Development of Hydrogen Selective Membranes/Modules as Reactors/Separators for Distributed Hydrogen Production

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## Overview

### Project Start Date
7/1/05

### Project End Date
12/31/12

### Percent Complete
95%

### Total project funding
- **DOE Share:** $2,592,350.
- **Contractor Share:** $648,087.

**FY11:** $410K

**Planned FY12:** $400K

No catalyst development activities due to funding limitation in the beginning of the project

### BARRIERS

**#1 Cooling Stability:** Performance stability through cooling in H₂ is essential for portable power generation, and is desirable for distributed H₂ production.

**#2 Cost vs Performance:** meeting US DOE and our end user cost vs performance targets.

**#3 Reactor Configuration:** a membrane reactor equipped with an integral cooling device and reliable seals between ceramic bundles and metallic housing.

### Key Personnel

- **Professor Theo T. Tsotsis**
  University of Southern California,
  Catalytic membrane reactor expert

- **Dr. Babak Fayyaz-Najafi**
  Chevron ETC,
  End User Participant

- **Dr. Hugh Stitt**
  Johnson Matthey,
  Catalyst Manufacturer

- **Mr. Pat Hearn**
  Ballard Power Systems
  Fuel Processing End User

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Overall Project Objectives - Relevance

1. Develop, fabricate and demonstrate field implementable hydrogen selective membranes/modules
2. Intensify/improve conventional hydrogen production process via a membrane reactor
3. Prepare field test modules and conduct a field test for hydrogen production/purification

Example of Conventional Process - Steam Methane Reforming (SMR)

**Objective #2**
Reduce HTS/LTS reactors & inter-stage coolers into a single stage LTS/MR operation (Barrier #3)

Objective #1
Develop a cost acceptable hydrogen selective membrane for end users, i.e., $100/ft² (Barrier #1 & 2).

**Objective #3**
Fabricate full-scale membrane/modules and perform field test for hydrogen separation (Barrier #3).

HTS: High Temperature Shift
LTS: Low Temperature Shift
PROX: Preferential Oxidation
PEM: Proton Exchange Membrane
MR: Membrane Reactor
PSA: Pressure Swing Adsorption

Project Goal
Field Test
Specific Objectives and Technical Approach for FY11-12

- Develop improved palladium membranes with cooling stability in presence of H₂
- Design and fabricate a catalytic membrane reactor for field test

Develop 3rd generation membrane with cooling stability in the H₂ charged environment (Barrier #1&2).

- Screen commercial Pd alloy foils to select a promising alloy exhibiting cooling stability.
- Deposit the thin film of the selected Pd alloy on our ceramic membranes as substrate.
- Evaluate the cooling stability of the Pd alloy membranes prepared.
- Optimize the Pd-Cu alloy membrane in terms of permeance vs selectivity.

Design and fabricate full-scale membrane bundles with the 3rd generation membrane as a membrane reactor (Barrier #3)

- Design and fabricate membrane bundles to accommodate (i) heat transfer requirement and (ii) the flexibility in catalyst volume/membrane surface area ratio for the WGS reaction.
- Fabricate membrane reactors with the above features for field test.

Prepare the test unit and system for field test (Barrier #3)

- Assemble a test unit for our membrane reactor.
- Conduct a field test.

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**Completed the foil evaluation to choose a promising palladium alloy for asymmetric membrane development.**
Commercially available Pd-Cu, Pd-Ag, and Pd-Au foils along with the Pd foil (as control) were evaluated for their stability of cooling in hydrogen. The Pd-Cu foil shows structure stability through multiple cooling cycles in H$_2$ (i.e., >60 cycles), not Pd–Ag and Pd-Au.

**Developed palladium-copper alloy membranes meeting the cost vs performance target set by US DOE.**
Pd-Cu thin film (~5 µm) was successfully deposited on our commercial ceramic substrate with a H$_2$ permeance of 10-15 m$^3$/m$^2$/hr/bar at 350°C (i.e., 50-75 scfh @ 20 psig) and the selectivity of H$_2$/N$_2$ of 200 to >1,000, meeting the DOE 2015 cost vs performance target.

**Verified the cooling stability in the presence of hydrogen**
More than 10 PdCu membranes are currently undergoing cooling stability testing, i.e., cooling from 350°C to room temperature in the presence of H$_2$. Several of them have experienced >85 cycles with no signs of performance degradation.
TECHNICAL ACCOMPLISHMENTS – FY11-12

- Designed and constructed membrane bundles which can accommodate (i) heat transfer requirement and (ii) flexibility in catalyst volume to membrane surface area ratio.
  Our unique membrane bundling configuration permits a membrane reactor that can be integrated with internal cooling coils without significant modifications to the membrane housing and module for the exothermic WGS reaction. In addition, the bundling configuration allows flexibility in catalyst volume to surface area ratio.

