Experimental Materials Development in Mixed Matrix Membranes for Post-Combustion Carbon Capture

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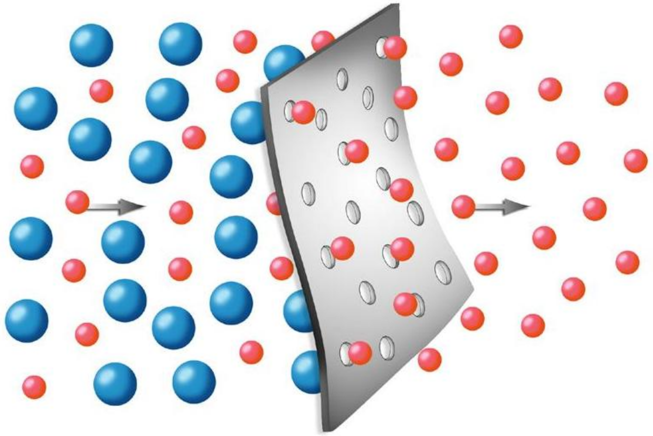
August 21st 2017

Membranes for carbon capture

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



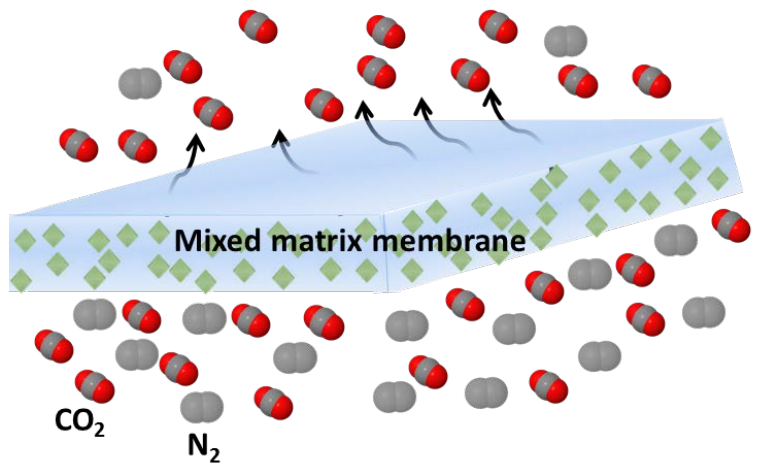
Selection of membrane materials

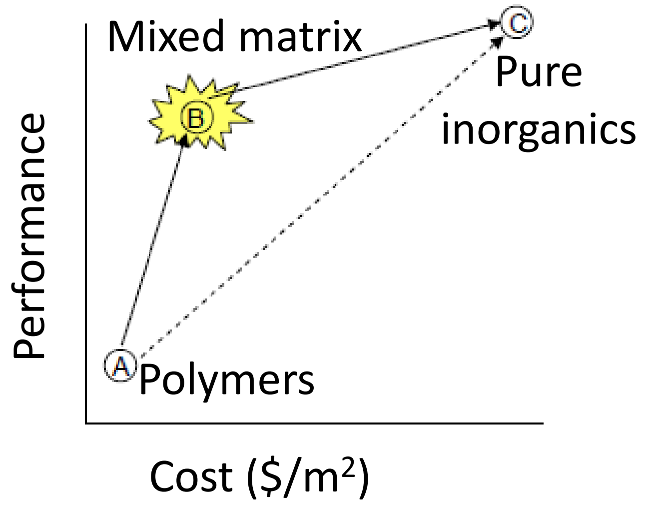
Permeability (flux)
Selectivity
Processability
Mechanical Properties
Chemical/thermal stability
Long term performance

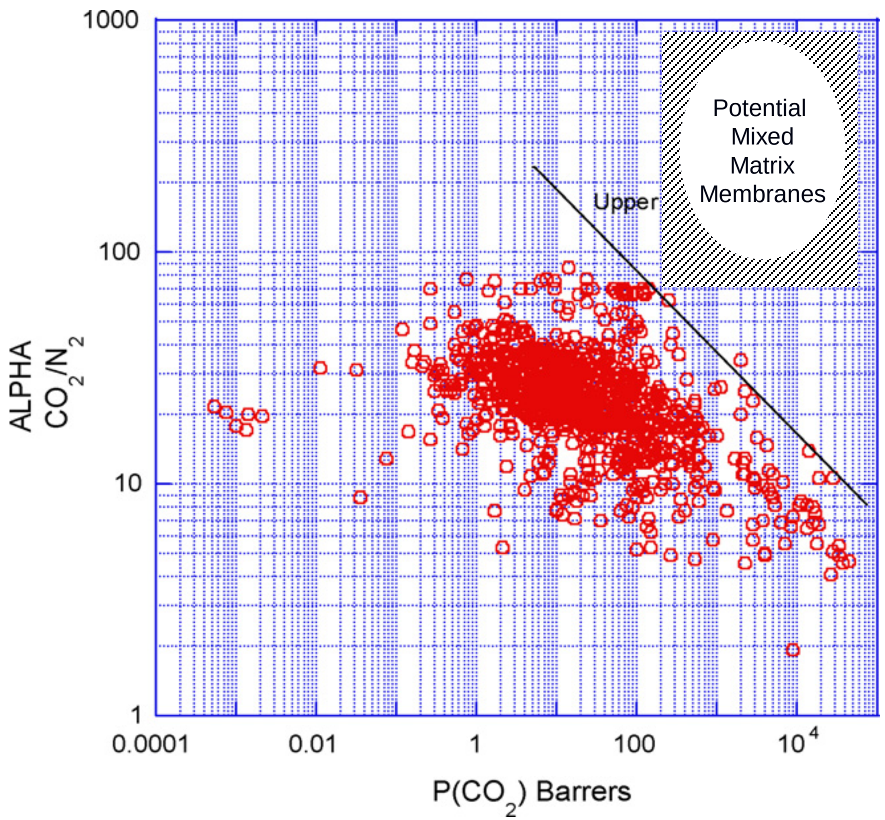
Goals for membrane performance to be economically practical
Permeance of >1,000 GPU
CO_2/N_2 selectivity of >30

Merkel et al., J. Membrane Science, 359 (2010) 126-139encyclopedia.che.engin.umich.edu/

