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

(DE-FC26-07NT43055)

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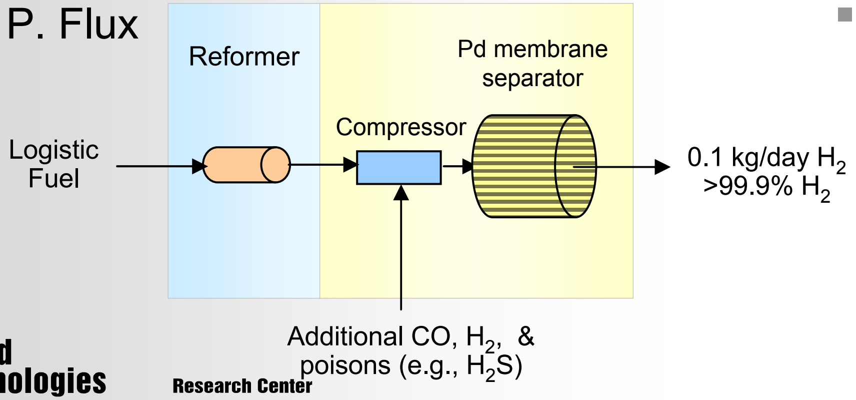
United Technologies Research Center

13 June 2008

Project ID #PD41

Overview & Objectives

- Timeline
  - 6/15/07 to 6/14/09
  - 42% complete
- Budget
  - \$1497k (\$1198k from DOE)
- Partners
  - Power+Energy
    - Membrane separator fabrication
  - Metal Hydride Technologies
    - H_2 solubility measurements
- 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 $m^3m^{-2}atm^{-0.5}h^{-1}$ 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

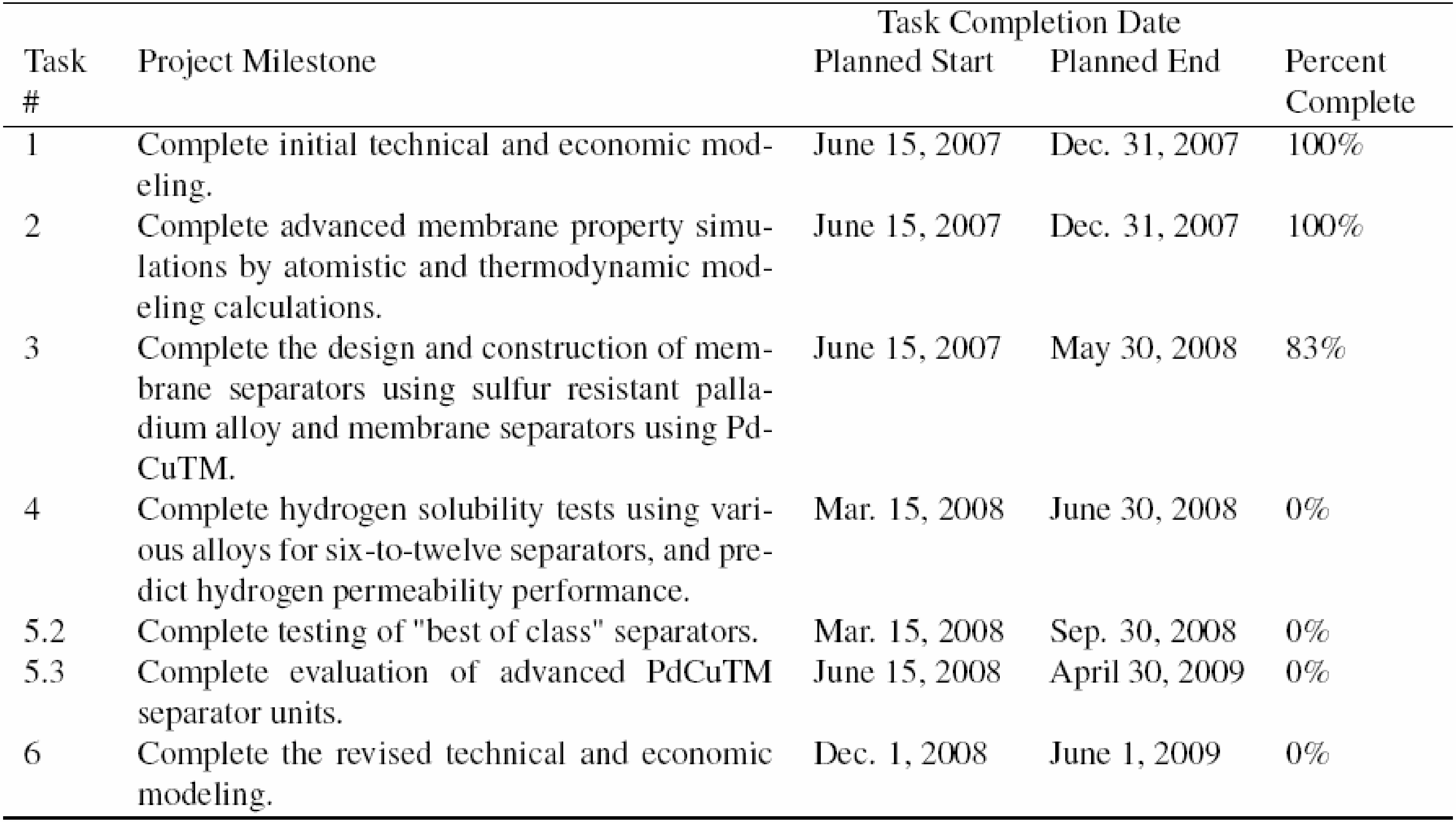
DE-FC26-07NT43055 Project Status Scorecard

