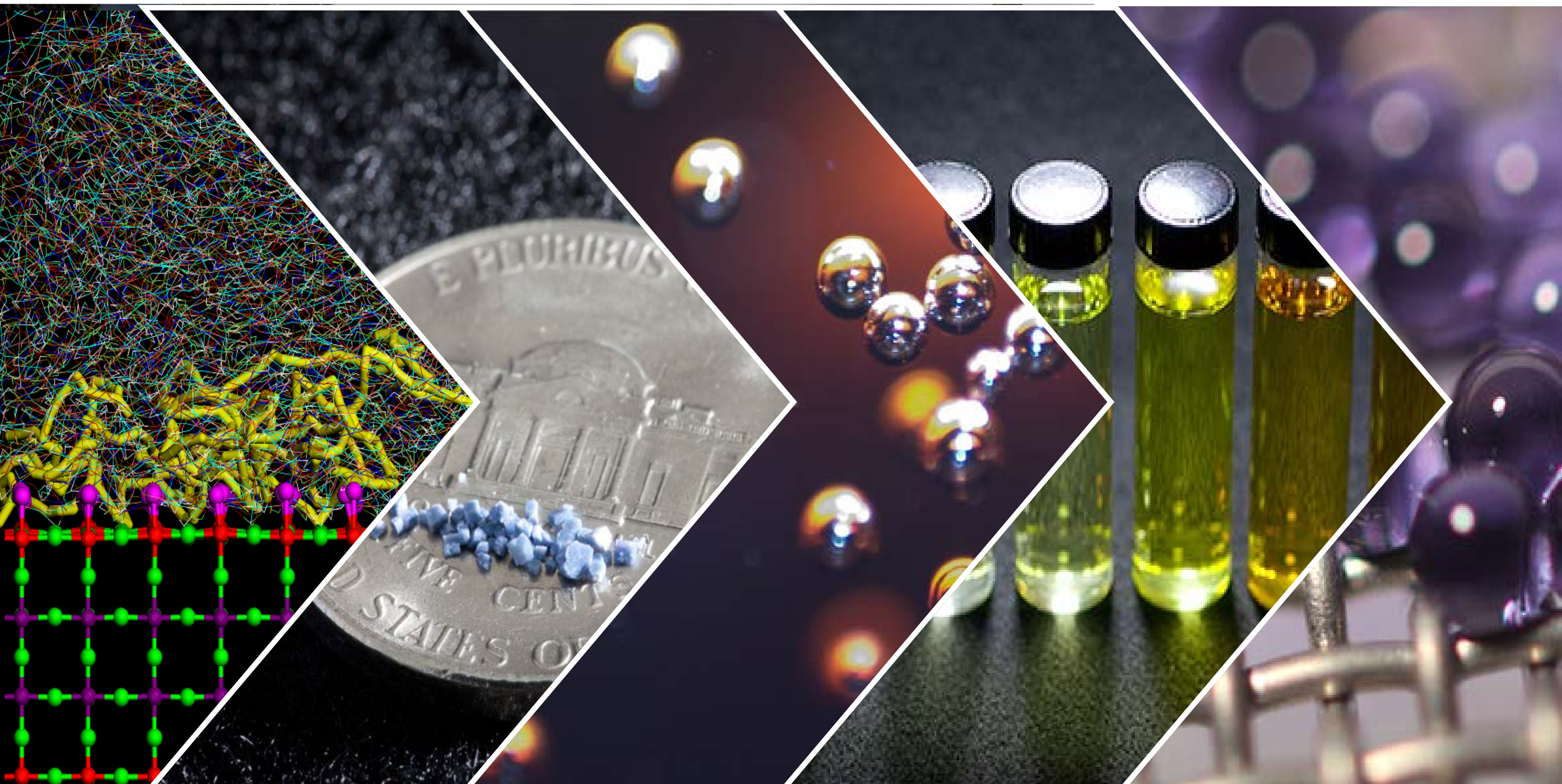
NATIONAL ENERGY TECHNOLOGY LABORATORY

A Combined Computational and Experimental Approach to Mixed Matrix Membranes for CO_2 Capture

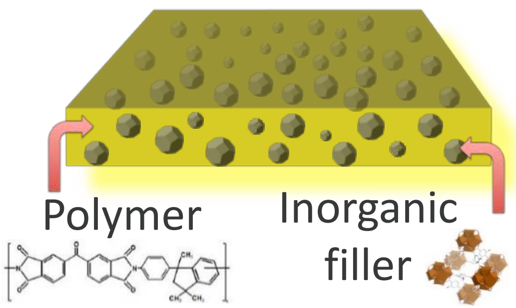
Dave Hopkinson, Surendar Venna, Ali Sekizkardes, Sameh Elsaidi, Samir Budhathoki, Jan Steckel, and many others

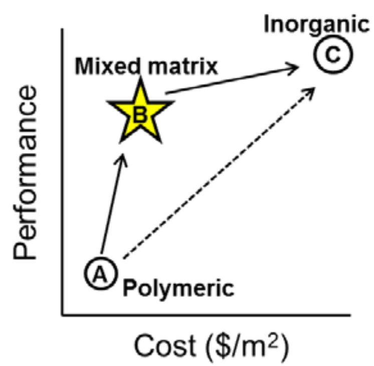


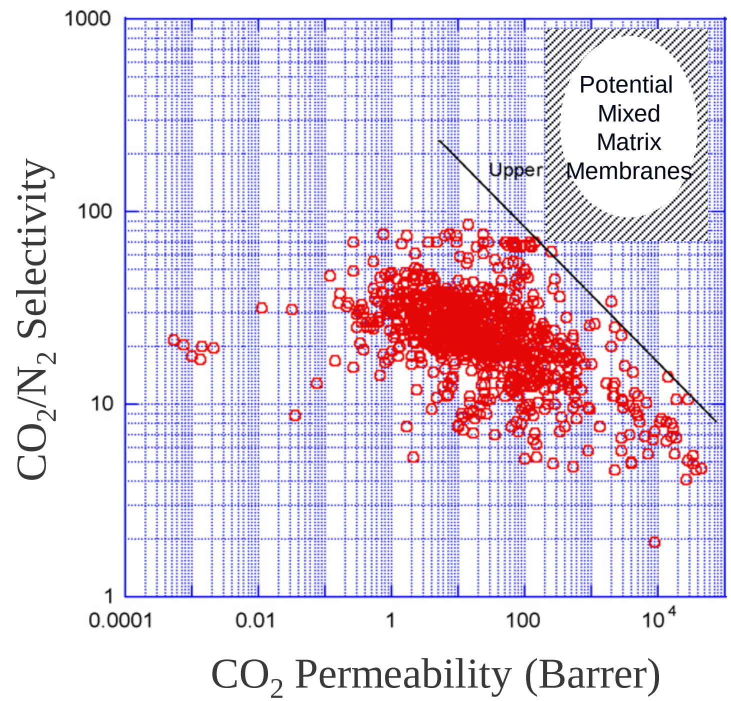
Membranes need very high performance to be used in CO_2 capture from fossil energy

