High-Performance, Durable, Palladium Alloy Membrane for Hydrogen Separation and Purification

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Pall Corporation
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Project PD 07

Project ID: pd_07_acquaviva

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Overview

Timeline
• July, 2005 start date
• June 30, 2010 end date
• 80% complete

Barriers
• Operational durability
• Compatibility to impurities
• Manufacturing cost

Budget
• $4 Million Project Total
  – $2.4M DOE share
  – $1.6M Contractor share
• $1.52 Million DOE cumulative obligations as of March 2009

Partners
• Colorado School of Mines
• ORNL – High Temperature Materials Lab
The project objective is development, demonstration and economic analysis of a Pd-alloy membrane that enables the production of 99.99% pure H₂ from reformed ethanol at a cost of $2-3/gge by 2010.

The objectives from June 08-May 09 were to:

- Fabricate a series of membranes covering a specific range of alloy composition and functional layer thickness
- Optimize the membrane formation process
- Test the membranes in pure gas streams prior to WGS testing
- Complete the equipment needed for extended WGS testing
- Obtain initial WGS test results
- Initiate the techno-economic modeling as soon as the combined membrane reactor model is available from DTI
Relevance - Impact on Barriers

• **Operational Durability**
  – Addressed through:
    • Alloy and composite membrane structure
    • Process conditions
    • Operational procedures

• **Compatibility to Impurities**
  – Alloy selection based on application specific requirements
  – Confirm compatibility through long term testing at actual conditions

• **Manufacturing Cost**
  – Cost estimate based on sale price to end user for membrane in a module
  – Manufacturing scale-up increases yield and reduces cost
# DOE HFI Membrane Performance Targets*

<table>
<thead>
<tr>
<th>Performance Criteria</th>
<th>2006 Status</th>
<th>2010 Target</th>
<th>2015 Target</th>
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<tbody>
<tr>
<td>Flux SCFH/ft² @20 psi ∆P H₂ partial pressure, 400ºC (Pure H₂ gas)</td>
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<td>Membrane Cost, $/ft² (including all module costs)</td>
<td>1500</td>
<td>1000</td>
<td>&lt;500</td>
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<td>∆P Operating Capability, system pressure, psi</td>
<td>200</td>
<td>400</td>
<td>400 - 600</td>
</tr>
<tr>
<td>Hydrogen Recovery (% of total gas)</td>
<td>60</td>
<td>&gt;80</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Hydrogen Permeate Quality</td>
<td>99.98%</td>
<td>99.99%</td>
<td>&gt;99.99%</td>
</tr>
<tr>
<td>Stability/Durability</td>
<td>&lt;1 year</td>
<td>2 years</td>
<td>&gt;5 years</td>
</tr>
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</table>

Approach - Overall Technical Approach

• Develop a commercially viable Pd alloy membrane to enable the design of economical processes for hydrogen production
  – Pd alloy membrane has been shown to have both high flux rate and high separation factor for separating H₂ from ethanol/NG reformate gas
  – Commercial scale-up of high quality porous metal substrate along with alloy development, deposition methods and module design pursued

• Increase the overall energy efficiency of a H₂ reforming system through use of membrane technology for process intensification
  – Membranes with high operating temperatures can be heat integrated to reduce thermal loss within the system
  – Membranes with high separation factor can reduce system complexity, size and operating cost
  – Membrane reactors can reduce the cost of pressure vessels, reduce catalyst volumes and overall capital and operating cost
Approach – Progress FY08/09

• **Membrane Development**
  – Consistently produced substrate and initiated manufacturing scale up
  – Improved deposition methods and post treatment during fabrication of Pd-alloy membrane inventory
  – Analyzed alloy composition and microstructure
  – Evaluated alloy composition, process conditions and operational procedures as variables affecting membrane performance

• **Economic Evaluation**
  – Updated costs based on scaled up membrane manufacturing
  – Design and cost evaluation of modules
  – Estimated H₂ production cost using combined membrane reactor model though interaction with DTI
### Milestones – Technical Accomplishments

