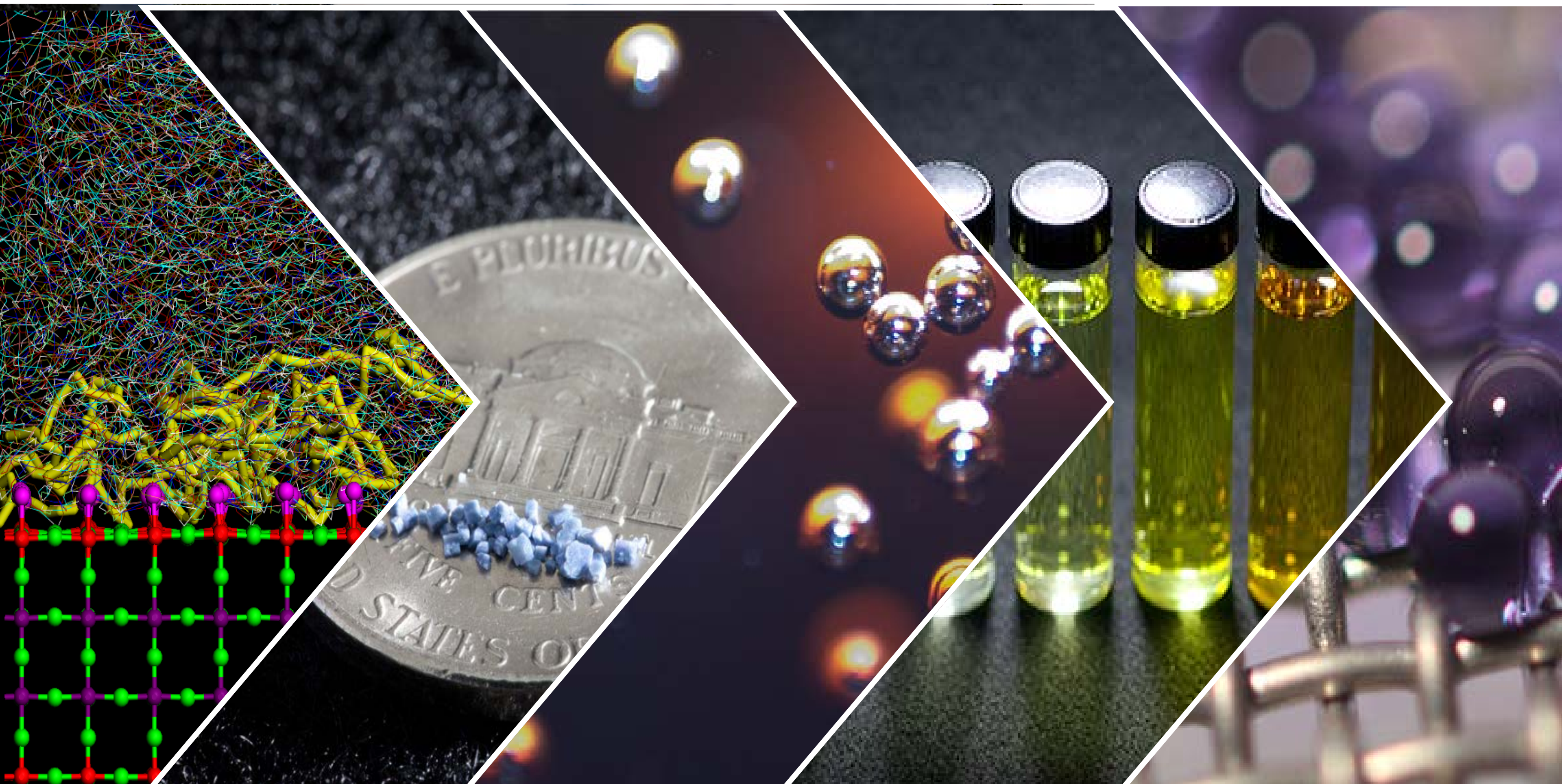
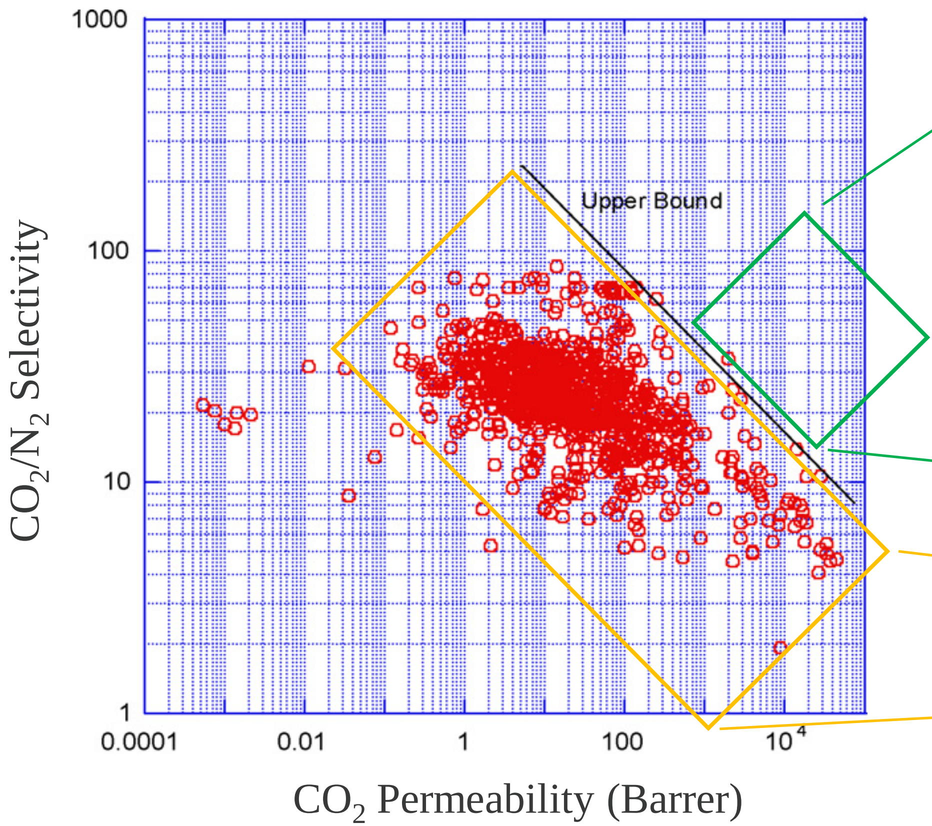
Membrane Development for Post-Combustion CO_2 Capture

Dave Hopkinson, NETL Research and Innovation Center



Membranes need very high performance to be used in CO_2 capture from fossil energy

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



Region of interest for post-combustion CO_2 capture requires next generation membranes:

- Mixed matrix
- Facilitated transport
- Carbon molecular sieve

Conventional polymer membranes

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, CO_2 permeance of 4000 GPU and CO_2/N_2 selectivity of 25 is needed

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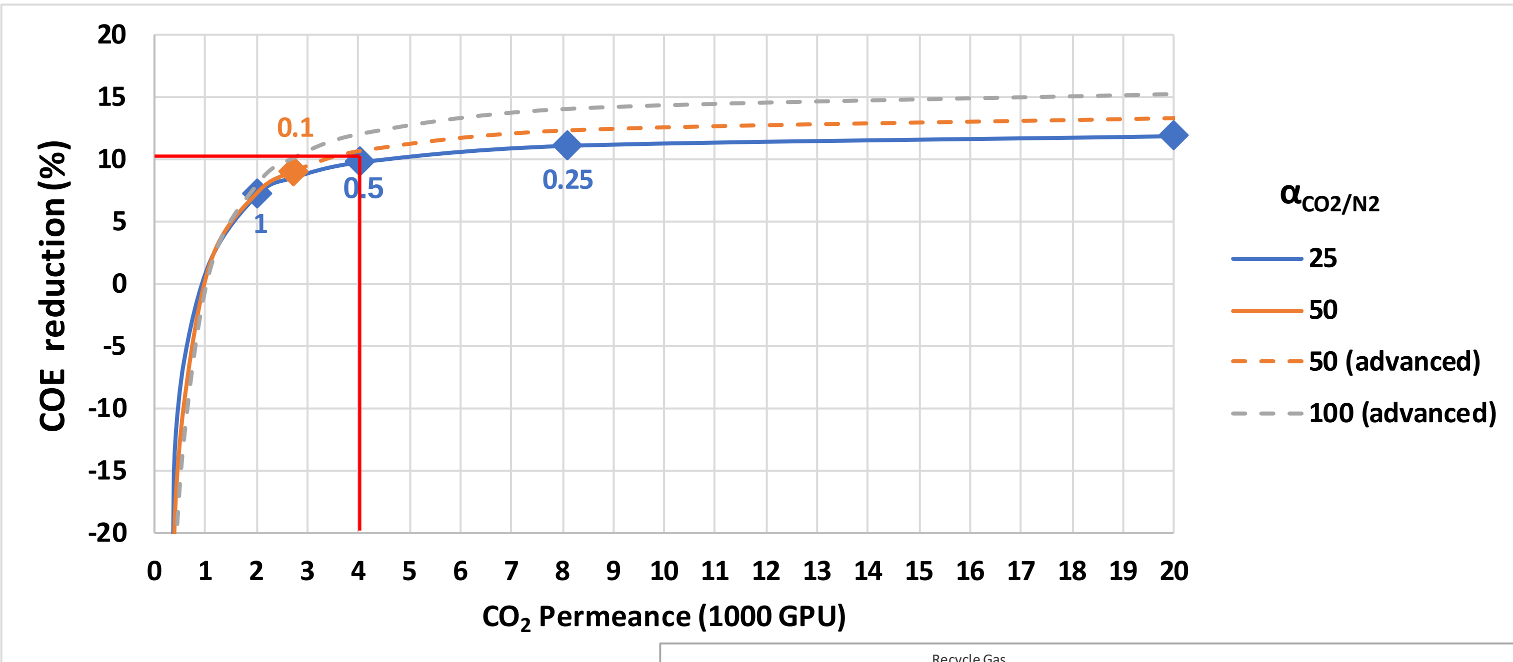
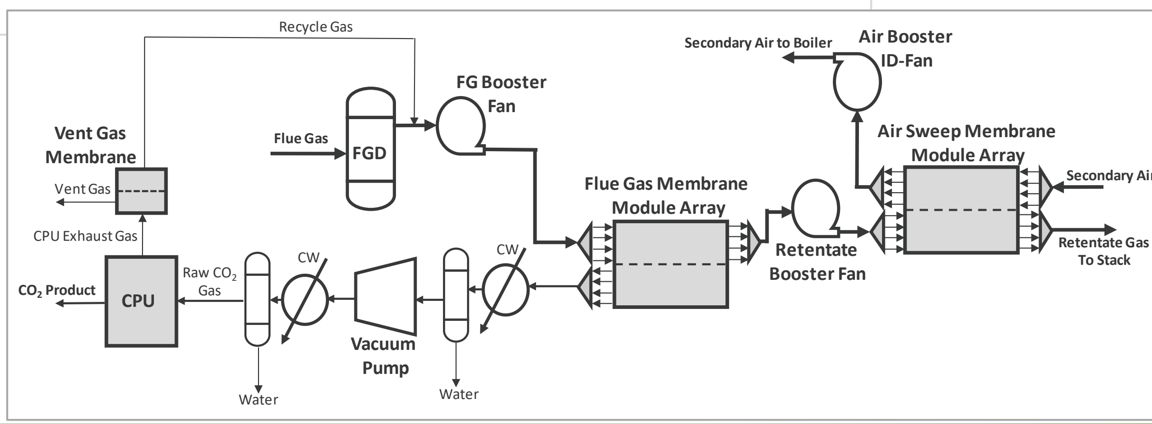


