Development of Robust Hydrogen Separation Membranes

Dr. Bryan D. Morreale

Reaction Chemistry & Engineering Research Group Leader
NETL Office of Research & Development

2010 DOE Hydrogen Program Review
Project ID# PD008
Reaction Chemistry & Engineering Group Members

**U.S. DOE - NETL**
Dr. Bryan Morreale
Dr. Bret Howard
Dr. Dirk Link
Dr. Charles Taylor

**NETL Research Faculty**
Dr. Andrew Gellman, CMU
Dr. James Miller, CMU
Casey O’Brien, CMU
William Michalak, CMU
Dr. Robert Enick, PITT
Kate Barillas
Dr. Goetz Vesser, PITT
Dr. Sittichai Natesakhawat, PITT
Dr. Nate Weiland, WVU

**NETL Site Support Contractors**
Dr. Fan Shi, URS
Dr. Adefemi Egbebi, URS
Dr. Mike Ciocco, URS
Dr. Sonia Hammache, URS
Dr. Brian Kail, URS
Dr. Janice Panza, URS
Paul Zandhuis, URS
Nick Means, URS
Overview

Timeline
• Project start date: 10/1/2009
• Project end date: 9/30/2010
• Percent complete: 58%

Budget
• FY10 Funding: $681
• FY09 Funding: $746k
• FY08 Funding: $1,000k
• FY07 Funding: $1,230k

Barriers(1)
• (G) H₂ Embrittlement
• (H) Thermal cycling
• (I) Poisoning of catalytic surface
• (J) Loss of structural integrity and performance

Partners
• Carnegie Mellon University
• University of Pittsburgh
• Gas Technology Institute
• Los Alamos National Lab.
• NETL Computational Chemistry

(1) 2008 Hydrogen from Coal Program: Research, Development and Demonstration Plan
Background

(Relevance)

• Overall goal
  – Development of robust hydrogen separation membranes for integration into coal conversion processes, including integrated WGSMR

• Studies suggest that incorporating separation membranes into coal conversion processes can reduce costs by 8%
Facilities & Capabilities

- **3 Membrane Test Rigs**
  - Continuous, bench-scale units
  - T to 1000°C, P to 1000 psi

- **2 Laboratory Membrane Screening Rigs**
  - Continuous, lab-scale units
  - T to 1000°C, P to 30 psi

- **Materials Lab**
  - Depositions chamber
  - Vacuum arc-melter
  - Micro-welder
  - High-T box and annealing ovens
  - XRD w/hot-stage
  - SEM w/EDS
  - TGA for use with H$_2$S
  - UHV analysis capabilities

- **High Throughput Materials Science**
  - Deposition tools
  - Spatially resolved characterization

- **Computation**
  - DFT, Kinetic Monte-Carlo, COMSOL CFD
Task 1: Performance testing of external membranes and the “NETL H₂ Membrane Test Protocol”
Task 2: Robust Metal Membrane Development

- Objective
- Approach
- Technical Accomplishments
- Collaborations
- Proposed Future Work
Task 1: H$_2$ Membrane Test Protocol

**Objective**
- Define a H$_2$-membrane test protocol that
  - will advance the technology towards application to coal conversion processes
  - is consistent with overall FE program metrics, and
  - yields a basis for an “apples-to-apples” comparison

**Approach**
- Apply understanding of engineering principles, membrane technology and coal conversion processes to define a sequential protocol