Enhancing the polymeric membrane gas transport properties

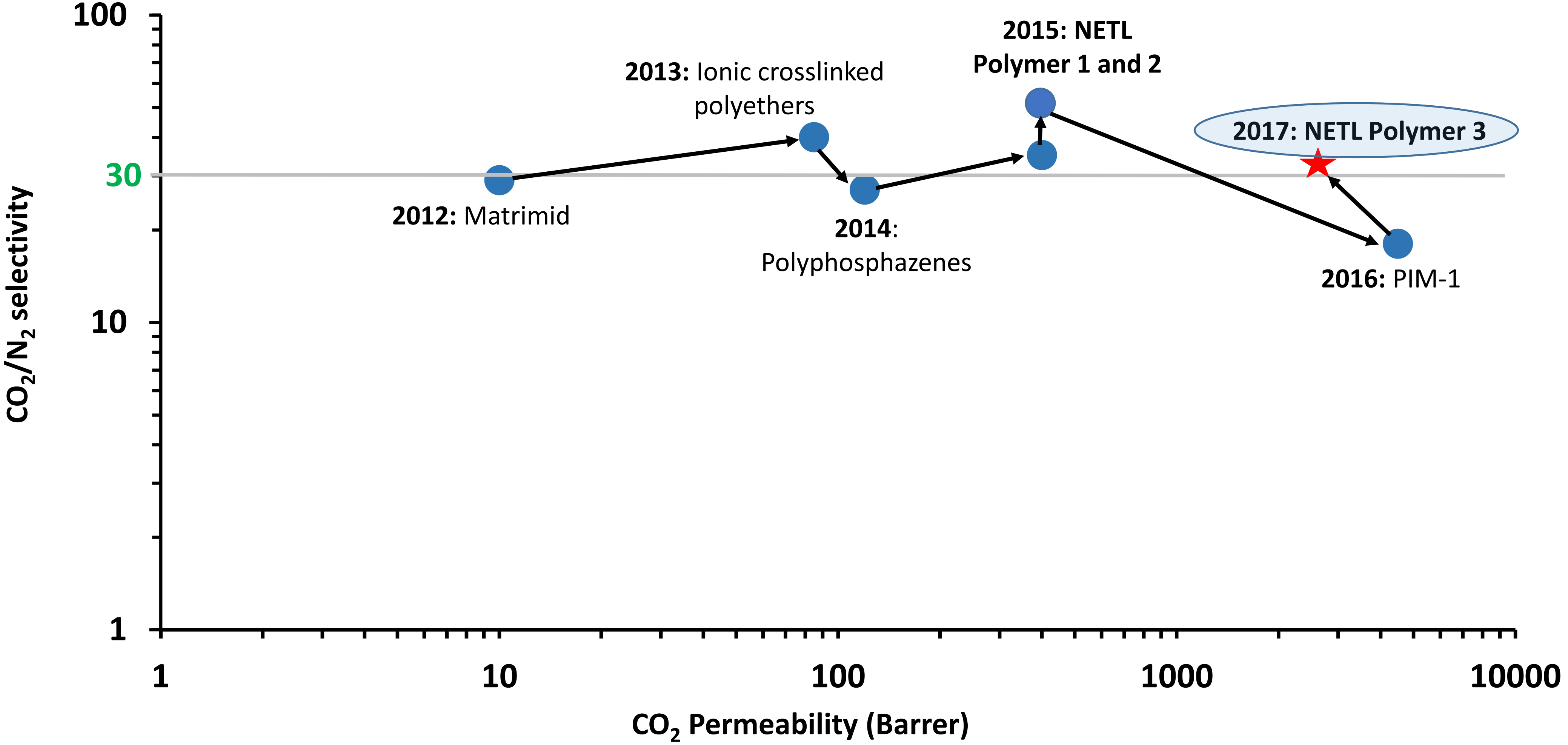






Lloyd M.Robeson, Journal of Membrane Science, 320, 2008, 390-400
Performance vs cost plot, Courtesy: William Koros

Developed high performance polymeric membranes at NETL



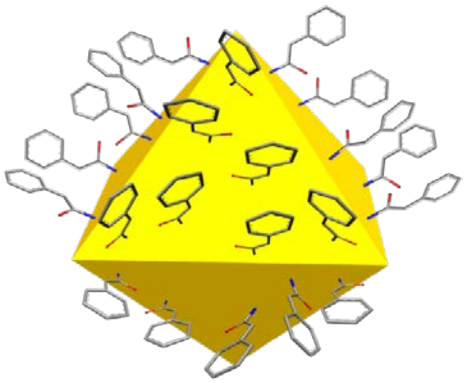
Venna et al., J. Membr. Sci., 535, 2017, 103–112
Zhou et al, European Polymer Journal, 84, 2016, 65–76
Kusuma, Sekizkardes et al, Manuscript in preparation.

High performance porous fillers to enhance polymer properties

NATIONAL ENERGY TECHNOLOGY LABORATORY

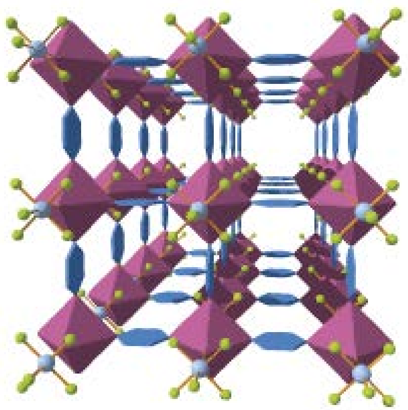
Selection criteria
- Good interaction with the polymer
- Optimum CO_2 heat of sorption, pore size.

UiO-66



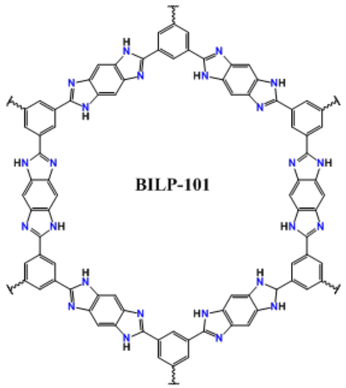
Surface functionalized to engineer the interface properties

SIFSIX-NETL



Developed to make MMM with polyphospazenes

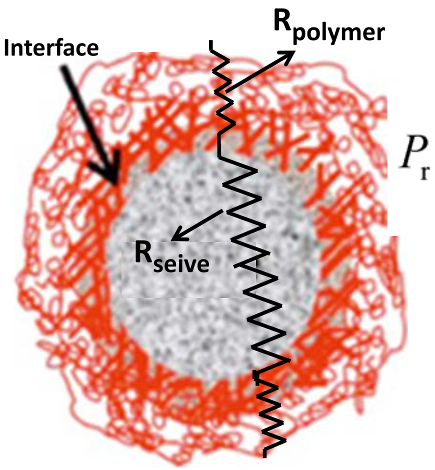
BILP-101



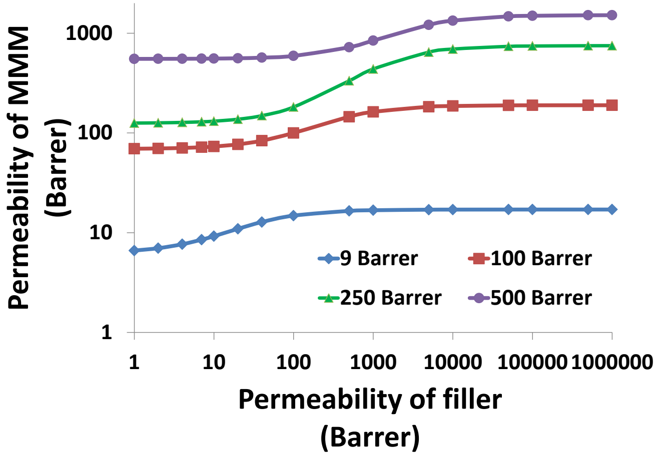
Synthesized to improve properties of porous polymers

Venna et al., J. Mater. Chem. A, 2015,3, 5014-5022, Feng et al, Polymer, 2017 103, 189-195
Marti et al, SIFSIX-NETL synthesis, manuscript preparation
Sekizkardes et al., Chem. Commun., 2016,52, 11768-11771