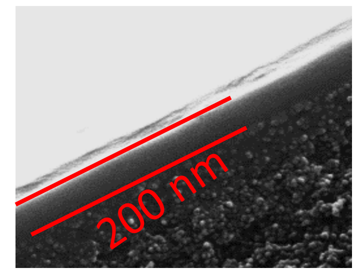
Two stage membrane process with air sweep

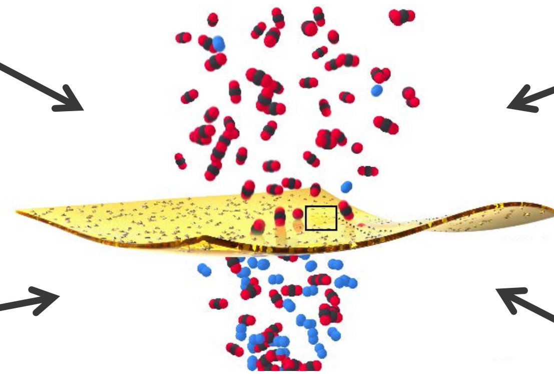


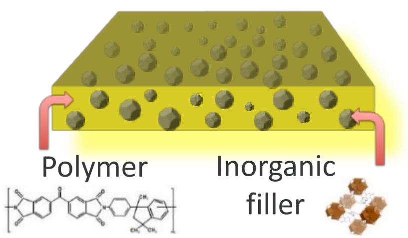
NETL is taking a multi-faceted approach to membrane development for CO_2 capture

High performance polymers

Thin film composite fabrication







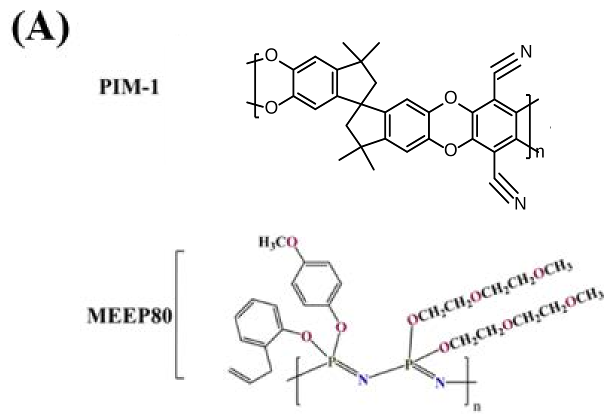
Filler particle optimization for mixed matrix membranes

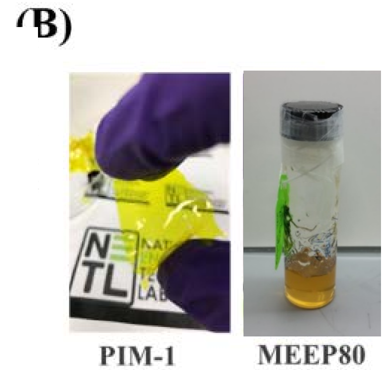
High throughput materials screening and systems analysis

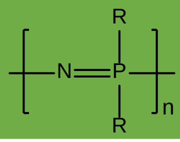
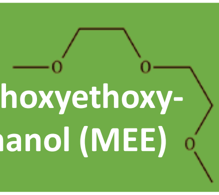
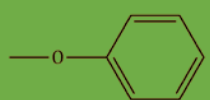
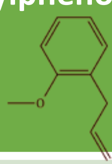
Two polymers of interest for CO_2 capture: PIM-1 and MEEP polyposphazene

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

MEEP PPZ: Moderate Permeability
High Selectivity
Gummy films

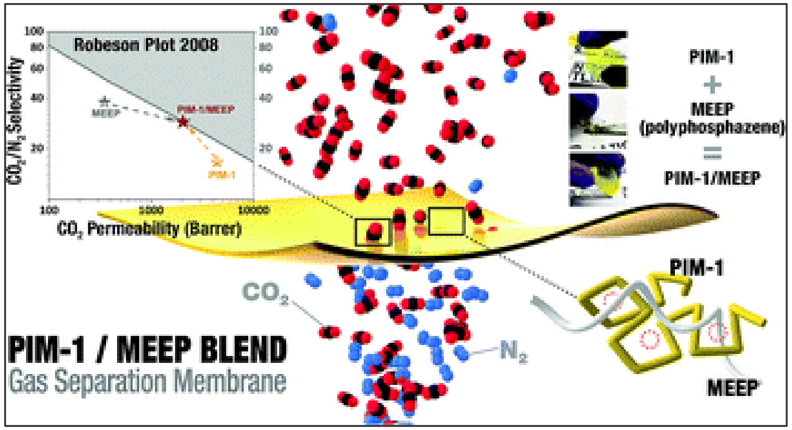




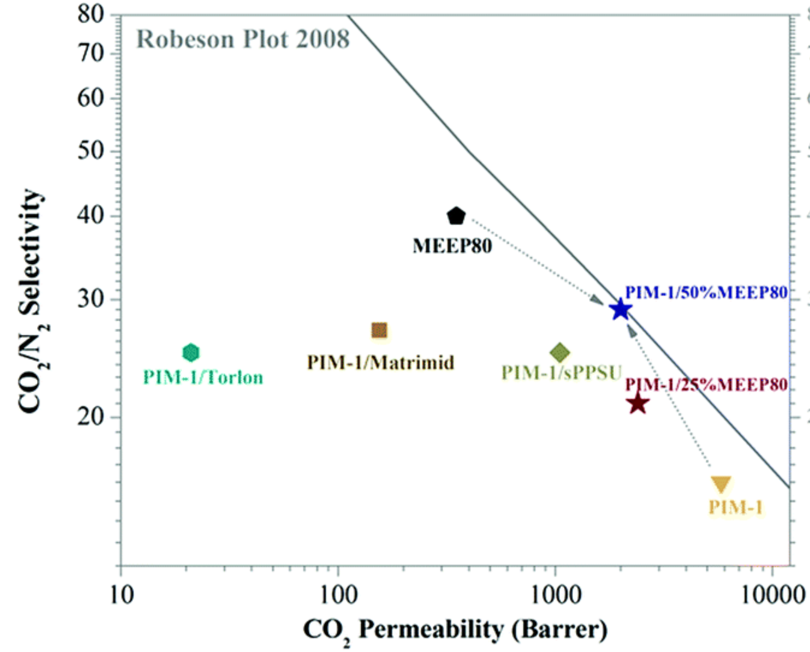
Terminology 	 methoxyethoxy-ethanol (MEE)	4-methoxyphenol (4-MEOP) 	phenoxy 	2-allylphenol (2-AP) 
MEEP80-PPZ	80%	15%	0%	5%
PPOP-PPZ	0%	0%	97%	3%

