Development of Robust Hydrogen Separation Membranes

National Energy Technology Laboratory-Regional University Alliance
NETL-RUA

PD008

2011 DOE Hydrogen Program Review

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H_2 Separation Membrane Team Members

(Collaborators)

U.S. DOE - NETL

Dr. Bryan Morreale, PIT (ChemE)

Dr. Bret Howard, PIT (InorgChem)

Dr. David Alman, ALB (MatSci)

Dr Omer Dogan, ALB (MatSci)

Dr Michael Gao, ALB (MatSci)

NETL Research Faculty

Dr. Andrew Gellman, CMU (ChemE)

Dr. James Miller, CMU (ChemE)

Dr. Petro Kondratyuk, CMU (Chem)

Dr Michael Widom, CMU (Phys)

Dr. Brian Gleeson, Pitt (MatSci)

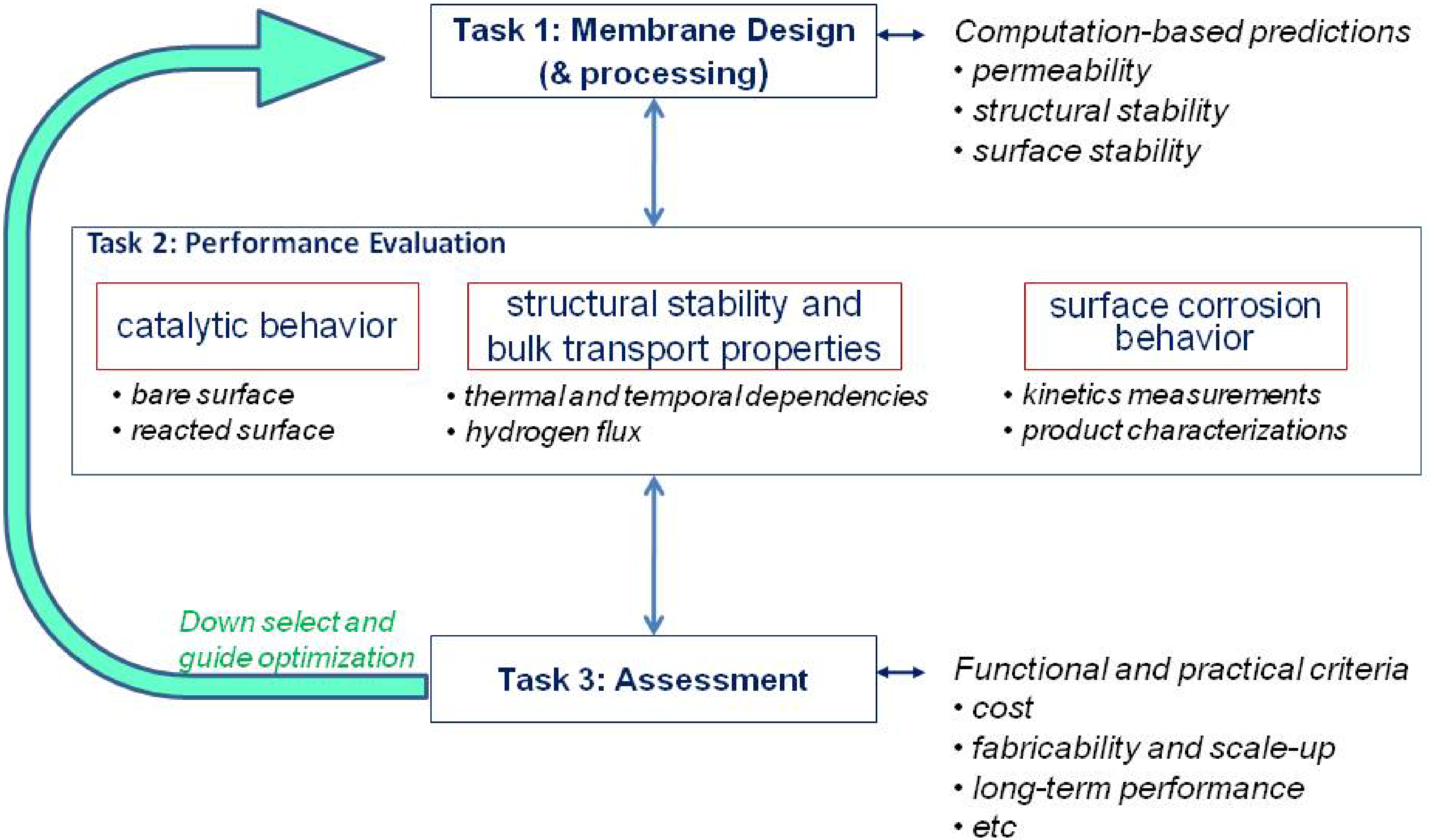
Dr. Ted Oyama, VT (ChemE)

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

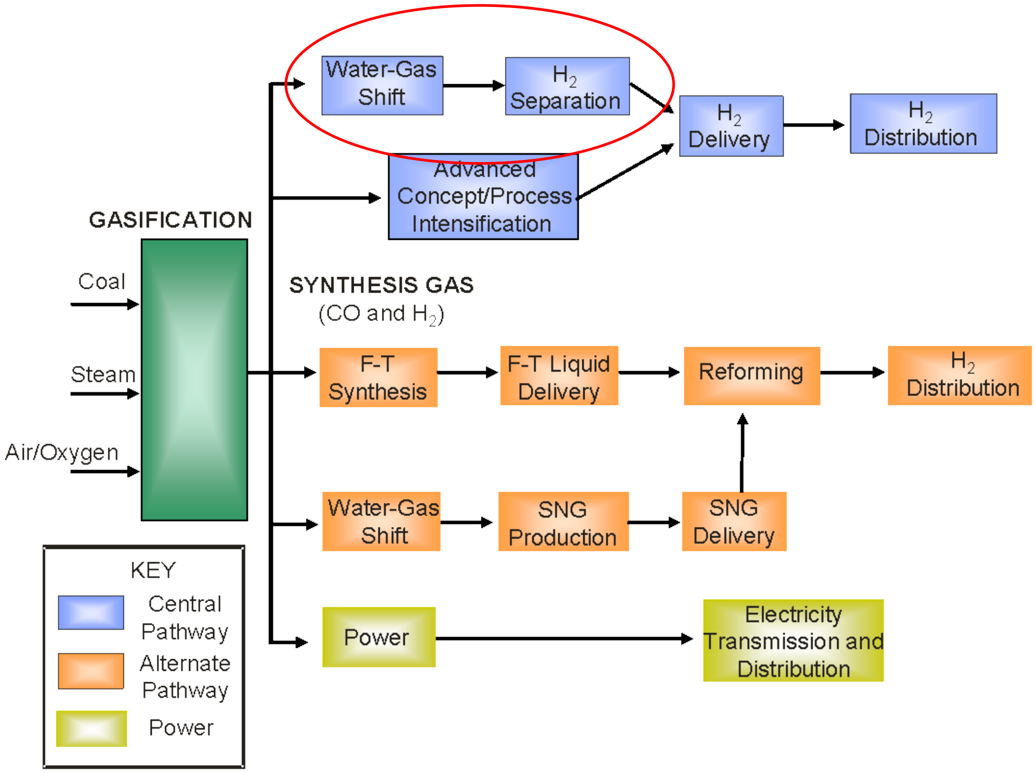
- Carnegie Mellon University
- University of Pittsburgh
- Virginia Tech
- NCCC, Wilsonville