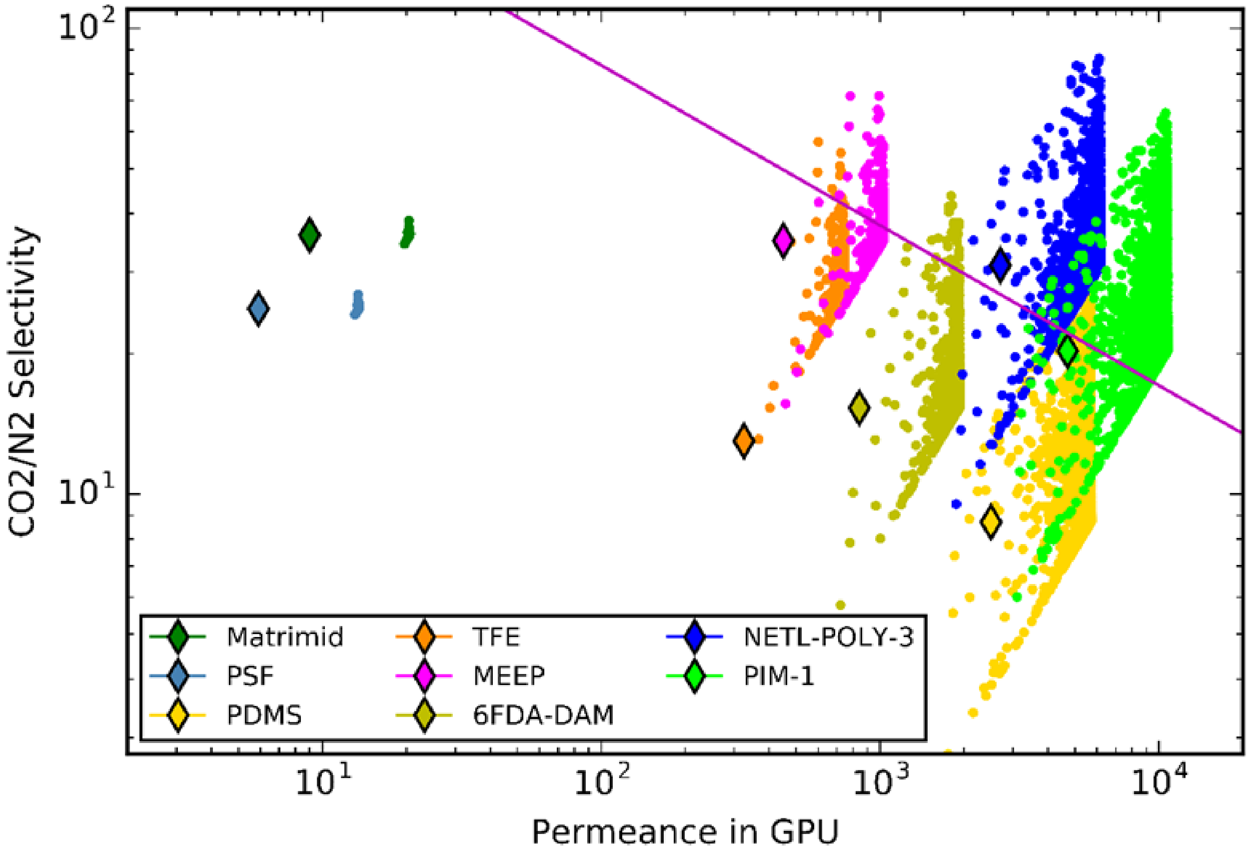
Better way to select the MOFs using molecular simulations



$$P_r = \frac{P}{P_m} = \frac{2(1-\varphi_d)+(1+2\varphi_d)\lambda_{dm}}{(2+\varphi_d)+(1-\varphi_d)\lambda_{dm}}$$



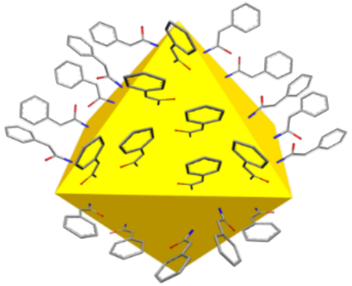
Measure the true permeability of MOFs is a challenge.

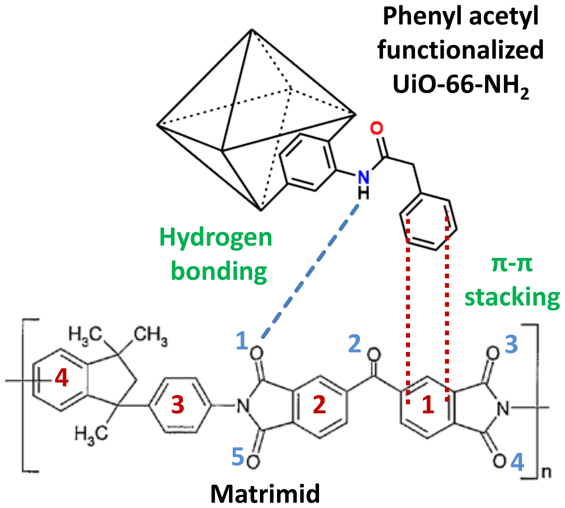


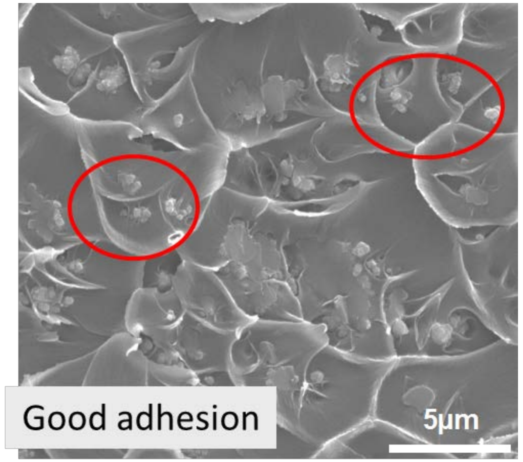
Screening of MOF materials using high throughput tools

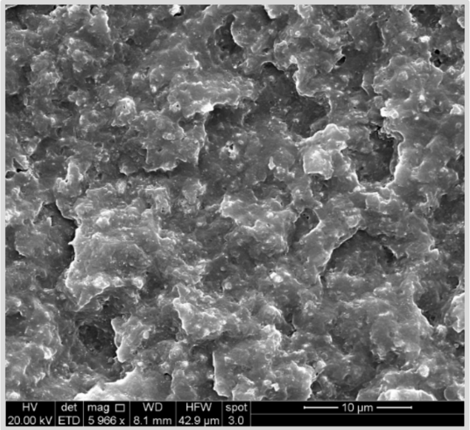
Engineered the materials to optimize the interface structure

