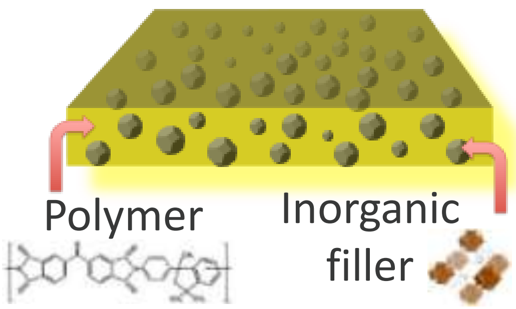
A Combined Computational and Experimental Approach to Ultra-High Permeability Mixed Matrix Membranes for Post-Combustion CO_2 Capture

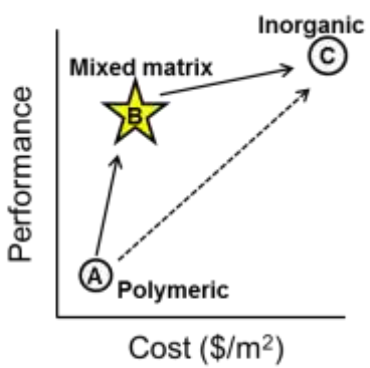
Dave Hopkinson, Surendar Venna, Ali Sekizkardes, Sameh Elsaidi, Samir Budhathoki, and Jan Steckel

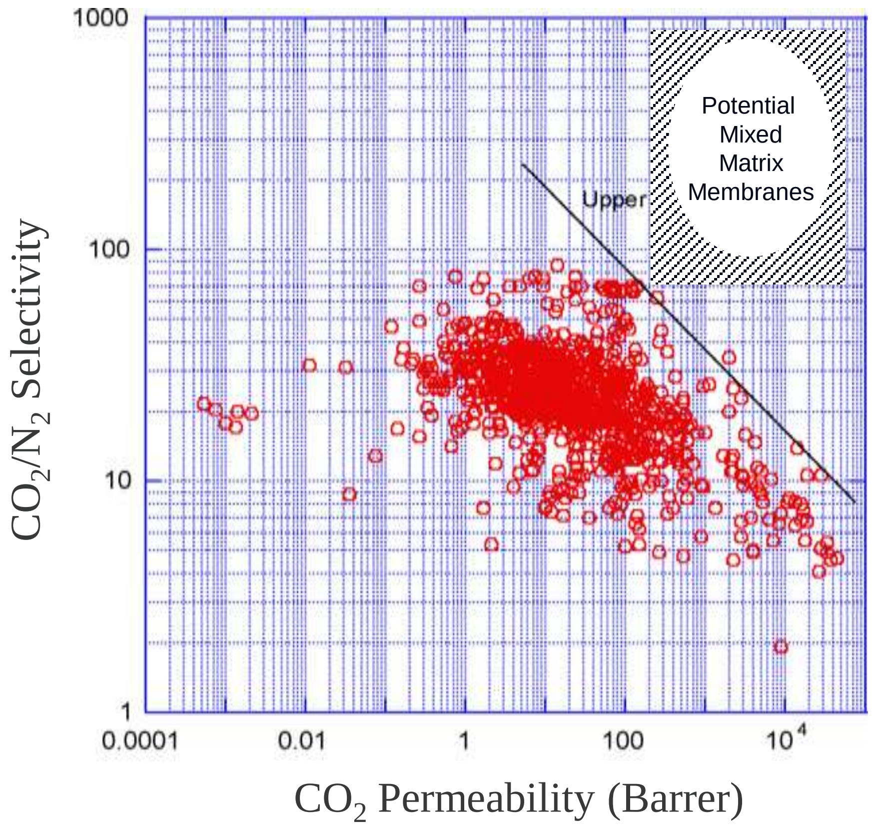
Membranes need very high performance to be used in CO_2 capture from fossil energy

Challenge: Need to process large amount of gases with low available driving force