[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

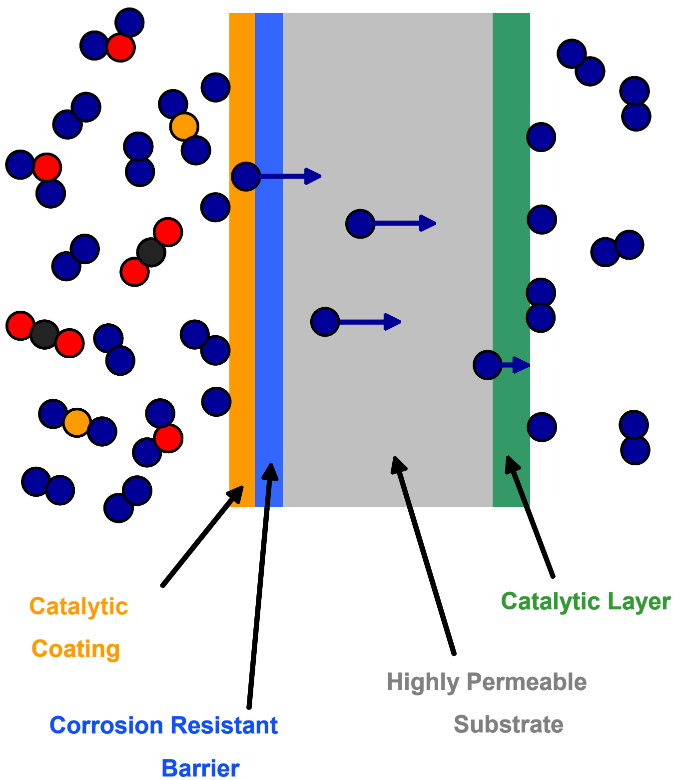
Robust Metal Membrane Development

(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

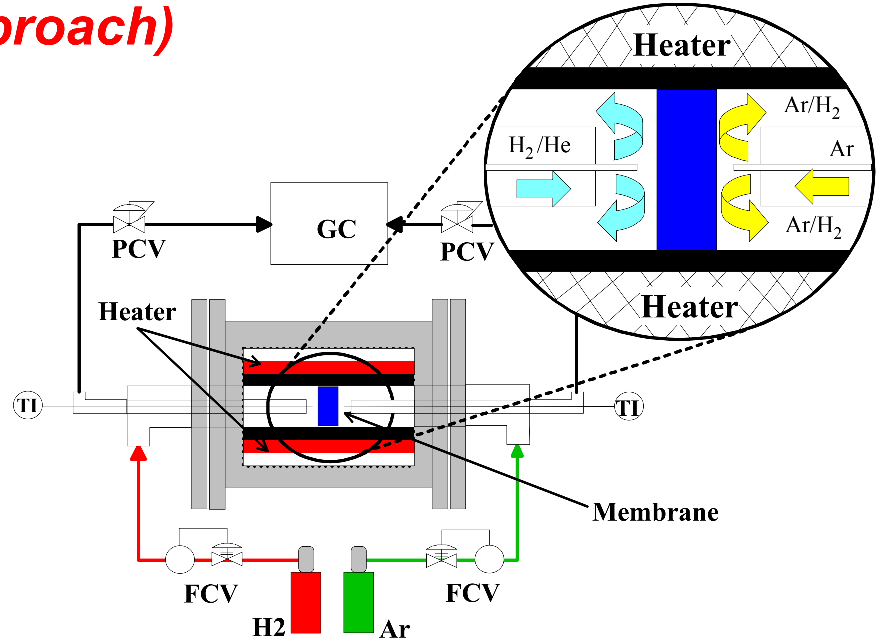
Multi-layer Membrane Concept



Facilities & Capabilities

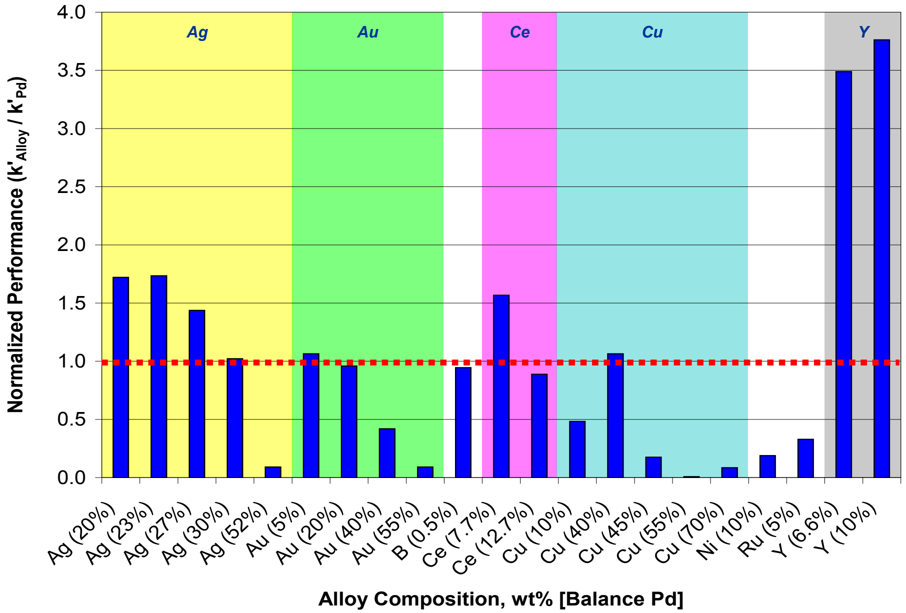
(Approach)

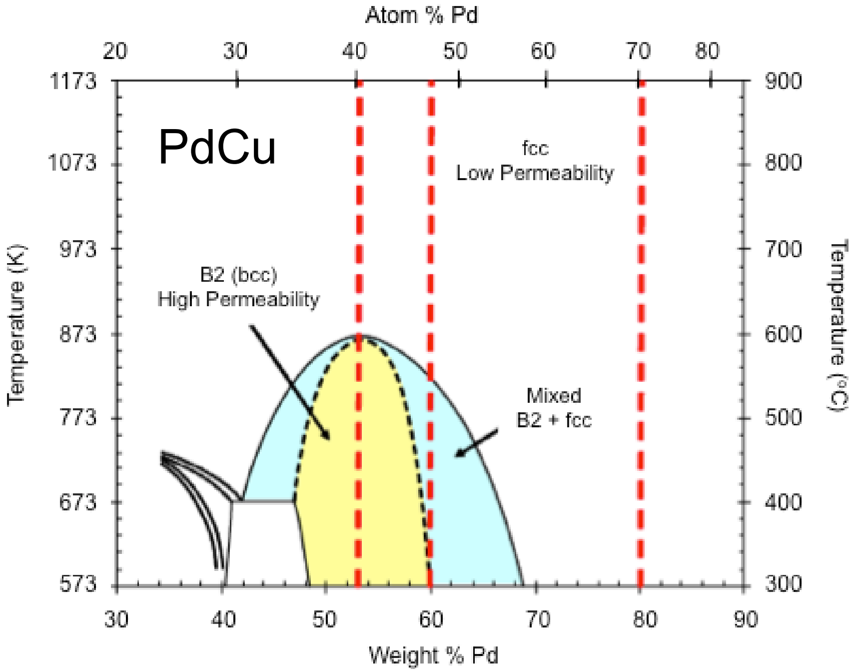
- **3 Membrane Test Rigs**
  - Continuous, bench-scale units
  - T to 1000°C, P to 1000 psi
- **2 Laboratory Membrane Screening Rigs**
  - Continuous, lab-scale units
  - T to 1000°C, P to 30 psi
- **Materials Lab**
  - Deposition chamber(s)
  - High-T box and annealing ovens
  - XRD w/hot-stage
  - 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,

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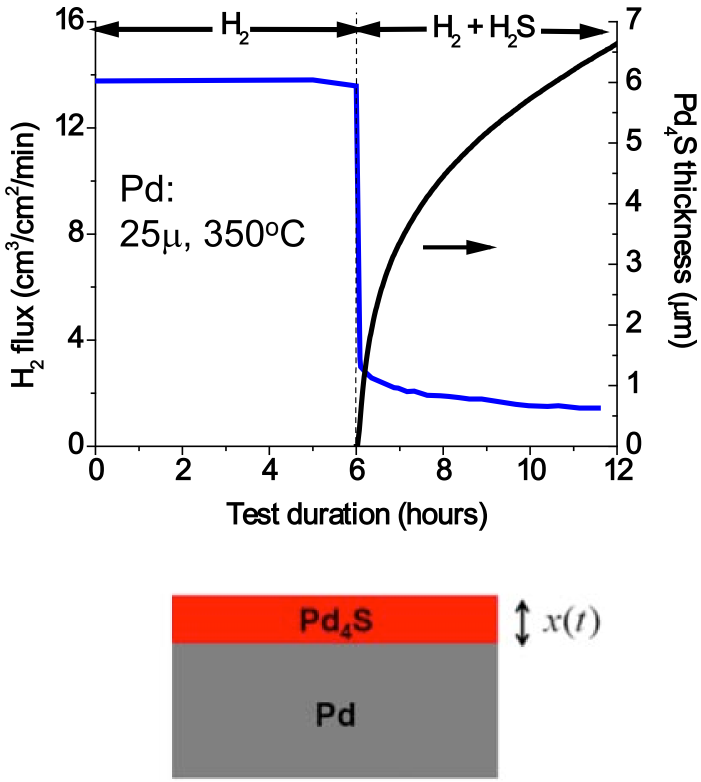
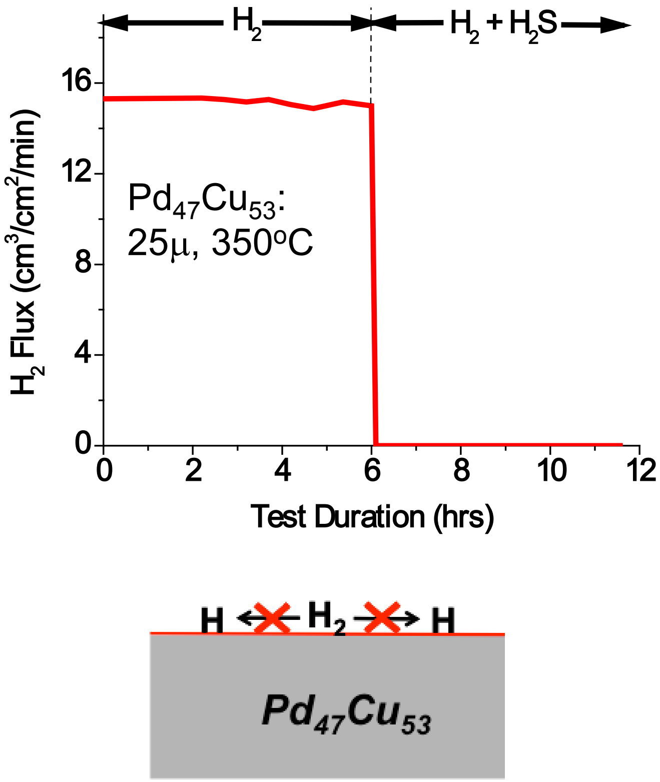
Robust Metal Membrane Development

(Background: previous results)