Functionalization of UiO-66

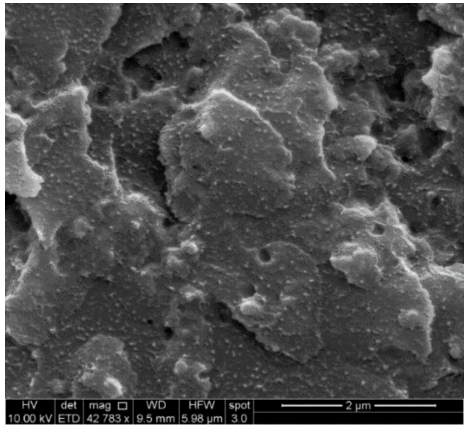




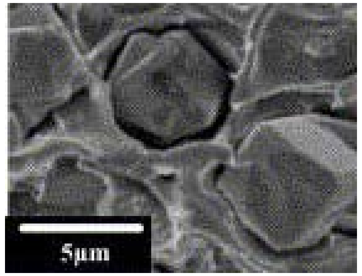




Polyphosphazene-SIFSIX MOF MMM



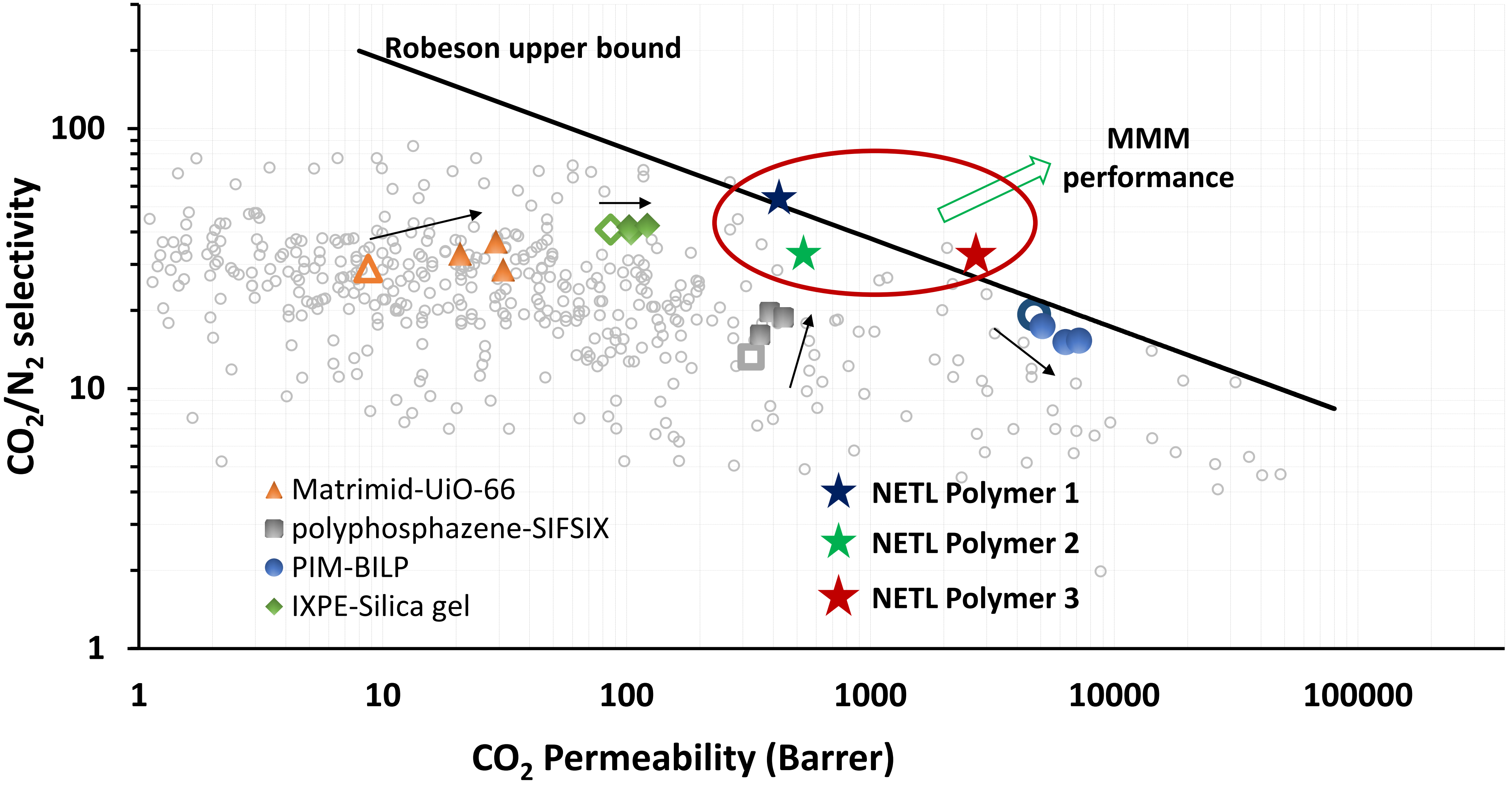
PIM-BILP MMM



Example of bad adhesion

Venna et al., J. Mater. Chem. A, 2015,3, 5014-5022,
Venna et al., J. Membr. Sci., 535, 2017, 103–112
Sekizkardes et al., Chem. Commun., 2016,52, 11768-11771

Enhancement of polymer properties using MMM



Venna et al., J. Mater. Chem. A, 2015,3, 5014-5022, Venna et al., J. Membr. Sci., 535, 2017, 103–112
Sekizkardes et al., Chem. Commun., 2016,52, 11768-11771
Sekizkardes et al., Sep. Purif. Tech., Under revisions

We need thinner films of these high performance polymers to process large amount of flue gas

Permeability :

$$P_i = D_i \cdot S_i = \frac{(\text{Flux})_i \cdot l}{\Delta p_i}$$

$$\text{Barrer} = 10^{-10} \frac{\text{cm}^3(\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{sec} \cdot \text{cm Hg}}$$

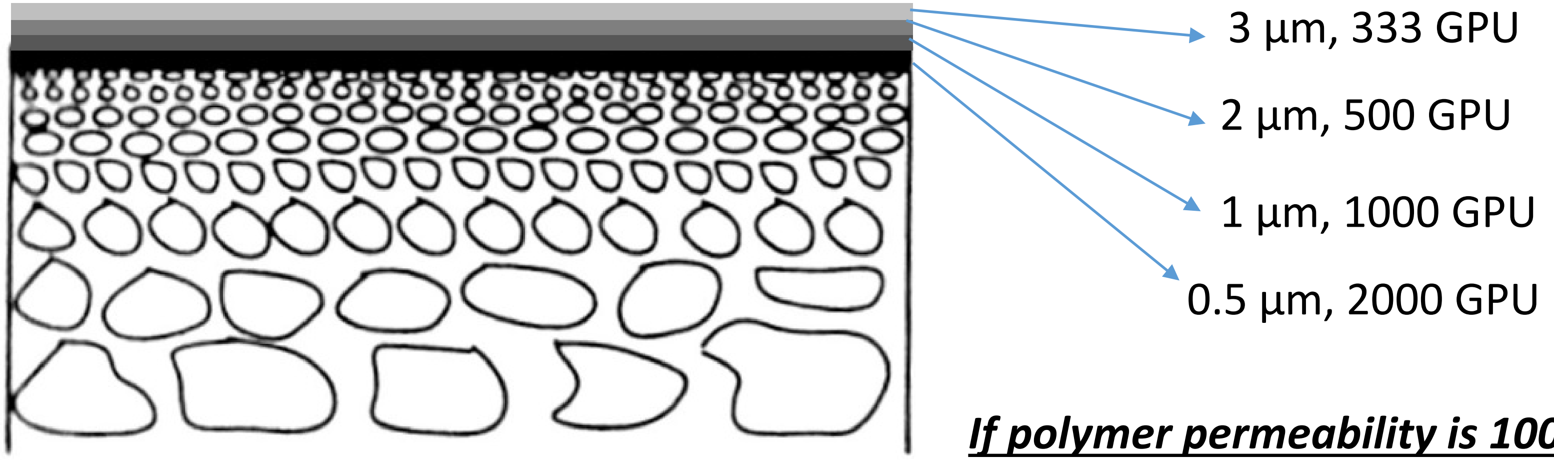
Permeance :

$$\left(\frac{P}{l}\right)_i = \frac{(\text{Flux})_i}{\Delta p_i}$$

$$\text{GPU} = 10^{-6} \frac{\text{cm}^3(\text{STP})}{\text{cm}^2 \cdot \text{sec} \cdot \text{cm Hg}}$$

Permeability is independent of thickness

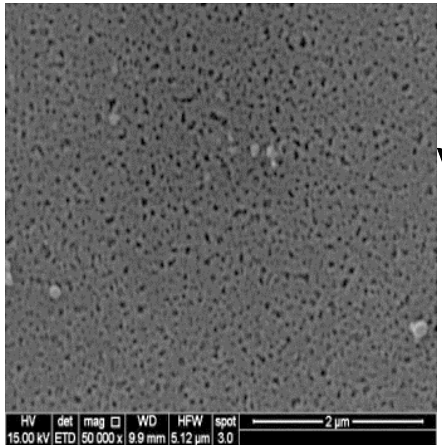
Permeance changes with thickness



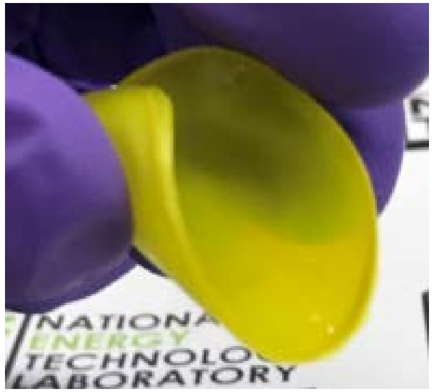
If polymer permeability is 1000 Barrer

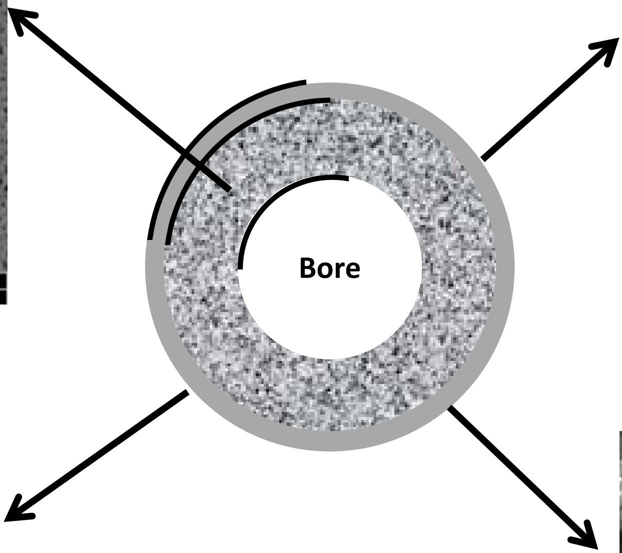
Thin film coating on porous hollow fiber supports is challenging