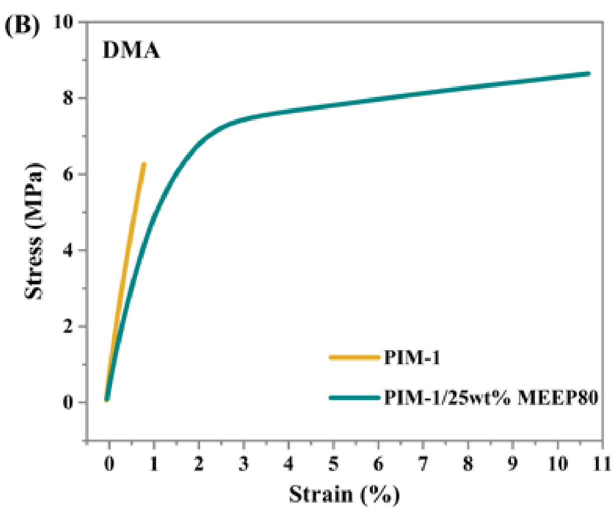
J. Mat. Chem. A **2018**,*6*, 22472

PIM-1/MEEP PPZ blend has high permeability and excellent mechanical properties

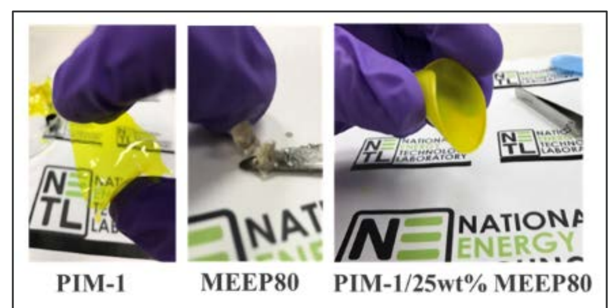


High P_{CO2}, Moderate $\alpha_{CO2/N2}$

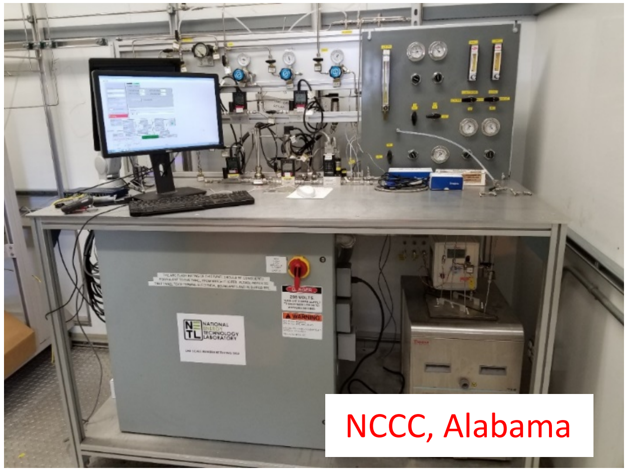


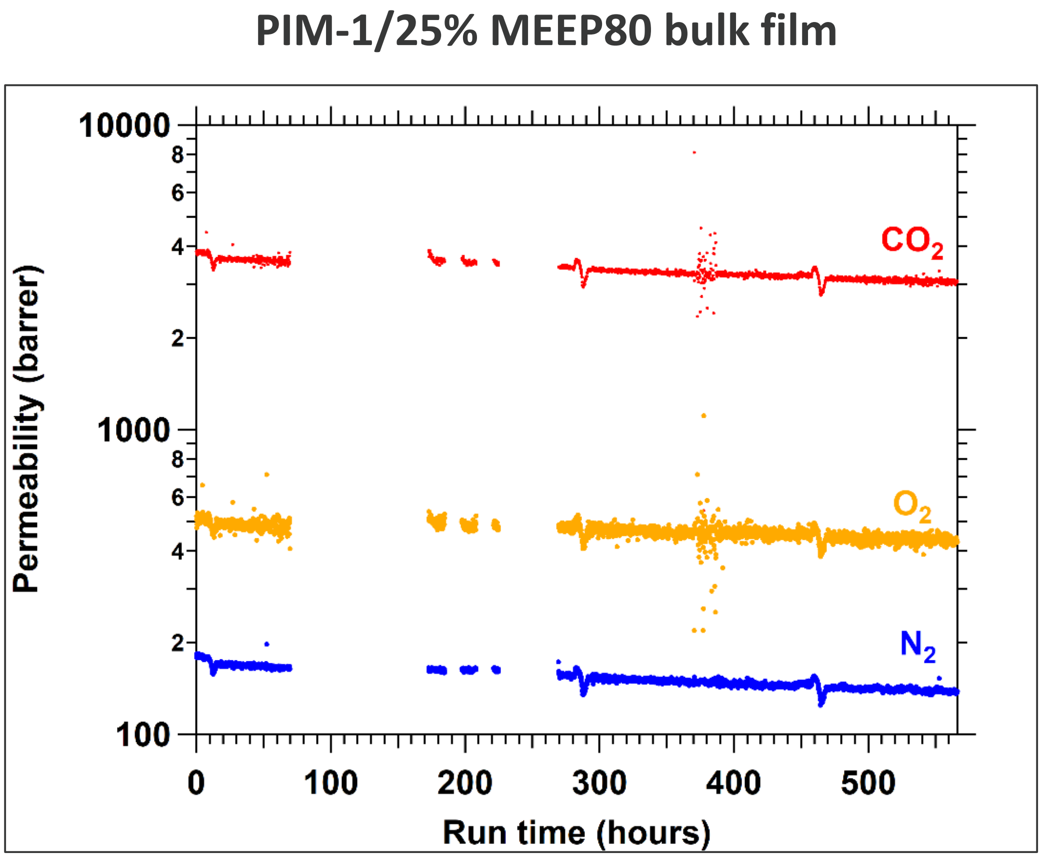


Strong and flexible films

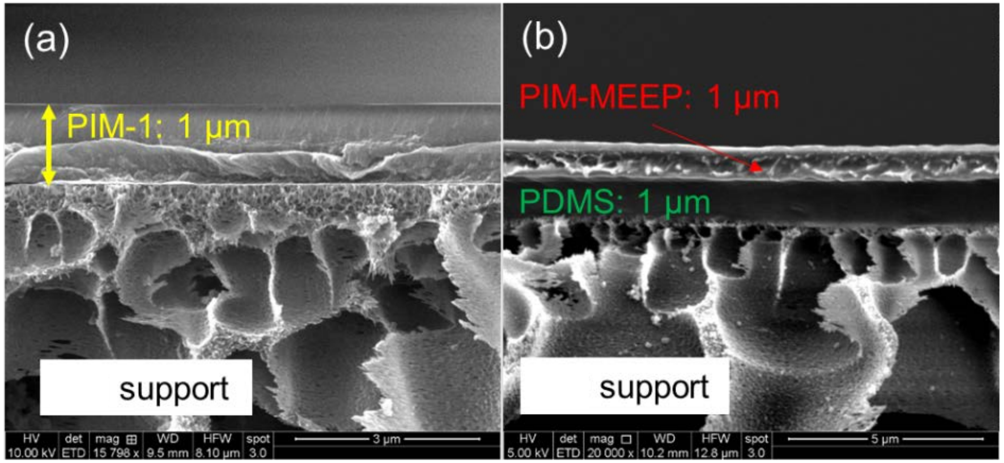


PIM-1/MEEP shows comparable performance to lab tests with real flue gas

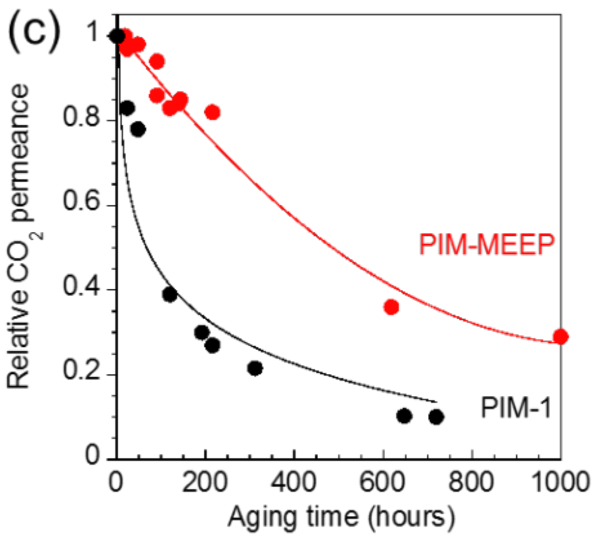


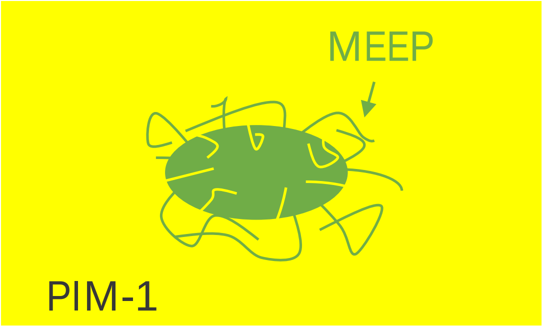


Thin film PIM-1/MEEP has reduced aging compared with neat PIM-1



Thin films





PIM-MEEP suffers less aging than PIM-1 due to:

(1) chain-chain entanglement

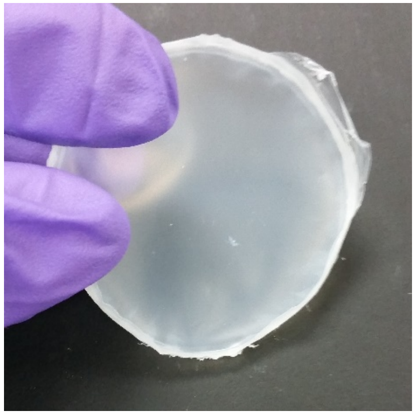
(2) MEEP chain/PIM-1 pore intercalations

