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

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### Overview

<table>
<thead>
<tr>
<th>Project Start Date</th>
<th>7/1/05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Project End Date</td>
<td>6/30/11</td>
</tr>
<tr>
<td>Percent Complete</td>
<td>70%</td>
</tr>
</tbody>
</table>

#### BARRIERS

1. **Testing/Analysis**: few commercial scale membrane- and membrane reactor-based processes in operation
2. **Permeate Flux/Selectivity**: cost vs performance target meeting our end user requirements
3. **Stability**: lack of long term membrane and membrane reactor performance data under our target field conditions

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

<table>
<thead>
<tr>
<th>FY09</th>
<th>$0</th>
</tr>
</thead>
<tbody>
<tr>
<td>FY10 Plan</td>
<td>$100K</td>
</tr>
</tbody>
</table>

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

### Participants

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

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**Media and Process Tech Inc.**
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 membranes/modules and conduct a field test for hydrogen separations

Example of Conventional Process - Steam Methane Reforming (SMR)

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

Field Test on MR in Phase II
• **Fabricating the Field Test Module for H₂ Recovery (Barrier #1&2)**
  - improved the field test module design to minimize module leaking potential experienced in the 1ˢᵗ field test.
  - performed the test to verify the thermal cycling stability and permeate flux of the improved field test module.
  - pursued 2ⁿᵈ generation membrane/module development to meet cost vs performance criteria set by our commercialization partner.

• **Conducting the membrane reactor test using full-scale membrane tubes (Barrier #1)**
  - experimentally verified the performance based upon process simulation.
  - provided design basis for our field test unit in Phase II.

• **Performing field tests on H₂ recovery (Barrier #1&3)**
  - conducting a field test using a 150 scfh H₂ separator in 2ⁿᵈ Q
TECHNICAL ACCOMPLISHMENTS – FY09-10

- **Balanced performance vs cost for our H\(_2\) Selective Membrane**
  Through evaluation of a range of ceramic membrane substrates with various permeances, we have been successful in developing our H\(_2\) selective membrane product to meet the low cost feature requested by our commercialization partner.

- **Corrected leakage issue of the 1\(^{st}\) generation module and ready for the field test**
  Our 1\(^{st}\) field test failed due to module leakage. This leak of the 1\(^{st}\) generation module has been corrected and the module is now ready for the field test scheduled in 2\(^{nd}\) Q.

- **Designed and fabricated the 2\(^{nd}\) generation module using ceramic membrane bundles**
  We have successfully developed the membrane bundle for our tubular H\(_2\) selective membrane. This bundle approach can minimize module leak and reduce the module cost, and will be used for our field test in Phase II.

- **Conducted membrane reactor test using our full-scale membrane tubes**
  The WGS-MR process we developed from a bench-scale unit previously has been verified experimentally using a full-scale tubular membrane. ~99% CO conversion, >83% H\(_2\) recovery and >99.9% purity H\(_2\) were achieved with this full-scale membrane reactor module.
1. Low temperature operation (WGS-LTS), thus, no exotic engineering/materials are required to develop for a membrane reactor and separator.

2. Our commercial low cost ceramic membranes/modules as platform; thus, capital cost can be justified due to low permeate flux at a low temperature.

**Unique Advantages of our Membranes/Membrane Reactors**
M&P CERAMIC MEMBRANES - Low Cost
for harsh environment applications

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

Developmental Work Required
1. Deposition of an additional thin film for hydrogen separation
2. Fabrication of bundle/housing suitable for working environment

Proposed Applications
• Hydrogen recovery from reformate
• Water gas shift (WGS) membrane reactor at 200 to 350°C
M&P Emerging Inorganic Membranes

M&P’s Core Technology: Thin film deposition on porous substrates

Inorganic Substrate

Ceramic Substrate

Carbon molecular sieve (porous, sulfur resistance)

Palladium (dense, excellent selectivity)

Unique features of Supported Membranes

• Low cost, no Pd supply challenge
• Module/housing for high temperature/pressure use
### Cost Analysis for Stationary Power Generators: Challenges for Membrane-based Processes

<table>
<thead>
<tr>
<th>Component</th>
<th>Typical Equipment</th>
<th>Cost [$]</th>
<th>$/kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stack</td>
<td>Fuel cell stack</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Fuel Processor</td>
<td>Reformer, fuel pumps, catalytic burner, air compressor</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Purifier</td>
<td>Pd membrane*</td>
<td>400</td>
<td>80</td>
</tr>
<tr>
<td>Other BOP</td>
<td>Cathode compressor, gas to gas humidifiers, plumbing, wiring, heat exchangers, power/control electronics</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Electrical</td>
<td>Power and control electronics</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Packaging</td>
<td>Chassis, insulation, sound proofing</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>5,250</strong></td>
<td><strong>1,050</strong></td>
</tr>
</tbody>
</table>

- The benefits offered by the membrane reactor was not taken into consideration in this analysis.
- Proprietary information of our end user participant.
- (Courtesy of Ballard Power Systems)
1. Performance Characterization (typical)

![Graph showing H2 permeance and H2/N2 selectivity at 350C for Pd-500-1]

