Mixed Matrix Membranes for Post-Combustion CO_2 Capture

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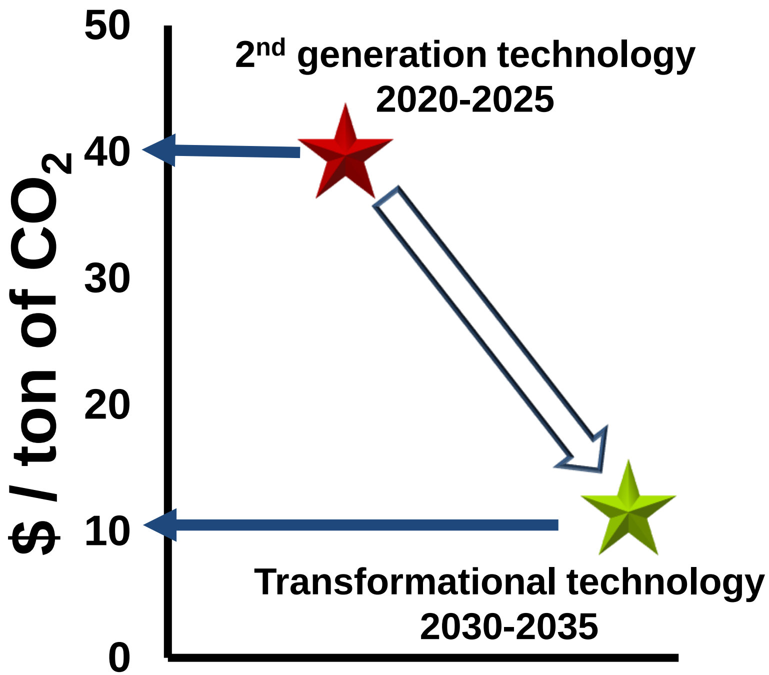
Research Engineer

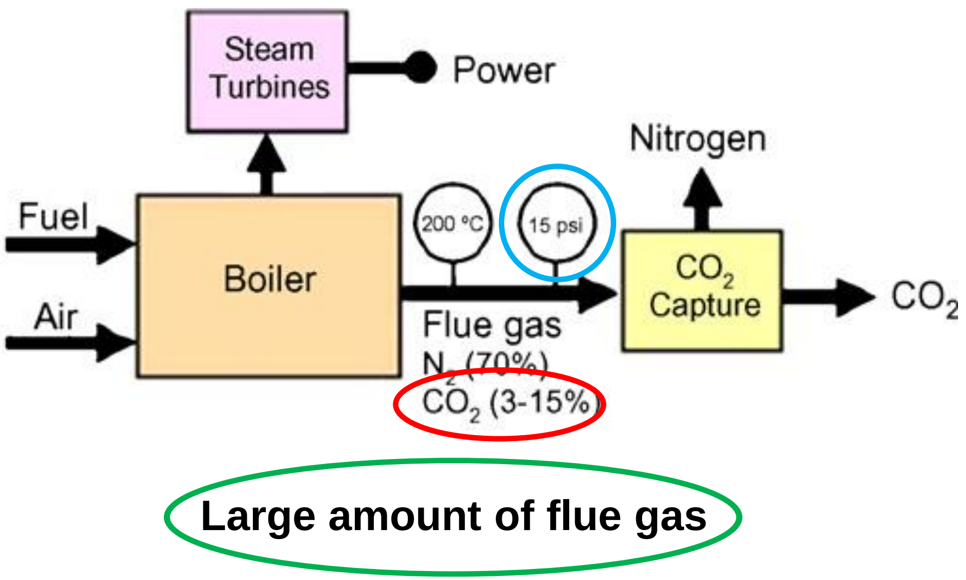
CO_2 Capture Technology Meeting

23rd June, 2015

U.S. DEPARTMENT OF ENERGY | National Energy Technology Laboratory

Project Objectives

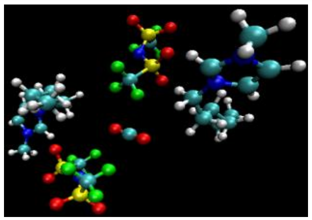




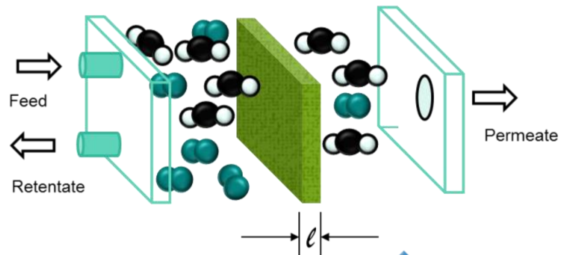
Goal is to fabricate *thin, CO_2 selective membrane* with *good mechanical, chemical & thermal stability* while achieving the DOE goals of CO_2 capture with *cost optimized process scheme*

Integrated Research Approach

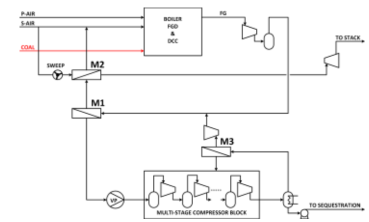
Computational Modeling



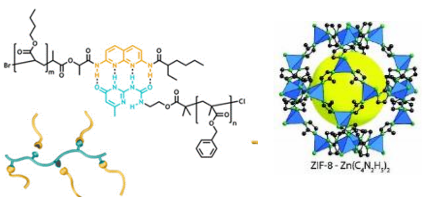
membrane technology development



Techno-economic analysis

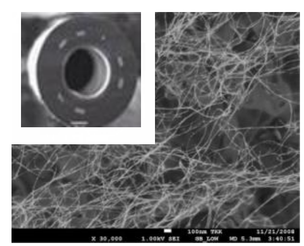


Synthesis

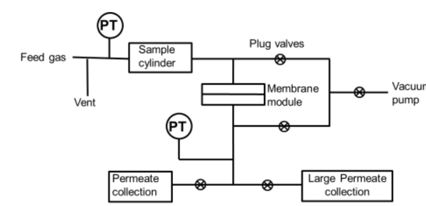


Characterization

Fabrication



Performance Testing



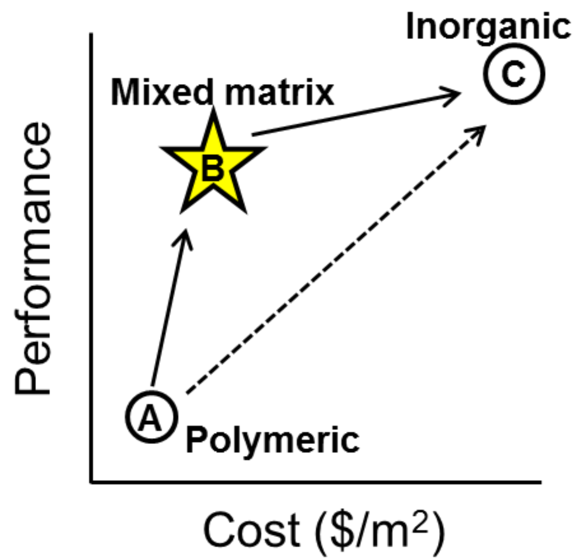
Multidisciplinary team helps to develop the best product.

