

Advanced Water Gas Shift Membrane Reactor (DE-FC26-05NT42453)

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2) QuesTek Innovations, Evanston, IL

3) Metal Hydride Technologies Inc., Burlington, VT

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Project ID: PD 17

Overview

Timeline

- Start – July 2005
- End – June 2007
- 95% Complete

Budget

- Total Project Funding
 - DOE share - \$849k
 - Contractor share - \$212k
- Funding Received in FY06
 - \$205k
- Funding for FY07
 - \$340k

Barriers

- Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan
 - Section 3.1.4.2.3: Separations and Other Cross-Cutting Hydrogen Production Barriers (DOE Office of Energy Efficiency and Renewable Energy)
 - M. Impurities
- Hydrogen from Coal – Research, Development, and Demonstration Plan
 - Section 5.1.5 Technical Barriers – Central Production Pathway (DOE Office of Fossil Energy)
 - D. Impurity Intolerance/Catalyst Durability
 - I. Poisoning of Catalytic Surfaces
 - Q. Impurities in Hydrogen from Coal

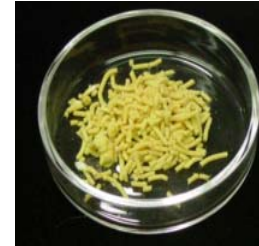
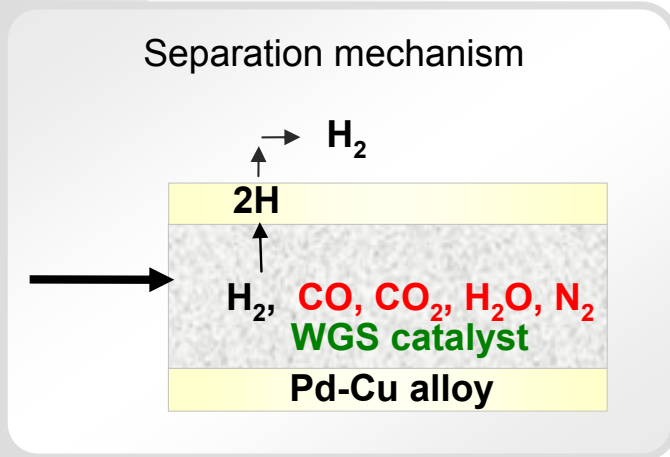
Partners

- QuesTek Innovations LLC
- Metal Hydride Technologies

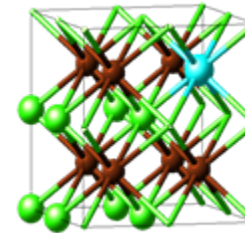
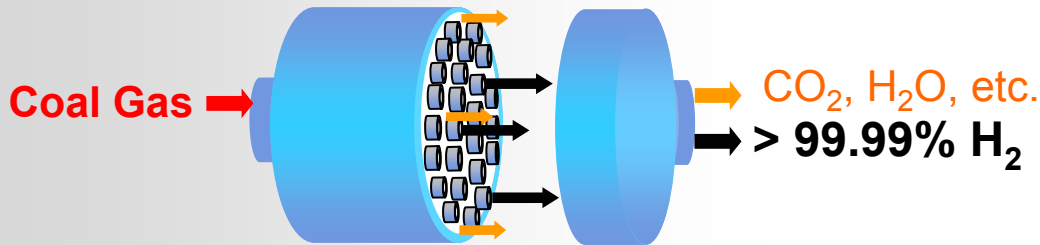
Objectives

- Identify through Atomistic and Thermodynamic modeling a suitable Pd-Cu tri-metallic alloy membrane with high stability and commercially relevant hydrogen permeation in the presence of carbon monoxide and trace amounts of sulfur.
- Identify and synthesize a Water Gas Shift (WGS) catalyst with a high operating life that is sulfur and chlorine tolerant at low concentrations (0.004 atm Partial Pressure at 42 atm total pressure) of these impurities.

Concept



**Water Gas Shift Catalyst
(Modeling & Experimental)**



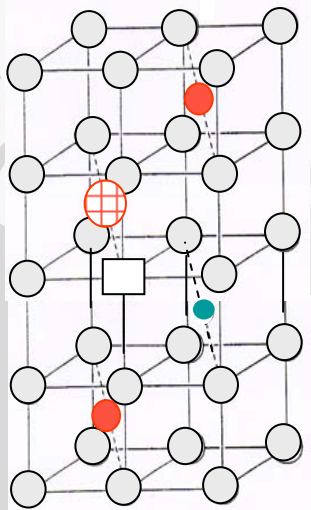
Pd Membrane Alloy (Modeling)

- Process intensification by removing equilibrium limitations on water gas shift (WGS) reaction & producing $>99.99\%$ pure H_2
- Atomistic and thermodynamic modeling of sulfur tolerant Pd-Cu tri-metallic alloys
- WGS catalyst with a high operating life that is sulfur and chlorine tolerant

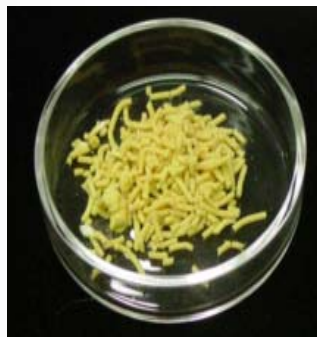
UTRC Catalyst Discovery Approach

Atomistic catalyst design, synthesis, characterization, reaction studies & kinetic analysis

Conceptual Catalyst Design

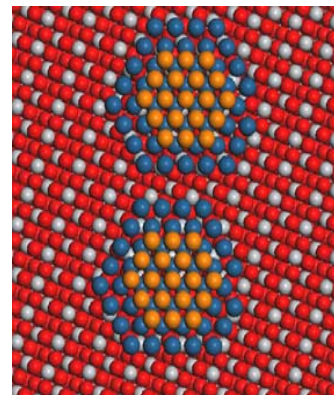


Catalyst Synthesis

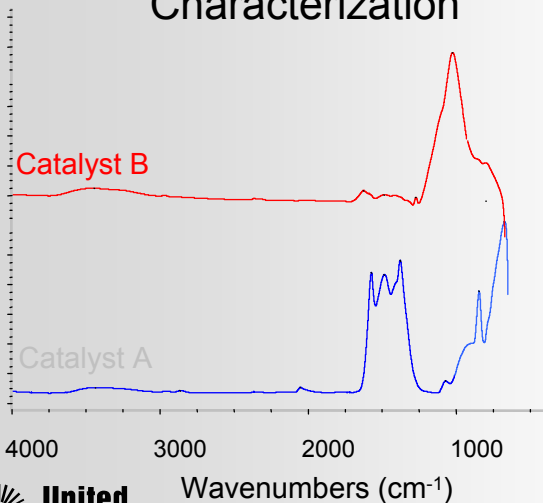


High active surface area
Nanocrystalline structure
~100% NM dispersion

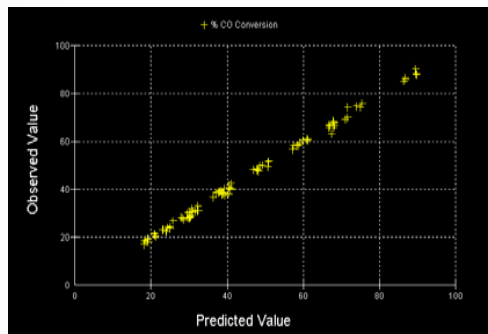
Quantum Mechanical Atomistic
Modeling for advanced catalyst design



