Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production

(DE-FC26-07NT43055)

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United Technologies Research Center

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Project ID #PD011

Overview & Objectives (Relevance)

- Timeline
  - 6/15/07 to 6/30/10
  - 97% complete
- Budget
  - $2571k ($2057k from DOE)
  - FY09 funding: $1024k
  - FY10 funding: $0k
- Partners
  - Power+Energy
    - Membrane separator fabrication
  - Metal Hydride Technologies
    - H_2 solubility measurements
  - Pall Corporation
    - Support tube development
- Barriers
  - K. Durability
  - L. Impurities
  - N. Hydrogen Selectivity
  - P. Flux

- Objectives
  - **Confirm the high stability and resistance of a PdCu trimetallic alloy** to carbon and carbide formation and, in addition, resistance to sulfur, halides, and ammonia
  - **Develop a sulfur, halide, and ammonia resistant alloy membrane** with a projected hydrogen permeance of 25 $m^3 m^{-2} atm^{-0.5} h^{-1}$ at 400 °C and capable of operating at pressures of 12.1 MPa (~120 atm, 1750 psia)
  - **Construct and experimentally validate the performance of 0.1 kg/day H_2 PdCu trimetallic alloy membrane separators** at feed pressures of 2 MPa (290 psia) in the presence of H_2S, NH_3, and HCl

DE-FC26-07NT43055 Project Status Scorecard

Dense metallic membranes can meet most DOE targets

Metric	2010 DOE Target	Current Project Status	Notes
Hydrogen Flux	200 $ft^3 ft^{-2} h^{-1}$	**61 $ft^3 ft^{-2} h^{-1}$ (P+E alloy)** **45 $ft^3 ft^{-2} h^{-1}$ (P+E alloy)**	• P+E alloy at 600 °C; 100 psig H_2 • P+E alloy at 450 °C; 200 psia H_2
Temperature	300–600 C	**350–600 C**	• UTRC ternary alloy limited to 475 °C
Sulfur tolerance	20 ppmv	**78 ppmv H_2S (P+E alloy)** 9 ppmv NH_3 (P+E alloy)	• Demonstrated with P+E alloy at 450 °C • Demonstrated 487±4 ppmv for 4 hours • Demonstrated 9 ppmv NH_3 for 175 hours
ΔP operating capability	Up to 400 psi ΔP	**200 psig**	• Current tube thicknesses limited to ≈200 psia
CO tolerance	Yes	**Yes**	• Demonstrated up to 13.3% CO at 90 psia total pressure; >9% CO at 304.7 psia
Hydrogen purity	99.5%	**99.9999%**	• P+E manufacturing design and manufacturing ensures no leaks • CO < 1 ppm, S < 15 ppbv desired for fuel cell applications

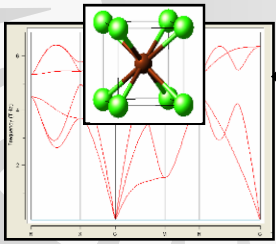
Milestone Schedule (Approach)

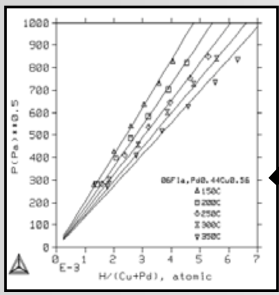
Project is on track to meet milestones; effort focused on Tasks 3 & 5

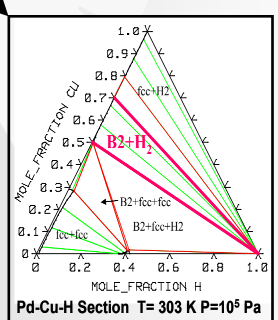
Task #	Project Milestone	Planned Start Date	Planned End Date	Percent Complete
1	Complete initial technical and economic modeling.	June 15, 2007	Dec. 31, 2007	100%
2	Complete advanced membrane property simulations by atomistic and thermodynamic modeling calculations.	June 15, 2007	Dec. 31, 2007	100%
3	Complete the design and construction of membrane separators using sulfur resistant palladium alloy and membrane separators using PdCuTM.	June 15, 2007	May 30, 2008	83%
3.1	Complete initial evaluation of Pd-alloy/nanoporous oxide membrane test articles.	Apr. 1, 2009	July 31, 2009	100%
4	Complete hydrogen solubility tests using various alloys for six-to-twelve separators, and predict hydrogen permeability performance.	Mar. 15, 2008	June 30, 2008	100%
5.2	Complete testing of "best of class" separators.	Mar. 15, 2008	Sep. 30, 2008	100%
5.2	Complete evaluation of Pd-alloy/nanoporous oxide membranes	Apr. 1, 2009	Mar. 31, 2010	70%
5.3	Complete evaluation of advanced PdCuTM separator units.	June 15, 2008	Apr. 30, 2009	0%
6	Complete the revised technical and economic modeling.	Dec. 1, 2008	Mar. 31, 2010	100%
6	Make recommendation for best development path to commercialization of hydrogen separation membranes.		Mar. 31, 2010	100%