Project status

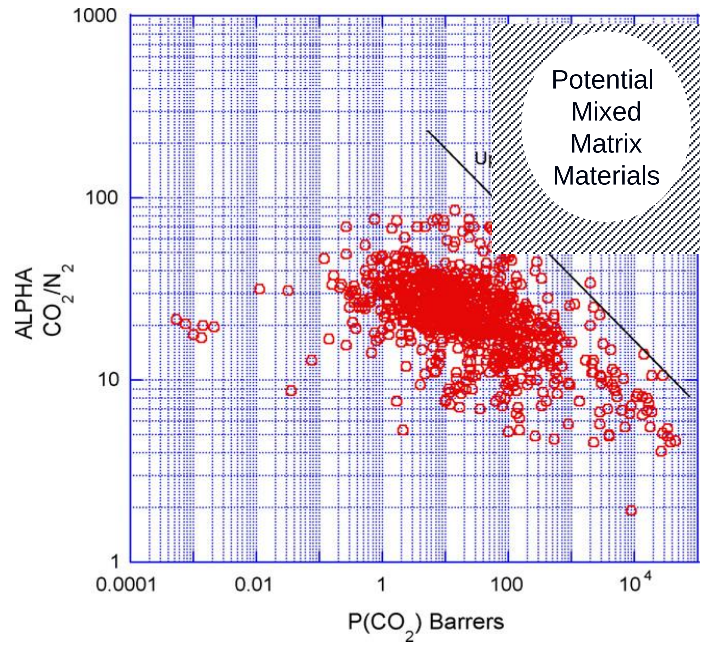
- **Budget period : 1 of 2 budget periods.**
- **60% of $1,509,046 total funds.**
- **Project is 62% complete.**
- **Current TRL: 3 End of Project TRL: 4**

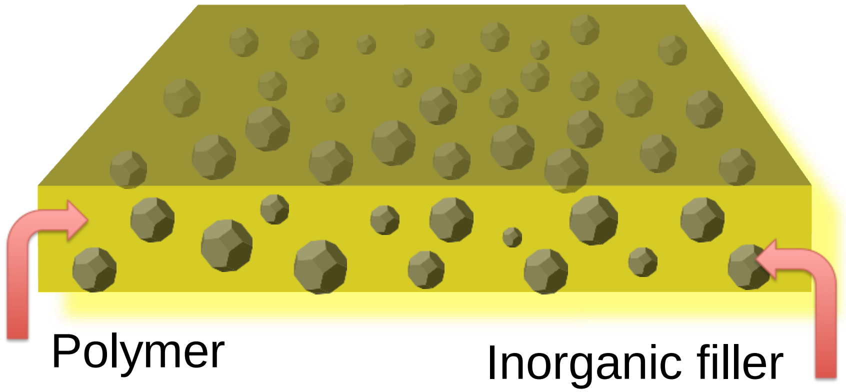
Milestone Number and Task	Milestone Title	Planned Completion Date	Actual Completion Date	Variance Comment
1	Complete testing of two down selected hollow fiber membranes in simulated pulverized coal power plant flue gas	9/30/2014	9/30/2014	None
2	Complete the construction of a membrane test skid for use with a slipstream of real flue gas.	9/30/2015		On Schedule
3	Complete the gas permeance testing of two membranes using a slipstream of real flue or fuel gas.	9/30/2016		On Schedule

