NATIONAL ENERGY TECHNOLOGY LABORATORY

Development of Robust Hydrogen Separation Membranes

National Energy Technology Laboratory-Regional University Alliance

NETL-RUA

PD008

2011 DOE Hydrogen Program Review

U.S. DEPARTMENT OF ENERGY

H_2 Separation Membrane Team Members

(Collaborators)

U.S. DOE - NETL

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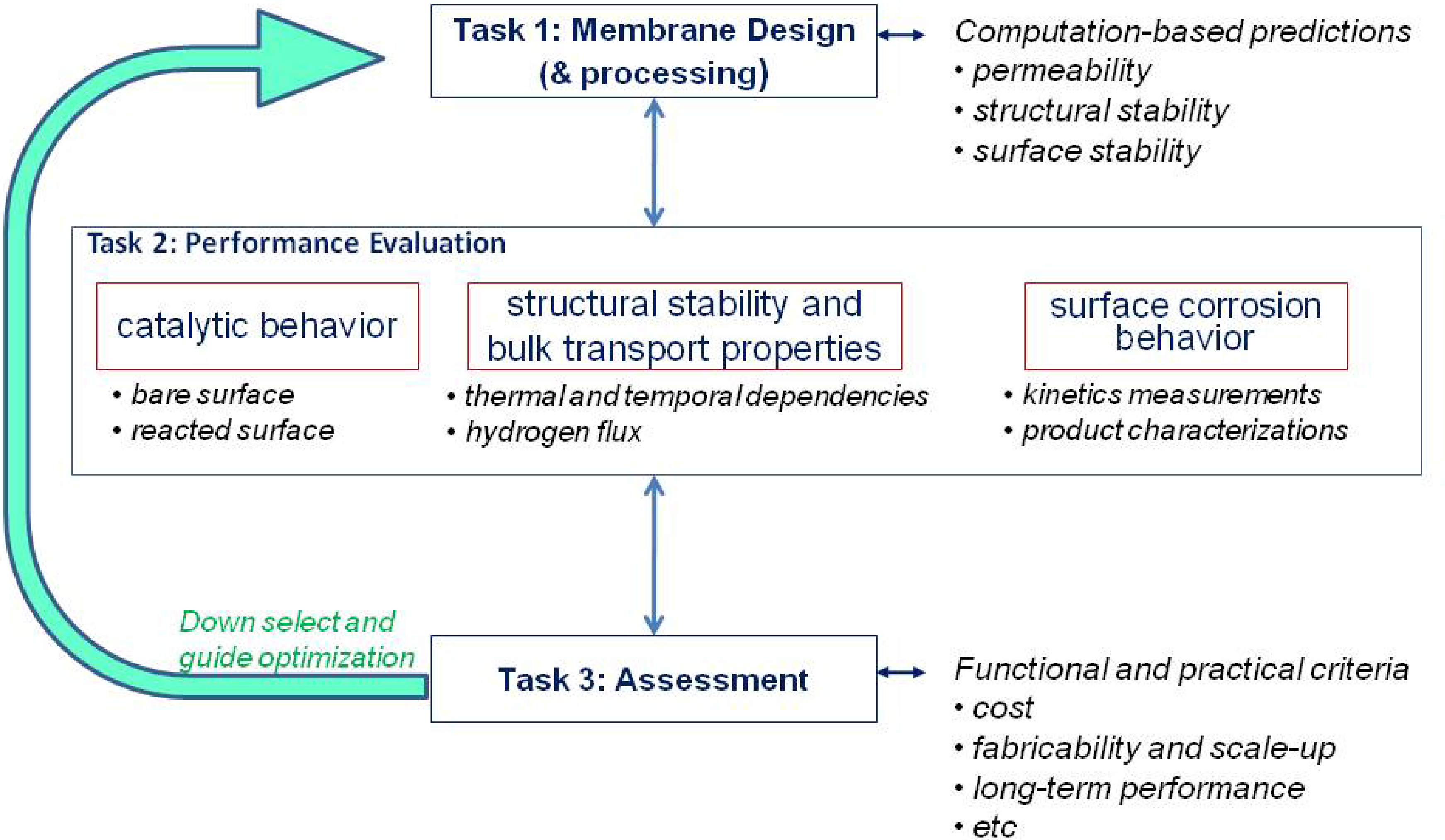
NETL Site Support Contractors

Dr. Mike Ciocco, PIT

H_2 Separation Membrane Team Structure

(Approach)



Overview

Timeline

- Project start date: 10/1/2010
- Project end date: 9/30/2011
- 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

- FY11 funding: $1,361k
- FY10 Funding: $681k
- FY09 Funding: $746k
- FY08 Funding: $1,000k
- FY07 Funding: $1,230k

Partners

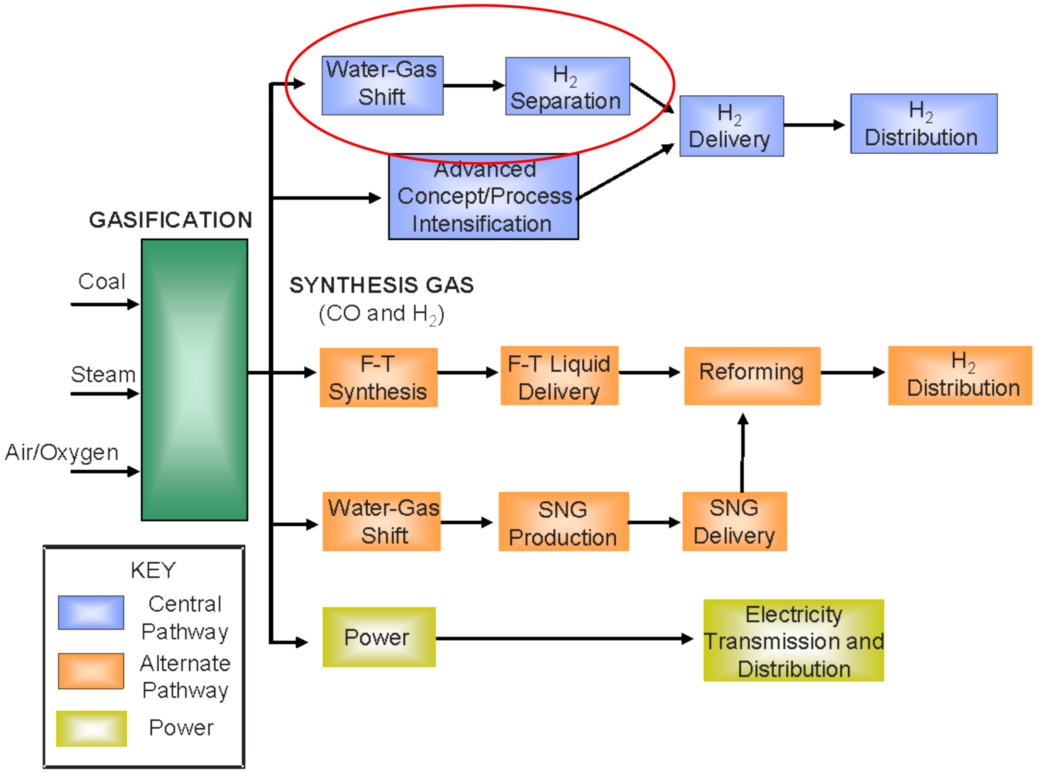
- Carnegie Mellon University
- University of Pittsburgh
- Virginia Tech
- NCCC, Wilsonville

(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%.



Hydrogen separation performance targets

(Relevance)

Performance Criteria	Units	Current Status [a] (H_2-permeable cermet)	2010 Target	2015 Target
Flux [b]	$ft^3/hour/ft^2$	~220	200	300
Temperature	°C	300–400	300–600	250–500
S Tolerance	ppmv	Yes (~20 ppmv)	20	>100
Cost	$\$/ft^2$	<200	100	<100
WGS Activity	-	N/A	Yes	Yes
ΔP Operating Capability [c]	psi	1,000 (tested)	Up to 400	Up to 800 to 1,000
Carbon Monoxide Tolerance	-	Yes	Yes	Yes
Hydrogen Purity [d]	%	>99.999%	99.5%	99.99%
Stability/Durability	years	0.9 (tested)	3	5

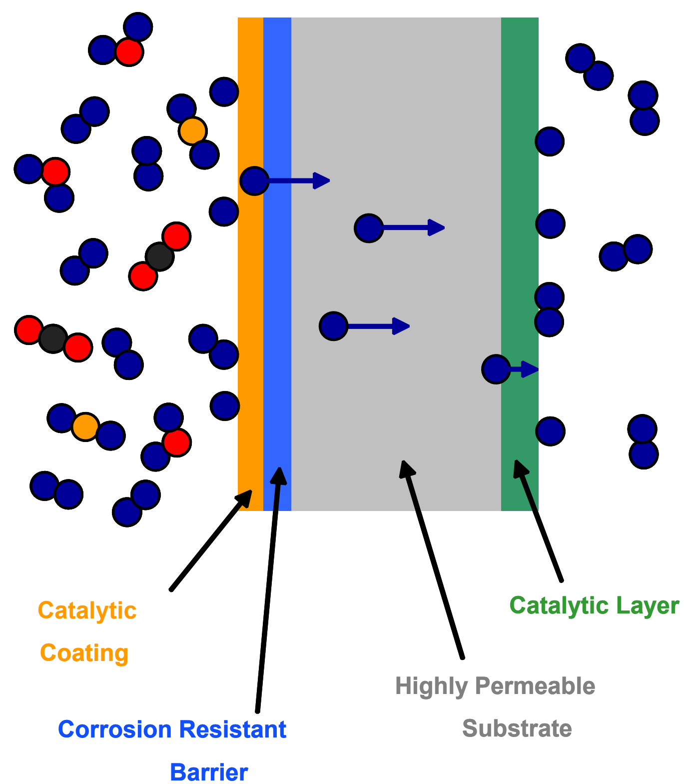
Hydrogen from Coal Program, RD&D Plan, External Draft, U.S. Department of Energy, Office of Fossil Energy, NETL, September 2008

Robust Metal Membrane Development

(Approach)

- **Develop an advanced membrane system for hydrogen separation**
  - High activity for hydrogen dissociation
  - High H-atom permeability
  - Resistance to S-poisoning
  - Mechanically robust
- **Apply computation and experiment**
  - Characterization of H_2 dissociation kinetics
  - Identification of third component that broadens the high-permeability region
  - Characterization of corrosion kinetics/products
  - Demonstrate performance of promising candidates
  - Coupon testing of promising candidate materials at NCCC