<table>
<thead>
<tr>
<th>Milestones</th>
<th>Progress Notes</th>
<th>Comments</th>
<th>% Comp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demonstrate progress toward $H_2$ quality goal</td>
<td>Achieved $\geq 99.9%$ in a 80hr WGS mixed gas test w/ max value 99.98%</td>
<td>- The potential of Pd-alloy membranes to achieve very high levels of $H_2$ purity has been confirmed</td>
<td>80%</td>
</tr>
<tr>
<td>Demonstrate progress on 2010 $H_2$ recovery goal</td>
<td>Achieved 78% in a WGS mixed gas test</td>
<td>- Likely to achieve 80% or greater by optimizing process conditions. Modeling indicates this is a reasonable target for economic viability</td>
<td>70%</td>
</tr>
<tr>
<td>Demonstrate achievement of $\Delta P$ goal</td>
<td>Test program in process at HTML for thin foil and substrate. Specialized pressure collapse test equipment currently being modified</td>
<td>- Empirical data at high temperature measured for foil strength. Substrate tube data to be collected at temperature to verify calculated operating pressure rating</td>
<td>65%</td>
</tr>
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<td>% Comp</td>
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<tr>
<td>---------------------------------------------------------------------------</td>
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<td>---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>--------</td>
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| Membrane module cost analysis to meet 2010 goal                          | Achieved 2010 goal of $1000/ft² module. Design in progress                     | - Increased yield and reduced production cost through scale up of substrate manufacturing process  
- Reliable deposition of the functional layer below 5 micron reduces cost of precious metal                                           | 60%    |
| Report on progress to achieve H₂ flux goal                               | Achieved 245 scfh/ft² on a WGS mixed gas test w/ differential pressure = 170 psi, T = 400 °C | - Established feasibility and repeatability across a range of samples  
- H₂ flux used as a metric for control of deposition process along with separation factor  
- Process flux will vary significantly based on operational conditions                                              | 70%    |
# Milestones – Technical Accomplishments

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| Predictive modeling report on progress toward durability goal             | Testing for over 100 hours conducted and reported                            | - Extended testing to be done with recently completed test stands  
- Multiple thermal cycle testing to be done for predictive modeling | 50%    |
| Report on system economic/energy model compared to 2010 goal             | Input provided to Directed Technologies used for initial analysis            | - Continue to interact with Directed Technologies to provide feedback on latest version of H2A that includes integrated membrane reactor | 20%    |
Approach – Key Milestones and Decision Points

- **Phase 2 Milestone:** Use projected cost estimate for membrane modules (area & $/ft^2) and DTI’s H2A based analysis to **establish economic viability** for integrated membrane reactor in a NG and/or Ethanol reformer system
  - Go/no go decision November 2009

- **Scope of Phase 3:** **Confirm stable performance** ($H_2$ flux, purity and recovery) of Pd-alloy membrane under typical post WGS operating conditions
Technical Accomplishments & Progress
Summary of Previous Accomplishments

• **Develop substrate process:** Porous metal media substrate tubes made from 310SC alloy stainless steel and rated for use at 550°C and 20 bar that can be made in longer lengths and ZrO₂ diffusion barrier fabrication process is scaled up to 12-inch lengths

• **Improve membrane deposition process:** Modified deposition methods to repeatedly produce thin Pd alloy membranes (≤2 microns) with high separation factors (greater than 20,000)

• **Fabricate test samples:** Produced various Pd-Au alloy tubular membranes 5-30% Au and thickness 1.0-3.5 microns

• **Design membrane for high ΔP:** Carried out tensile strength and strain at failure for Pd-alloy foils over the composition range of 0-38 mass % Au to determine high pressure operating capability for the functional membrane layer

• **Performed preliminary testing in mixed gas streams:** A limited amount of testing was carried out in mixed gas test streams to determine effect of other gas components

• **Estimated cost:** Module design, fabrication techniques and materials for a stand alone membrane separator device show that $1,000 per ft² of area cost to end user is achievable

• **Initiated techno-economic analysis:** Directed Technologies’ used Pall provided information in a modified H2A economic model. Initial results showed the cost of the separation device (PSA or membrane) is a small percent (<10%) of capital cost of the reforming system, so membrane module cost is not the dominating factor. Membrane separation enables a more efficient reforming system, reducing operating cost and lowering the cost per Kg of H₂, so membrane performance and process integration are key
Technical Accomplishments & Progress
Summary of Accomplishments for June 08 - May 09

• Developed new membrane synthesis process (air oxidation and layering sequences) to improve membrane performance
• Established an inventory of membranes with various Pd-Au composition (0-30% Au) and thickness (1.0-3.5 microns)
• Analyzed the effect of alloy composition, process conditions and operational procedures on membrane performance
• Fabricated two WGS test stands, one for sensitivity analysis, the second for long-term durability analysis
• Conducted preliminary H2 production cost analysis using DTI’s H2A based model and Pall provided costs

Significant progress towards establishing viability
**Tubes**

**Gas Separation Membrane**

**Substrate Development**

"It is all about substrate!!! - Prof. Douglas Way"

- Ceramic Coated Porous Stainless Steel Substrates
- Available in 316 and 316 SS with welded fitting

- Uniform pore size distribution
- Average Pore Size = 70 nm
- First Bubble/Largest Pore > 30 psig
- Air Permeance = 1.0 x 10^-10 cm^2 s^-1 Pa^-1 m^-1

- Excellent adhesion between Stainless Steel and ceramic layer.