2. Thermal Cycling Stability

![Graph showing membrane cost for 5kW genset]

<table>
<thead>
<tr>
<th>Membrane Cost for 5kW Genset</th>
<th>Targets</th>
<th>H2 Flux*</th>
<th>Cost [$/5 kW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Target</td>
<td>250</td>
<td>2,000</td>
<td></td>
</tr>
<tr>
<td>M&amp;P current</td>
<td>121</td>
<td>416</td>
<td></td>
</tr>
</tbody>
</table>

* in scfh/ft² at 20 psig

3. Thermal/ Hydrothermal Stability

![Graph showing long term hydrothermal stability test of hydrogen selective membrane]

1. Our Pd membranes have been comprehensively evaluated under multiple temperature cycles and extended thermal/hydrothermal test.

2. Our cost/performance ratio meets/exceeds the DOE target. More importantly, the membrane is prepared on existing commercial ceramic membrane products.

3. 121 scfh/ft² at 20 psig with $100/ft² can meet the cost target set by our commercialization partner.
## M&P H₂ Selective Pd Membranes

**Effect of substrate on Permeance and Product Cost**

<table>
<thead>
<tr>
<th>M&amp;P Substrate</th>
<th>Substrate N₂ Permeance [m³/m²/hr/bar]</th>
<th>Pd Permeance [m³/m²/hr/bar]</th>
<th>Selectivity [H₂/N₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early Stage</td>
<td>50 to 70</td>
<td>3 to 5</td>
<td>800 to 2,000</td>
</tr>
<tr>
<td>Current Standard</td>
<td>50 to 70</td>
<td>10 to 15</td>
<td>1,000 to &gt;10,000</td>
</tr>
<tr>
<td>Next Generation</td>
<td>120 to 150</td>
<td>20 to 25</td>
<td>350 to 500 (need improvement)</td>
</tr>
<tr>
<td>High Permeance Experimental Substrate</td>
<td>&gt;790</td>
<td>40 to 50</td>
<td>40 to 100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate Configuration</th>
<th>Features for Pd Film Deposition</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetric</td>
<td>Metallic foil</td>
<td>Thicker film; lower flux</td>
</tr>
<tr>
<td>Asymmetric</td>
<td>Porous Ceramic</td>
<td>Higher quality surface topography</td>
</tr>
<tr>
<td></td>
<td>Porous SS</td>
<td>Requiring diffusion barrier</td>
</tr>
</tbody>
</table>

However, seal for the ceramic membrane to the metallic housing is considered complicated.
Our Standard Full-scale Pd Membranes

Pd Thin Film Coated on the Outside
of Our Tubular Commercial Ceramic Membranes as Substrate

<table>
<thead>
<tr>
<th>Layer Location</th>
<th>Tube Diameter [cm]</th>
<th>Tube Length [in]</th>
<th>Surface Area [m²/30&quot;L tube]</th>
<th>Surface Area Ratio [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inside</td>
<td>0.57</td>
<td>0.35</td>
<td>30</td>
<td>0.0084</td>
</tr>
<tr>
<td>Outside</td>
<td>0.57</td>
<td>0.35</td>
<td>30</td>
<td>0.0136</td>
</tr>
</tbody>
</table>
Field Test Activities in FY09-10

M&P H₂ Selective Membranes for fuel processing to produce 152 scfh Hydrogen

Picture: Design of 5 kWh fuel-cell power generation unit (courtesy of Ballard Corp)

Current Status:
Leak was encountered in the 1ˢᵗ test. scheduled to perform the 2ⁿᵈ test in 2ⁿᵈ Q 2010

M&P Pd Membrane Module – 1ˢᵗ Generation (~1.3 m²)
1st Generation M&P Membrane Module Overview and Membrane Tube Packing
Stability of the 1st Generation Module through Thermal Cycling

N₂ permeance measurement for each individual tube at room temperature after 25 to 350°C thermal cycling

- Since the leaking trend does not follow the sequence of thermal cycles for most tubes, we conclude that the tube seal is stable through multiple thermal cycles.
- N₂ measurement of ~0.08 m³/m²/hr/bar in average is equivalent to ~0.006 m³/m²/hr/bar at 350°C based upon Knudsen diffusion, which is consistent with the measurement on the module basis as shown in the next slide.
Evaluation of the 1st Generation Field Test Module for H₂ Separation: hydrogen permeance, selectivity and leak potential through thermal cycling

- Hydrogen permeance of 7-8 m³/m²/hr/bar was obtained, consistent with our measurement from single tubes.
- Selectivity of >1,000 was obtained, indicating leaking is acceptable.
- Combining the results from this and the previous slides indicates that the 1st generation module is acceptable in terms of stability and performance after improvement of packing.
MEMBRANE BUNDLE AND HOUSING PREPARATION
as 2nd Generation Module for Phase II Field Test

These membranes and modules were adapted from our existing commercial ceramic membrane products and modules.