Mixed Matrix Membrane







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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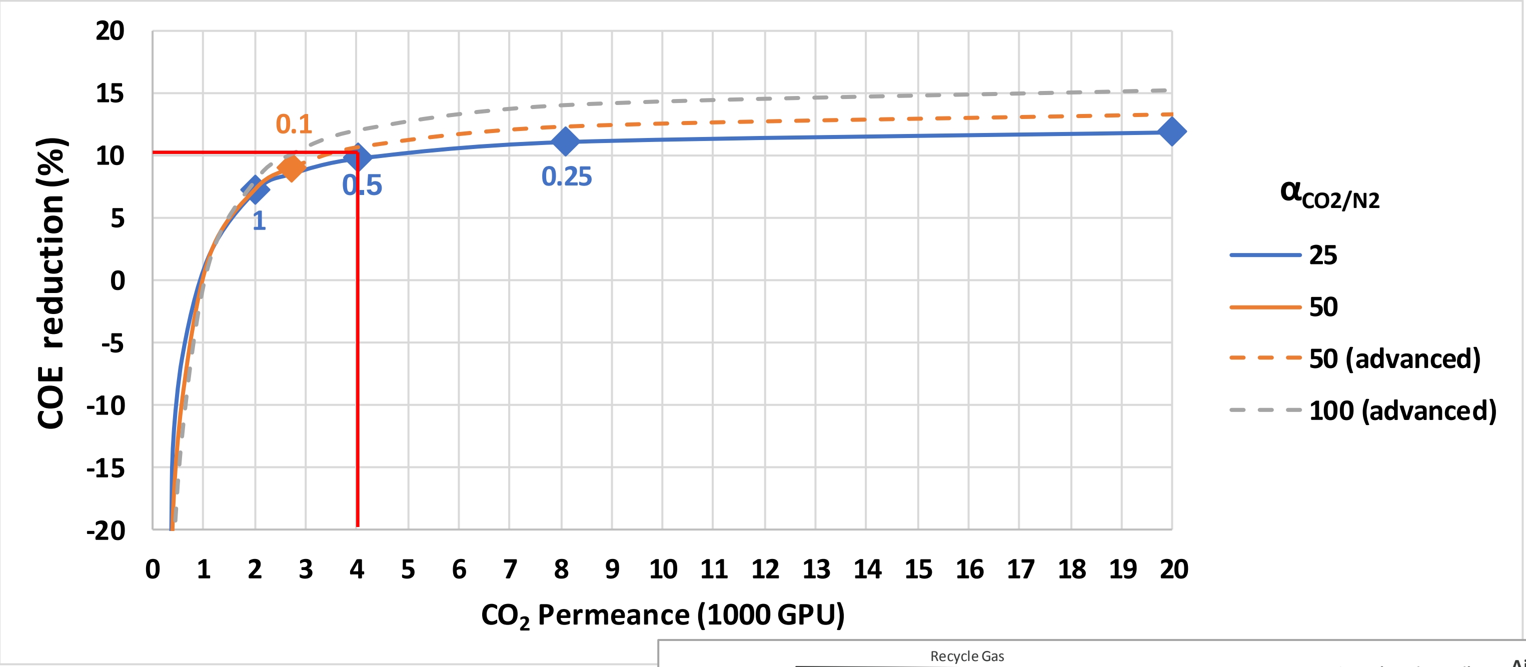
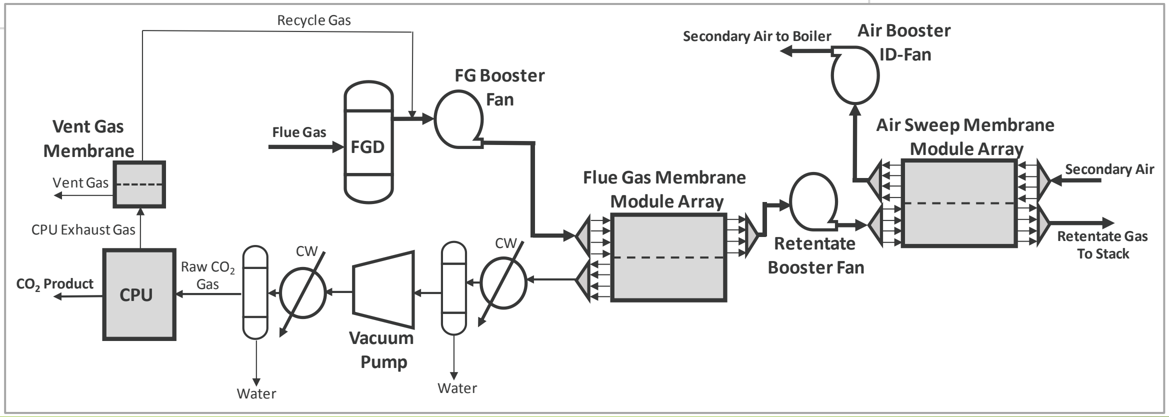
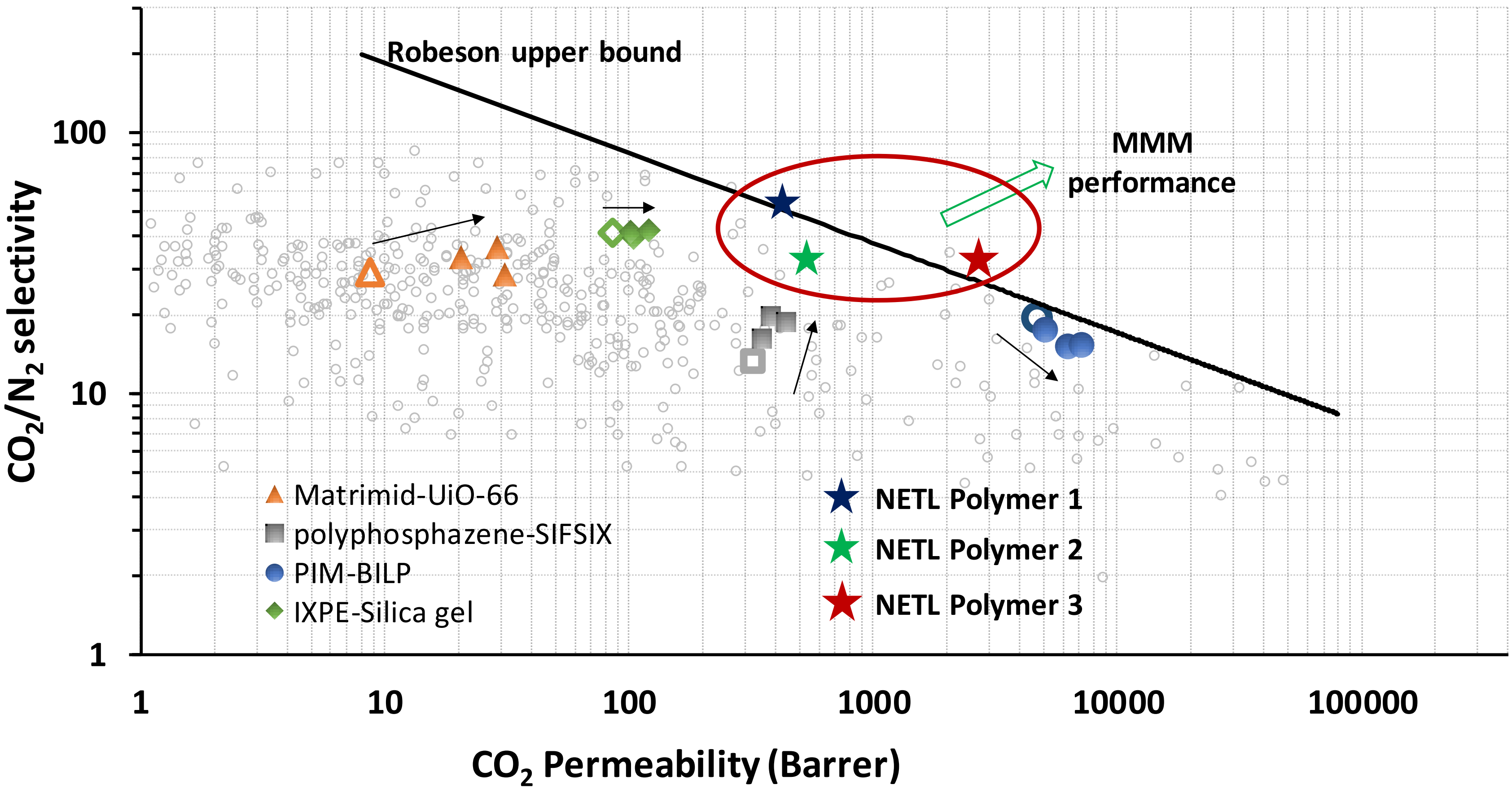


Two stage membrane process with air sweep



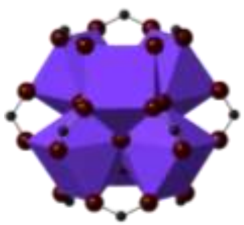
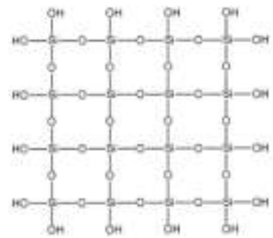
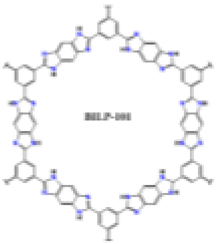
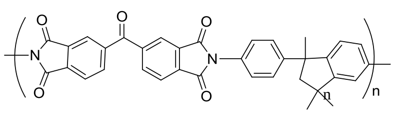
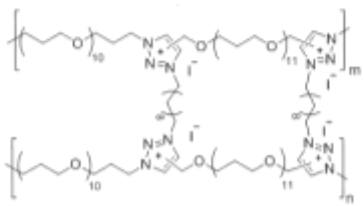
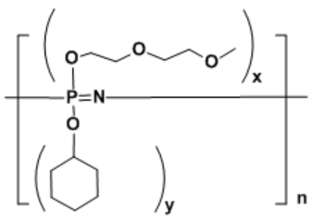
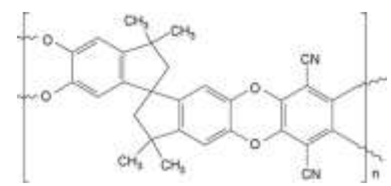
Keairns et al, A cost and performance analysis of polymeric membrane-based post-combustion carbon capture, In review

MMMs can increase membrane performance beyond the Robeson Upper Bound



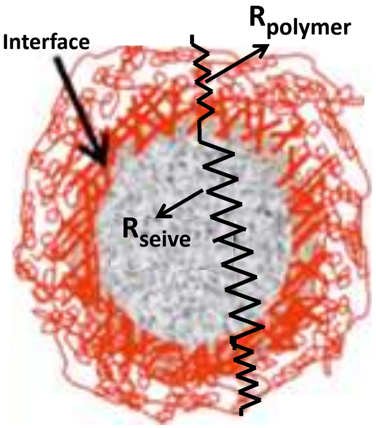
Assumptions of Robeson UB: pure polymers; 35 ^{o}C; pure gas; solution-diffusion

How do we choose the best pair of polymer and filler particle? By chemical intuition?

