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

United Technologies Research Center

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

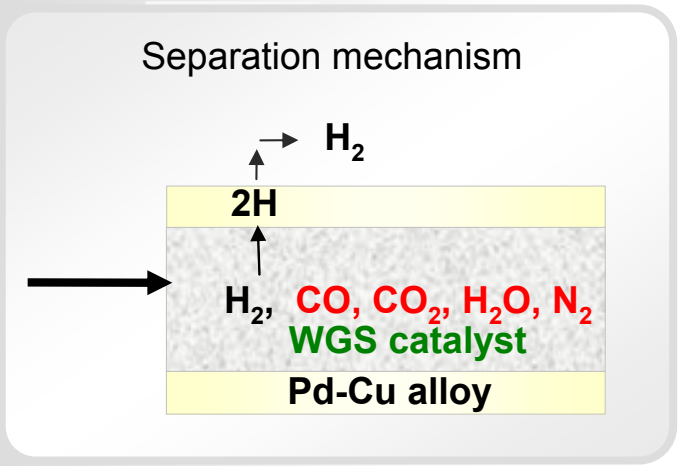
Partners
- QuesTek Innovations LLC
- Metal Hydride Technologies

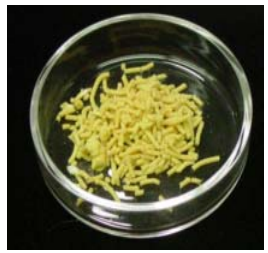
Objectives

- 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.

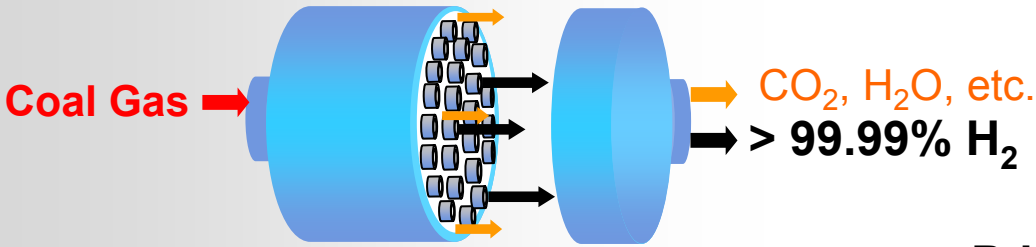
- Identify and synthesize a Water Gas Shift (WGS) catalyst with a high operating life that is sulfur and chlorine tolerant at low concentrations (0.004 atm Partial Pressure at 42 atm total pressure) of these impurities.

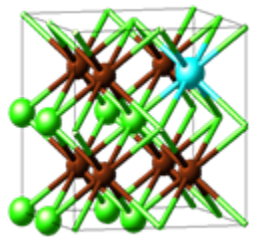
Concept





Water Gas Shift Catalyst (Modeling & Experimental)





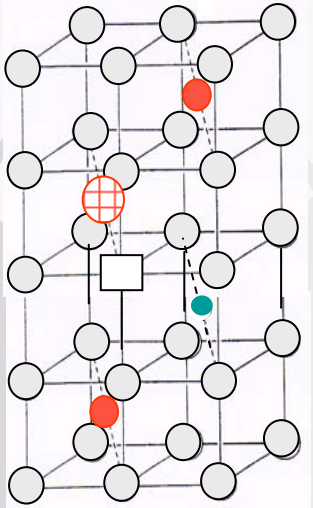
Pd Membrane Alloy (Modeling)

- 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

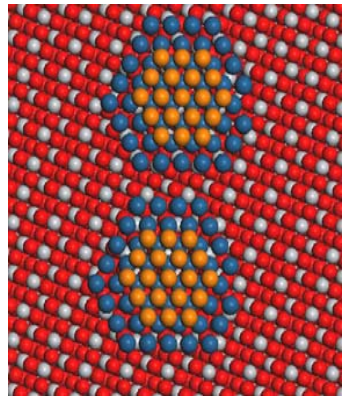
Atomistic catalyst design, synthesis, characterization, reaction studies & kinetic analysis