Mixed Matrix Membranes - Advantages



Courtesy : William J Koros



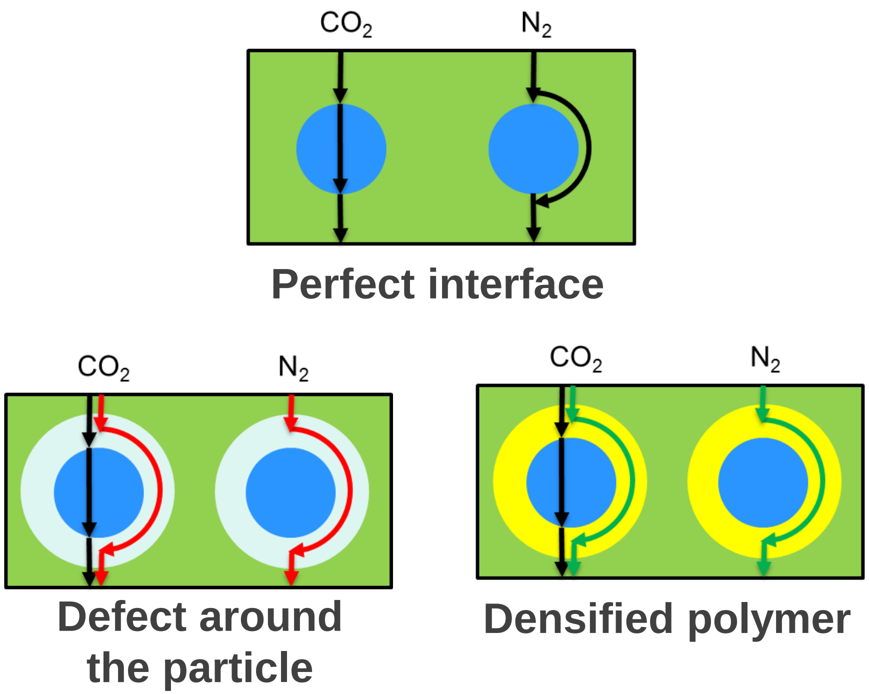


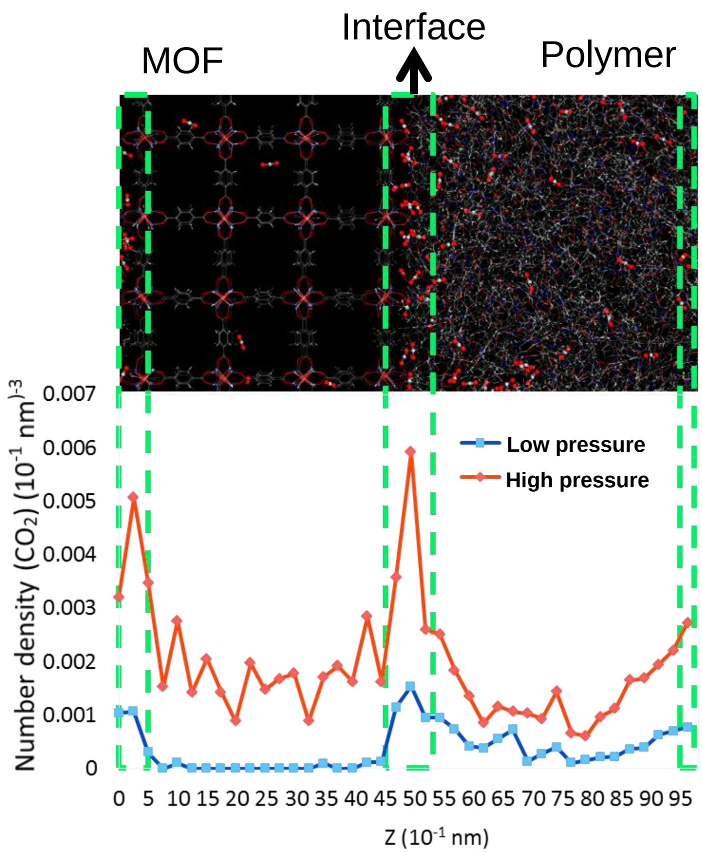
Goals for membrane performance to be economically practical:

– Permeance of >1,000 GPU.

– CO_2/N_2 selectivity of >30.

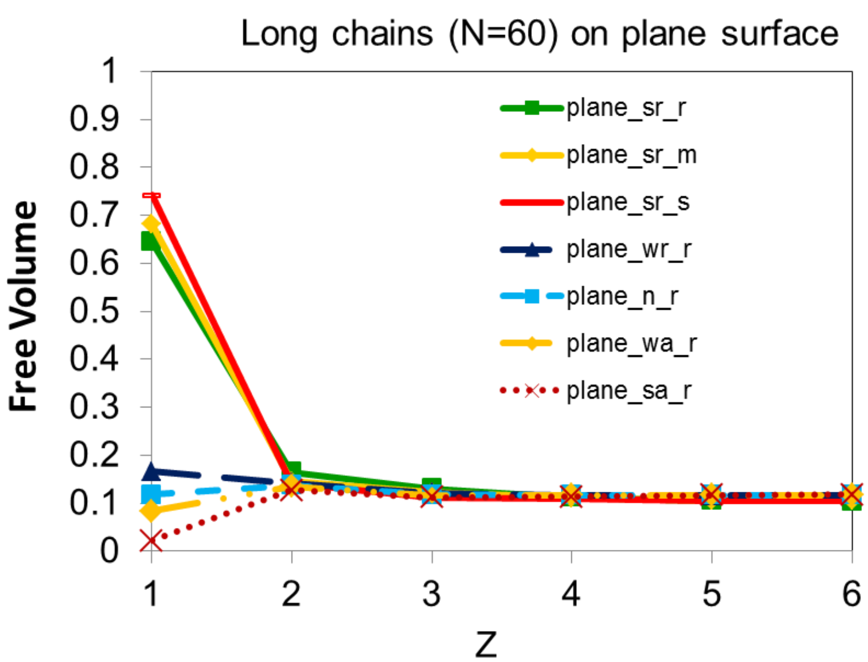
Polymer - filler interface is important

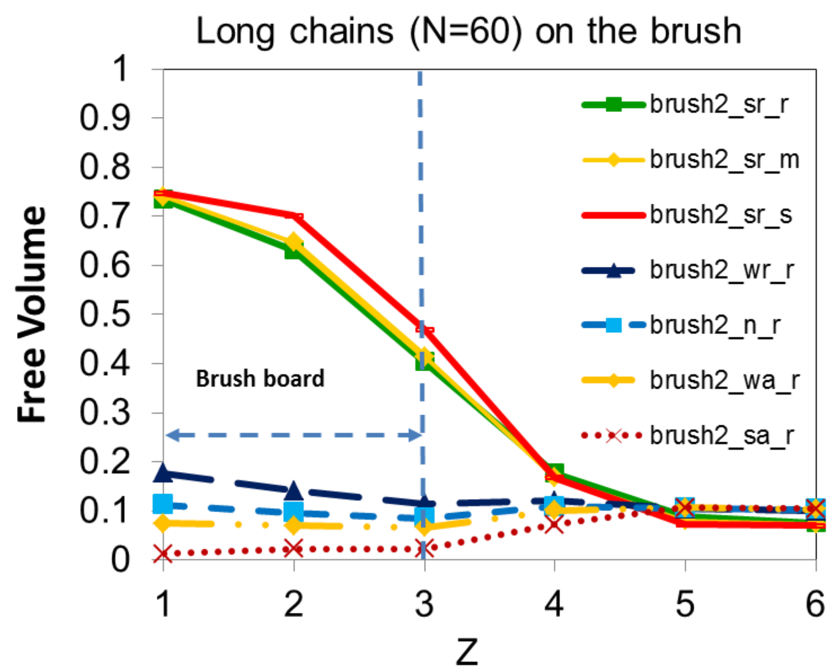




Control of nanoscale interfaces is very important to achieve improved performance

Tuning the interface structure

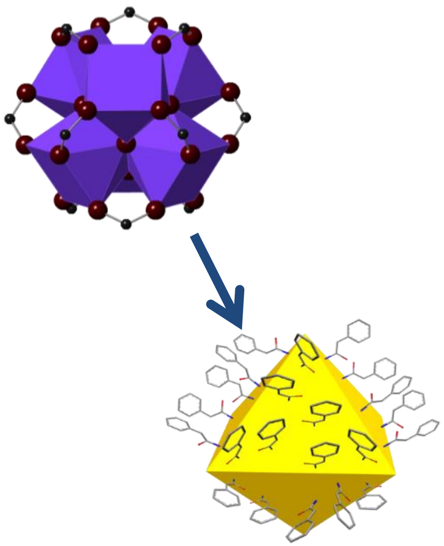




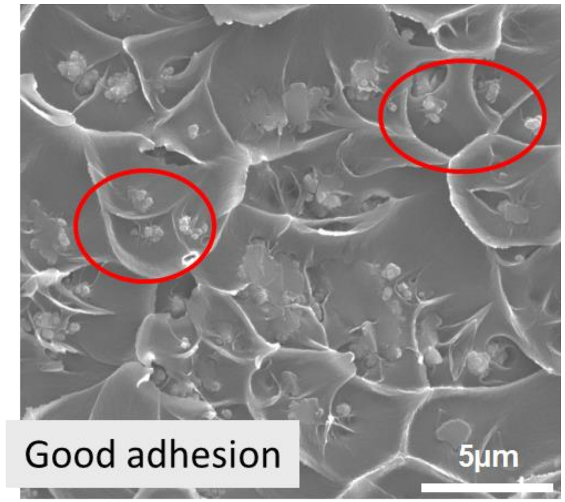
- **Filler surface:** Plane and brush
- **Polymer chain flexibility:** Rigid, intermediate and soft
- **Interaction between polymer and MOF:** Strong repulsion, weak repulsion, neutral, weak interaction and strong interaction

