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

(DE-FC26-07NT43055)

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United Technologies Research Center

22 May 2009

Project ID #PD_48_Emerson

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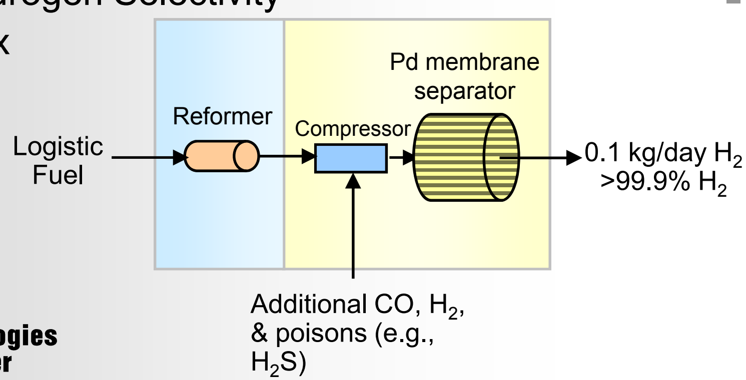
DOE Hydrogen Program

Overview & Objectives (Relevance)

- Timeline
  - 6/15/07 to 6/14/09
  - 88% complete
- Budget
  - $1497k ($1198k from DOE)
  - FY08 funding: $535k
  - FY09 funding: $163k
- 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

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DE-FC26-07NT43055 Project Status Scorecard (Relevance)

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

Metric	2012 DOE Target	Current Project Status	Notes
Hydrogen Flux	200 $ft^3ft^{-2}h^{-1}$	**61 $ft^3ft^{-2}h^{-1}$ (P+E alloy)** **200 $ft^3ft^{-2}h^{-1}$ (UTRC alloy prediction)**	▪ P+E alloy at 600 °C; 100 psig H_2 ▪ UTRC alloy predicted to be 200 $ft^3ft^{-2}h^{-1}$ by atomistic modeling at ≈475 °C with current tube thicknesses
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	**290 psig**	▪ Facilities & current separator design limited to 20.7 atm (290 psig) testing
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

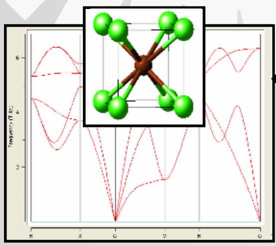
Milestone Schedule (Approach)

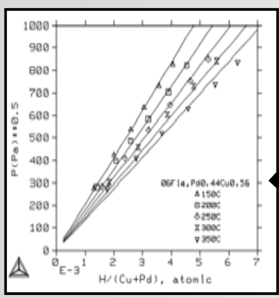
Project is on track to meet milestones; effort focused on Tasks 3 & 5

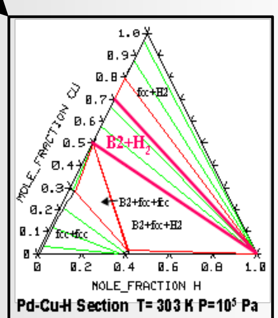
Task #	Project Milestone	Planned Start Date	Planned End Date	Percent Complete
1	Complete initial technical and economic modeling.	June 15, 2007	Dec. 31, 2007	100%
2	Complete advanced membrane property simulations by atomistic and thermodynamic modeling calculations.	June 15, 2007	Dec. 31, 2007	100%
3	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%
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	50%
5.3	Complete evaluation of advanced PdCuTM separator units.	June 15, 2008	April 30, 2009	50%
6	Complete the revised technical and economic modeling.	Dec. 1, 2008	June 1, 2009	0%

Technical Approach

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







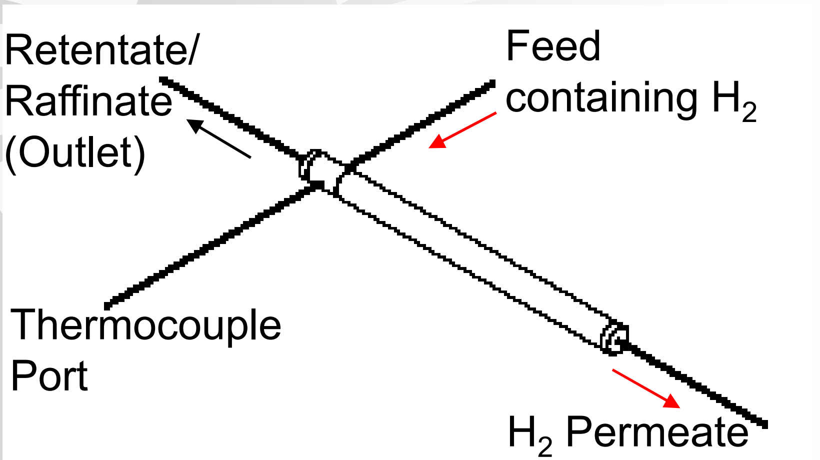
Virtual modeling of phase behavior & properties

Construction of "best commercial" & virtually developed alloy separators

Low pressure laboratory screening: quantify performance

High pressure screening: quantify durability & poison resistance

Power+Energy Membrane Separators (Approach)



- Robust, scalable commercial design
- Design minimizes external mass transfer resistances
- Tubular design allows for membrane growth & leak free sealing