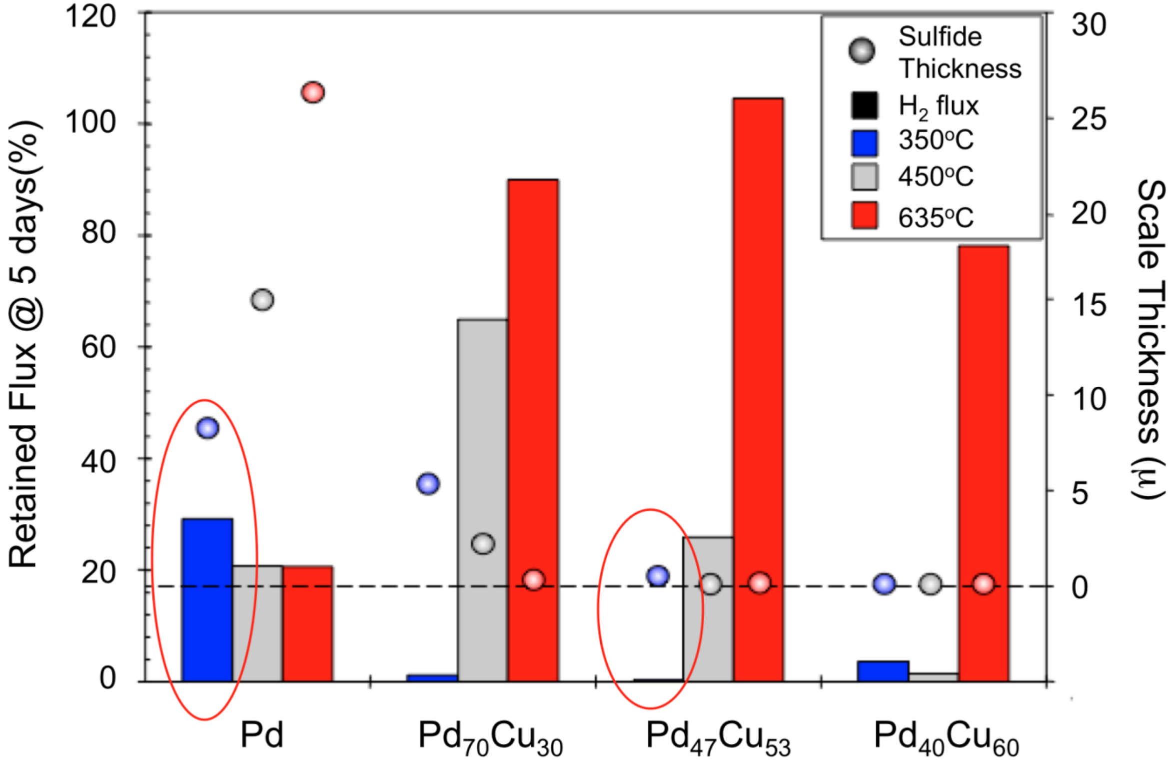




Two mechanisms of performance deterioration caused by exposure to H_2S: (L) growth of low permeabilty sulfide scale on Pd and (R) catalytic poisoning of alloy surface.

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

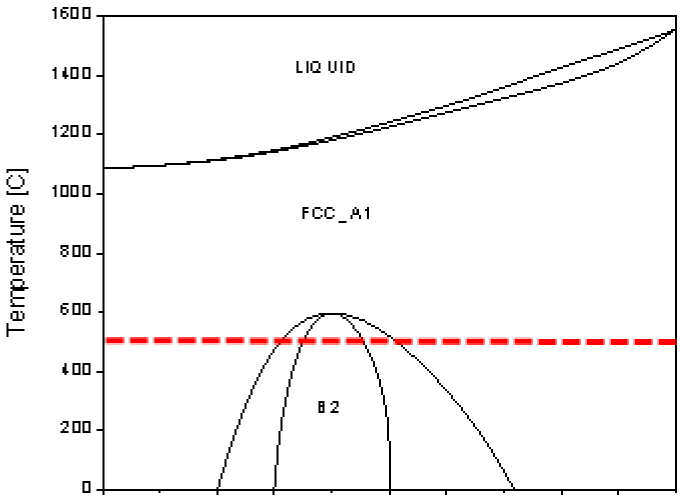
Current activities:

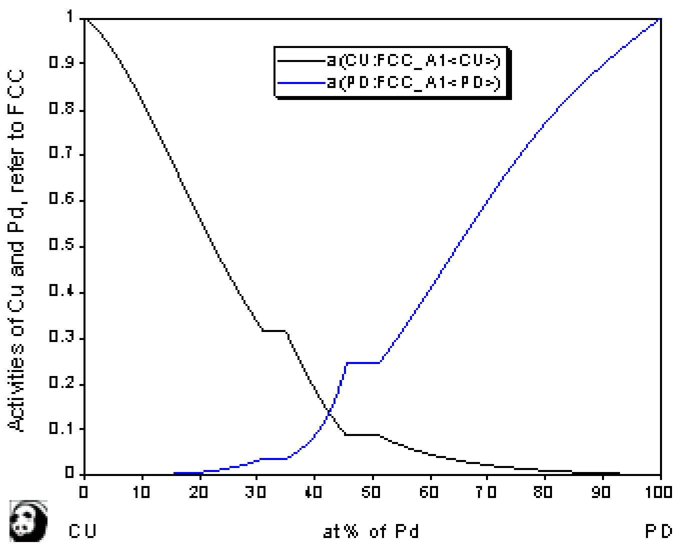
- basic understanding of PdCu
- expansion to ternary alloys

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

Material Thermodynamics

(Technical Accomplishments – Stability & Scale Prediction)

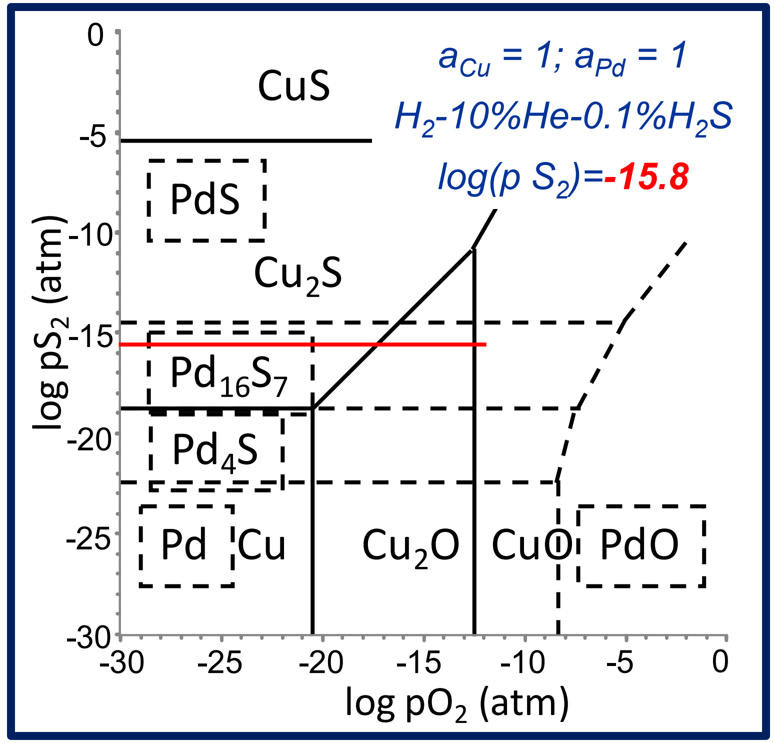




$$aM + bH_2S \leftrightarrow M_aS_b + bH_2$$

Predicted Stability

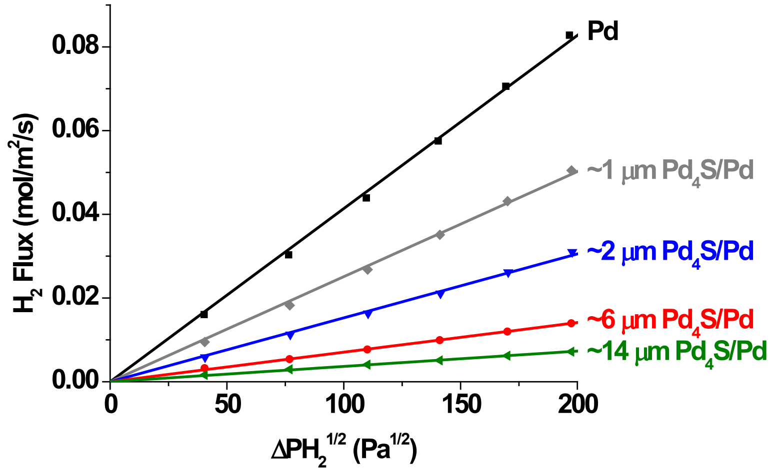
gas	gas	gas
$Pd_{16}S_7$	Cu_2S	$Pd_{16}S_7$
Pd_4S		Pd_4S
Pd	Cu	$Pd_{70}Cu_{30}$