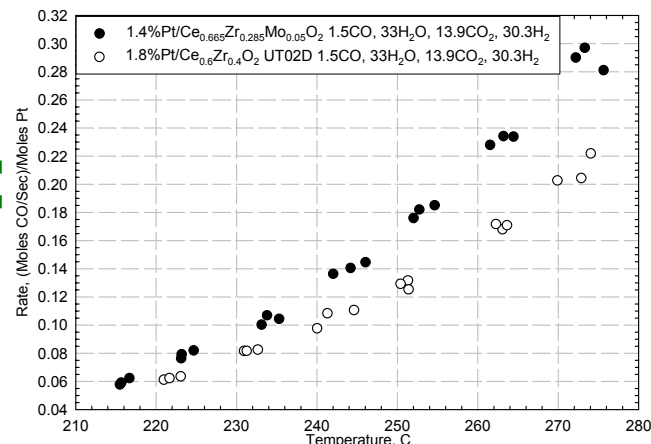
Characterization



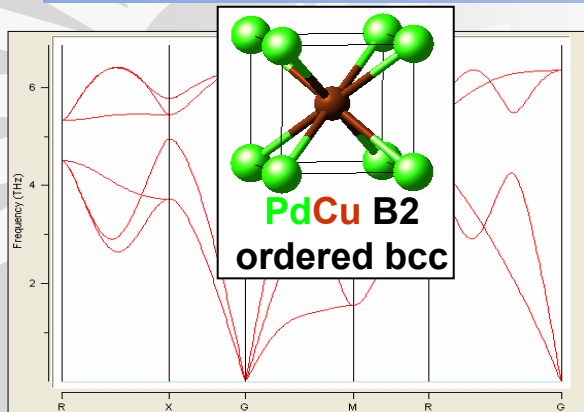
Kinetic Expressions Derived
From Reaction Data