Hydrogen Separation Module delivered to US Navy for Logistic Fuels Processing for 50 kW Fuel Cell Demonstration

Second Generation membrane assembly incorporates sulfur tolerant membranes

P+E performs 100% inspection and testing of incoming membranes in its Automated Testing and Inspection Area

Next generation PE9000S Hydrogen Purifiers incorporating P+E microchannel membranes

Each 24” unit has a capacity of 1370 slpm

Power+Energy™
Fueling the Hydrogen Economy

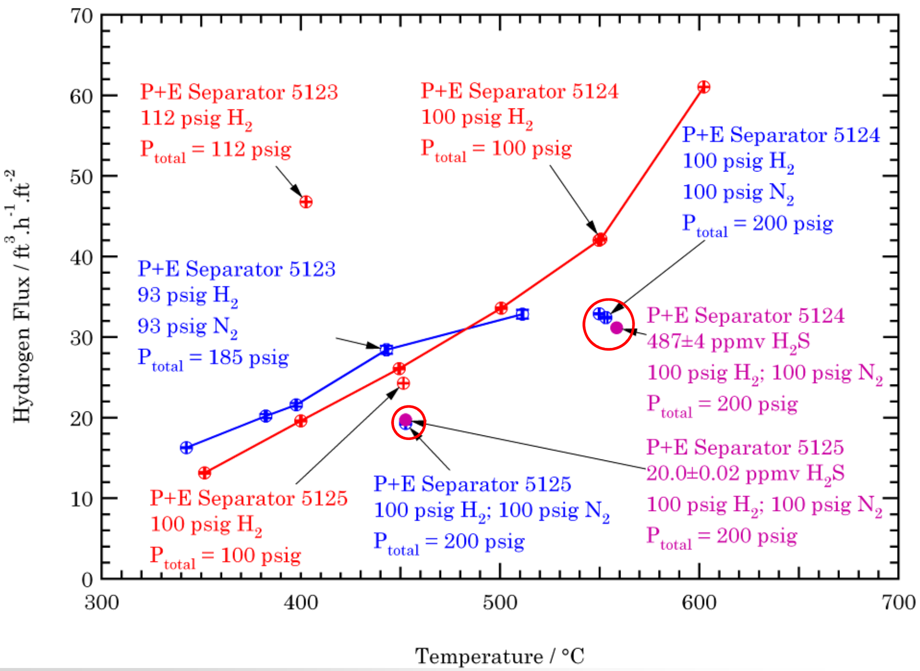
Technical: Membrane Separator Testing

Task 5 Summary

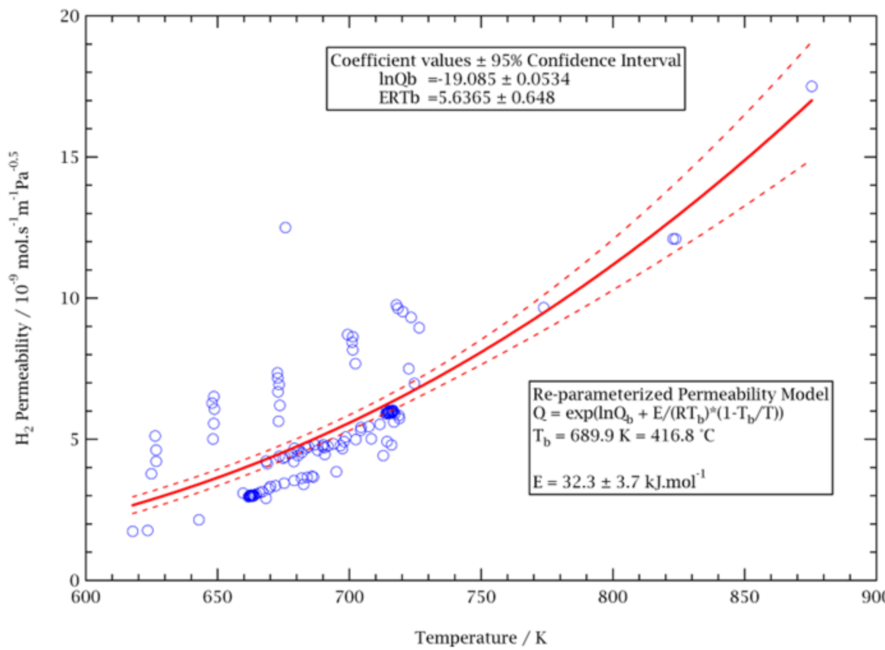
- Logistic fuel reformer test stand completed (high pressure test rig)
  - More difficult than expected to integrate rig components
  - Necessary to avoid prohibitive costs of gas cylinders & enable testing with "real" reformate gases for durability testing
- Tests of fcc PdCu alloy performed at high pressure
  - Demonstrated flux of 61 scfh/ft^2 with 100 psig H_2
  - Pressures of 290 psig with high temperatures can result in failures of membrane tubes with defects
- Achieved DOE sulfur target
  - 26 scfh/ft^2 stable flux with 20 ppmv H_2S at 200 psig (100 psig H_2), 450 °C
  - Operated >100 h with 33–78 ppmv H_2S with no loss in flux
- Next six months of project focused on durability testing
  - Evaluate separators for durability in the presence of H_2S, NH_3, and HCl
  - Demonstrate 500-2000 h durability