- Excellent adhesion to zirconia layer uniform thickness, surface contour following of Pd-alloy metal film.

**Hydrogen Separation Membrane**

- Palladium-Alloy membranes
  - Composite and alloy development in collaboration with CSM
  - Extensive fabrication and testing
  - Robust: Thermal stability and start-up/shut-down cycling test
  - Module design and innovation to improve performance
  - 15m² modules available for field testing

- Engineering design optimization for enhanced performance. Data at 400 C; 75 psig feed pressure; 70/30% H₂/Ar, Atmospheric permeate

**Polybenzimidazole Membrane**

- High temperature polymeric membrane development in collaboration with Los Alamos National Laboratory
- Long term stability at temperatures exceeding 250 C
- Exceptional stability in H₂ and CO environment
- Innovative composite design for 25-fold performance improvement

**Progressing towards Industrial Scale**

- Large scale manufacturing capability
- Unique weld design developed and commercialized
- Porous stainless steel and ceramic coated stainless substrates suitable for high temperature and pressure gas and vapor separation applications

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Technical Accomplishments & Progress

- CSM developed membrane and process
- Deposition method and alloy composition varied
- Air purge cycle added to the test
- Showed surface effects were reversible with the right alloy and process conditions

CSM235 1.9 micron Pd$_{92}$Au$_{8}$ increase in Hydrogen Flux and pure gas selectivity at 400 °C with successive air purges at 300 °C
In Situ, High Temperature XRD

• Test has proved useful for membrane characterization at operational temperature
• Alloying is not complete but appears to be stable
• Further analysis to be conducted

Discussion

The front most scans show two distinct pairs of diffraction peaks corresponding to the Pd and Au starting layers. As the temperature is increased, the Au peaks shift to higher diffraction angle, corresponding to a smaller lattice spacing, which may be interpreted as alloying of the Au with smaller Pd atoms. Two features stand out from this data set. First, that there are no equivalent shifts of the Pd peaks, meaning that there remains an unalloyed Pd layer under the Au-Pd alloy. Second, the peak shift stops at some temperature well below 400°C, meaning that the Au-Pd alloy is stable and in equilibrium with the underlying Pd layer. This demonstrates that the process yields a Pd membrane protected by a thin Au-Pd alloy layer of uniform composition. These results are yet to be quantified, and will be supplemented by an electron microprobe analysis through the thickness of the foil.
Technical Accomplishments & Progress

Inventory of Membranes for WGS Performance Testing

Pd alloy membranes with Au content ranging from 0-30% and thickness from 1.0-3.5 microns. Alloy composition can affect:
- Stable operational flux rate
- Cost
- Purity
- Operating limits
- Manufacturability
- Application viability

CSM fabricated membranes on Pall provided substrates
Selection of tubes of varying Pd-Au alloys ready for testing on the automated water gas shift test stand
Technical Accomplishments & Progress
High Pressure WGS Test

<table>
<thead>
<tr>
<th>CSM Membrane Sample #</th>
<th>201</th>
<th>199</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Gas (SCFH/ft².atm⁰.⁵)</td>
<td>303</td>
<td>331</td>
</tr>
<tr>
<td>Mixed Gas (SCFH/ft².atm⁰.⁵)</td>
<td>219</td>
<td>149</td>
</tr>
<tr>
<td>Flux - Mixed Gas (SCFH/ft²)</td>
<td>245</td>
<td>216</td>
</tr>
<tr>
<td>H₂ Recovery (%)</td>
<td>67</td>
<td>60</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>99.5</td>
<td>99.96</td>
</tr>
<tr>
<td>Test time (hrs)</td>
<td>120</td>
<td>75</td>
</tr>
</tbody>
</table>

- Feed gas: 50% H₂, 1% CO, 30% CO₂, 19% H₂O
- T = 400°C, dP= 180 psid
- Feed pressure = 12.6 bar (182 psia)
- Permeate pressure = 0.8 bar (12 psia)
- Testing done at TDA Research Inc, Wheat Ridge, CO

Reduced flux likely due to concentration polarization
Technical Accomplishment – Thermal Cycle Durability

Stable Flux Rate

Test Cycle
- Increase from 50c to 400c in 45 minutes
- Decrease from 400c to 50 c in 45 minutes

No leak
Technical Accomplishment – Operational Conditions

- S/C ratio of 1 is a minimum to prevent carbon formation
- Pd alloy allows for stable operation even in low steam conditions
- Need to match alloy to process conditions for optimized performance

Conditions for membrane testing:
Feed H₂ 70%
CO 15%
H₂O/CO changed
CO₂ balance
Pressure 80 PSIG
Temperature 400°C
H₂ Recovery 65-70%