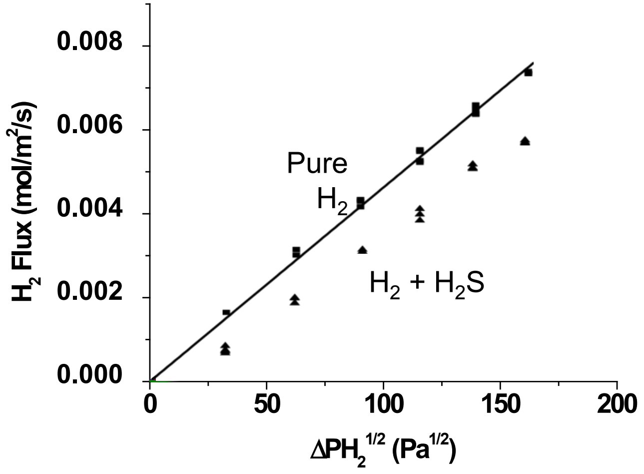
Robust Metal Membrane Development

(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

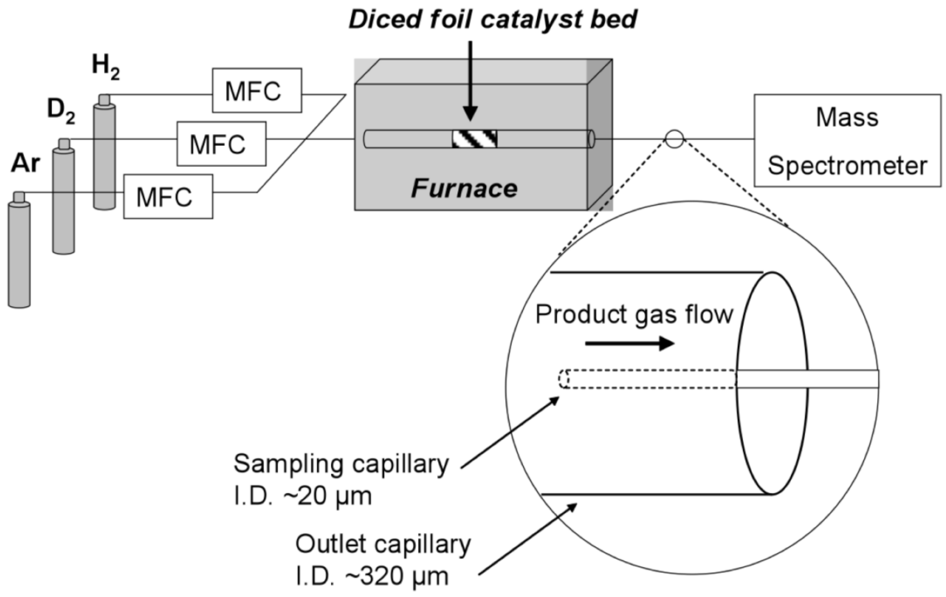


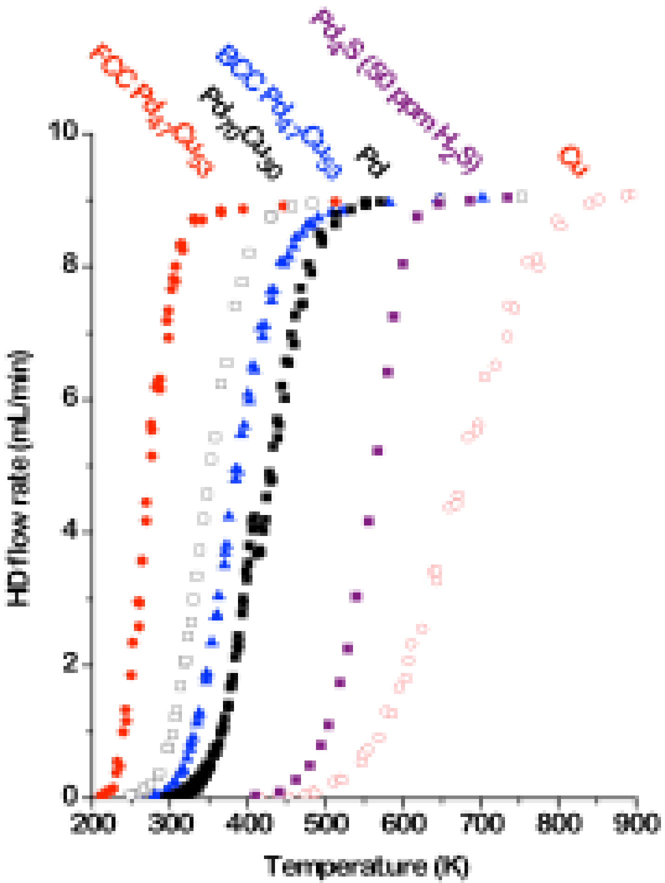
- **H_2S causes incremental flux decline**
  - Likely mechanism is site blocking (link to H-D exchange work)



Robust Metal Membrane Development

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



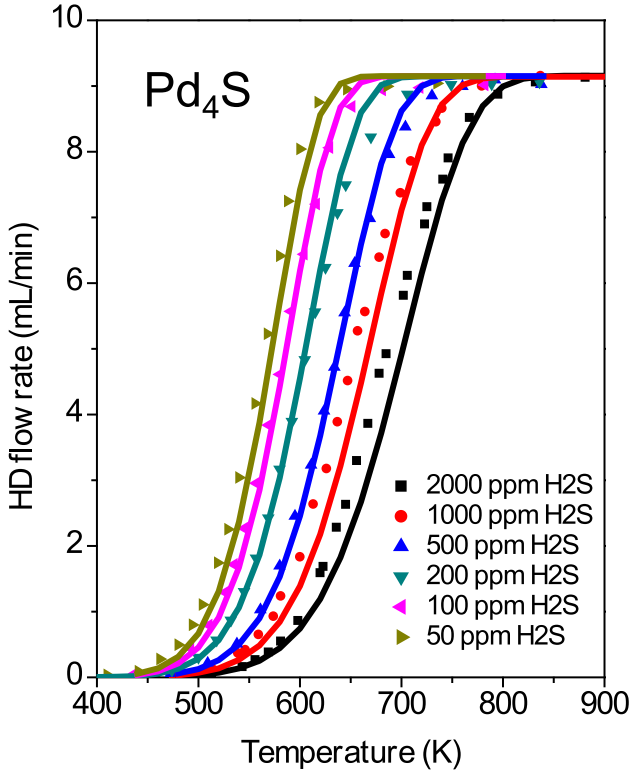


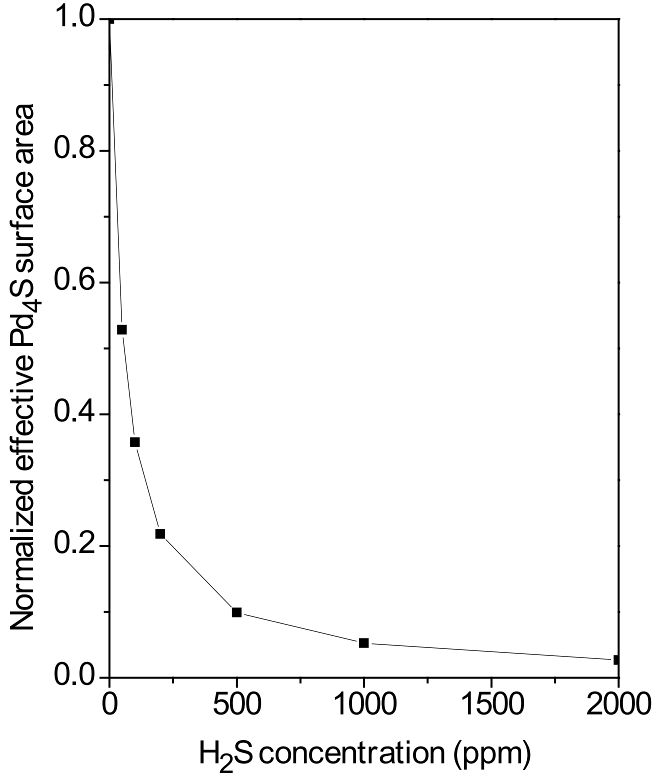
$H_2 + D_2 \longleftrightarrow 2HD$

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)



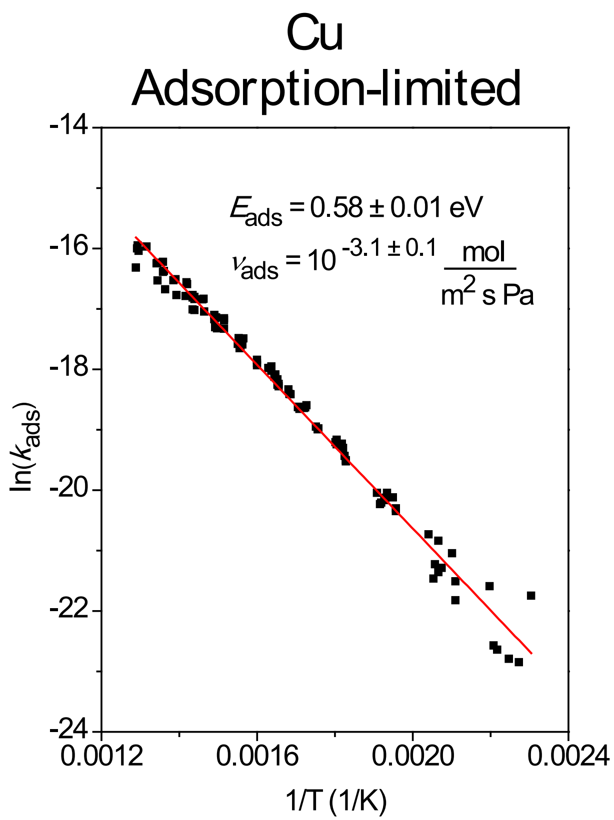


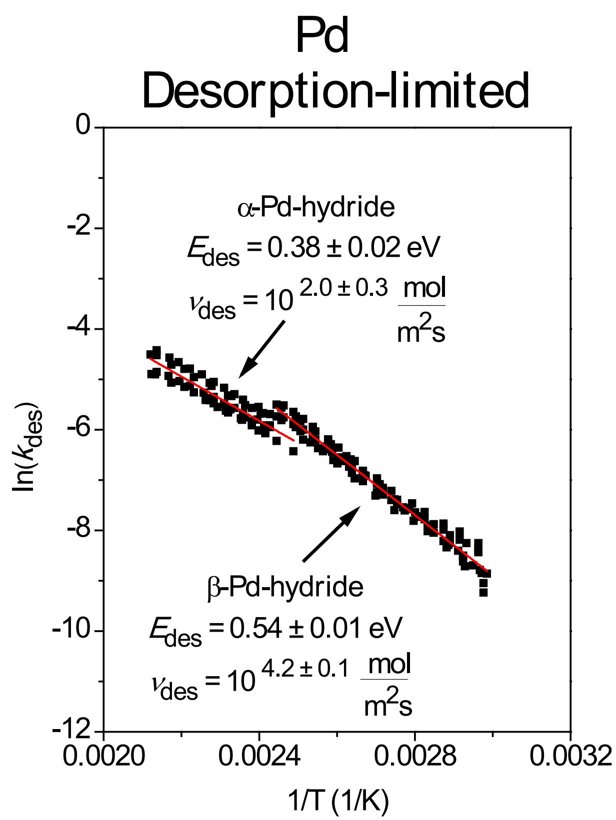
$H_2 + D_2 \longleftrightarrow 2HD$

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)