Dense Metallic Pd Membranes Technical Approach

Experimental verification of commercial fcc & novel bcc-stabilized PdCu alloys



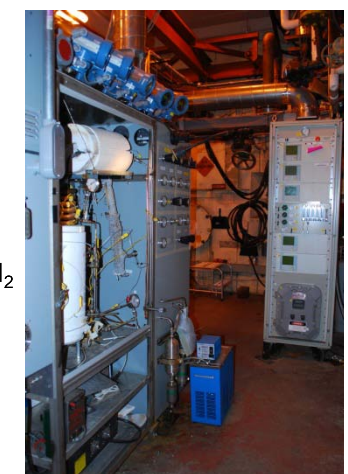




Virtual modeling of phase behavior & properties

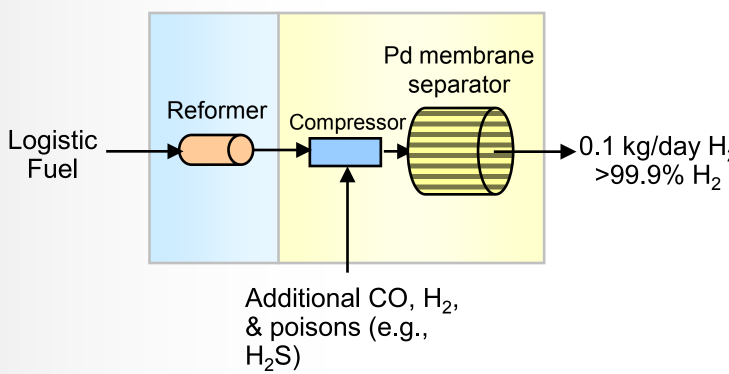
Construction of "best commercial" & virtually developed alloy separators

Low pressure laboratory screening: quantify performance



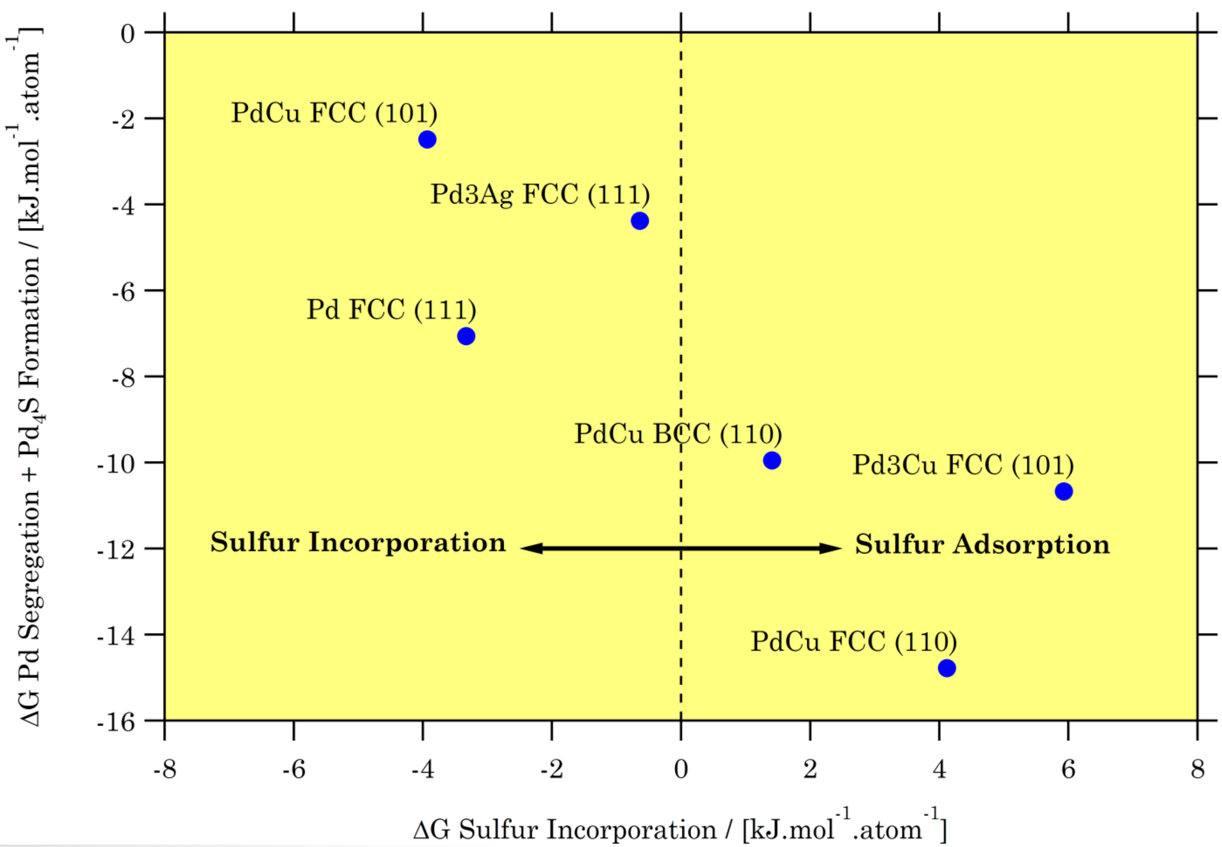
High pressure screening: quantify durability & poison resistance