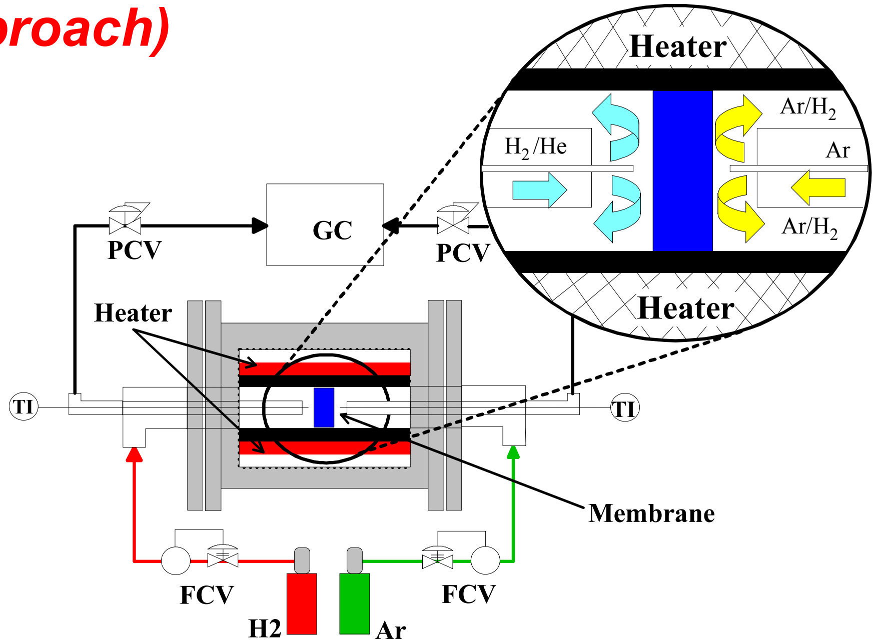
Multi-layer Membrane Concept



Facilities & Capabilities

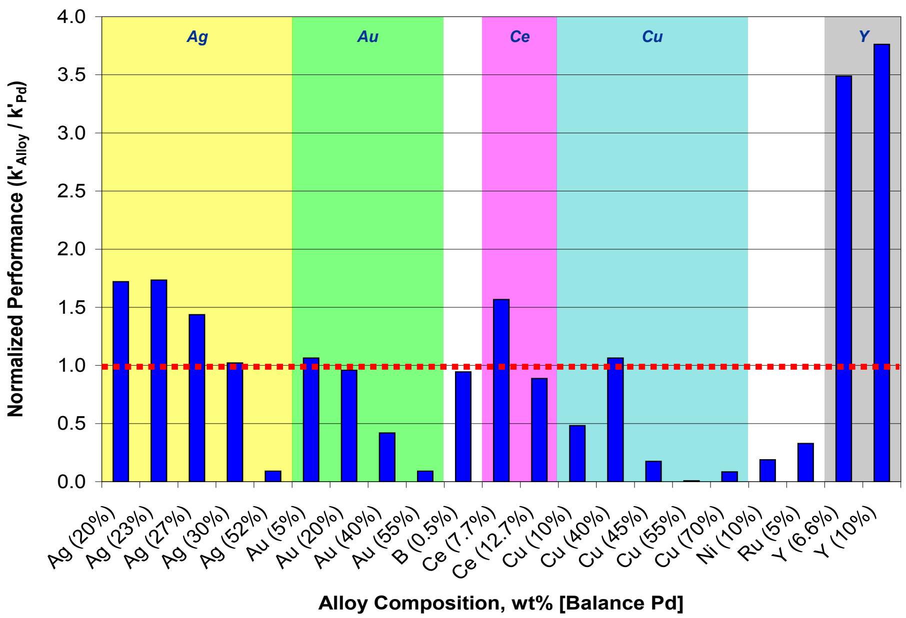
(Approach)

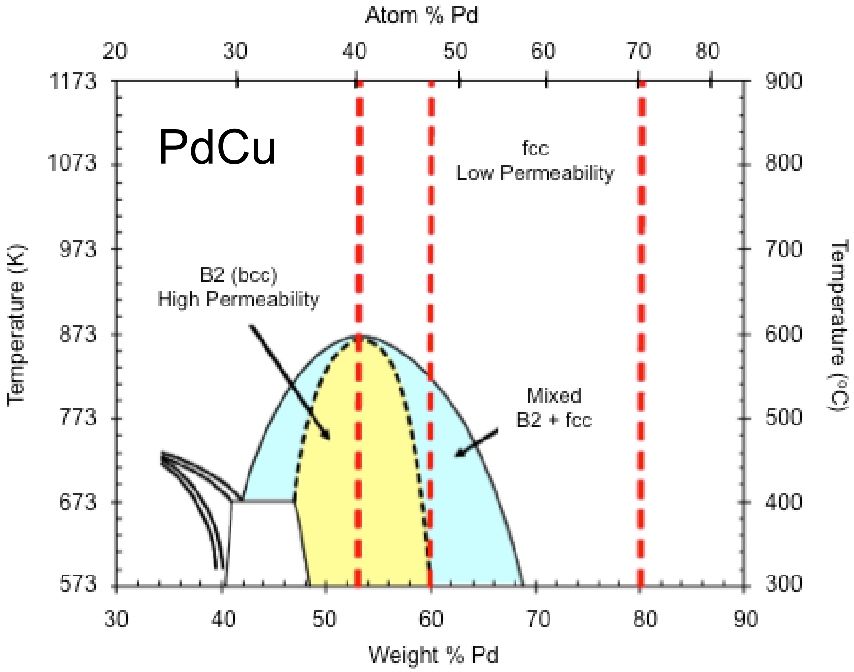
- **3 Membrane Test Rigs**
  - Continuous, bench-scale units
  - T to 1000°C, P to 1000 psi
- **2 Laboratory Membrane Screening Rigs**
  - Continuous, lab-scale units
  - T to 1000^{o}C, P to 30 psi
- **Materials Lab**
  - Deposition chamber(s)
  - High-T box and annealing ovens
  - XRD w/hot-stage
  - SEM w/EDS, EBSD
  - TGA for use with H_2S
  - Imaging XPS
  - He^{+} ion scattering
- **High Throughput Materials Science**
  - Deposition tools
  - Spatially resolved characterization
- **Computation**
  - DFT, Kinetic Monte-Carlo, COMSOL CFD



Robust Metal Membrane Development

(Approach)



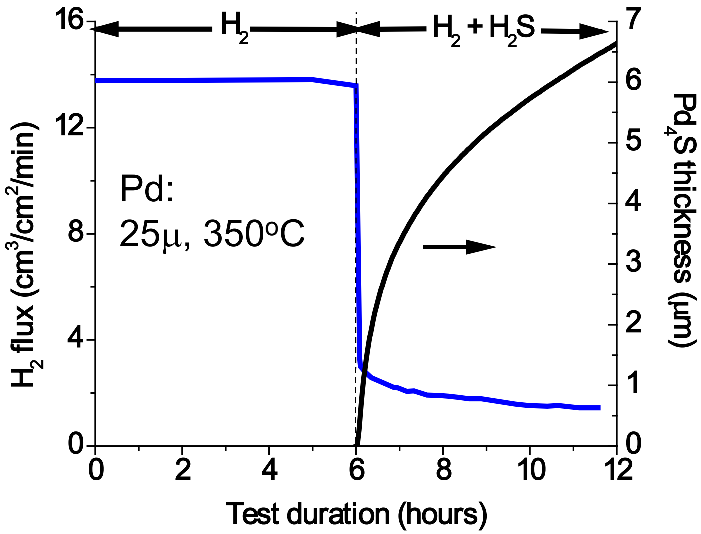


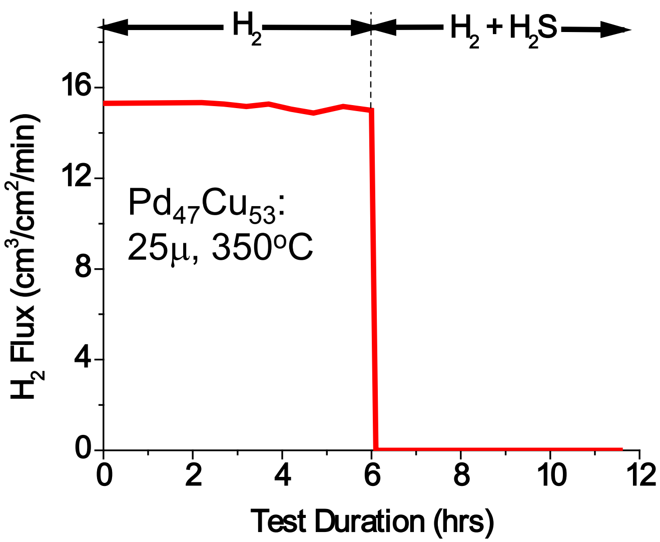
Alloying Pd with minor component(s) can:

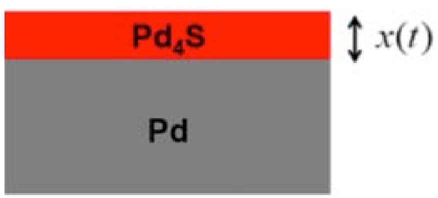
- improve mechanical robustness and sulfur tolerance
- maintain Pd's surface activity and high permeance,

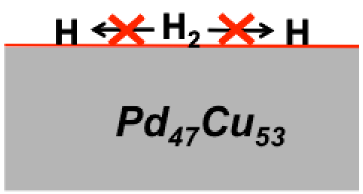
Robust Metal Membrane Development

(Background: previous results)





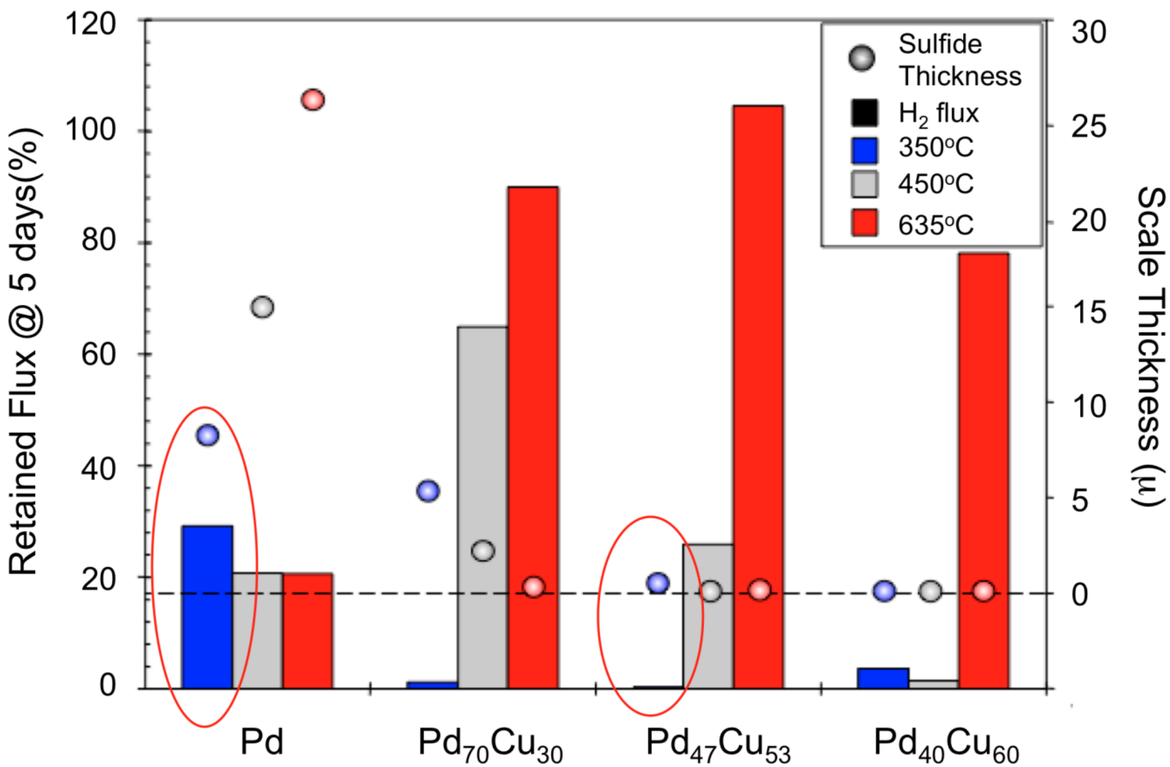




Two mechanisms of performance deterioration caused by exposure to H_2S: (L) growth of low permeabilty sulfide scale on Pd and (R) catalytic poisoning of alloy surface.