Conceptual Catalyst Design



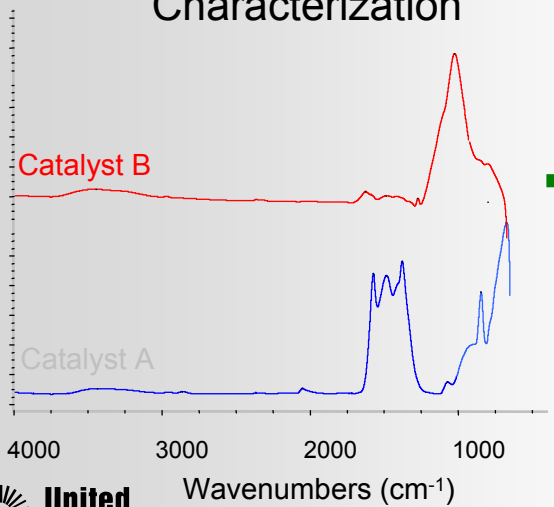
Catalyst Synthesis

Quantum Mechanical Atomistic Modeling for advanced catalyst design

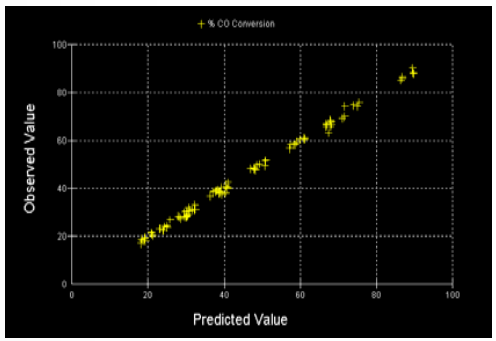


High active surface area
Nanocrystalline structure
~100% NM dispersion

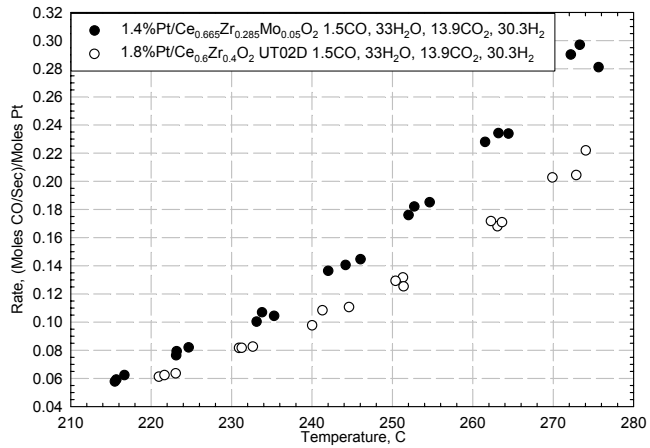
Characterization



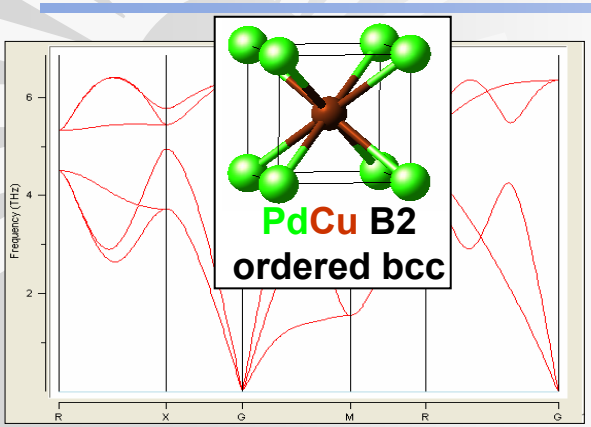
Kinetic Expressions Derived From Reaction Data



Superior Performance

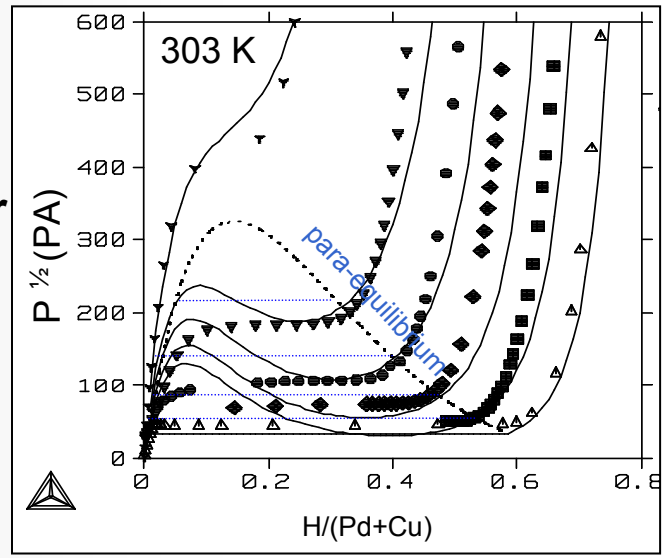


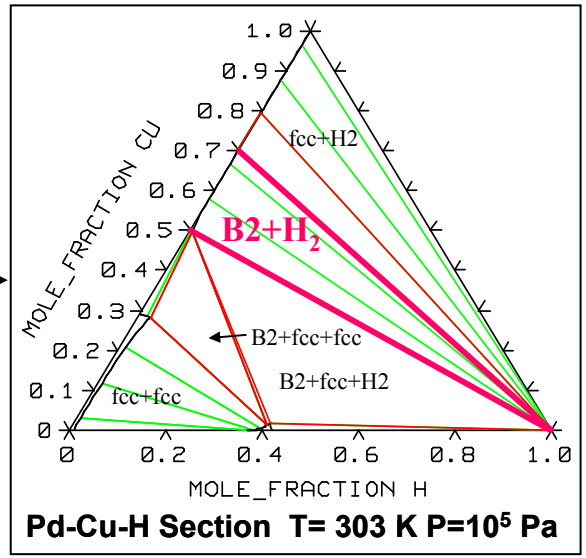
High Permeability Alloy Design



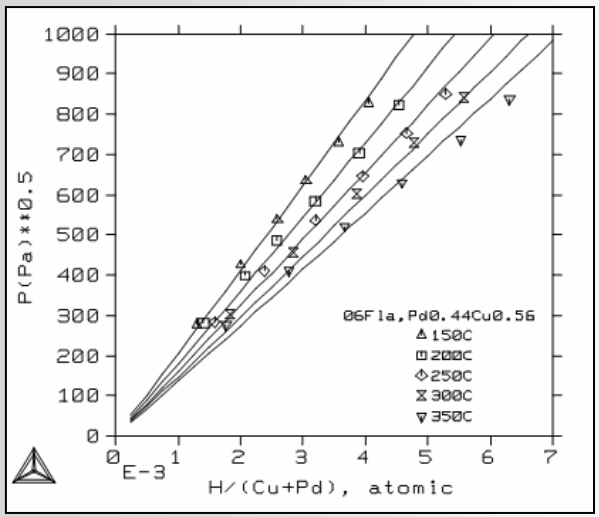
Predicted lattice dynamics for diffusivity & thermodynamics