Crosslinked MEEP has good gas separation performance without aging

MEEP80-PPZ

excellent gas separation performance
semi-solid material that flows

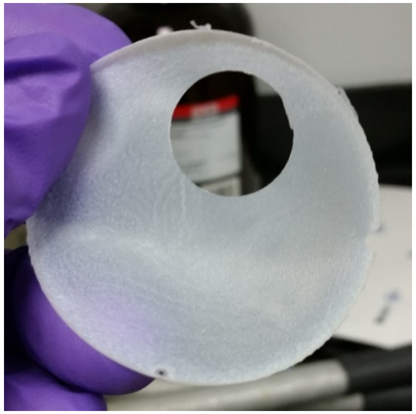
+



PPOP-PPZ

poor gas separation performance
excellent mechanical robustness

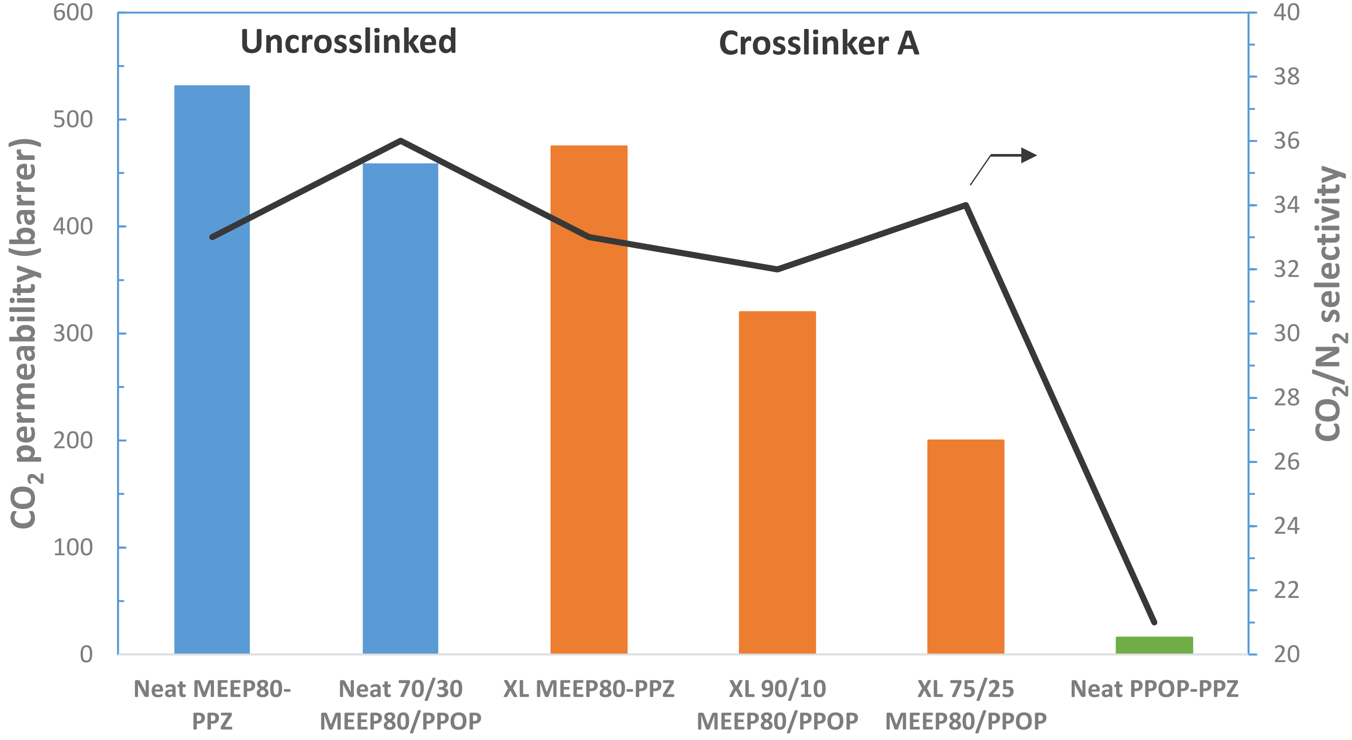
Cross-linking agent →



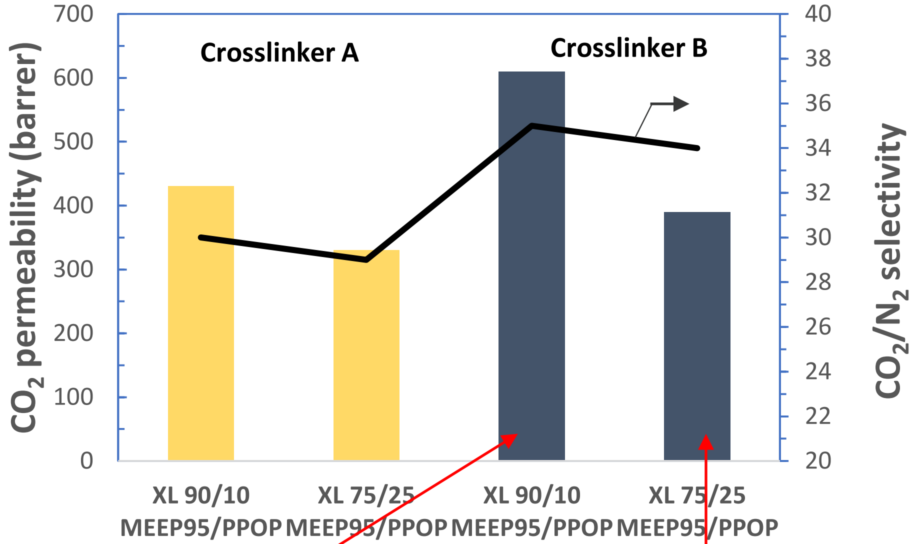
XL MEEP

excellent gas separation performance
good mechanical robustness
solid material that does not flow

Crosslinking of MEEP dramatically improves film durability with some decrease in gas permeability



Crosslinked MEEP gas separation performance can be further improved based on composition and crosslinker



Crosslinked MEEP shows stable performance with real flue gas

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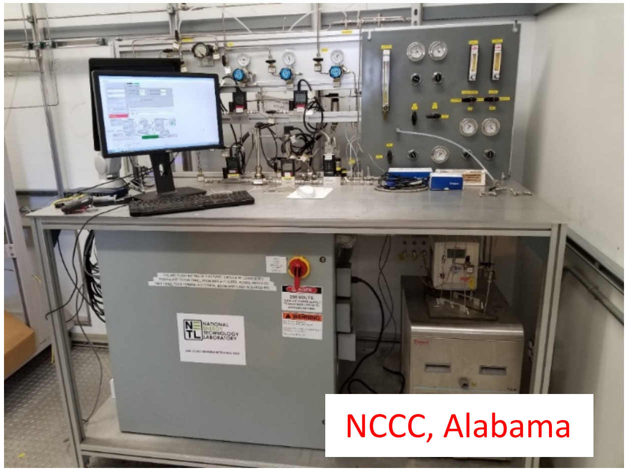
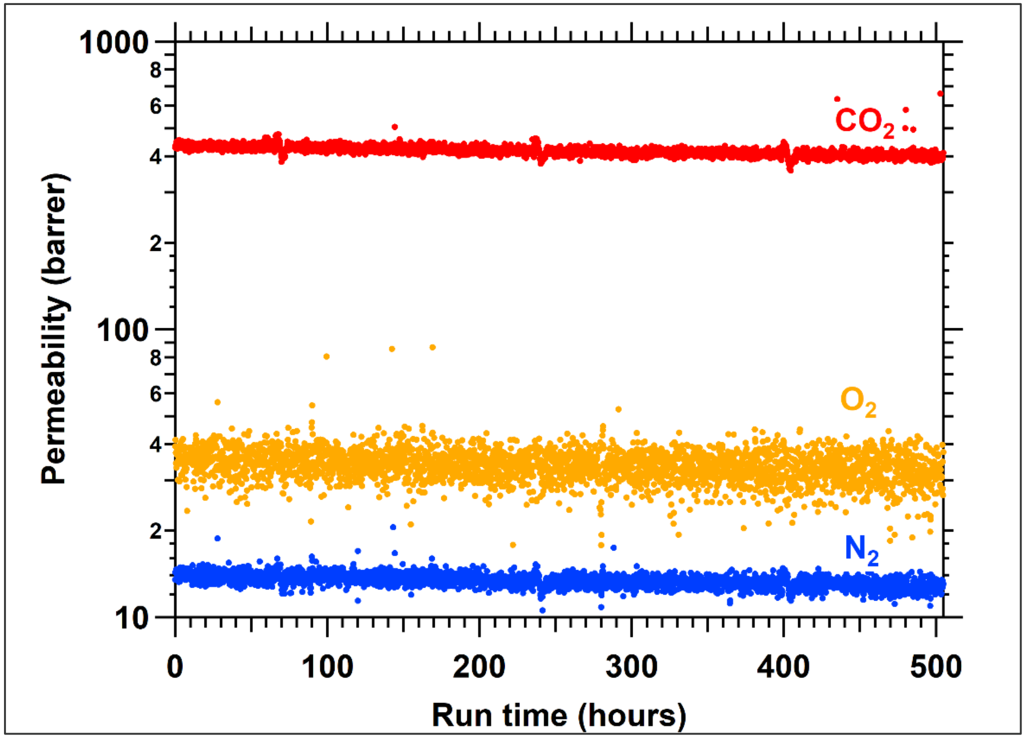
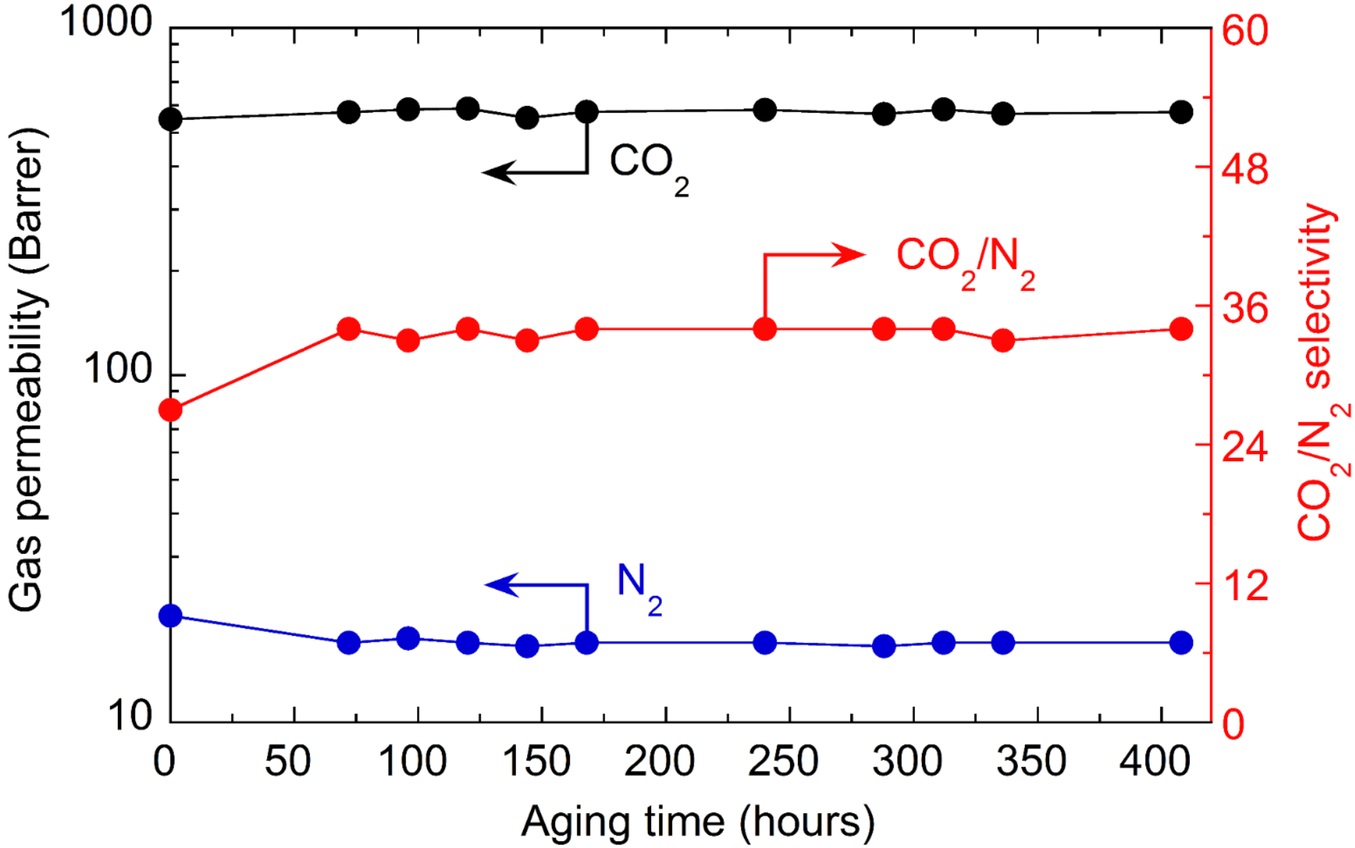