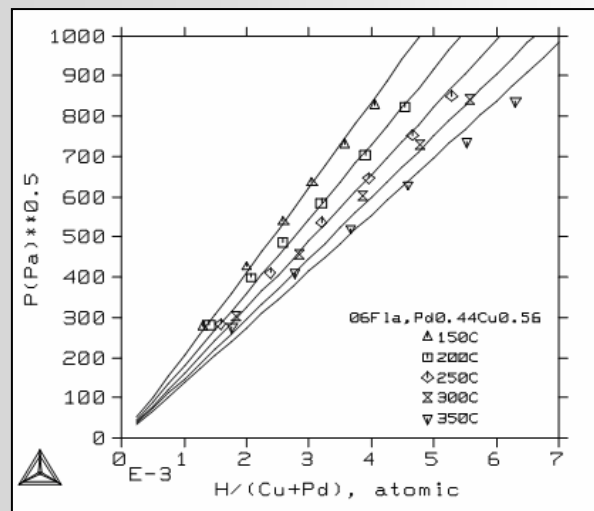
Superior Performance



High Permeability Alloy Design

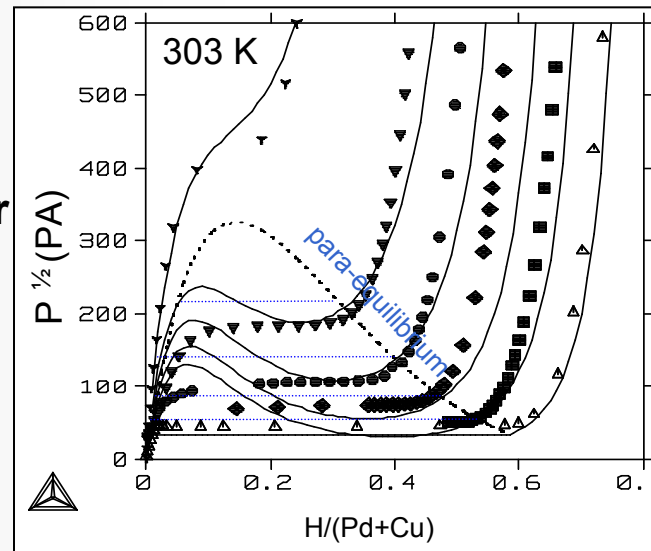


Predicted lattice dynamics for diffusivity & thermodynamics

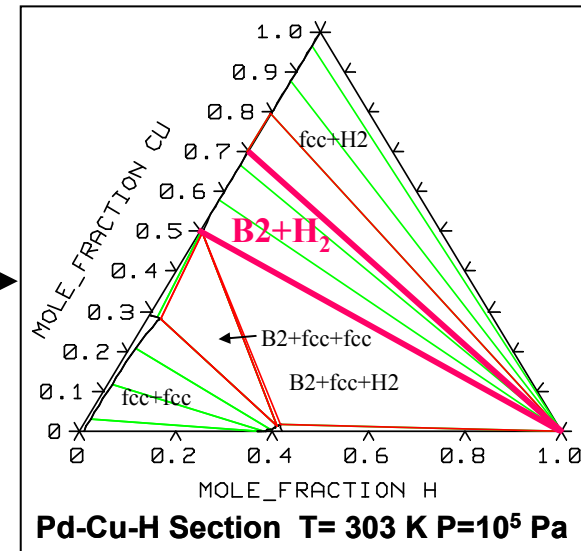


Thermodynamic H solubility measurements

Seek to maximize H permeability:
permeability = diffusivity x solubility



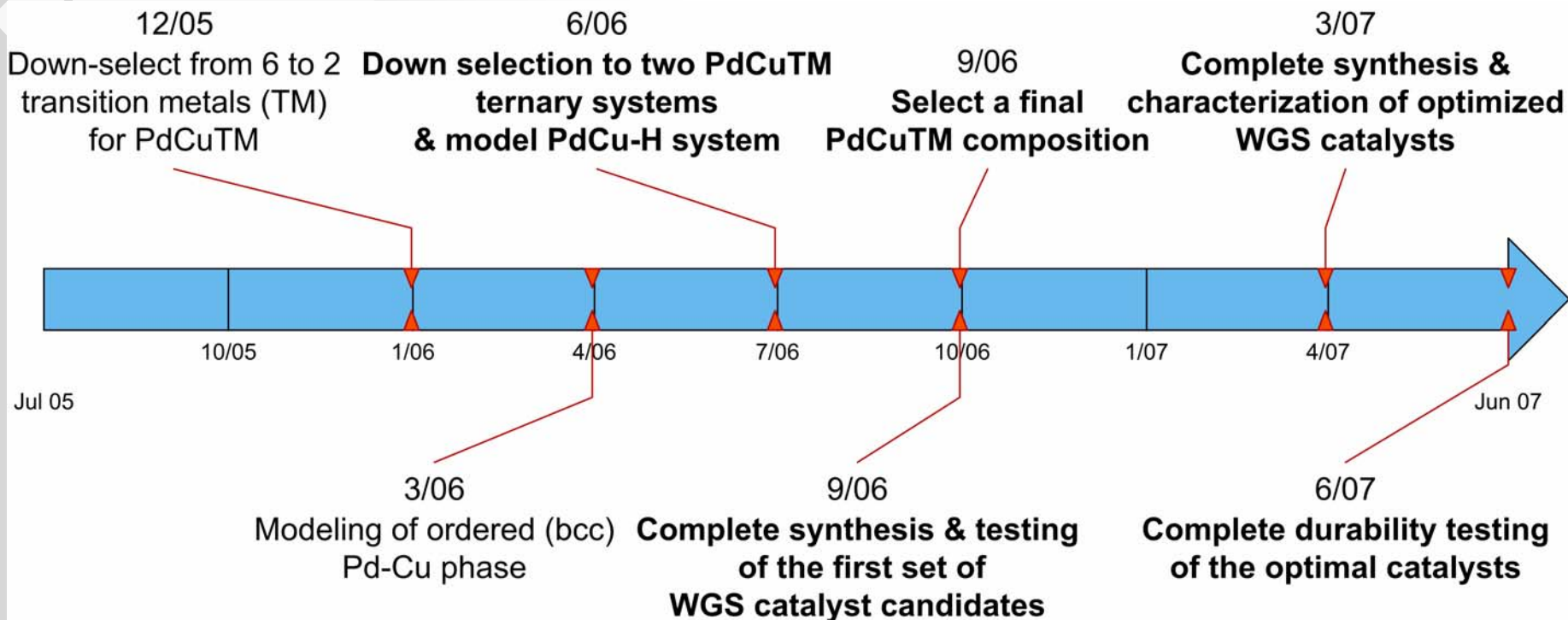
Assessment, and validation of thermodynamic model against literature data



Modeling of phase behavior and properties

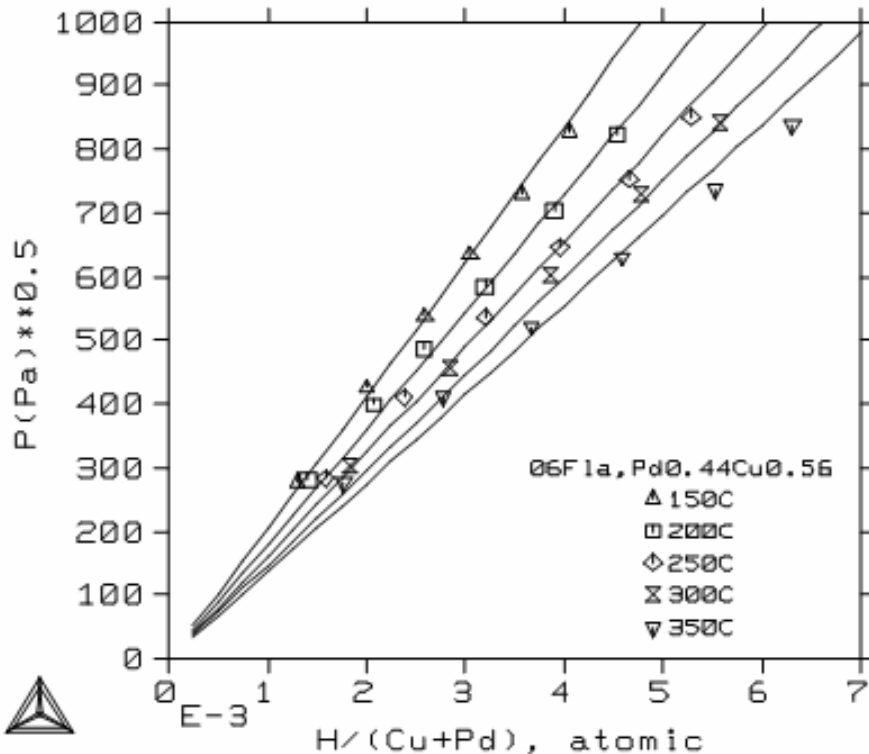
PdCu bcc H diffusion activation barriers lower than those in fcc PdCu. Design more stable ternary bcc PdCuTM phase.