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

Mixed Matrix Membrane



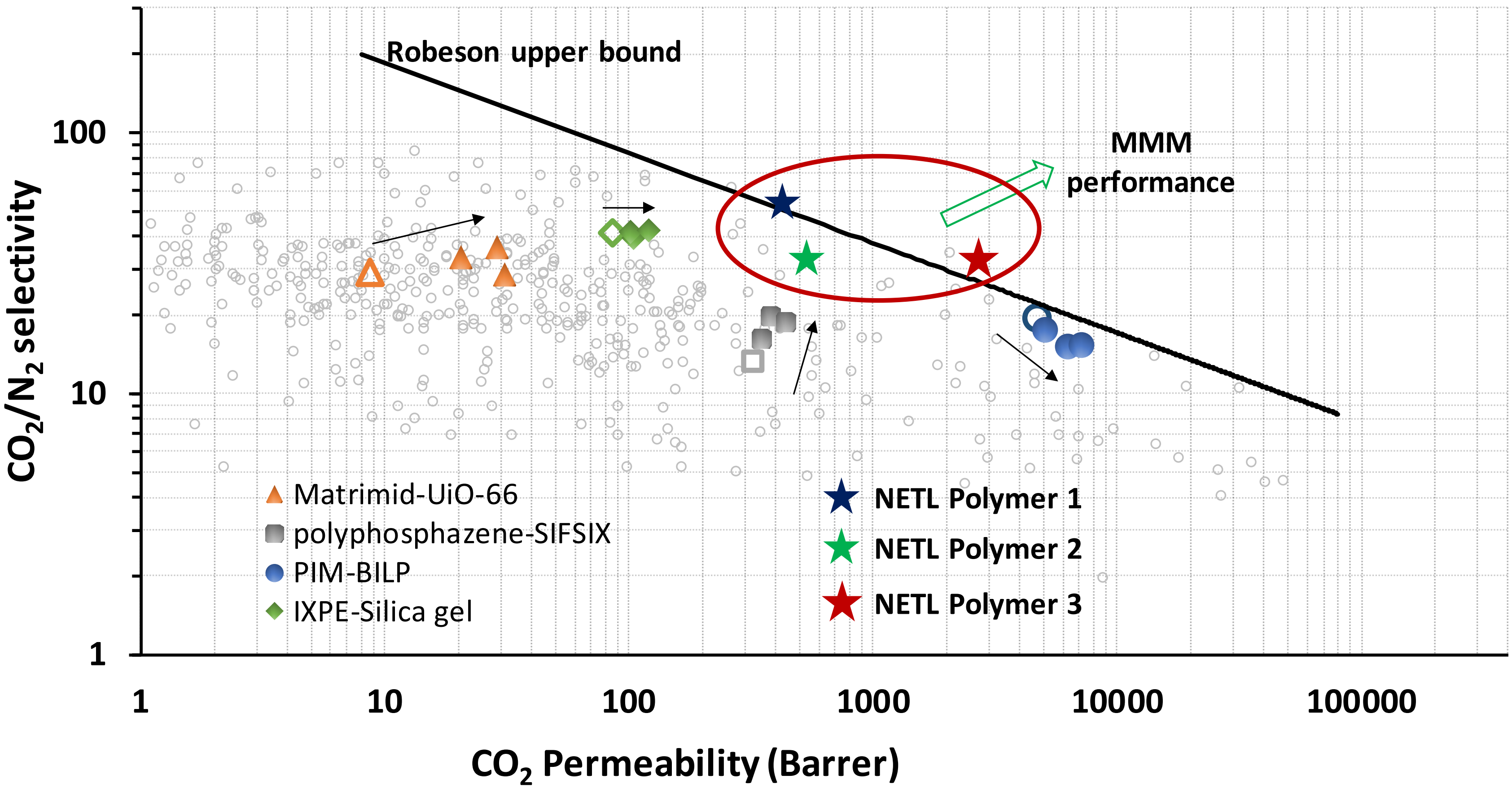




Permeance of 4000 GPU, CO_2/N_2 selectivity of 25
For 10% COE reduction compared with reference plant

Lloyd M.Robeson, Journal of Membrane Science, 320, 2008, 390-400
Performance vs cost plot, Courtesy: William Koros

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?

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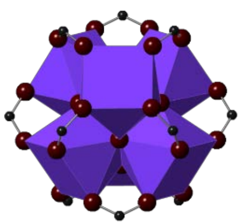
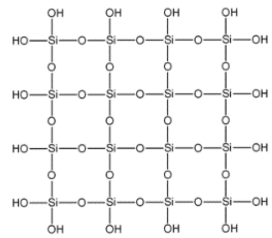
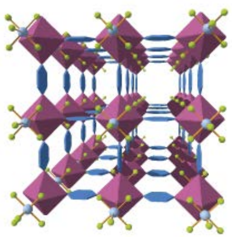
UiO-66



Silica

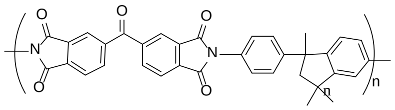


SIFSIX

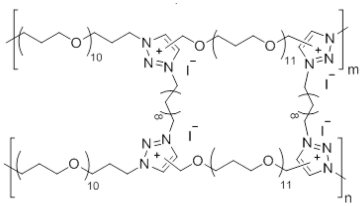


POP

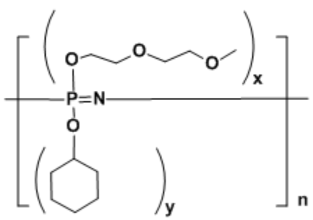
Polyimide



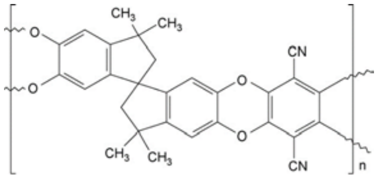
Ionic XL Polyethers



Polyphosphazenes

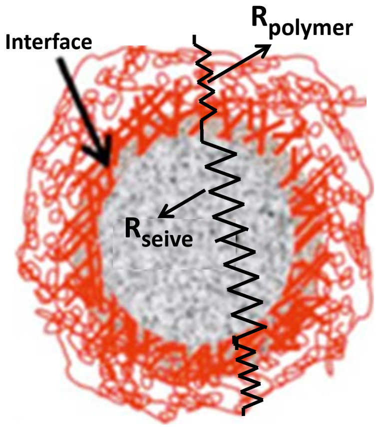


Microporous Polymers



Normally filler particles are paired with polymers by chemical intuition

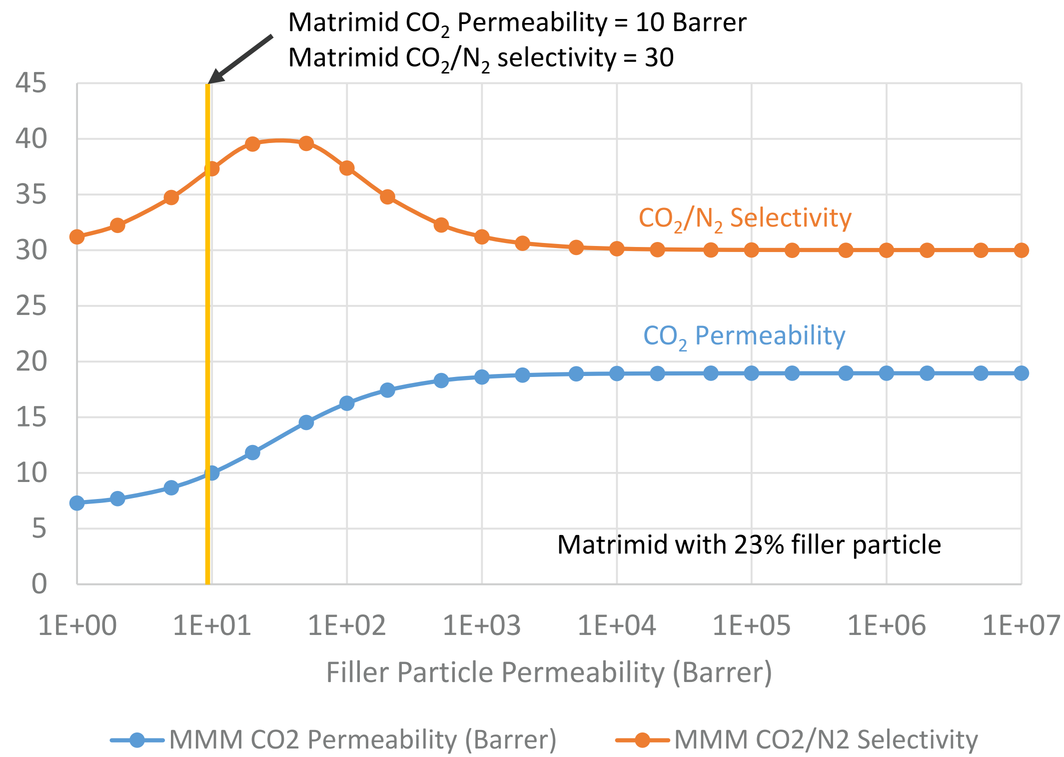
According to the Maxwell Model, properties of the polymer and filler must be complementary



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

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

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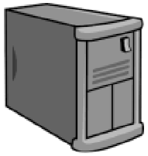
MOF Properties
(Predicted by Calculations)

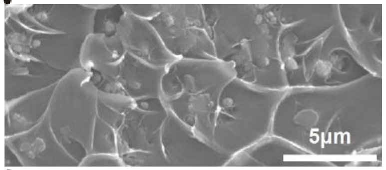
DB of ~137,000
Hypo-MOFs
DB of ~2,500 MOFs
CORE-MOFs



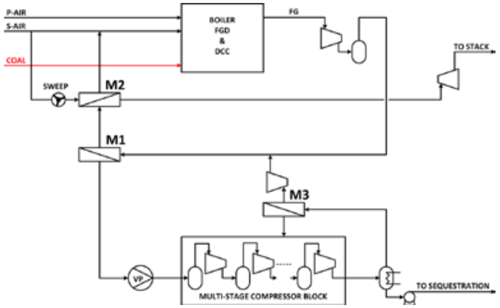
Pure Membrane Properties
for ~10 polymers
measured experimentally

Maxwell Eq.