XL MEEP bulk film



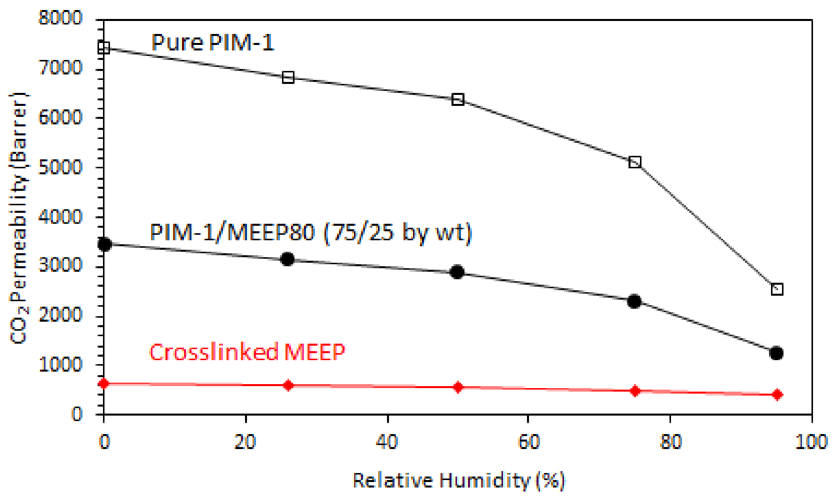
Aging has no significant effect on Crosslinked MEEP thin film in lab tests