UiO-66	Silica	SIFSIX	POP
			
Polyimide	**Ionic XL Polyethers**	**Polyphosphazenes**	**Microporous Polymers**
			

Polyphosphazene polymer development for mixed matrix membranes using SIFSIX-Cu-2i as performance enhancement filler particles, Journal of Membrane Science, 535 (2017) 103-112.
Incorporation of benzimidazole linked polymers into Matrimid to yield mixed matrix membranes with enhanced CO_2/N_2 selectivity, Journal of Membrane Science, 554 (2018).
Carbon Dioxide Separation from Flue Gas by Mixed Matrix Membranes with Dual Phase Microporous Polymeric Constituents, Chemical Communications, 52 (2016) 11768-11771.

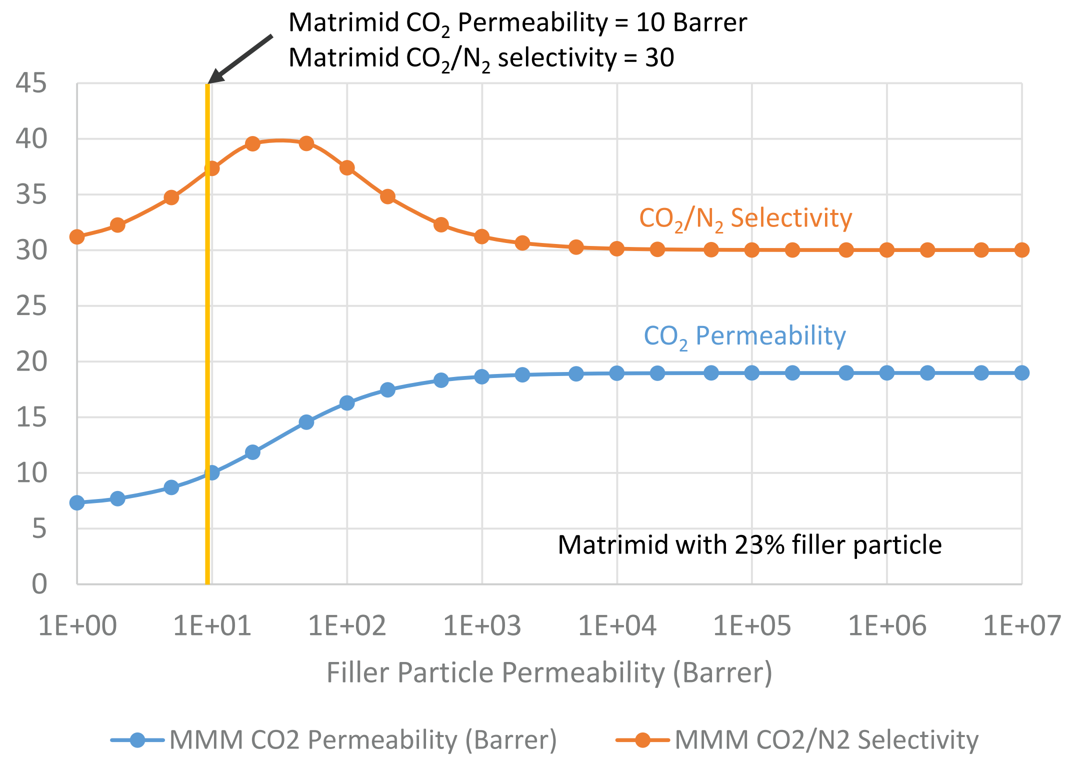
According to the Maxwell Model, properties of the polymer and filler must be complementary



$$P_{eff} = P_c \left[\frac{P_d + 2P_c - 2\emptyset_d(P_c - P_d)}{P_d + 2P_c + \emptyset_d(P_c - P_d)} \right]$$

Assumptions of Maxwell Model:

- Resistors in series
- No particle agglomeration
- Low particle loading, spherical
- Ideal interface



- For optimum selectivity, permeability of particle should be < 100X greater than polymer
- MMM permeability improvement has limitations

Computational modeling is used to predict MOF and MMM properties

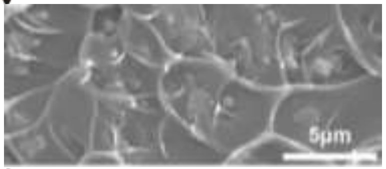
MOF Properties
(Predicted by Calculations)

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

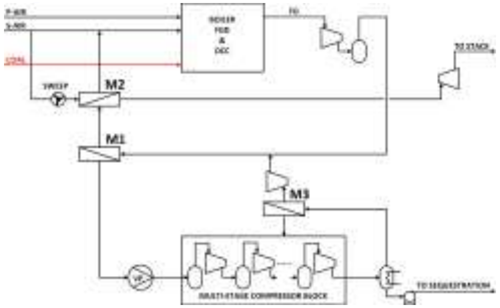
Pure Membrane Properties
for ~10 polymers
measured experimentally

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

Permeability of MOFs is calculated based on pore geometry

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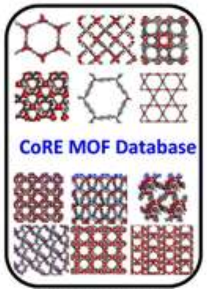
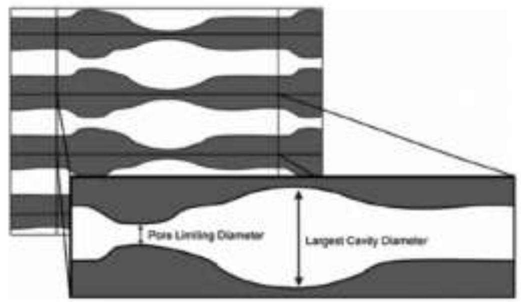
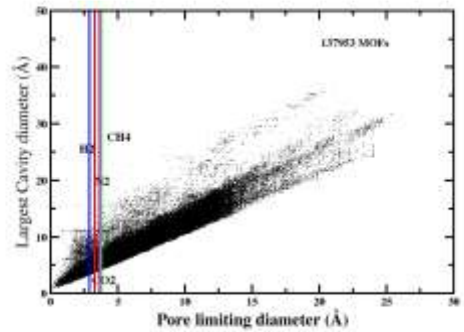
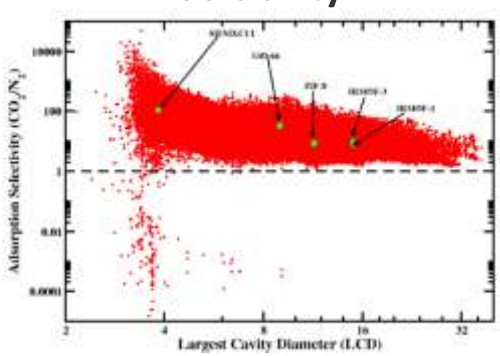




Pore Limiting Diameter

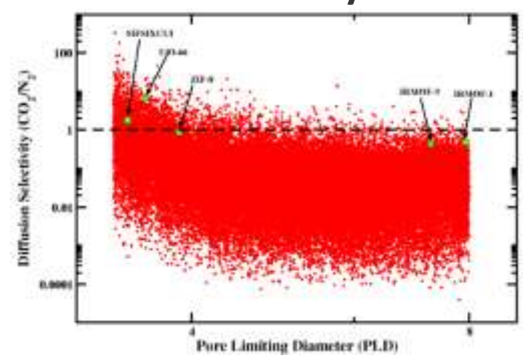


Solubility



Grand Canonical Monte Carlo simulations are used to calculate CO_2 and N_2 solubility for rigid MOFs

