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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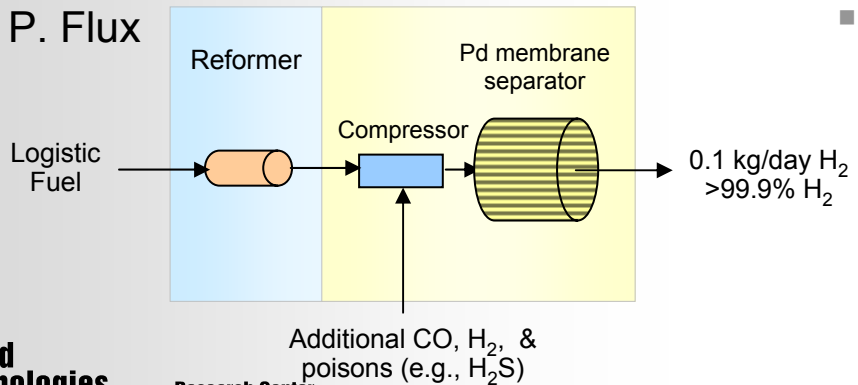
Project ID #PD41

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



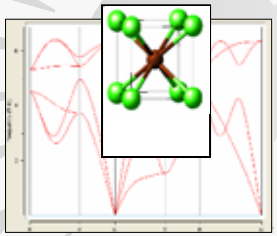
- Objectives
  - **Confirm the high stability and resistance of a PdCu trimetallic alloy** to carbon and carbide formation and, in addition, resistance to sulfur, halides, and ammonia
  - **Develop a sulfur, halide, and ammonia resistant alloy membrane** with a projected hydrogen permeance of 25 $m^3m^{-2}atm^{-0.5}h^{-1}$ 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

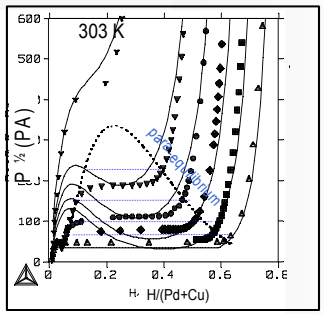
DE-FC26-07NT43055 Project Status Scorecard

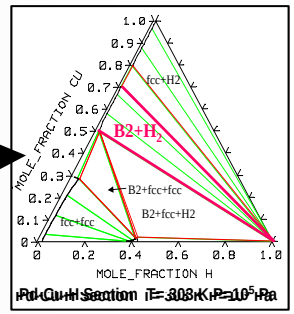
P+E & UTRC alloy separators can meet or exceed DOE targets

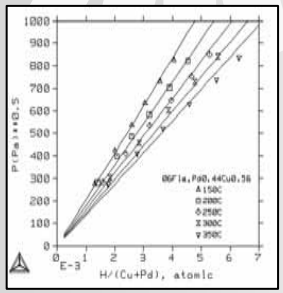
Metric	2010 DOE Target	Current Project Status	Notes
Flux rate	200–250 $ft^3ft^{-2}h^{-1}$	**525 $ft^3ft^{-2}h^{-1}$ (UTRC alloy prediction)** **120 $ft^3ft^{-2}h^{-1}$ (P+E alloy, 400 °C)** **252 $ft^3ft^{-2}h^{-1}$ (P+E, 530 °C)**	▪ Alloy modeling predicts permeabilities much greater than PdCu (fcc) 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 $/ft^2$	137–600 $/ft^2$ 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

Technical Approach









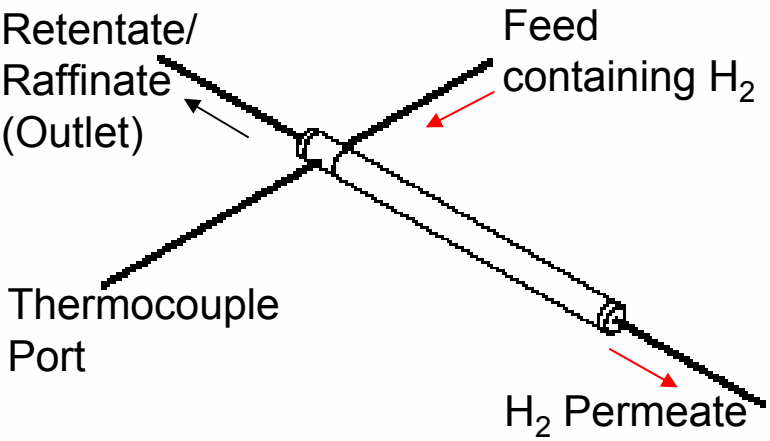
Virtual modeling of phase behavior and properties