XL MEEP thin film

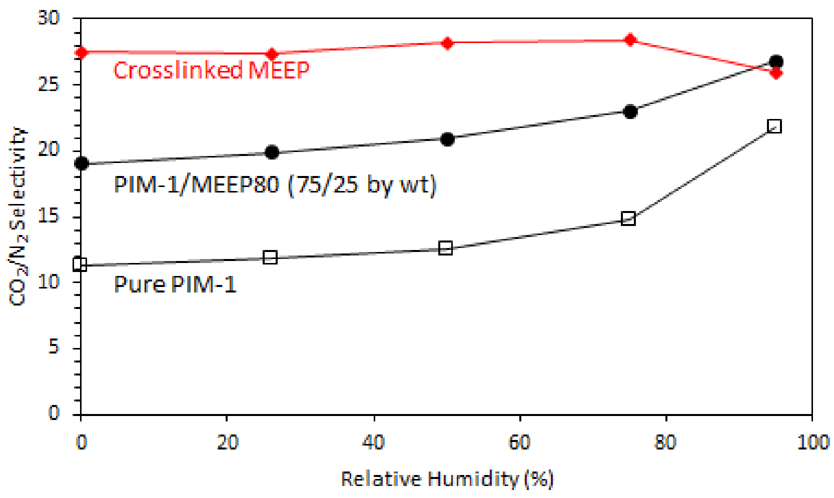


Humidity has only minor effect on XL-MEEP gas separation performance

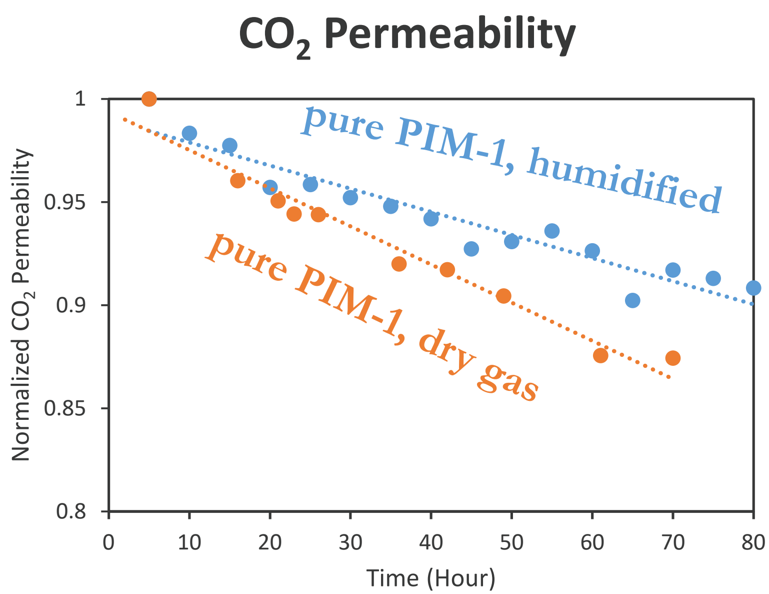
CO_2 Permeability

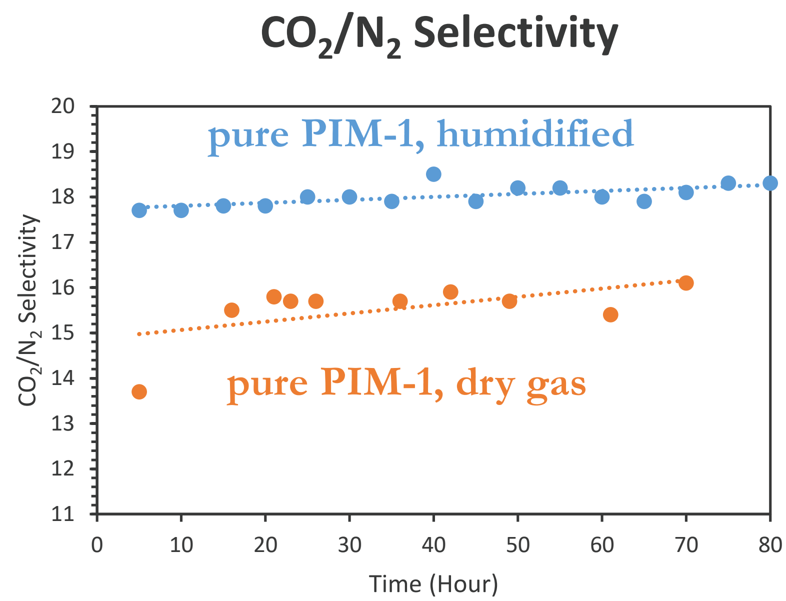


CO_2/N_2 Selectivity

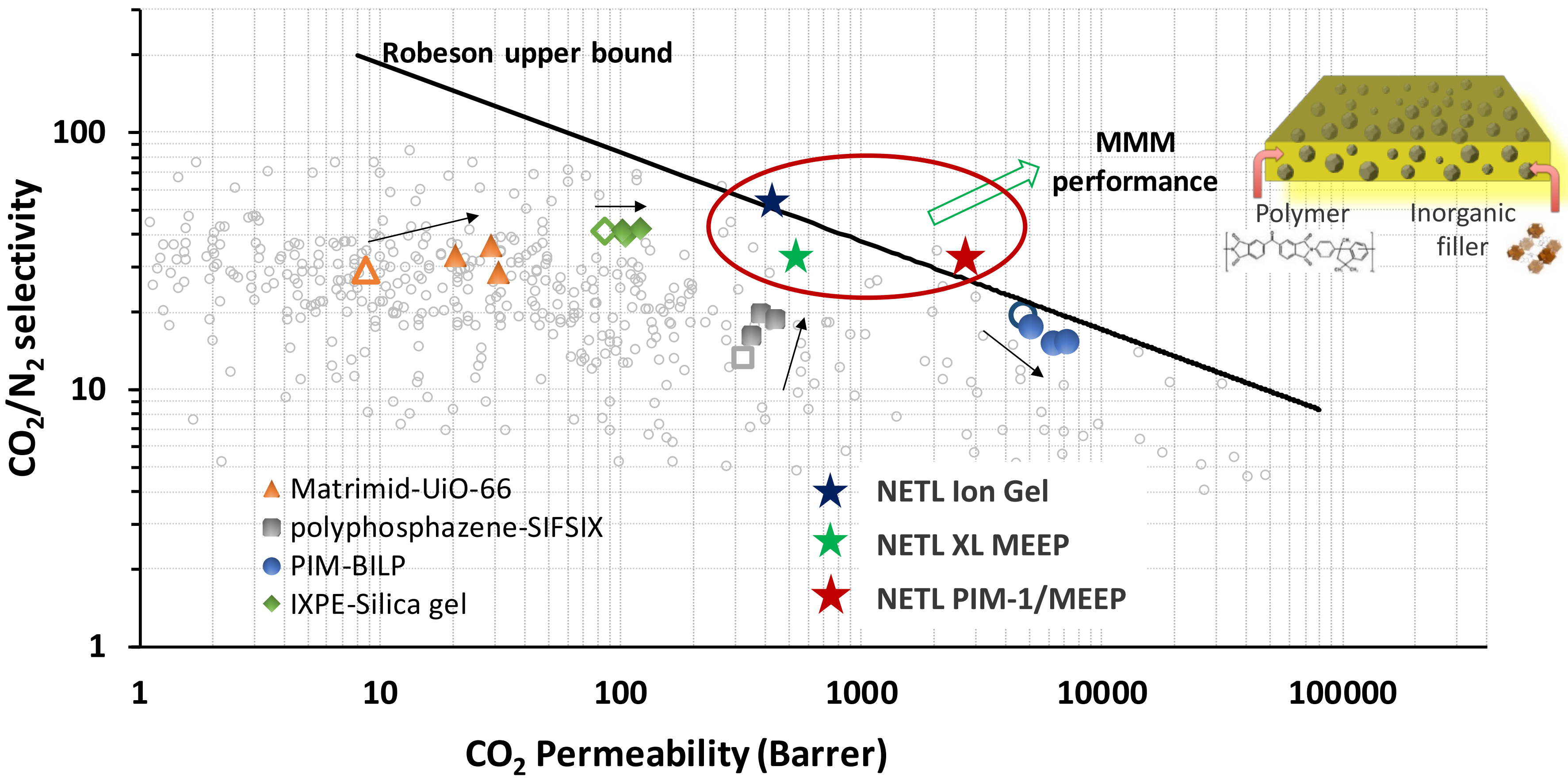


Humidity causes a small reduction in aging in PIM-1; boost in CO_2/N_2 selectivity





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

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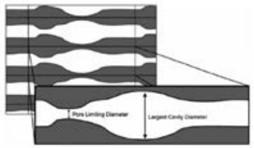
MOF Properties
(Predicted by Calculations)

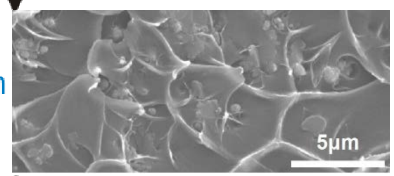
DB of ~137,000 Hypo-MOFs
DB of ~2,500 MOF CORE-MOFs



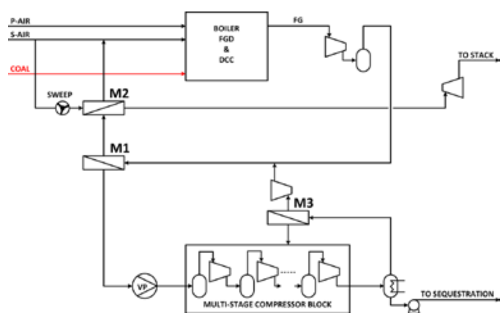
Pure Membrane Properties for ~10 polymers measured experimentally

Maxwell Eq.

Predicted Properties for well over a million possible MMMs



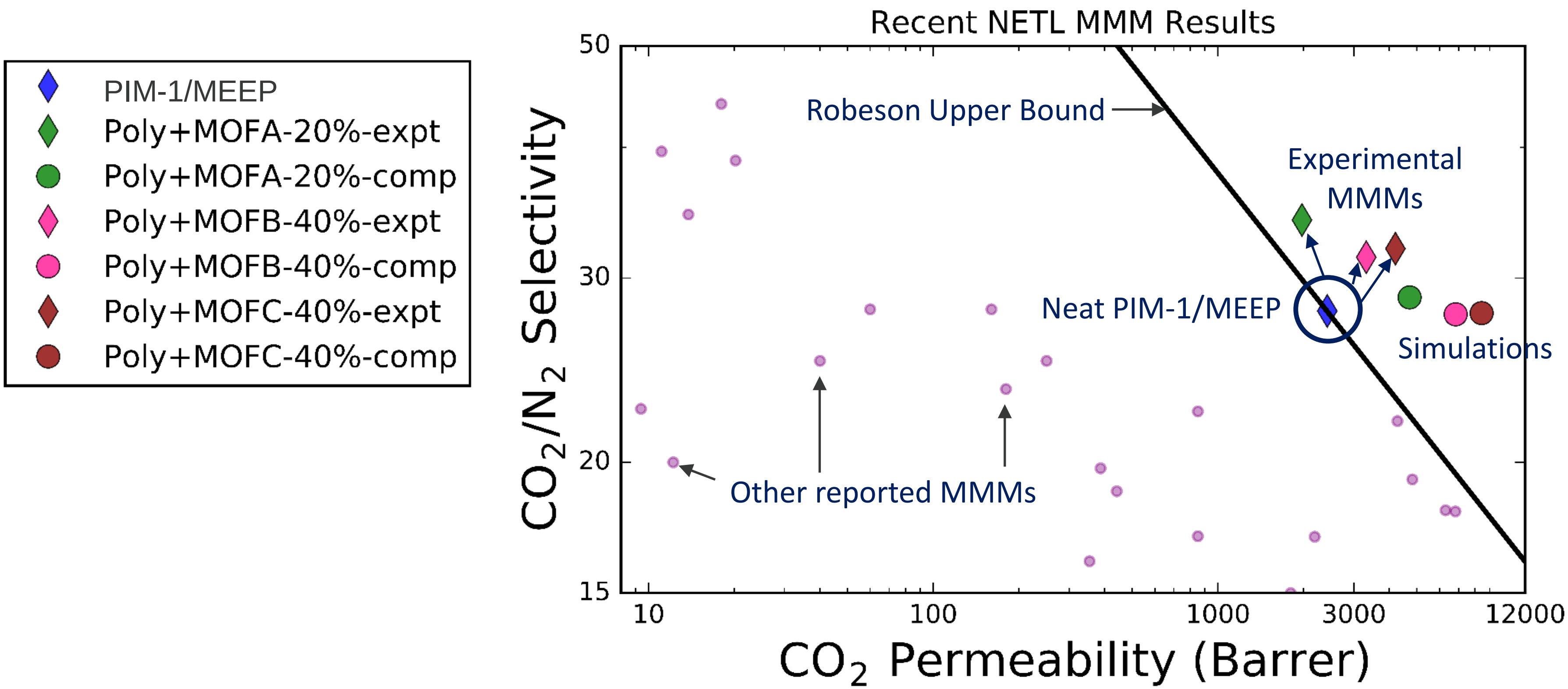
Estimate of Cost of Carbon Capture based on an assumed configuration



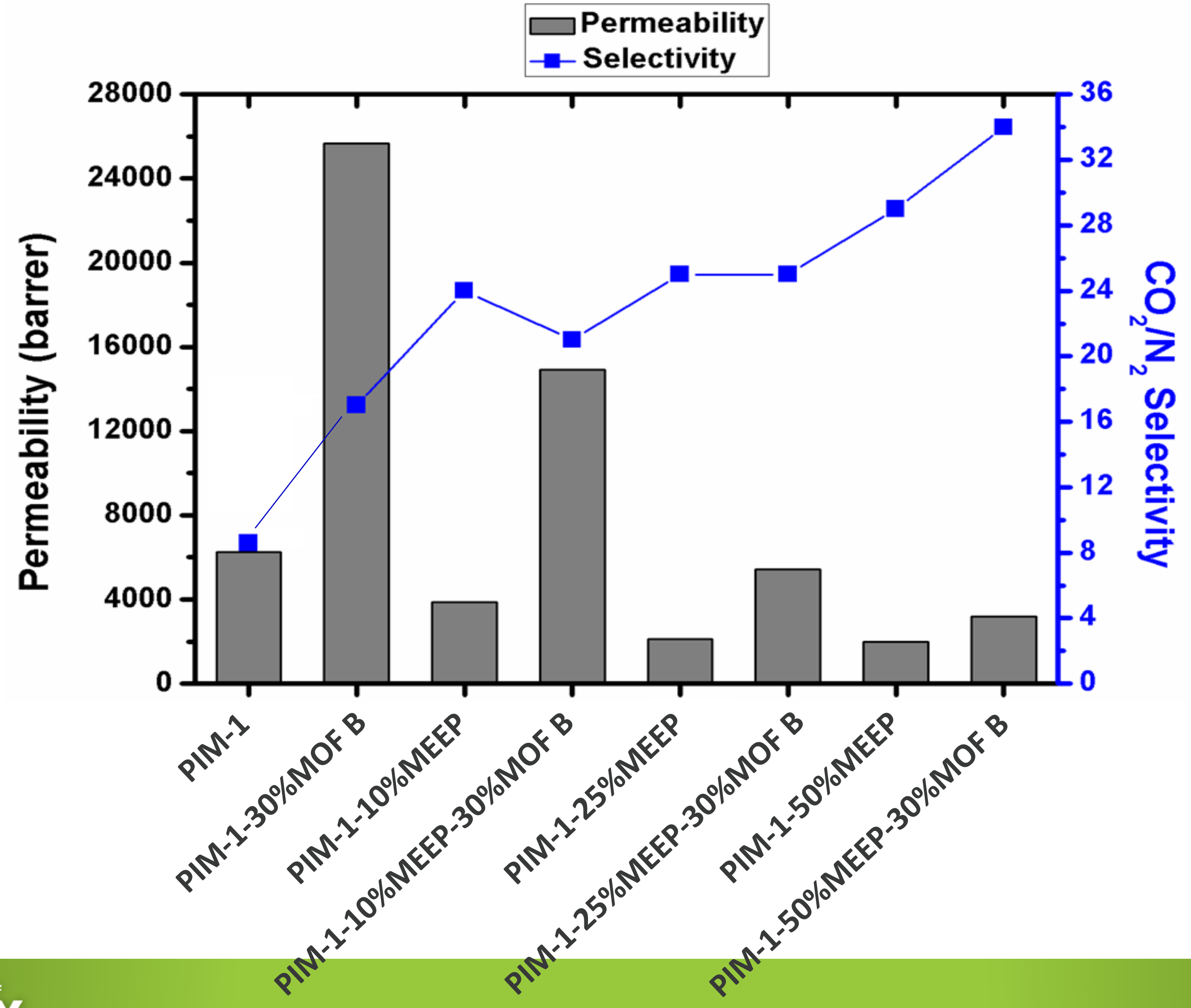
CCSI[2]
Carbon Capture Simulation for Industry Impact