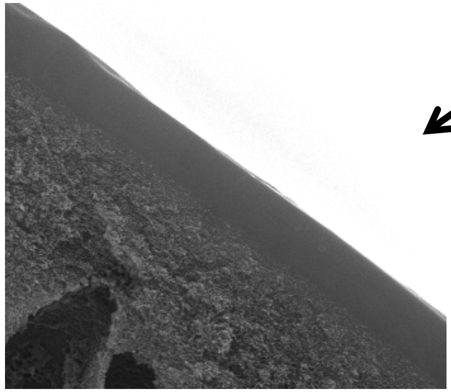
1 **Fiber support with optimum pore size and density**



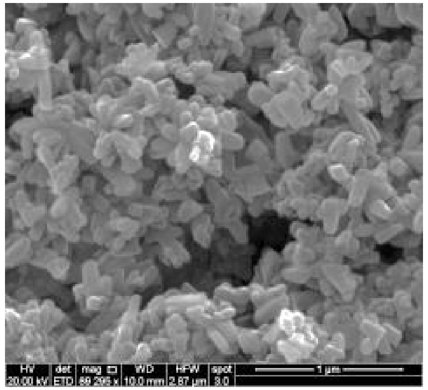
2 **Polymers with good gas transport properties and mechanical properties**





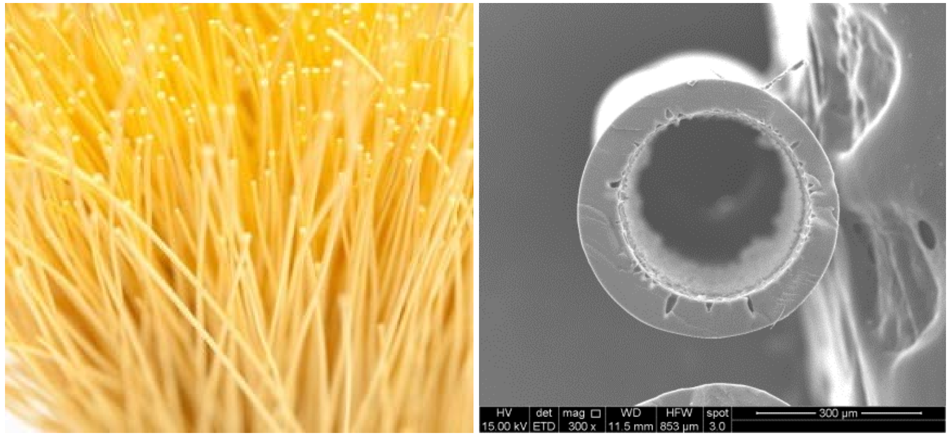


4 **Good interaction between support and selective layer**

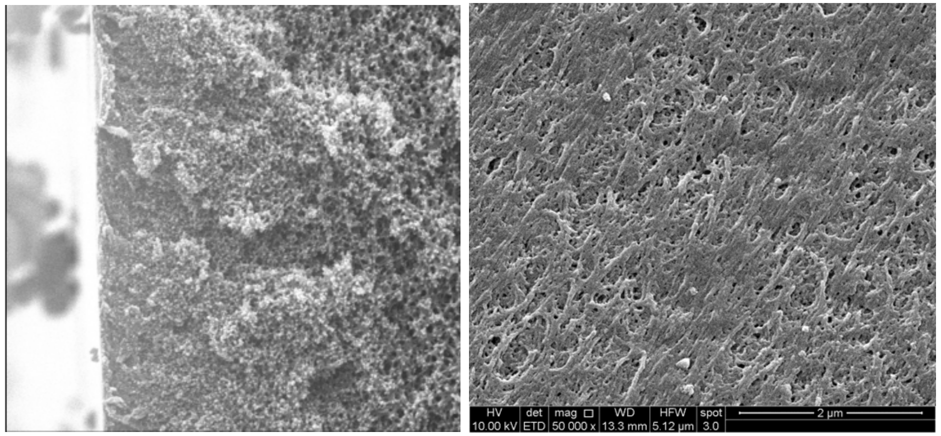


3 **< 100 nm particles**

Structural properties of porous supports are critical for thin film coating



Optimum wall thickness and bore diameter



Higher surface pore density with optimum pore size

*Fiber support should have at least **an order of magnitude higher gas fluxes** compared to selective layer flux in order to avoid the mass transfer problems.*

High performance, flexible and durable membranes were fabricated

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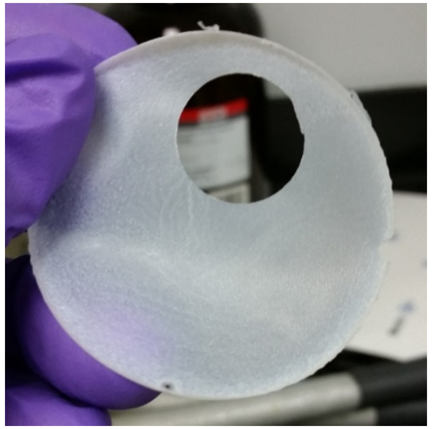
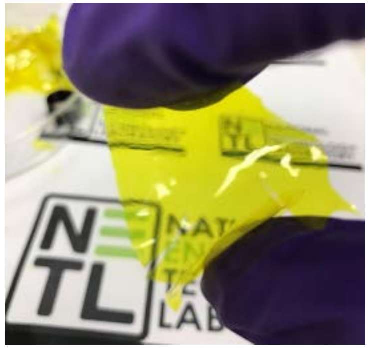
Gel-like Polymer

Low tack, weak, transparent

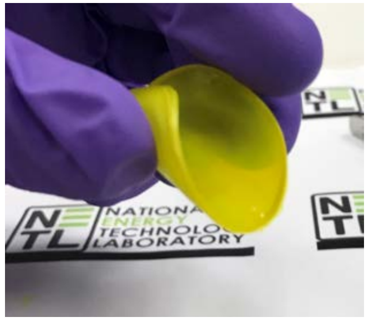


NETL Polymer -2,
no tack, tough, good flexibility

Glassy,
brittle polymer

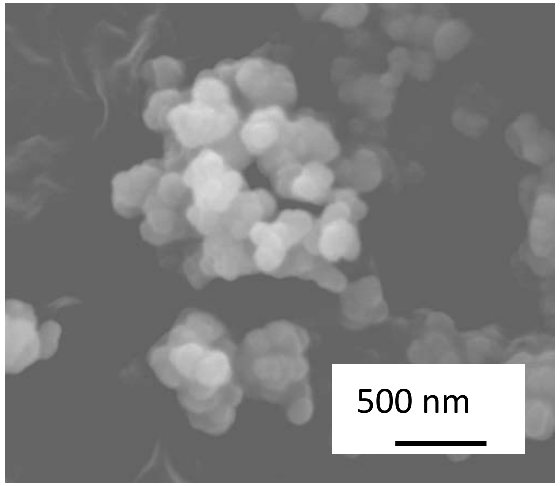


Additives

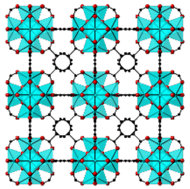


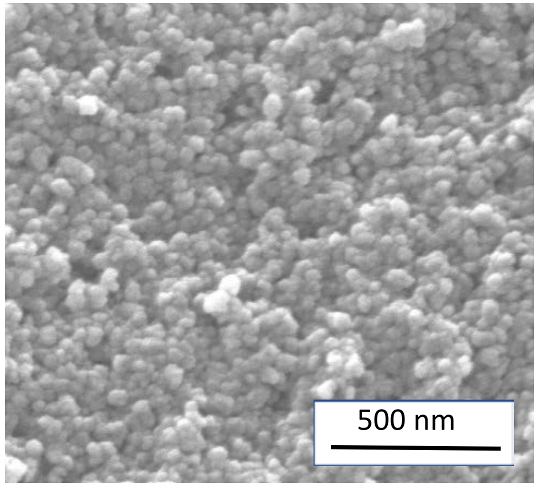
NETL Polymer 3,
strong and flexible polymer

