Sorption Enhanced Mixed Matrix Membranes for H₂ Purification and CO₂ Capture (DE-FE0026463)

Lingxiang Zhu¹, Deqiang Yin¹, Shailesh Konda¹, Hien Nguyen¹, Mark Swihart¹, and Haiqing Lin¹, Jay Kniep² and Tim Merkel²
Andrew Placido³ and Kunlei Liu³

¹University at Buffalo, State University of New York (UB)
²Membrane Technology and Research, Inc. (MTR)
³Center for Applied Energy Research, University of Kentucky (CAER)

NETL CO₂ Capture Technology Project Review Meeting
Pittsburgh, PA
8/14/2018
Sorption Enhanced Mixed Matrix Membranes for H₂ Purification and CO₂ Capture

Award number: DE-FE0026463

Project period: 10/1/15 to 12/31/18

Funding:
$1,485,099 DOE
$ 376,837 UB and MTR contribution
$1,861,936 total

Program manager: Steve Mascaro

Participants: University at Buffalo (UB); Membrane Technology and Research, Inc. (MTR); and University of Kentucky (CAER)

Project Objectives:
Develop industrial membranes with H₂ permeance of 500 GPU and H₂/CO₂ selectivity of 30; and
Conduct parametric tests with real syngas at CAER.
**Project Scope**

**BP1:** Prepare mixed matrix materials with H₂ permeability of 50 Barrers and H₂/CO₂ selectivity of 30 (*Q1-Q4*)

**BP2:** Prepare thin film composite membranes with H₂ permeance of 500 GPU and H₂/CO₂ selectivity of 30 (*Q5-Q10*)

**BP3:** Conduct a 20-day field test of membranes with real syngas at CAER (*Q11-Q13*)

![Nanostructured materials](image1)

![Industrial membranes](image2)

Field test
Our Approach:  
**H₂/CO₂ Solubility Selectivity**

\[
\alpha = \frac{P_{H_2}}{P_{CO_2}} = \frac{S_{H_2}}{S_{CO_2}} \times \frac{D_{H_2}}{D_{CO_2}}
\]

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temp. (°C)</th>
<th>H₂ solubility cm³(STP)/(cm³ atm)</th>
<th>H₂/CO₂ solubility selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(dimethyl siloxane)</td>
<td>35</td>
<td>0.10</td>
<td>0.078</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>35</td>
<td>0.075</td>
<td>0.036</td>
</tr>
<tr>
<td>Matrimid®</td>
<td>35</td>
<td>0.12</td>
<td>0.035</td>
</tr>
<tr>
<td><strong>Pd metal</strong></td>
<td><strong>25</strong></td>
<td><strong>38,000</strong></td>
<td><strong>&gt; 1,000</strong></td>
</tr>
</tbody>
</table>

* Calculated at 0.02 bar H₂
Our Approach:
Sorption Enhanced Mixed Matrix Materials

Polybenzimidazole (PBI)

Mixed matrix materials (MMMs)

Pd nanoparticles

Membrane Materials Meeting the BP1 Target

**Mixed-gas:**
50% H₂/50% CO₂

**Temperatures:**
150-175-200-225 °C from left to right.

<table>
<thead>
<tr>
<th>Tasks (BP2)</th>
<th>Start date</th>
<th>End date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 7 Scale up Polymer Synthesis</td>
<td>10/1/2016</td>
<td>3/31/2017</td>
</tr>
<tr>
<td>Task 8. Scale up Synthesis of Pd-based Nanomaterials</td>
<td>10/1/2016</td>
<td>3/31/2017</td>
</tr>
<tr>
<td>Task 9. Prepare Thin Film Composite Membranes</td>
<td>1/1/2017</td>
<td>9/30/2017</td>
</tr>
<tr>
<td>Task 10. Conduct Parametric Tests of Membranes for H$_2$/CO$_2$ Separation</td>
<td>1/1/2017</td>
<td>12/31/2017</td>
</tr>
<tr>
<td>Task 11. Design and Modify Membrane Stamp Test Unit for CAER Field Test</td>
<td>6/1/2017</td>
<td>12/31/2017</td>
</tr>
</tbody>
</table>

**Milestone f: Mixed matrix membranes with superior H$_2$/CO$_2$ separation properties prepared**

| Task 13. Run 20-Day Field Test at CAER                                    | 6/1/2018   | 11/30/2018  |
| Task 14. Analyze Field Test Results / Membrane Post-analysis             | 10/1/2018  | 12/31/2018  |

**Milestone h: Successful field test completed**
Polymer Development and Scale-up

- Commercial PBIs are identified
- Modification of PBIs has been demonstrated to improve performance