Predicted Properties
for well over a million
possible MMMs



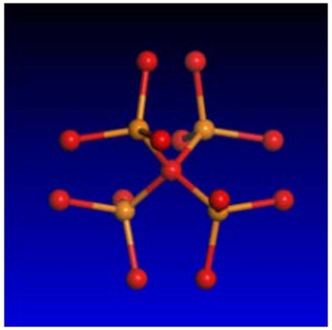
Estimate of Cost
of Carbon Capture
based on an
assumed configuration



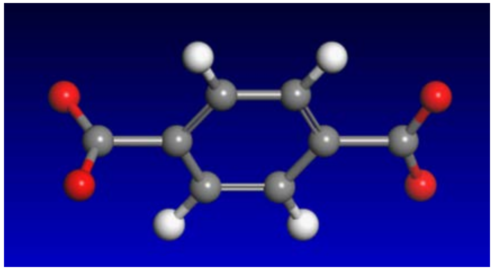
CCSI²
Carbon Capture Simulation for Industry Impact

A database of 137,000 hypothetical MOFs was made by combining MOF building blocks

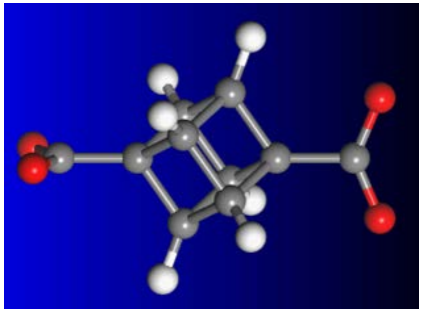
1: Metal Center



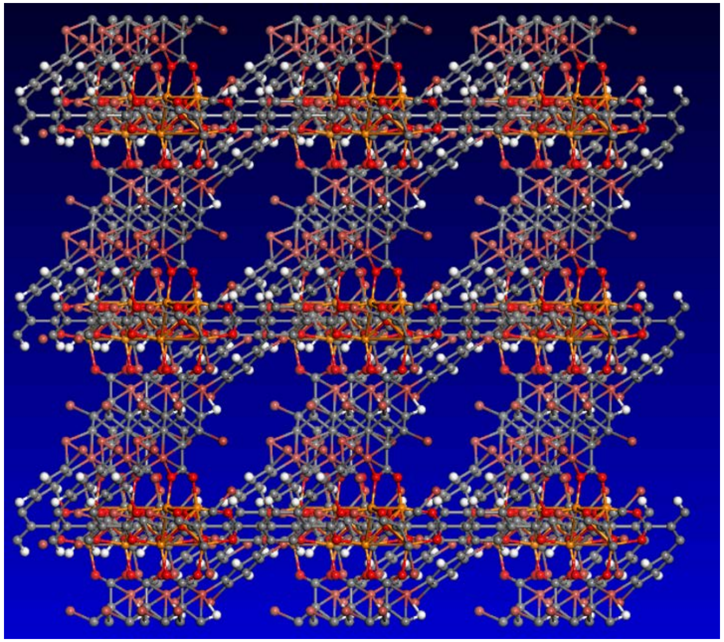
2: Organic Linkers



3: Functional Groups
e.g. –Br, -Cl, phenyl, etc.

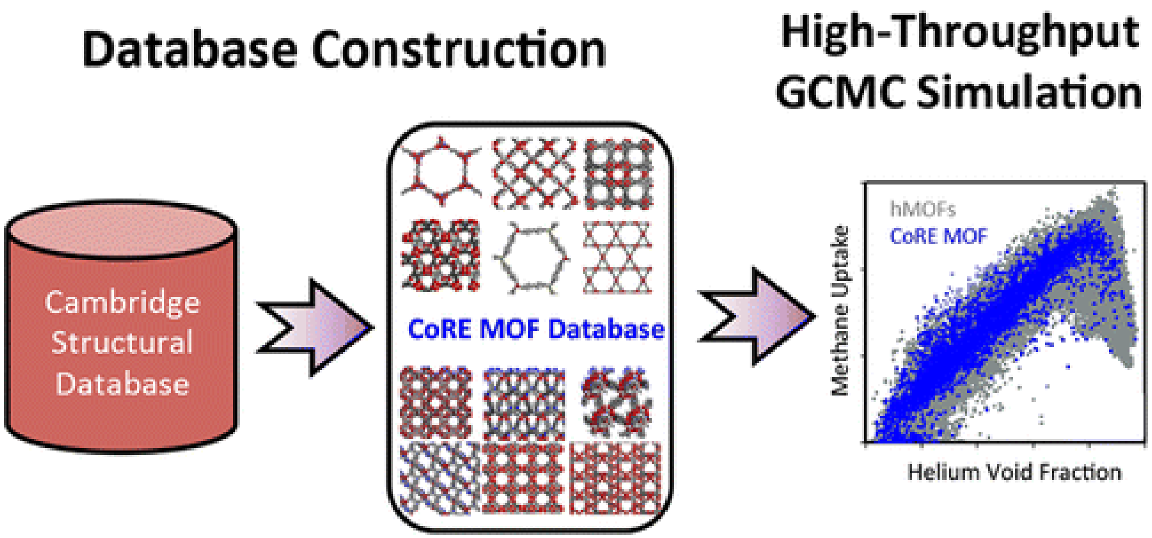


Building blocks re-combined using simple geometrical rules to create periodic, 3D structures



C. E. Wilmer et al., **Nature Chemistry**, 2012, 4, 83–89.

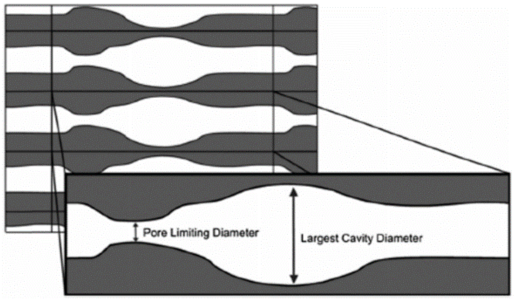
The CoRE database details properties of MOFs that have been synthesized before



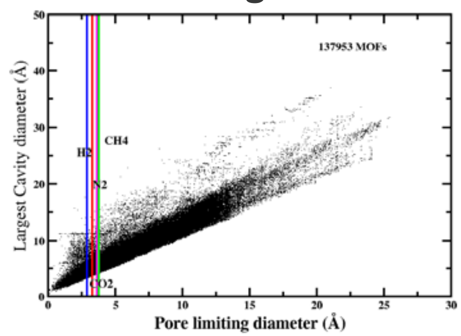
- **Automated screening of the Cambridge Structural Database was used to clean experimentally obtained structure files:**
  - Solvent molecules removed
  - Other disorder removed
- **6,000 structures available in CoRE database**
- **We have completed calculations on ~2,500 CoRE MOFs**