- Pure Pd Membrane
  H₂O/CO ratio = 0

- Pure Pd Membrane
  H₂O/CO ratio = 1

- Pd Alloy Membrane
  H₂O/CO ratio = 0.5

![Graph showing H₂ impurities over time for different conditions]
Technical Accomplishment - Module Design/Cost Estimate

3.3 ft² area
100 Kg/day capacity at typical conditions
Technical Accomplishments & Progress
Techno-Economic Modeling Background

• Membrane cost analysis done by Pall Corp. as part of manufacturing scale-up evaluation and includes economies of scale estimates for volume production
• Membrane “cost” is based on sales price to end user of a membrane in a pressure vessel (ie: membrane module)
• Directed Technologies Inc. has developed a H₂ production model for cost analysis of medium temperature ethanol integrated reformer/WGS/membrane separator system coupled with H2A forecourt model
• H₂ production cost in “gallon of gas equivalent” (GGE) is determined for given process, operating conditions and capital costs
• Preliminary sensitivity analysis was conducted by DTI for determining the influence of membrane permeance and overall H₂ recovery on the cost of H₂ for 1500 kg/d H₂ production rate
### Technical Accomplishments & Progress

**Techno-Economic Modeling Preliminary Results**

<table>
<thead>
<tr>
<th>H$_2$ Compressed to 300 psig</th>
<th>H$_2$ Recovery</th>
<th>Cost of H$_2$ – ($/kg)</th>
<th>Integrated ethanol reformer/WGS/membrane separator</th>
<th>H$_2$ production rate: 1500 kg/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane H$_2$ flux (400 C, 20 psid)</td>
<td>150 scfh/ft$^2$</td>
<td>200 scfh/ft$^2$</td>
<td>250 scfh/ft$^2$</td>
<td></td>
</tr>
<tr>
<td>70 %</td>
<td>$3.19$</td>
<td>$3.18$</td>
<td>$3.18$</td>
<td></td>
</tr>
<tr>
<td>80 %</td>
<td>$3.08$</td>
<td>$3.07$</td>
<td>$3.06$</td>
<td></td>
</tr>
<tr>
<td>90 %</td>
<td>$3.01$</td>
<td>$3.00$</td>
<td>$2.98$</td>
<td></td>
</tr>
</tbody>
</table>

- Membrane flux rate (area/cost) has minor impact on cost of H$_2$
  - Cost of membranes <10% of total capital cost
- Increasing hydrogen recovery decreased cost of H$_2$ in this range
- Ethanol efficiency – 68.87% at 90% H$_2$ recovery, 63.36% at 70% H$_2$ recovery
- Increasing ethanol efficiency to 79.4% was shown to reduce the cost of hydrogen to $2.67/kg by DTI in last year’s AMR presentation

*Preliminary results approach DOE target of $2-$3 per GGE*
Collaborations

- **Colorado School of Mines**: Sub-contractor focused on the material science. Responsibility includes selection of Pd-alloy compositions, fabrication of membranes and testing for compatibility. Extensive collaboration for compositional/process development, analytical testing and WGS testing will continue.

- **ORNL-HTML**: Sub-contractor focused on the evaluation of material properties using unique test equipment and techniques. Includes mechanical properties and alloy structure at operating temperature.

- **Directed Technologies Inc.**: Independent contractor to the DOE. Used module costs and membrane performance estimates provided by project team to estimate H2 production cost. Uses computer model for both stand alone membrane separator and combined membrane/water gas shift reactor configurations. Plan to collaborate more interactively to analyze process variations that could reduce cost for both NG and Ethanol reforming.
Future Work

• Increase test time to establish membrane durability
  – Focus on post WGS test conditions for applicable reforming process
  – Use physical analysis and accelerated aging techniques to predict membrane life
• Improve membrane formation process
  – Increase separation factor / H₂ purity
  – Reduce cost
• Evaluate the effect of process variables and operating procedures on membrane performance
• Develop knowledge base to be used for selecting optimum alloy composition, process conditions and/or operating procedures
  – Match to system requirements for applications of interest
• Refine the techno-economic analysis to include optimized membrane and reforming process

Establish overall economic viability for H₂ production via membrane based reforming
Summary
Technical Accomplishments Achieved This Year

• Improved **membrane deposition** & conditioning
• Produced **membrane inventory** of various alloy compositions and thickness
• Obtained initial **performance and durability data** on high pressure WGS test
• Began development of **knowledge base** for matching alloy composition, process conditions and operating procedures
• Fabricated two **WGS test stands**, one for sensitivity analysis, the second for long-term durability analysis.
• Established baseline **economic analysis** showing feasibility of achieving DOE target
FY08 & FY09 Progress Against Targets

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* Permeate quality in excess of 99.99% consistently achieved