Robust Metal Membrane Development

(Background: previous results)



True S-tolerance exists in the PdCu binary, but at conditions of low "base permeance": High Cu content + elevated temperature

Illustrates potential of Pd alloys and teaches how to frame the problem

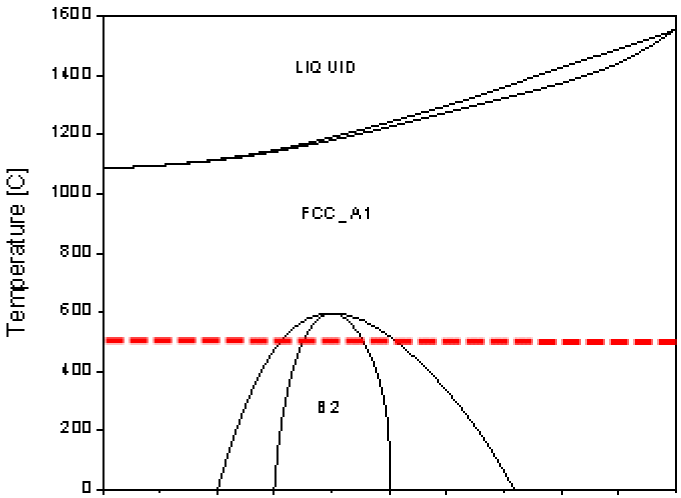
Current activities:

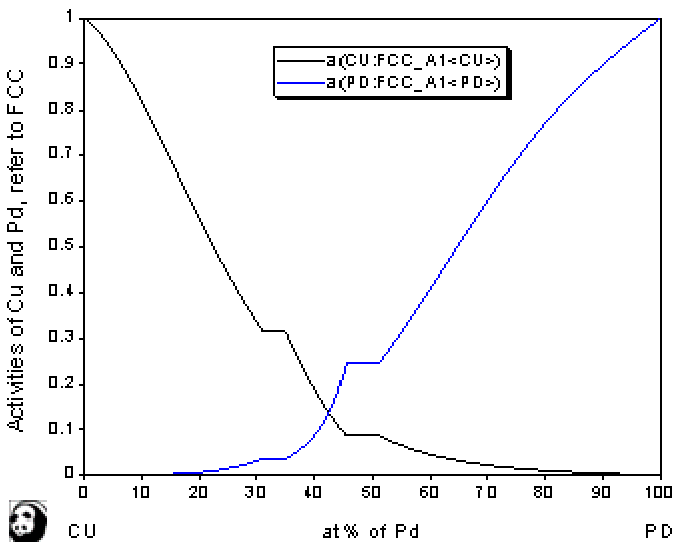
- basic understanding of PdCu
- expansion to ternary alloys

1000ppm H_2S in H_2, steady state flux typically obtained after 5 days on stream

Material Thermodynamics

(Technical Accomplishments – Stability & Scale Prediction)

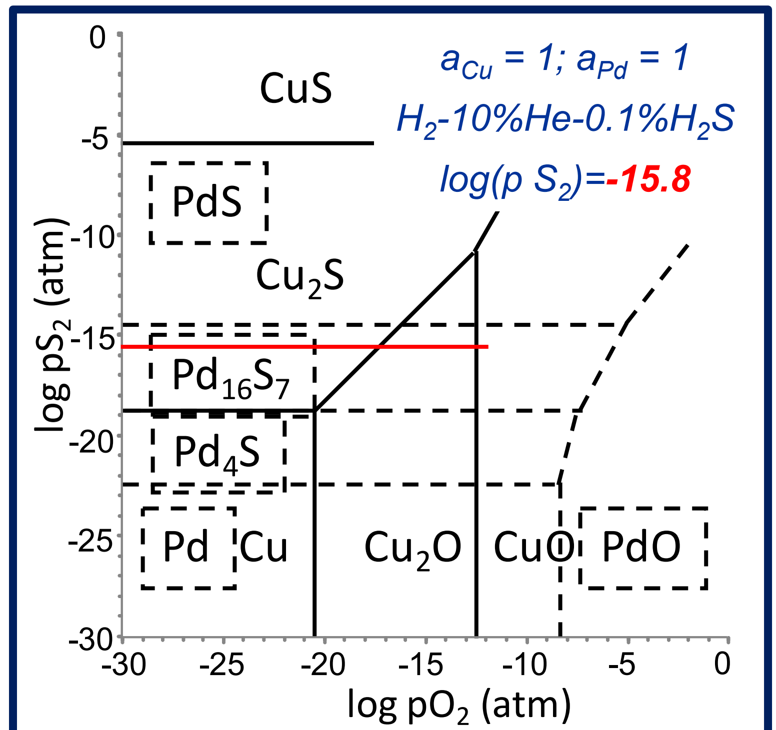




$$aM + bH_2S \leftrightarrow M_aS_b + bH_2$$

Predicted Stability

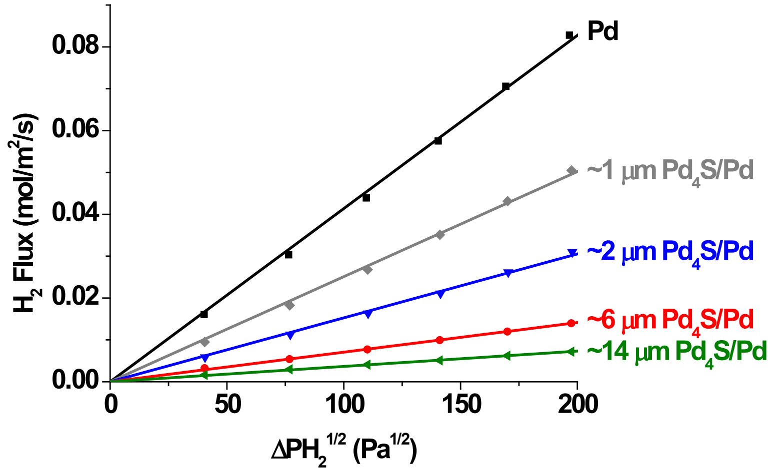
gas	gas	gas
$Pd_{16}S_7$	Cu_2S	$Pd_{16}S_7$
Pd_4S		Pd_4S
Pd	Cu	$Pd_{70}Cu_{30}$



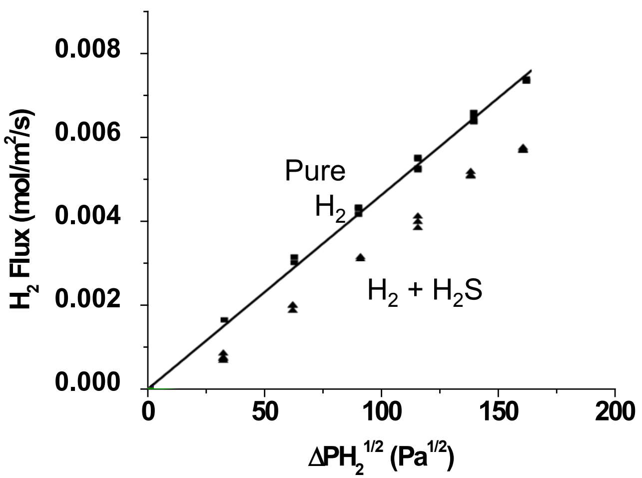
Robust Metal Membrane Development

(Technical Accomplishments – Stability, Scale Growth & Transport)

- **Direct measurement of Pd_4S permeability**
  - In the presence of H_2, appears to follow Sievert's law
  - Permeability of Pd_4S is ~10x less than Pd