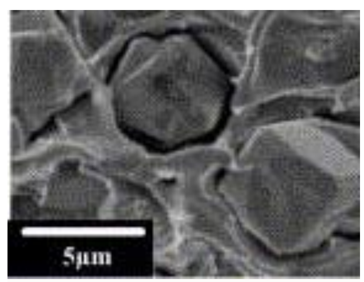
Interface optimization by MOF functionalization

<u>Functionalization of UiO-66</u>

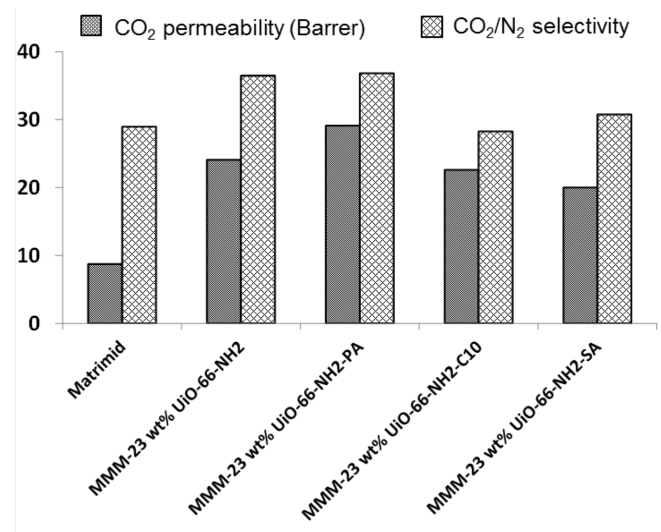


<u>Functionalities</u>
C10 amide,
Phenyl acetyl amide,
Succinimide





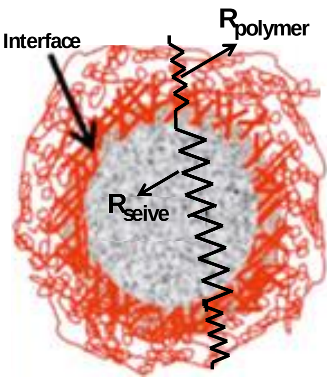
Example of bad adhesion



It is possible to optimize the interface by engineering the materials

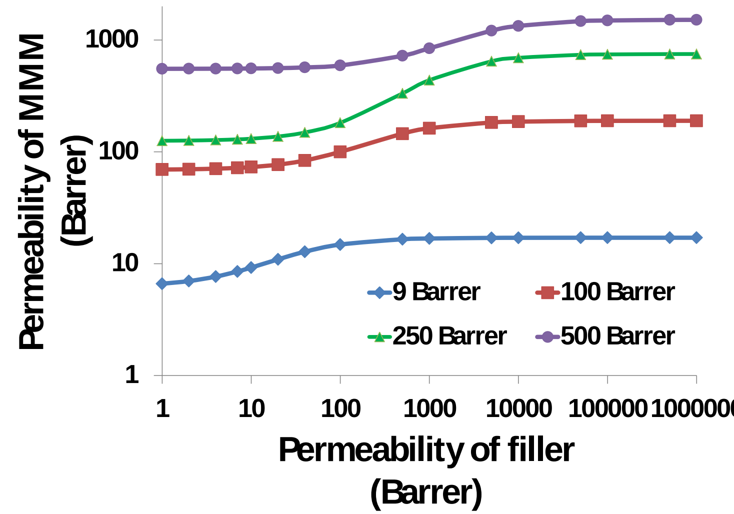
Venna et. al., J. Mater. Chem. A, 2015,3, 5014-5022

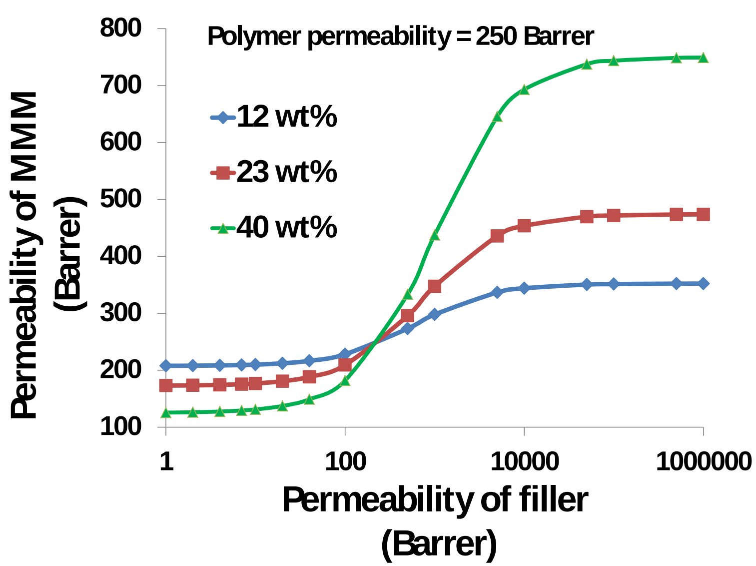
Membrane performance - Targets

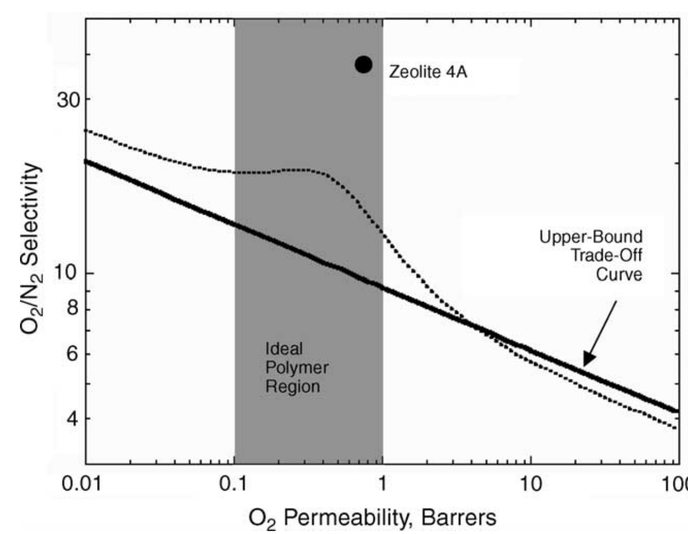


$$P_c = P_m\left[\frac{P_s + 2P_m - 2\Phi_s(P_m - P_s)}{P_s + 2P_m + \Phi_s(P_m - P_s)}\right]$$