Nano-size MOFs are critical to thin film coating

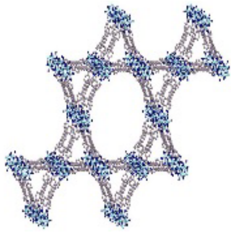


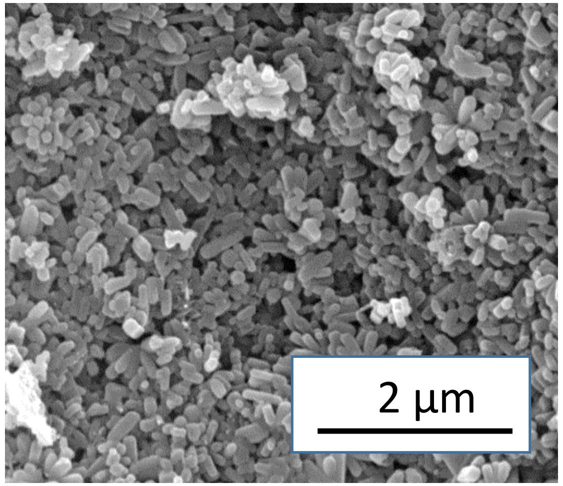
UiO-66
Zr MOF, size
~100-200 nm



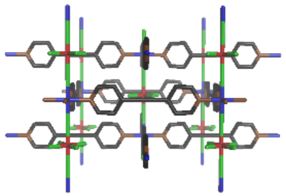


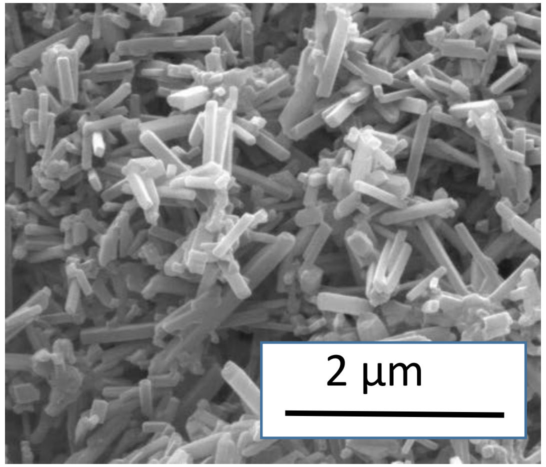
NU-1000
Zr MOF,
size: <50 nm



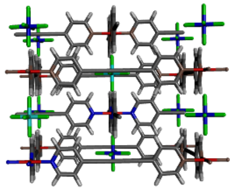


SIFSIX-2Cui
Cu MOF,
size ~100-200 nm



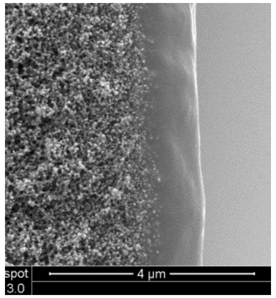


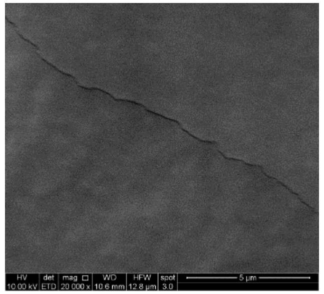
SIFSIX-NETL
Cu MOF
size ~200-300 nm



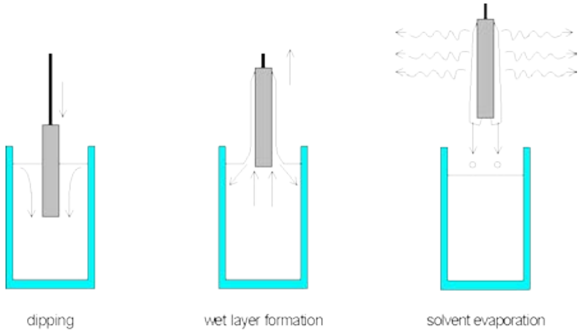
Coating techniques used for formation of thin films

