Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production
(DE-FC26-07NT43055)

United Technologies Research Center
22 May 2009
Project ID #PD_48_Emerson

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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
    - H₂ 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 m³m⁻²atm⁻⁰.⁵h⁻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 H₂ PdCu trimetallic alloy membrane separators** at feed pressures of 2 MPa (290 psia) in the presence of H₂S, NH₃, and HCl
# Project Status Scorecard (Relevance)

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

<table>
<thead>
<tr>
<th>Metric</th>
<th>2012 DOE Target</th>
<th>Current Project Status</th>
<th>Notes</th>
</tr>
</thead>
</table>
| Hydrogen Flux    | 200 ft³ft⁻²h⁻¹  | 61 ft³ft⁻²h⁻¹ (P+E alloy) 200 ft³ft⁻²h⁻¹ (UTRC alloy prediction) | - P+E alloy at 600 °C; 100 psig H₂  
- UTRC alloy predicted to be 200 ft³ft⁻²h⁻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 H₂S (P+E alloy) 9 ppmv NH₃ (P+E alloy) | - Demonstrated with P+E alloy at 450 °C  
- Demonstrated 487±4 ppmv for 4 hours  
- Demonstrated 9 ppmv NH₃ 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

<table>
<thead>
<tr>
<th>Task #</th>
<th>Project Milestone</th>
<th>Planned Start Date</th>
<th>Planned End Date</th>
<th>Percent Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Complete initial technical and economic modeling.</td>
<td>June 15, 2007</td>
<td>Dec. 31, 2007</td>
<td>100%</td>
</tr>
<tr>
<td>2</td>
<td>Complete advanced membrane property simulations by atomistic and thermodynamic modeling calculations.</td>
<td>June 15, 2007</td>
<td>Dec. 31, 2007</td>
<td>100%</td>
</tr>
<tr>
<td>3</td>
<td>Complete the design and construction of membrane separators using sulfur resistant palladium alloy and membrane separators using PdCuTM.</td>
<td>June 15, 2007</td>
<td>May 30, 2008</td>
<td>83%</td>
</tr>
<tr>
<td>4</td>
<td>Complete hydrogen solubility tests using various alloys for six-to-twelve separators, and predict hydrogen permeability performance.</td>
<td>Mar. 15, 2008</td>
<td>June 30, 2008</td>
<td>100%</td>
</tr>
<tr>
<td>5.2</td>
<td>Complete testing of &quot;best of class&quot; separators.</td>
<td>Mar. 15, 2008</td>
<td>Sep. 30, 2008</td>
<td>50%</td>
</tr>
<tr>
<td>5.3</td>
<td>Complete evaluation of advanced PdCuTM separator units.</td>
<td>June 15, 2008</td>
<td>April 30, 2009</td>
<td>50%</td>
</tr>
<tr>
<td>6</td>
<td>Complete the revised technical and economic modeling.</td>
<td>Dec. 1, 2008</td>
<td>June 1, 2009</td>
<td>0%</td>
</tr>
</tbody>
</table>
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

Retentate/Raffinate (Outlet) -> Feed containing H₂ -> Thermocouple Port -> H₂ Permeate

- 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

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
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/ft² with 100 psig H₂
  - Pressures of 290 psig with high temperatures can result in failures of membrane tubes with defects

- Achieved DOE sulfur target
  - 26 scfh/ft² stable flux with 20 ppmv H₂S at 200 psig (100 psig H₂), 450 °C
  - Operated >100 h with 33–78 ppmv H₂S with no loss in flux

- Next six months of project focused on durability testing
  - Evaluate separators for durability in the presence of H₂S, NH₃, and HCl
  - Demonstrate 500-2000 h durability
Technical: Summary of fcc PdCu Performance