- New capital installed for high pressure laboratory testing since DOE protocol established
- No longer a need to compress reformate



Technical: Atomistic Modeling

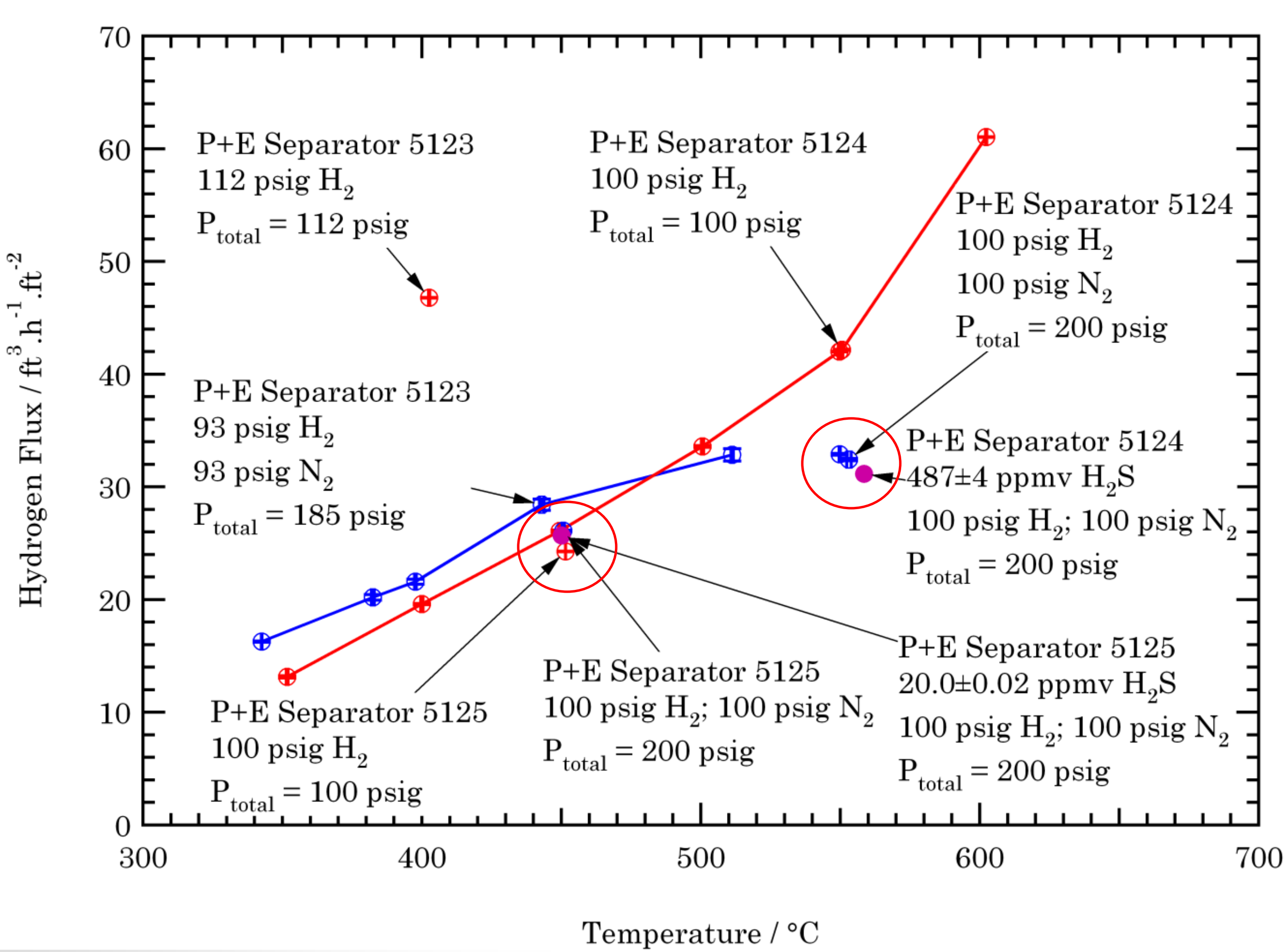
Development of modeling methodology to explain sulfur tolerance