Accomplishments

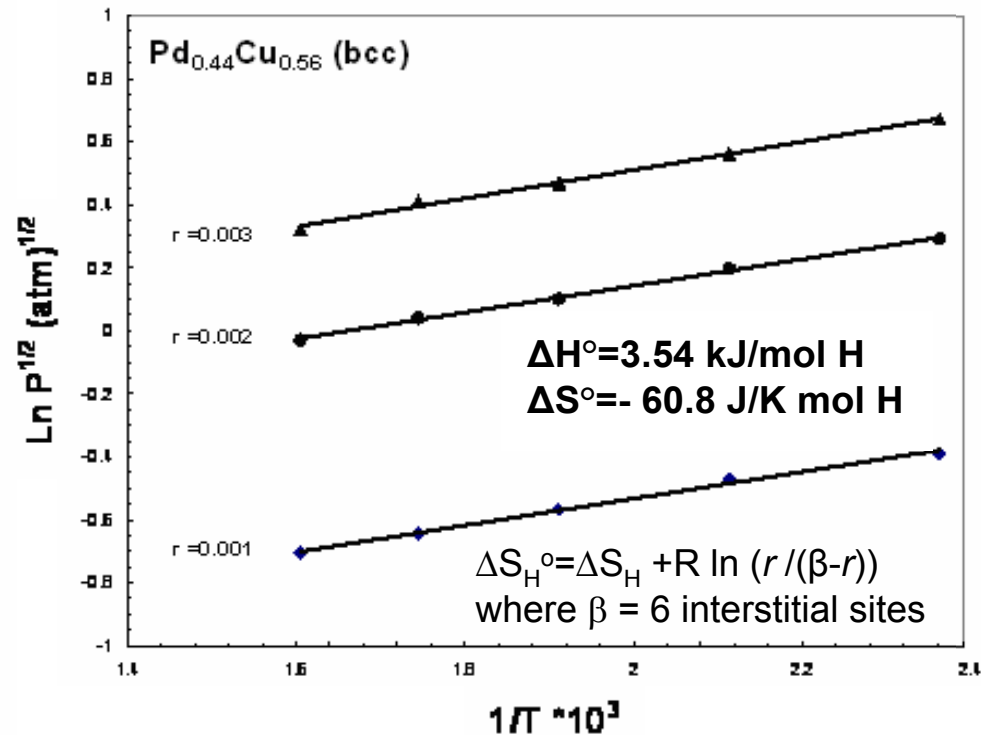


Pd_{0.44}Cu_{0.56} B2 Alloy H Solubility Measurements

Dilute H solubility regime
measured from Δ pressure
using Sievert's apparatus

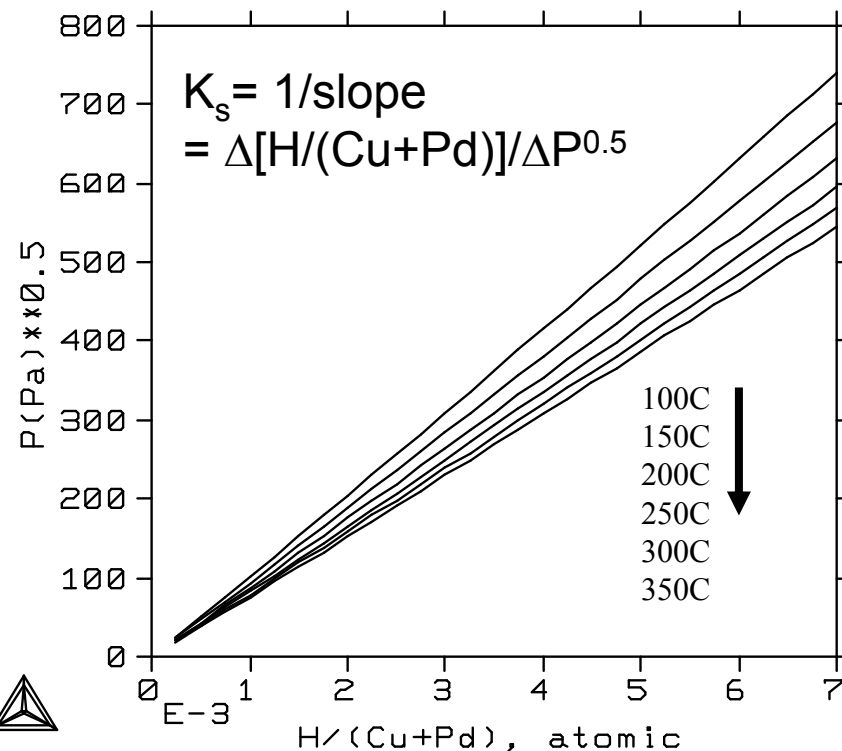
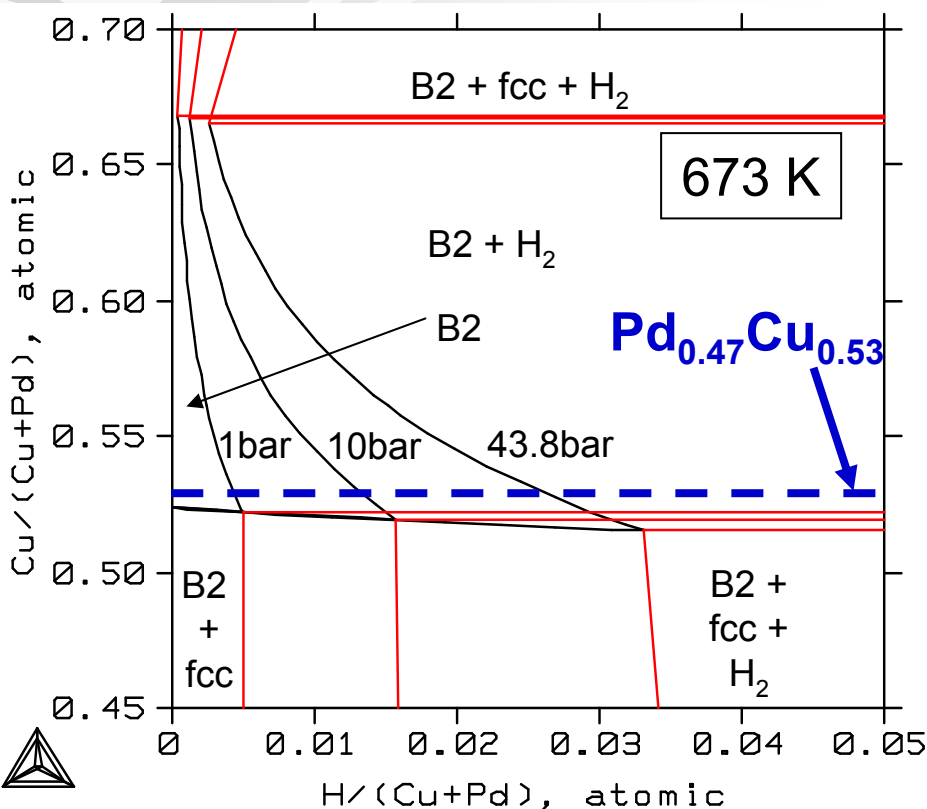


Partial molar quantities
from van't Hoff plot
at fixed concentrations



H solubility is small and endothermic: solubility increases with temperature, contrary to H behavior in other Pd alloys. Thus, increased solubility at a fixed diffusivity yields higher permeability.

Thermodynamic Modeling: H Solubility in PdCu B2

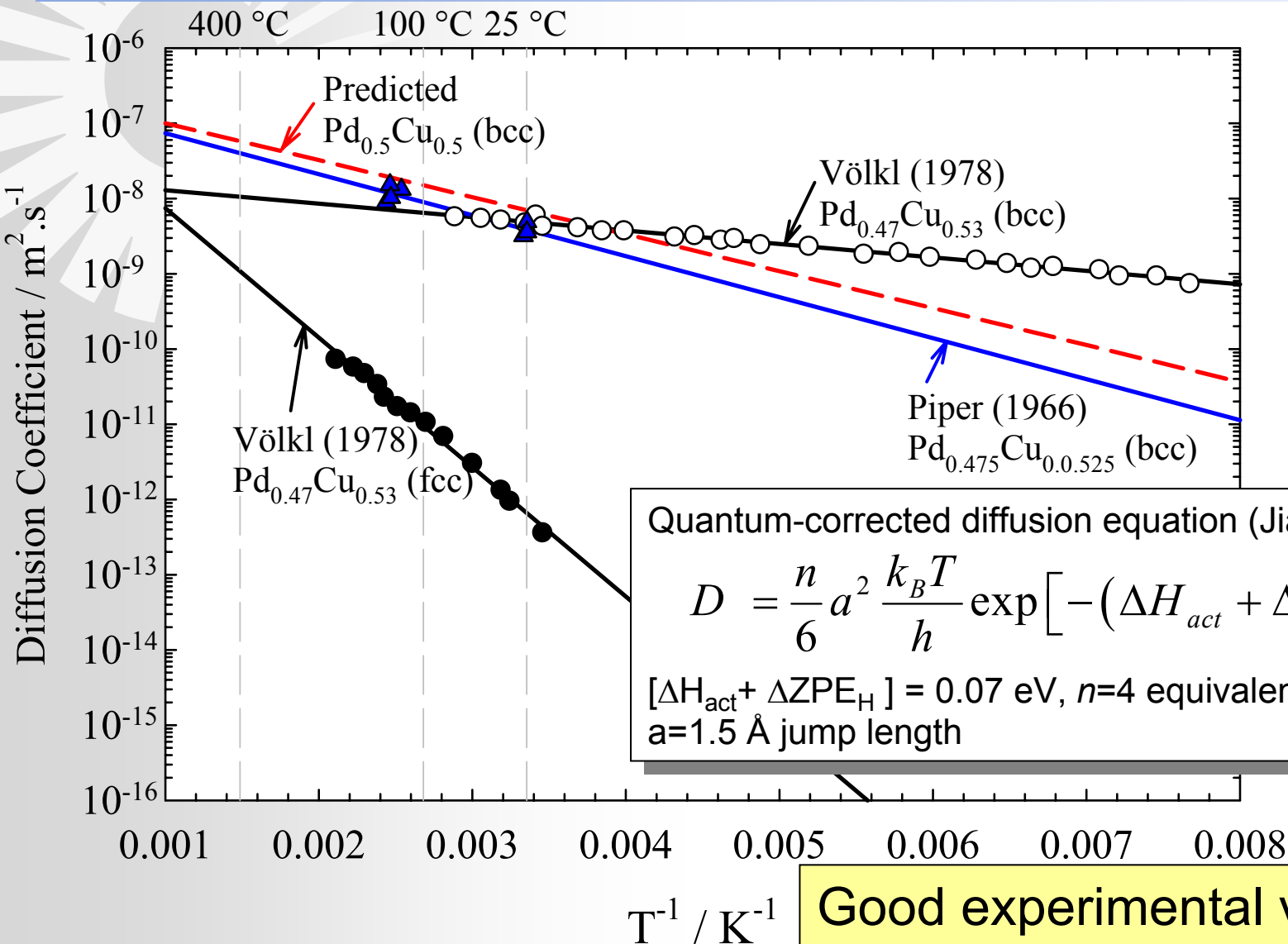


Pd-Cu boundaries independent of P.
B2 H solubility \uparrow & B2 range shifts to lower Cu compositions with $\uparrow P_{H_2}$.

Modeled H solubility in the Pd_{0.47}Cu_{0.53} B2 phase increases with temperature.

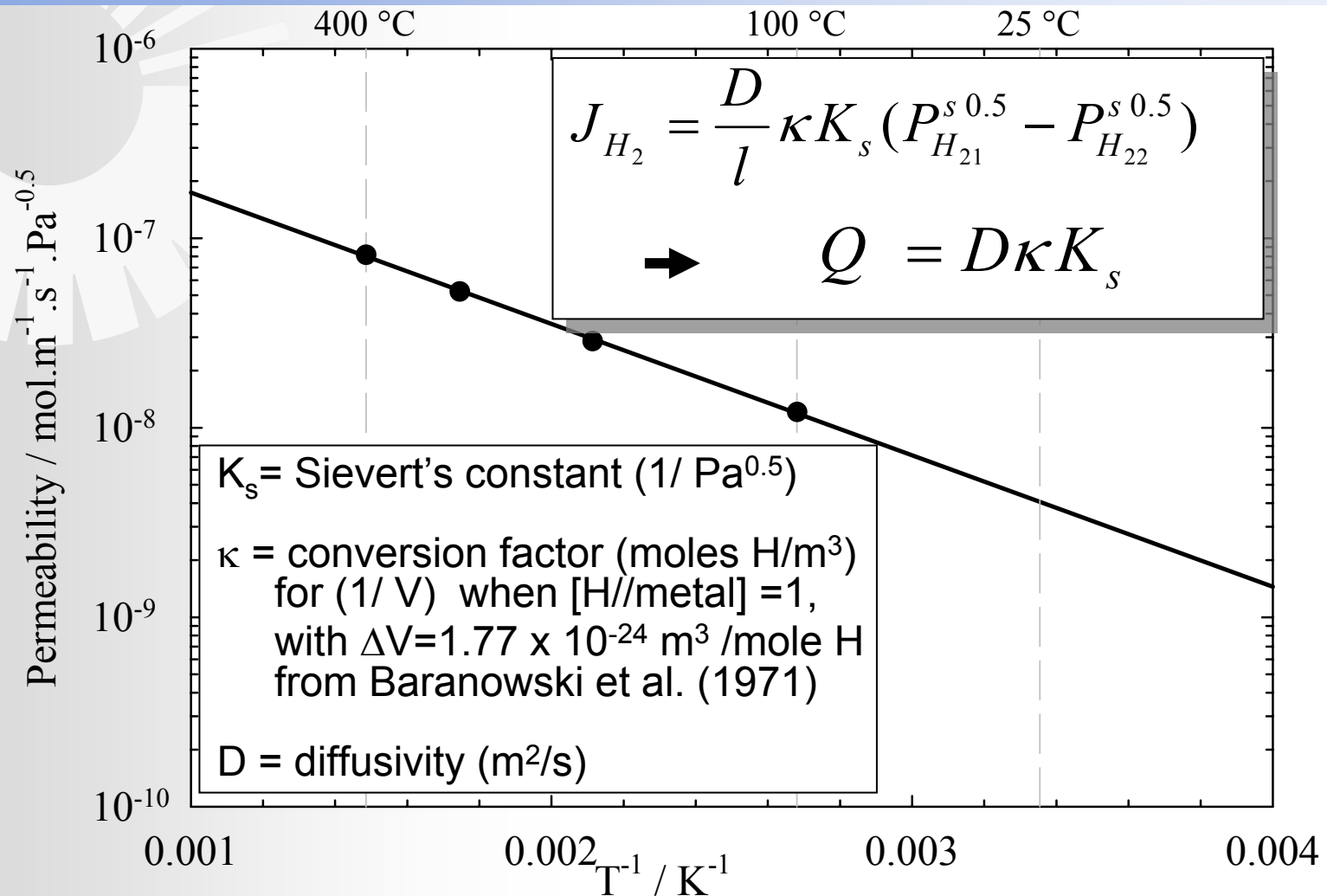
Thermodynamic modeling delineates boundaries for max. H solubility in high diffusivity Pd_{0.47}Cu_{0.53} B2 phase.

Comparison FP Predictions & Experiment



Good experimental vs. predicted
Diffusion Coefficient agreement.

Prediction of H Permeability in Pd_{0.47}Cu_{0.53}



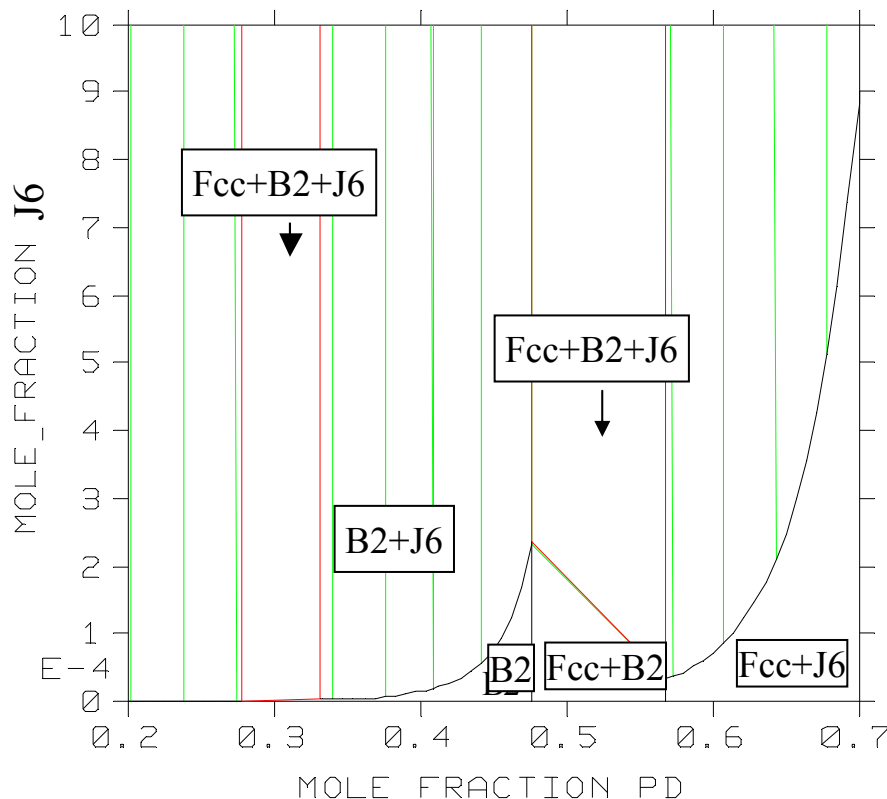
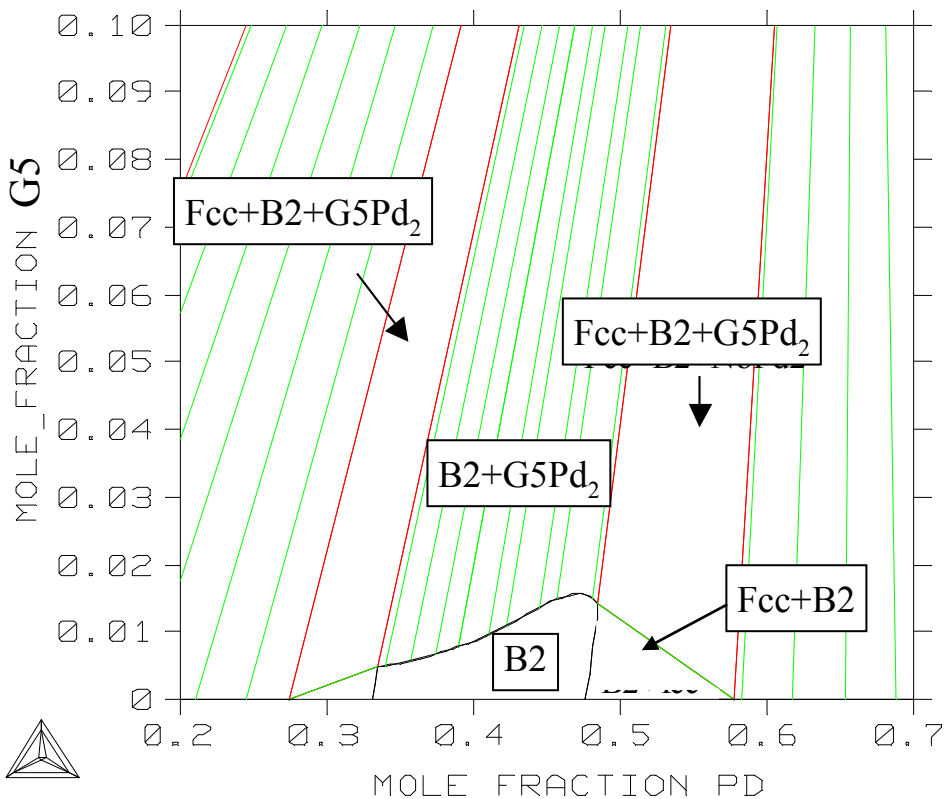
Bulk H permeability (Q) predicted from our experiments, & thermodynamic assessments in agreement with Ma et al. (2003).

Pd-Cu-Transition Metal Ternary Assessments

PdCuTM (TM= transition metal) ternary assessments with TM= G5 and J6, showing poor solubility of J6.

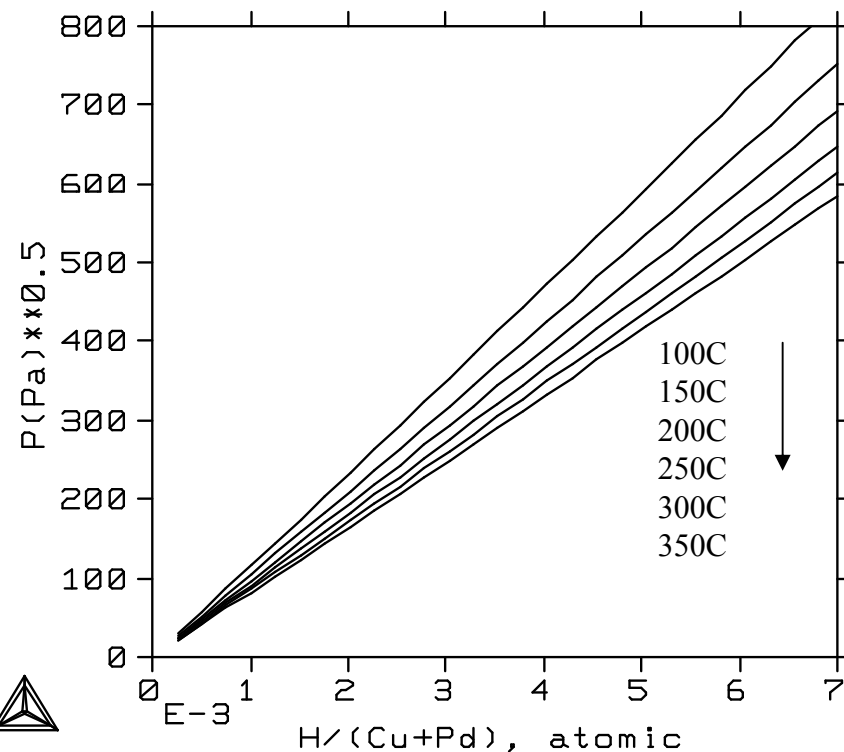
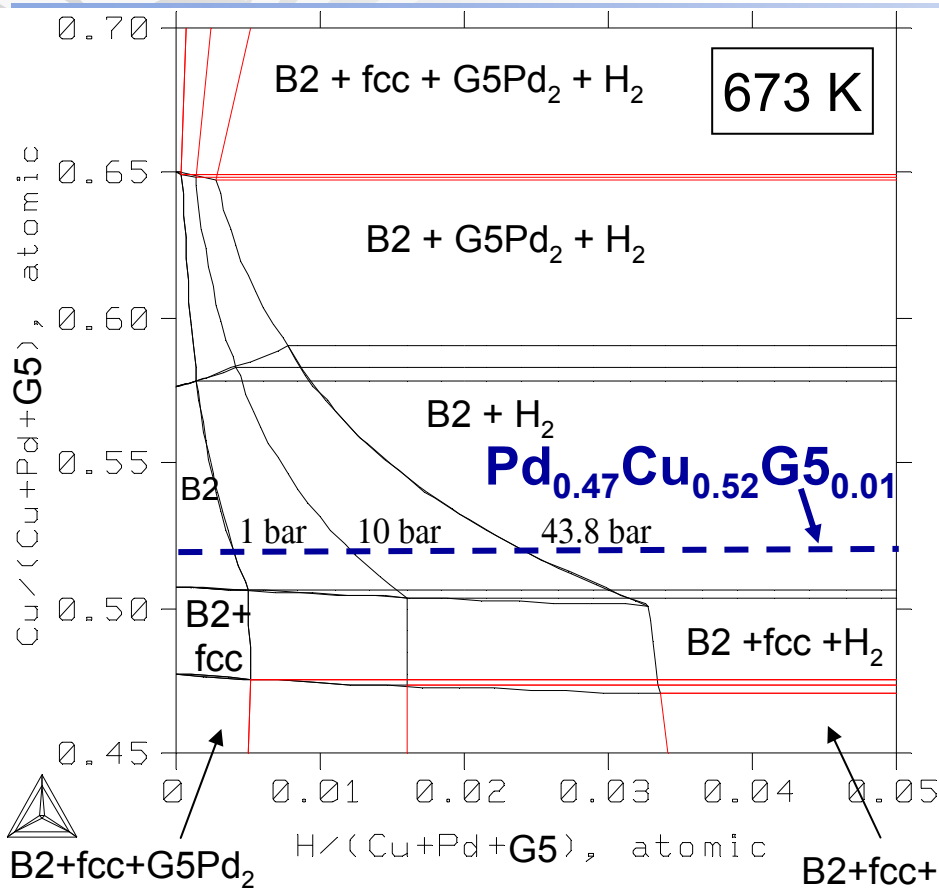
PdCuG5

PdCuJ6



G5 shows maximum solubility of 1.5 atomic % in PdCu B2 phase.

Predicted H Solubility for Selected Ternary Alloy



1% G5 addition widens B2 region while maintaining H solubility.

Predicted H solubility in the Pd_{0.47}Cu_{0.52}G5_{0.01} B2 phase.

Pd_{0.47}Cu_{0.52}G5_{0.01} ternary alloy less susceptible to phase separation with thermal cycling and compositional fluctuations.

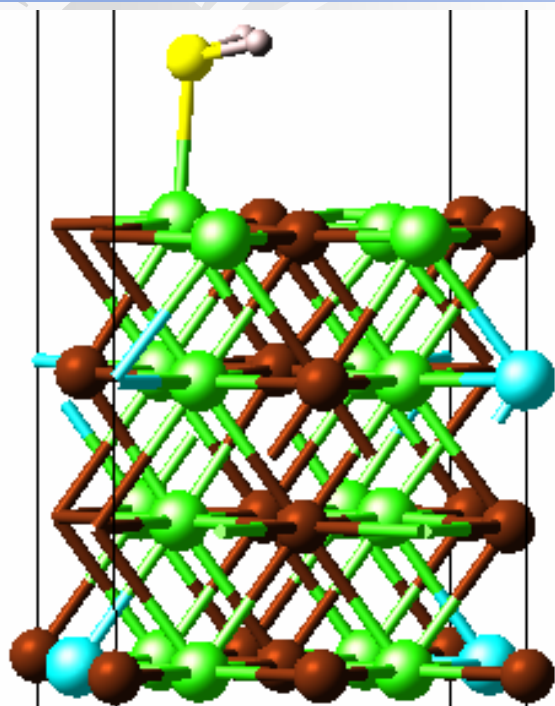
Diffusivity and Permeability of Selected Alloy

Comparison at AWGSMR Conditions: 400 °C and 43.8 bar.

Composition	H solubility, Ks	Predicted Diffusivity, D	Predicted Permeability, Q	Typical experimental Permeability, Q
	Pa ^{0.5}	m ² .s ⁻¹	mol.s ⁻¹ .m ⁻¹ .Pa ^{-0.5}	mol.s ⁻¹ .m ⁻¹ .Pa ^{-0.5}
Pd _{0.47} Cu _{0.52} G5 _{0.01}	1.17×10 ⁻⁵	9.69×10 ⁻⁹	1.11×10 ⁻⁸	
Pd _{0.47} Cu _{0.52} (bcc)	1.25×10 ⁻⁵	6.30×10 ⁻⁸	7.89×10 ⁻⁸	
Pd _{0.77} Cu _{0.23} (fcc)				≈ 4×10 ⁻⁹

Selected alloy is predicted to have at least twice the permeability of the best candidate fcc phase, with thermal and chemical stability.

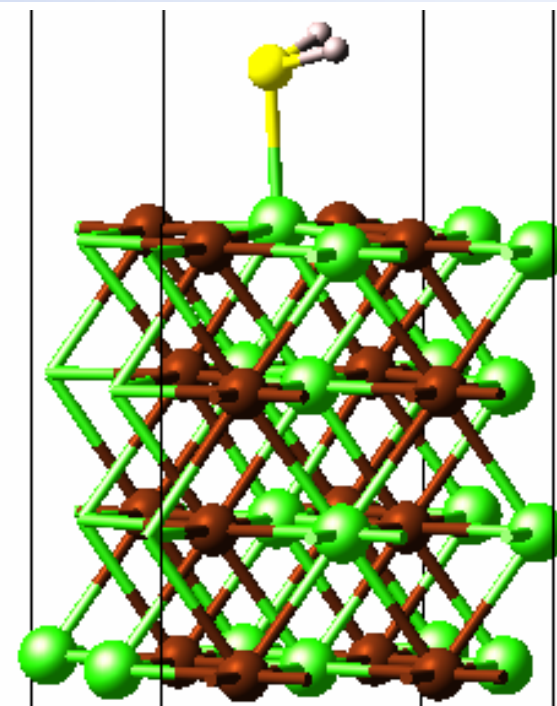
Sulfur Resistance of Ternary Alloy



H₂S on Pd₈Cu₇G5 (110)

Pd Cu G5 H S

Optimal
H₂S binding
configurations
predicted at
ground state



H₂S on Pd₈Cu₈ (110)

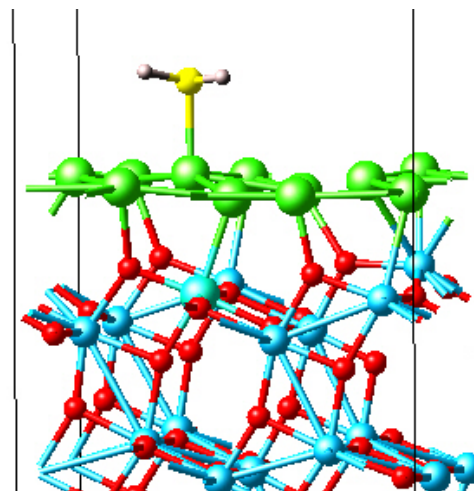
- G5 ternary element preferentially substitutes for subsurface Cu.
- H₂S binding is ≈ 10 kJ/mole weaker on the Pd₈Cu₇G5 B2 (110) surface compared to binding on PdCu B2 (110) surface.

Ternary alloy predicted to have the sulfur resistance comparable to fcc PdCu alloys with the higher permeability of bcc PdCu alloys.

Results: Lower Sulfur Binding Energy Predicted

Low CO Binding Energy Preferred For 42 atm, high CO partial press. Coal Gas

	CO, eV	H ₂ O, eV	H ₂ S, eV
TiO ₂ - Anatase	-0.32	-0.64	-1.93
TiO ₂ - Rutile	-0.09	-1.16	-0.90
Ti _{0.96} J6 _{0.04} O ₂	-0.34	-0.72	-2.09
Ce _{0.5} Zr _{0.4} J6 _{0.1} O ₂	-0.63	-0.74	-2.14
Ce _{0.5} Zr _{0.4} E4 _{0.1} O ₂	-0.97	-1.01	-2.43
Ce_{0.33}Zr_{0.33}E4_{0.33}O₂	-0.01	-0.83	-0.29



Pt O J6 Ti S H

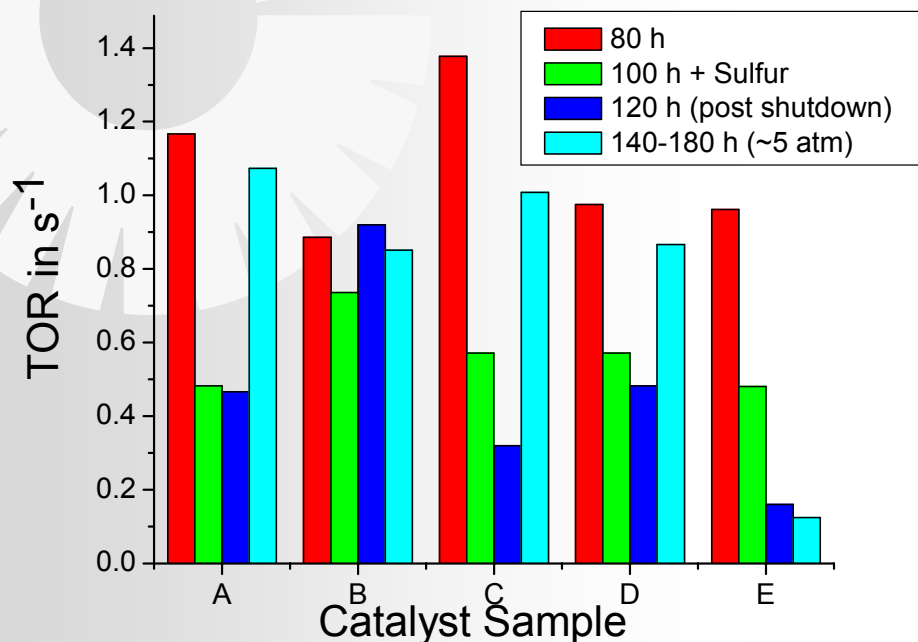
H₂S/Pt/J6-Doped TiO₂ Anatase(101)
Binding Energy: -2.02 eV/H₂S

	CO, eV	H ₂ S, eV
Pt / TiO ₂ - Anatase	-1.67	-2.37
Pt / Ti _{0.96} J6 _{0.04} O ₂	-0.97	-2.02
Pt / Ce _{0.5} Zr _{0.4} J6 _{0.1} O ₂	-1.74	-3.66
Pt / Ce_{0.33}Zr_{0.33}E4_{0.33}O₂	-0.32	-1.84

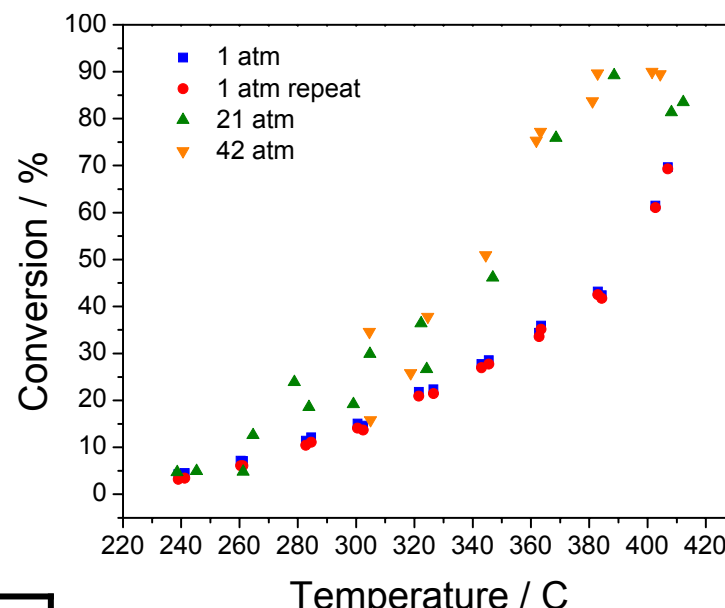
The electronic structure of doped oxides modifies that of Pt monolayer thus lowering CO, H₂S binding energies to Pt.

Catalyst Test Results Consistent with Modeling

RATE DATA AT 400 C - Normalized to 2% Pt



3.1%Pt-1.6%Re / Ce_{0.36}Zr_{0.33}E4_{0.31}O₂



Temperature / C
7.2% CO, 7.8% CO₂, 6% H₂, 39.2% H₂O

		% Pt	% Re
A	Pt/Re-Ce _{0.36} Zr _{0.33} E4 _{0.31} O ₂	3.1	1.6
B	Pt/Re-Ce _{0.52} Zr _{0.39} E4 _{0.09} O ₂	2.3	1.2
C	Pt/Re-Ce _{0.36} Zr _{0.22} E4 _{0.42} O ₂	3.4	1.7
D	Pt/Re-Ce _{0.69} E6 _{0.25} J6 _{0.05} O ₂	2.8	1.4
E	Pt/Re-Ti _{0.9} J6 _{0.1} O ₂	3.6	1.8

- High Pressure, high CO operation very challenging
- Remaining effort focused on Sulfur durability run.

Future Work

- (Apr-Jun '07) Complete evaluation and durability tests of final set of catalysts and deliver final report.

Advanced Membrane Reactor Water Gas Shift Summary

Relevance Lower cost high purity H_2 production from precleaned coal gas:
Eliminates need for: 1) complete sulfur scrubbing, 2) separate H_2 extraction/purification train and retentate gas is $>90\%$ CO_2 on a dry basis.

Approach

- Atomistic and thermodynamic modeling to design high stability BCC Pd-Cu based trimetallic alloy with commercial relevant permeance.
- Design synthesize and test catalyst tailored to needs of advanced membrane reactor

Accomplishments

- Two “stabilized” BCC alloys $Pd_{0.5}Cu_{(0.5-x)}G5_x$ and $Pd_{0.5}Cu_{(0.5-x)}J6_x$ investigated.
- Permeance, stability, and composition of $Pd_{0.5}Cu_{(0.5-x)}G5_x$ predicted
- WGS catalyst family potentially resistant to H_2S identified

Issues

- Completing 1500-h durability run at high pressure