P+E & UTRC alloy separators can meet or exceed DOE targets

Metric	**2010 DOE Target**	**Current Project Status**	**Notes**
Flux rate	200–250 $ft^3ft^{-2}h^{-1}$	**525 $ft^3ft^{-2}h^{-1}$ (UTRC alloy prediction)** **120 $ft^3ft^{-2}h^{-1}$ (P+E alloy, 400 °C)** **252 $ft^3ft^{-2}h^{-1}$ (P+E, 530 °C)**	- Alloy modeling predicts permeabilities much greater than PdCu (fcc) alloys - P+E alloy can exceed DOE target at temperatures ≈>480°C
Impurity tolerance	20 ppmv Sulfur CO/Coke tolerant	**5 ppmv H_2S (P+E alloy)** **11 ppmv NH_3 (P+E alloy)** CO/Coke tolerant	- P+E alloy tested subscale up to 200 hours at UTRC with no degradation - P+E demonstrated 800 h operation with 100 ppmv H_2S - Plan to test with >40 ppmv H_2S, HCl; and 10 ppmv NH_3
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
ΔP and T operating capability	Up to 400 psi ΔP 300–600 °C	**290 psid** **350 °C – 475 °C** (UTRC alloy) **350 °C – 600 °C** (P+E alloy)	- Facilities & current separator design limited to 20 atm testing
Cost	100–1000 $/ft²	137–600 $/ft² initial estimate	- Based on initial estimate of $5/scfh H_2
Durability	3 years	200 h (P+E alloy at UTRC)	- P+E proven more than 2 years operation - Planned demonstration up to 2000 h

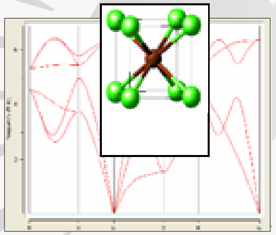
Milestone Schedule (DE-FC26-07NT43055)

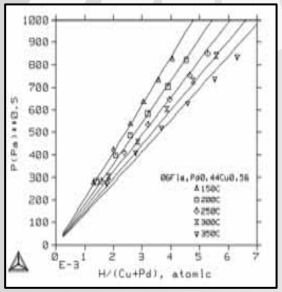
Project is on track to meet milestones

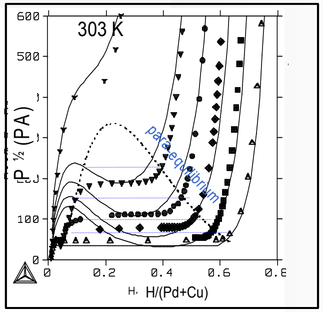


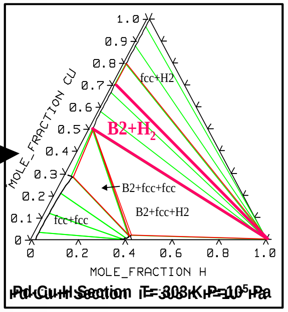
		Task Completion Date		
Task #	Project Milestone	Planned Start	Planned End	Percent Complete
1	Complete initial technical and economic modeling.	June 15, 2007	Dec. 31, 2007	100%
2	Complete advanced membrane property simulations by atomistic and thermodynamic modeling calculations.	June 15, 2007	Dec. 31, 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%
4	Complete hydrogen solubility tests using various alloys for six-to-twelve separators, and predict hydrogen permeability performance.	Mar. 15, 2008	June 30, 2008	0%
5.2	Complete testing of "best of class" separators.	Mar. 15, 2008	Sep. 30, 2008	0%
5.3	Complete evaluation of advanced PdCuTM separator units.	June 15, 2008	April 30, 2009	0%
6	Complete the revised technical and economic modeling.	Dec. 1, 2008	June 1, 2009	0%