Diffusivity



Molecular dynamics simulations are used to calculate CO_2 and N_2 diffusivity

MOF Permeability = Solubility X Diffusivity

Mixed Matrix Membrane Permeability is from the Maxwell Model

Predictions of MMM permeability are in good agreement with literature data

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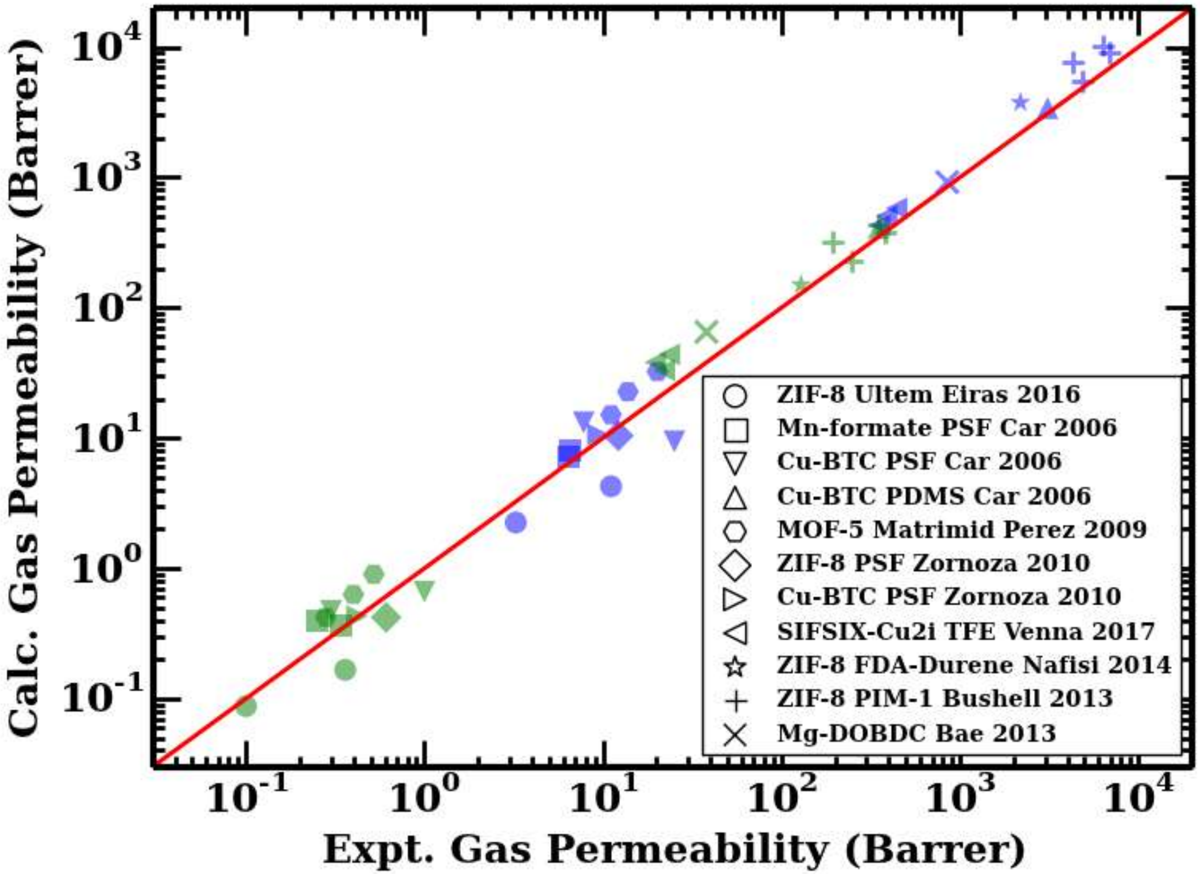
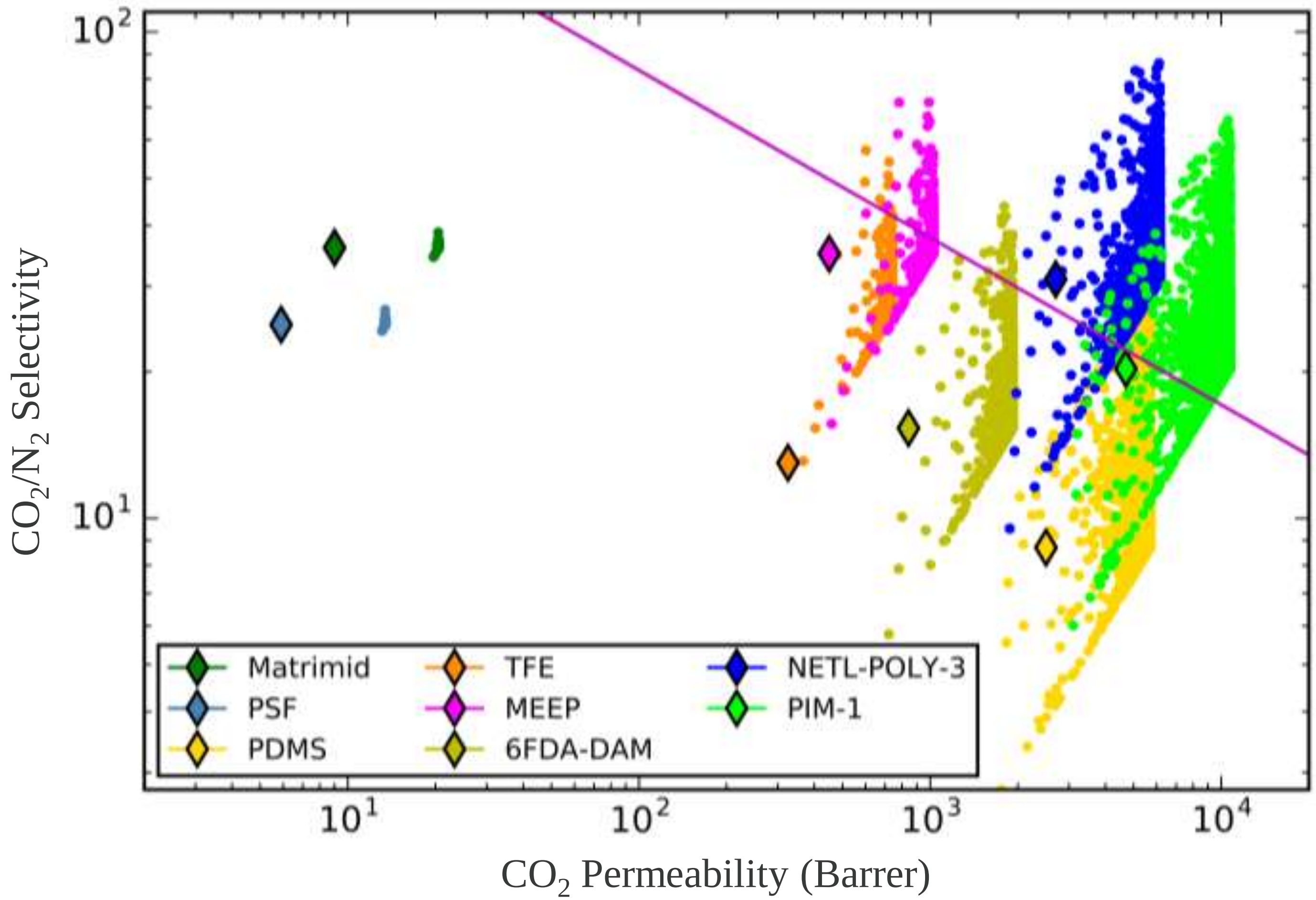
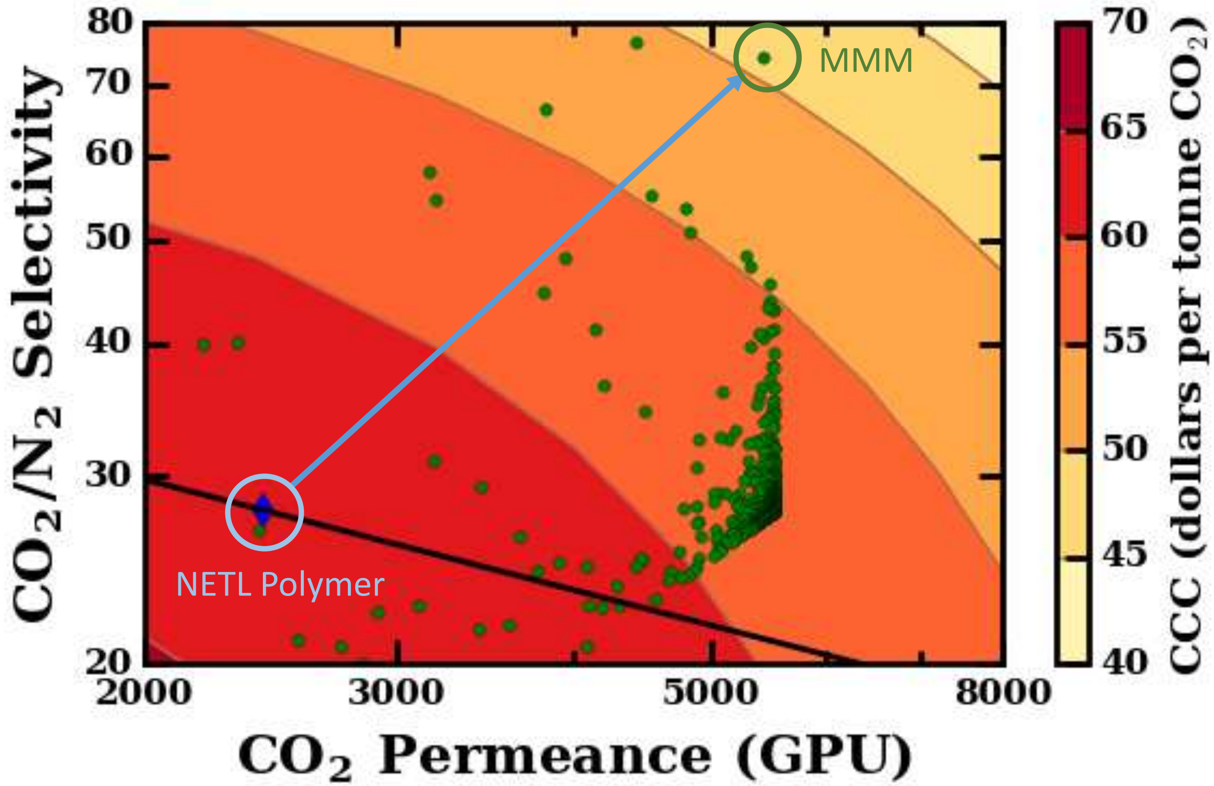


