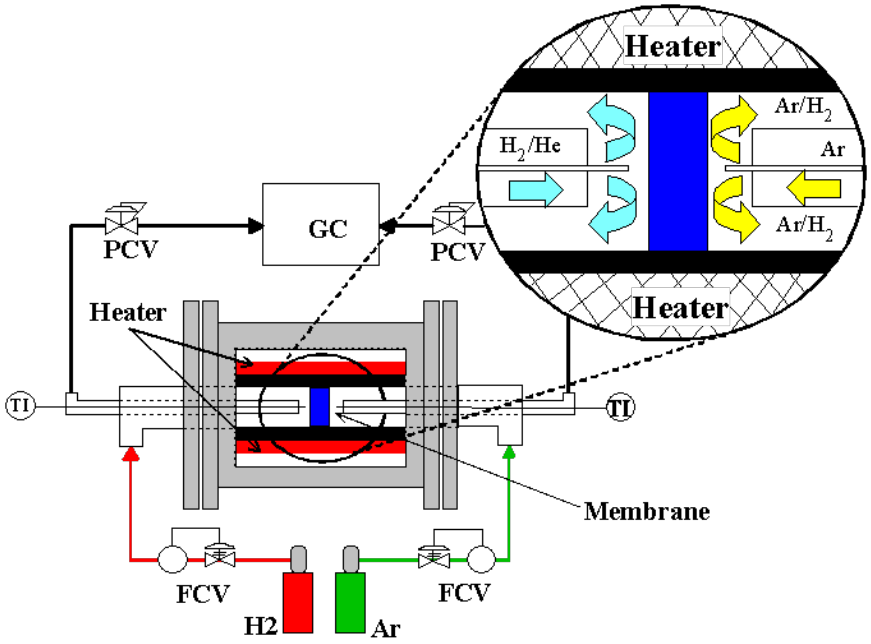
Background
(Relevance)

- **Overall goal**
  - Development of robust dense metal, hydrogen separation membranes for integration into coal conversion processes
- **Studies suggest that incorporating separation membranes into coal conversion processes can reduce costs by…**



Facilities & Capabilities

- **Reactor Systems**
  - Reactor and separation configurations
    - Continuous or batch
  - Major and minor syngas constituents
  - T to 1000°C, P to 1000 psi
- **Fabrication Lab**
  - Depositions chamber
  - Vacuum arc-melter
  - Micro-welder
  - High-T box and annealing ovens
- **Characterization Instruments**
  - UHV chambers
    - Gradient doser, AES, XPS, LEIS, TPD, PVD
  - XRD w/hot-stage
  - SEM w/EDS
  - TGA for use with H_2S



Outline

Task 1: H_2 Membrane Test Protocol

Task 2: PdCu System

Task 3: 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

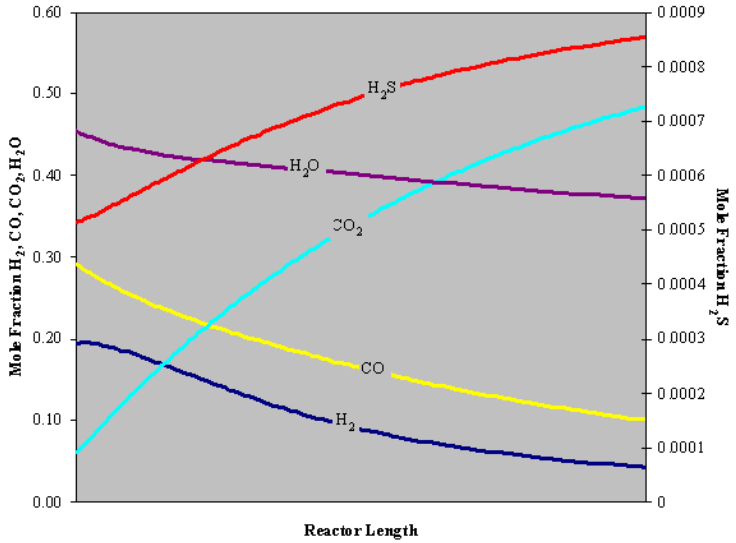
Performance Criteria	Units	2007 Target	2010 Target	2015 Target
Flux [a]	sccm/cm^2	51	102	152.4
Temperature	°C	400–700	300–600	250–500
S Tolerance	ppmv	----	20	>100
Cost	$/ft^2	150	100	<100
WGS Activity	-	Yes	Yes	Yes
?P Operating Capability [b]	psi	100	Up to 400	Up to 800 to 1,000
Carbon Monoxide Tolerance	-	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