$\alpha_{A/B} = P_{cA}/P_{cB}$ from above model



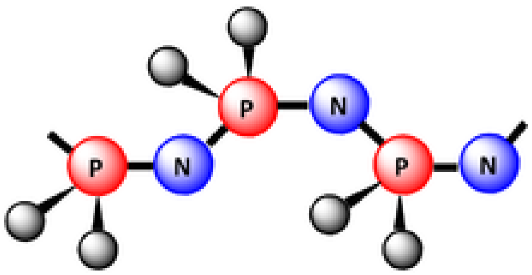




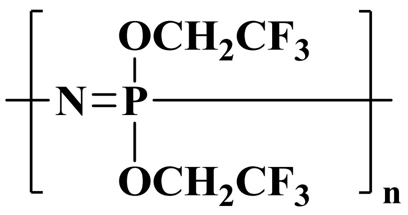
Moore, T.T and Koros, W.J., Journal of molecular structure, 2005, 739, 87

Polyphosphazene membranes

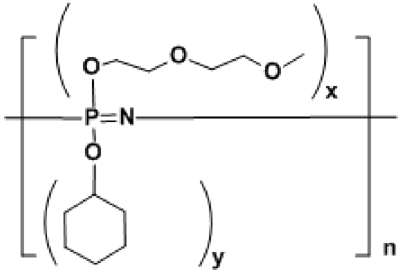
Polyphosphazene was chosen because of its high tunability, mechanical properties and gas transport properties



Over 700 Different Polyphosphazenes Have Been Synthesized So Far



Poly(bis(trifluoroethoxy)) phosphazene

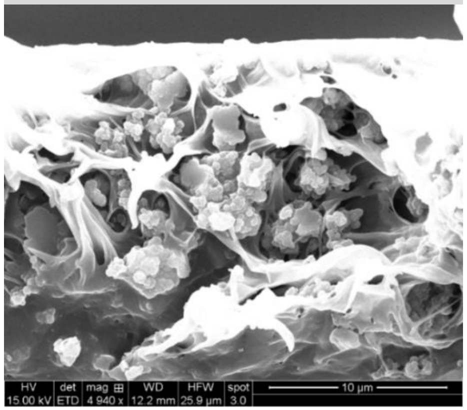


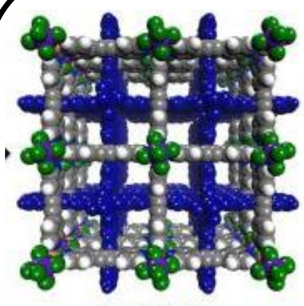
Poly(cyclohexanol - methoxyethoxyethoxy) phosphazene

	CO_2 Permeability (Barrer)	N_2 Permeability (Barrer)	CO_2/N_2 selectivity
Poly(bis(trifluoroethoxy)) phosphazene	325	25	13
Poly(cyclohexanol-methoxyethoxy ethoxy) phosphazene	110	4.1	27

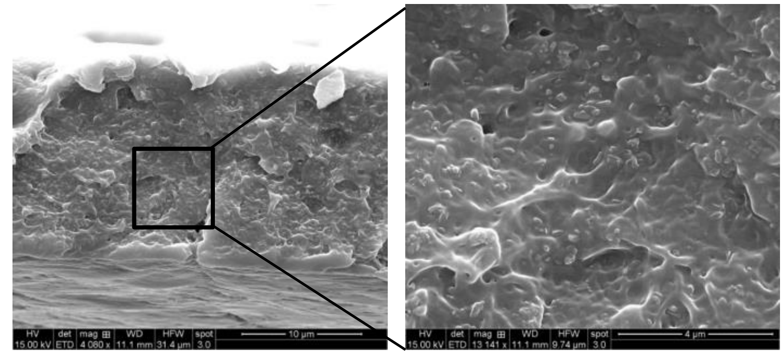
Polyphosphazene MMM

UiO-66-NH_2 with poor adhesion & agglomeration





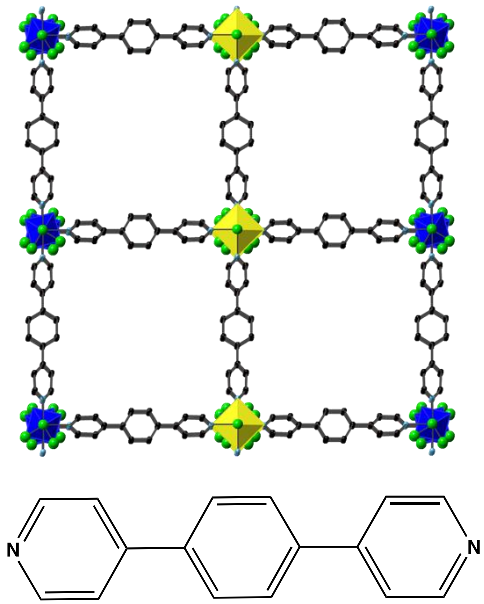
SIFSIX-2-Cu-i

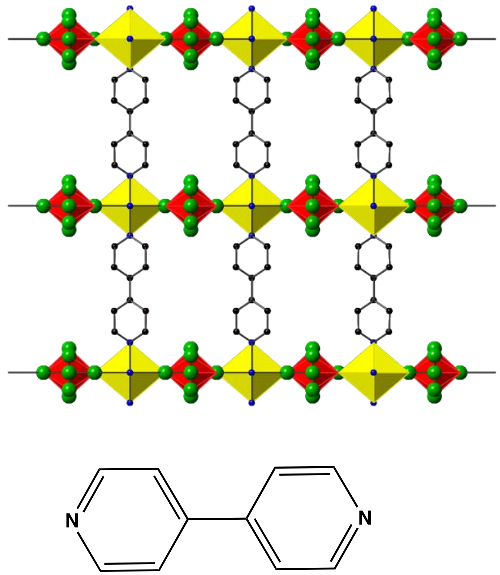


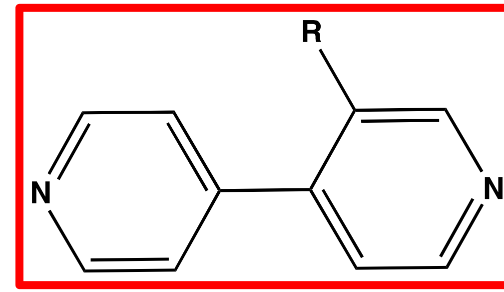
Defect free membrane with well dispersed particles

	CO_2 Permeability (Barrer)	CO_2/N_2 selectivity
Poly(bis(trifluoroethoxy)) phosphazene	325	13
MMM -TFE PZ 10 wt% of SIFSIX	354	16.1