Technical: Summary of fcc PdCu Performance

Best expt. flux of 61 $ft^3ft^{-2}h^{-1}$at current thickness; membranes H_2S resistant



Flux data for fcc PdCu alloy



Permeability data for fcc PdCu alloy

- Best measured flux of 61 scfh/ft^2 on pure H_2
- Flux with >20 ppmv H_2S identical to sulfur free flux
- Some variation in separator performance
- Furnace temperatures of 400 °C–770 °C ***and 290 psig*** result in defective tube failures (lowering pressure to 250 psig mitigates failure)

Technical: Revised Model of Species Effect on fcc PdCu

Reversible adsorption of gases: H_2S >> CO > CO_2, N_2, H_2O

$$Q_{\text{eff}} = \frac{Q_{H_2}}{1 + K_{CO}p_{CO} + K_{CO_2}p_{CO_2} + K_{H_2O}p_{H_2O} + K_{N_2}p_{N_2} + K_{H_2S}p_{H_2S}}$$

$$Q_{H_2} = \exp\left(-19.085 + 5.6365\left(1 - \frac{689.9\text{ K}}{T}\right)\right) = 1.4434 \times 10^{-6} \exp\left(\frac{-32330}{RT}\right)$$

$$K_{CO} = \exp\left((-12.748 \pm 1.008) + \ln\frac{T}{689.9\text{ K}}\right) = 4.22 \times 10^{-9} T$$

$$K_{CO_2} = \exp\left((-15.107 \pm 2.340) + \ln\frac{T}{689.9\text{ K}}\right) = 3.98 \times 10^{-10} T$$

$$K_{N_2} = \exp\left((-14.859 \pm 1.046) + \ln\frac{T}{689.9\text{ K}}\right) = 5.11 \times 10^{-10} T$$

$$K_{H_2O} = \exp\left((-15.386 \pm 1.531) + \ln\frac{T}{689.9\text{ K}}\right) = 3.01 \times 10^{-10} T$$

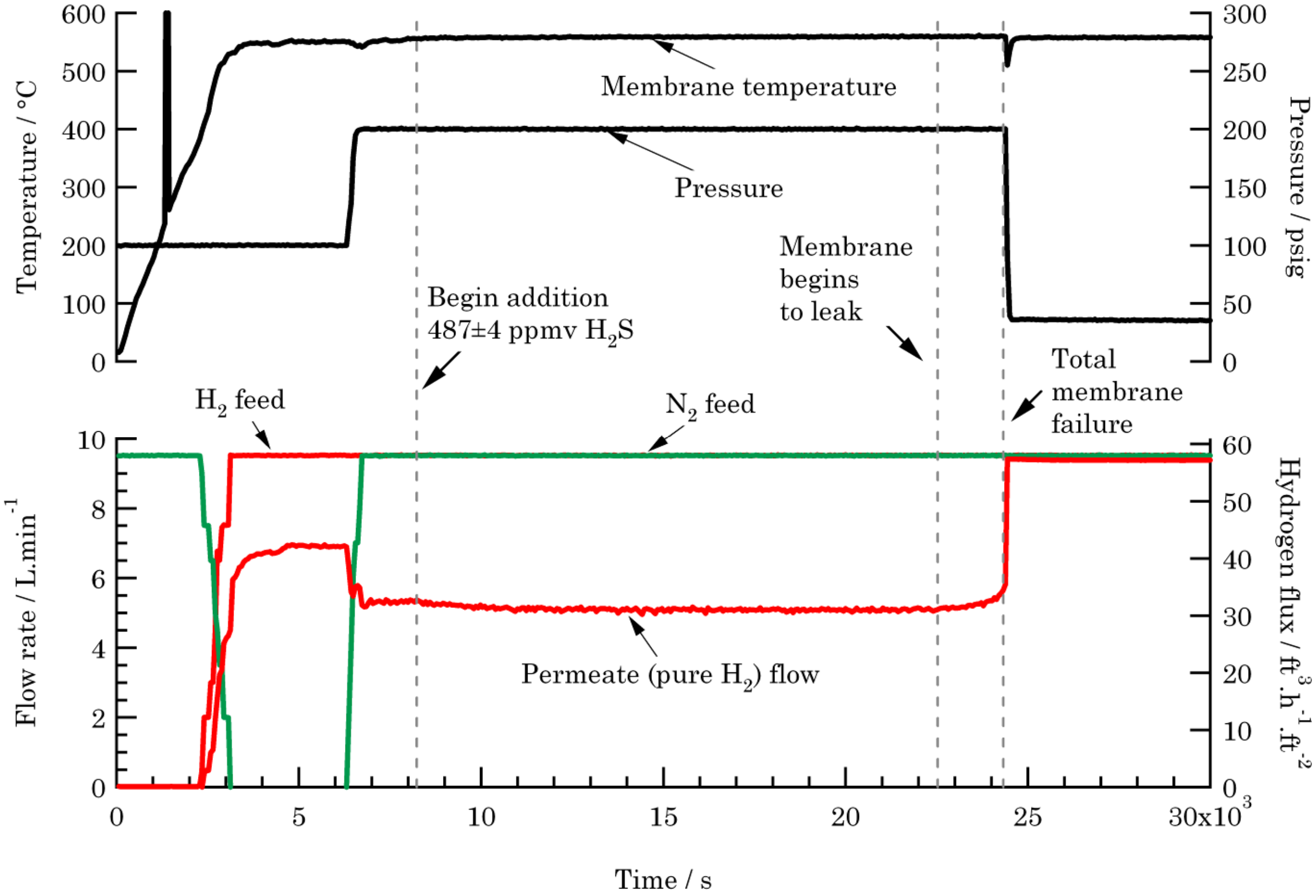
$$K_{H_2S} = \exp\left((-4.569 \pm 1.345) + \ln\frac{T}{689.9\text{ K}}\right) = 1.50 \times 10^{-5} T$$