Seek to maximize H permeability:
permeability = diffusivity x solubility





Pd-Cu-H Section T= 303 K P=10^5 Pa



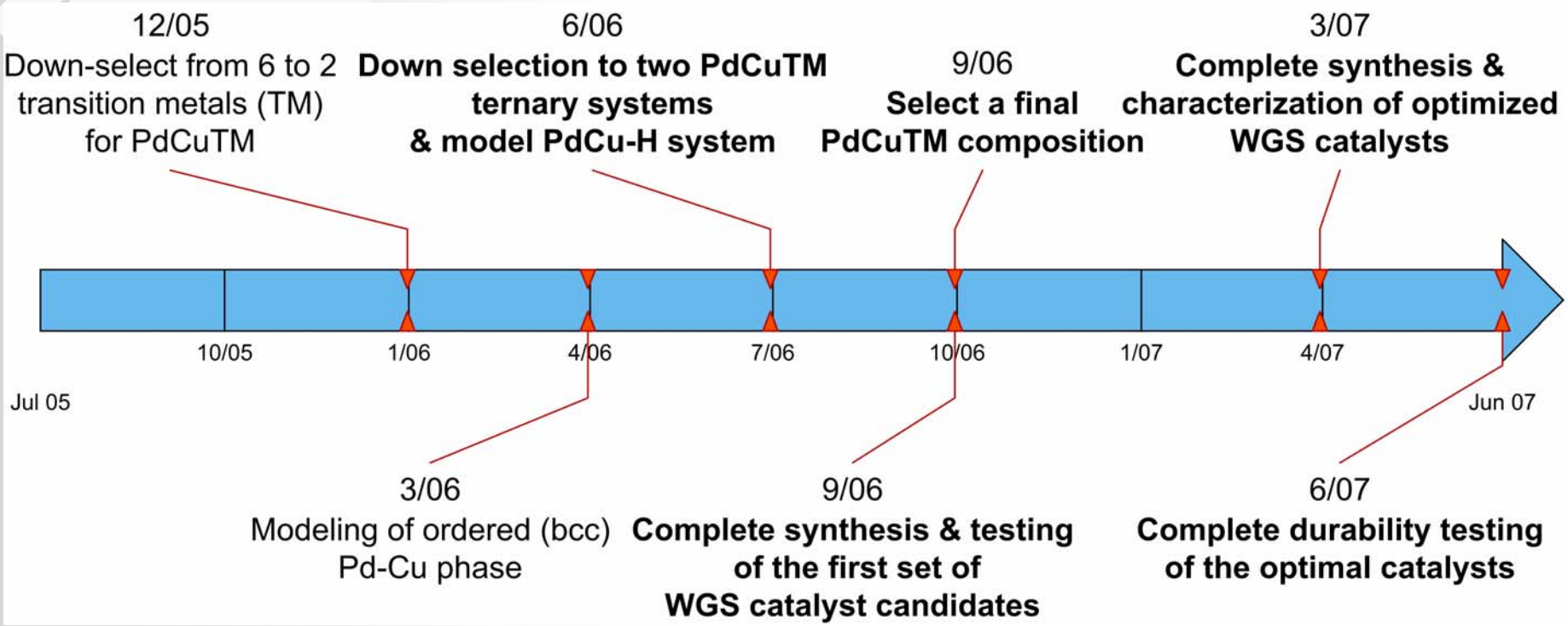
Thermodynamic H solubility measurements

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.