(Technical Accomplishments)

- **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

(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 for biomass co-feed
  - Integration of WGS reactor and Membrane separator
    - (WGSMR)

Task 2: PdCu System

- **Objective**
  - Complete a comprehensive performance evaluation of the PdCu system at conditions consistent with coal conversion processes
- **The intent of the study is to**
  - gain a fundamental understanding of the PdCu system
  - address discrepancies observed in literature
  - develop property-performance relationships
  - provide design guidance for fabrication of membranes at commercial scales and thicknesses

Performance Criteria	Units	2007 Target	2010 Target	2015 Target
Flux [a]	scm/cm^2	51	102	152.4
Temperature	°C	400–700	300–600	250–500
S Tolerance	ppmv	----	20	>100
Cost	$/ft^2$	150	100	<100
WGS Activity	-	Yes	Yes	Yes
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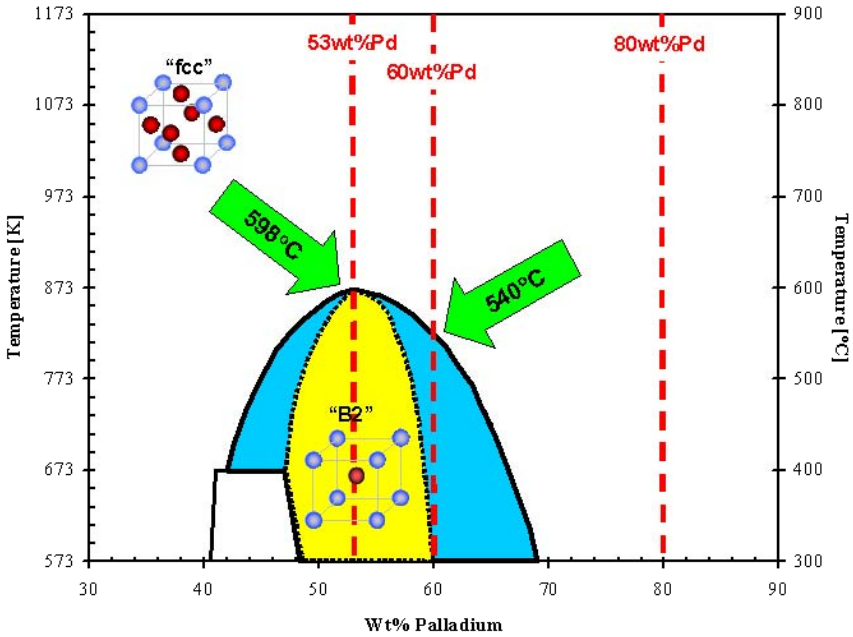
[a] For 100 psi ΔP (hydrogen partial pressure basis)
[b] ΔP = total pressure differential across the membrane reactor

Task 2: PdCu System

(Approach)

- **Utilize several PdCu compositions**
  - 100, 80, 60, 53wt%Pd-Cu
- **Fabricated by "cold rolling" techniques**
- **Membrane thickness was generally ~100μm**
  - Ease of operation and minimize failures
- **Temperatures consistent with post gasification and allowed variation in crystalline structure**
  - 350, 450 and 635°C
- **Sour gas studies**
  - 8hrs in clean 10%He-H_2 (baseline)
  - 120hrs in 0.1%H_2S-10%He-H_2

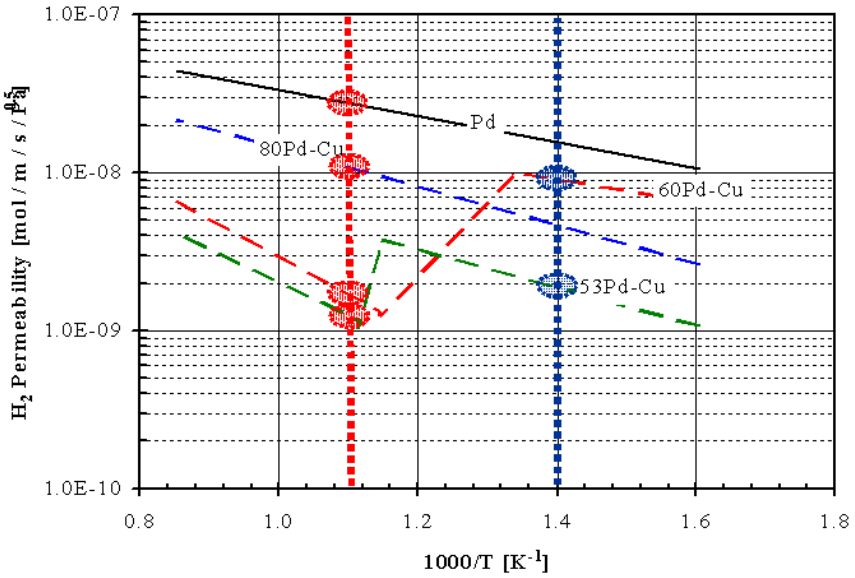


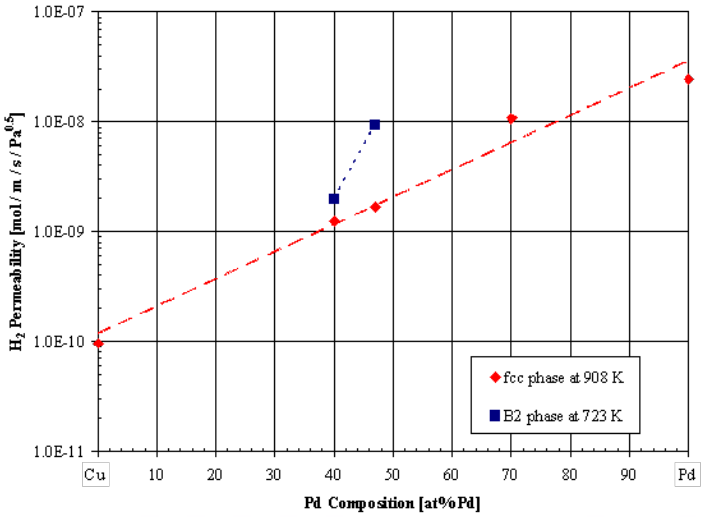
Subramanian, Laughlin, Binary Alloy Phase Diagrams, Second Ed., ASM International, (1990) 1454-1456.

Task 2: PdCu System

(Technical Accomplishments)

- **Completed evaluation of hydrogen permeability of Pd and PdCu**
  - 60Pd-Cu exhibits the highest permeability at temperatures below ~500°C, corresponding to a B2 crystalline structure.
  - 80Pd-Cu exhibits the highest permeability at temperatures above ~500°C, corresponding to a fcc crystalline structure.
  - In general, Pd-Cu permeability increases with increasing Pd content.

