Mixed Matrix Membranes for Post-Combustion CO$_2$ Capture

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Goal is to fabricate *thin, CO$_2$ selective membrane* with *good mechanical, chemical & thermal stability* while achieving the DOE goals of CO$_2$ capture with *cost optimized process scheme*.
Multidisciplinary team helps to develop the best product.
**Project status**

- Budget period: 1 of 2 budget periods.
- 60% of $1,509,046 total funds.
- Project is 62% complete.
- Current TRL: 3  
  End of Project TRL: 4

<table>
<thead>
<tr>
<th>Milestone Number and Task</th>
<th>Milestone Title</th>
<th>Planned Completion Date</th>
<th>Actual Completion Date</th>
<th>Variance Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Complete testing of two down selected hollow fiber membranes in simulated pulverized coal power plant flue gas</td>
<td>9/30/2014</td>
<td>9/30/2014</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>Complete the construction of a membrane test skid for use with a slipstream of real flue gas.</td>
<td>9/30/2015</td>
<td></td>
<td>On Schedule</td>
</tr>
<tr>
<td>3</td>
<td>Complete the gas permeance testing of two membranes using a slipstream of real flue or fuel gas.</td>
<td>9/30/2016</td>
<td></td>
<td>On Schedule</td>
</tr>
</tbody>
</table>
Mixed Matrix Membranes - Advantages

Goals for membrane performance to be economically practical:

- Permeance of >1,000 GPU.
- CO₂/N₂ selectivity of >30.

Courtesy: William J Koros
Control of nanoscale interfaces is very important to achieve improved performance.
Tuning the interface structure

- **Filler surface**: Plane and brush
- **Polymer chain flexibility**: Rigid, intermediate and soft
- **Interaction between polymer and MOF**: Strong repulsion, weak repulsion, neutral, weak interaction and strong interaction
It is possible to optimize the interface by engineering the materials.

Venna et. al., J. Mater. Chem. A, 2015, 3, 5014-5022
Membrane performance - Targets

\[ P_c = P_m \left[ \frac{P_s + 2P_m - 2\Phi_s (P_m - P_s)}{P_s + 2P_m + \Phi_s (P_m - P_s)} \right] \]

\[ \alpha_{A/B} = \frac{P_{cA}}{P_{cB}} \text{ from above model} \]

Polyphosphazene membranes

Polyphosphazene was chosen because of its high tunability, mechanical properties and gas transport properties.

Over 700 Different Polyphosphazenes Have Been Synthesized So Far

<table>
<thead>
<tr>
<th></th>
<th>CO₂ Permeability (Barrer)</th>
<th>N₂ Permeability (Barrer)</th>
<th>CO₂/N₂ selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(bis(trifluoroethoxy)) phosphazene</td>
<td>325</td>
<td>25</td>
<td>13</td>
</tr>
<tr>
<td>Poly(cyclohexanol-methoxyethoxy ethoxy) phosphazene</td>
<td>110</td>
<td>4.1</td>
<td>27</td>
</tr>
</tbody>
</table>
Polyphosphazene MMM

UiO-66-NH₂ with poor adhesion & agglomeration

Defect free membrane with well dispersed particles

<table>
<thead>
<tr>
<th>Material</th>
<th>CO₂ Permeability (Barrer)</th>
<th>CO₂/N₂ selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(bis(trifluoroethoxy)) phosphazene</td>
<td>325</td>
<td>13</td>
</tr>
<tr>
<td>MMM - TFE PZ 10 wt% of SIFSIX</td>
<td>354</td>
<td>16.1</td>
</tr>
</tbody>
</table>
Development of potential MOFs

N\textsubscript{2} Adsorption:
Pore size: 5.9 Å
Surface area: ~1800 m\textsuperscript{2}/g
Pore volume 0.9 cc/g

CO\textsubscript{2} uptake at 40°C
Ionic cross-linked polyethers (IXPE)

Tunable properties
Oligomer length
Crosslinker and its length
Anion

![Chemical structure of IXPE](image)

![Graph showing CO₂ permeability and CO₂/N₂ selectivity](image)

- CO₂ permeability (Barrer)
- CO₂/N₂ selectivity

- Cerenol-250 C3 X-linker
- Cerenol-250 C10 X-linker
- Cerenol-650 12wt% C10 X-linker
- Cerenol-650 22wt% C10 X-linker
- Cerenol-650 36wt% C10 X-linker
- Cerenol-650 Cerenol-250 X-linker
IXPE – mixed matrix membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>CO$_2$ Permeability (Barrer)</th>
<th>N$_2$ Permeability (Barrer)</th>
<th>CO$_2$/N$_2$ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerenol 650</td>
<td>86</td>
<td>2.1</td>
<td>40.9</td>
</tr>
<tr>
<td>10 wt% UiO-66-NH$_2$ in Cerenol 650</td>
<td>59.3</td>
<td>0.78</td>
<td>75</td>
</tr>
</tbody>
</table>
MMM using low cost fillers

CO₂ Permeability (Barrer)  CO₂/N₂ Selectivity

- Cerenol 650
- 10 wt% UiO-66 - IXPE 650
- 10 wt% Silica gel - IXPE 650
- 20 wt% Silica gel - IXPE 650
- 30 wt% Silica gel - IXPE 650
Coating a sufficiently thin, selective membrane with industrially viable fluxes.

Fabricating the right hollow fiber support with ideal pore size and density.

Particle size of MOF must be lower than 50 nm without any agglomeration.

The materials should show good mechanical properties as a thin membrane.
Development of hollow fiber membranes

Matrimid hollow fiber supports

<table>
<thead>
<tr>
<th>Details</th>
<th>CO$_2$ Permeance (GPU)</th>
<th>CO$_2$/N$_2$ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure polymer</td>
<td>55.3</td>
<td>12.9</td>
</tr>
<tr>
<td>PZ-SIF SiX MMM</td>
<td>94.1</td>
<td>15.4</td>
</tr>
</tbody>
</table>

Pore structure optimization
Testing Conditions:
Gas composition - "CO$_2$" : O$_2$ : SO$_2$ : NO$_2$ : N$_2$ = 14 : 4 : 50PPM : 1PPM : BAL Humidity - 80%RH"

Performance testing with simulated flue gas

- with contaminants
- without contaminants

CO$_2$ Permeance (GPU)

Time (Hr)
Membrane testing at NCCC

P&ID of the test skid is ready and construction is in progress. Will be ready for testing soon.
Conclusions

Key challenges and Future Plans

- Continue development of materials to increase permeance
- Synthesizing the smaller MOF particles
- Technique to coat thin films on the hollow fiber supports
- Testing long term stability of the membranes under realistic conditions

Successfully transformed from Flat sheet to hollow fiber form

MMMs showed promising gas separation performance and stability under simulated flue gas conditions.
Acknowledgements

Membrane Fabrication and testing
• Erik Albenze, Victor Kusuma, Shan Wickramanayake, David Hopkinson

Polymer Synthesis
• Zhicheng Tian, Harry Allcock, Xu Zhou, Hunaid Nulwala

MOF synthesis and functionalization
• Anne Marti, Alex Spore, Nathaniel Rosi

Molecular simulations
• Jie Feng

System Analysis
• Olukayode Ajayi