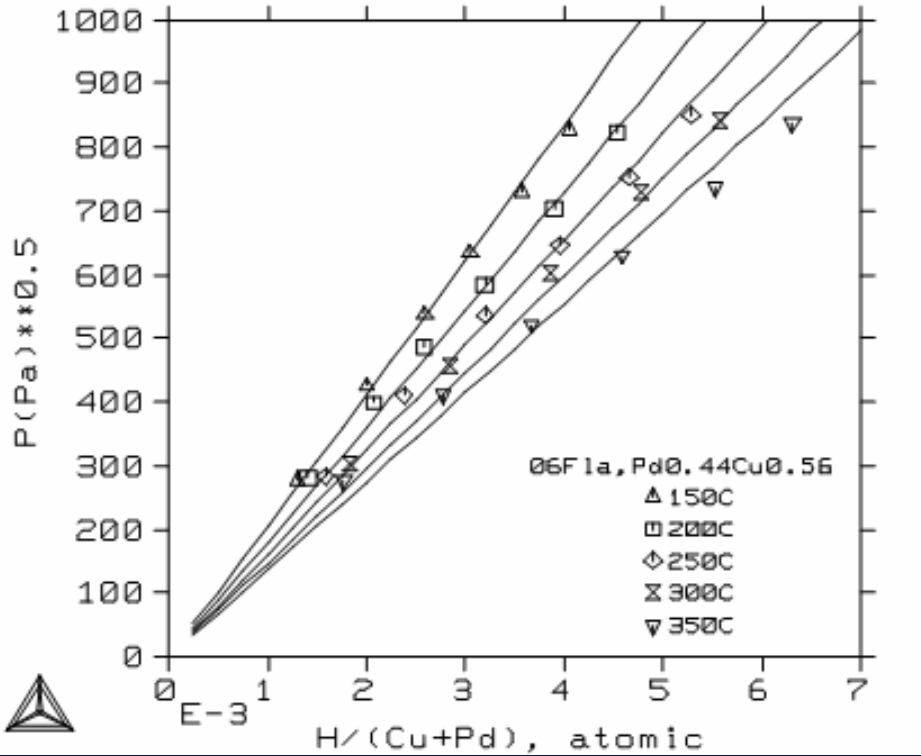
Accomplishments

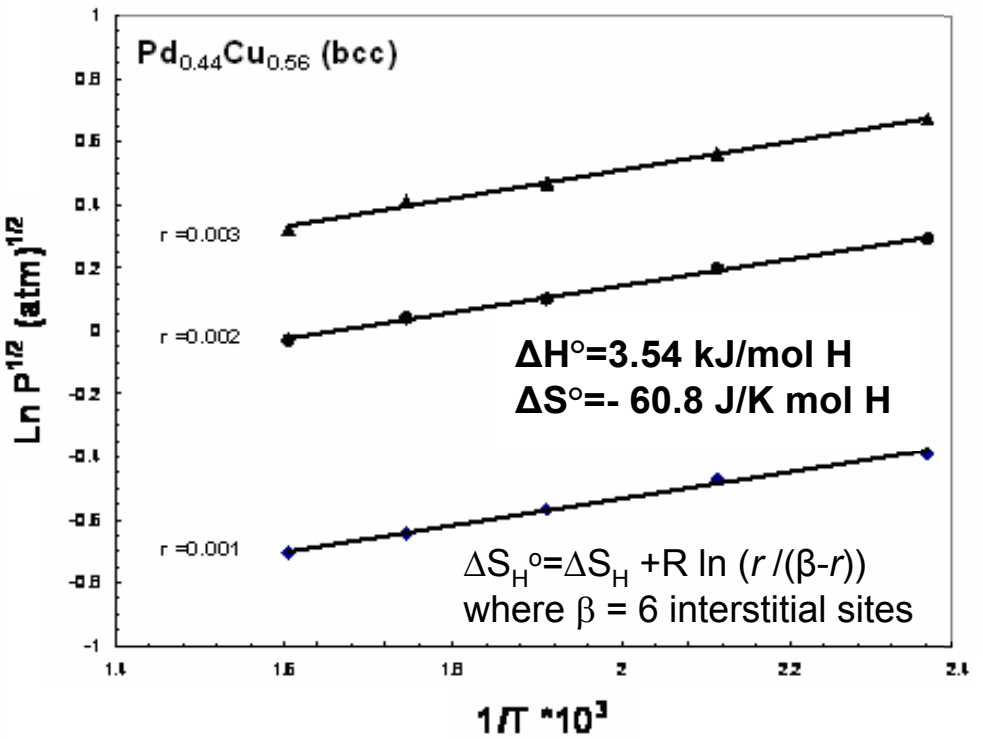


$Pd_{0.44}Cu_{0.56}$ B2 Alloy H Solubility Measurements

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

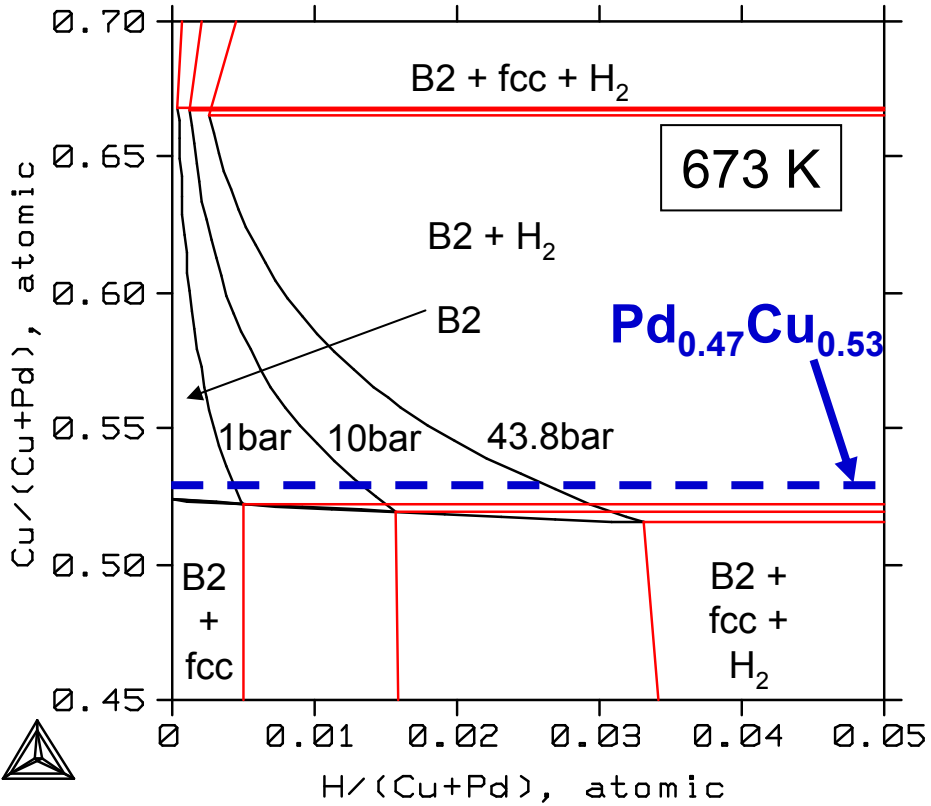
Partial molar quantities from van't Hoff plot at fixed concentrations

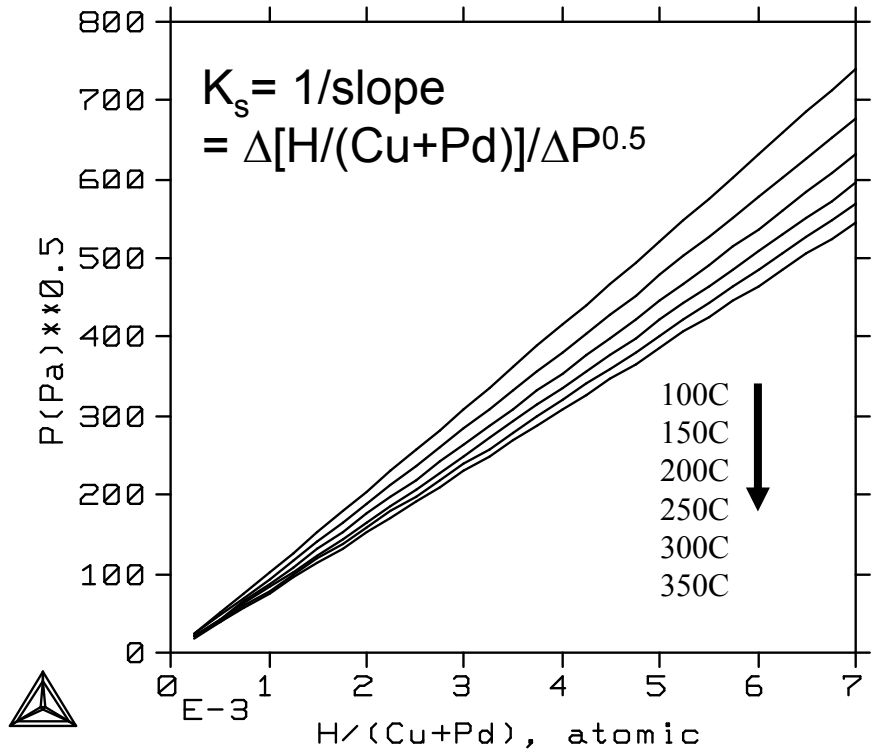




H solubility is small and endothermic: solubility increases with temperature, contrary to H behavior in other Pd alloys. Thus, increased solubility at a fixed diffusivity yields higher permeability.