Pilot Scale Membrane Bundle and Housing for High Pressure Intermediate Temperature Applications

- 1.5” Dia Bundles (top & right) and Housing (bottom),
- 20 x 5mm Membranes in candle filter configuration for CMS membrane (above)
- 20 x 5mm Membranes in two-end mounted configuration for Pd membrane (right)
- Thermal cycling tested at 20 to 220°C
- Pressure cycling tested at 0 to 1000 psig

Unique Features
- low cost
- existing engineering/materials know-how

Our Accomplishments
- successfully thermal/pressure cyclic tested

Our full-scale ceramic membrane module (3-4” dia, prototype) for gas applications
Performance and Thermal Cycling Stability of The 2<sup>nd</sup> Generation Module: Pd Membrane Bundle

Pilot Test at M&P with Synthetic Mixture

| 350°C, 14 psig, 4.5 liter/min |  
|-----------------------------|---|
| H<sub>2</sub> [vol%] | 80 |
| CO<sub>2</sub> | 20 |

<table>
<thead>
<tr>
<th>Reject [liter/min]</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt; [vol%]</td>
<td>68</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>32</td>
</tr>
</tbody>
</table>

Permeate [liter/min] 2.5
- H<sub>2</sub> [vol%] 99.9
- CO<sub>2</sub> 0.1

- Temperature Range: 25 to 350°C
- At 350°C, membrane was exposed to hydrogen
- At <350°C, membrane was exposed to nitrogen

- Bundle leaking is acceptable and stable through the multiple thermal cycling test.
- Pd bundle configuration for the 2<sup>nd</sup> generation module shown here will be used in the field test to be undertaken in Phase III.
Objective: using a full-scale H₂ selective membrane to demonstrate high CO conversion and high purity hydrogen product at a high hydrogen recovery ratio

Physical Characteristics and Operating Parameters

<table>
<thead>
<tr>
<th>Pd Membrane:</th>
<th>30&quot;L, 0.57cm OD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature:</td>
<td>300°C</td>
</tr>
<tr>
<td>Catalyst:</td>
<td>30g of Cu/ZnO</td>
</tr>
<tr>
<td>Feed:</td>
<td>H₂:CO:CO₂:CH₄:H₂O 5.22:1:0.48:0.22:2.8</td>
</tr>
<tr>
<td>Pressure:</td>
<td>30 to 50 psig</td>
</tr>
<tr>
<td>Sweep Ratio:</td>
<td>0 to 0.3</td>
</tr>
</tbody>
</table>

Membrane Performance Characteristics:

Single Component Gas Permeances at 300°C

<table>
<thead>
<tr>
<th>Gas</th>
<th>Permeance [m3/m2/h/bar]</th>
<th>Sepn Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>16.82</td>
<td>1</td>
</tr>
<tr>
<td>CO</td>
<td>0.01</td>
<td>2,369</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.01</td>
<td>2,951</td>
</tr>
<tr>
<td>Ar</td>
<td>0.01</td>
<td>2,474</td>
</tr>
<tr>
<td>N₂</td>
<td>0.01</td>
<td>2,548</td>
</tr>
</tbody>
</table>
Experimental Results from operation at 30 psig and with no sweep

**WGS/LTS Membrane Reactor Activities in FY09-10**

CO concentration of <50 ppm and H₂ Purity >99.9% were obtained experimentally.
WGS-LTS Membrane Reactor Activities in FY09-10
Experimental Results from the operation at 30 psig and sweep ratio = 0.3

WGS/MR Operating Conditions
Temperature: 300°C, Feed Pressure: 30 psig
Perm Pressure: 1 psig, Perm Sweep Ratio: 0.3

>99% CO Conversion is possible; 20-30% additional conversion over the level by the packed bed was accomplished.
• ~83% H₂ recovery ratio at >99.9% H₂ purity were obtained experimentally.
• The experimental results shown in this and the previous two slides demonstrate >99% conversion and >99.9% purity at >83% hydrogen recovery is possible by our WGS-MR.
The low cost Pd membranes supported on our ceramic substrate were developed, which can meet the very stringent cost target set by our commercialization partner.

We have improved the 1st generation module and successfully verified its stability (i.e., acceptable leak through thermal cycling) and performance, which is ready for the field test involving hydrogen separation (to be held in April 2010).

The 2nd generation module, i.e., Pd membrane bundle, which is more economical and less prone to leak, has been developed and successfully tested. This module will be used for field test in Phase II.

>99% CO conversion and >99.9% purity hydrogen at >83% hydrogen recovery ratio was demonstrated experimentally using a reactor packed with our full-scale Pd membrane and a commercial catalyst. We are now ready to move to the field test of the membrane reactor to be undertaken in Phase II.
Work Plan for Rest of Project Period

Phase I: Field Test on Membranes/Modules

1. Complete the field test for hydrogen separation at our commercialization partner site to demonstrate its commercial viability in the field (scheduled in April 2010).
2. Prepare the field test involving the WGS-Membrane Reactor (MR) with the 2nd generation module, which will be the focus of our Phase II project.

Phase II: Field Test Activities

1. Prepare 2nd generation membrane/modules for use as a full-scale WGS-MR.
2. Design and construct the full-scale membrane reactor for field test at Ballard Power Systems.
3. Conduct field test at the participated end user site.