Blue markers = CO_2 permeability; Green markers = N_2 permeability

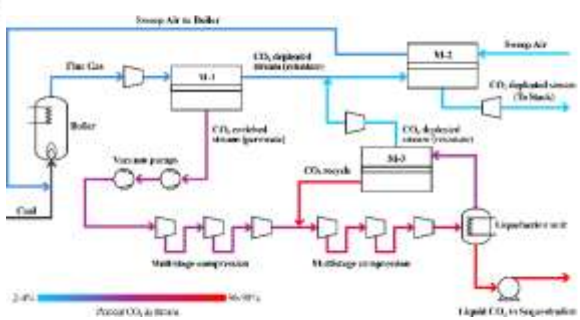
CO_2 permeability and CO_2/N_2 selectivity is calculated for MMMs with hypothetical MOFs



Compared to pure polymer, MMMs can dramatically reduce the cost of capture



CO$_2$ removal system: Two stage membrane with air sweep



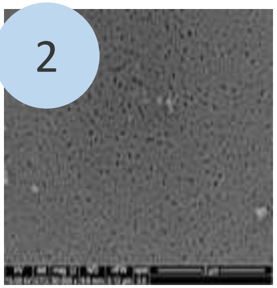
- Cost Reduction from ~\$61 to ~\$46 per tonne CO_2
- Reduction of ~24%