Development of potential MOFs







F, CF_3, NH_2, CH_3, and OCH_3

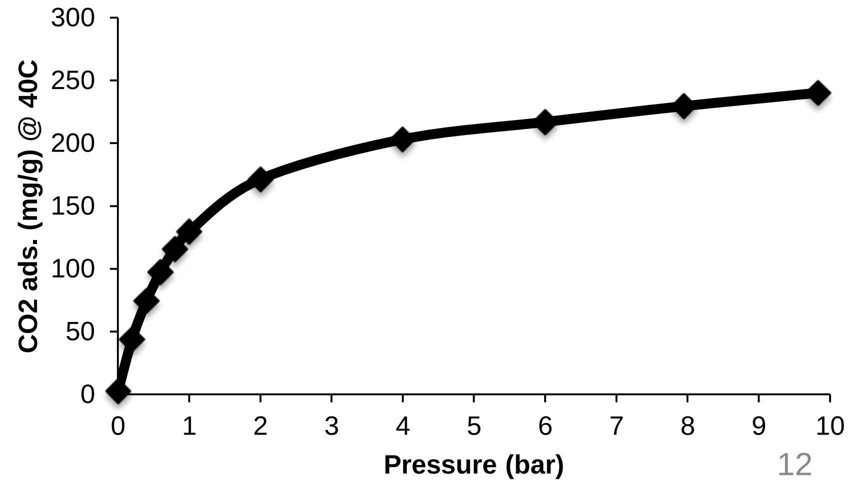
N_2 Adsorption:

Pore size: 5.9 Å

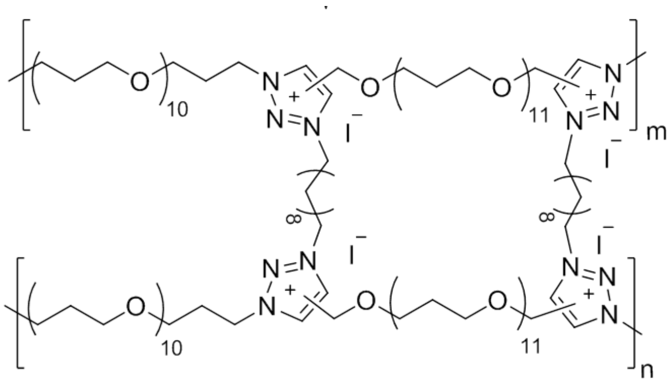
Surface area: ~1800 m^2/g

Pore volume 0.9 cc/g

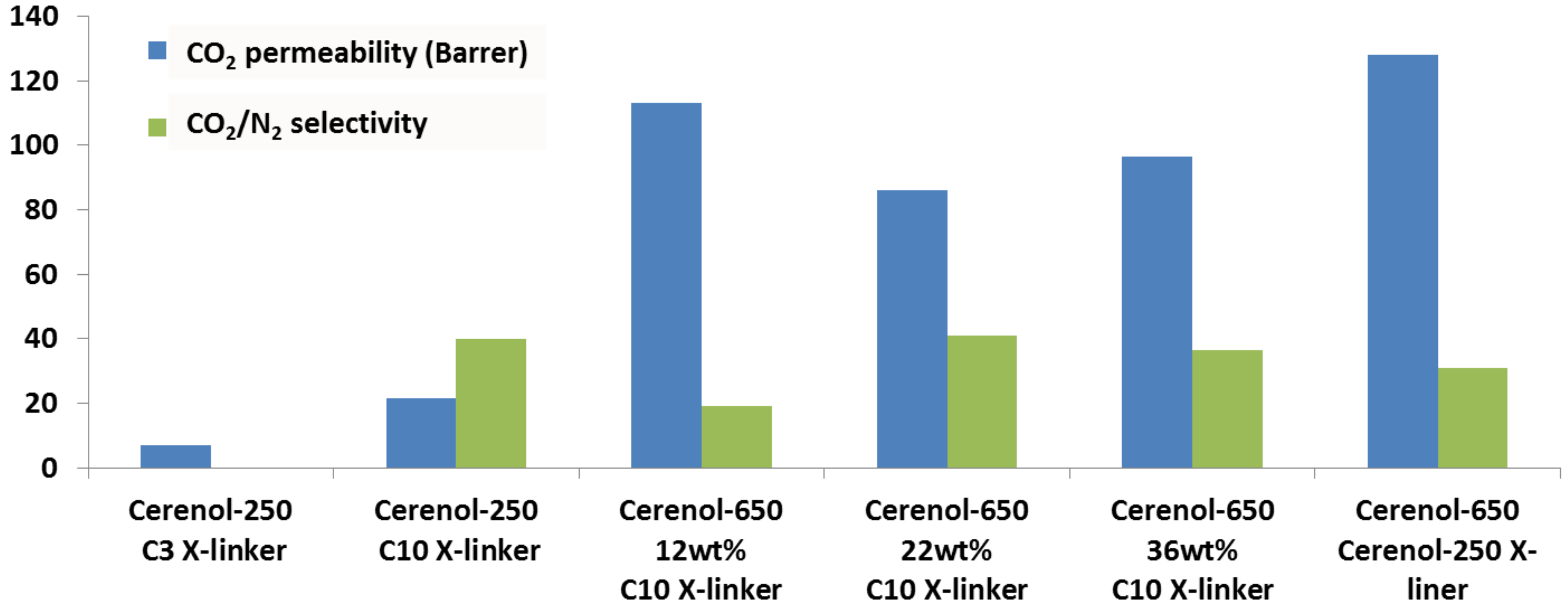
CO_2 uptake at 40ºC



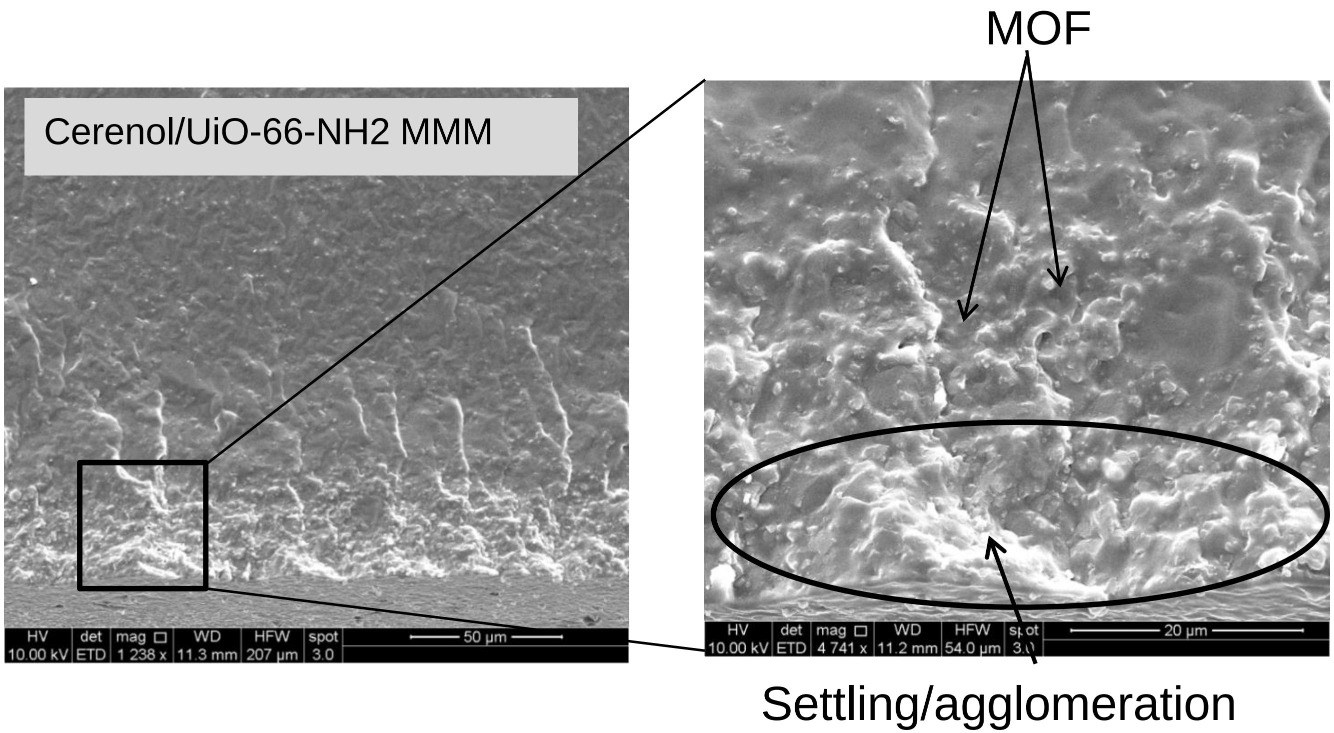
Ionic cross-linked polyethers (IXPE)



Tunable properties
Oligomer length
Crosslinker and its length
Anion

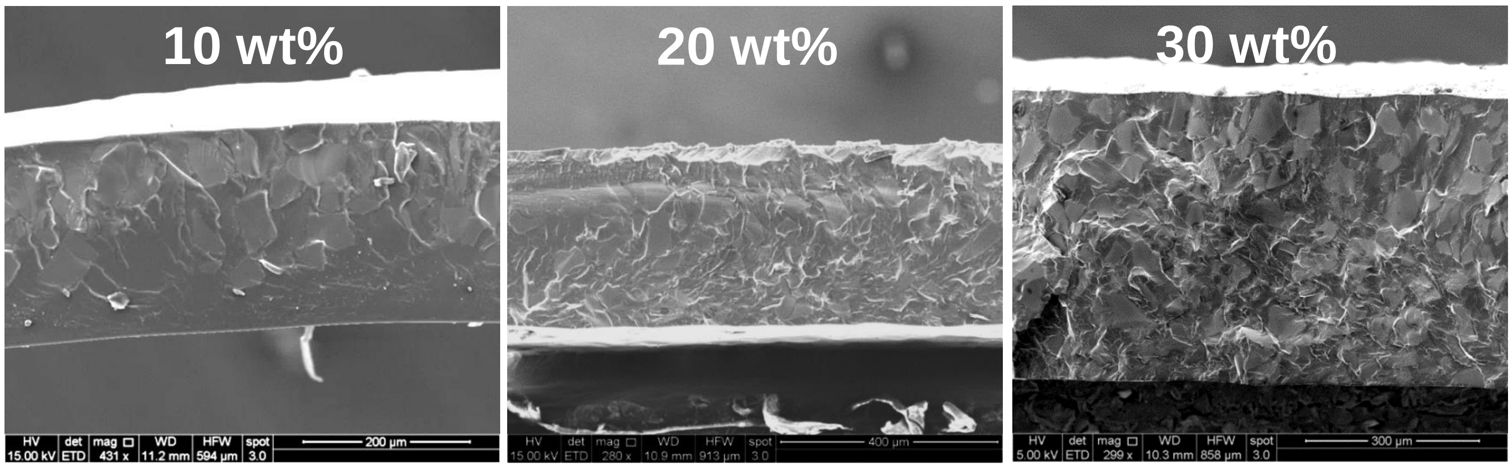


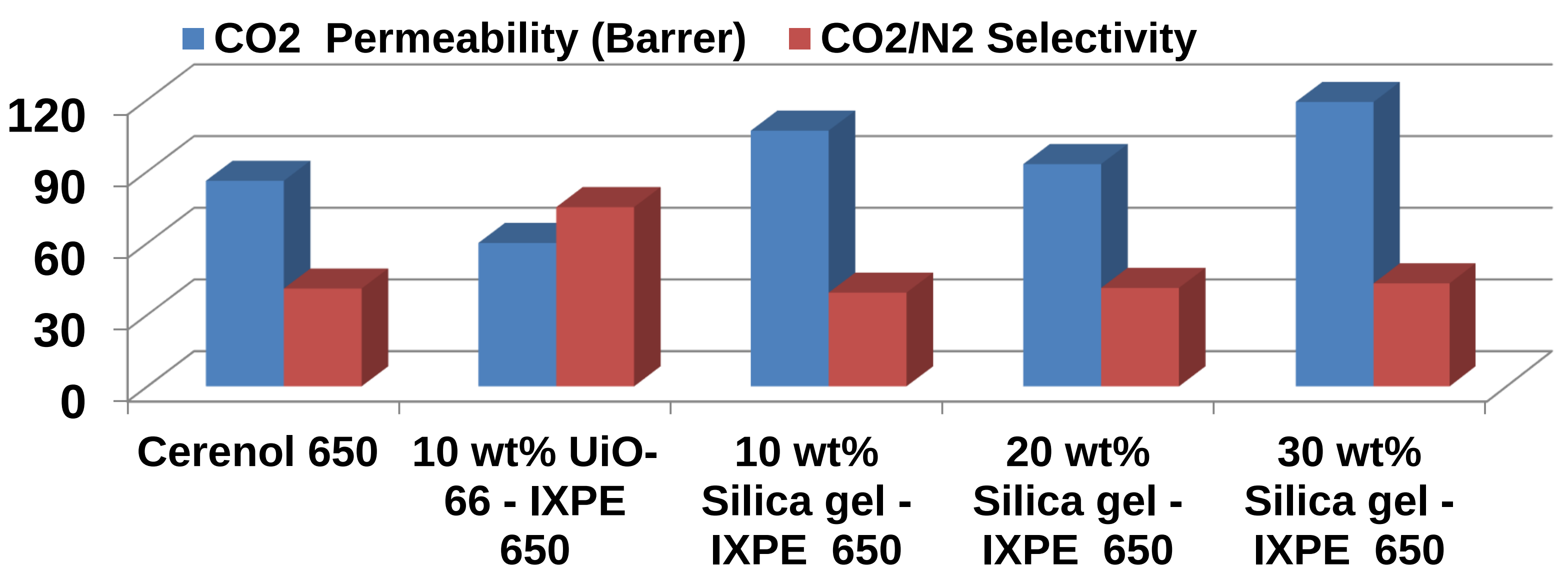
IXPE – mixed matrix membranes



Membrane	CO_2 Permeability (Barrer)	N_2 Permeability (Barrer)	CO_2/N_2 Selectivity
Cerenol 650	86	2.1	40.9
10 wt% UiO-66-NH_2 in Cerenol 650	59.3	0.78	75