Technical Approach

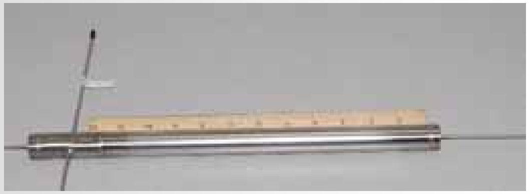








Virtual modeling of phase behavior and properties

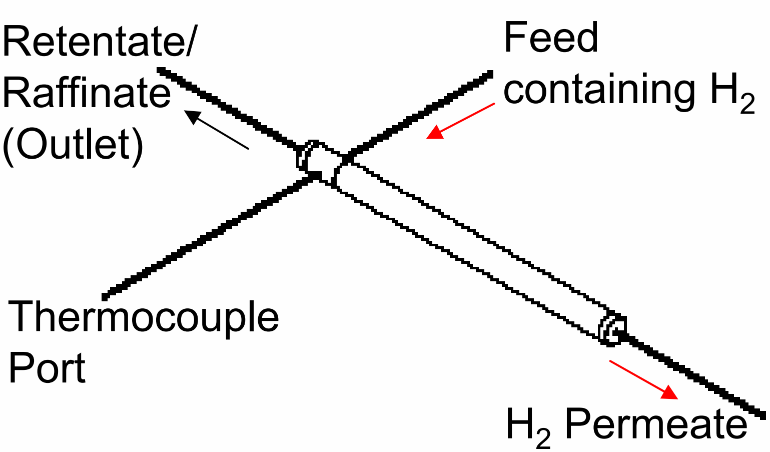


Construction of "best commercial" & virtually developed alloy separators

Low pressure laboratory screening: quantify performance

High pressure screening: quantify durability & poison resistance

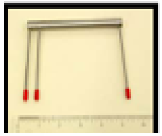
Power+Energy Membrane Separators



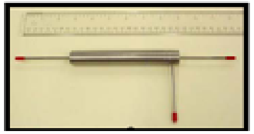
- Robust, scalable commercial design
- Design minimizes external mass transfer resistances
- Tubular design allows for membrane growth & leak free sealing
- Ten (10) separators delivered by P+E
    - Five (5) with P+E PdCu alloy
    - Five (5) with UTRC alloy
- Two (2) additional separators to be delivered mid-year

High Capacity 1300 slpm
Modular H_2 Purifier System

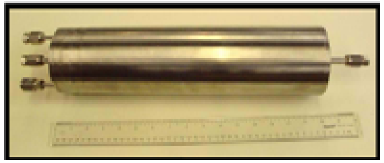
100 Watt
5" x 0.5"



500 Watt
6" x 0.75"



50 kWatt
16"x 4"



Laboratory Screening Rig (≤6 atm)

- Steam generator for H_2O addition to gas mixture
- Operation from 1–6 atm (absolute)
- Furnace capable of temperatures 300–650 °C
- Capable of simulating different gas compositions (CO, H_2, CO_2, N_2) from cylinders and house H_2
- Addition of poisons from gas cylinders or water supply
- Computer automated testing plans

Laboratory Screening Tests

Quantify separator permeability & effects of major gas species

Permeability

Flux

$$J = \underbrace{\frac{Q_{\text{eff}}}{l}}_{\text{Permeance}} \left(P_1^{0.5} - P_2^{0.5}\right)$$

Hydrogen driving force

Effective Permeability Neglecting External Mass Transfer Resistance

$$\begin{aligned} Q_{\text{eff}} &= \frac{aQ_0}{1+\sum K_i p_i} \\ &= \frac{aQ_{H_2}}{1+K_{CO}p_{CO}+K_{CO_2}p_{CO_2}+K_{H_2O}p_{H_2O}+K_{N_2}p_{N_2}} \end{aligned}$$

Experimental Objectives

- Obtain separators' permeability as a function of temperature with pure H_2 (Q_{H2})
- Quantify the effect of different non-poison gas species on H_2 permeability
- Determine adsorption coefficients (K_i) for each significant gas species

Pressurized Reformate Testing Rig (>10 atm)

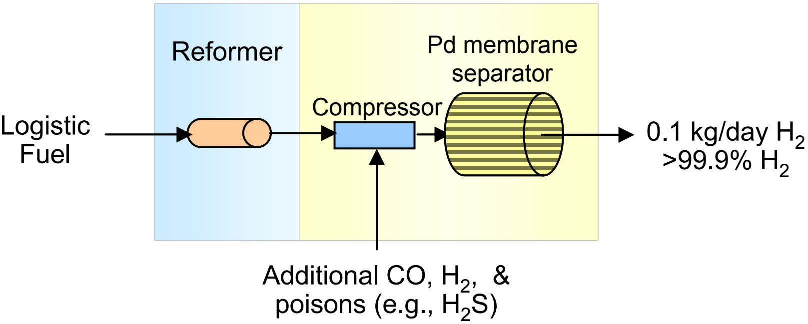
Rig is under construction. Reformer capability enabled; fully operational May.

Emissions Cart
(Gas conditioning
& analysis)

Test area
(Reformer,
Furnace, Steam
Generation, &
Membrane)

Real-time Controls
& Data Acquisition

Process Controls
Cabinet


Reformer

Pd membrane separator

Compressor

Logistic Fuel

0.1 kg/day H_2
>99.9% H_2

Additional CO, H_2, & poisons (e.g., H_2S)