Thermodynamic Modeling: H Solubility in PdCu B2



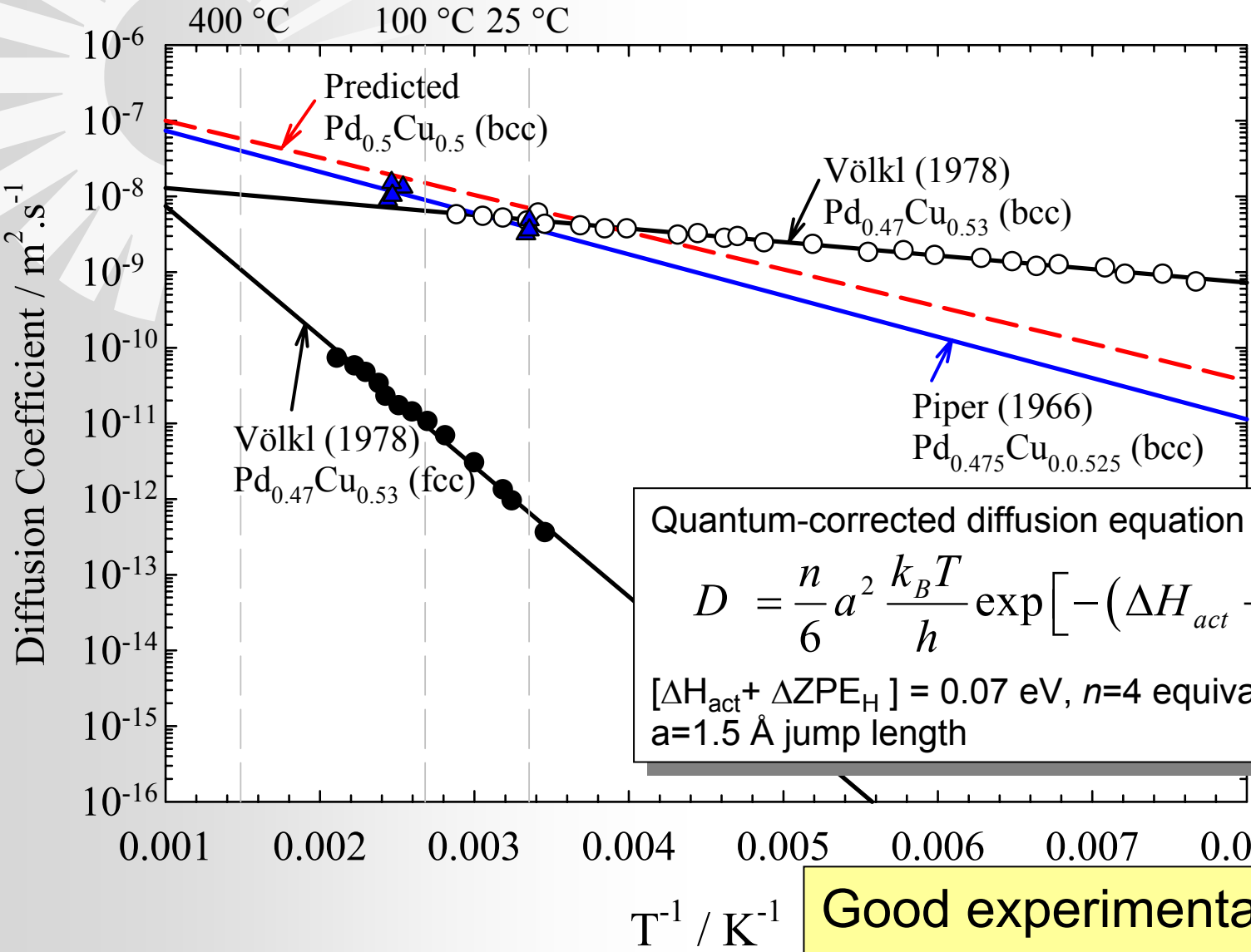


Pd-Cu boundaries independent of P. B2 H solubility ↑ & B2 range shifts to lower Cu compositions with ↑ P_{H2} .

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



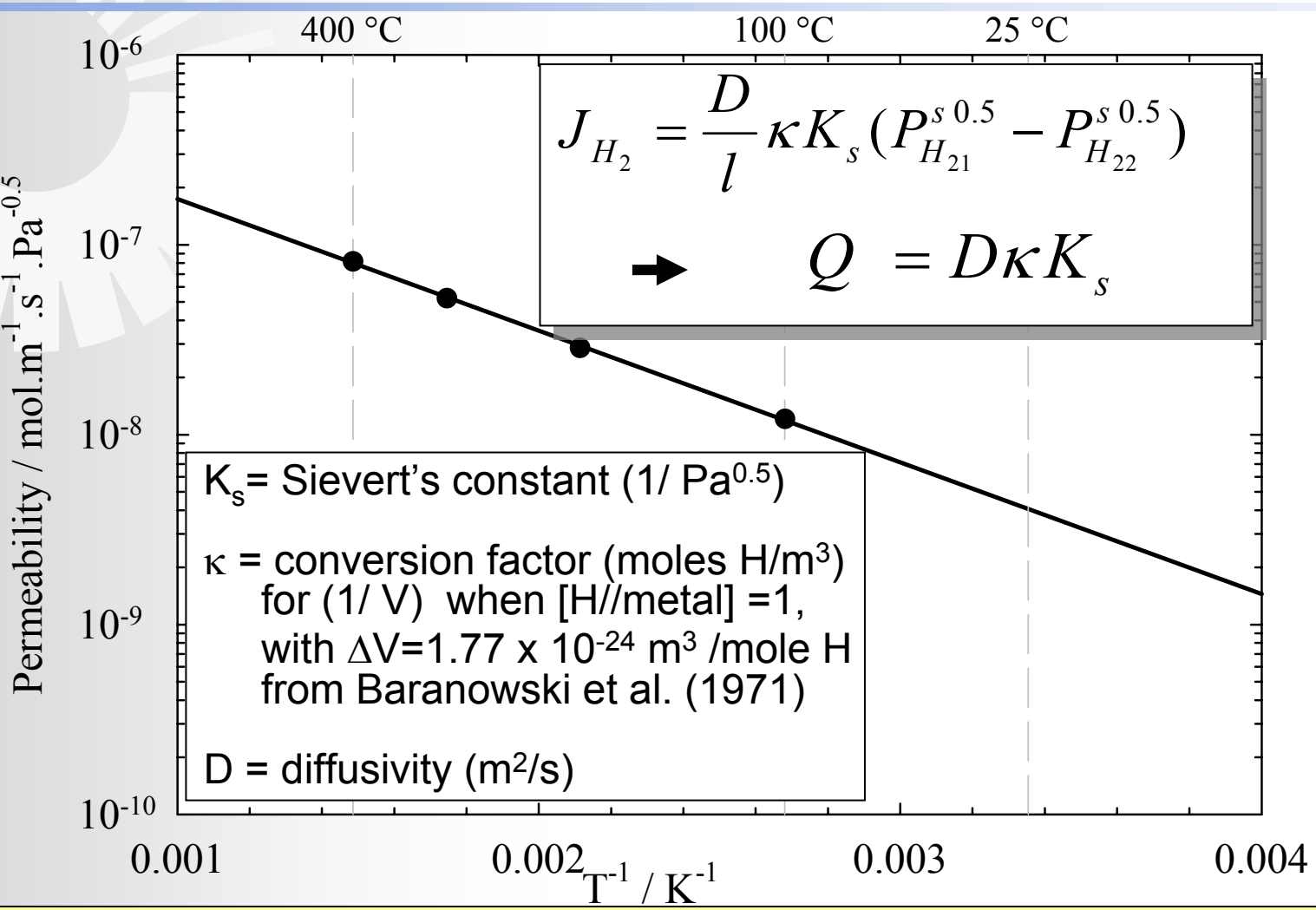
Quantum-corrected diffusion equation (Jiang, 2004):

$$D = \frac{n}{6} a^2 \frac{k_B T}{h} \exp\left[-\left(\Delta H_{act} + \Delta ZPE\right)/k_B T\right]$$

$[\Delta H_{act} + \Delta ZPE_H] = 0.07$ eV, n=4 equivalent paths
a=1.5 Å jump length

Good experimental vs. predicted Diffusion Coefficient agreement.

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

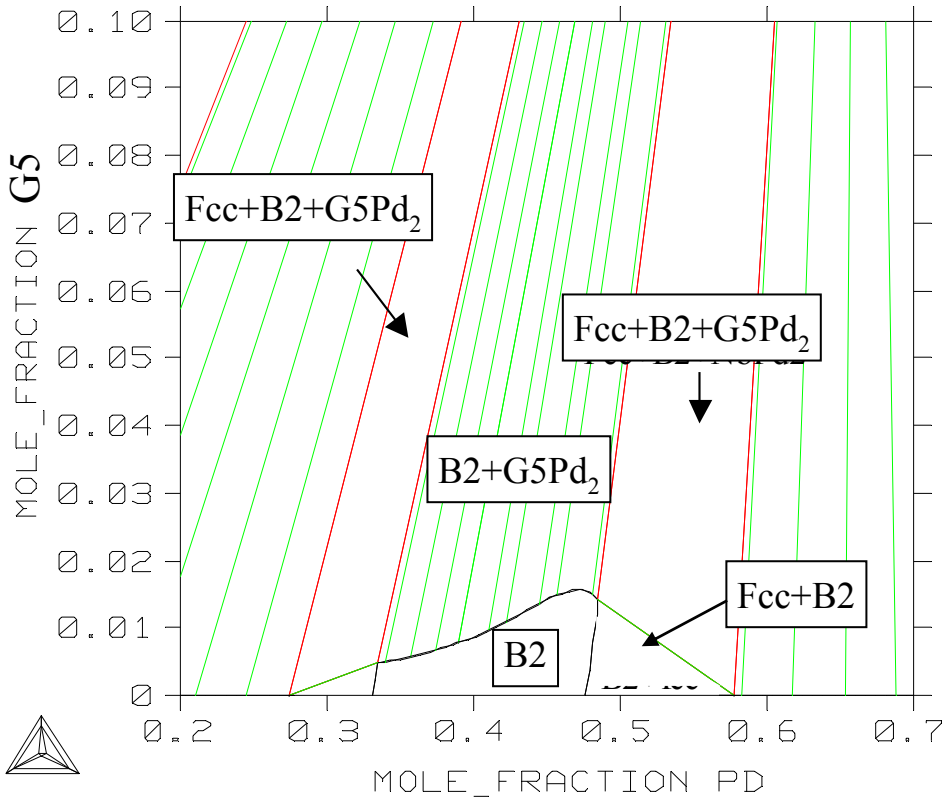


Bulk H permeability (Q) predicted from our experiments, & thermodynamic assessments in agreement with Ma et al. (2003).

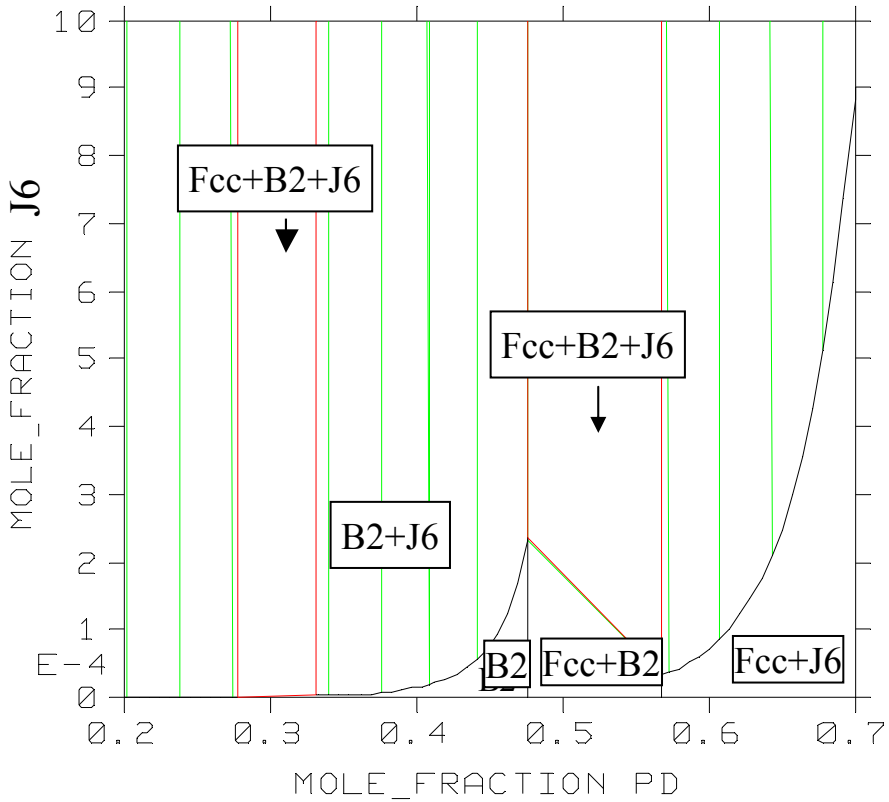
Pd-Cu-Transition Metal Ternary Assessments

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

PdCuG5

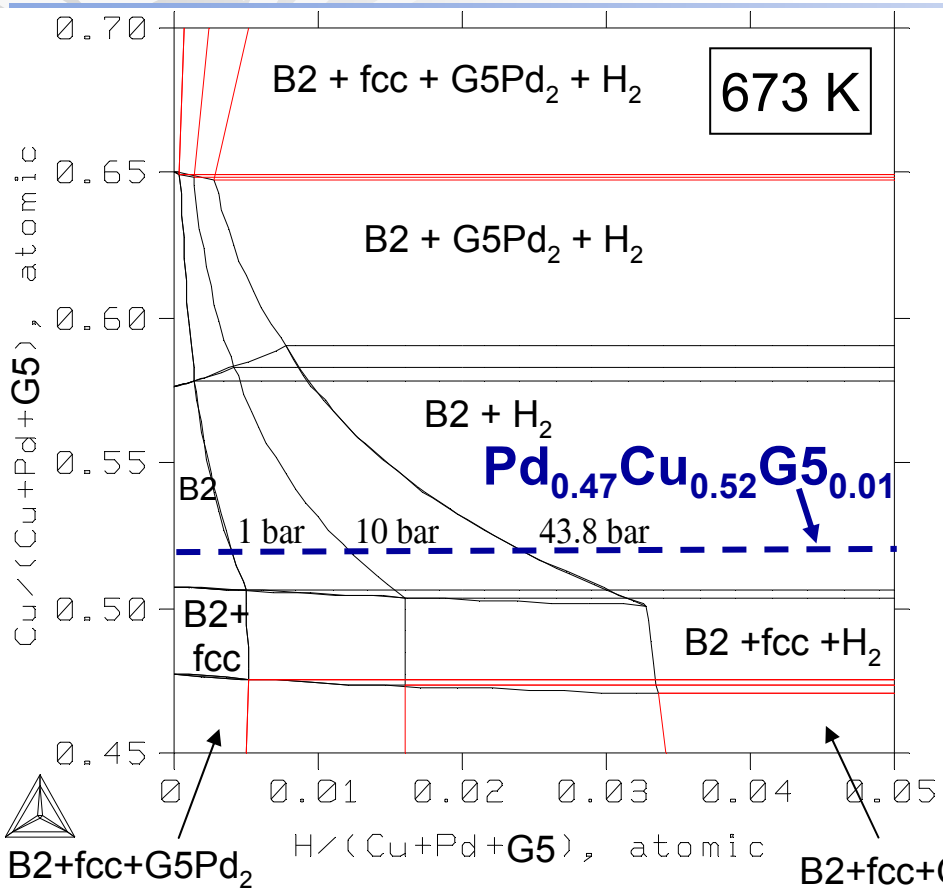


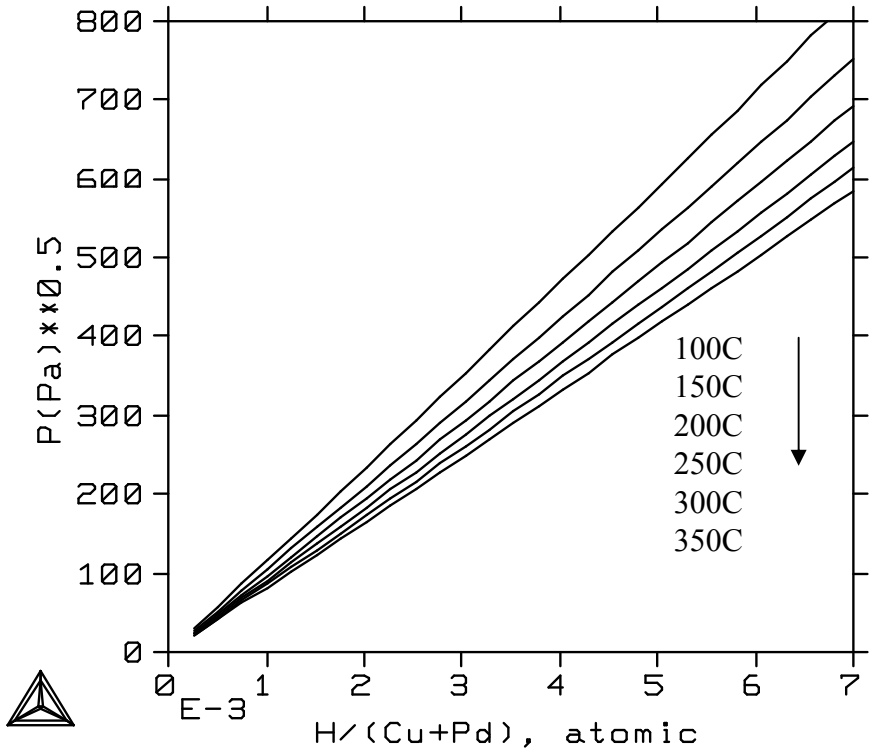
PdCuJ6



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.

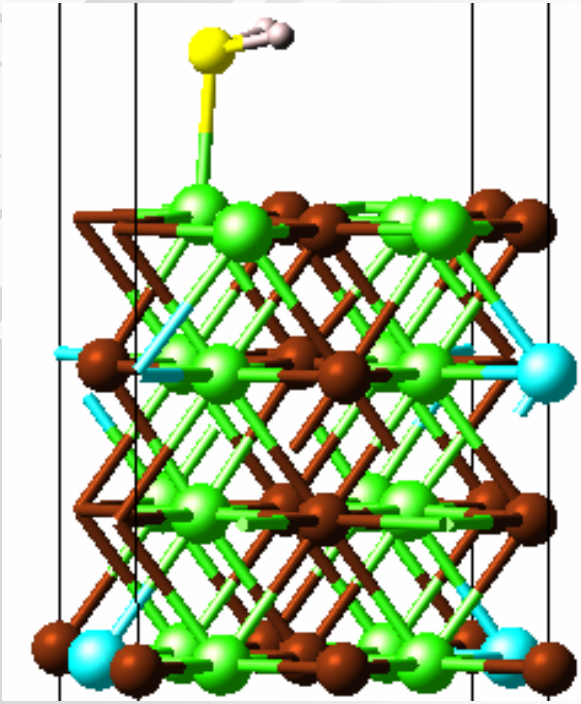
Diffusivity and Permeability of Selected Alloy

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)				$\approx 4\times10^{-9}$

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

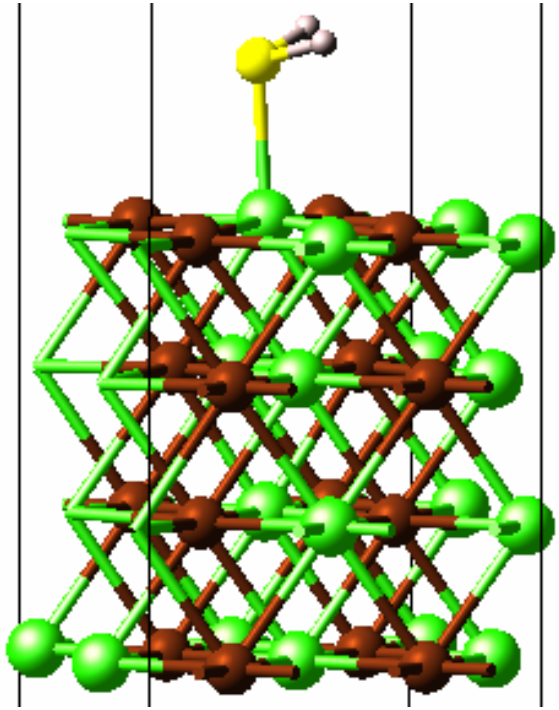
Sulfur Resistance of Ternary Alloy



H_2S on Pd_8Cu_7G5 (110)

Pd Cu G5 H S

Optimal H_2S binding configurations predicted at ground state



H_2S on Pd_8Cu_8 (110)

- G5 ternary element preferentially substitutes for subsurface Cu.
- H_2S binding is ≈10 kJ/mole weaker on the Pd_8Cu_7G5 B2 (110) surface compared to binding on PdCu B2 (110) surface.