<table>
<thead>
<tr>
<th>Performance Criteria</th>
<th>Units</th>
<th>2007 Target</th>
<th>2010 Target</th>
<th>2015 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux $^a$</td>
<td>sccm/cm$^2$</td>
<td>51</td>
<td>102</td>
<td>152.4</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>400–700</td>
<td>300–600</td>
<td>250–500</td>
</tr>
<tr>
<td>S Tolerance</td>
<td>ppmv</td>
<td>----</td>
<td>20</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Cost</td>
<td>$/ft^2$</td>
<td>150</td>
<td>100</td>
<td>&lt;100</td>
</tr>
<tr>
<td>WGS Activity</td>
<td>-</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>ΔP Operating Capability $^b$</td>
<td>psi</td>
<td>100</td>
<td>Up to 400</td>
<td>Up to 800 to 1,000</td>
</tr>
<tr>
<td>Carbon Monoxide Tolerance</td>
<td>-</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Hydrogen Purity</td>
<td>%</td>
<td>95%</td>
<td>99.5%</td>
<td>99.99%</td>
</tr>
<tr>
<td>Stability/Durability</td>
<td>years</td>
<td>1</td>
<td>3</td>
<td>5</td>
</tr>
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$^a$ For 100 psi ΔP (hydrogen partial pressure basis)
$^b$ ΔP = total pressure differential across the membrane reactor
Task 1: H₂ Membrane Test Protocol

*(Background)*

• Completed a survey to determine the effluent composition of a WGS unit

• Developed COMSOL model to predict the influence of WGS reaction and/or H₂ removal on overall gas composition

• Identified the test conditions and gas compositions that are relevant to syngas conversion flowsheet options:
  - **Test 1:** Shifted syngas, with no sulfur
  - **Test 2a:** Shifted syngas with 20ppm H₂S
  - **Test 2b:** Shifted syngas with ~50% H₂ removal
  - **Test 2c:** Shifted syngas with ~90% H₂ removal

<table>
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<tr>
<th></th>
<th>Test 1</th>
<th>Test 2a</th>
<th>Test 2b</th>
<th>Test 2c</th>
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<tbody>
<tr>
<td>H₂</td>
<td>50%</td>
<td>50%</td>
<td>33%</td>
<td>5%</td>
</tr>
<tr>
<td>CO</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>2%</td>
</tr>
<tr>
<td>CO₂</td>
<td>30%</td>
<td>30%</td>
<td>40%</td>
<td>57%</td>
</tr>
<tr>
<td>H₂O</td>
<td>19%</td>
<td>19%</td>
<td>25%</td>
<td>36%</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.0%</td>
<td>0.2%</td>
<td>0.3%</td>
<td>0.4%</td>
</tr>
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Temp: 300-600ºC
Pᵦₑᵦ: 200 psi
Pᵦₑᵦᵦ: atm
Task 1: H₂ Membrane Test Protocol

(Technical Accomplishments)

• **Infrastructure**
  – Moved the membrane test units to new location
  – Modified membrane units to accommodate the “test protocol”

• **Flow ranges and membranes to test**
  – Conducted detailed analysis of the flow requirements to test a variety of membranes being developed
    • Disks, tubes
    • Performing at 2015 targets
Task 1: $H_2$ Membrane Test Protocol

(Collaborations)

- NETL Technology Manager and Technology Team
  - The development of the test protocol was a team effort consisting of several participants of the Technology Team

- NETL funded $H_2$ Separation Projects
  - Provide unbiased performance verification testing
    - REB Research
    - ORNL
    - Eltron Research
    - WRI
**Task 1: H₂ Membrane Test Protocol**

*(Proposed Future Work)*

- Continue to support the development of test protocols to include more “commercially relevant” conditions
  - Higher transmembrane pressure differentials
  - Contaminants other than H₂S
    - For example, Cl- and N-compounds for biomass co-feed
  - Integration of WGS reactor and Membrane separator
Task 2: Robust Metal Membrane Development

Identify membrane compositions and configurations that meet the criteria outlined in FE H\textsubscript{2} from Coal RD&D plan per the NETL Membrane Test Protocol

Provide design guidance to collaborators who will fabricate membranes at commercial scales and thicknesses

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\textsuperscript{b} ΔP = total pressure differential across the membrane reactor
Task 2: Robust Metal Membrane Development

(Background)

Corrosive decay
- “turns on” slowly
- Associated with formation of $\text{Pd}_4\text{S}$ scale
  \[ 4\text{Pd} + \text{H}_2\text{S} \rightarrow \text{Pd}_4\text{S} + \text{H}_2 \]
- Flux never = 0
Task 2: Robust Metal Membrane Development