Construction of “best commercial” & virtually developed alloy separators

Low pressure laboratory screening: quantify performance

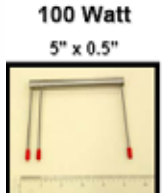
High pressure screening: quantify durability & poison resistance

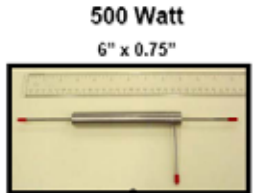
Power+Energy Membrane Separators

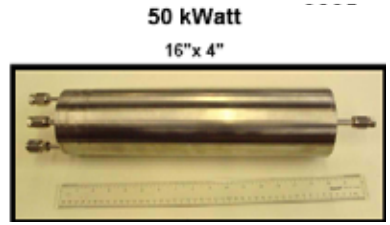


- Robust, scalable commercial design
- Design minimizes external mass transfer resistances
- Tubular design allows for membrane growth & leak free sealing
- Ten (10) separators delivered by P+E
  - Five (5) with P+E PdCu alloy
  - Five (5) with UTRC alloy
- Two (2) additional separators to be delivered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

High Capacity 1300 slpm Modular H_2 Purifier System

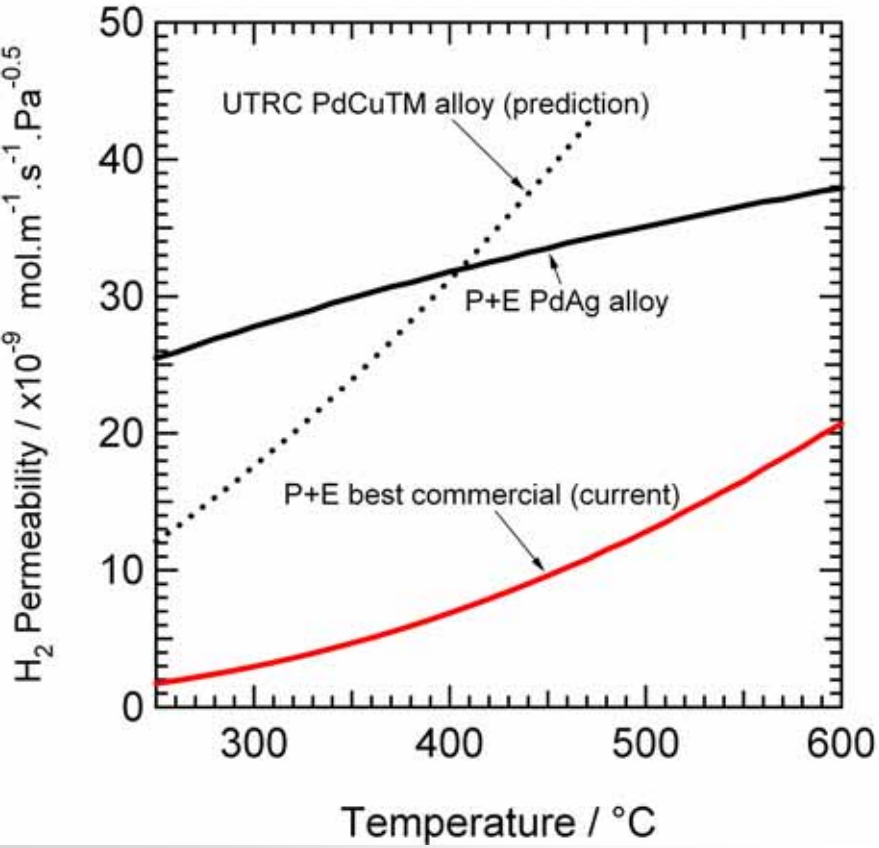


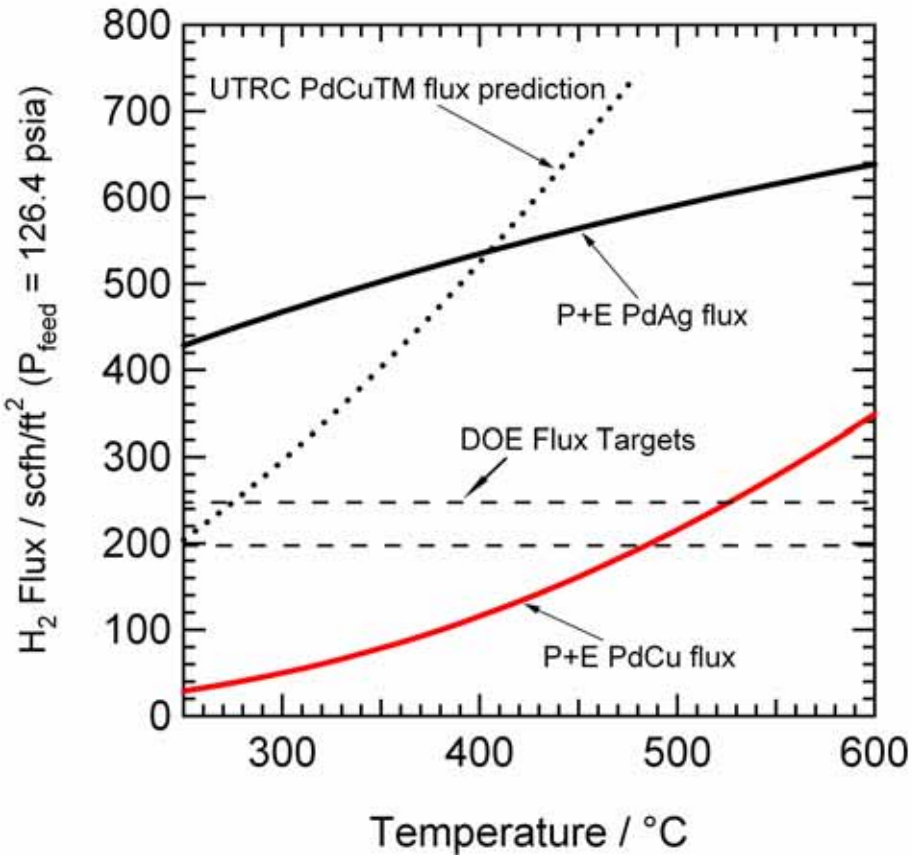




Hydrogen Flux/Permeability for Different Alloys

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

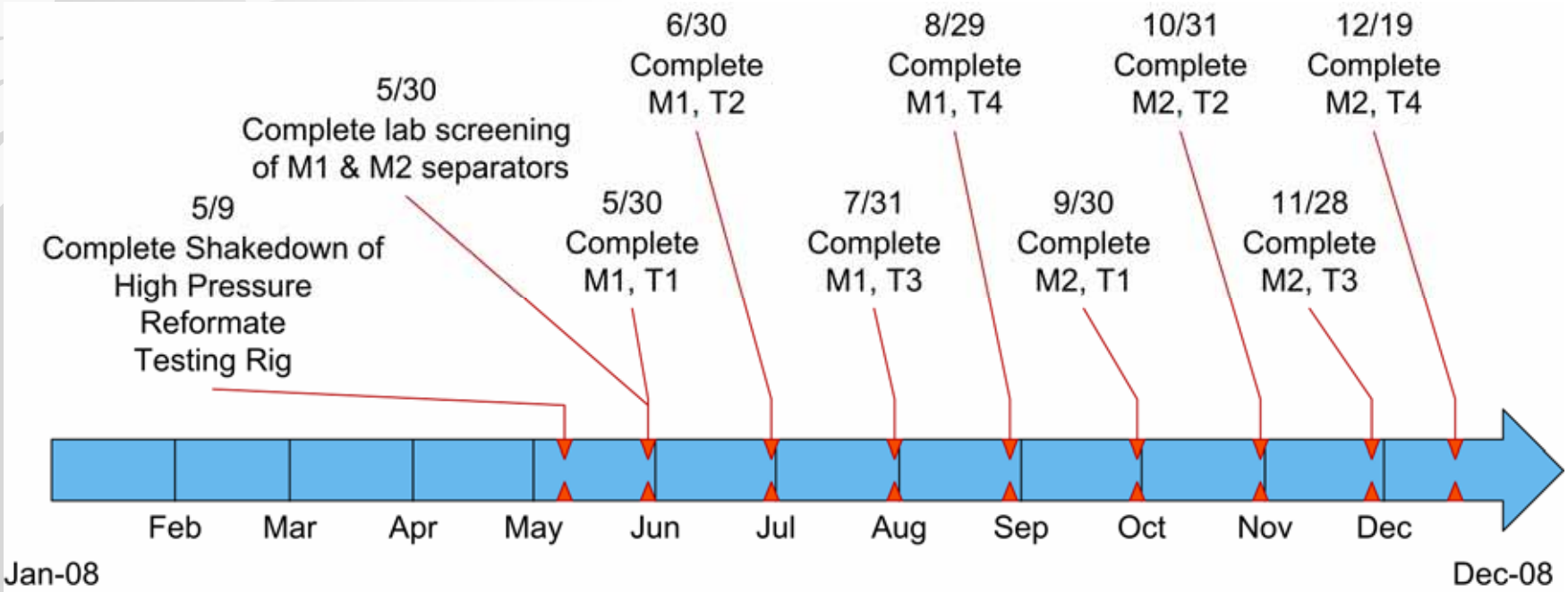




- Modeling projections for UTRC PdCu ternary alloy satisfy DOE flux targets at all operating temperatures
- P+E commercial PdCu alloy meets DOE targets above 480 °C

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

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