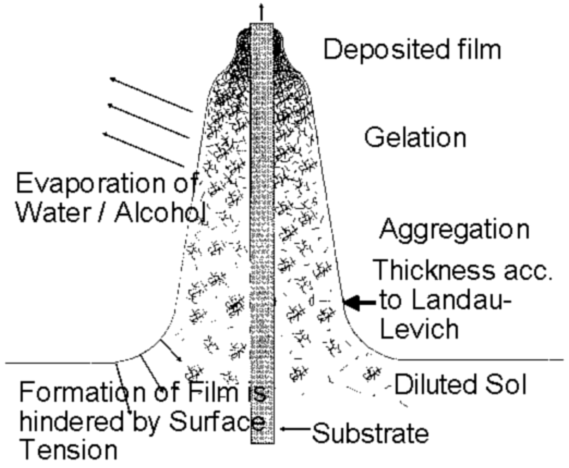
Spray coating



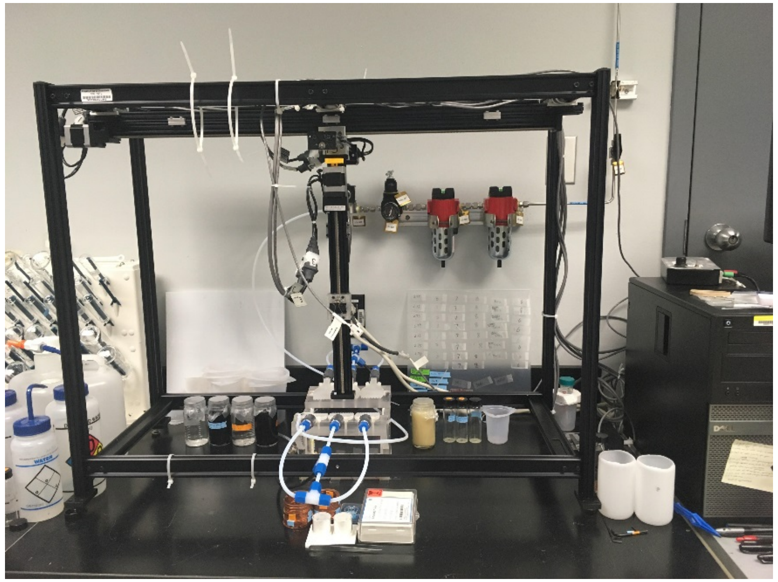


Dip coating





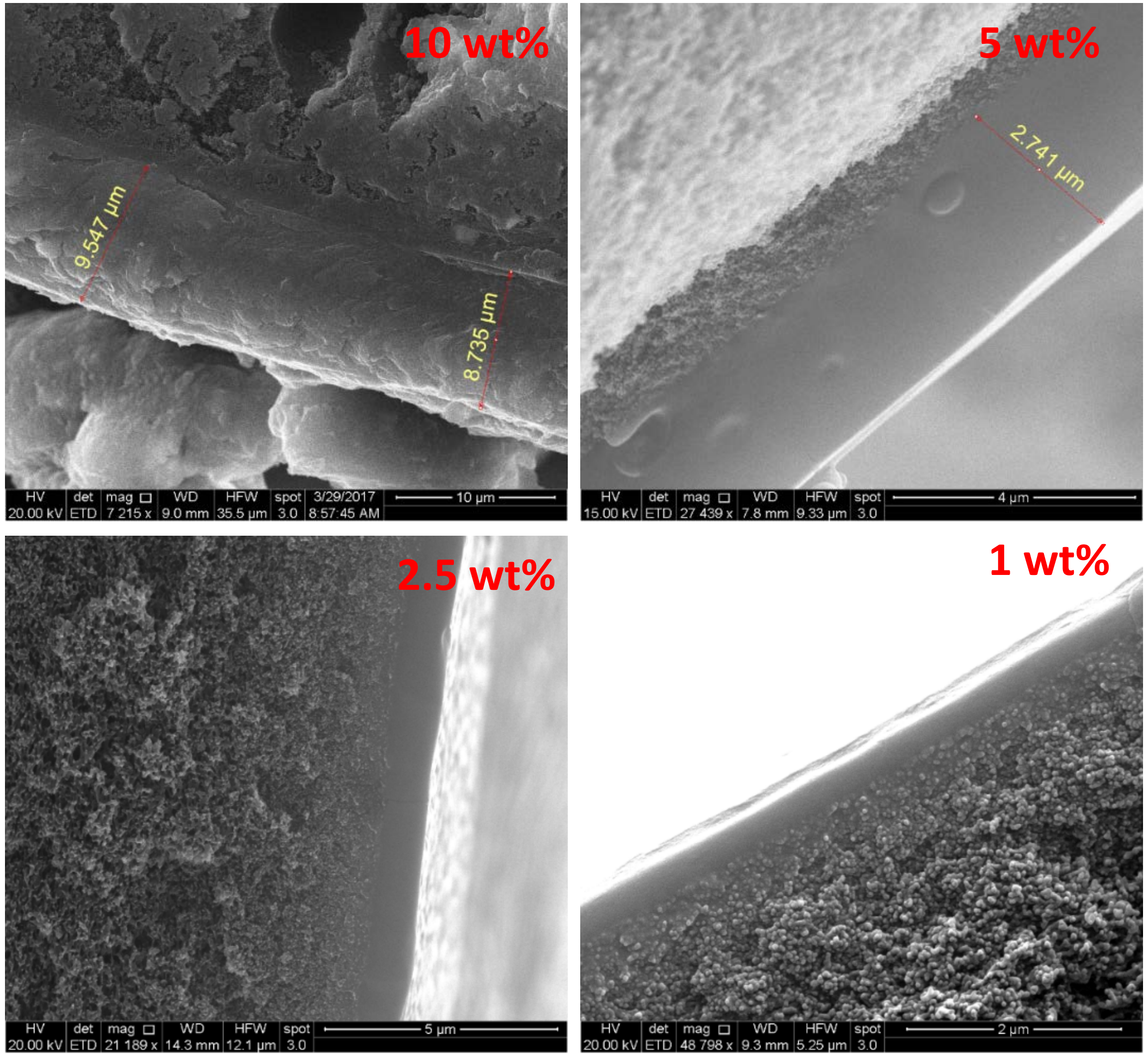
Programmable hollow fiber dip coater



Parameter studied:
Polymer concentration, single vs double coating, draw speed

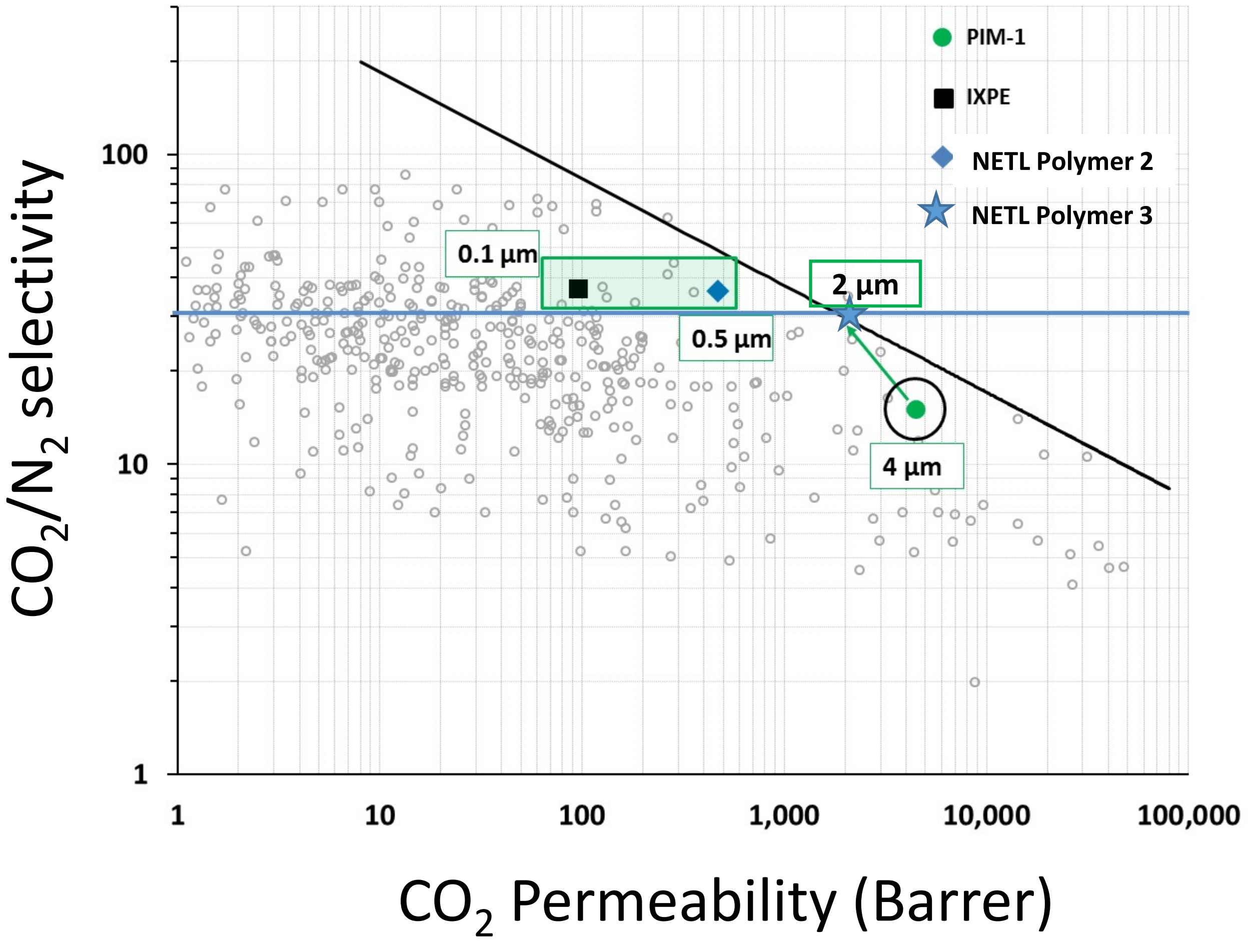
http://www.solgel.com/articles/Nov00/mennig.htm

Effect of polymer concentration on film thickness



As the polymer concentration decreases, the thickness of the film decreased. At 1 wt%, thickness of the film is ~ 200 nm

What is the minimum thickness needed for in-house developed membranes to achieve goals?