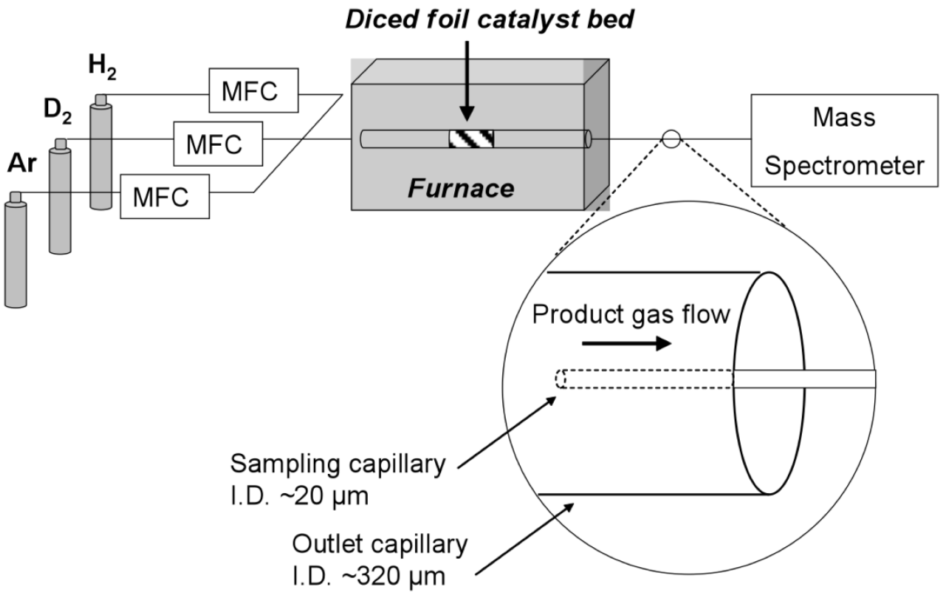


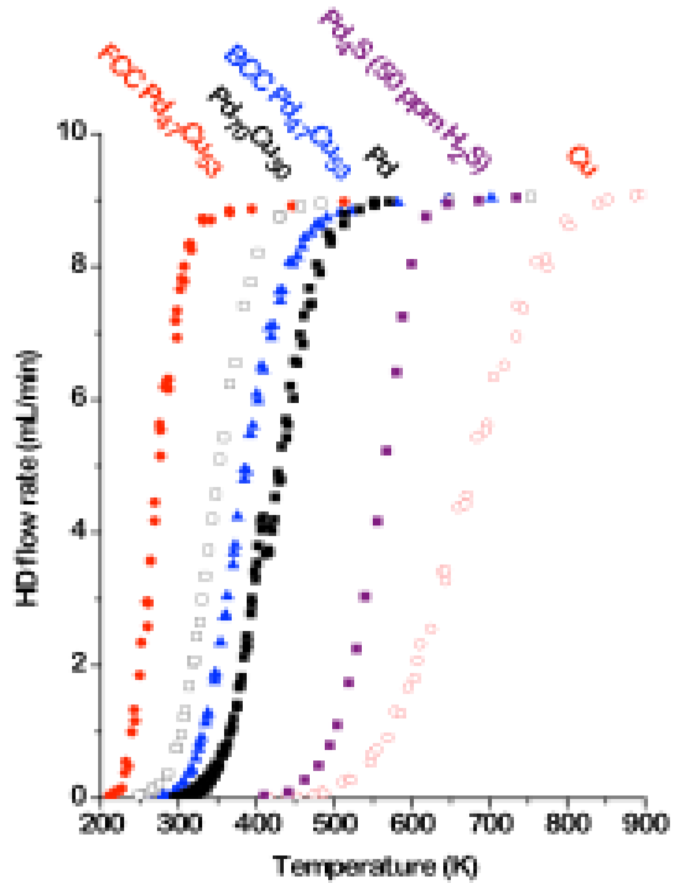
- **H_2S causes incremental flux decline**
  - Likely mechanism is site blocking (link to H-D exchange work)



Robust Metal Membrane Development

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



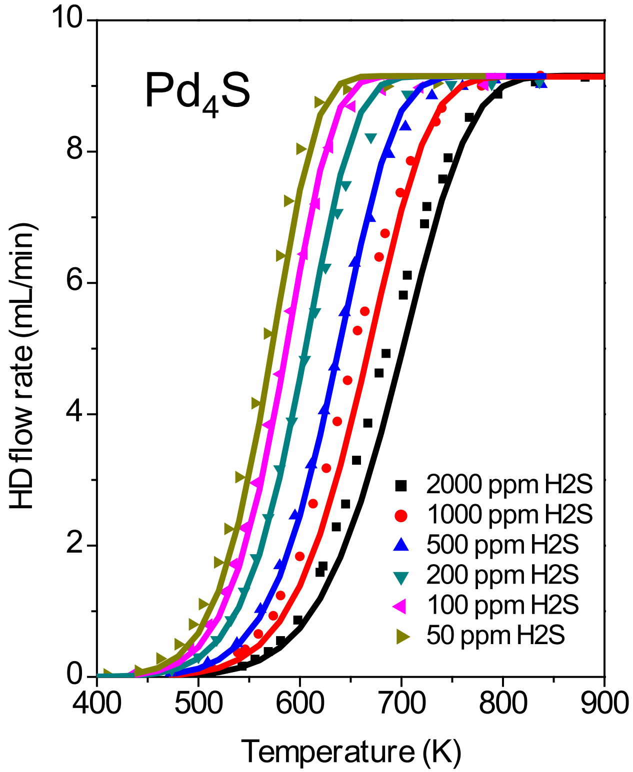


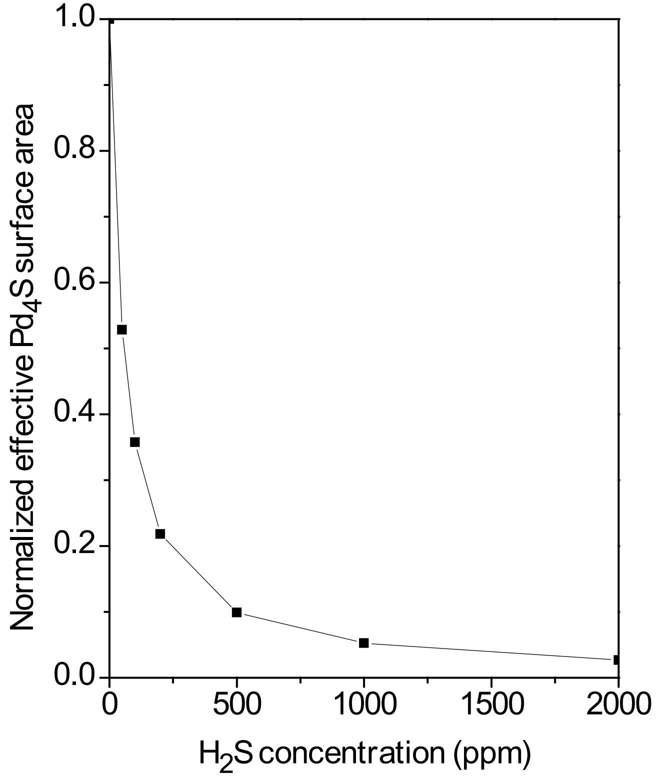
$H_2 + D_2 \longleftrightarrow 2HD$

H_2-D_2 exchange provides fundamental insight into hydrogen dissociation on model membrane surfaces—across alloy composition *and* in the presence of H_2S