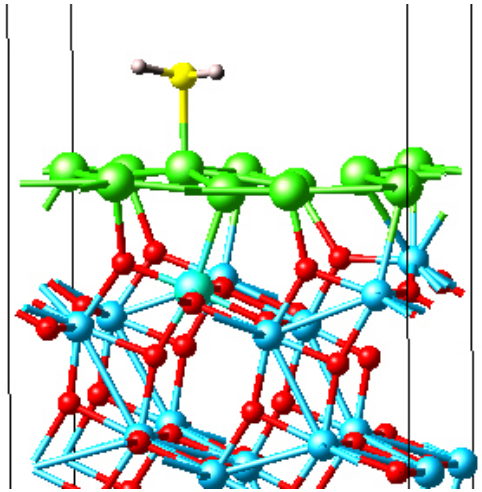
Ternary alloy predicted to have the sulfur resistance comparable to fcc PdCu alloys with the higher permeability of bcc PdCu alloys.

Results: Lower Sulfur Binding Energy Predicted

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

	CO, eV	H_2O, eV	H_2S, eV
TiO_2 - Anatase	-0.32	-0.64	-1.93
TiO2 - 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
$Ce_{0.33}Zr_{0.33}E4_{0.33}O_2$	**-0.01**	**-0.83**	**-0.29**

	CO, eV	H_2S, 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 / **$Ce_{0.33}Zr_{0.33}E4_{0.33}O_2$**	**-0.32**	**-1.84**

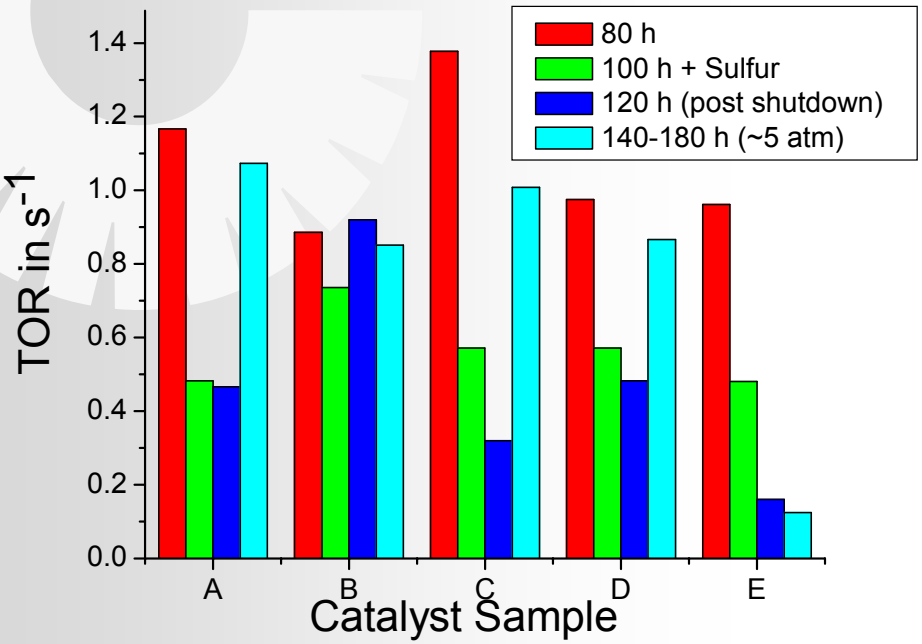


H_2S/Pt/J6-Doped TiO_2 Anatase(101)
Binding Energy: -2.02 eV/H_2S

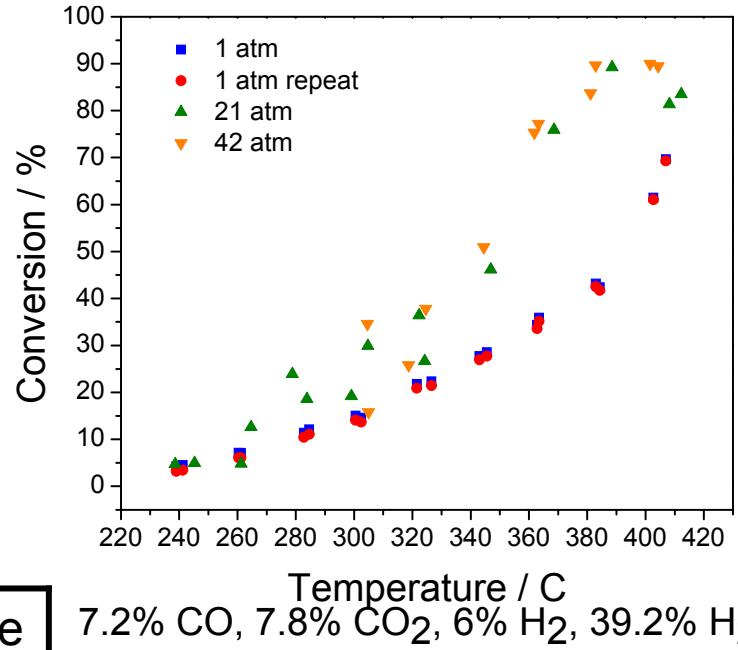
The electronic structure of doped oxides modifies that of Pt monolayer thus lowering CO, H_2S binding energies to Pt.

Catalyst Test Results Consistent with Modeling

RATE DATA AT 400 C - Normalized to 2% Pt



3.1%Pt-1.6%Re / $Ce_{0.36}Zr_{0.33}E4_{0.31}O_2$



7.2% CO, 7.8% CO_2, 6% H_2, 39.2% H_2O

		% 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