Y. G. Chung et al., Chemistry of Materials, 2014, *26* (21), 6185–6192.

Permeability of MOFs is calculated based on pore geometry

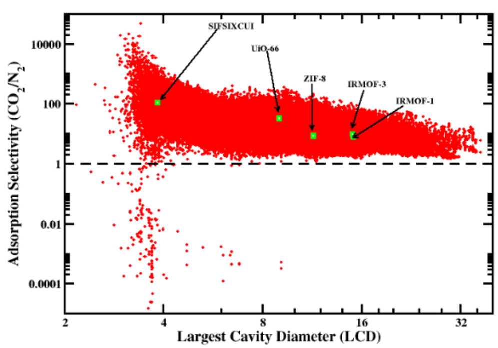


Pore Limiting Diameter



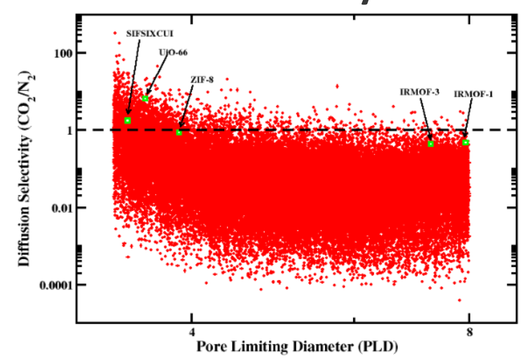
MOFs from the hypothetical and CoRE databases are analyzed based on largest cavity diameter (LCD), pore limiting diameter (PLD), and surface area

Solubility



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

Diffusivity

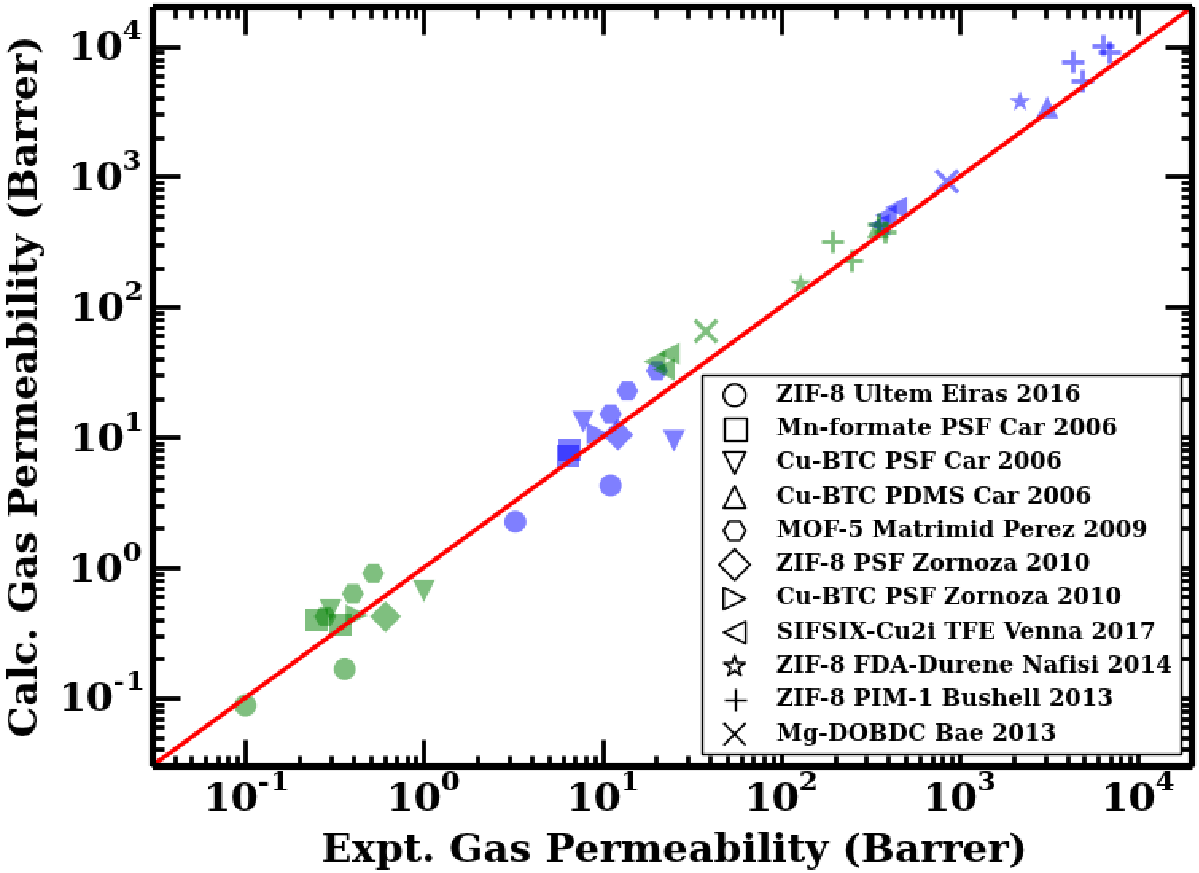


Molecular dynamics simulations are used to calculate CO_2 and N_2 diffusivity

MOF Permeability = Solubility X Diffusivity

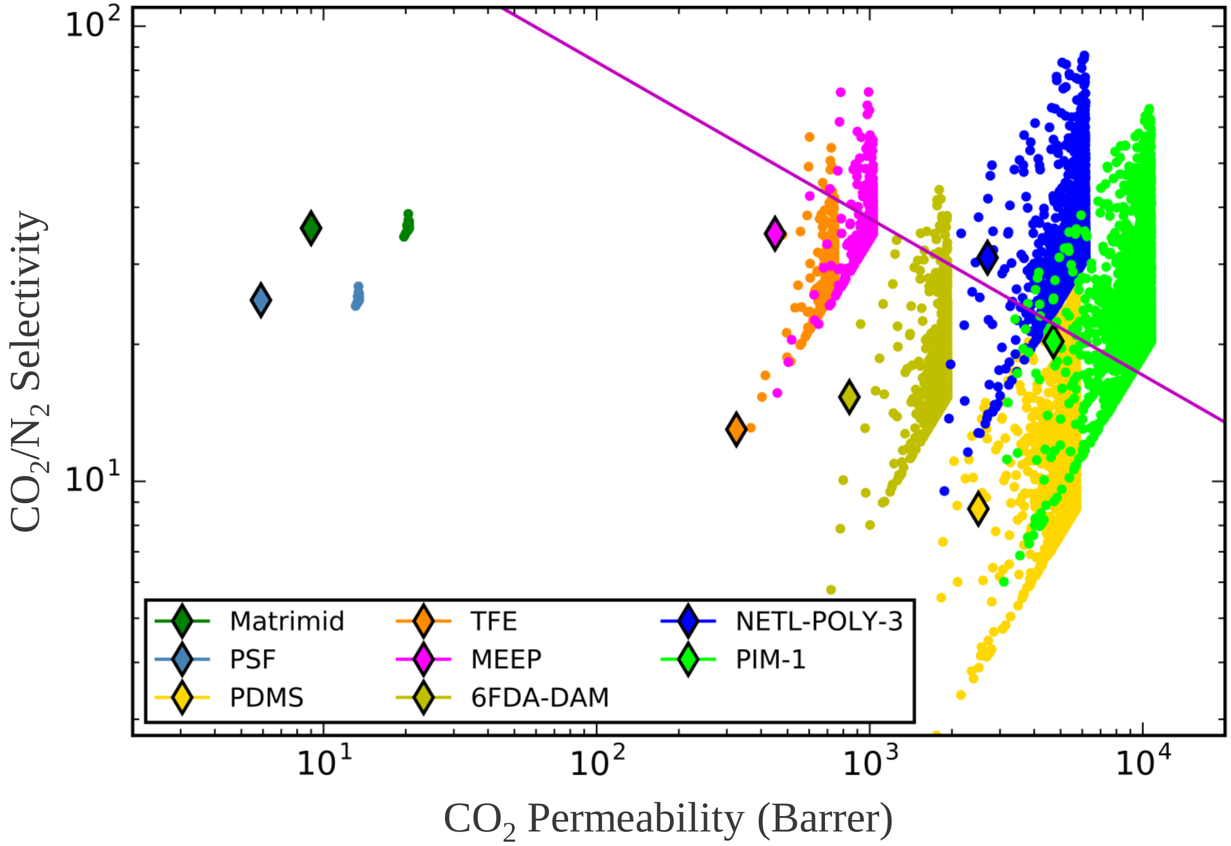
Mixed Matrix Membrane Permeability is from the Maxwell Model