- Assembling a test system for the field test
  We currently are assembling the test unit/system around the membrane reactor to perform the field test in the 3rd & 4th Quarter of 2012. The reformer and the membrane subunit have been fully tested to meet syngas productivity and separation and purification requirements (i.e., 16 liter/min syngas and <10 ppm CO).

- Continuing the long term thermal stability test of the Pd and Pd-Cu membranes
  Thermal stability testing of our Pd membrane bundle is continuing as part of the test requirement to verify that the DOE performance specification is met. Stability for > 9,000 -10,000 hours at 350°C has been demonstrated for Pd and >600 hrs for PdCu membranes.
MPT CERAMIC MEMBRANES - Low Cost
for harsh environment applications

Examples of Commercial Installations
• Oil filtration applications at 150ºC and 80 psi
• Water vapor recovery from flue gas at ~75ºC

Proposed Applications
• Hydrogen recovery from reformate
• Water gas shift (WGS) membrane reactor at 200 to 350ºC

Developmental Work Required
1. Deposition of an additional thin film for hydrogen separation
2. Fabrication of bundle and housing suitable for the application environment
MPT Advanced Inorganic Membranes

Our Core Technology: Thin film deposition on porous substrates

Inorganic Substrate

Ceramic Substrate

Carbon molecular sieve (porous, sulfur resistant)

Palladium (dense, excellent selectivity)

Unique feature of Supported Membranes

• Low cost, no Pd supply challenge
Advantages of Ceramic Membranes:
• High temperature and chemical stability
• Well defined porous structure (in comparison with SS, or others)
• Low cost (at least 50% or more cheaper)

An ideal platform for high temperature gas separations
   e.g., H₂ separation and purification for
   H₂ production via reforming of hydrocarbons and biomass

Key Barriers:
• Effective and reliable seal between metallic housing and ceramic membranes, i.e., thermal mismatch (completed)
• Metallic thin film cracks from its ceramic substrate, in particular for palladium under cooling in H₂ charged environment (FY11-12)
Accomplishments in FY 11-12:
Demonstrated Long Term Thermal Stability of Palladium Membrane Bundles

Pd-Cu Alloy Thermal Stability: Long term thermal stability testing of the MPT Pd-Cu membrane is currently underway. Over 600 hours of stable performance has been demonstrated.
Literature Review: Cooling Stability of Existing Palladium Membranes
(Asymmetric Composite Membranes, Cooling in Hydrogen Charged Environment)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Alloy</th>
<th>Porous Support</th>
<th>Preparation Method</th>
<th>Pd:X [%]</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PdCu</td>
<td>Alumina</td>
<td>Electroless plating</td>
<td>44 to 63:56:37</td>
<td>H₂:cooling, H₂: heating</td>
</tr>
<tr>
<td>2</td>
<td>PdCuNi</td>
<td>Nickel</td>
<td>Sputtering</td>
<td>90:7:3</td>
<td>H₂:cooling, H₂: heating</td>
</tr>
<tr>
<td>3</td>
<td>PdAg</td>
<td>Alumina</td>
<td>Electroless plating</td>
<td>75:25</td>
<td>H₂:cooling, H₂: heating</td>
</tr>
<tr>
<td>4</td>
<td>PdAg</td>
<td>Alumina</td>
<td>Electroless plating</td>
<td>80:20:15:5:10</td>
<td>H₂:cooling, N₂: heating</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature Cycling [°C]</th>
<th>No. of Cycles</th>
<th>Stable [Y/N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400</td>
<td>150</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>25</td>
<td>500</td>
</tr>
<tr>
<td>3</td>
<td>350</td>
<td>200</td>
<td>350</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>100</td>
<td>300</td>
</tr>
</tbody>
</table>

**No supported Pd membranes have demonstrated stability with an extended number of cooling cycles in H₂ charged environment, in particular with ceramic substrate. Nevertheless cooling stability is an important feature for small scale power generation.**

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**Treatment:**
Cooling in the presence of H₂ from 350°C to room temperature

**Sample:**
Our Pd membranes supported on commercial ceramic substrate

**Results:**
Our Pd membrane is not stable as shown by the morphological changes after treatment (as most Pd membranes reported). During FY 11-12, we have focused on the development of a Pd membrane that is stable during cooling in H₂.
**Our Approach**

Evaluation of Commercially Available Pd Alloy Foils for Cooling Stability in H₂ Atmosphere