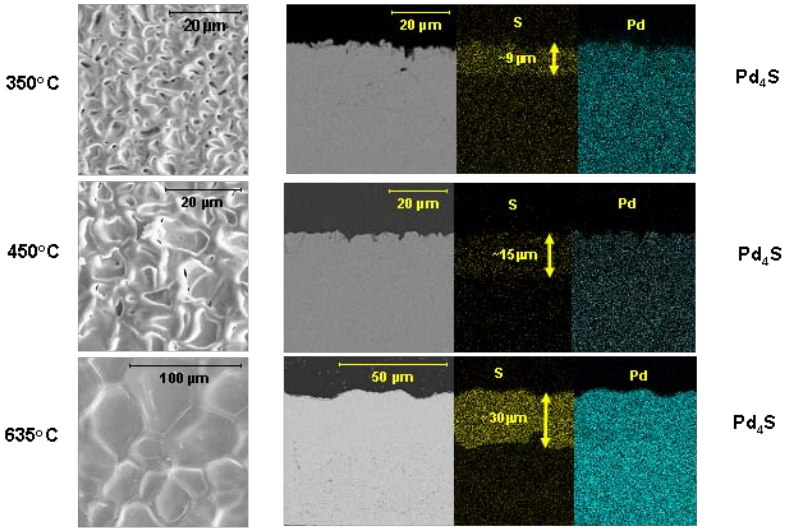




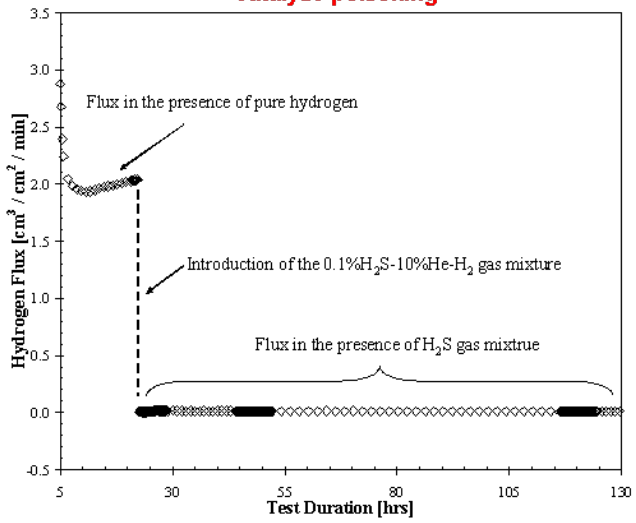
Task 2: PdCu System

(Technical Accomplishments)

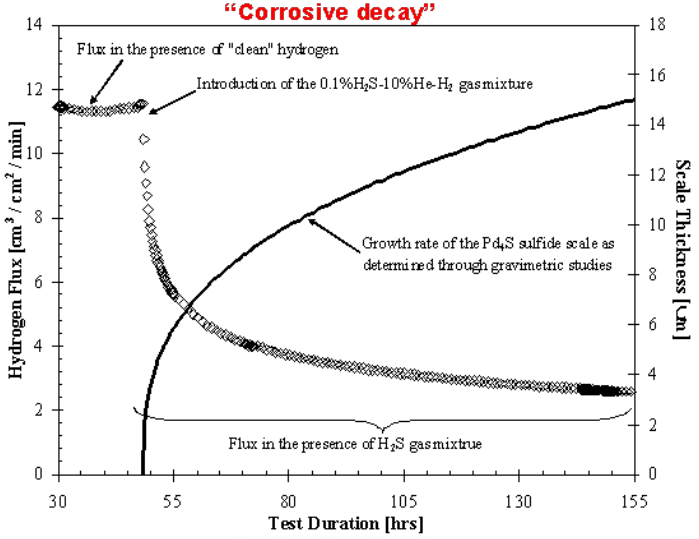
- **Completed evaluation of Pd and PdCu alloys in presence of H_2S**
  - Catalytic poisoning: Immediate decrease: no significant surface scale
    - 60Pd-Cu, 53Pd-Cu
  - Corrosive decay: Gradual decrease: significant surface scale
    - Pd, 80Pd-Cu
  - No change in performance upon the introduction of H_2S: no surface scale.
    - 80Pd-Cu, 60Pd-Cu, 53Pd-Cu at T>450°C



"Catalytic poisoning"



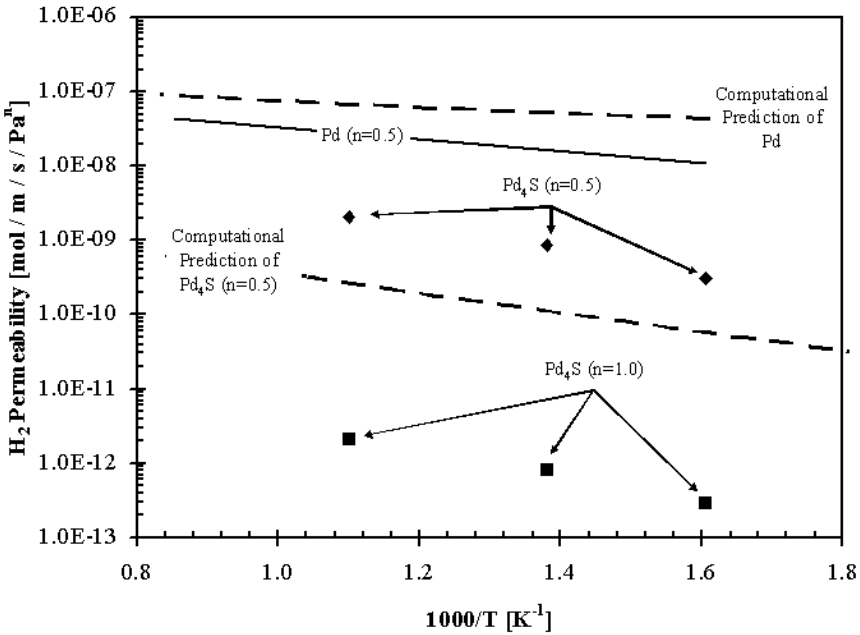
"Corrosive decay"

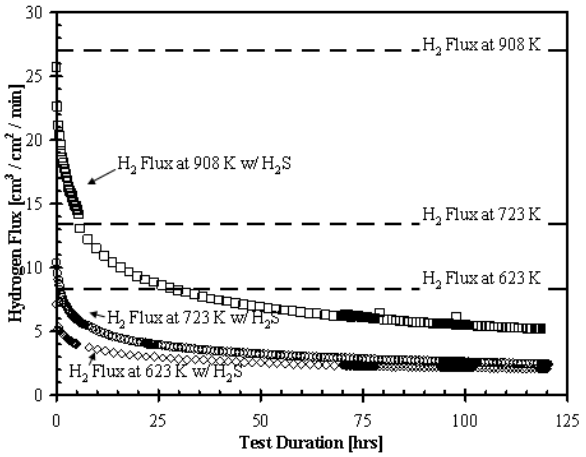


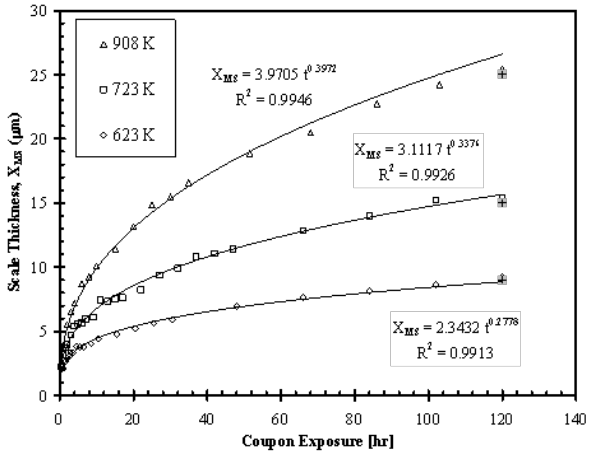
Task 2: PdCu System

(Technical Accomplishments)

- **Reported the first ever permeability of Pd_4S using both experimental and computational techniques**
  - Approach can be used for developing new membrane systems
- **Pd_4S permeability is ~1/10 Pd permeability**







Task 2: PdCu System

(Collaborations)

- **The research team conducting the work on the PdCu system consisted of participants from local universities**
  - University of Pittsburgh
    - Provided technical support
    - Performance testing of the membranes
    - Membrane characterization
  - Georgia Institute of Technology
    - Utilized computational method to predict the first reported permeability of palladium-sulfide

Task 2: PdCu System

(Proposed Future Work)

- **Characterization of the PdCu system in clean and H_2S-contaminated environments has been successfully completed**
- **No additional work specific to PdCu is planned**
- **The results of our work with PdCu will help set the direction of future Robust Metal Membrane Development (Task 3):**
  - how to think about and characterize interaction of sulfur with multicomponent materials, like alloys
  - alloys' contribution to corrosion resistance
  - the role of minor components in imparting sulfur tolerance to metal membrane systems

Task 3: 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
Flux [a]	sccm/cm^2	51	102	152.4
Temperature	°C	400–700	300–600	250–500
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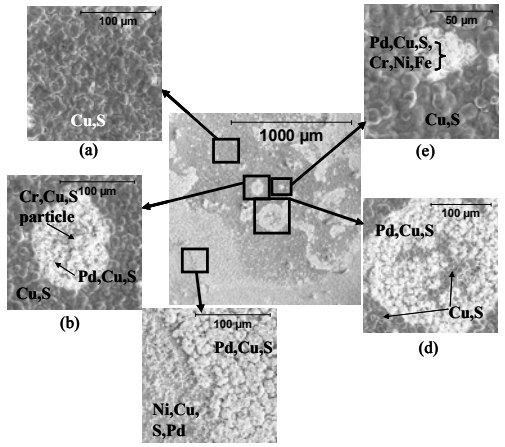
Stability/Durability	years	1	3	5

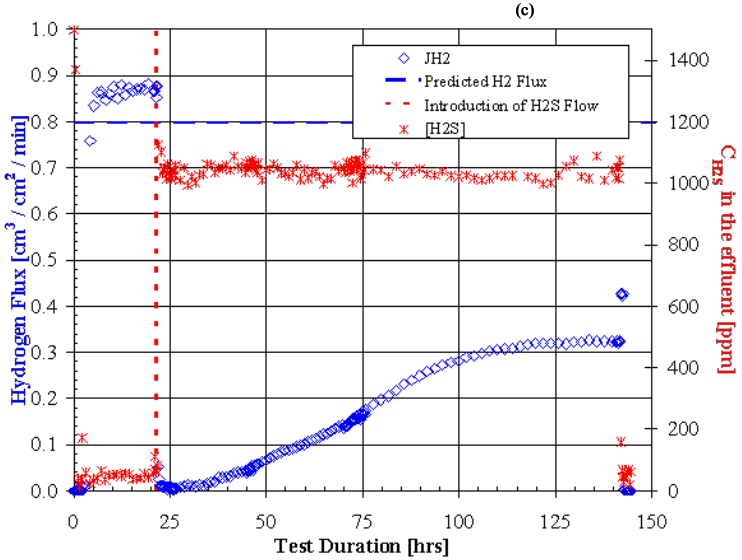
[a] For 100 psi ΔP (hydrogen partial pressure basis)
[b] ΔP = total pressure differential across the membrane reactor

Task 3: Robust Metal Membrane Development

(Approach)

- **Building on the PdCu foundation, apply fundamental and applied science to engineer membrane alloys and composites suitable for coal conversion processes**
  - Corrosion resistance
    - fundamental thermodynamics,
    - gravimetric analysis
  - Surface activity
    - H_2/D_2 exchange
    - computational studies
  - H_2-transport





Task 3: Robust Metal Membrane Development

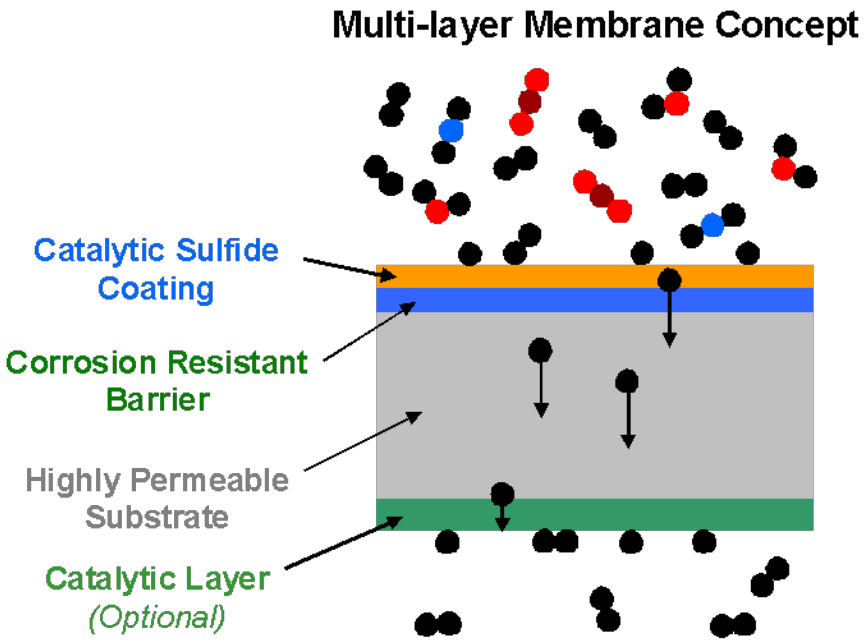
(Technical Accomplishments)

- **Provisional Patent Filed:**

"Sulfur Induced H_2-Membrane"

  - Concept: Use B2-structured Pd-Cu alloy as sulfide corrosion barrier in multilayered membrane structure
  - Utilize "S-based surface catalyst" to provide atomic hydrogen for transport

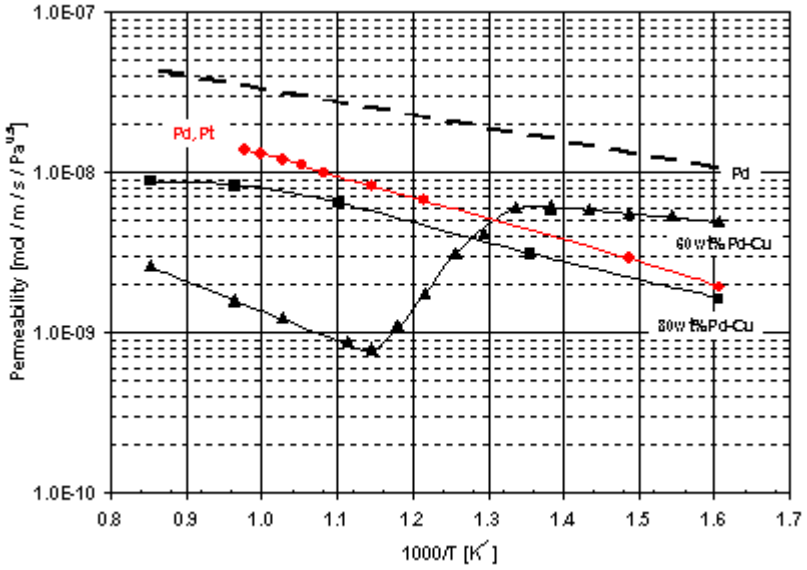
- **New capabilities developed**
  - preparation and characterization of H-atom transport through multi-layer structures in UHV
  - preparation and characterization of catalytic-sulfide top-layers for multi-layer structures

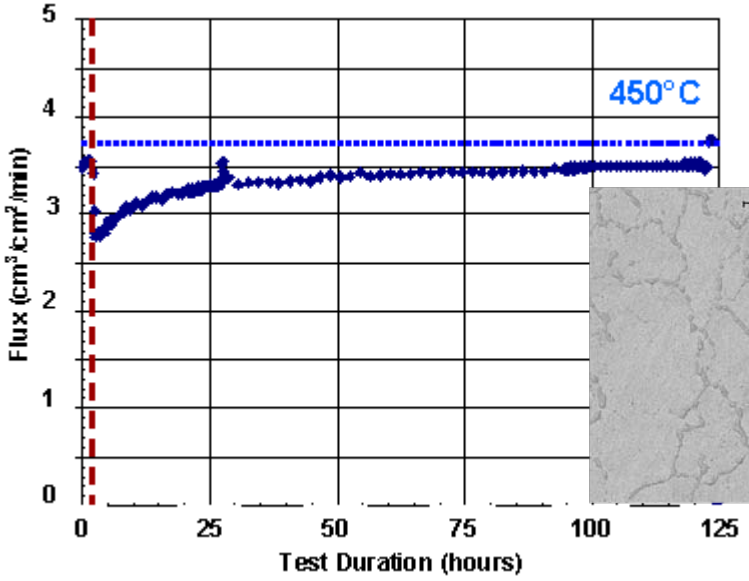


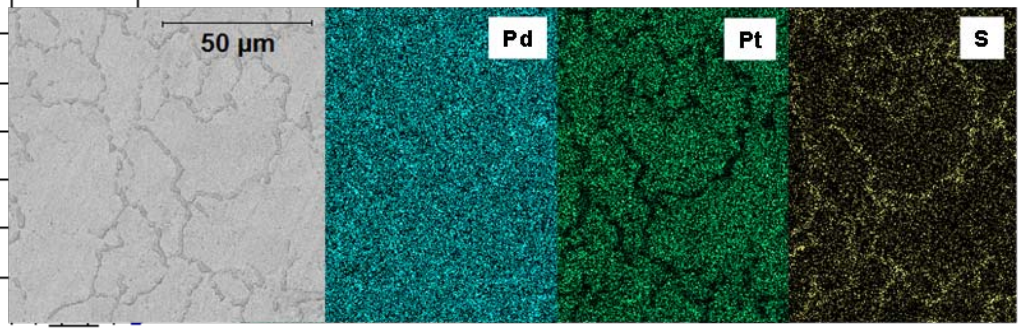
Task 3: Robust Metal Membrane Development

(Technical Accomplishments)

- **Several binary and tertiary metallic systems have been fabricated and screened**
  - Pd-Ag, Au, Co, Cu, Ni, Pt
- **PdPt alloy has shown significant promise for S-tolerance**







Task 3: Robust Metal Membrane Development

(Collaborations)

- **The research team conducting the work on the task consisted of participants from institutions**
  - Carnegie Mellon University
    - Provided technical support
    - Assisted performance testing of the membranes
    - Utilize UHV techniques to evaluate the energetics associated with H_2 activation on metal and sulfide surfaces.
  - NETL Computational Research Group
    - Provide fundamental computational studies evaluating the energetics associated with H_2 activation on metal and sulfide surfaces.

Task 3: Robust Metal Membrane Development

(Proposed Future Work)

- **Characterize H-atom transport across interfaces buried within multi-layer structures**
- **Develop options for sulfur-resistant top-layers and corrosion-resistant intermediate layers for layered structures**
- **Continue evaluation of binary and higher alloys for use alone or as functional layers in multi-component structures**
- **Provide design input to partners who fabricate membranes for practical implementation**

Summary

- **A test protocol has been developed that allows technological progression and comparisons for application to coal conversion processes**
- **A comprehensive study of the PdCu system has been completed**
  - Conditions of complete S-tolerance have been identified.
  - Corrosion/catalytic phenomena has been identified and will be used for further membrane development
- **Several alloy compositions have been fabricated and screened for performance**
  - Some alloys have shown potential for S-tolerance