- Weak temperature dependence over experimental range
  - Heats of adsorption statistically insignificant
  - Linear temperature dependency describes data
- Presence of other gases, especially H_2S can reduce flux by 50%

Test conditions	Test 1	Test 2a	Test 2b	Test 2c
H_2 / %	50.0	50.0	33.0	4.8
CO / %	1.0	1.0	1.3	2.0
CO_2 / %	30.0	30.0	40.0	57.0
H_2O / %	19.0	19.0	25.0	36.2
H_2S / %	0.000	0.002	0.003	0.004
N_2 / %	0.000	0.000	0.000	0.000
Total feed pressure / psia	200	200	200	200
Temperature / °C	400	400	400	400
Absorption factor	1.20	1.48	1.69	1.95
Flux target / [SCFH/ft^2]	200	200	200	200
Required Pure H_2 Flux / [SCFH/ft^2]	241	296	337	390

Estimated required pure H_2 flux needed to achieve 200 ft^{3}ft^{2}h^{-1} in DOE test protocol

Technical: Separator Failure at High T & P

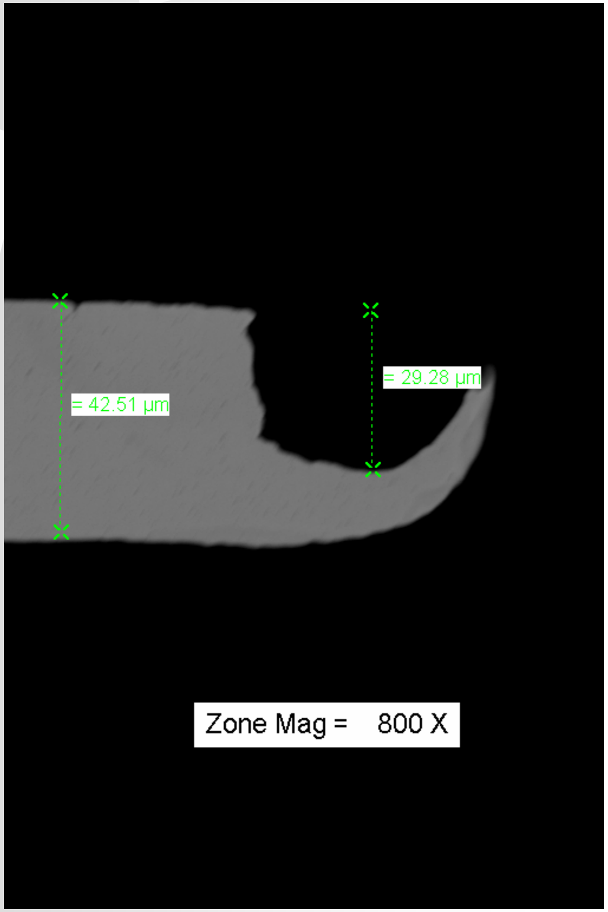


Single tube failure

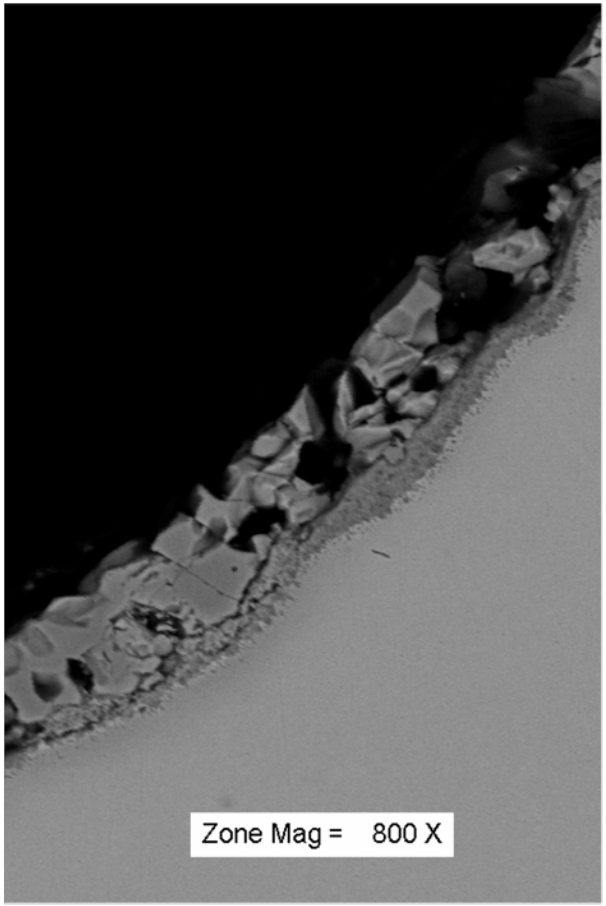
- Sustained 4 hours leak-free operation at 559 °C with 487±4 ppmv H_2S
- Separator failure after 4.5 hours
- Single tube defect failure plus some corrosion of internal stainless steel elements