Best measured flux of 61 scfh/ft² on pure H₂

Flux with >20 ppmv H₂S 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: \( \text{H}_2\text{S} \gg \text{CO} > \text{CO}_2, \text{N}_2, \text{H}_2\text{O} \)

\[
Q_{\text{eff}} = \frac{Q_{\text{H}_2}}{1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}} + K_{\text{N}_2} p_{\text{N}_2} + K_{\text{H}_2\text{S}} p_{\text{H}_2\text{S}}} \\
Q_{\text{H}_2} = \exp \left( -19.085 + 5.6365 \left( 1 - \frac{689.9 \text{ K}}{T} \right) \right) = 1.4434 \times 10^{-6} \exp \left( -\frac{32330}{RT} \right) \\
K_{\text{CO}} = \exp \left( -12.748 \pm 1.008 + \ln \left( \frac{T}{689.9 \text{ K}} \right) \right) = 4.22 \times 10^{-9} T \\
K_{\text{CO}_2} = \exp \left( -15.107 \pm 2.340 + \ln \left( \frac{T}{689.9 \text{ K}} \right) \right) = 3.98 \times 10^{-10} T \\
K_{\text{N}_2} = \exp \left( -14.859 \pm 1.046 + \ln \left( \frac{T}{689.9 \text{ K}} \right) \right) = 5.11 \times 10^{-10} T \\
K_{\text{H}_2\text{O}} = \exp \left( -15.386 \pm 1.531 + \ln \left( \frac{T}{689.9 \text{ K}} \right) \right) = 3.01 \times 10^{-10} T \\
K_{\text{H}_2\text{S}} = \exp \left( -4.569 \pm 1.345 + \ln \left( \frac{T}{689.9 \text{ K}} \right) \right) = 1.50 \times 10^{-5} T
\]

- Weak temperature dependence over experimental range
- Heats of adsorption statistically insignificant
- Linear temperature dependency describes data
- Presence of other gases, especially \( \text{H}_2\text{S} \) can reduce flux by 50%

<table>
<thead>
<tr>
<th>Test conditions</th>
<th>Test 1</th>
<th>Test 2a</th>
<th>Test 2b</th>
<th>Test 2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 ) / %</td>
<td>50.0</td>
<td>50.0</td>
<td>33.0</td>
<td>4.8</td>
</tr>
<tr>
<td>( \text{CO} ) / %</td>
<td>1.0</td>
<td>1.0</td>
<td>1.3</td>
<td>2.0</td>
</tr>
<tr>
<td>( \text{CO}_2 ) / %</td>
<td>30.0</td>
<td>30.0</td>
<td>40.0</td>
<td>57.0</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} ) / %</td>
<td>19.0</td>
<td>19.0</td>
<td>25.0</td>
<td>36.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} ) / %</td>
<td>0.000</td>
<td>0.002</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td>( \text{N}_2 ) / %</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Total feed pressure / psia</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Temperature / °C</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Absorption factor</td>
<td>1.20</td>
<td>1.48</td>
<td>1.69</td>
<td>1.95</td>
</tr>
<tr>
<td>Flux target / [SCFH/ft²]</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Required Pure ( \text{H}_2 ) Flux / [SCFH/ft²]</td>
<td>241</td>
<td>296</td>
<td>337</td>
<td>390</td>
</tr>
</tbody>
</table>

Estimated required pure \( \text{H}_2 \) flux needed to achieve 200 ft³/ft²/h⁻¹ in DOE test protocol
Technical: Separator Failure at High T & P

- Sustained 4 hours leak-free operation at 559 °C with 487±4 ppmv H₂S
- 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 $\text{H}_2\text{S}$ affects stainless steel only; Defect failure at high T & P

- 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 $\text{H}_2\text{S}$

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

- Separator tested for >200 hours with 20–90 ppmv $\text{H}_2\text{S}$ 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
Technical: Operation with Reformate for >300 hours

Presence of additional gases with 39 psia H₂ lowers flux to 2.5–4 ft³/ft²/h⁻¹

- Separator tested for >300 hours with 20–90 ppmv H₂S at 400 °C–450 °C
- H₂S and NH₃ 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

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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: 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

- 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 H₂S, CO, CO₂, N₂, and H₂O on H₂ 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 H₂S, HCl, and NH₃ on H₂ 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