Predictions of MMM permeability are in good agreement with literature data



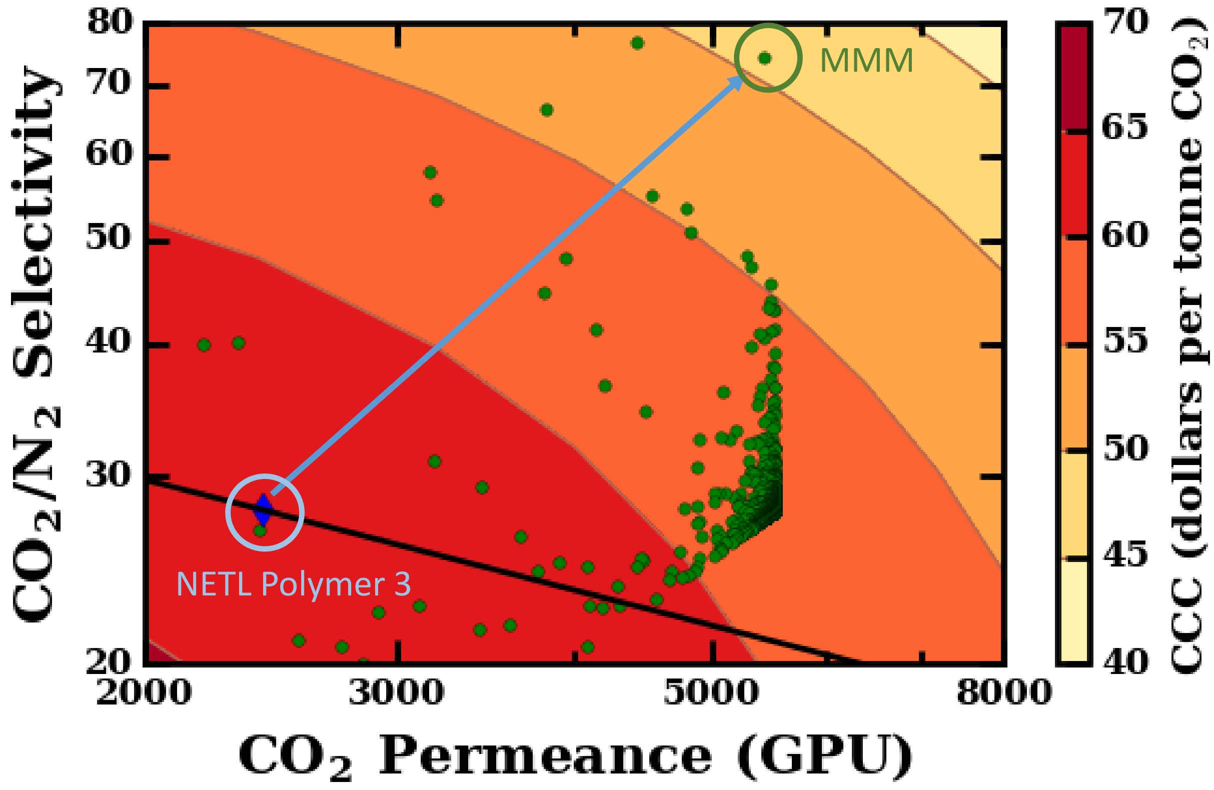
Blue markers = CO_2 permeability; Green markers = N_2 permeability

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

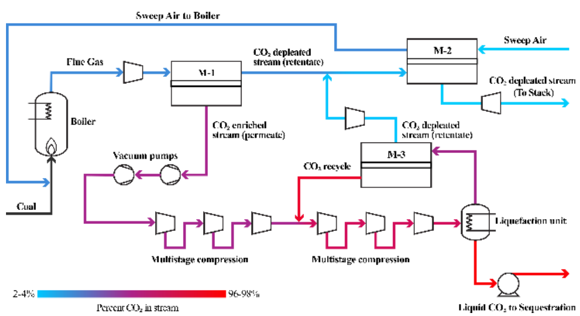


- For low permeability polymers, any MOF leads to an increase in permeability
- For high permeability polymers, only some MOFs will cause an improvement in permeability *and* selectivity

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

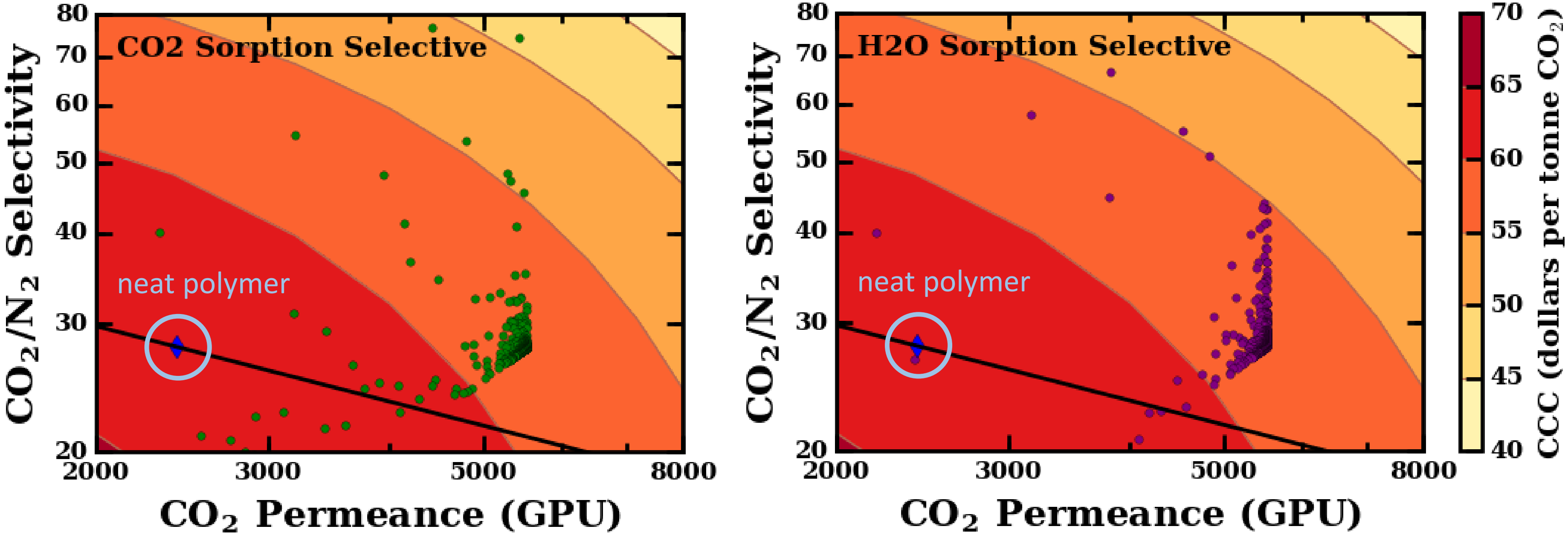


CO_2 removal system: 2 stage membrane with air sweep



- Cost Reduction from ~$63 to ~$48 per tonne CO_2
- Reduction of ~24%

Many of the MOFs in the CoRE database are sorption selective to CO_2 over H_2O

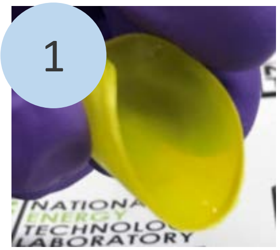


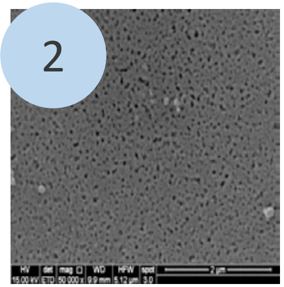
Henry's Constants for H_2O in CoRE MOFs courtesy of:

Li, S.; Chung, Y. G.; Snurr, R. Q. High-Throughput Screening of Metal–Organic Frameworks for CO_2 Capture in the Presence of Water. *Langmuir* **2016**, *32* (40), 10368–10376.