Technical: Membrane Tube Failure Root Cause Analysis

487 ppmv H_2S affects stainless steel only; Defect failure at high T & P



Cross-section of membrane failure point

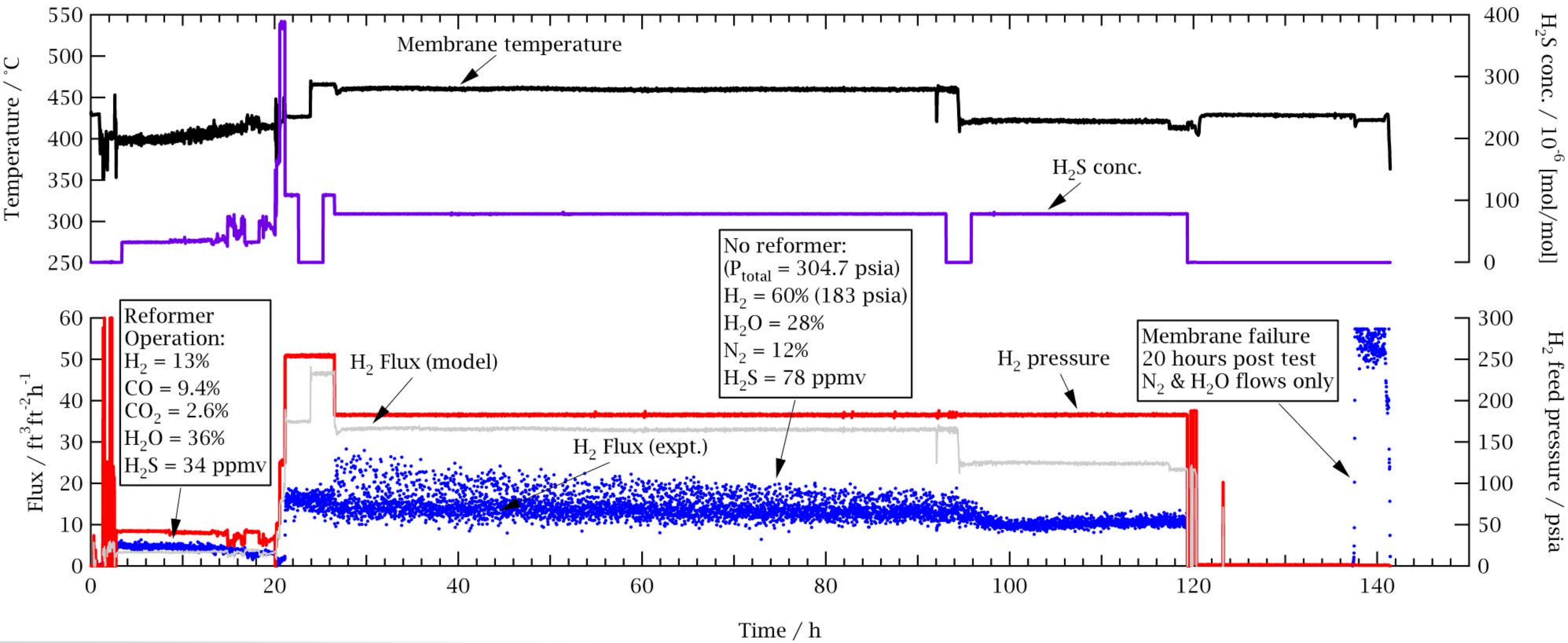


Cross-section of stainless steel portion of separator

- No sulfur found in PdCu alloy cross-section elemental map
- Failure point had a 30-µm defect in membrane tube
- 487 ppmv sulfur corroded stainless steel components, forming metal sulfides
- Newer inspection procedures in place to screen out membranes with defects

Technical: Stable Operation with 78 ppmv H_2S

Sulfur has no effect on PdCu alloys; Defective tubes can fail at 290 psig



- Separator tested for >200 hours with 20–90 ppmv H_2S at 410 °C–450 °C
- Sulfur concentrations at temperatures of 400 °C–500 °C have no impact on membrane performance
- Operation at pressures of 290 psig causes failures in defective membrane tubes