There are many practical considerations for a high performance membrane

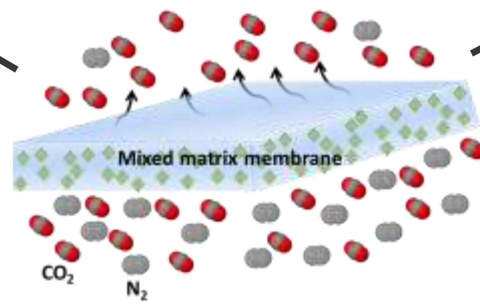
High performance polymer

1

2

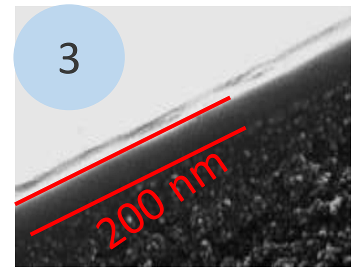


Support with optimum pore size and density

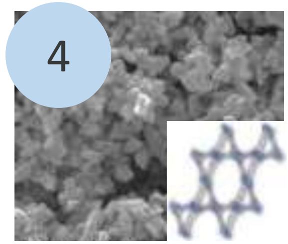


Ultra-thin, defect-free selective layer

3



4



Nano-size MOF with matched properties

PIM-1/MEEP-Polyphosphazene polymers combine the best properties of each

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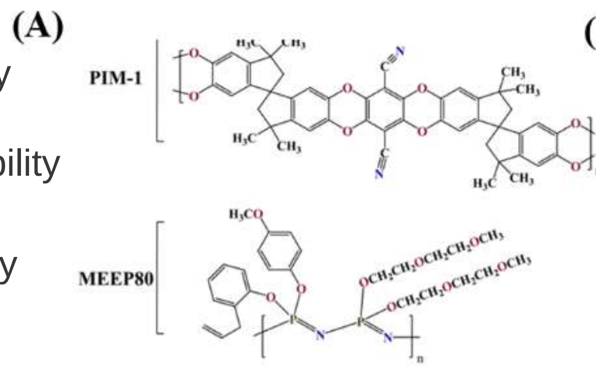
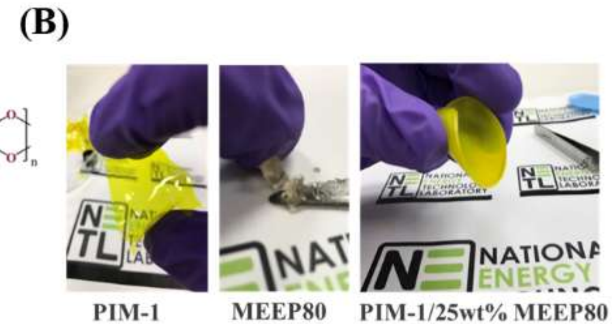
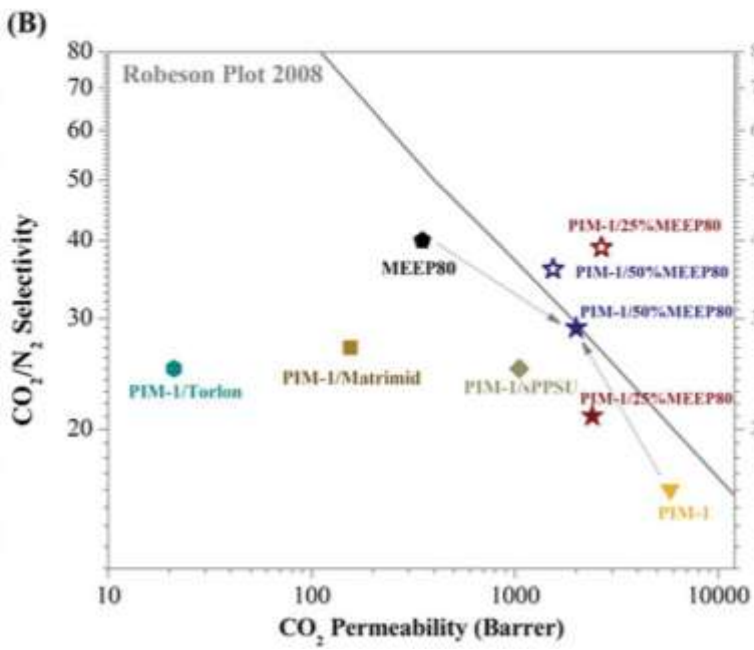
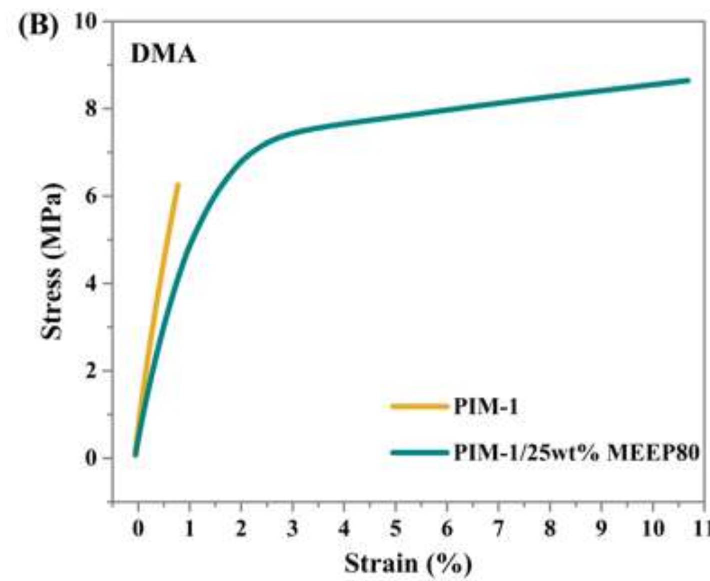
PIM-1: High Permeability Low Selectivity
Brittle films
Physical aging reduces permeability