Budhathoki et al, Energy Environ. Sci. 2019, 12, 1255

Several NETL MMMs were demonstrated to have performance above the Robeson Upper Bound



Increasing MEEP concentration trades lower P_{CO2} for higher $\alpha_{CO2/N2}$



Increasing MOF concentration improves P_{CO2} with little effect on $\alpha_{CO2/N2}$

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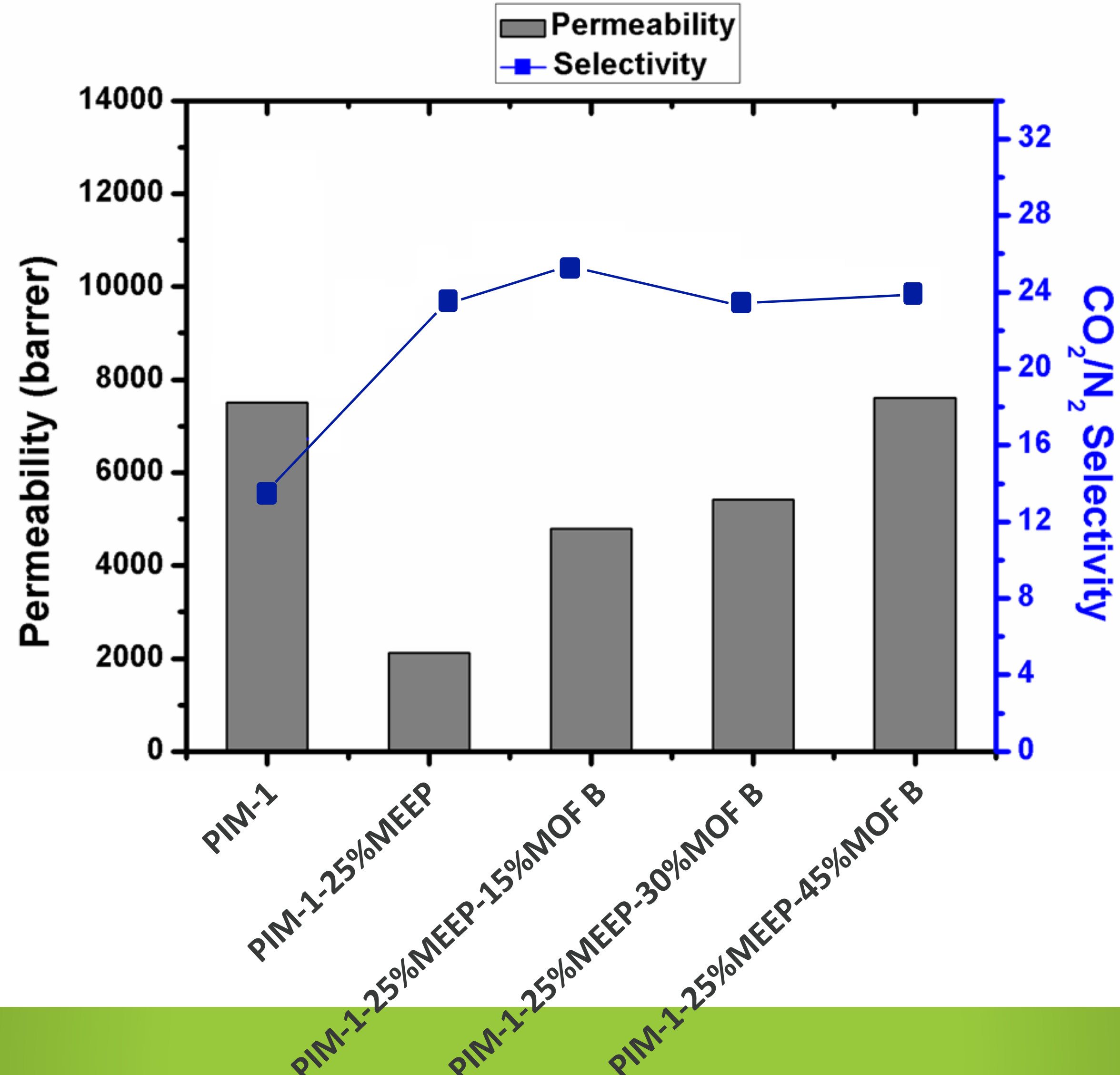
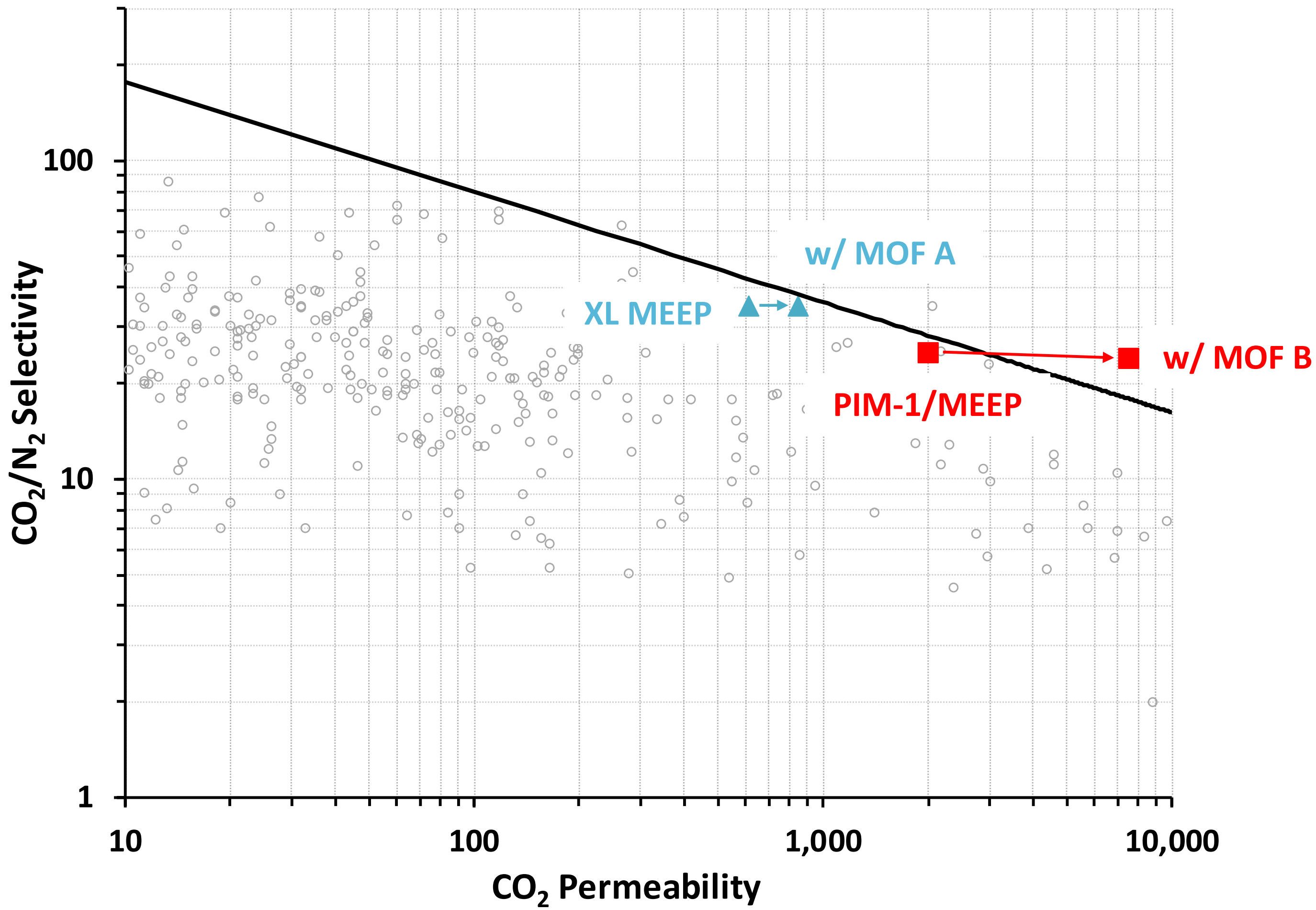
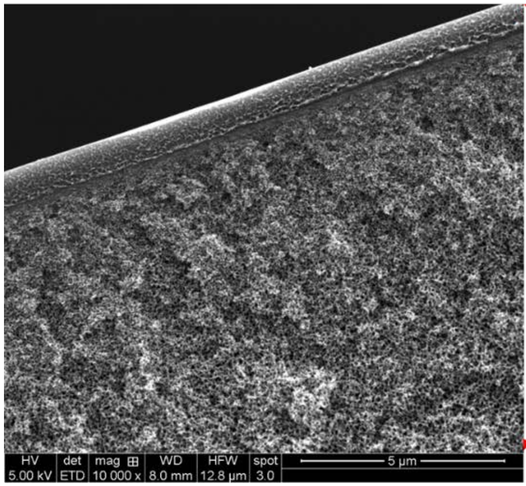
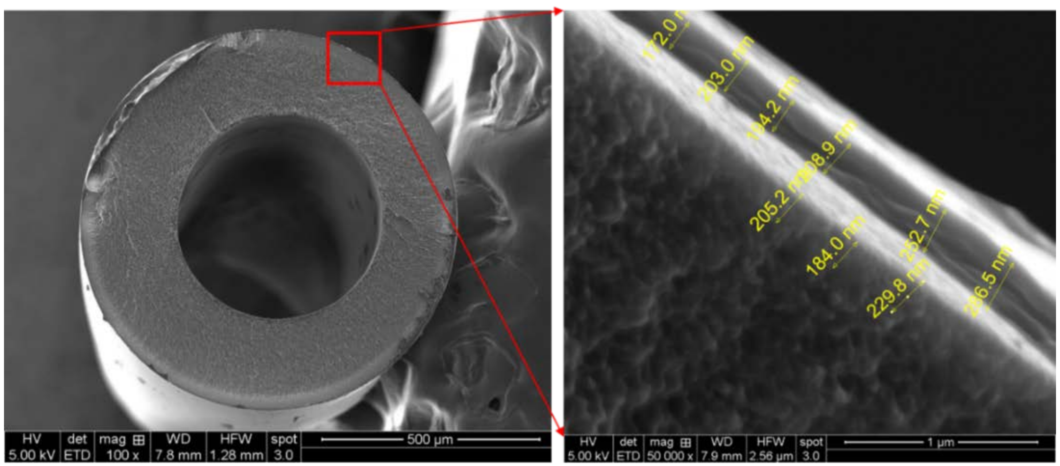