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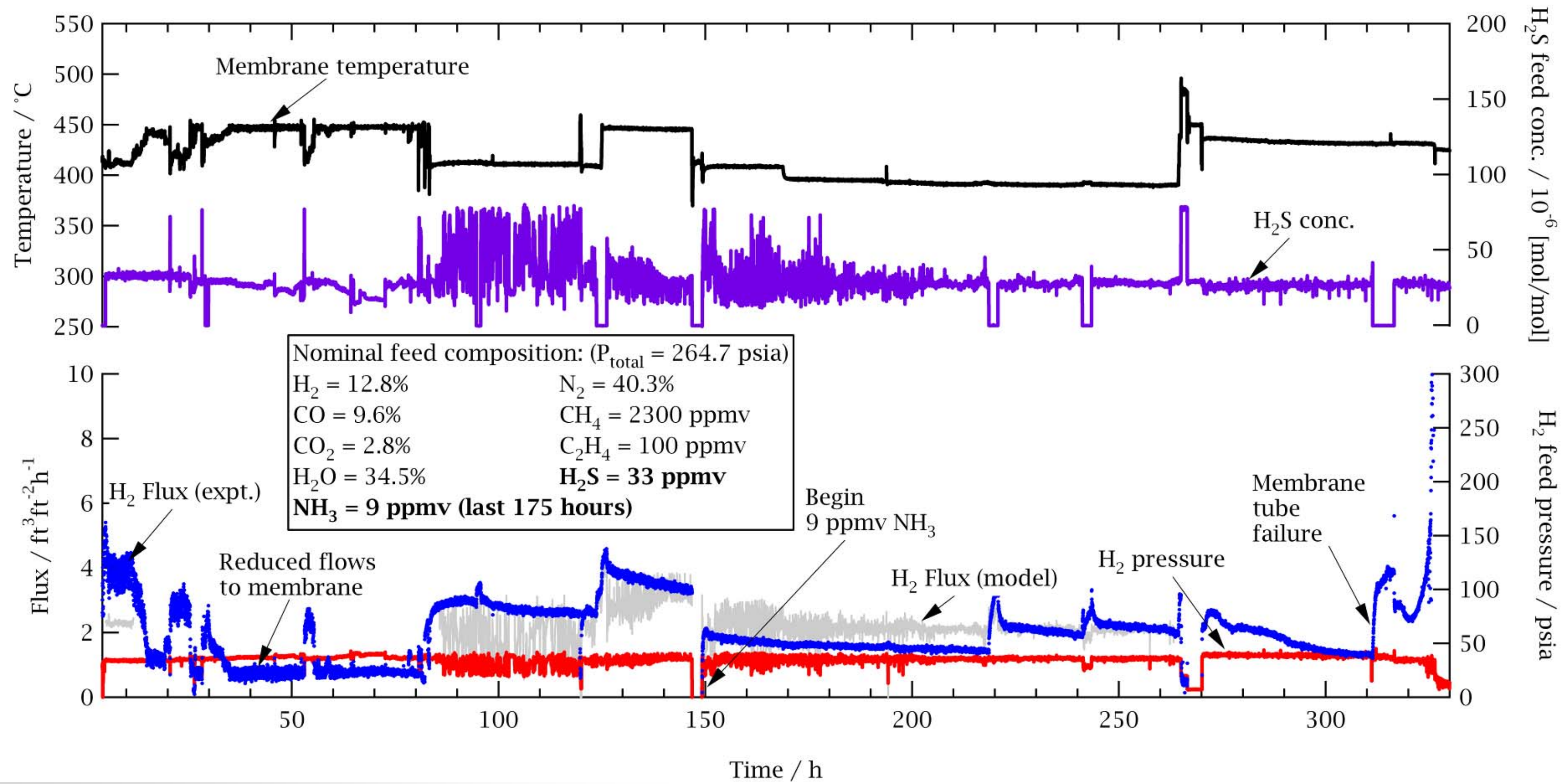
Technical: Operation with Reformate for >300 hours

Presence of additional gases with 39 psia H_2 lowers flux to 2.5–4 $ft^3ft^{-2}h^{-1}$



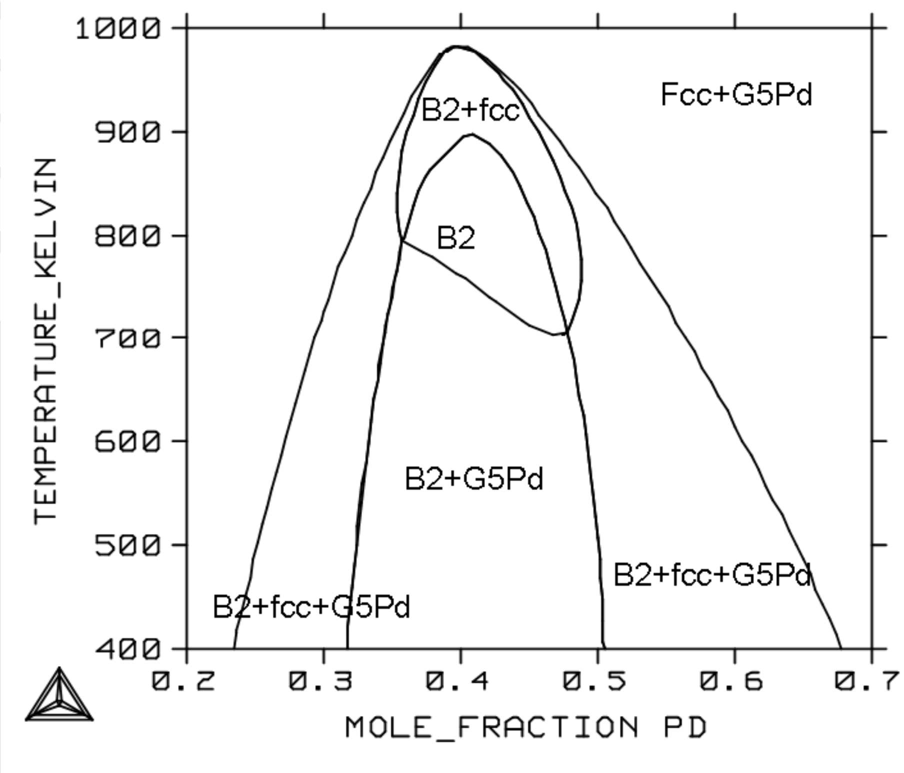
- Separator tested for >300 hours with 20–90 ppmv H_2S at 400 °C–450 °C
- H_2S and NH_3 at temperatures of 400 °C–500 °C have negligible impact on membrane performance
- Operation at pressures of >250 psig causes failures in defective membrane tubes

