Development of Robust Metal Membranes for Hydrogen Separation

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

2009 DOE Hydrogen Program Review
## Reaction Chemistry & Engineering

### Group Members

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- Dr. Bryan Morreale
- Dr. Bret Howard
- Dr. Dirk Link
- Dr. Charles Taylor

#### NETL Research Faculty
- Dr. Andrew Gellman, CMU
- Dr. James Miller, CMU
- Dr. Robert Enick, PITT
- Dr. Goetz Vesser, PITT
- Dr. Sittichai Natesakhawat, PITT

#### NETL Site Support Contractors
- Dr. Mike Ciocco, Parsons
- Dr. Sonia Hammache, Parsons
- Paul Zandhuis, Parsons
- Nick Means, Parsons
- Technical staff, Parsons
Overview

Timeline
• Project start date: 10/1/2008
• Project end date: 9/30/2009
• Percent complete: 67%

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

Barriers\(^{(1)}\)
• (G) H\(_2\) 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
• REB Research
• 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 dense metal, hydrogen separation membranes for integration into coal conversion processes

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

• Reactor Systems
  – Reactor and separation configurations
    • Continuous or batch
  – Major and minor syngas constituents
  – T to 1000°C, P to 1000 psi

• Fabrication Lab
  – Depositions chamber
  – Vacuum arc-melter
  – Micro-welder
  – High-T box and annealing ovens

• Characterization Instruments
  – UHV chambers
    • Gradient doser, AES, XPS, LEIS, TPD, PVD
  – XRD w/hot-stage
  – SEM w/EDS
  – TGA for use with H₂S
Outline

Task 1: H₂ Membrane Test Protocol
Task 2: PdCu System
Task 3: 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>
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<td>$/ft^2$</td>
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<tr>
<td>WGS Activity</td>
<td>-</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
<td>?P Operating Capability (b)</td>
<td>psi</td>
<td>100</td>
<td>Up to 400</td>
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<tr>
<td>Hydrogen Purity</td>
<td>%</td>
<td>95%</td>
<td>99.5%</td>
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<td>Stability/Durability</td>
<td>years</td>
<td>1</td>
<td>3</td>
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* a For 100 psi $\Delta P$ (hydrogen partial pressure basis)
  b $\Delta P = $ total pressure differential across the membrane reactor
**Task 1: H₂ Membrane Test Protocol**

*(Technical Accomplishments)*

- 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 20 ppm H₂S
  - **Test 2b**: Shifted syngas with ~50% H₂ removal
  - **Test 2c**: Shifted syngas with ~90% H₂ removal

<table>
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<tr>
<th>Component</th>
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<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>
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<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>
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<tr>
<td>H₂S</td>
<td>0.0%</td>
<td>0.2%</td>
<td>0.3%</td>
<td>0.4%</td>
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- Temp: 300-600°C
- P_{Ref}: 200 psi atm
Task 1: H₂ 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 H₂ Separation Projects
  – Provide unbiased performance verification testing
    • REB Research
    • ORNL
    • Eltron Research
    • WRI
Task 1: $\text{H}_2$ 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 $\text{H}_2\text{S}$
    - For example, Cl and N for biomass co-feed
  - Integration of WGS reactor and Membrane separator
    - (WGSMR)
Task 2: PdCu System

• Objective
  – Complete a comprehensive performance evaluation of the PdCu system at conditions consistent with coal conversion processes

• The intent of the study is to
  – gain a fundamental understanding of the PdCu system
  – address discrepancies observed in literature
  – develop property-performance relationships
  – provide design guidance for fabrication of membranes at commercial scales and thicknesses

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(a) For 100 psi ΔP (hydrogen partial pressure basis)
(b) ΔP = total pressure differential across the membrane reactor
Task 2: PdCu System

(Approach)

- Utilize several PdCu compositions
  - 100, 80, 60, 53wt%Pd-Cu
- Fabricated by “cold rolling” techniques
- Membrane thickness was generally ~100 μm
  - Ease of operation and minimize failures
- Temperatures consistent with post gasification and allowed variation in crystalline structure
  - 350, 450 and 635°C
- Sour gas studies
  - 8hrs in clean 10%He-H2 (baseline)
  - 120hrs in 0.1%H2S-10%He-H2

Task 2: PdCu System

(Technical Accomplishments)

- Completed evaluation of hydrogen permeability of Pd and PdCu
  - 60Pd-Cu exhibits the highest permeability at temperatures below ~500°C, corresponding to a B2 crystalline structure.
  - 80Pd-Cu exhibits the highest permeability at temperatures above ~500°C, corresponding to a fcc crystalline structure.
  - In general, Pd-Cu permeability increases with increasing Pd content.
Task 2: PdCu System

(Technical Accomplishments)