As a guideline for our membrane material development

<table>
<thead>
<tr>
<th>Alloy Types Tested</th>
<th>Size</th>
<th>Vendor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>25mm x 25mm x 0.025mm</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>(77%Pd) / (23%Ag)</td>
<td>25mm x 25mm x 0.025mm</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>(90%wtPd) / (10%wtAu)</td>
<td>25mm x 25mm x 0.025mm</td>
<td>Refining system, Inc</td>
</tr>
<tr>
<td>(60%wt)Pd / (40%wtCu)</td>
<td>25mm x 25mm x 0.025mm</td>
<td>Refining system, Inc</td>
</tr>
</tbody>
</table>

Test Cells for Pd Alloy Foils

**Pd Alloy Discs after 34 Cooling Cycles:**
Pd-Cu was intact, Pd-Ag showed wrinkle near the edge, Pd and Pd-Au failed.
Overall, visual and SEM inspection of the unsupported foils following H₂ thermal cycling indicated that the foil stability goes as Pd-Cu(40) ~ Pd-Ag(23) >> Pd-Au(10) >> Pd.
Cooling Stability in H$_2$ Charged Environment: PdAg vs PdCu
H$_2$ and N$_2$ Permeances vs thermal cycles

**Test Protocol**: flat disc membranes following thermal cycling between RT and 350°C with cooling in H$_2$

**Implication**: Pd-Cu (~40%) alloy may deliver the cooling stability required.

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Accomplishments in FY11-12
Summary of Some MPT Pd Alloy Membranes Prepared in FY11-12

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>H₂</th>
<th>N₂</th>
<th>Selectivity</th>
<th>n&lt;sup&gt;th&lt;/sup&gt; Cooling Cycle</th>
<th>Cu [wt%]</th>
<th>Thickness [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCu-500-51</td>
<td>11.9</td>
<td>0.044</td>
<td>271</td>
<td>65</td>
<td>44.5</td>
<td>5.0</td>
</tr>
<tr>
<td>PdCu-500-52</td>
<td>10.3</td>
<td>0.075</td>
<td>138</td>
<td>65</td>
<td>45.3</td>
<td>4.7</td>
</tr>
<tr>
<td>PdCu-500-53</td>
<td>9.1</td>
<td>0.007</td>
<td>1,379</td>
<td>Fail</td>
<td>45.4</td>
<td>5.4</td>
</tr>
<tr>
<td>PdCu-500-54</td>
<td>11.4</td>
<td>0.008</td>
<td>1,354</td>
<td>Fail</td>
<td>43.3</td>
<td>3.8</td>
</tr>
<tr>
<td>PdCu-500-57</td>
<td>10.9</td>
<td>0.010</td>
<td>1,136</td>
<td>16</td>
<td>42.8</td>
<td>3.0</td>
</tr>
<tr>
<td>PdCu-500-58</td>
<td>11.5</td>
<td>0.053</td>
<td>219</td>
<td>16</td>
<td>44.3</td>
<td>5.1</td>
</tr>
<tr>
<td>PdCu-500-60</td>
<td>7.9</td>
<td>0.032</td>
<td>248</td>
<td>26</td>
<td>40.3</td>
<td>5.0</td>
</tr>
<tr>
<td>PdCu-500-62</td>
<td>6.2</td>
<td>0.010</td>
<td>616</td>
<td>6</td>
<td>41.5</td>
<td></td>
</tr>
<tr>
<td>PdCu-500-63</td>
<td>10.6</td>
<td>0.015</td>
<td>695</td>
<td>3</td>
<td>43.2</td>
<td></td>
</tr>
<tr>
<td>PdCu-500-64</td>
<td>15.4</td>
<td>0.038</td>
<td>403</td>
<td>3</td>
<td>45.0</td>
<td></td>
</tr>
</tbody>
</table>

We have successfully deposited the Pd-Cu (~44wt%) film on the ceramic substrate with permeances of 10-15 m³/m²/h/b and selectivity up to >1,000 at 350°C.

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Accomplishments in FY 11-12:
Demonstrated MPT Pd-Cu Membranes with Cooling Stability under H$_2$ Charged Atmosphere

In comparison with the literature, this unique stability has not been reported for a Pd/ceramic asymmetric membrane.
Use of low cost ceramic substrate as support for our Pd membranes is mainly responsible for meeting this cost vs performance target. On the other hand, through this project we have overcome the barriers associated with the use of ceramic substrate for high temperature gas separations.

Our Pd-Cu membranes developed in FY11-12 meet the 2015 DOE cost vs performance target.
Development of Catalytic Membrane Reactor for Water Gas Shift Reaction – Overview

Our previous laboratory study has demonstrated the performance potential of the membrane reactor for WGS reaction.

Key barriers associated with the ceramic membrane reactor and our accomplishments in FY 11-12 are presented below:

- Lack of flexible means to accommodate catalysts vs. membrane surface area
  Multi-tube membrane bundle with module (completed, prior to FY11-12);

- Lack of simple means for in-situ heat transfer to remove exothermic heat
  An innovative ceramic membrane reactor integrated with internal cooling coils has been developed. Thus, the in-situ heat transfer requirement can be accommodated without mechanical complication and cost increase (our focus in FY11-12).

WGS-MR Results

- >99% CO conversion
- >99.9% H₂ purity
- >83% H₂ recovery
- <50 ppm CO
- <3 ppm CO with post-treatment.
Accomplishments in FY 11-12:
Engineering and fabricating a commercially viable membrane reactor which can accommodate in-situ heat transfer

Pd Membrane Bundle with Cooling Channel(s)

Our Key Innovations:
Membrane reactors shown here are equipped with:
• Cooling coils which can be easily integrated into the module.

In addition, from our work in previous years, our candle filter configuration offers:
• Flexibility in catalyst volume vs membrane surface area,
• Effective and reliable seal between metallic housing and ceramic membranes.

In summary, a commercially viable ceramic membrane reactor has been developed successfully.
Tests completed:
1. Syngas at 16L/min produced by the reforming subunit
2. Hydrogen purification with the palladium membrane subunit, delivering hydrogen with ≤ 10 ppm CO from reformate.

Units under Construction:
1. Membrane reactor subunit with integrated post treatment to further reduce CO.

Test to be completed by 3rd Q:
1. Water gas shift reaction and hydrogen separation via the membrane reactor.
Accomplishments in FY 11-12:
Reformer and Pd Membranes have been prepared/installed and fully tested.

Gas Compositions

<table>
<thead>
<tr>
<th></th>
<th>Reformate (Feed to Membrane)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>61.6%</td>
</tr>
<tr>
<td>H₂O</td>
<td>19.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>19.0</td>
</tr>
<tr>
<td>CO</td>
<td>0.3</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Membrane Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>H₂O</td>
<td>NA</td>
</tr>
<tr>
<td>CO₂</td>
<td>800 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>&lt;10 ppm</td>
</tr>
<tr>
<td>CH₄</td>
<td>ND</td>
</tr>
</tbody>
</table>

H₂ separation and purification results from actual reformate are consistent with previous results obtained from synthetic mixtures. The membrane reactor will be installed and tested by 2nd Q ready for the field test in July 2012.
Performance stability during thermal cycling in the presence of hydrogen is essential for the palladium membrane to be viable for portable power generation applications. Through a screening study with the commercially available Pd alloy foils, PdCu was identified as a promising alloy candidate. PdCu shows no sign of degradation for >60 cycles while PdAg shows degradation from the 2nd cycle in our screening study.

During this year, we have successfully deposited the PdCu alloy thin film (~5µm) on our commercial ceramic substrate as an asymmetric Pd alloy membrane in terms of performance, and thermal and cooling stability.

The Pd alloy membrane thus developed meets the cost performance target set by US DOE for Yr 2015, i.e., 0.6 scfh @ Δp=20 psi/unit $ membrane cost. In general, the permeance is 10-15 m³/m²/hr/bar with the selectivity of ≥~1,000 at 350°C.

The Pd alloy membranes thus developed demonstrated performance stability during cooling from 350°C to room temperature in H₂ for >85 cycles as of today.

A full-scale membrane reactor packed with our PdCu membrane bundle and equipped with an internal cooling device has been designed and is currently under fabrication. The reformer and the membrane subunits have been fully tested. The entire system is scheduled to be ready for field test by 2nd Q 2012.
1. Complete the field test system assembly which is equipped with a full-scale PdCu membrane bundle and integrated with internal cooling coils by 2\textsuperscript{nd} Q 2012.

2. Conduct a field test for 1 month (i.e., ~700 hrs) in 3\textsuperscript{rd} Q 2012. The target performance is 99.999% purity and >83% recovery of H\textsubscript{2}.

3. Upgrade the permeance of the 3\textsuperscript{rd} generation Pd alloy membrane* we have developed by the end of 2012 to the level similar to our existing 2\textsuperscript{nd} generation Pd membrane, i.e., H\textsubscript{2} permeance increase from 15 to 25 m\textsuperscript{3}/m\textsuperscript{2}/hr/bar.

*with the cooling stability under the hydrogen charged environment