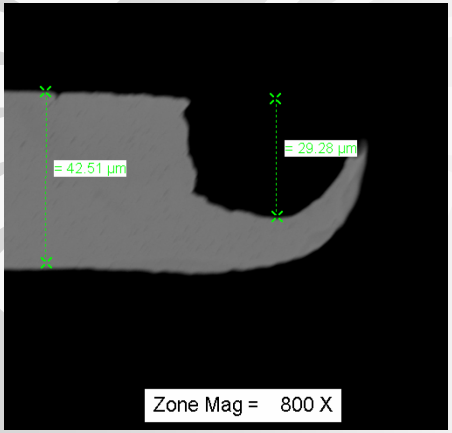
- PdAg alloys known to be sulfur intolerant
- NETL has shown that Pd can irreversibly convert to Pd_4S
- P+E PdCu alloys are sulfur resistant & do not irreversibly convert to Pd_4S
- Alloys that can incorporate sulfur into their lattice have an opportunity to make Pd_4S

Technical: Sulfur Tolerance & Flux

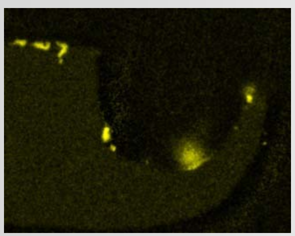
P+E fcc PdCu alloy performance ≥450 °C for H_2S in H_2/N_2 mixtures identical to runs without H_2S



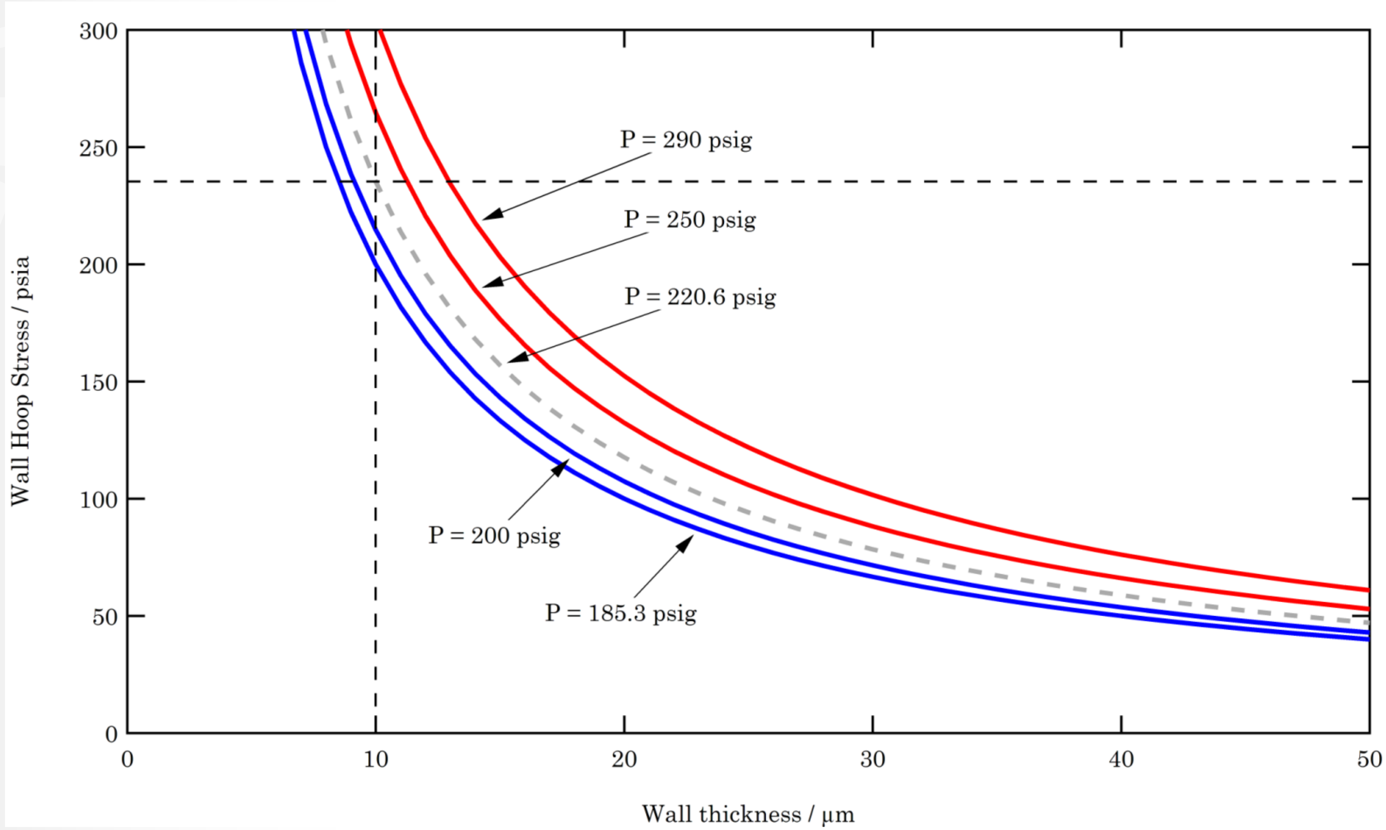
Technical: Tube Defects Reduce Operating Pressure



Cross-section of membrane failure point



EDS Sulfur Map



- Reported tube failures in 2009 on PdCu separators
  - Failures are not related to sulfur
- 10% of tubes have a defect from the manufacturing process
  - Mitigate with screening procedures & changes to process
- Tube defects limit operation to less than 220 psig
- Operation for >500 h demonstrated for 200 psia without failure

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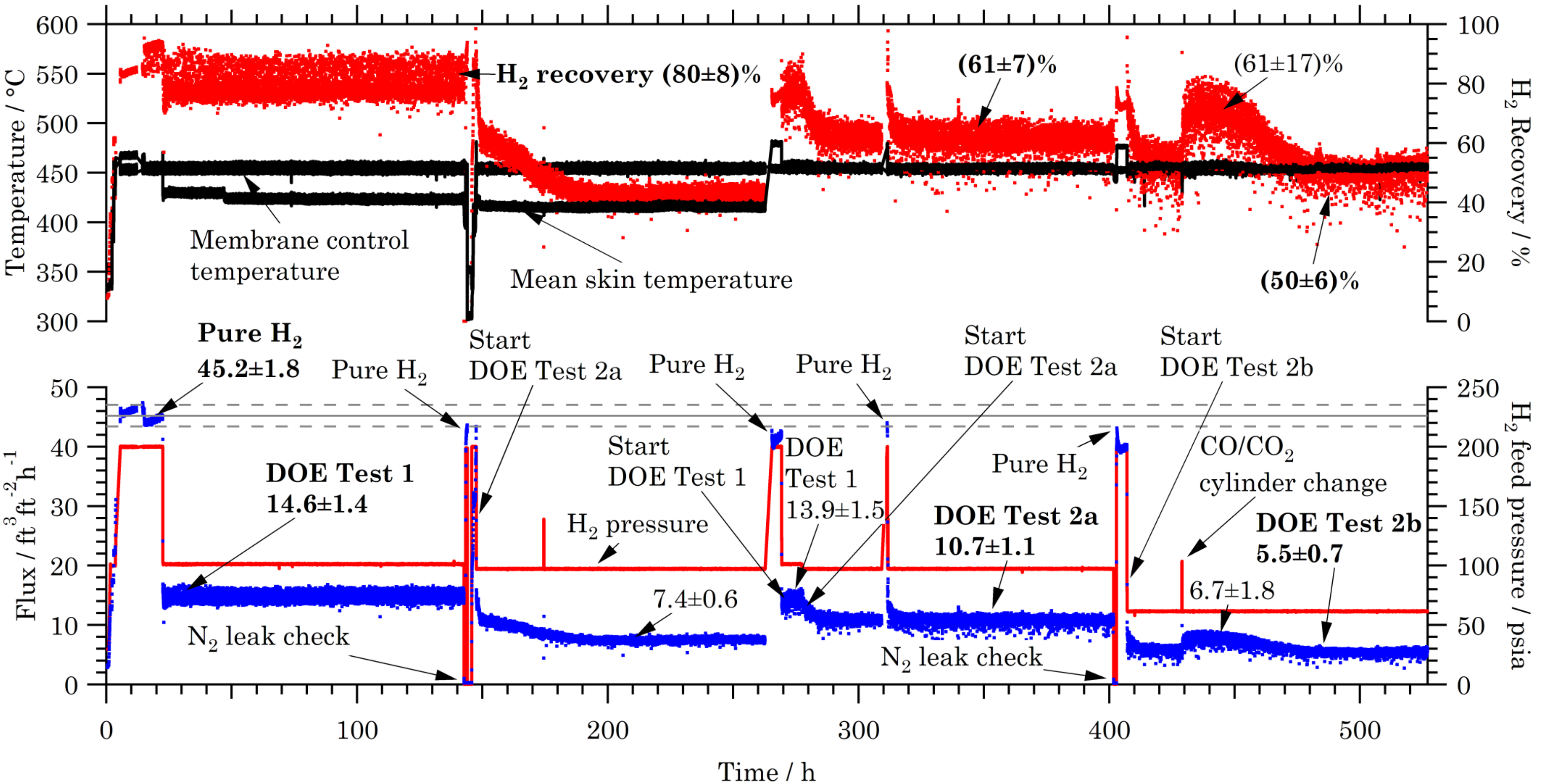
Technical: DOE Protocol Testing on fcc PdCu



- P+E Separator 5127
- 527 h at 450 °C & 200 psia
- DOE conditions 1, 2a, & 2b

Test condition	Hydrogen flux / $ft^3ft^{-2}h^{-1}$	Hydrogen recovery / %
Pure H_2	45.2±1.8	>80
Test 1	14.6±1.4	80±8
Test 1 repeat	13.9±1.5	
Test 2a	10.7±1.1	61±7
Test 2b	5.5±0.7	50±6

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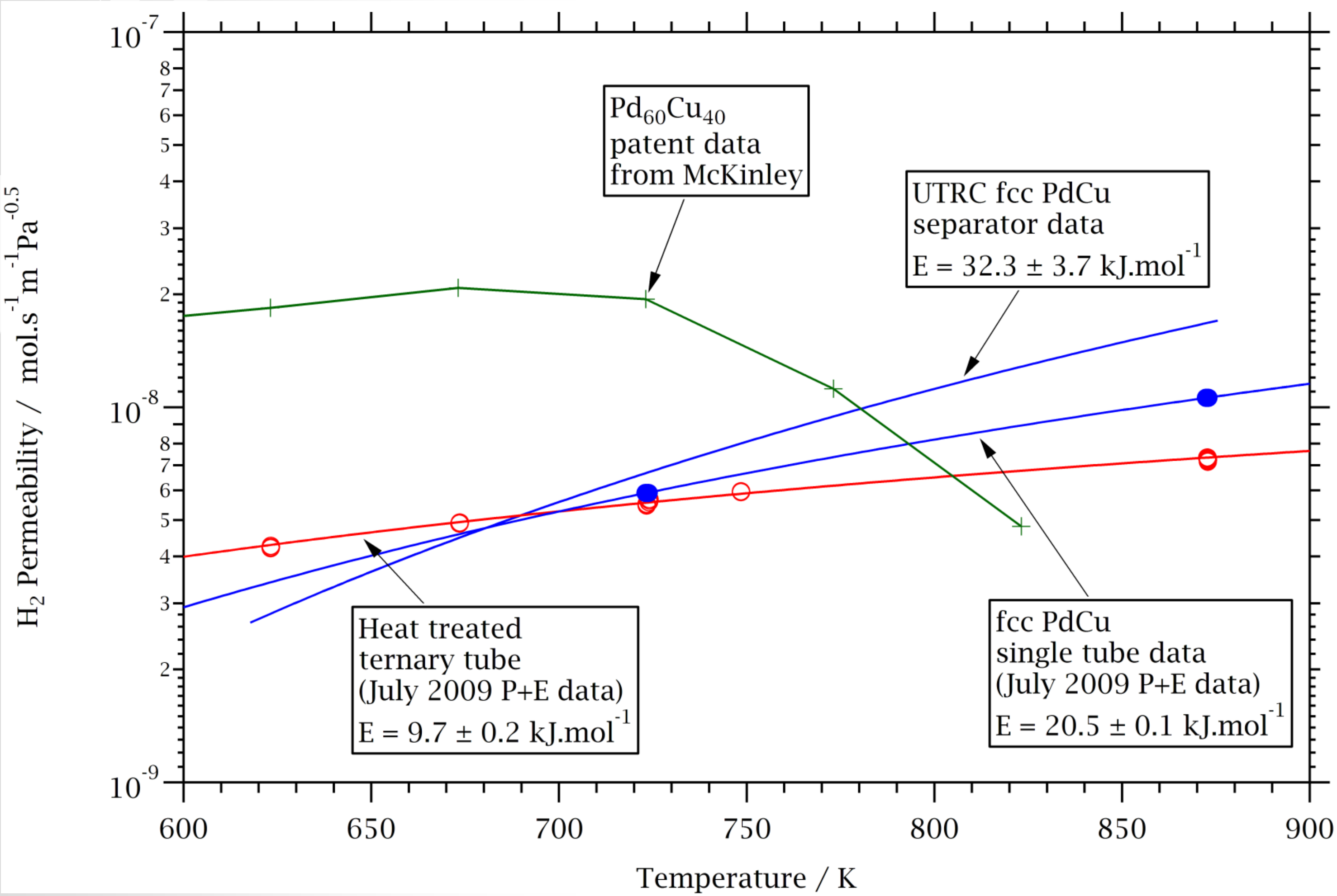
Technical: 2009 UTRC Ternary Alloy Performance



- Performance comparable to P+E fcc PdCu alloy
- Tube is 100% bcc on surfaces and in bulk, but appears to have TM oxide segregation that alters Cu/Pd ratio & thus H_2 diffusivity

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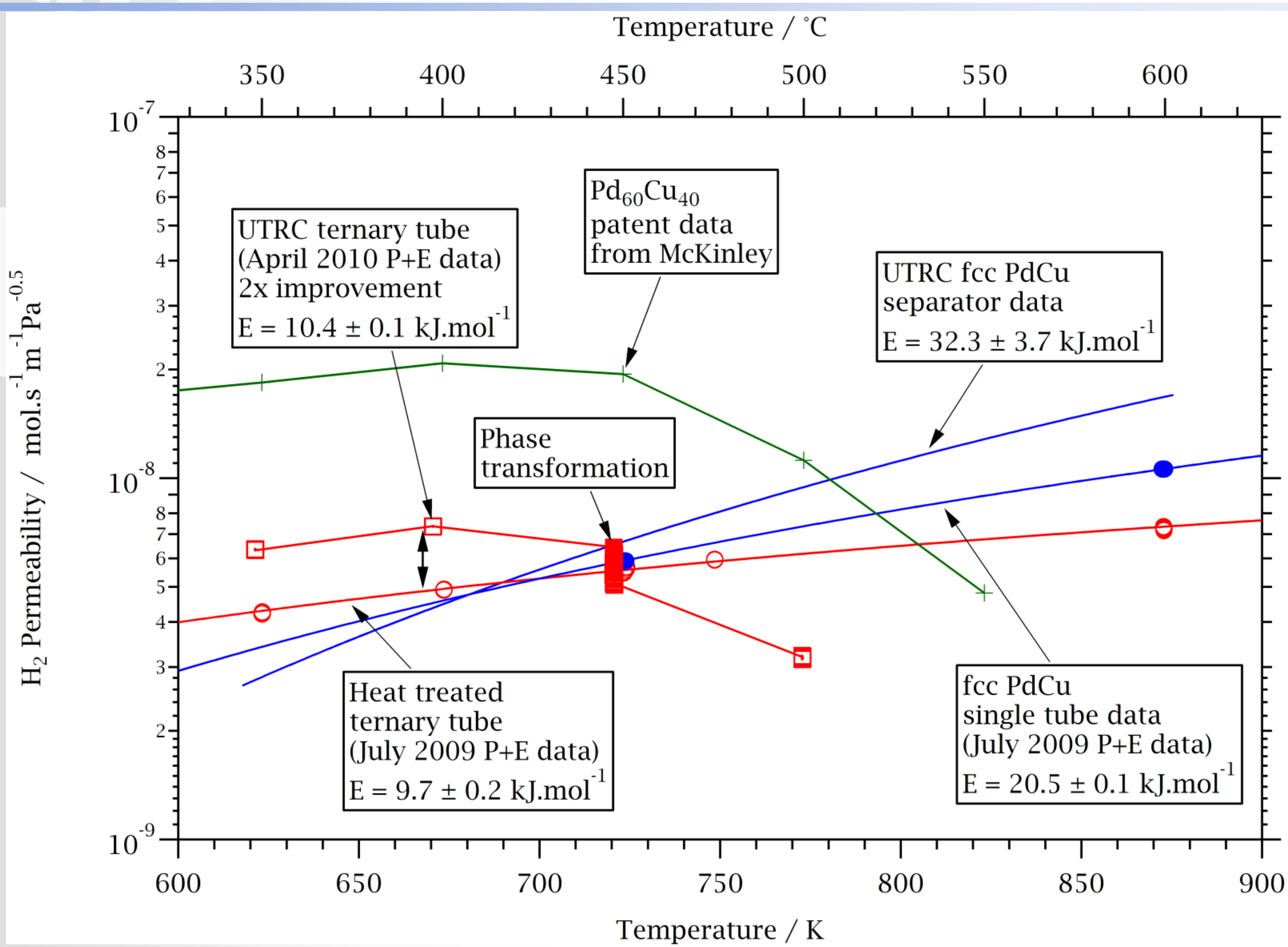
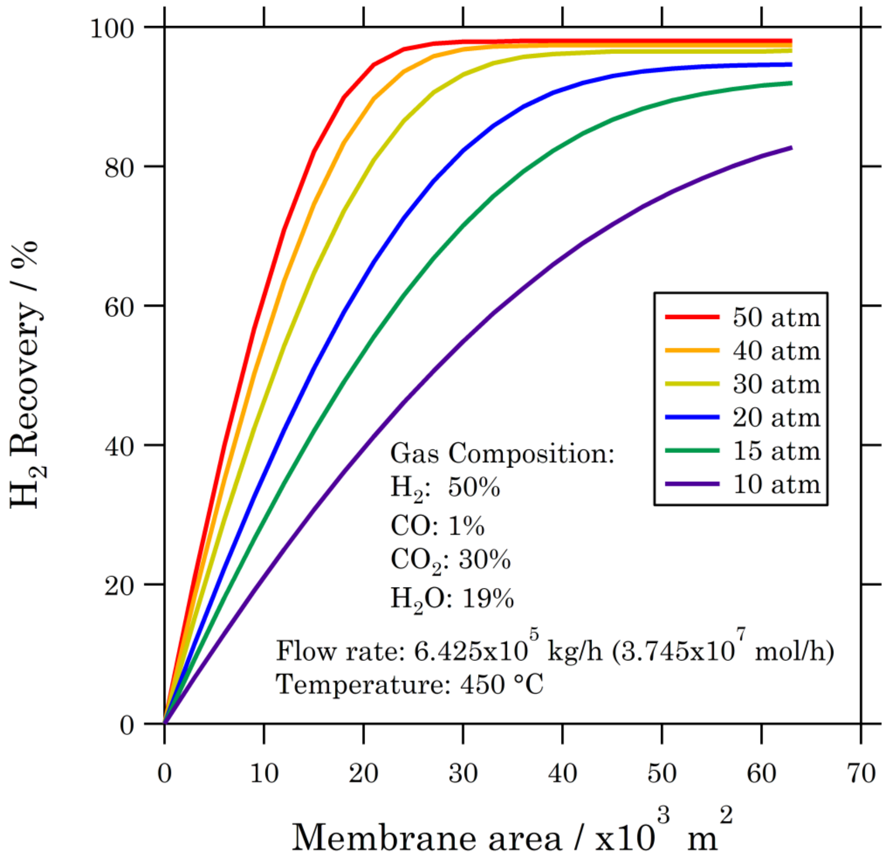
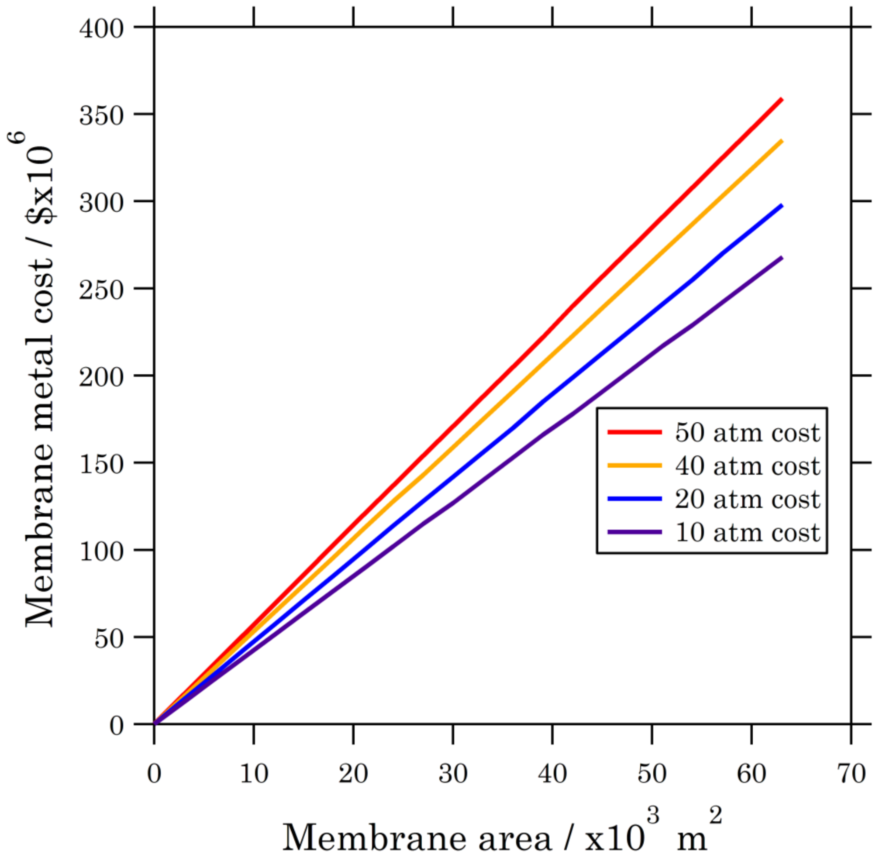
Technical: Surface Modification Improves Ternary 2X



- Additional characterization performed & polishing procedure implemented to remove surface layers
- Performance is 2× 2009 results

Technical: Techno-Economic Analysis for PdCu





- Flow rate typical of 520–640 MW gasifier systems
- Metal cost for dense metallic tubes = 400–530 $\$/ft^2$
  - Cost of Pd = \$9.38/g (7-year average); Cost of Cu = \$0.004/g
  - Total separator cost is approximately 2–4 times the metal cost
- Operating pressure affects tube thickness and H_2 recovery and thus cost
- Leasing and recycling of metal necessary to reduce separator cost

Collaborations

- Partners
  - Power+Energy (Industry)
    - Manufacture of hydrogen separators
    - UTRC alloy fabrication
  - Metal Hydride Technologies (Ted Flanagan from Univ. of Vermont)
    - Fundamental experiments on hydrogen solubility
    - Experimental measurements of alloy systems for thermodynamic phase modeling
- Technology Transfer
  - Colorado School of Mines (Robert Braun from Colorado School of Mines)
    - DOE project: *Coal/Biomass Gasification at the Colorado School of Mines*
    - Transferred permeability model for trade studies on using membranes in system analysis of integrated gasification fuel cell power plants (IGFC)

Future Work

Focus on UTRC alloy improvements & testing

- Construct ternary alloy separator for testing
- Conduct DOE testing protocol tests to validate performance and durability
- Move to larger scale demonstration (e.g., 100 lb/day H_2) with real gasifier exhaust in a follow on effort

Project Summary

- Developed an atomistic modeling screening approach for sulfur tolerance
  - Can virtually screen materials to see if they are susceptible to sulfur attack
- Evaluated performance of fcc PdCu separators under DOE testing protocol
  - Reconfirmed sulfur resistance & stability of PdCu alloy
  - Demonstrated understanding of tube defect issue limitation on current operating pressure levels
- Produced single tube separator with UTRC ternary composition
  - Compositional barrier formed on outer surface of membrane
  - Polishing process identified to remove surface barrier
  - Performance of membrane improved by 2x versus 2009 results