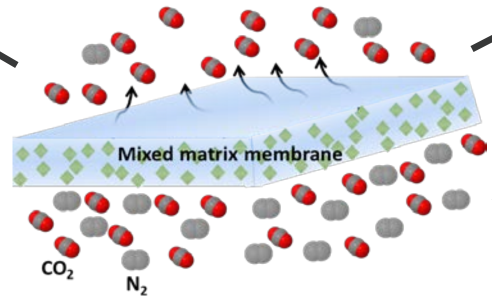
There are many practical considerations for a high performance membrane

High performance polymer

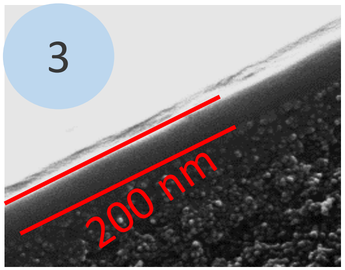


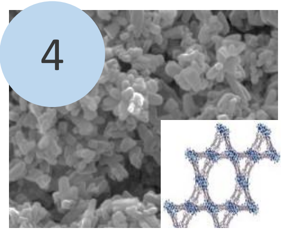


Support with optimum pore size and density



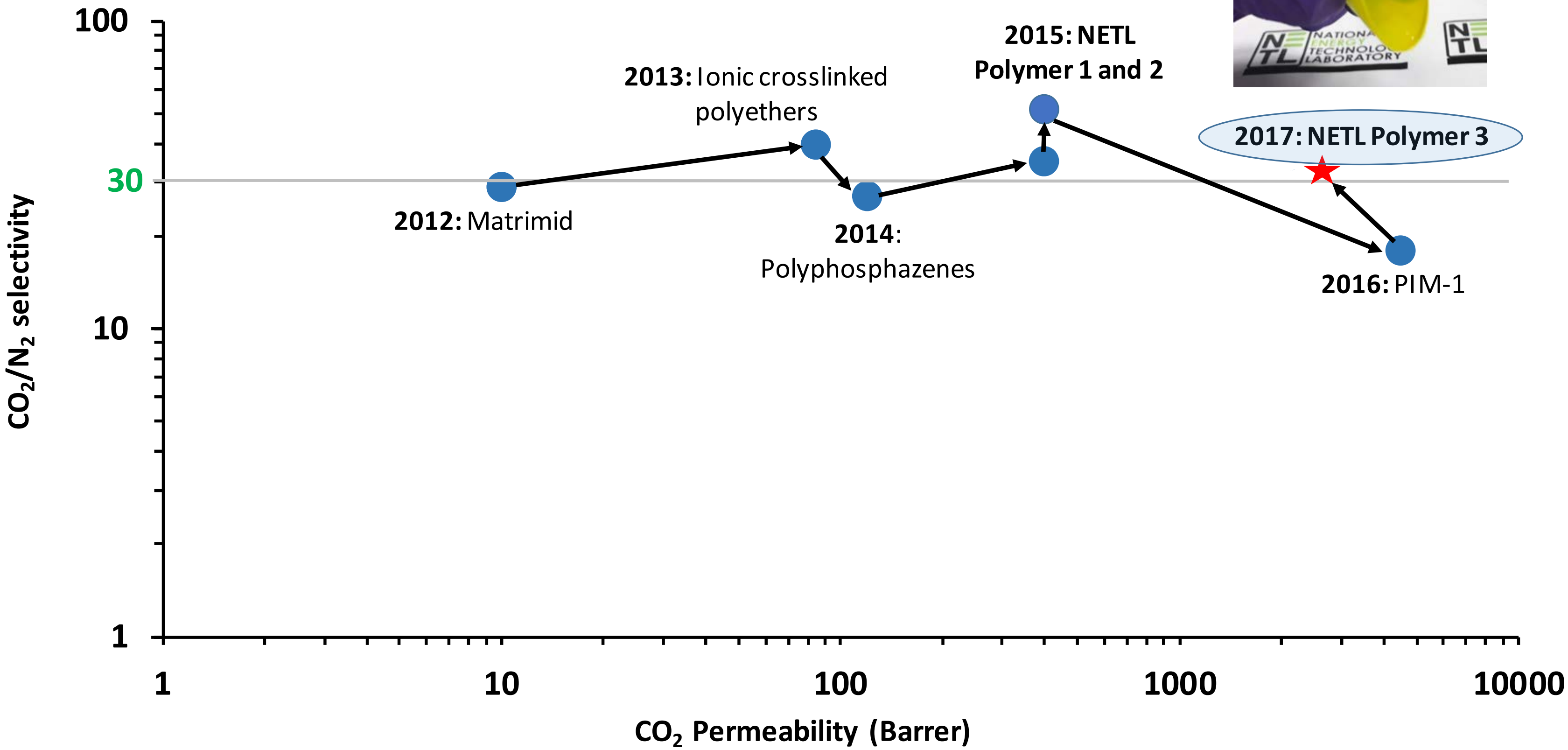
Ultra-thin, defect-free selective layer





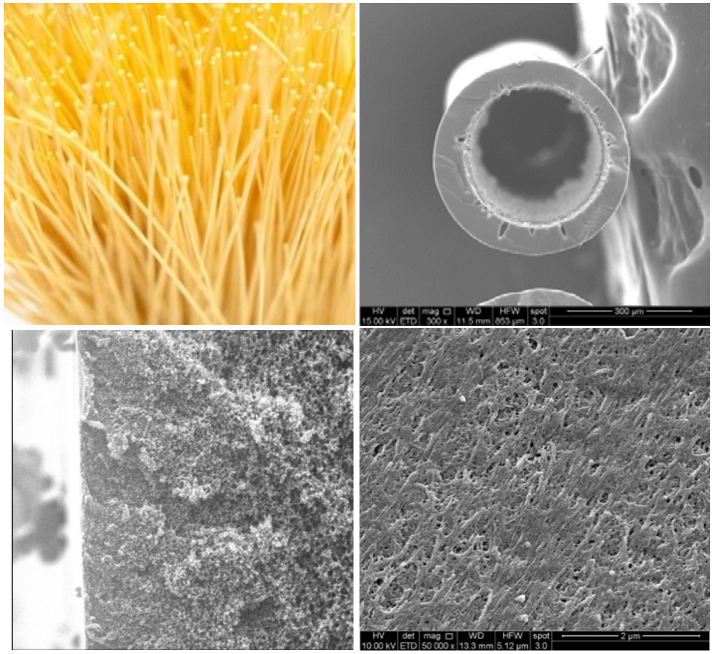
Nano-size MOF with matched properties

A high performance MMM requires a high performance polymer



Venna et al., J. Membr. Sci., 535, 2017, 103–112
Zhou et al, European Polymer Journal, 84, 2016, 65–76

A hollow fiber support needs optimized pore density and pore size

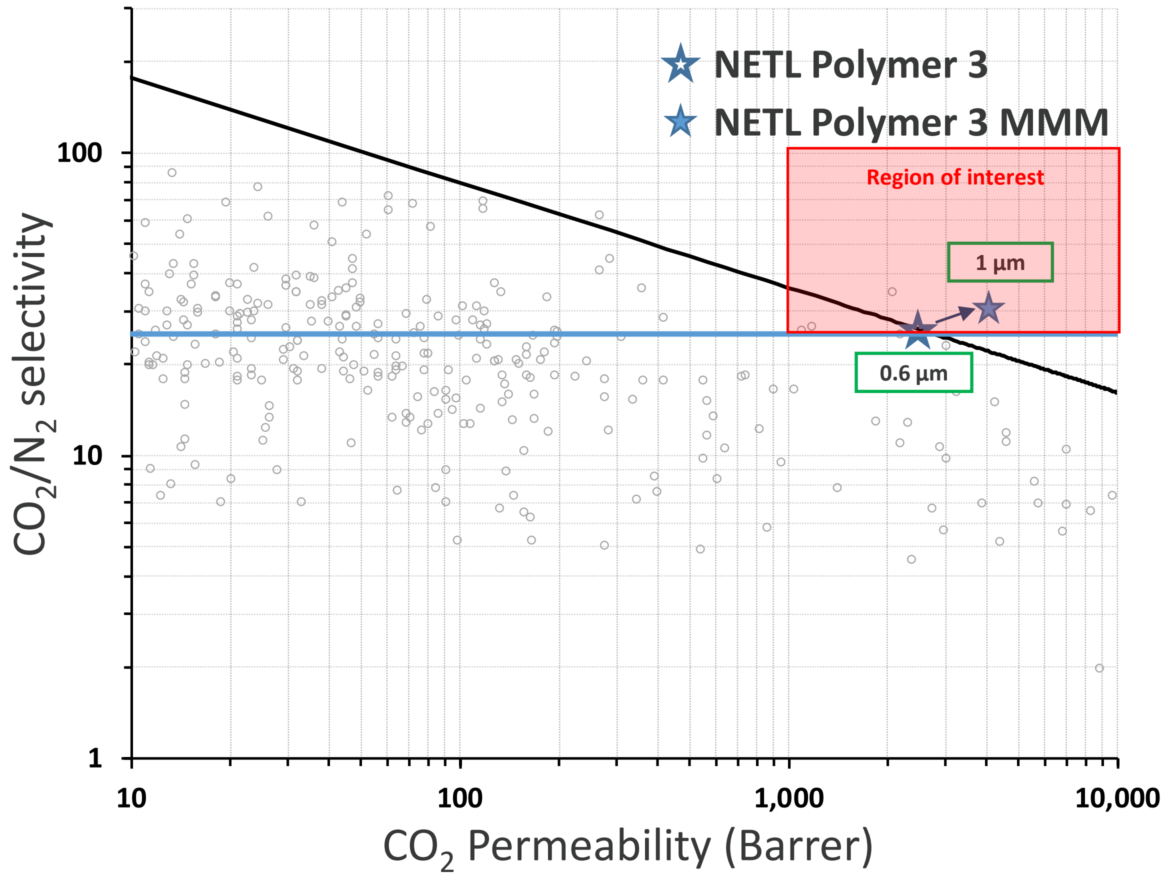


Optimum wall thickness and bore diameter

Higher surface pore density with optimum pore size

The support should have at least an order of magnitude higher gas flux compared to selective layer

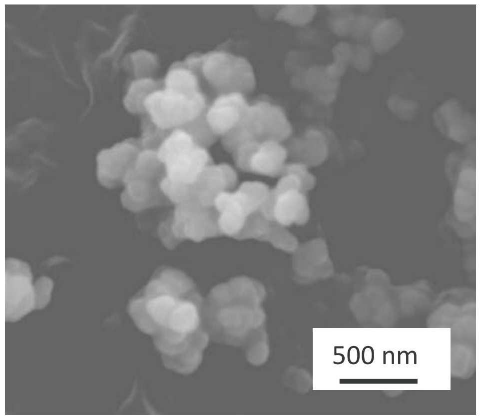
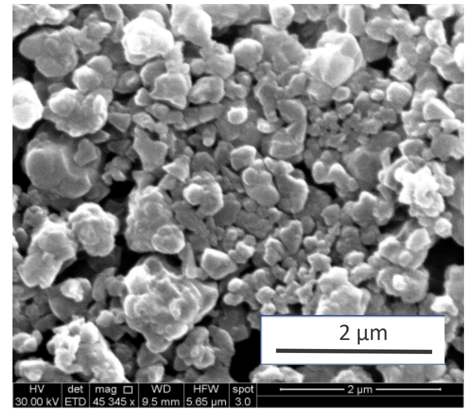
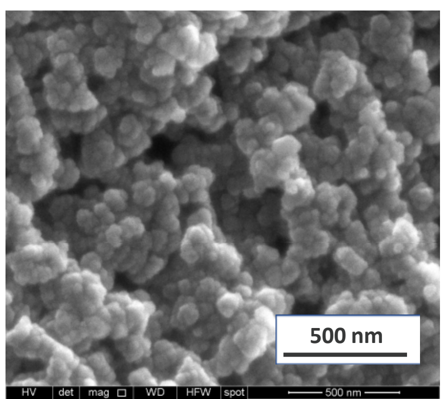
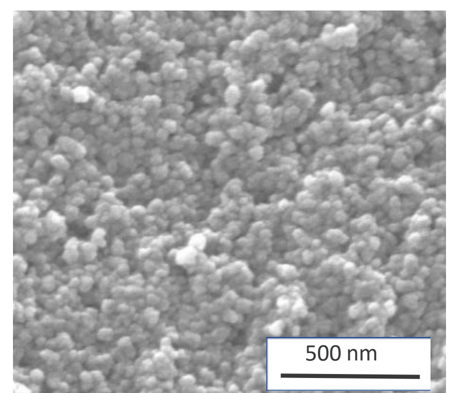
What is the max allowable selective layer thickness needed to achieve our performance goals?



Thickness needed for NETL Polymer 3 to achieve 4000 GPU is ~ 600 nm
For the NETL Polymer 3 MMM, the thickness needed is > 1000 nm

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

Nano-size MOFs are needed for thin film coating, and can be achieved

MOF A, 100-200 nm	MOF B, 100-200 nm
	
MOF C, 40-80 nm	MOF D, <50 nm
	

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

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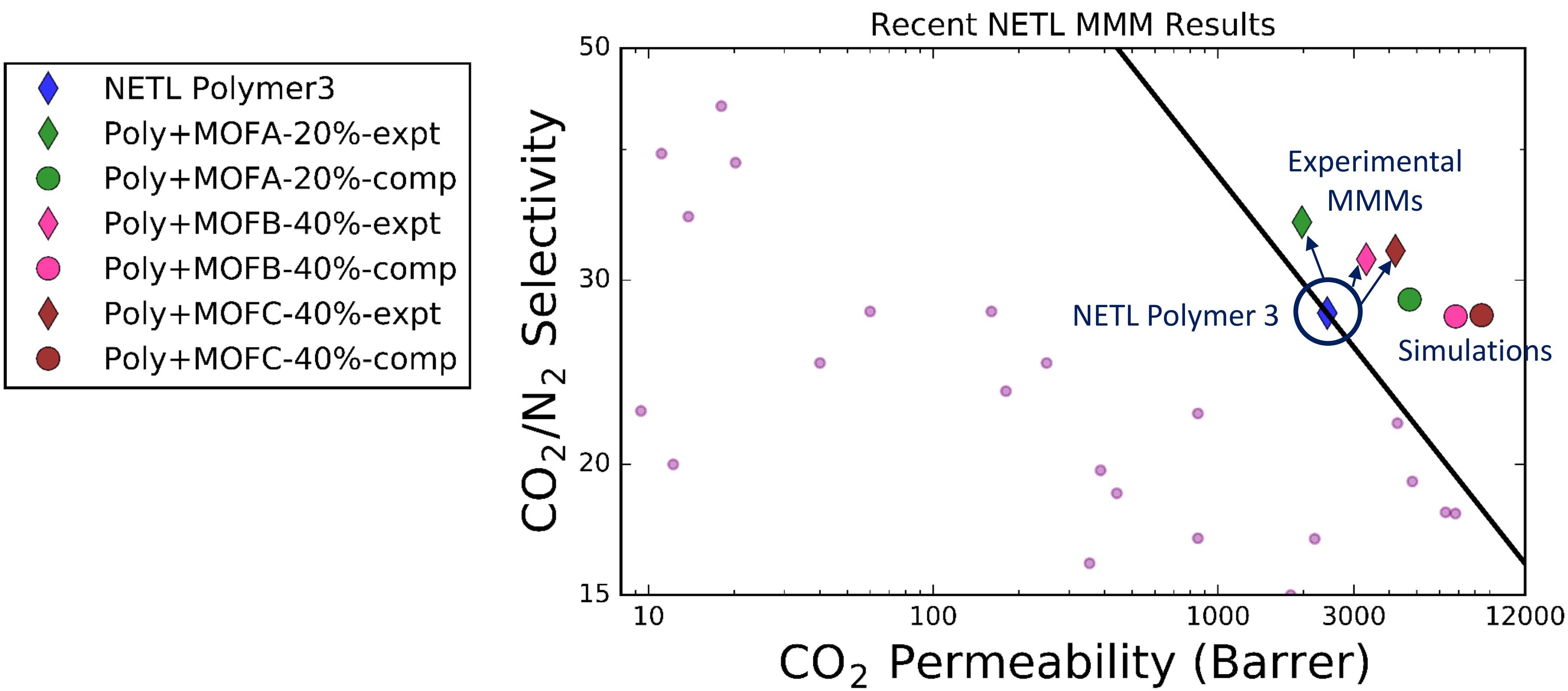
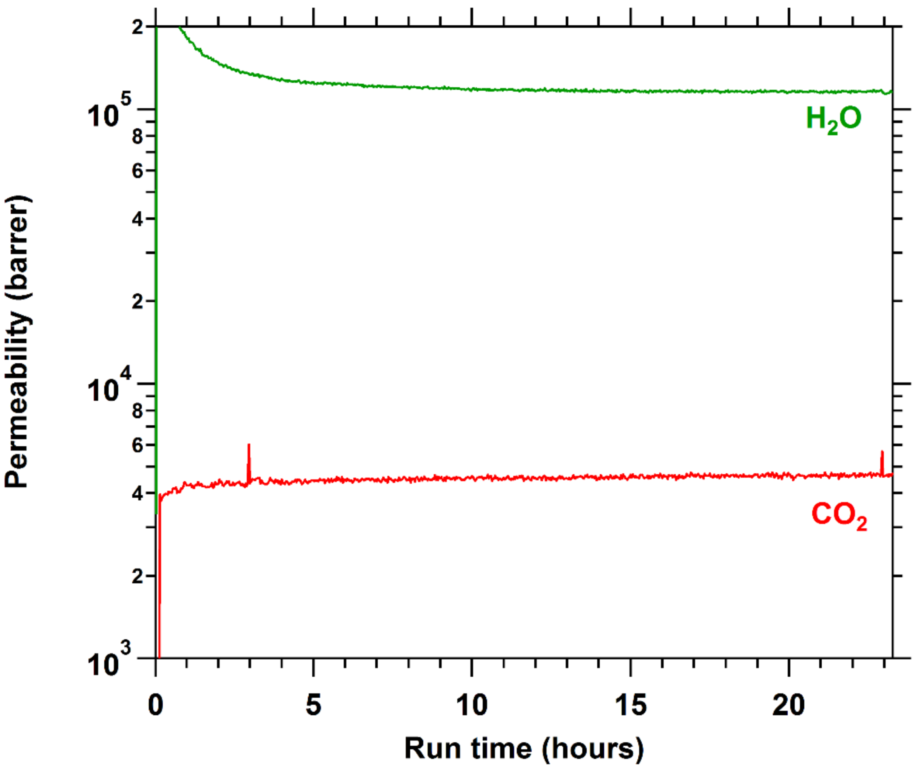