Test Configuration

High Pressure Tests on Real Reformate

Quantify separator durability & effects of poisons

Effective Permeability Neglecting External Mass Transfer Resistance

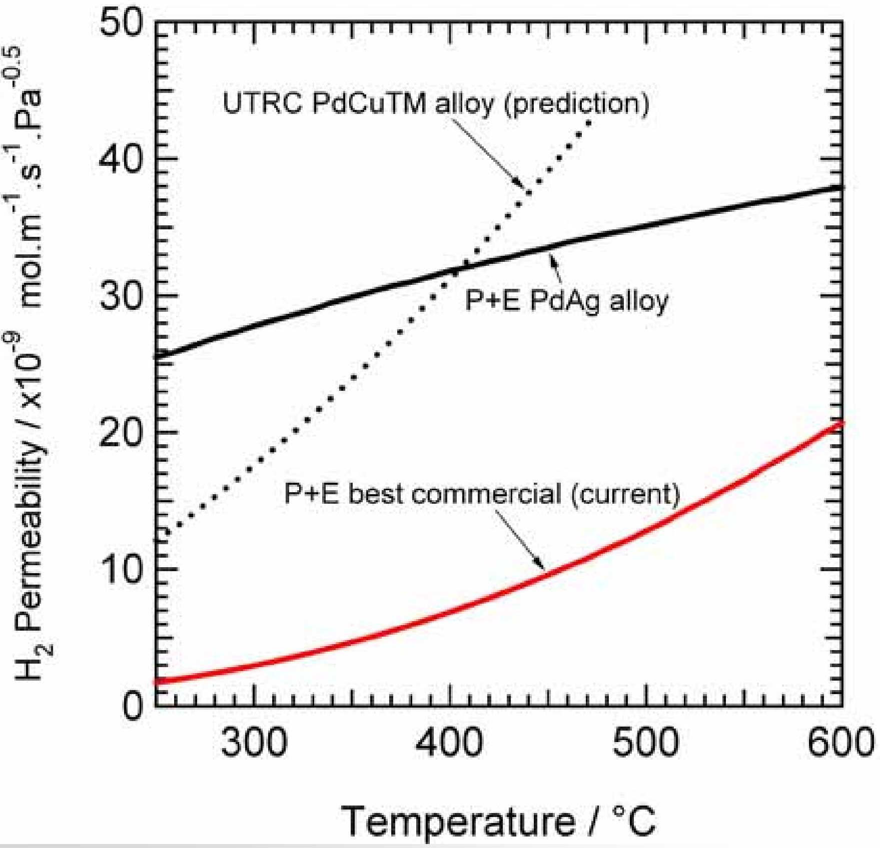
$$Q_{\mathrm{eff}} = \frac{aQ_{H_2}}{1 + \underbrace{K_{CO}p_{CO} + K_{CO_2}p_{CO_2} + K_{H_2O}p_{H_2O} + K_{N_2}p_{N_2}}_{\text{Values from laboratory experiments}} + \underbrace{K_{H_2S}p_{H_2S} + K_{HCl}p_{HCl} + K_{NH_3}p_{NH_3}}_{\text{Quantify during reformate higher pressure tests}}}$$

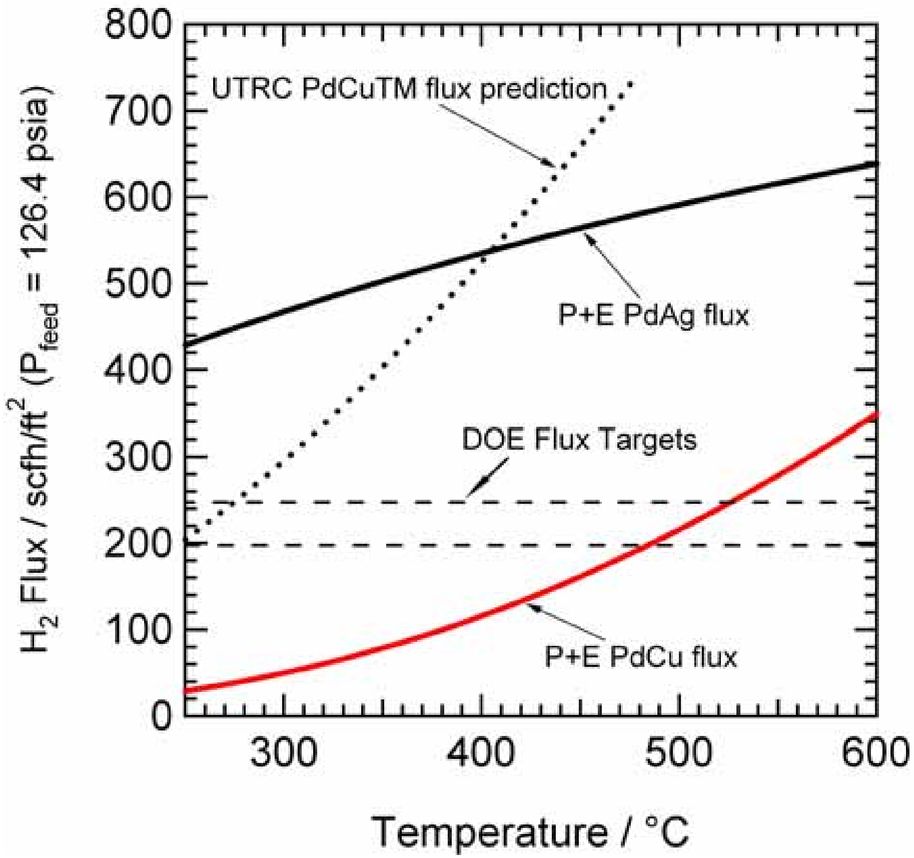
Experimental Objectives

- Quantify effect of three poisons on separators' H_2 permeability
- Operate separators off of "real" gas generated from reformed diesel
- Evaluate 500-h durability of separators
- Downselect best separator alloy for longer durability testing (2000 h)

Hydrogen Flux/Permeability for Different Alloys

Commercial P+E alloy separator can satisfy DOE's membrane requirements





- Modeling projections for UTRC PdCu ternary alloy satisfy DOE flux targets at all operating temperatures
- P+E commercial PdCu alloy meets DOE targets above 480 °C