MEEP: Low Permeability High Selectivity
Gummy films



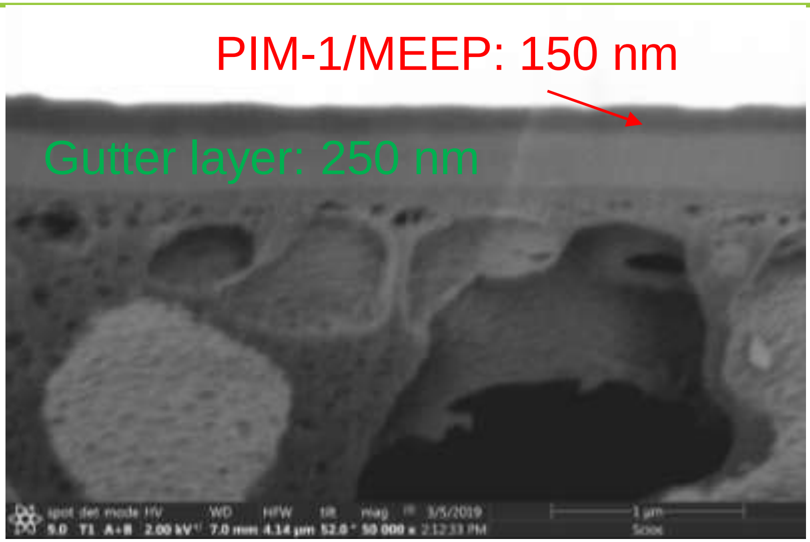


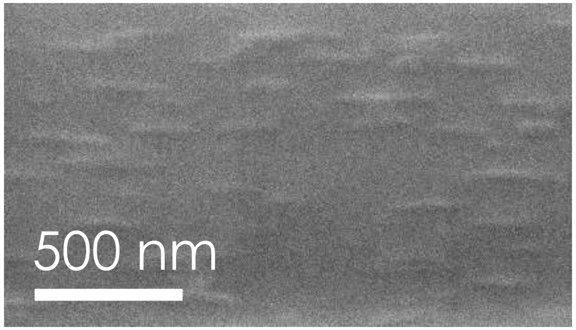


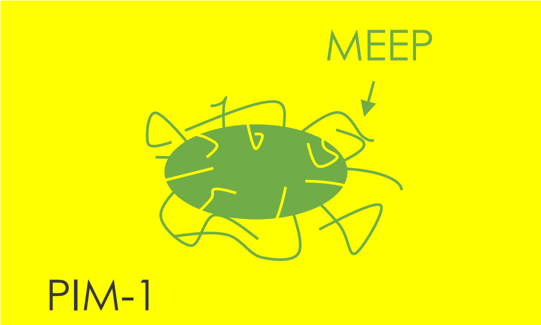


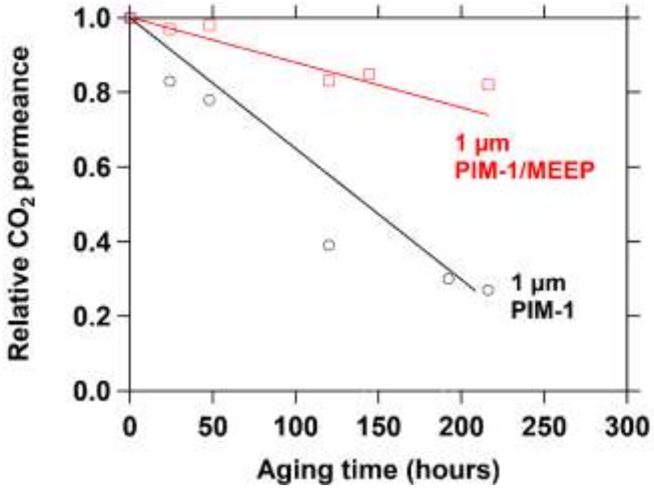
U.S. DEPARTMENT OF ENERGY

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







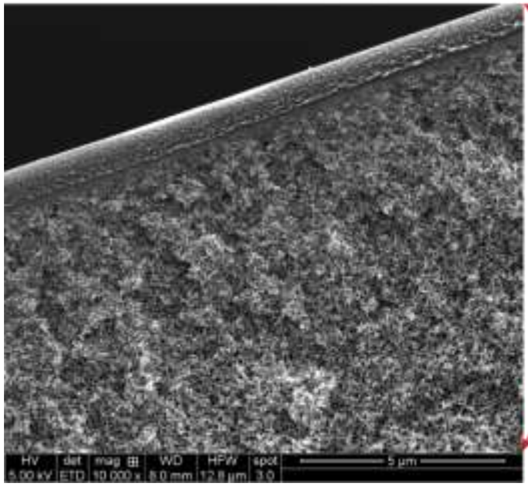


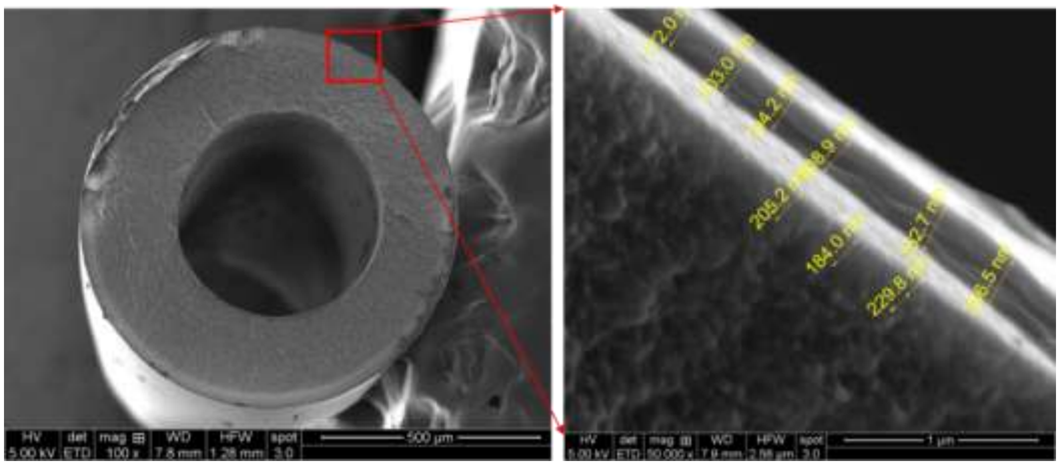
PIM-MEEP suffers less aging than PIM-1 due to

(1) chain-chain entanglement

(2) MEEP chain/PIM-1 pore intercalations

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



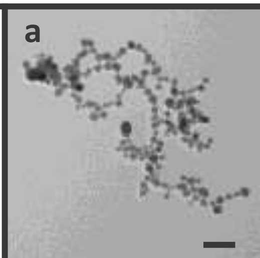
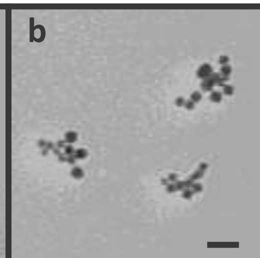
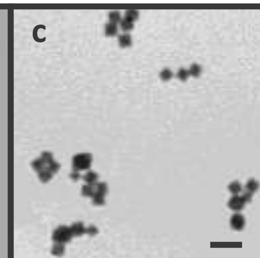
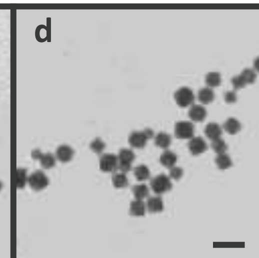
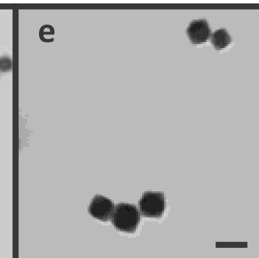
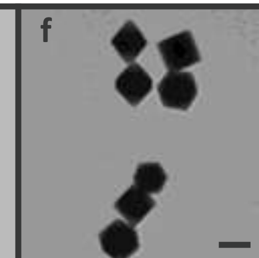


Our current hollow fiber membrane supports:

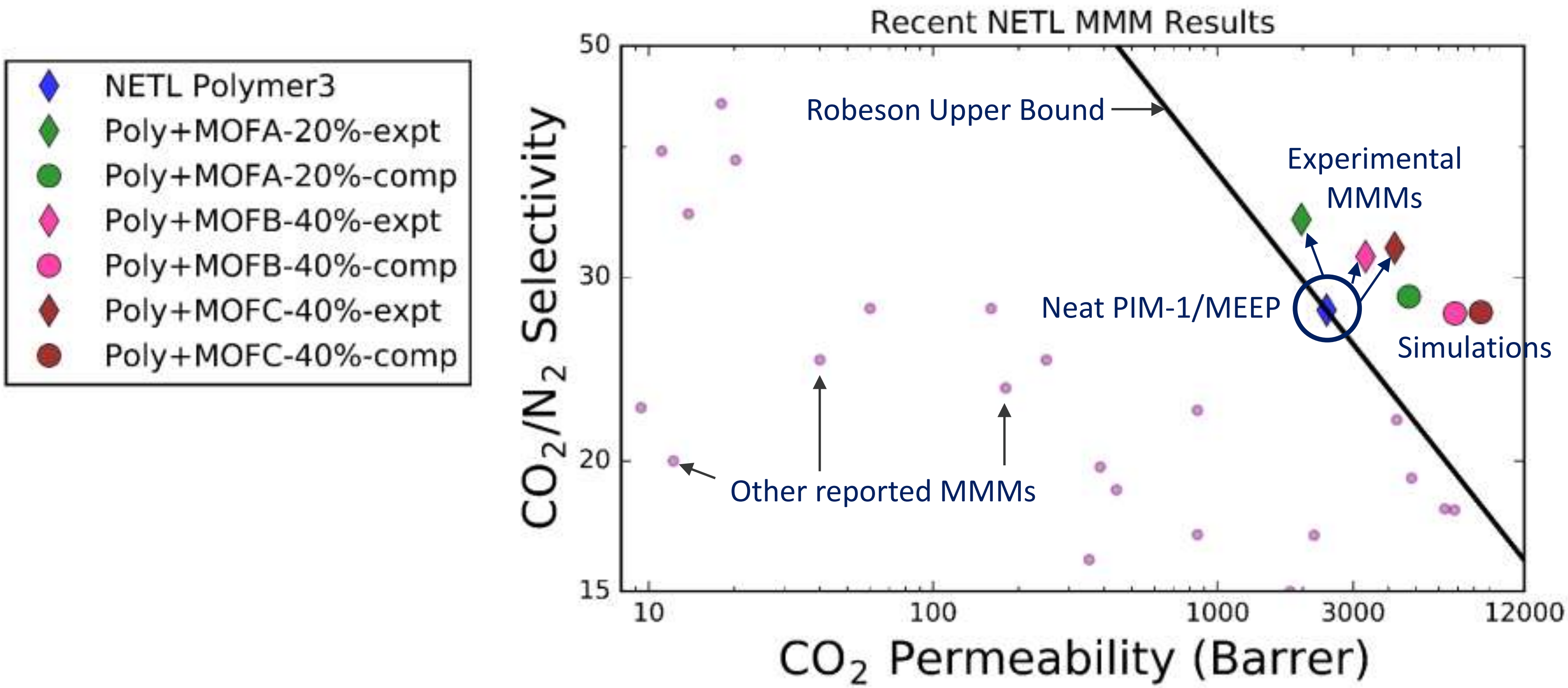
- N_2 permeance >100,000 GPU
- CO_2/N_2 selectivity ~ 0.8 (Knudsen diffusion)
- Surface pore size ~ 20 nm
- Resistant to mild solvents

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

TEM Images (scale bars = 200 nm)						
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

NETL MMMs are above the Robeson Upper Bound with high CO_2 permeability



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

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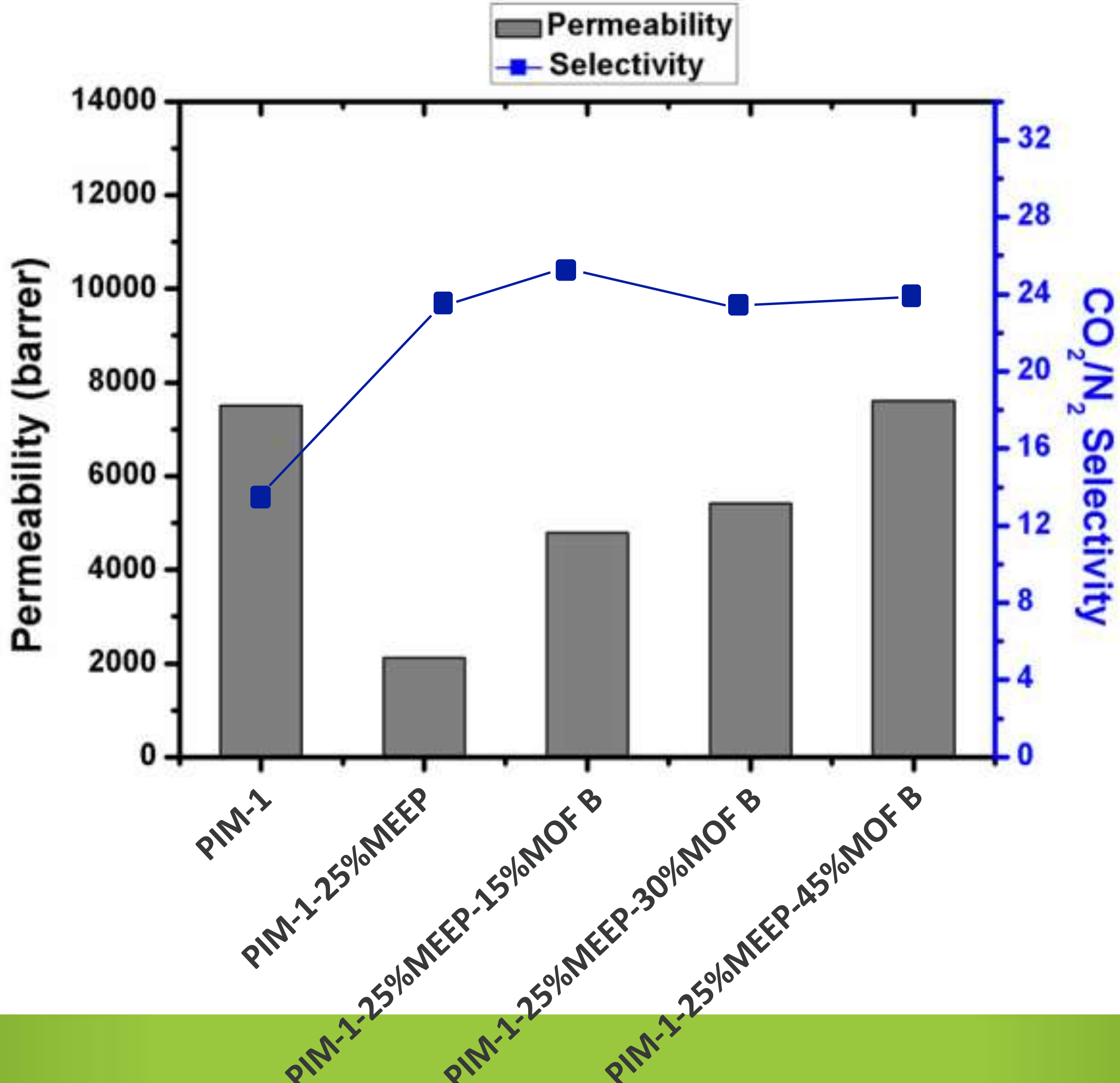

MMMs show stable performance when tested in actual flue gas with contaminants

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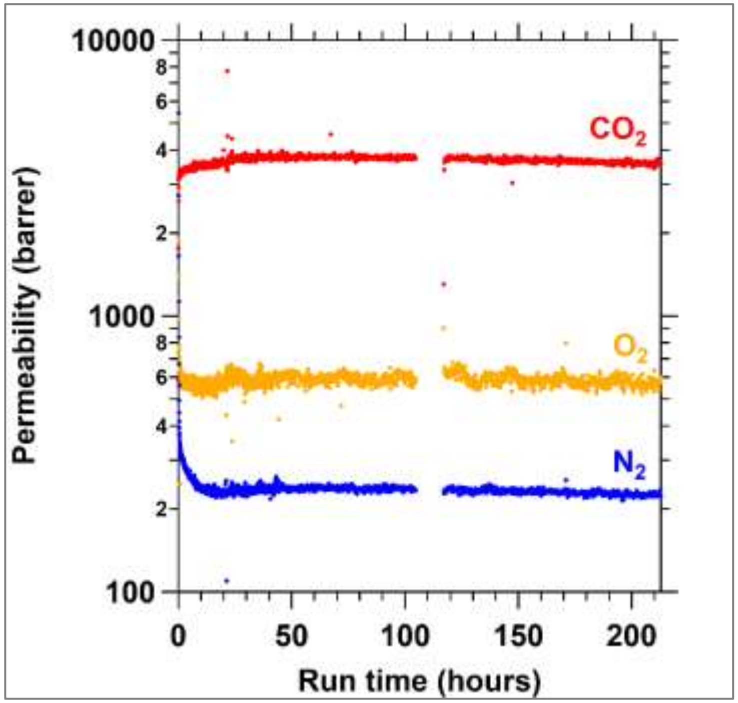
NETL's membrane flue gas test unit at the National Carbon Capture Center



MMM with MOF A

Kusuma et al.,Journal of Membrane Science, 533, 2017, 28–37

Summary: NETL has taken a multifaceted approach to MMM development for low cost CO_2 capture

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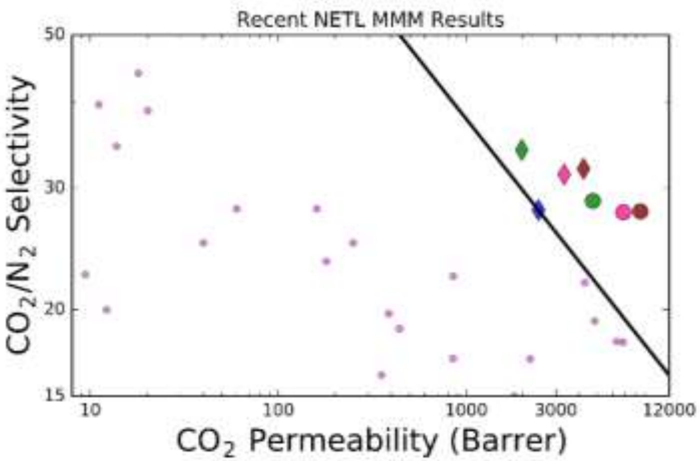
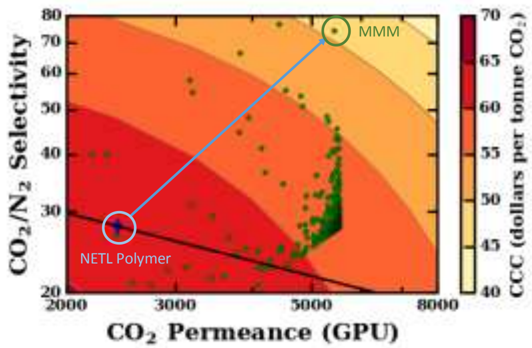
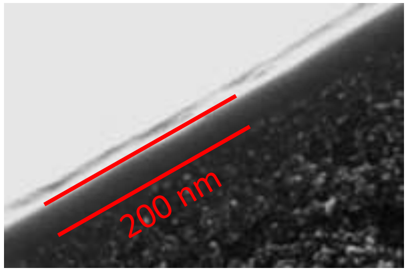


- MMMs developed at NETL are above the Robeson Upper Bound



- Using high throughput computational techniques, properties of polymer/MOF can be matched to make better MMMs
- For an NETL polymer, the cost of capture can be reduced from \$61 to \$46/tonne CO_2



- High permeance hollow fiber supports have been fabricated
- Techniques for thin film coatings of MMMs are being developed

- MMMs have been tested at NCCC with real flue gas and show stable performance

Thanks to our team!

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Nathaniel Rosi
Patrick Muldoon

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James Baker

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