- Completed evaluation of Pd and PdCu alloys in presence of H₂S
  - Catalytic poisoning: Immediate decrease: no significant surface scale
    - 60Pd-Cu, 53Pd-Cu
  - Corrosive decay: Gradual decrease: significant surface scale
    - Pd, 80Pd-Cu
  - No change in performance upon the introduction of H₂S: no surface scale.
    - 80Pd-Cu, 60Pd-Cu, 53Pd-Cu at T>450°C

“Catalytic poisoning”

“Corrosive decay”
Task 2: PdCu System
(Technical Accomplishments)

- Reported the first ever permeability of Pd₄S using both experimental and computational techniques
  - Approach can be used for developing new membrane systems
- Pd₄S permeability is ~1/10 Pd permeability
Task 2: PdCu System
(Collaborations)

• The research team conducting the work on the PdCu system consisted of participants from local universities
  – University of Pittsburgh
    • Provided technical support
    • Performance testing of the membranes
    • Membrane characterization
  – Georgia Institute of Technology
    • Utilized computational method to predict the first reported permeability of palladium-sulfide
Task 2: PdCu System

(Proposed Future Work)

• Characterization of the PdCu system in clean and \( \text{H}_2\text{S} \)-contaminated environments has been successfully completed

• No additional work specific to PdCu is planned

• The results of our work with PdCu will help set the direction of future Robust Metal Membrane Development (Task 3):
  – how to think about and characterize interaction of sulfur with multicomponent materials, like alloys
  – alloys’ contribution to corrosion resistance
  – the role of minor components in imparting sulfur tolerance to metal membrane systems
Task 3: Robust Metal Membrane Development

• Identify membrane compositions and configurations that meet the criteria outlined in FE H₂ 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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| WGS Activity          |            | Yes         | Yes         | Yes         |
| 7F Operating          |            |             | Up to 400   | Up to 800   |
| Capability (b)        | psi        | 100         |             | 1,000       |
| Carbon Monoxide       |            | Yes         | Yes         | Yes         |
| Tolerance             |            |             |             |             |
| Hydrogen Purity       | %          | 95%         | 99.5%       | 99.99%      |
| Stability/Durability  | years      | 1           | 3           | 5           |

(a) For 100 psi ΔP (hydrogen partial pressure basis)
(b) ΔP = total pressure differential across the membrane reactor
Task 3: Robust Metal Membrane Development

(Approach)

- Building on the PdCu foundation, apply fundamental and applied science to engineer membrane alloys and composites suitable for coal conversion processes
  - Corrosion resistance
    - fundamental thermodynamics,
    - gravimetric analysis
  - Surface activity
    - $\text{H}_2/\text{D}_2$ exchange
    - computational studies
  - $\text{H}_2$-transport
Task 3: Robust Metal Membrane Development

(Technical Accomplishments)

• Provisional Patent Filed:
  “Sulfur Induced H₂-Membrane”
  – Concept: Use B2-structured Pd-Cu alloy as sulfide corrosion barrier in multilayered membrane structure
  – Utilize “S-based surface catalyst” to provide atomic hydrogen for transport

• New capabilities developed
  – Preparation and characterization of H-atom transport through multi-layer structures in UHV
  – Preparation and characterization of catalytic-sulfide top-layers for multi-layer structures
Task 3: Robust Metal Membrane Development

(Technical Accomplishments)

• Several binary and tertiary metallic systems have been fabricated and screened
  – Pd-Ag, Au, Co, Cu, Ni, Pt
• PdPt alloy has shown significant promise for S-tolerance
Task 3: Robust Metal Membrane Development

(Collaborations)

• The research team conducting the work on the task consisted of participants from institutions
  – Carnegie Mellon University
    • Provided technical support
    • Assisted performance testing of the membranes
    • Utilize UHV techniques to evaluate the energetics associated with H₂ activation on metal and sulfide surfaces.
  – NETL Computational Research Group
    • Provide fundamental computational studies evaluating the energetics associated with H₂ activation on metal and sulfide surfaces.
Task 3: Robust Metal Membrane Development

(Proposed Future Work)

- Characterize H-atom transport across interfaces buried within multi-layer structures
- Develop options for sulfur-resistant top-layers and corrosion-resistant intermediate layers for layered structures
- Continue evaluation of binary and higher alloys for use alone or as functional layers in multi-component structures
- Provide design input to partners who fabricate membranes for practical implementation
Summary

• A test protocol has been developed that allows technological progression and comparisons for application to coal conversion processes

• A comprehensive study of the PdCu system has been completed
  – Conditions of complete S-tolerance have been identified.
  – Corrosion/catalytic phenomena has been identified and will be used for further membrane development

• Several alloy compositions have been fabricated and screened for performance
  – Some alloys have shown potential for S-tolerance