Preliminary Effect of Major Gas Species on PdCu Separators

Gas species compete reversibly with H_2; CO adsorption most dominant

Preliminary fcc permeability results

$$Q_{\text{eff}} = \frac{Q_{H_2}}{1 + K_{CO}p_{CO} + K_{CO_2}p_{CO_2} + K_{H_2O}p_{H_2O} + K_{N_2}p_{N_2}}$$

$$Q_{H_2} = exp\left(-18.795 + 4.8187\left(1 - \frac{673.15\text{ K}}{T}\right)\right) = 8.5\times10^{-7}exp\left(\frac{-26968}{RT}\right)$$

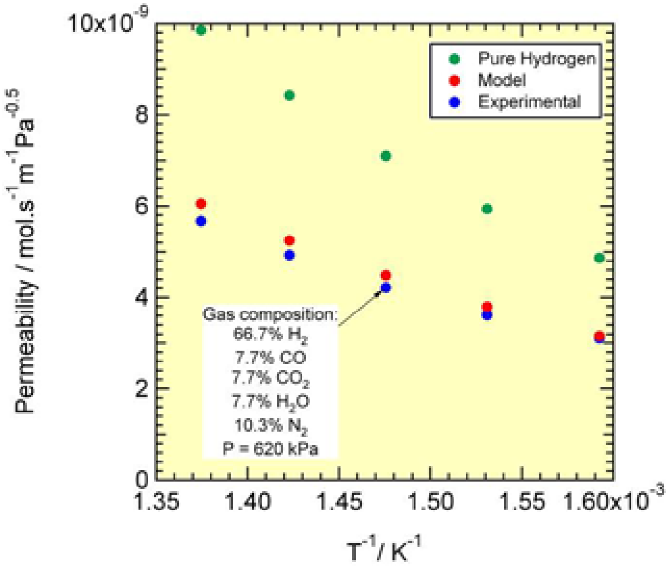
$$K_{CO} = exp\left((-11.831 \pm 0.115) + ln\frac{T}{673.15\text{ K}}\right) = 1.08\times10^{-8}T$$

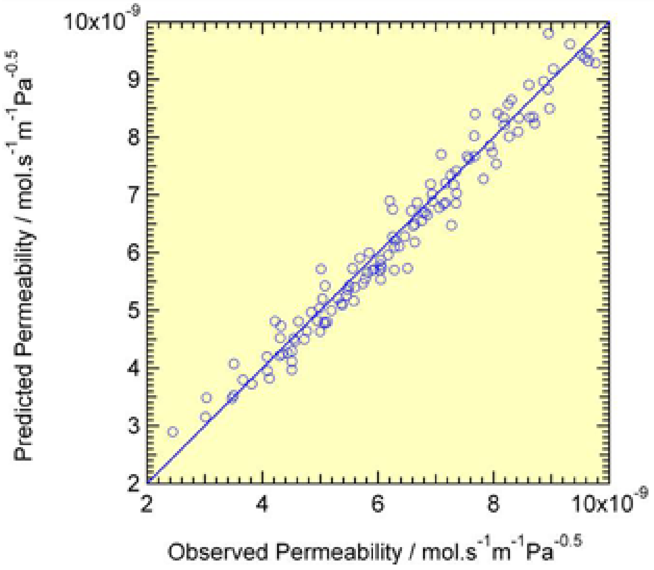
$$K_{CO_2} = exp\left((-13.134 \pm 0.223) + ln\frac{T}{673.15\text{ K}}\right) = 2.94\times10^{-9}T$$

$$K_{N_2} = exp\left((-13.551 \pm 0.111) + ln\frac{T}{673.15\text{ K}}\right) = 1.94\times10^{-9}T$$

$$K_{H_2O} = exp\left((-13.6 \pm 0.156) + ln\frac{T}{673.15\text{ K}}\right) = 1.84\times10^{-9}T$$

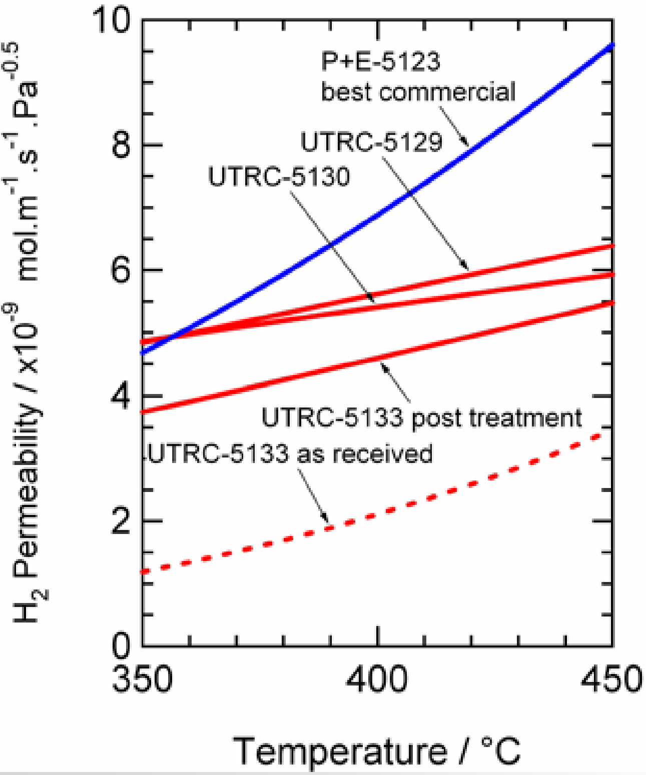
- Single separator preliminary results based on 123 experiments
  - T= 353 °C – 455 °C; P = 203 kPa – 620 kPa (29.4 – 89.9 psia)
  - Pure H_2 tests
  - Mixtures H_2–N_2, H_2–CO–H_2O, H_2–CO_2–H_2O, H_2–H_2O
- Weak temperature dependence on adsorption over experimental range (≈100 °C)
  - Heats of adsorption statistically insignificant
  - Linear temperature dependency describes data
- Model agreement within 5.2% on validation mixture composition
  - 66.7% H_2, 7.7% CO, 7.7% CO_2, 7.7%H_2O, 10.3% N_2

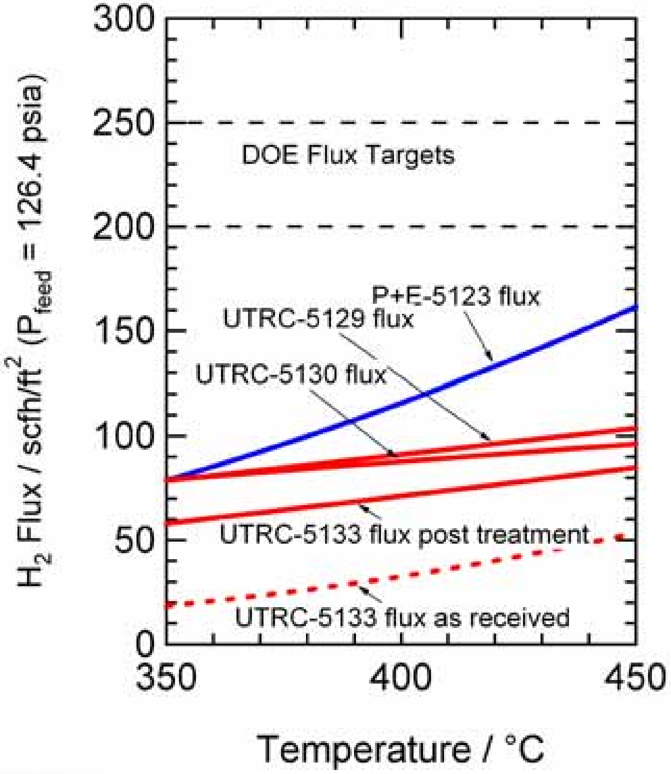


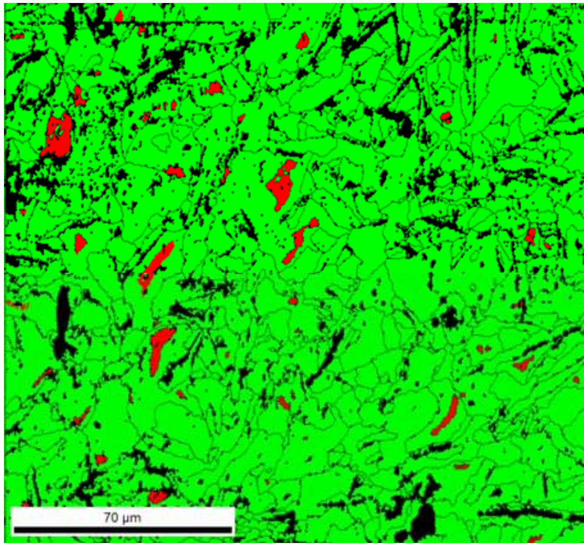


Permeability of UTRC Alloy Separators Less Than Expected

Characterization indicates presence of binary alloy on surface







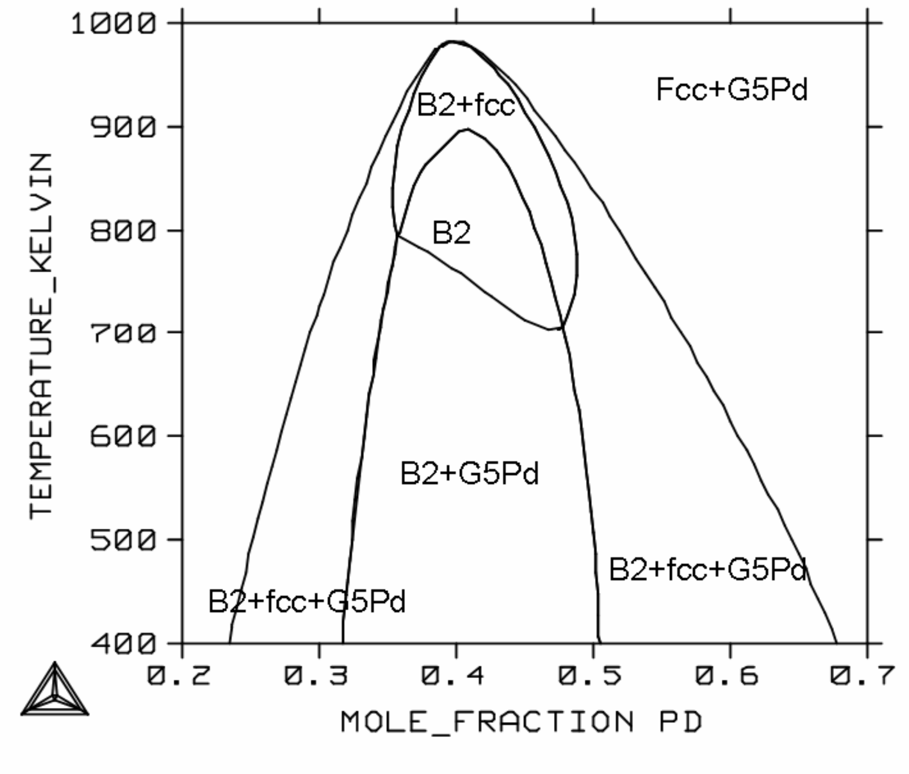
EBSD phase map

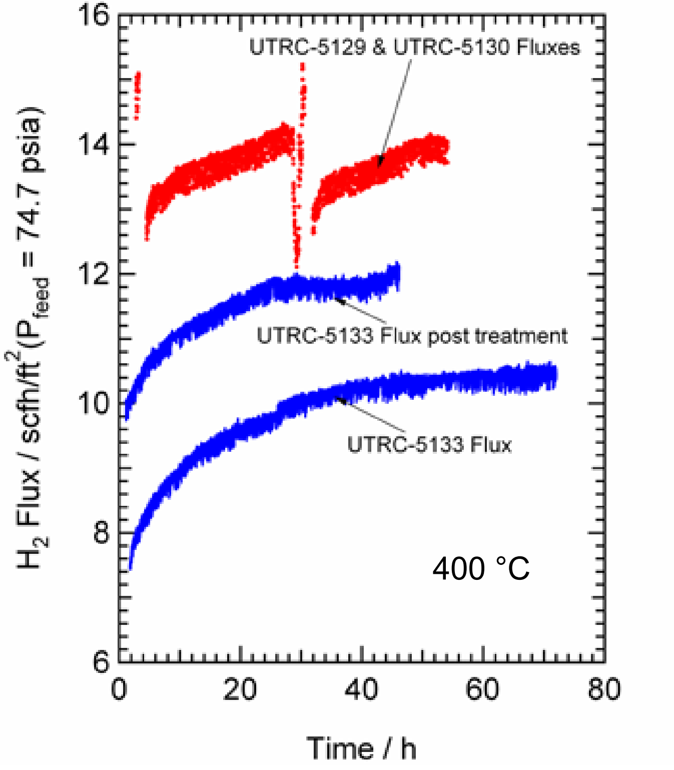
Green = PdG5; Red = PdCu

- Electron Backscatter Diffraction (EBSD) on individual tube indicates presence of binary Pd alloy covering surface of membrane
- Surface alloy layer 500 Å – 700 Å thick by microprobe analysis
- Heat treatments to desegregate/homogenize can improve membrane

Removal of Low Permeability Binary by Thermal Treatment

Homogenization/Desegregation work in progress

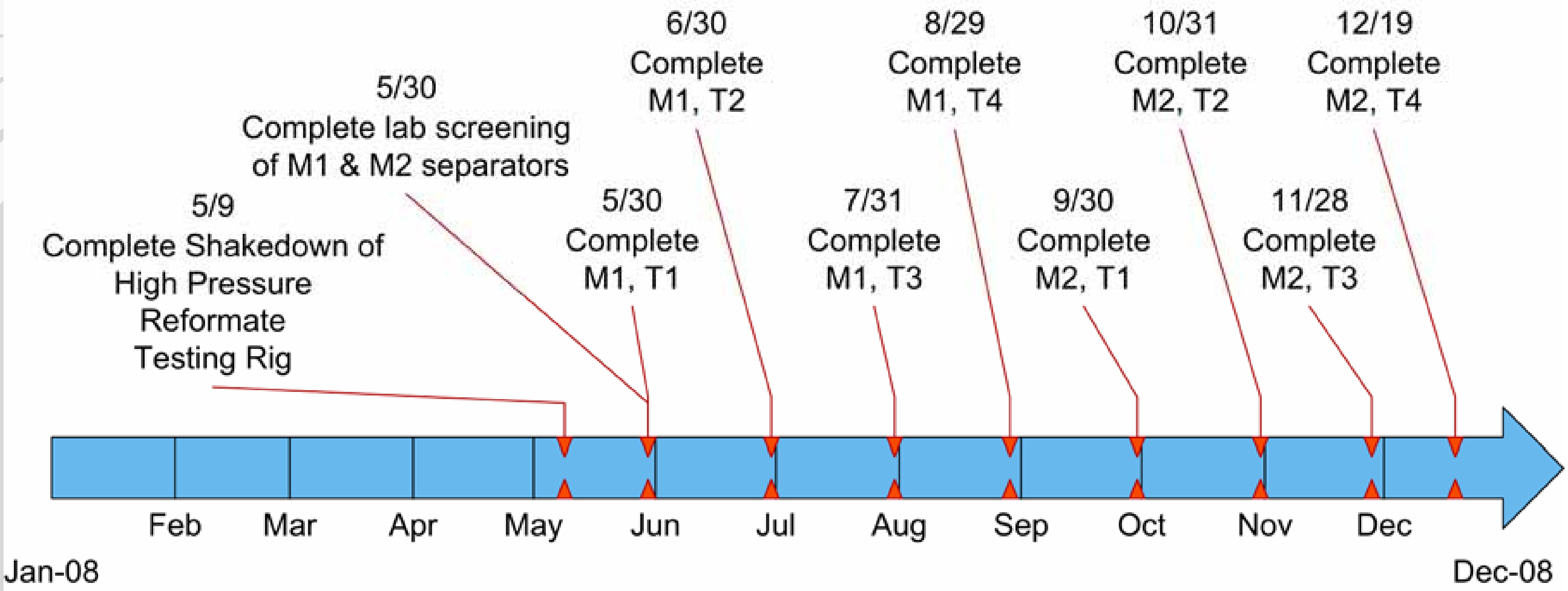




- UTRC alloy contains 47 at% Pd, targeting B2 phase
- Surface binary alloy between Pd & G5 element exists at low and high temperatures
- Binary could be formed during initial melt or during separator construction
- Heat treatments & quenching improves performance
- Etching may be necessary to remove surface resistance