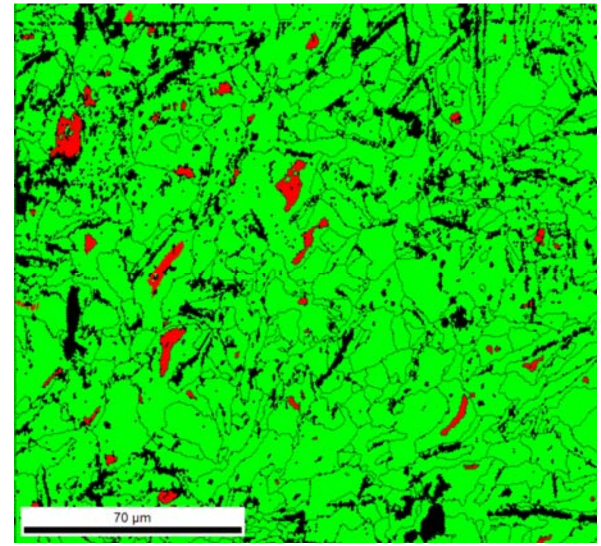
Technical: Design & Construction of Membrane Separators

Task 3 Summary

- Produced five separators with P+E fcc PdCu alloy
  - Four separators have been evaluated
  - Three of the four have been tested to failure
- Produced five separators with UTRC ternary bcc PdCuTM alloy
  - Separators produced with surface barrier (low flux binary alloy)
  - Etching process developed to remove surface barrier
- At least two additional ternary PdCuTM alloy separators to be produced in 2009
  - Test in May time frame
  - Perform ex situ etching if necessary prior to separator manufacture
  - Based on UTC (P&W) experience, an alternative approach to make alloy tubes can be done without etching, although not within the current project resources

Technical: Binary Alloy on Surface of Ternary Alloy (FY2008)





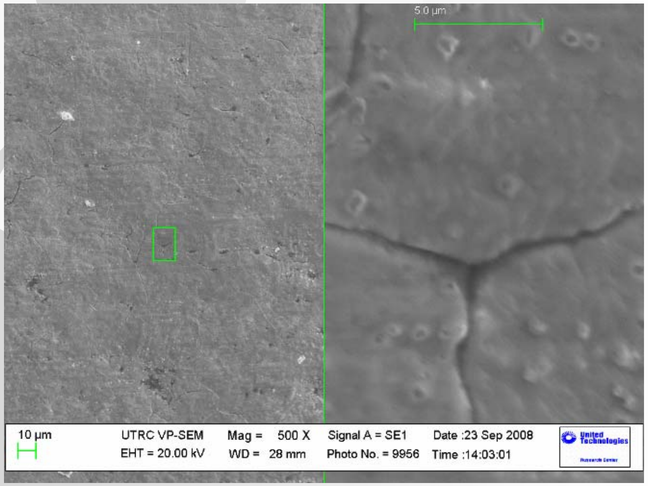
EBSD phase map

Green = PdG5; Red = PdCu

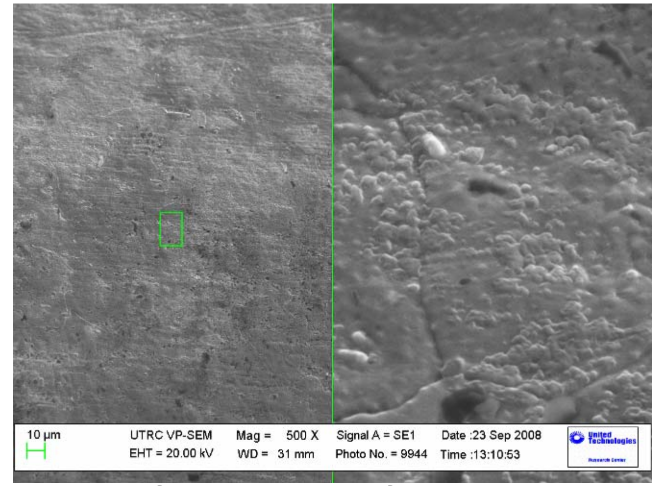
- X-ray diffraction confirmed formation of bcc PdCu as predicted
- Electron Backscatter Diffraction (EBSD) on individual tube indicates presence of binary Pd alloy covering surface of membrane
- Surface alloy layer 500 Å – 700 Å thick by microprobe analysis
- Heat treatments to desegregate/homogenize result in limited improvement
- Etching development chosen for in situ separator treatment