- MMMs using NETL Polymer 3 and three different MOFs are all above the Robeson Upper Bound
- Modeling results overpredict the performance of MMMs because of non-idealities that are not captured by the Maxwell model

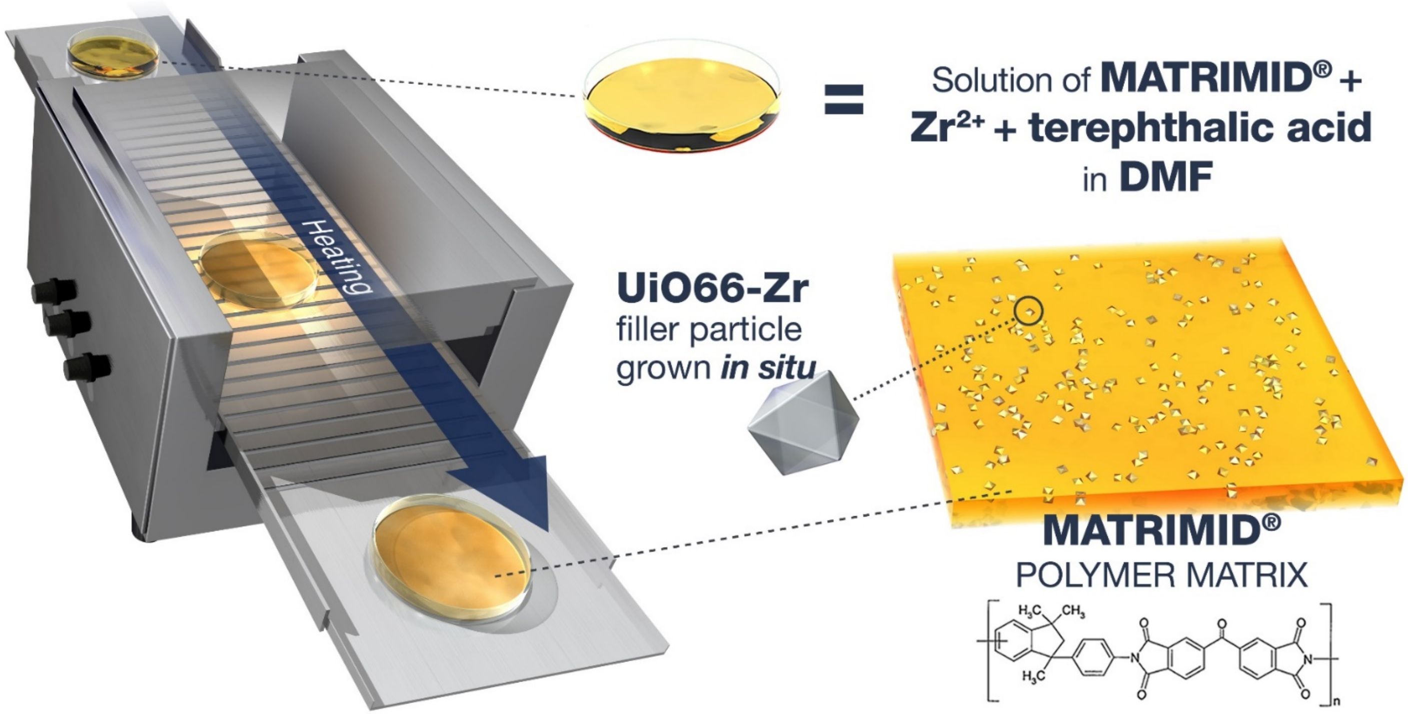
Long term stability of membranes is tested with actual flue gas

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



MMMs show stable performance when tested with humidity and contaminants

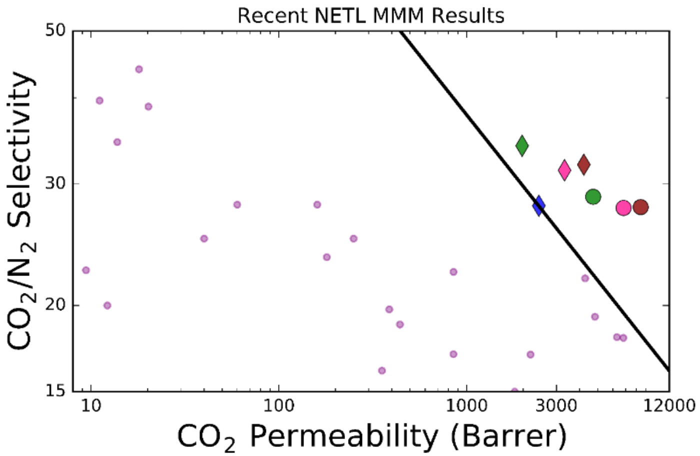
Future work is to scale up to a small hollow fiber module tested with flue gas



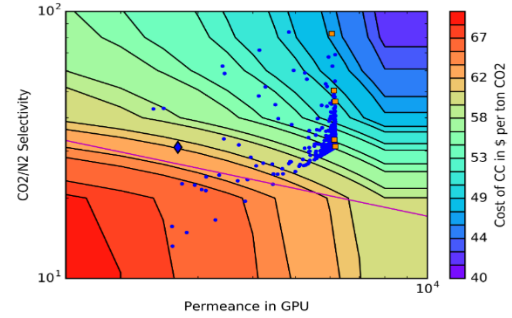
In-situ MOF growth is a possible scheme for reducing steps for scale-up manufacturing of mixed matrix membranes

A Simple Fabrication Method for Mixed Matrix Membranes with *In-situ* MOF Growth for Gas Separation, Anne M. Marti, Surendar R. Venna, Elliot A. Roth, Jeffrey T. Culp, and David P. Hopkinson, ACS Applied Materials and Interfaces

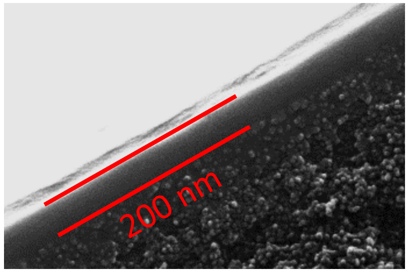
Summary: NETL has taken a multifaceted approach to MMM development for low cost CO_2 capture



- 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 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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Jeff Culp
Nathaniel Rosi
Patrick Muldoon

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James Baker
Megan Macala

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Samir Budhathoki
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Ganpat Dahe
Dave Luebke
Hunaid Nulwala
Erik Albenze
Alex Spore

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