Both PIM-1/MEEP and XL MEEP can be improved by using MOFs to form mixed matrix membranes



A hollow fiber support needs to be optimized for flux, pore size, and pore density





Our current hollow fiber membrane supports:

- N_2 permeance >100,000 GPU
- CO_2/N_2 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

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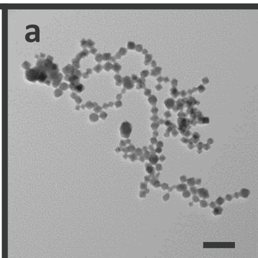
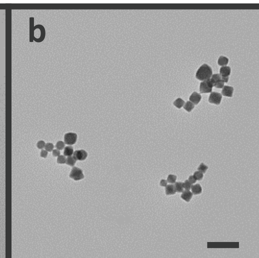
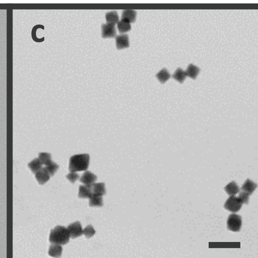
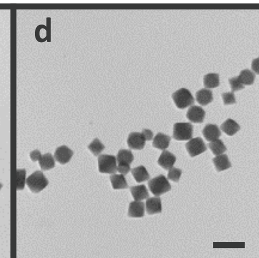
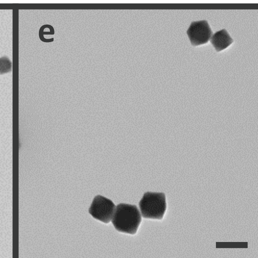
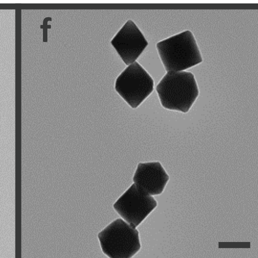
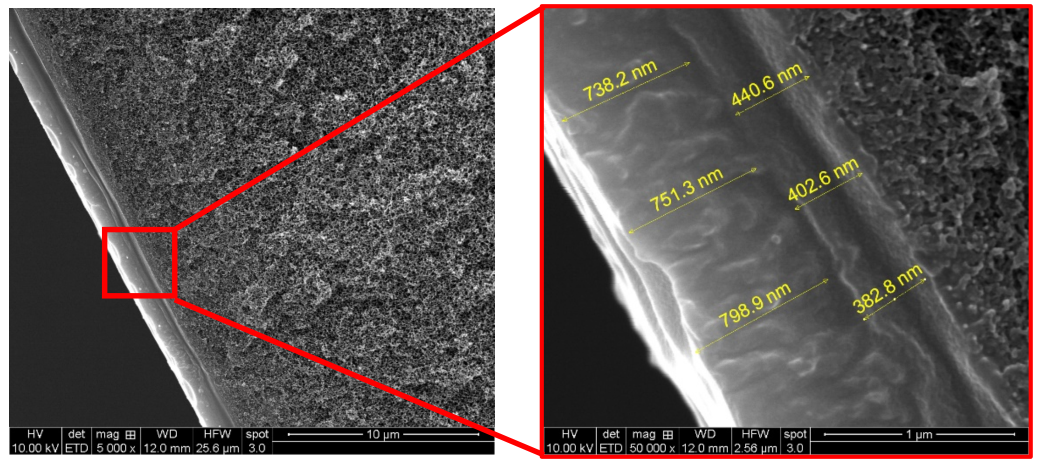
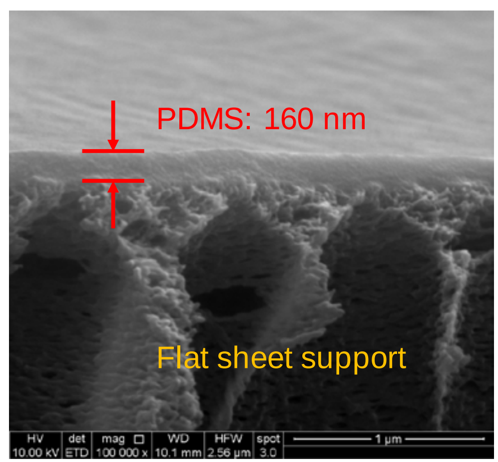
TEM Images (scale bars = 200 nm)	a 	b 	c 	d 	e 	f 
Diameter (nm)	43±9	67±11	82±12	**104±16**	151±24	248±34
Surface area (m^2/g, N_2 77 K)	1158±2	1353±3	1205±2	**1393±3**	1409±4	1410±4

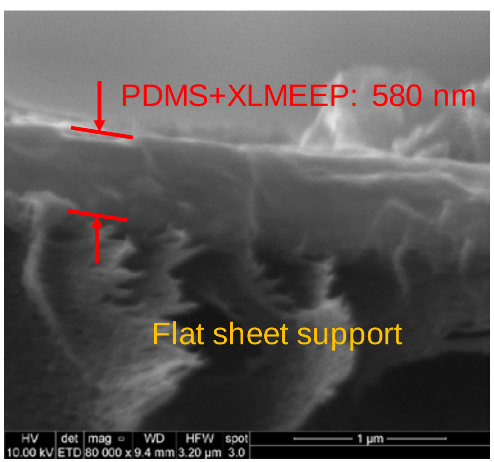
PIM-1/MEEP MMMs and XL MEEP have been demonstrated as thin film composites

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



- XL MEEP selective layer
- High flux flat sheet support



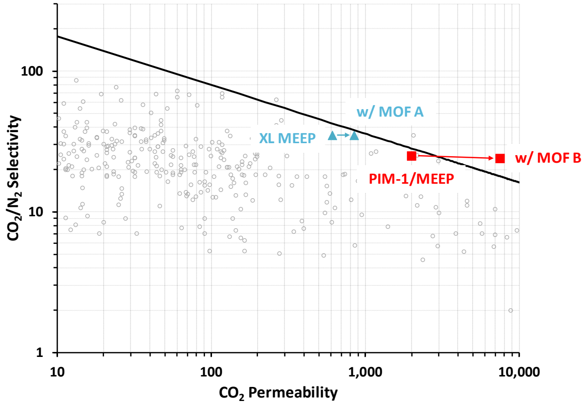


Summary: NETL has taken a multifaceted approach to membrane development for CO_2 capture

PIM-1/MEEP

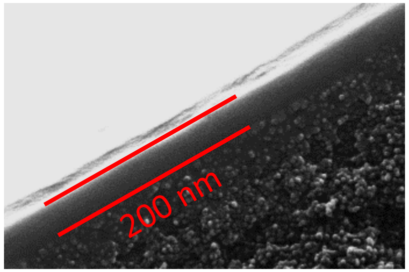
XL MEEP

- Two polymers show high CO_2/N_2 separation performance: PIM-1/MEEP, XL MEEP
- Both have excellent mechanical properties



- Both PIM-1/MEEP and XL MEEP show improved CO2 permeability by adding targeted MOFs to form MMMs

- Membranes tested at NCCC with real flue gas show comparable performance to lab tests



- 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!

MOF development:
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Jeff Culp
Nathaniel Rosi (U. Pitt.)
Patrick Muldoon (U. Pitt)

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James Baker
Josh McNally (INL)

Simulations and economic analysis:
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Wei Shi
Christopher Wilmer (U. Pitt.)

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Shouliang Yi
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Megan Macala

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Task 9: Advanced Polymer Membranes, $553K
Task 10: Mixed Matrix Membranes, $376K

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