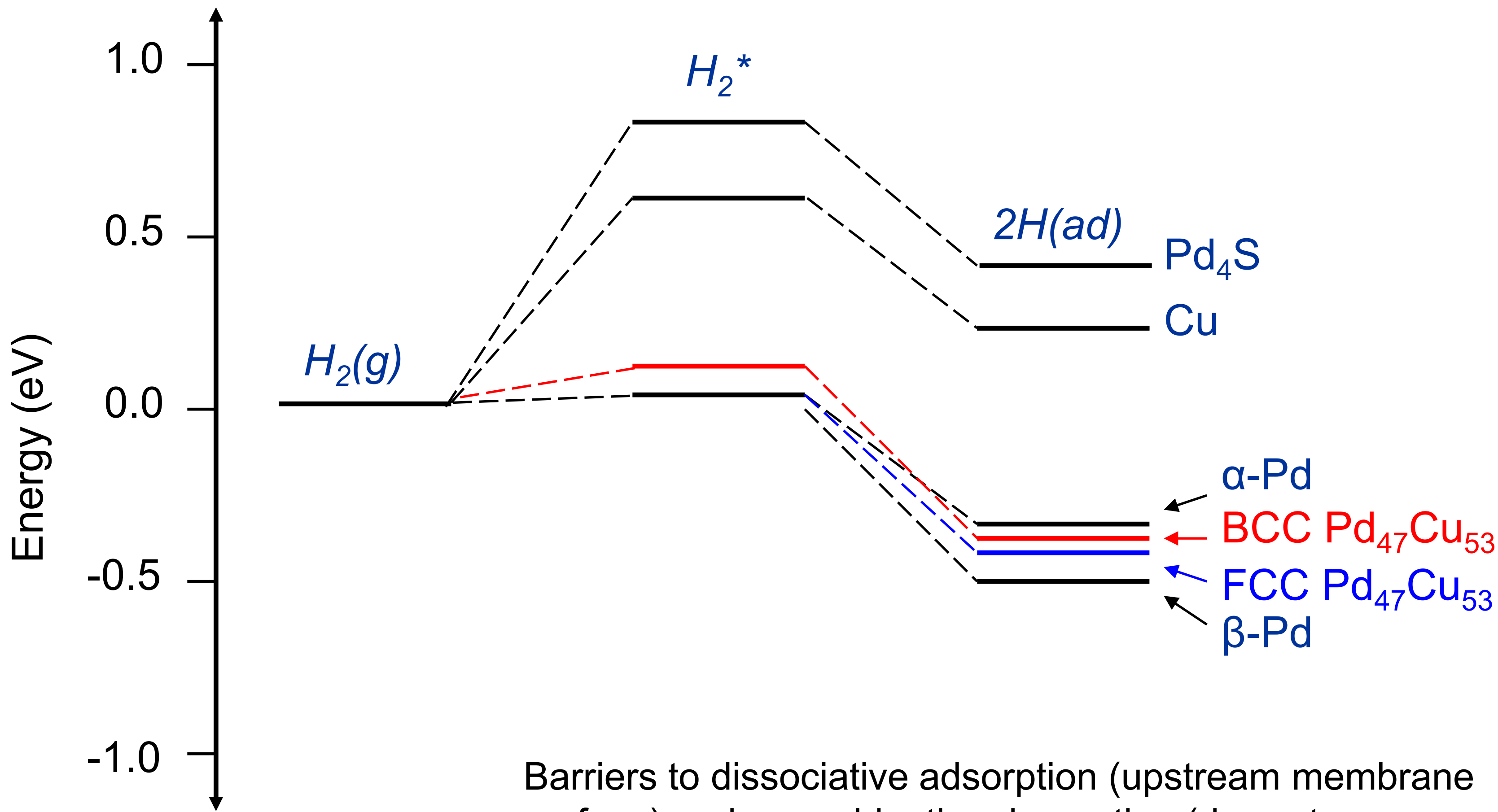


$H_2 + D_2 \longleftrightarrow 2HD$

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

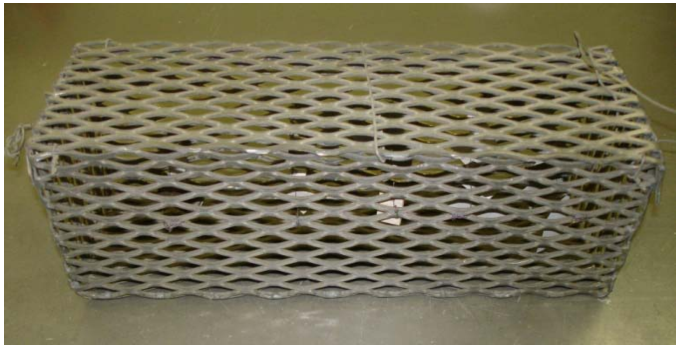
Robust Metal Membrane Development

(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

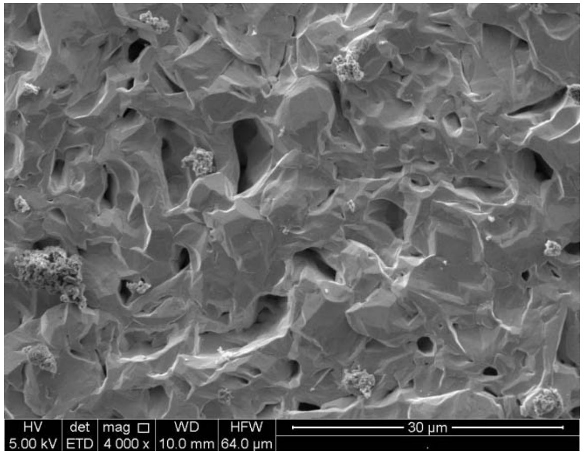
Robust Metal Membrane Development

(Technical Accomplishments – Stability, Scale Growth & Transport)

NCCC Coupon Testing: preliminary results

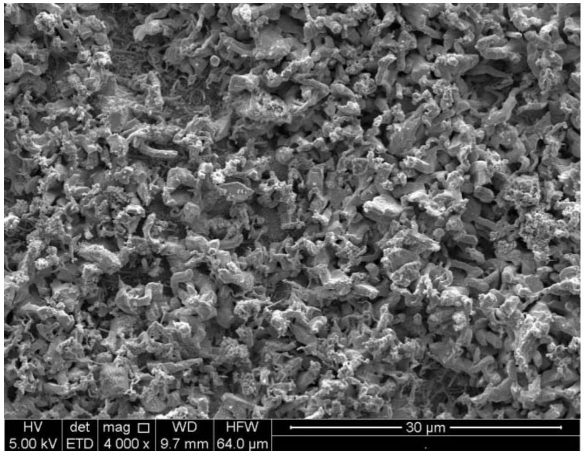
- **B2-structured alloys suffered much less corrosion**
- **Particulates observed to impact surface**
- **Trace component effects appear important**
    - **Arsenic detected in several coupons so far**
- **Surface morphology for some alloys very different than observed in lab tests**

Pd



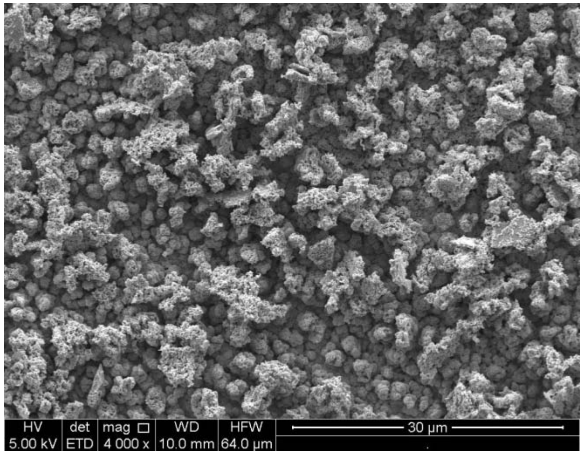
XRD: Pd_4S only phase detected (Pd coupon completely sulfided and fractured into pieces)

80wt%Pd-Cu



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

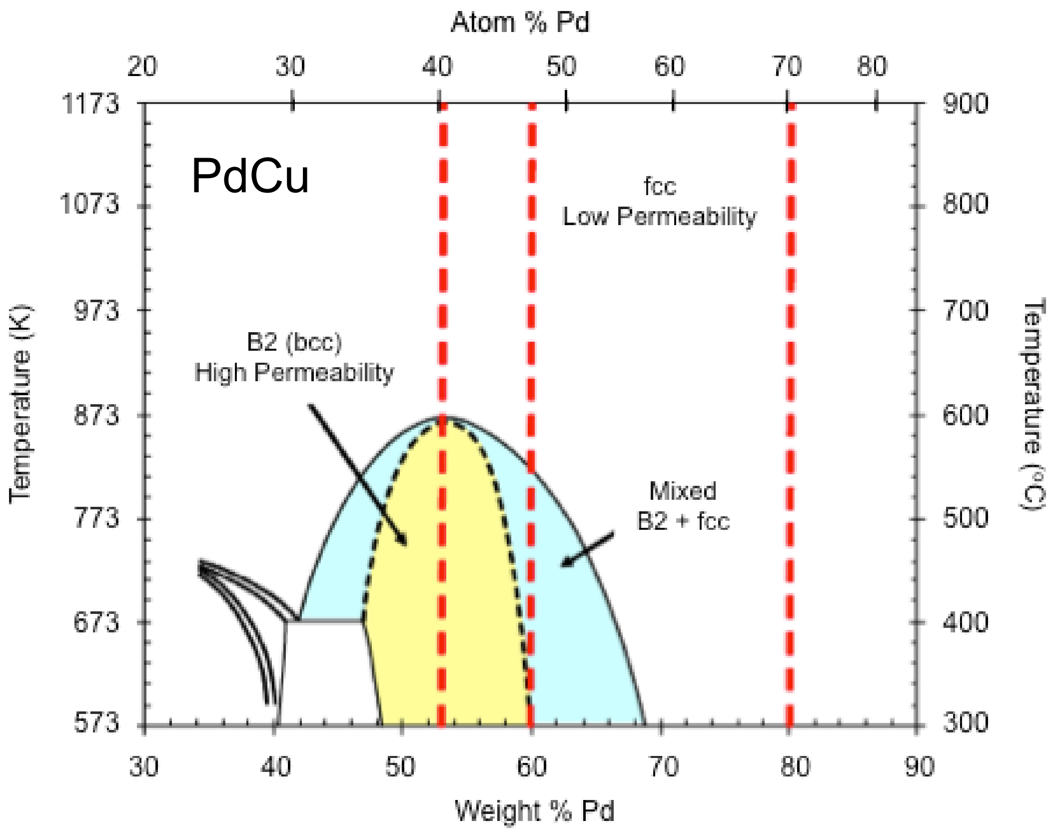
60wt%Pd-Cu



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)