Technical: Etching Development

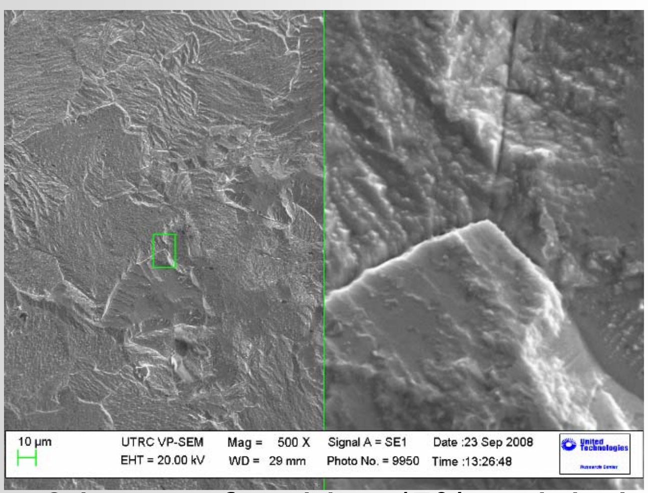
Etching solution can remove surface of membrane in the presence of stainless steel in less than 3 hours



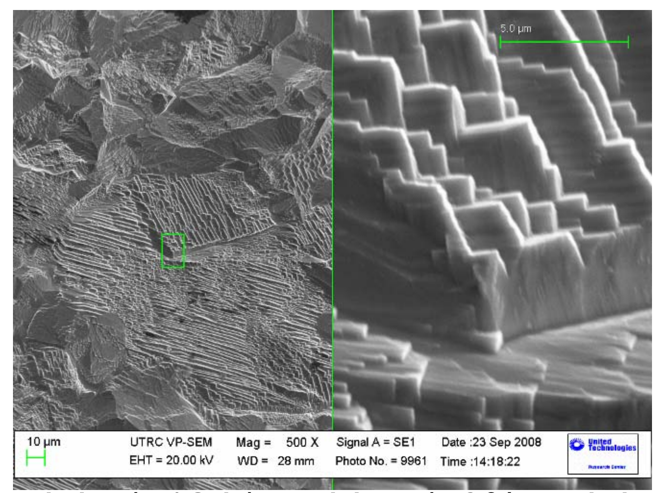
Unetched ternary alloy tube



After 1 hour of etching



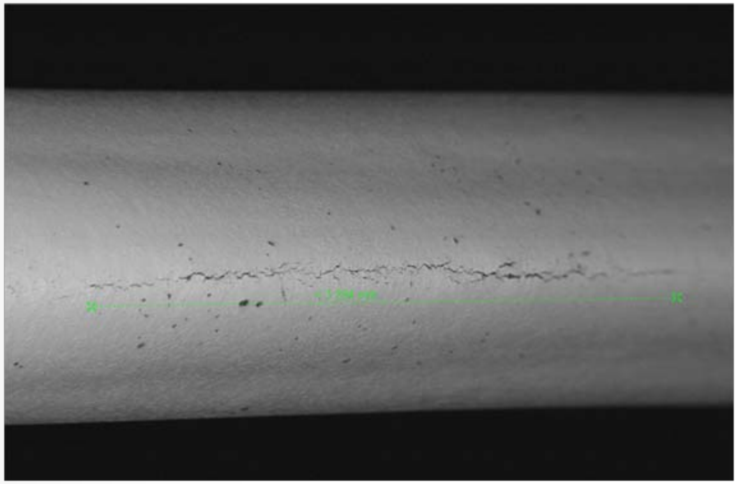
After 3 hours of etching (5% weight loss)



Over night (≈12 h) etching (50% weight loss)

Technical: Etching Development

Etching in situ resulted in stress fractures at defect sites on a few tubes when separators tested at 350 °C



Stress fracture in leaking etched tube

- Etched two separators
  - 1-h with no flux improvement
  - Another 1-h treatment yields leaks at 350 °C
  - 3-h treatment also leads to leaks at 350 °C
  - Tube failure rate approximately 11% (1/9)
- Etching does not degrade seals
- Moving to ex situ etching of new batch of alloy tubes if necessary
  - Allow P+E to screen out defective tubes before separator constructed

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 P+E alloy testing & UTRC alloy improvements

- First quarter 2009
  - Durability studies on fcc PdCu to further quantify resistance to poisons
  - Demonstrate >500 h durability
- Second quarter 2009
  - Evaluate performance of additional ternary alloy separators
  - Durability studies on bcc PdCuTM

Project Summary

- Constructed ten (10) commercially manufactured separators for evaluation
- Evaluated performance of fcc PdCu separators
  - Quantified effect of H_2S, CO, CO_2, N_2, and H_2O on H_2 permeability
  - Demonstrated sulfur resistance of PdCu alloy
- Produced five (5) separators with UTRC ternary composition
  - Secondary phase barrier formed on outer surface of membrane
  - Work in progress to improve performance in two additional separators
- Higher pressure experiments using poison-doped reformate to be conducted for remainder of project
  - Quantify effect of H_2S, HCl, and NH_3 on H_2 permeability
  - Demonstrate >500 h durability with poisons

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