Future Work

Focus on P+E alloy testing & UTRC alloy improvements



- Each reformate test will nominally be 500 h
- Nomenclature
  - M1 = P+E alloy; M2 = UTRC alloy
  - T1: Reformate with baseline sulfur in fuel
  - T2: Reformate plus H_2S (<100 ppm H_2S)
  - T3: Reformate plus NH_3 (<15 ppm NH_3)
  - T4: Reformate plus HCl (<100 ppm HCl)
- Follow-on tests (end 2008 to mid 2009)
  - Test with a reduced steam to carbon ratio for 500 h
  - 2000 h durability demonstration with poisons

Project Summary

- Constructed ten (10) commercially manufactured separators for evaluation

- Evaluated performance of first fcc PdCu separator
  - Quantified effect of CO, CO_2, N_2, and H_2O on H_2 permeability
  - Commercial unit can meet DOE flux targets for T>480 °C

- Produced five (5) separators with UTRC ternary composition
  - Phase segregation occurred on outer surface of membrane
  - Work in progress to improve current separator performance

- Opportunity to improve on UTRC alloy separator performance
  - Construction of two additional separators

- Higher pressure experiments using poison-doped reformate to be conducted this year
  - Quantify effect of H_2S, HCl, and NH_3 on H_2 permeability

Acknowledgments

- United Technologies Research Center
  - Testing: John Costello, Tom Hale, Robert Hebert, Gayle Marigliani, Jeffrey Walker, & Ying She
  - Atomistic Modeling: Susanne Opalka
  - Characterization: Jeff Covington, Bruce Laube, & C. Barila
  - Resources: Zissis Dardas, Dan Pfau, & Craig Walker

- Power+Energy
  - Albert Stubbmann & Peter Bossard

- Metal Hydride Technologies
  - Ted Flanagan

- U.S. Department of Energy
  - Arun Bose & Daniel Cicero

Additional Slides

- No responses to reviewers: project began in June 2007
- Publications & presentations
- Critical assumptions & issues

Publications & Presentations

Includes work from DE-FC26-05NT42453 & DE-FC26-07NT43055

S. M. Opalka, T. H. Vanderspurt, S. C. Emerson, W. Huang, D. Wang, T. Flanagan, and Y. She, “Modeling of B2 Phase PdCuTM Alloy Hydrogen Selective Membrane Performance,” invited presentation at 2008 TMS Annual Meeting, New Orleans, LA, March 9-13, 2008.

S. M. Opalka, W. Huang, D. Wang, T. B. Flanagan, O. M. Løvvik, S. C. Emerson, Y. She, and T. H. Vanderspurt, “Hydrogen interactions with the PdCu ordered B2 alloy,” J. Alloys Compd., 2007, 446-447, 583. doi:10.1016/j.jallcom.2007.01.130

W. Huang, S. M. Opalka, D. Wang, and T. B. Flanagan, “Thermodynamic Modeling of the Cu-Pd-H system,” CALPHAD, 2007, 31, 3. doi:10.1016/j.calphad.2007.02.002

S.M. Opalka, R. C. Benn, S. C. Emerson, T. B. Flanagan, W. Huang, Y. She, D. Wang, T.H. Vanderspurt, “Modeling of a stable, high permeability, sulfur resistant B2 phase PdCuTM alloy,” presentation at the 234th ACS National Meeting, Boston, MA, August 19-23, 2007.

S. M. Opalka, W. Huang, D. Wang, T. B. Flanagan, O. M. Løvvik, S. C. Emerson, Y. She, and T. H. Vanderspurt, “PdCu B2 Hydrogen Interactions under Advanced Water Gas Shift Membrane Reactor Conditions,” presented at the 20th North American Catalysis Society Meeting, Houston, TX, June 17-22, 2007.

O. M. Løvvik and S. M. Opalka, “Modeling the effect of adsorbates on the surface segregation of binary alloy surfaces,” presentation at the American Physical Society Annual Meeting, Denver, Co, March 5-9, 2007.

S. M. Opalka, W. Huang, O. M. Løvvik, D. Wang, T. B. Flanagan, S. C. Emerson, Y. She, and T. H. Vanderspurt, “Hydrogen interactions with the ordered BCC PdCu alloy,” invited presentation at International Symposium on Metal-Hydrogen Systems, Lahaina, HI, October 1-6, 2006.

Critical Assumptions & Issues

- Assumptions
    - Successful formation of UTRC ternary alloy on first attempt
    - Virtual modeling of alloy will result in high permeability material
    - UTRC alloy will be stable to temperature and poisons
- Issues
    - Need to perform further thermal and possibly chemical treatments of UTRC separators to increase performance
    - Need to manufacture final two separators to ensure UTRC alloy is formed without impurity phases on surface