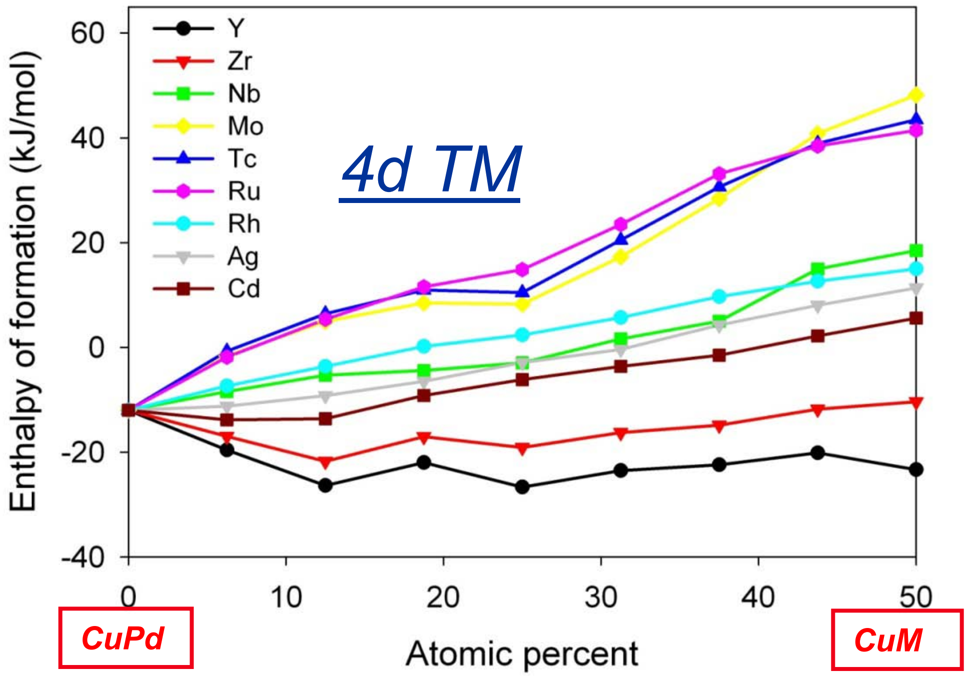


Add a third component to PdCu to:

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

Robust Metal Membrane Development

(Technical Accomplishments – New Materials Development)

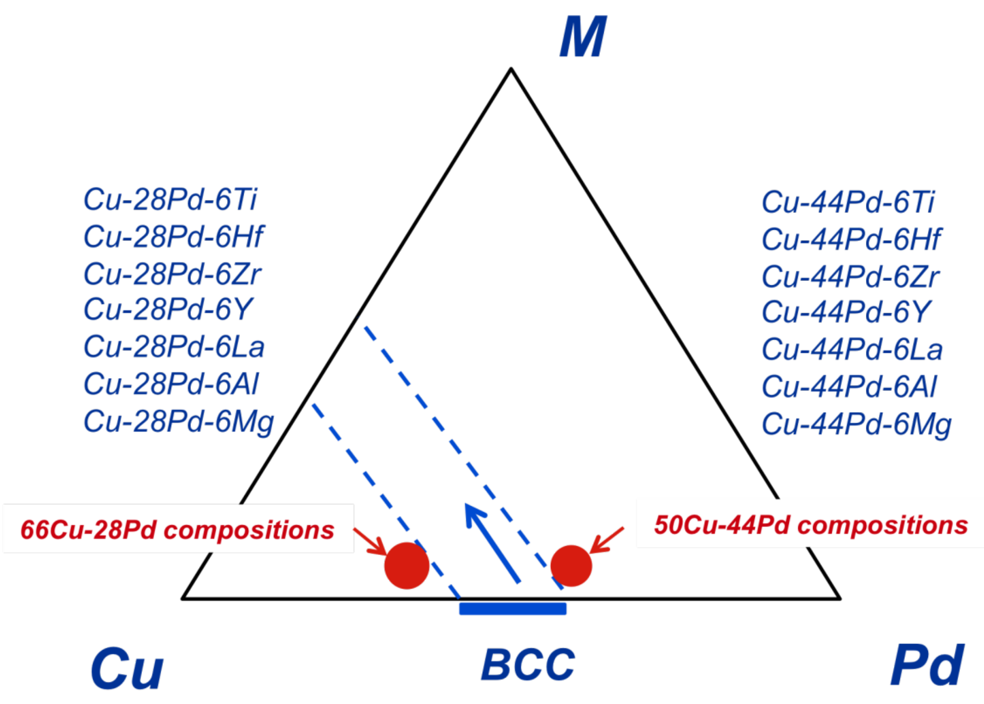


$Cu_{50}Pd_{(50-x)}M_x$

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)

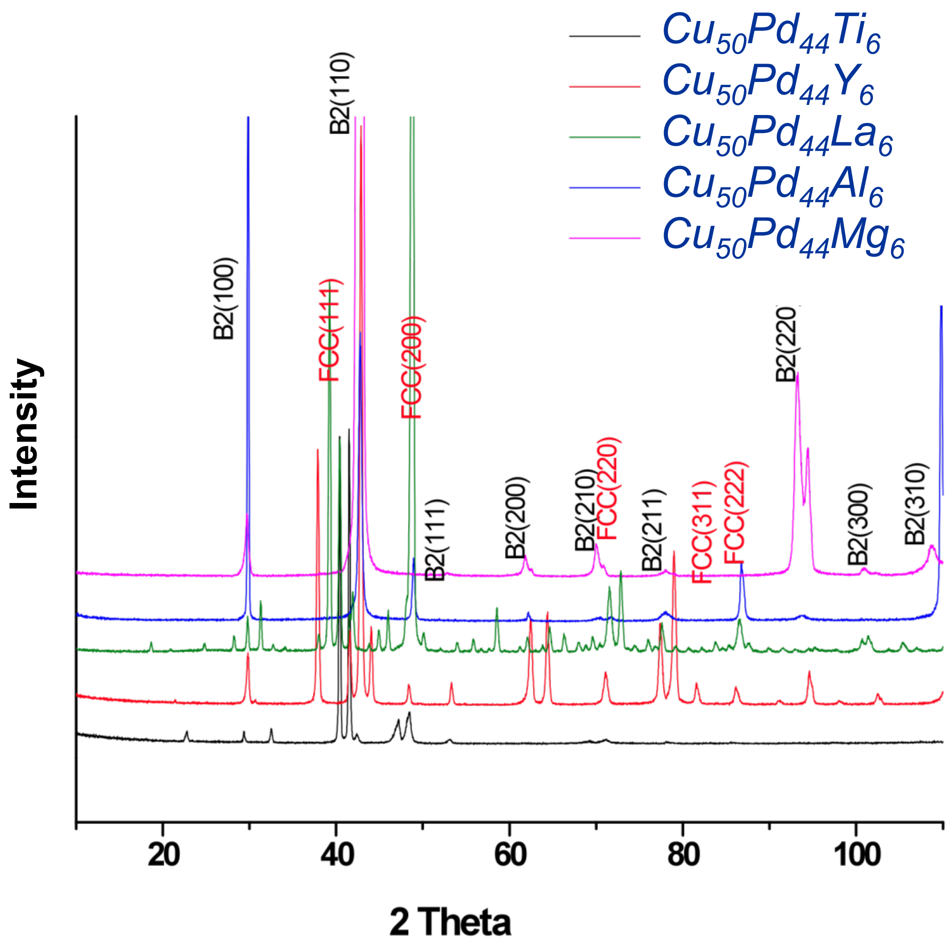


Strategy:

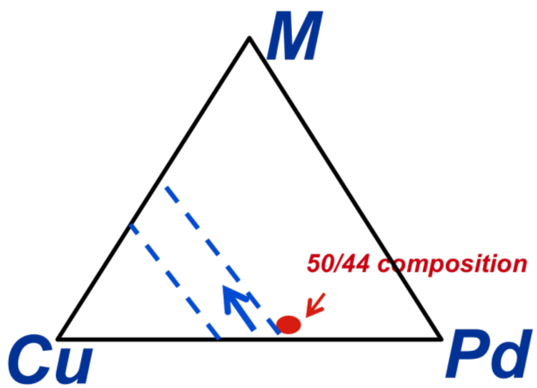
- Replace Pd with M at "BCC boundaries"
- Measure BCC region broadening w/HT XRD
- Evaluate for corrosion resistance
- Measure flux (future)
- Characterize for dissociation activity (future)

Robust Metal Membrane Development

(Technical Accomplishments – New Materials Development)



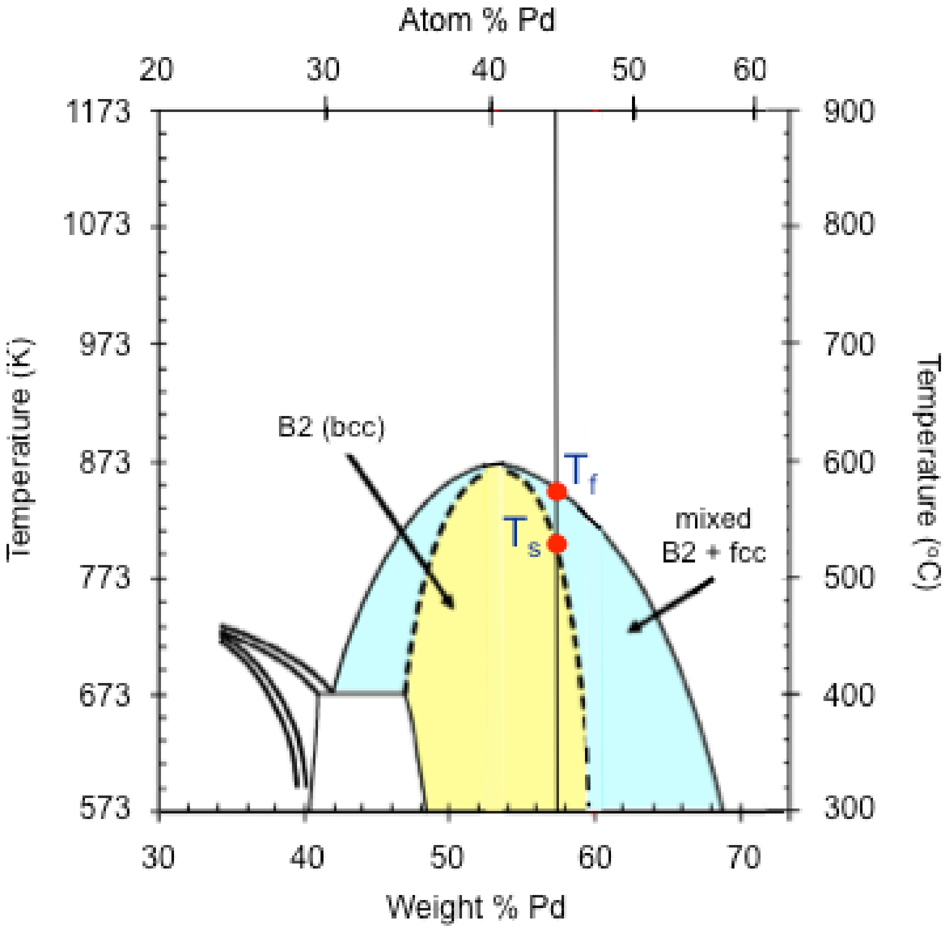
$Cu_{50}Pd_{44}M_6$ alloys that displayed a B2 phase at room temperature (L) were studied at elevated temperatures



Robust Metal Membrane Development

(Technical Accomplishments – New Materials Development)

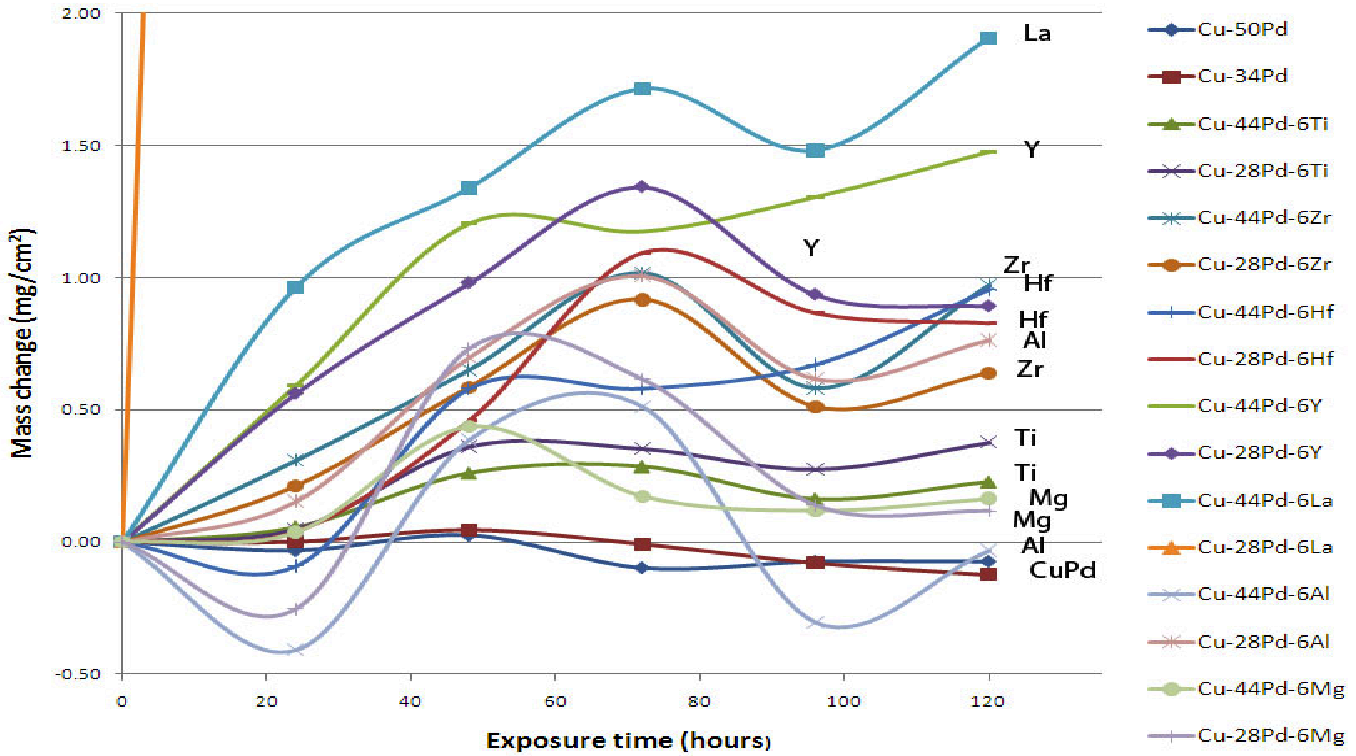
Alloy	T_s (C)	T_f (C)
$Cu_{56}Pd_{44}$	~530	~580
Cu-Pd-Mg	~640	>860
Cu-Pd-Y	575-600	675-700
Cu-Pd-Al	650-675	825-850
Cu-Pd-Ti	<400	775-800
Cu-Pd-La	<400	625-650



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

Robust Metal Membrane Development

(Technical Accomplishments – New Materials Development)



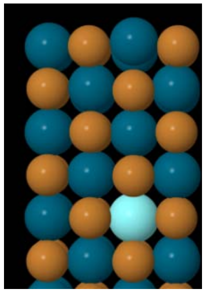
- **Temperature = 500°C**
- **Process gas composition**
  - 50%H_2, 30%CO_2, 1%CO, 19%H_2O, no H_2S
  - H_2S will be added in future trials

Except for La, no significant oxidation was observed

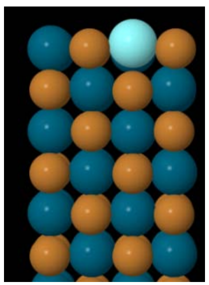
Robust Metal Membrane Development

(Technical Accomplishments – New Materials Development)

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

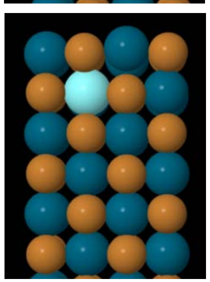


Y in Pd bulk position — *DFT* → $E(Y,bulk)$



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***

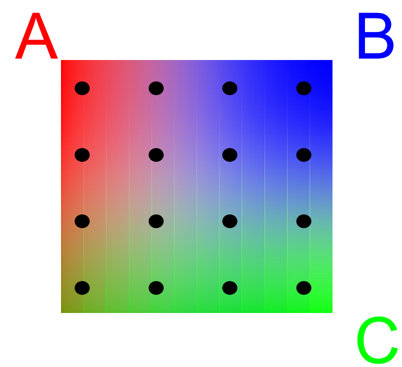
Robust Metal Membrane Development

(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}

$A_xB_yC_{1-x-y}$

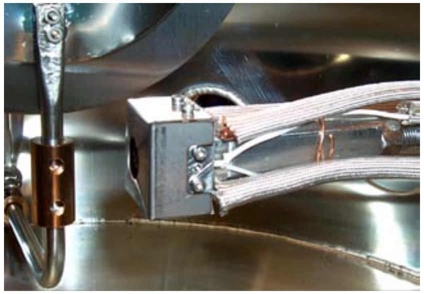


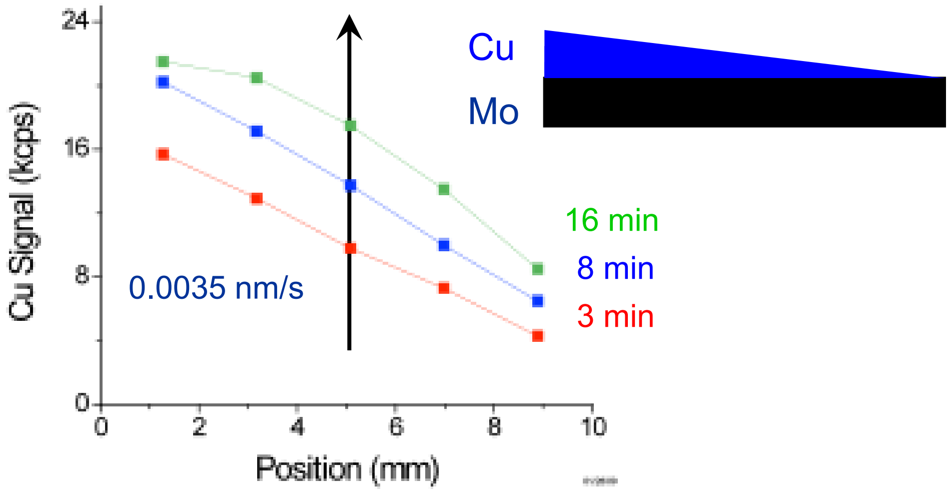
- Scientific/technical challenges
  - Tools for preparation and characterization of CSAFs are not commercially available and must be developed internally.

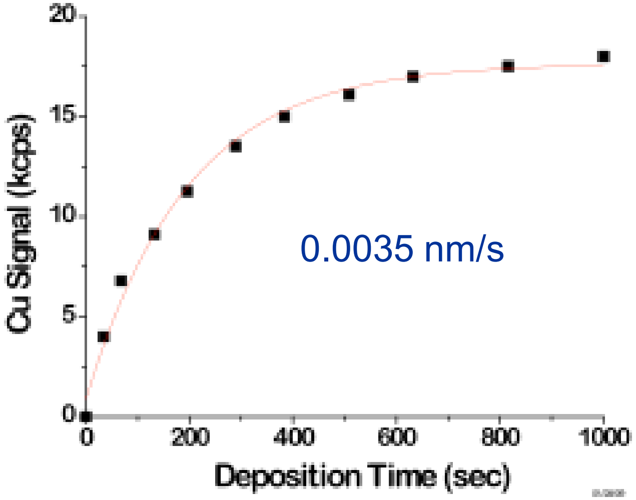
Robust Metal Membrane Development

(Technical Accomplishments – High Throughput Methods Development)

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

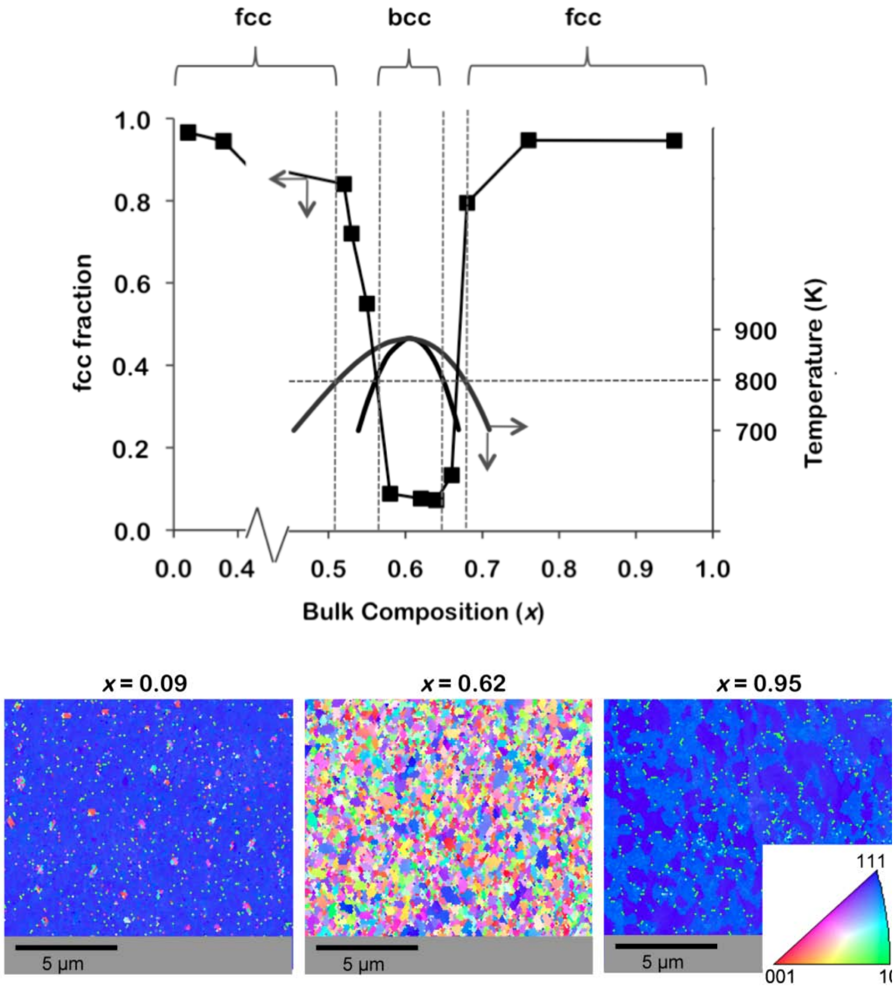






Robust Metal Membrane Development

(Technical Accomplishments – High Throughput Methods Development)

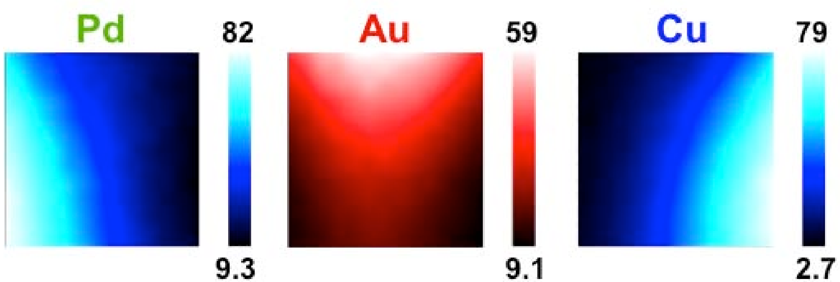


- Prepare 100 nm-thick Pd_xCu_{1-x} CSAF on Mo substrate
- Anneal at 800 K, then quench
- Characterize structure by Electron Backscatter Diffraction
- Phase diagram matches those reported in the literature
- Exciting capability for screening new membrane alloys and their responses to contaminants!

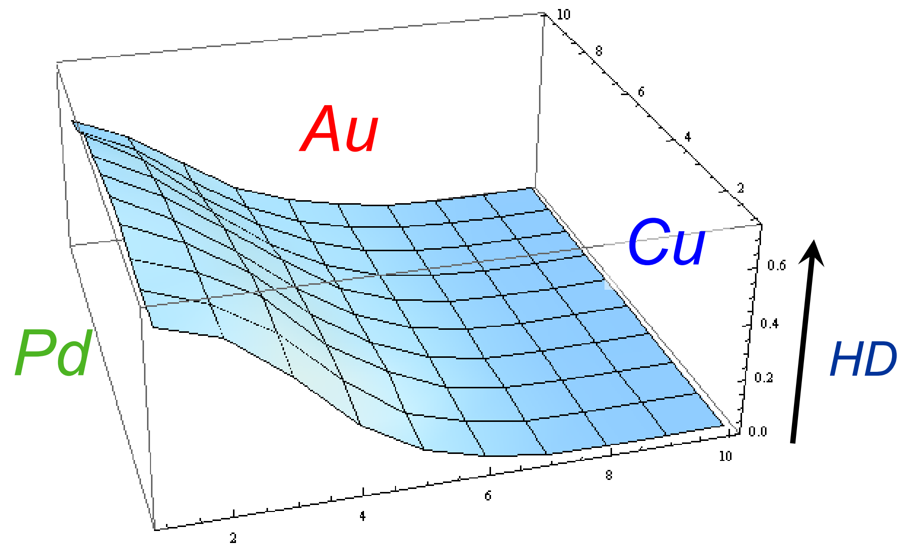
Robust Metal Membrane Development

(Technical Accomplishments – High Throughput Methods Development)

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



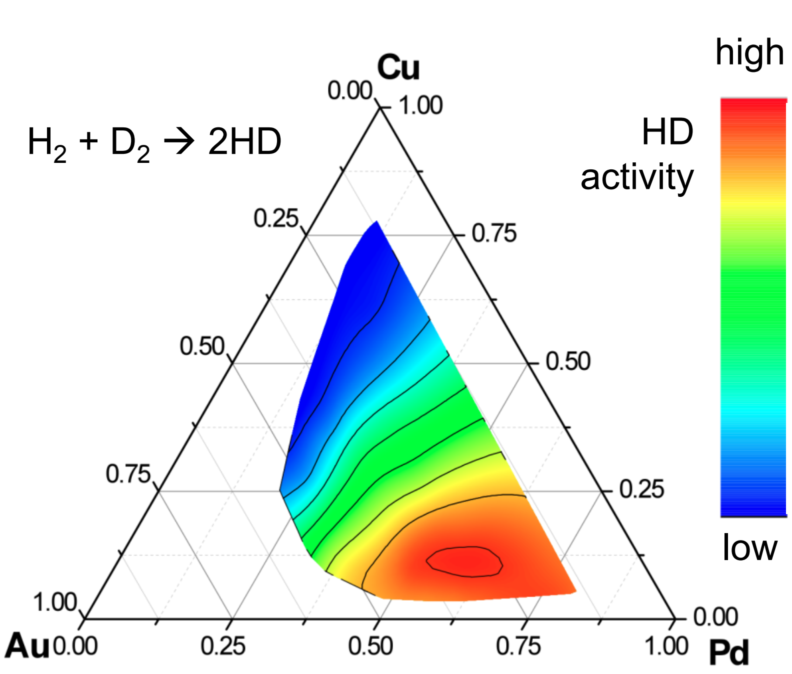
$Pd^{82}_{9.3}Cu^{79}_{2.7}Au^{59}_{9.1}$



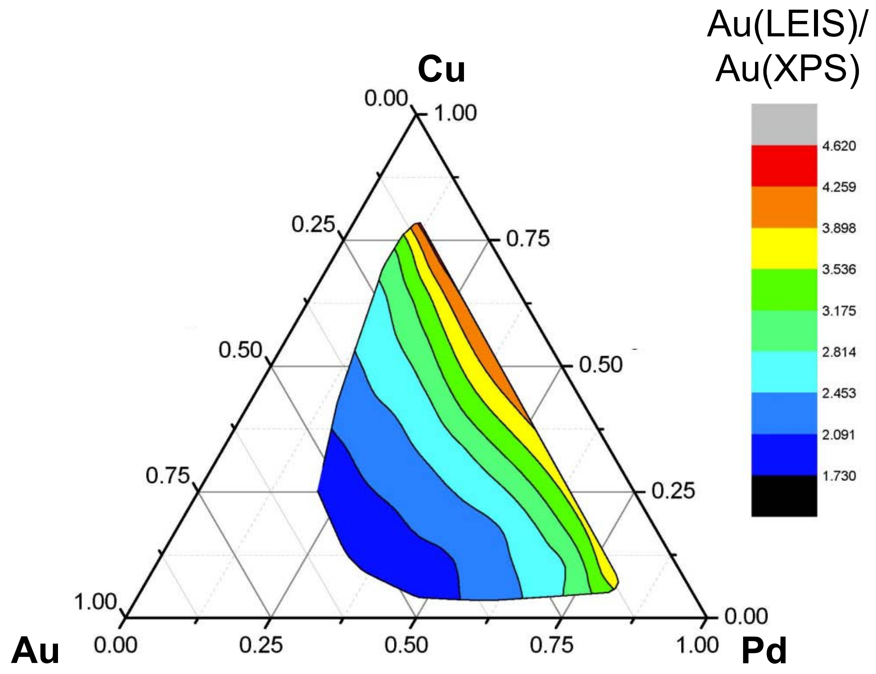
Rapid characterization of H_2 dissociation kinetics over broad composition space of relevance to the membrane application

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