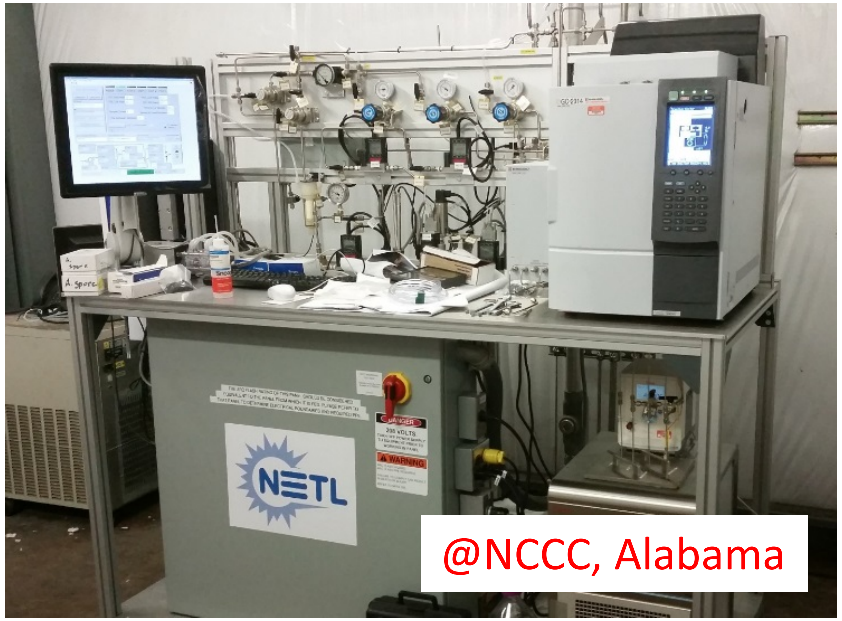


Thickness needed for high performance NETL polymer-3 is ~ 750 nm to achieve 4000 GPU

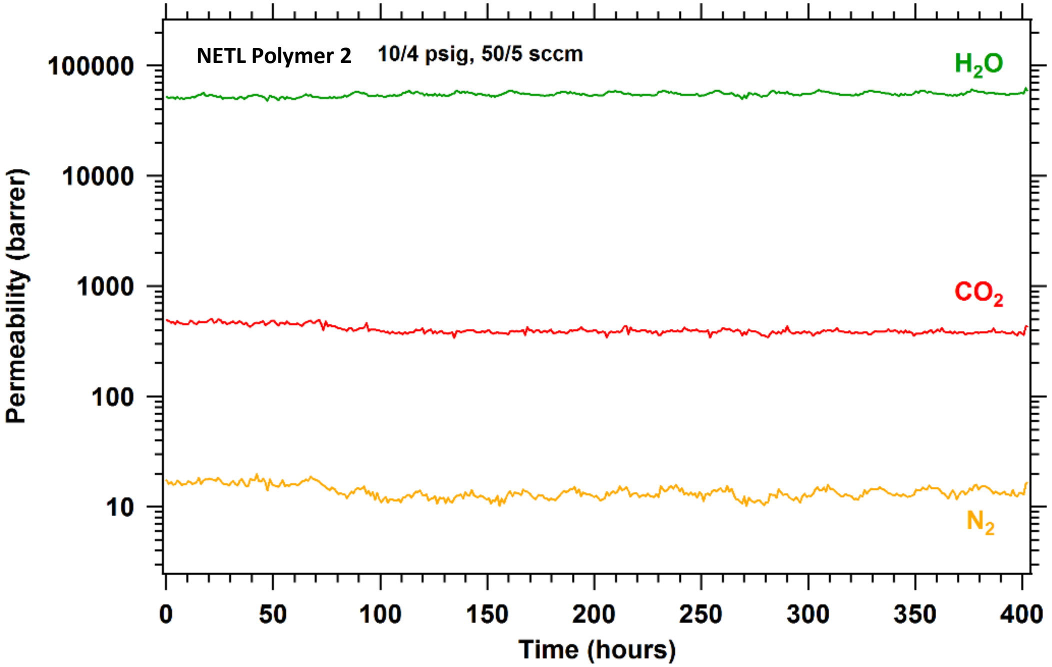
Lloyd M.Robeson, Journal of Membrane Science, 320, 2008, 390-400

Long term stability of these high performance materials with simulated and actual flue gas

Developed a capability at NETL to test the membranes with simulated flue gas conditions
Gas composition - $CO_2 : O_2 : SO_2 : NO_2 : N_2$ = 14 : 4 : 50PPM : 1PPM : BAL, Humidity - 80%RH

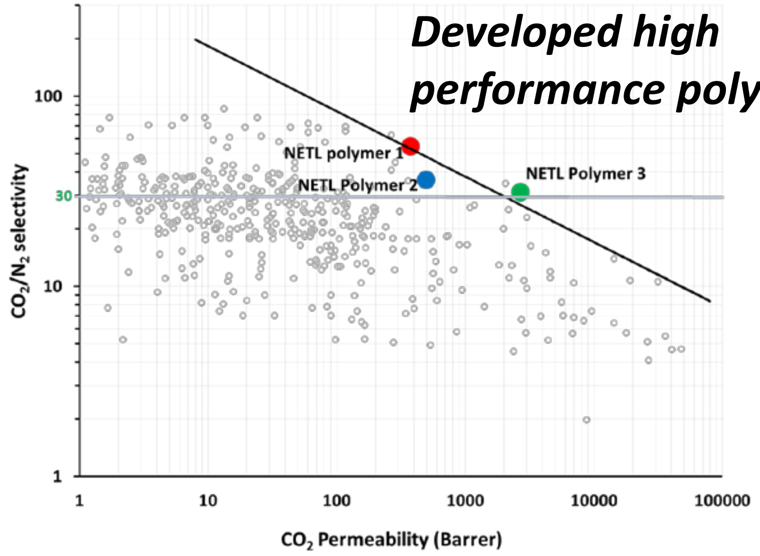


Skid for testing lab scale flat sheet and hollow fiber membranes at NCCC

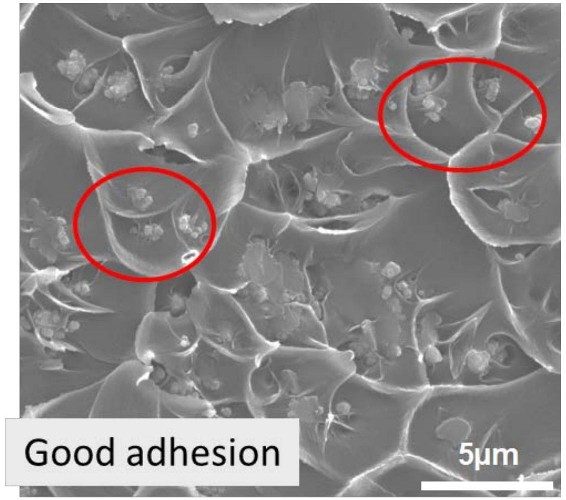


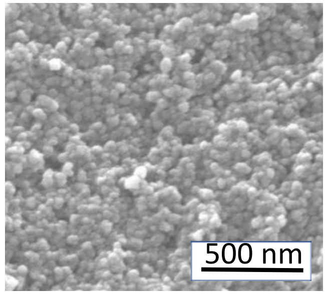
Gas composition @NCCC: CO_2 – 11-13, O_2 – 6-8, SO_2 and NO_2 <5 PPM, H_2O < 1%, N_2 – BAL

Summary



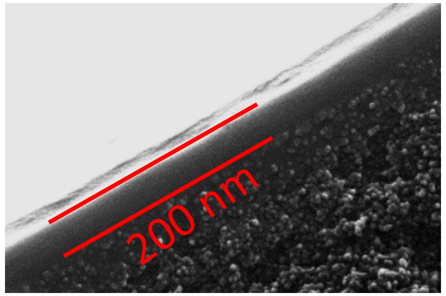
Developed high performance polymers





systematically matched the properties of polymer and MOFs

Fabricated porous hollow fiber support with desired structural properties



Thin films were coated on support and defect needs to be mitigated.

Skid for testing lab scale flat sheet and hollow fiber membranes at NCCC

Great Team!!!!

MOF development:
Anne Marti
Sameh Elsaidi
Jeff Culp

Polymer development:
Ali Sekizkardes
James Baker
Megan Macala

Simulations and economic analysis:
Olukayode Ajayi
Samir Budhathoki
Jan Steckel
Wei Shi

Membrane Fabrication and Testing:
Victor Kusuma
Shan Wickramanayake
Fangming Xiang

Team Lead:
David Hopkinson
Kevin Resnik

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Disclaimer: