Membrane Development for Post-Combustion CO$_2$ Capture

Dave Hopkinson, NETL Research and Innovation Center
Membranes need very high performance to be used in CO₂ capture from fossil energy

**Challenge:** Need to process high flow rate of gases with low available driving force

Region of interest for post-combustion CO₂ capture requires next generation membranes:
- Mixed matrix
- Facilitated transport
- Carbon molecular sieve

CO₂ Permeability (Barrer)

CO₂/N₂ Selectivity

Lloyd M. Robeson, Journal of Membrane Science, 320, 2008, 390-400

Performance vs cost plot, Courtesy: William Koros
For a 10% reduction in COE over reference plant, CO₂ permeance of 4000 GPU and CO₂/N₂ selectivity of 25 is needed.

Two stage membrane process with air sweep

Keairns et al, A cost and performance analysis of polymeric membrane-based post-combustion carbon capture, In review
NETL is taking a multi-faceted approach to membrane development for CO$_2$ capture.

- High performance polymers
- Filler particle optimization for mixed matrix membranes
- Polymer
- Inorganic filler
- Thin film composite fabrication
- High throughput materials screening and systems analysis
Two polymers of interest for CO₂ capture: PIM-1 and MEEP polyposphazene

PIM-1: High Permeability
   Low Selectivity
   Brittle films
   Aging reduces permeability

MEEP PPZ: Moderate Permeability
   High Selectivity
   Gummy films

Terminology

<table>
<thead>
<tr>
<th>Terminology</th>
<th>MEEP80-PPZ</th>
<th>4-methoxyphenol (4-MEOP)</th>
<th>phenoxy</th>
<th>2-allylphenol (2-AP)</th>
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<tbody>
<tr>
<td>methoxyethoxyethanol (MEE)</td>
<td>80%</td>
<td>15%</td>
<td>0%</td>
<td>5%</td>
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<tr>
<td>PPOP-PPZ</td>
<td>0%</td>
<td>0%</td>
<td>97%</td>
<td>3%</td>
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</table>
PIM-1/MEEP PPZ blend has high permeability and excellent mechanical properties


High $P_{CO_2}$, Moderate $\alpha_{CO_2/N_2}$

Strong and flexible films
PIM-1/ MEEP shows comparable performance to lab tests with real flue gas

NCCC, Alabama

PIM-1/25% MEEP80 bulk film

![Graph showing permeability (barrier) over run time (hours) for CO₂, O₂, and N₂.](image)
Thin film PIM-1/MEEP has reduced aging compared with neat PIM-1

PIM-MEEP suffers less aging than PIM-1 due to:
(1) chain-chain entanglement
(2) MEEP chain/PIM-1 pore intercalations
Crosslinked MEEP has good gas separation performance without aging.

- **MEEP80-PPZ**: excellent gas separation performance, semi-solid material that flows.
- **PPOP-PPZ**: poor gas separation performance, excellent mechanical robustness.
- **XL MEEP**: excellent gas separation performance, good mechanical robustness, solid material that does not flow.

Cross-linking agent
Crosslinking of MEEP dramatically improves film durability with some decrease in gas permeability.

The graph shows the CO$_2$ permeability (in barrers) and CO$_2$/N$_2$ selectivity for various samples:
- Neat MEEP80-PPZ
- Neat 70/30 MEEP80/PPOP
- XL MEEP80-PPZ
- XL 90/10 MEEP80/PPOP
- XL 75/25 MEEP80/PPOP
- Neat PPOP-PPZ

The crosslinker A results in a decrease in CO$_2$ permeability and an increase in CO$_2$/N$_2$ selectivity.
Crosslinked MEEP gas separation performance can be further improved based on composition and crosslinker.

The graph shows the CO$_2$ permeability (barrer) and CO$_2$/N$_2$ selectivity for different compositions and crosslinkers. The CO$_2$ permeability increases with the crosslinker content, and the CO$_2$/N$_2$ selectivity also shows a trend with the crosslinker type and composition.
Crosslinked MEEP shows stable performance with real flue gas

XL MEEP bulk film

NCCC, Alabama
Aging has no significant effect on Crosslinked MEEP thin film in lab tests.

The graph shows the gas permeability (in Barrer) and CO₂/N₂ selectivity over aging time (in hours). The permeability of CO₂, N₂, and CO₂/N₂ selectivity remain relatively constant with aging time, indicating no significant change in permeability due to aging.
Humidity has only minor effect on XL-MEEP gas separation performance

**CO₂ Permeability**

- Pure PIM-1
- PIM-1/MEEP80 (75/25 by wt)
- Crosslinked MEEP

**CO₂/N₂ Selectivity**

- Crosslinked MEEP
- PIM-1/MEEP80 (75/25 by wt)
- Pure PIM-1
Humidity causes a small reduction in aging in PIM-1; boost in CO$_2$/N$_2$ selectivity

**CO$_2$ Permeability**

- Pure PIM-1, humidified
- Pure PIM-1, dry gas

**CO$_2$/N$_2$ Selectivity**

- Pure PIM-1, humidified
- Pure PIM-1, dry gas
Mixed matrix membranes can increase membrane performance beyond the Robeson Upper Bound.
Computational modeling was used for high throughput screening of MOF and MMM gas separation properties.

MOF Properties
(Predicted by Calculations)
DB of ~137,000 Hypo-MOFs
DB of ~2,500 MOF CORE-MOFs

Pure Membrane Properties
for ~10 polymers measured experimentally

Predicted Properties for well over a million possible MMMs

Estimate of Cost of Carbon Capture based on an assumed configuration

Budathoki et al, Energy Environ. Sci. 2019, 12, 1255
Several NETL MMMs were demonstrated to have performance above the Robeson Upper Bound.

- PIM-1/MEEP
- Poly+MOFA-20%-expt
- Poly+MOFA-20%-comp
- Poly+MOFB-40%-expt
- Poly+MOFB-40%-comp
- Poly+MOFC-40%-expt
- Poly+MOFC-40%-comp

![Graph showing CO₂/N₂ Selectivity vs. CO₂ Permeability (Barrer)]
Increasing MEEP concentration trades lower $P_{CO_2}$ for higher $\alpha_{CO_2/N_2}$.
Increasing MOF concentration improves $P_{\text{CO}_2}$ with little effect on $\alpha_{\text{CO}_2/\text{N}_2}$
Both PIM-1/MEEP and XL MEEP can be improved by using MOFs to form mixed matrix membranes.
A hollow fiber support needs to be optimized for flux, pore size, and pore density

Our current hollow fiber membrane supports:
- N₂ permeance >100,000 GPU
- CO₂/N₂ selectivity ~ 0.8 (Knudsen diffusion)
- Surface pore size ~ 20 nm
- Resistant to mild solvents

The support should have at least an order of magnitude higher gas flux compared to selective layer
MOF A can now be synthesized in a variety of particle sizes with the same structure.

<table>
<thead>
<tr>
<th>TEM Images (scale bars = 200 nm)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
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<tr>
<td>Diameter (nm)</td>
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<td>Surface area (m²/g, N₂ 77 K)</td>
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PIM-1/ MEEP MMMs and XL MEEP have been demonstrated as thin film composites

- PIM-1/MEEP/10% MOF A MMM selective layer
- High flux hollow fiber support

- XL MEEP selective layer
- High flux flat sheet support
Summary: NETL has taken a multifaceted approach to membrane development for CO₂ capture

- Two polymers show high CO₂/N₂ separation performance: PIM-1/MEEP, XL MEEP
- Both have excellent mechanical properties
- Membranes tested at NCCC with real flue gas show comparable performance to lab tests
- Both PIM-1/MEEP and XL MEEP show improved CO₂ permeability by adding targeted MOFs to form MMMs
- High permeance flat sheet and hollow fiber supports have been fabricated
- Thin film coatings have been demonstrated for PIM-1/MEEP and XL MEEP
Thanks to our team!

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**Membrane fabrication and testing:**
Victor Kusuma
Fangming Xiang
Shouliang Yi
Lingxiang Zhu
Zi Tong

**Team leads:**
Dave Hopkinson
Kevin Resnik

**Program management:**
Tim Fout
Lynn Brickett
John Litynski

**Past team members:**
Surendar Venna
Anne Marti
Olukayode Ajayi
Jie Feng
Ganpat Dahe
Dave Luebke
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