(Background)

Catalytic poisoning
- Immediate
- Usually partially reversible
- No bulk Pd-S compound formation
- Characteristic of alloy at low temperatures

![Image of Membrane Surface and Cross Section]
Task 2: Robust Metal Membrane Development

(Approach)

- Develop a multi-layered membrane system that utilizes the catalytic activity shown with Pd₄S and the corrosion resistance of select PdCu alloys

- Use computational and experimental techniques to understand the
  - catalytic activity at the gas-scale interface
    - Pd, Cu, Mo, Fe, Ni, Co, etc.
  - Hydrogen transport properties of the layers and interfaces
  - stability and growth scale
Task 2: Robust Metal Membrane Development
(Technical Accomplishments – Catalytic Activity, Gas-Scale Interface)

Surface Stability
- Pd-terminated surfaces are least stable
- S-Pd-terminated surfaces are most stable

Catalytic Activity
- Incorporation of S into the Pd system decreases catalytic activity
- Pd-participation in the surface reaction allows rates high enough to meet DOE targets
  - Pd-terminated
  - Sub-surface Pd
Task 2: Robust Metal Membrane Development
(Technical Accomplishments – Catalytic Activity, Gas-Scale Interface)

HD-Exchange Experiments

- Modified quartz reactor system
- Developed kinetic model
- Initiated experimentation on Pd, Cu and 80Pd-Cu
  - The 80Pd-Cu system is “more catalytic” than pure Pd in H₂
Synthesized multi-layered membranes
– Continuous and dispersed overlayers
– 25µm PdCu substrate (corrosion resistance)
Synthesized multi-layered membranes
- Mono-layer Mo film
- Expected performance in H₂
- H₂S catalyzed the corrosion of PdCu substrate
Task 2: Robust Metal Membrane Development
(Technical Accomplishments – Stability, Scale Growth & Transport)

- Directly measured the permeability of Pd$_4$S
  - In the presence of H$_2$, appears to follow Sievert's law
  - Permeability of Pd$_4$S is ~10x less than Pd
  - and consistent with fcc-phase 60Pd-Cu
Task 2: Robust Metal Membrane Development

(Collaborations)

• The research team conducting the work on the task consisted of participants from
  – Carnegie Mellon University
  – NETL Reaction Chemistry & Engineering Group
  – NETL Computational Research Group
  • Dominic Alfonso
Task 2: Robust Metal Membrane Development

*Proposed Future Work*

Identify membrane compositions and configurations that meet the criteria outlined in FE H₂ from Coal RD&D plan per the NETL Membrane Test Protocol

- **Catalytic activity**
  - Utilize computational and experimental approaches to screen the H₂-dissociation properties of potential membrane surfaces (metals, oxides, sulfides, carbides, glasses)
    - High-activity, thermally stable and corrosion resistant
  - High-throughput methodologies that can measure properties over the entire composition spectrum of up to 4-components

- **Hydrogen transport properties**
  - Utilize computational and experimental approaches to quantify the permeability of base materials and scales that form during operation
    - High permeability, high mechanical strength

- **Scale growth and stability**
  - Quantify the scale growth of corrosion products, and stability of membrane overlayers at relevant conditions

- **Membrane fabrication**
  - Utilize the observations above to synthesize membranes for characterization per the NETL Test Protocol
Summary

• A test protocol has been developed and NETL’s test systems have been modified to allow testing of various membrane geometries and performance levels.

• Evaluation of the catalytic activity of potential membrane catalyst layers has been initiated utilizing DFT, kinetic Monte Carlo and H$_2$-D$_2$ exchange.
  – In the presence of H$_2$, 80Pd-Cu appears more catalytic than Pd.
  – Pd$_4$S shows catalytic properties for H$_2$ dissociation.

• Several multi-layered membrane systems have been fabricated using both continuous and dispersed catalysts.
  – Thin catalyst layers appear to catalyze the corrosion of a corrosion resistance PdCu alloy.

• The characterization of sulfide permeability has been initiated.
  – Pd4S is approximately 10x lower than pure Pd.