H₂/CO₂ selectivity vs. H₂ permeability (Barrer)

Long-term Stability of a PBI-(H$_3$PO$_4$)$_{0.16}$ Film in Simulated Syngas (H$_2$, CO$_2$ and H$_2$O)

Test time (h)

Mixed-gas permeability (Barrel)

H$_2$/CO$_2$ selectivity

- 50%H$_2$:50%CO$_2$ @ 150 °C
- Dry
- H$_2$O: 0.3 mol%
Nanoparticle Synthesis Scale-up: Gas Phase Synthesis

- Scaled up the nozzle diameter
- Achieved plugging-free production
- Can produce 2 g of Pd-Cu alloy NPs in 8 h

Stability of Mixed Matrix Materials against H$_2$S

**PBI-Pd-58/13**: 58 wt% or 13 vol% Pd nanoparticles
Thin Film Composite (TFC) Membranes

Conventional TFC membranes


Thermally stable TFC membranes
Surface of PBI-supports: SEM Characterization

Aver. pore size: 14 nm
Surface porosity: ~15%
Cross-section of PBI-supports: SEM Characterization

500 nm
Reduce PBI/Pd Selective Layer Thickness to below 900 nm

PBI-Pd-58/13

H₂ permeance: ca. 40 GPU
H₂/CO₂ selectivity: 40

Note: The PDMS gutter layer has an H₂ permeance of ~400 GPU

Measurement condition: 150 °C, 150 psig; 50% H₂/50% CO₂
Stability with H$_2$S for PBI-Pd-58/13-based TFC Membrane

PBI-Pd-58/13: 58 wt% or 13 vol% Pd nanoparticles
175 ºC; 150 psig
Benchmarking Our TFC Membranes

- Thin film (70 nm)
- 230 °C

Gasifier at University of Kentucky Center for Applied Energy Research (CAER)

Syngas produced at atmospheric pressure, cooled to 40 °C, and then compressed to 450 psig

Photos provided by Andy Placido of CAER
Membrane Testing Apparatus

UK-CBTL

- 33 lb/h → ASU
- <90 lb/h → UB
- 10 lb/h → UB
- <47 lb/h → Other

![Test unit](image1.png)

![Test cell](image2.png)
Project Plan and Milestones

10/15  High performance materials development
10/16  Thin film composite membranes developed
       (1)
       Modify a testing unit
       (2)
6/18   20-days testing
       (3)

(1) High performance mixed matrix materials identified;
(2) High performance thin film composite membranes prepared;
    Testing skid modified;
(3) Parametric testing of membranes using real syngas
# Project Milestones

<table>
<thead>
<tr>
<th>Budget Period</th>
<th>ID</th>
<th>Description</th>
<th>(Planned) Completion Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a</td>
<td>Updated Project Management Plan</td>
<td>11/30/15</td>
</tr>
<tr>
<td>1</td>
<td>b</td>
<td>Kickoff Meeting</td>
<td>12/31/15</td>
</tr>
<tr>
<td>3</td>
<td>c</td>
<td>Final report</td>
<td>12/31/18</td>
</tr>
<tr>
<td>1</td>
<td>d</td>
<td>Polymers and nanomaterials with promising $\text{H}_2/\text{CO}_2$ separation properties identified and prepared</td>
<td>6/30/16</td>
</tr>
<tr>
<td>1</td>
<td>e</td>
<td>Mixed matrix materials with superior $\text{H}_2/\text{CO}_2$ separation properties prepared</td>
<td>9/30/16</td>
</tr>
<tr>
<td>2</td>
<td>f</td>
<td>Mixed matrix membranes with superior $\text{H}_2/\text{CO}_2$ separation properties</td>
<td>3/31/18</td>
</tr>
<tr>
<td>2</td>
<td>g</td>
<td>Field test unit modified</td>
<td>3/31/18</td>
</tr>
<tr>
<td>3</td>
<td>h</td>
<td>Successful field test</td>
<td>11/30/18</td>
</tr>
</tbody>
</table>
Summary

**H₂/CO₂ selectivity vs. H₂ permeability (Barrer)**

- PBI-Pd-58/13
- PBI-Pd-46/8.2
- PBI-Pd-22/3.0

2008 upper bound at 150 °C

**Target region**

Target region for PBI-ZIF 8 and MTR Proteus™.

**DOE/NETL**
- Develop MMMs

**UB**
- Coordinate

**CAER/UK**
- Host field test

**MTR**
- Modify a test unit
- Run the test at CAER

This study

Polyamide

SRI PBI

PBI-ZIF 8

MTR Proteus™

H₂/CO₂ Selectivity vs. H₂ Permeance (GPU)
Acknowledgments

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Kunlei Liu