Robust Metal Membrane Development

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



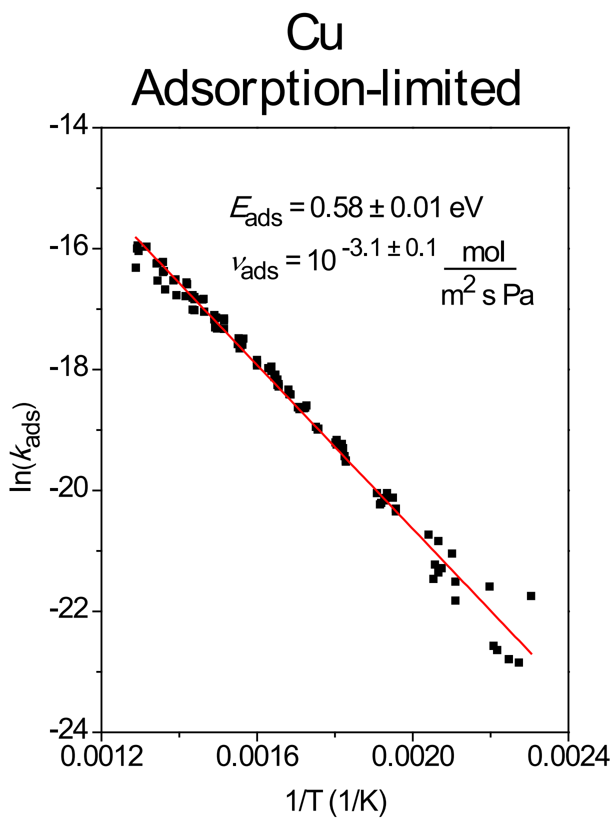


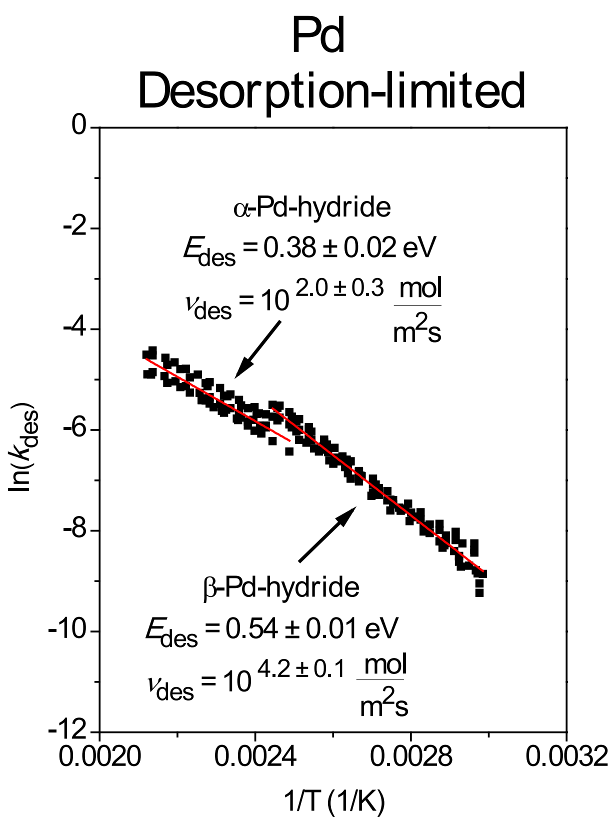
$H_2 + D_2 \longleftrightarrow 2HD$

H_2S adsorption onto Pd_4S reduces effective surface area for H_2 adsorption

Robust Metal Membrane Development

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



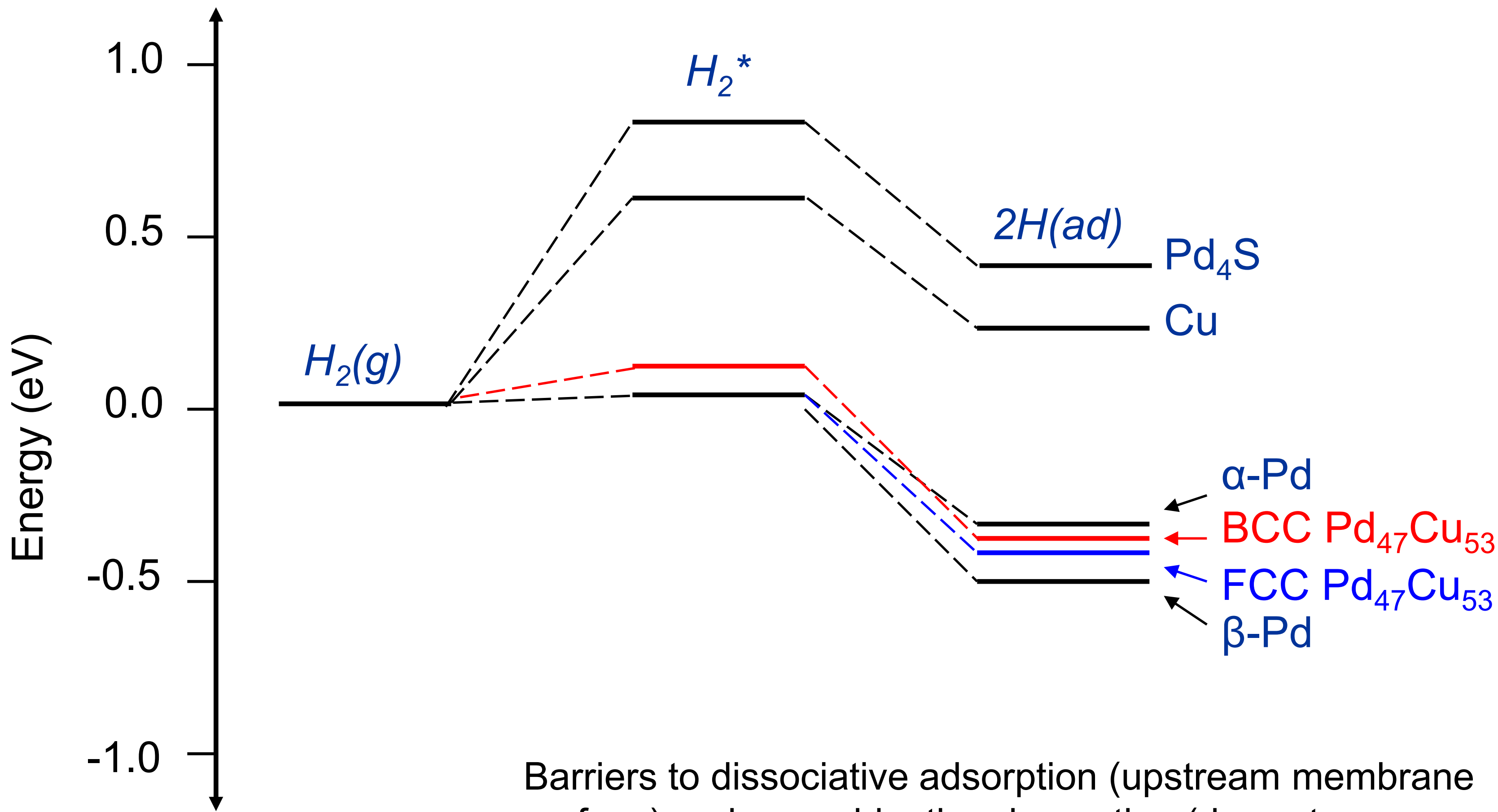


$H_2 + D_2 \longleftrightarrow 2HD$

Interpret H_2-D_2 exchange data via a micro-kinetic model to estimate activation barriers and pre-exponentials—a rational basis for comparing membrane surface activities

Robust Metal Membrane Development

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



$H_2 + D_2 \longleftrightarrow 2HD$

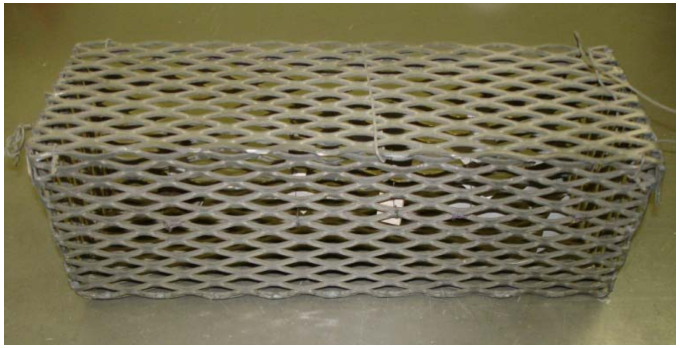
Barriers to dissociative adsorption (upstream membrane surface) and recombinative desorption (downstream membrane surface) both depend on surface composition

Robust Metal Membrane Development
(Approach – Stability, Scale Growth & Transport)

Metal coupons consisting of materials of interest to NETL were exposed to an actual gasifier syngas at the National Carbon Capture Center in Wilsonville, Alabama to evaluate real-world corrosion effects versus those observed under laboratory conditions.

Coupon exposure test conditions (average)

- **Fuel: Coal**
- **Duration: 5 weeks**
- **Temperature: 400ºC**
- **Hydrogen concentration: 7.5% (dry basis)**
- **Hydrogen sulfide concentration: 250 ppm**



Coupon types exposed

- **Membrane (NETL Pittsburgh)**
    - **19 samples (coupons approximately 100 μm thick)**
        - **Pd, PdCu (5 samples), PdCuX (4 samples), PdX (7 samples), 2 misc. alloys**
- **Supported membrane (WPI)**
    - **6 samples (composite Pd and PdCu on porous SS)**
- **Structural alloy (NETL Albany)**
    - **4 samples**

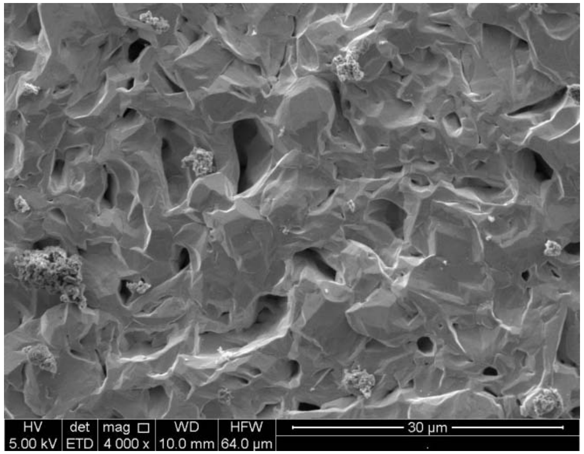
Robust Metal Membrane Development

(Technical Accomplishments – Stability, Scale Growth & Transport)

NCCC Coupon Testing: preliminary results

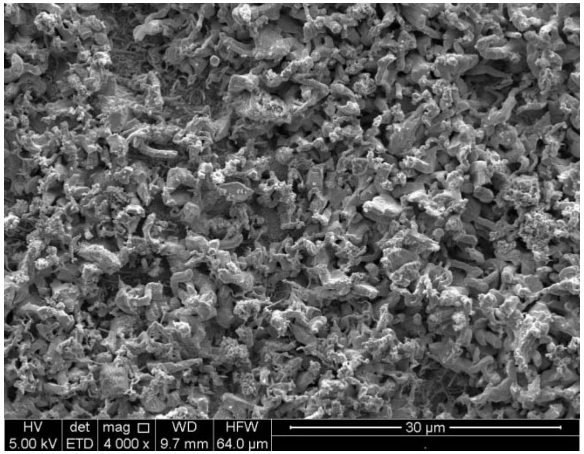
- B2-structured alloys suffered much less corrosion
- Particulates observed to impact surface
- Trace component effects appear important
    - Arsenic detected in several coupons so far
- Surface morphology for some alloys very different than observed in lab tests

Pd



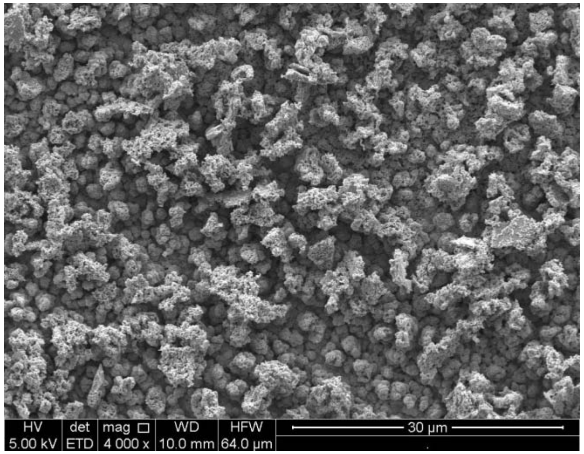
XRD: Pd_4S only phase detected (Pd coupon completely sulfided and fractured into pieces)

80wt%Pd-Cu



XRD: $Pd_{13}Cu_3S$ with trace of Pd_4S (thick sulfide corrosion layer - metal not detected)

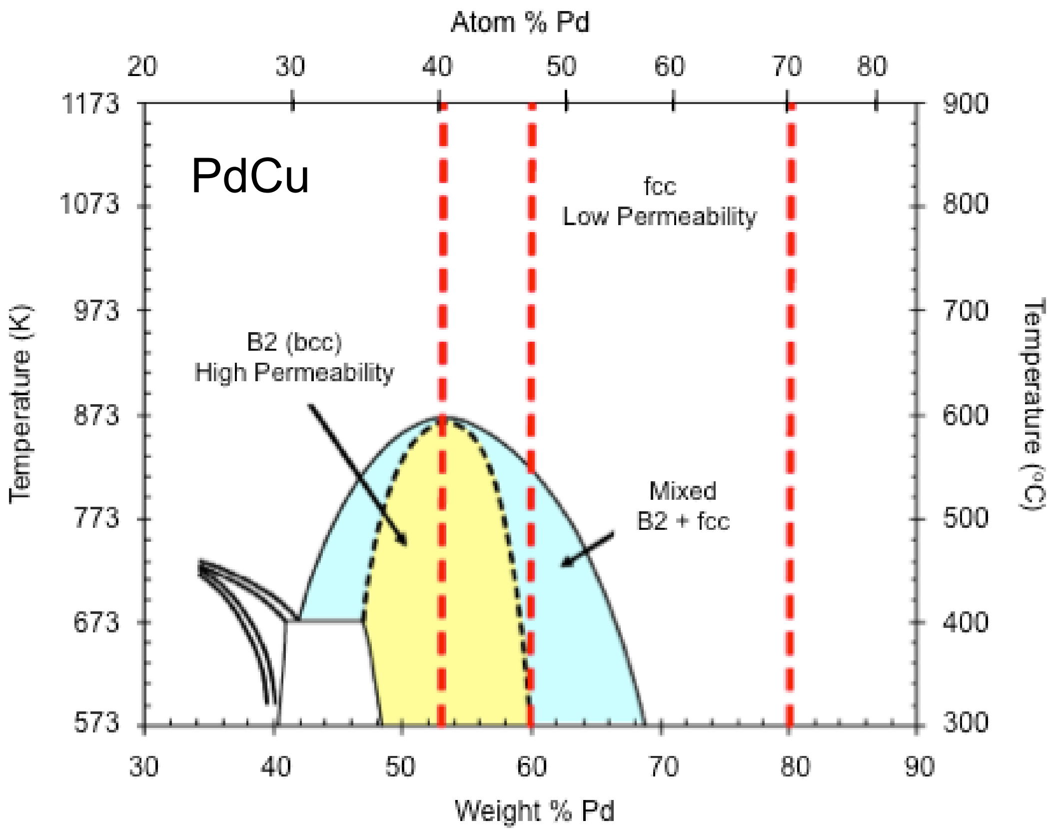
60wt%Pd-Cu



XRD: Only B2 PdCu detected (sulfides visible by SEM are below detection limit of standard XRD scan conditions used)

Robust Metal Membrane Development

(Approach – New Materials Development)

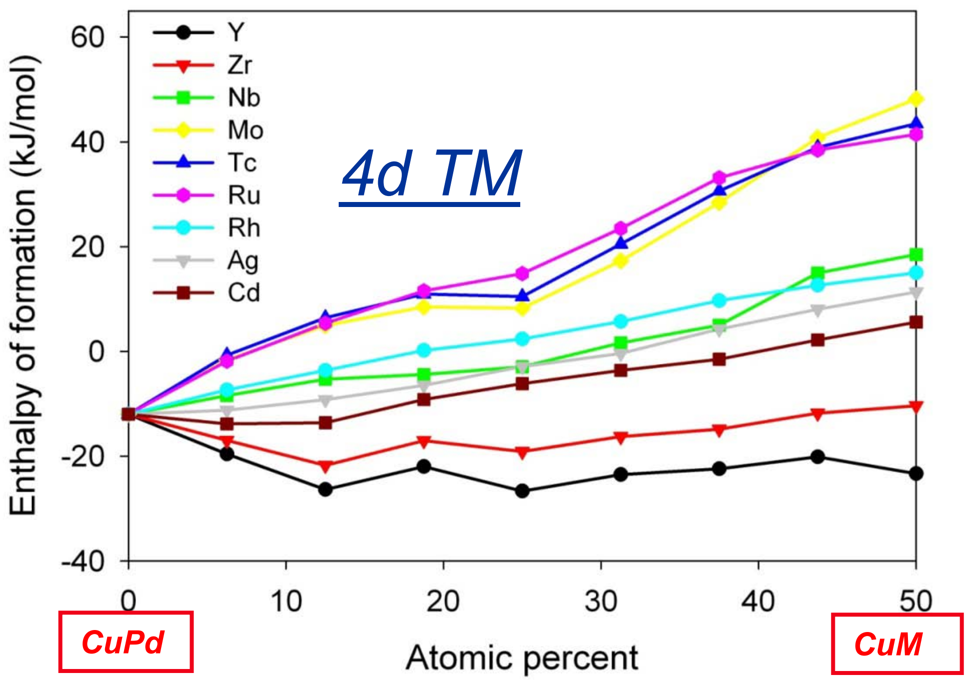


Add a third component to PdCu to:

- Broaden B2 phase field
- Enhance H_2 permeability
- Improve sulfur poisoning resistance

Robust Metal Membrane Development

(Technical Accomplishments – New Materials Development)

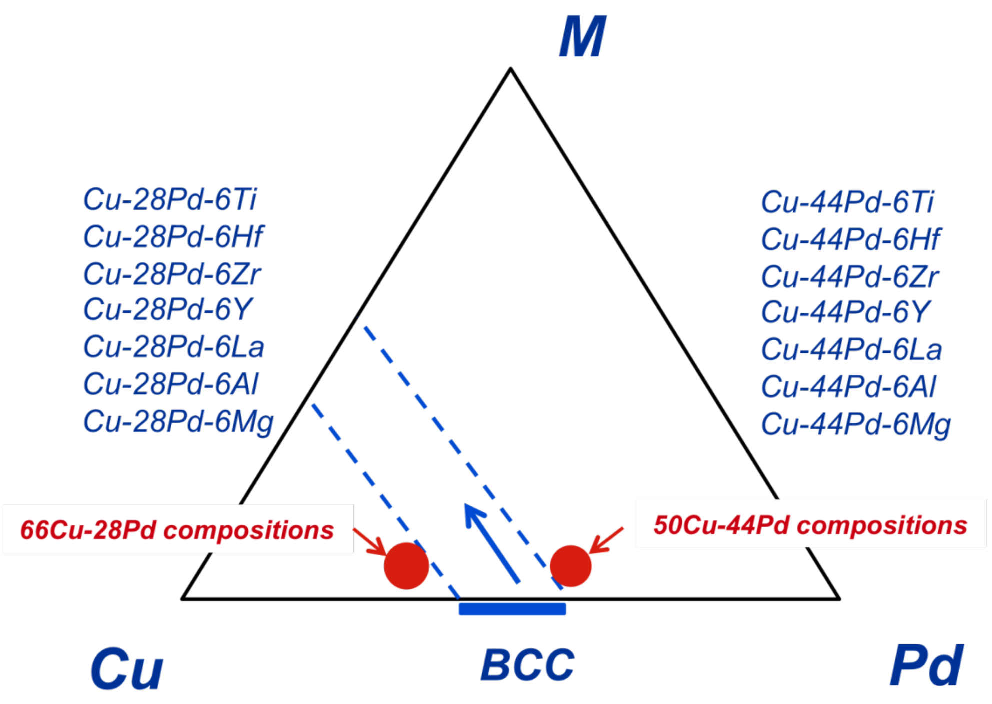


$Cu_{50}Pd_{(50-x)}M_x$

Calculation of enthalpy of formation using *ab initio* density functional theory (DFT) methods identifies most stable ternary alloys

Robust Metal Membrane Development

(Approach – New Materials Development)

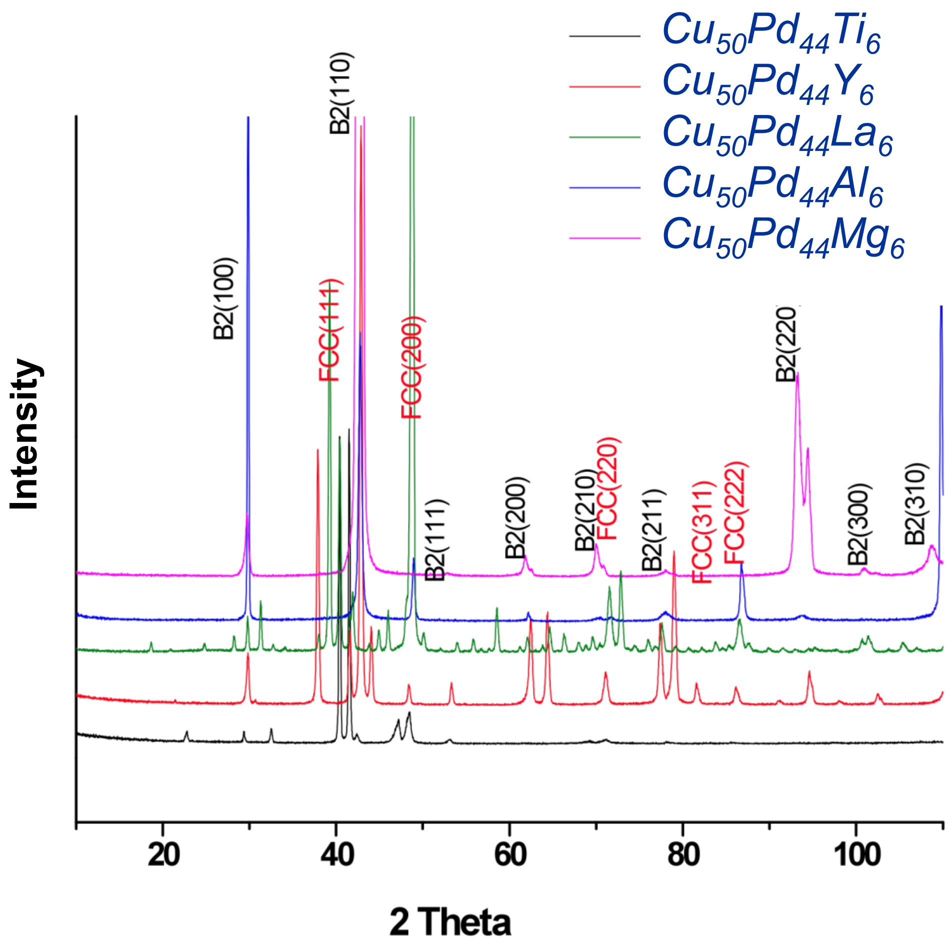


Strategy:

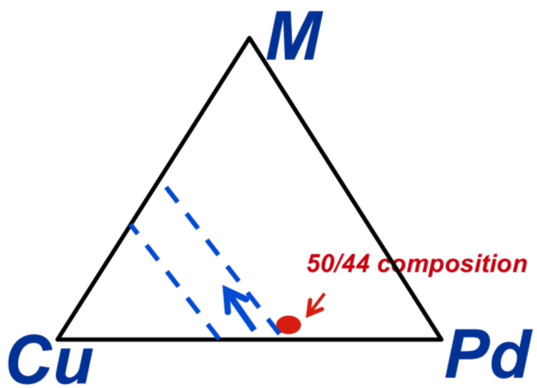
- Replace Pd with M at "BCC boundaries"
- Measure BCC region broadening w/HT XRD
- Evaluate for corrosion resistance
- Measure flux (future)
- Characterize for dissociation activity (future)

Robust Metal Membrane Development

(Technical Accomplishments – New Materials Development)



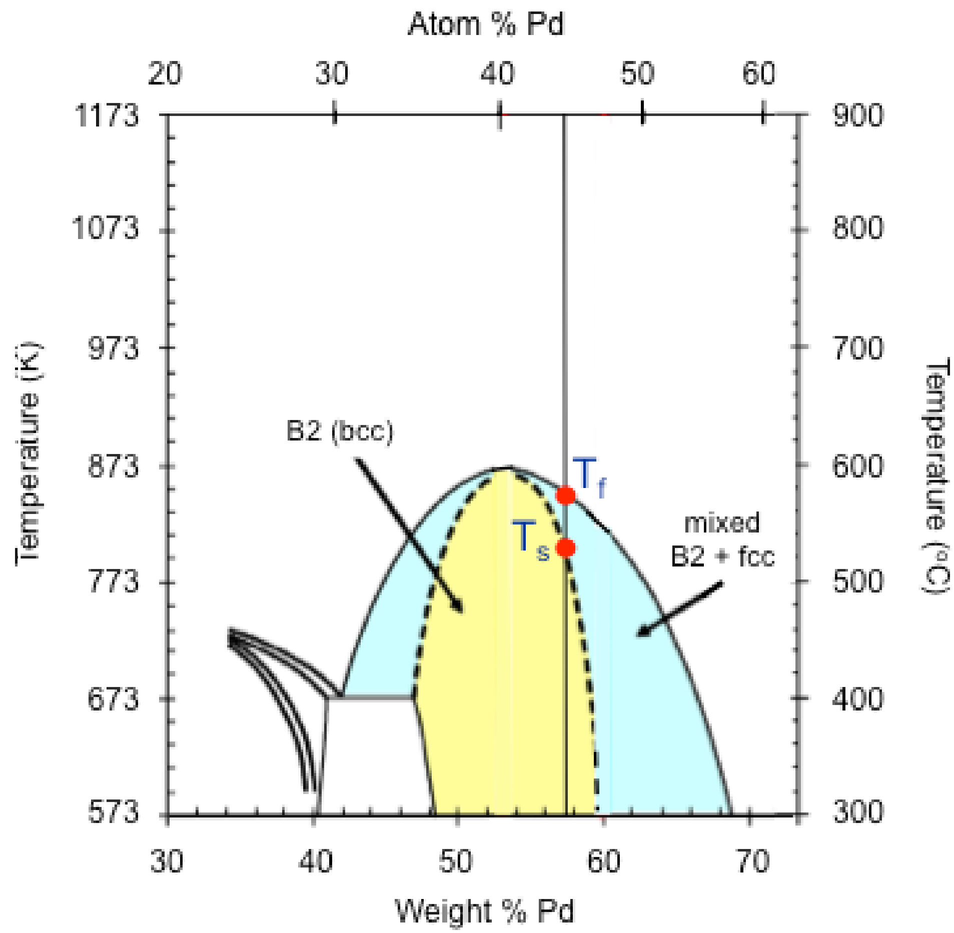
$Cu_{50}Pd_{44}M_6$ alloys that displayed a B2 phase at room temperature (L) were studied at elevated temperatures



Robust Metal Membrane Development

(Technical Accomplishments – New Materials Development)

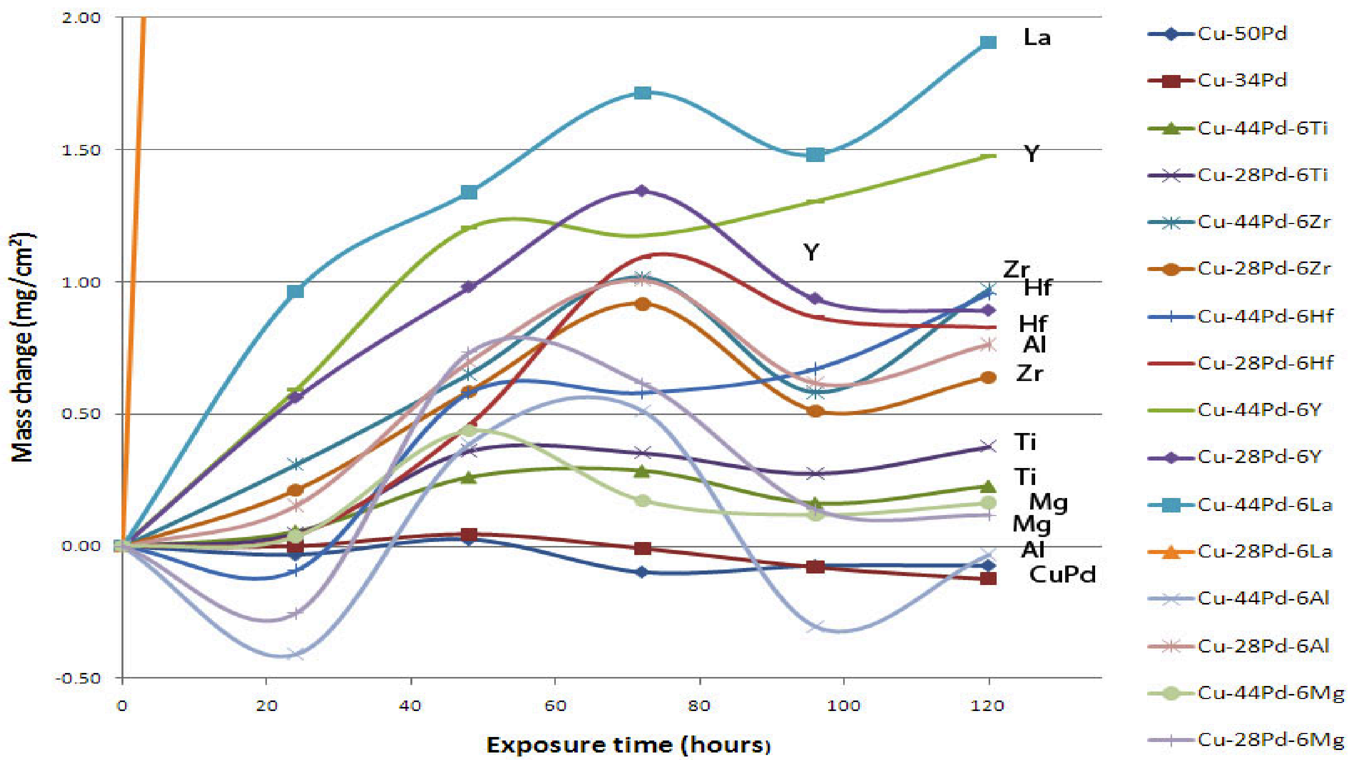
Alloy	T_s (C)	T_f (C)
$Cu_{56}Pd_{44}$	~530	~580
Cu-Pd-Mg	~640	>860
Cu-Pd-Y	575-600	675-700
Cu-Pd-Al	650-675	825-850
Cu-Pd-Ti	<400	775-800
Cu-Pd-La	<400	625-650



Addition of third component (M) expands range of B2 stability

Robust Metal Membrane Development

(Technical Accomplishments – New Materials Development)

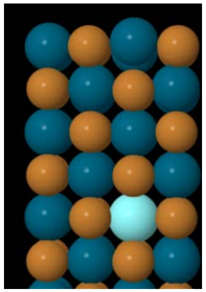


- **Temperature = 500°C**
- **Process gas composition**
  - 50%H_2, 30%CO_2, 1%CO, 19%H_2O, no H_2S
  - H_2S will be added in future trials

Except for La, no significant oxidation was observed

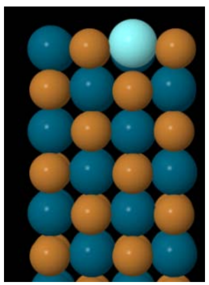
Robust Metal Membrane Development

(Technical Accomplishments – New Materials Development)



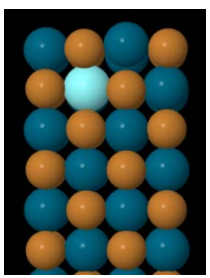
Y in Pd bulk position — DFT → $E(Y, bulk)$

Computational study of surface segregation of Y on CuPd (011) alloy



Y in Pd surface position — DFT → $E(Y, surf)$

$$E_{segr}^{surf} = E(Y, surf) - E(Y, bulk)$$



Y in Pd sub-surface position — DFT → $E(Y, sub-surf)$

$$E_{segr}^{sub-surf} = E(Y, sub-surf) - E(Y, bulk)$$

$$E_{segr}^{surf} = -0.23\ eV \ > \ E_{segr}^{sub-surf} = -0.33\ eV$$

→ *Y atoms migrate to the sub-surface*

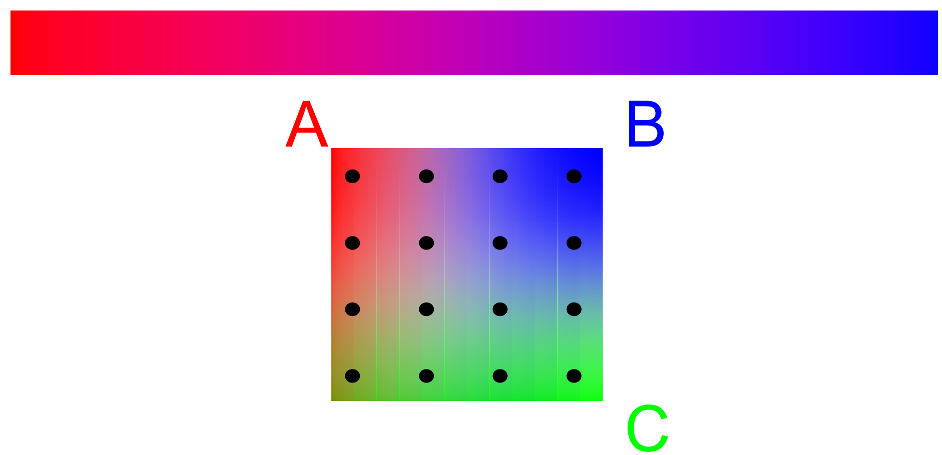
Robust Metal Membrane Development

(Technical Accomplishments – High Throughput Methods Development)

- Screening all possible compositions is prohibitive
  - Prepare Composition Spread Alloy Films (CSAFs) with all possible compositions on a single substrate

A_xB_{1-x}

$A_xB_yC_{1-x-y}$

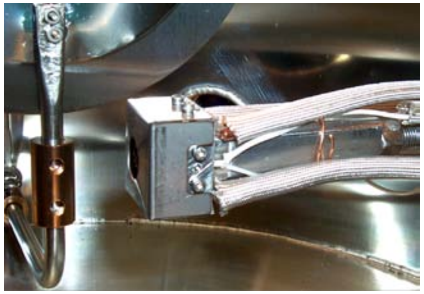


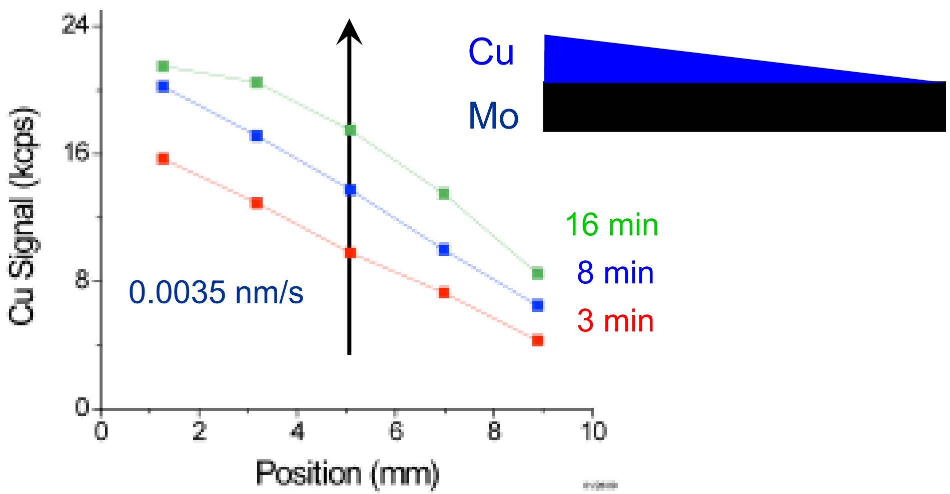
- Scientific/technical challenges
  - Tools for preparation and characterization of CSAFs are not commercially available and must be developed internally.

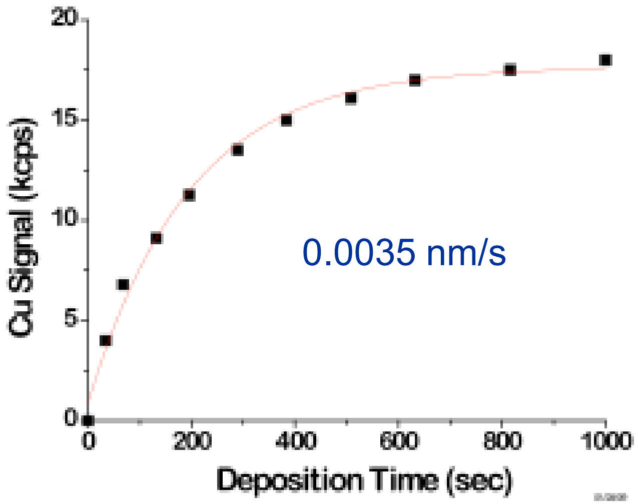
Robust Metal Membrane Development

(Technical Accomplishments – High Throughput Methods Development)

- Physical vapor deposition by evaporation.
- Flux distribution across surface determined by precise placement of filaments.

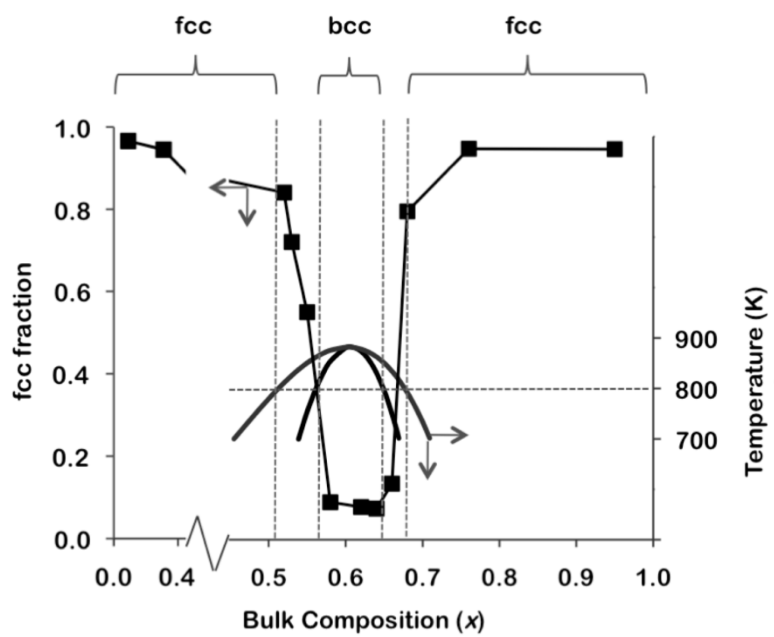


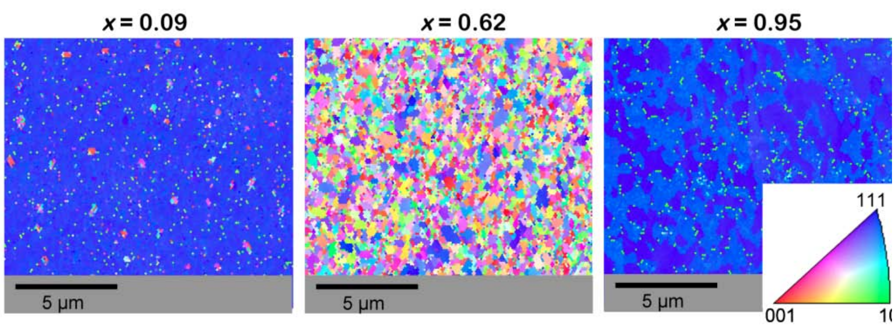




Robust Metal Membrane Development

(Technical Accomplishments – High Throughput Methods Development)



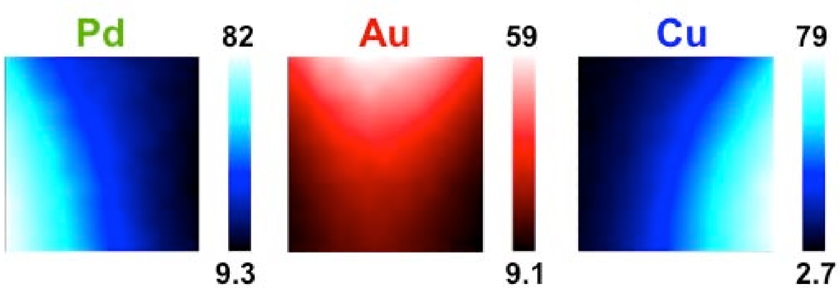


- Prepare 100 nm-thick Pd_xCu_{1-x} CSAF on Mo substrate
- Anneal at 800 K, then quench
- Characterize structure by Electron Backscatter Diffraction
- Phase diagram matches those reported in the literature
- Exciting capability for screening new membrane alloys and their responses to contaminants!

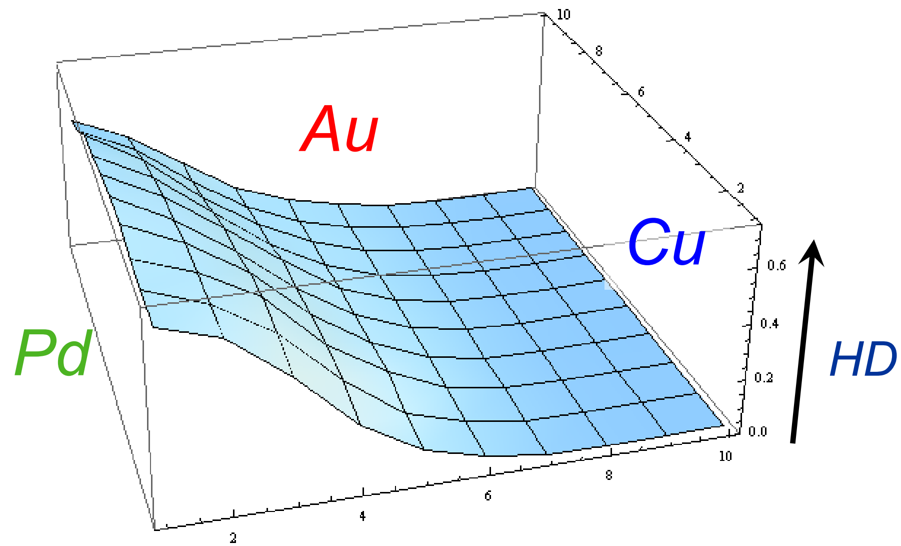
Robust Metal Membrane Development

(Technical Accomplishments – High Throughput Methods Development)

- PdCuAu CSAF
- H_2-D_2 exchange at ~130 ^{o}C
- XPS used to analyze the composition of CSAF
- Au and Cu suppress HD exchange.



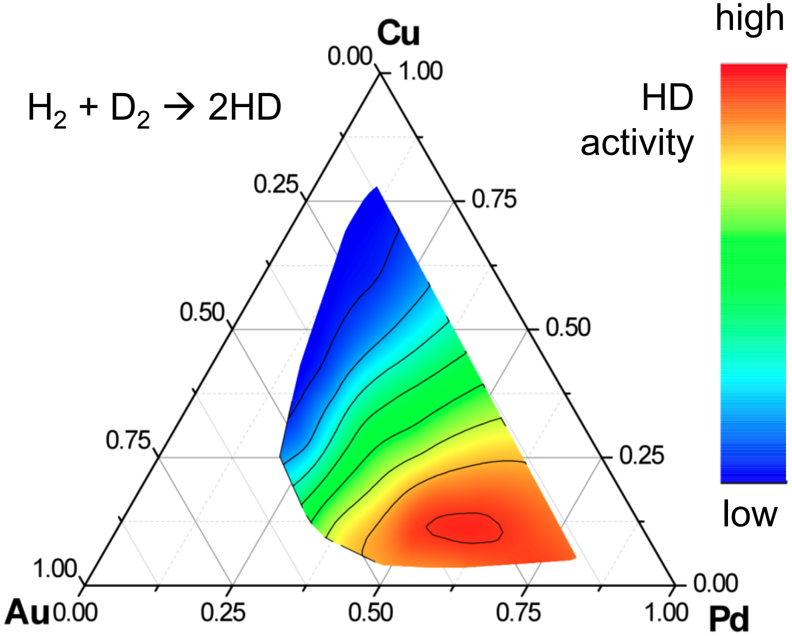
$Pd_{9.3}^{82}Cu_{2.7}^{79}Au_{9.1}^{59}$



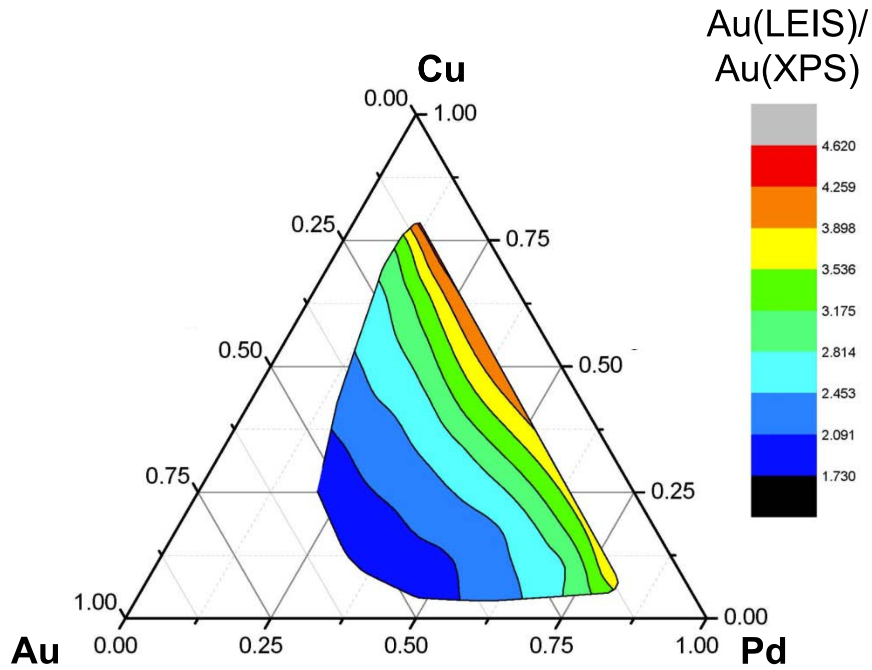
Rapid characterization of H_2 dissociation kinetics over broad composition space of relevance to the membrane application

Robust Metal Membrane Development

(Technical Accomplishments – High Throughput Methods Development)



H_2-D_2 exchange activity (from previous slide)



Characterization of surface segregation

Robust Metal Membrane Development

(Proposed future work)

- Computational evaluation of PdCuX alloys' surface compositions and interactions with H_2 and important contaminant molecules
- Fabrication of PdCuX alloys for experimental characterization of
  - Corrosion resistance (in process)
  - H_2 permeance (according to protocol, just started)
  - Coupon exposure tests at NCCC (in process)
- Application of HT methods to measure PdCuX alloy properties across complex composition space
  - H_2 dissociation activity in a contaminant environment
  - Phase stability in a contaminant environment
- Development of HT permeation reactor (started)
- Fabrication and demonstration of membrane systems

Summary

- Diverse, cross-functional team…
  - Materials scientists, surface scientist, engineers students
  - NETL, CMU, Pitt, Virginia Tech

- …with a wide range of capabilities
  - Computational chemistry
  - Alloy fabrication
  - Materials characterization
  - Surface analysis
  - Membrane screening
  - Membrane performance testing

- Development of design basis for robust metal membrane
  - Complete, fundamental understanding of PdCu
    - Identification of dual S-deactivation mechanisms
    - Characterization of corrosion products' activity, permeability
    - Measurement of hydrogen dissociation activity across alloys, and in presence of H2S
  - Extension to PdCuM
    - Computational evaluation of stability, potential for interactions for S
    - Preparation, corrosion characterization of alloys designed to expand "high permeabiity window"

- New capability in high-throughput materials and surface science
  - Rapid screening/understanding of PdCuM properties across composition space