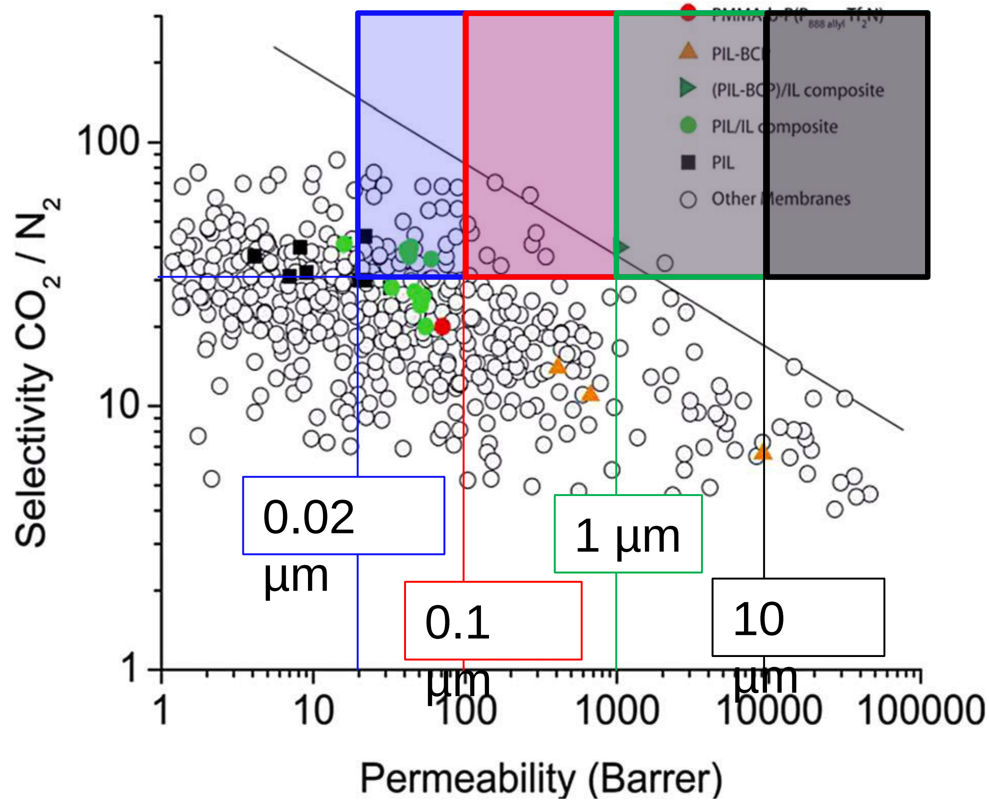
MMM using low cost fillers





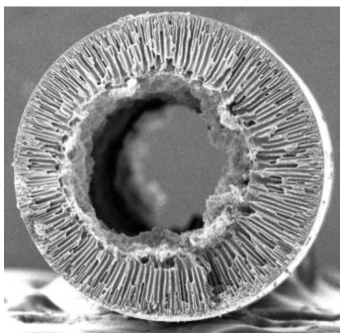
Thin membranes: Challenges

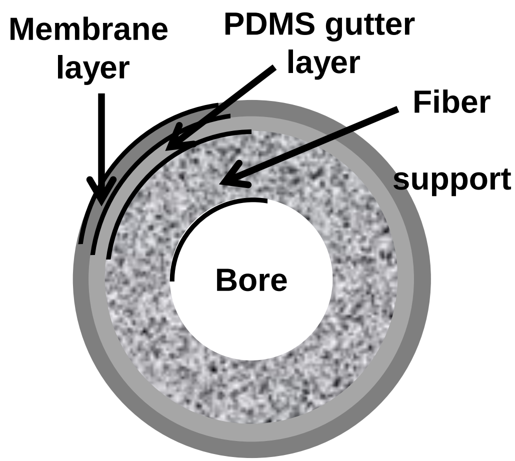
- Coating a sufficiently thin, selective membrane with industrially viable fluxes.
- Fabricating the right hollow fiber support with ideal pore size and density.
- Particle size of MOF must be lower than 50 nm without any agglomeration
- The materials should show good mechanical properties as a thin membrane.



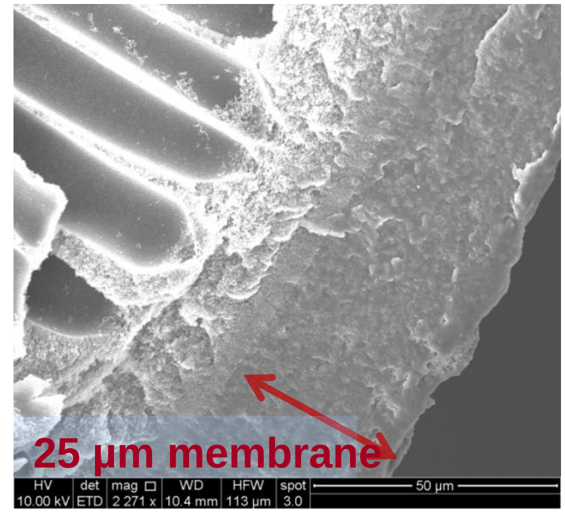
Development of hollow fiber membranes

Matrimid hollow fiber supports

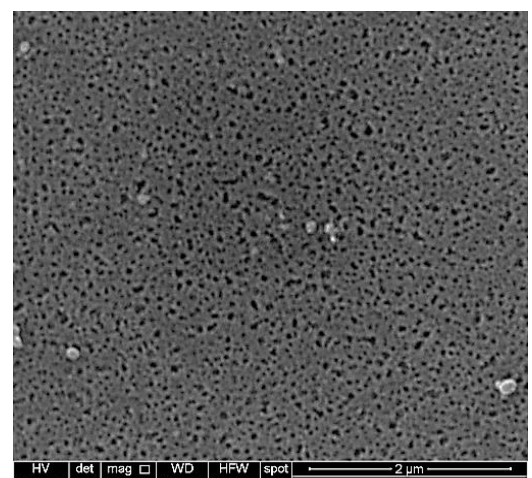




MMM coating on the hollow fiber supports using dip coating



Pore structure optimization

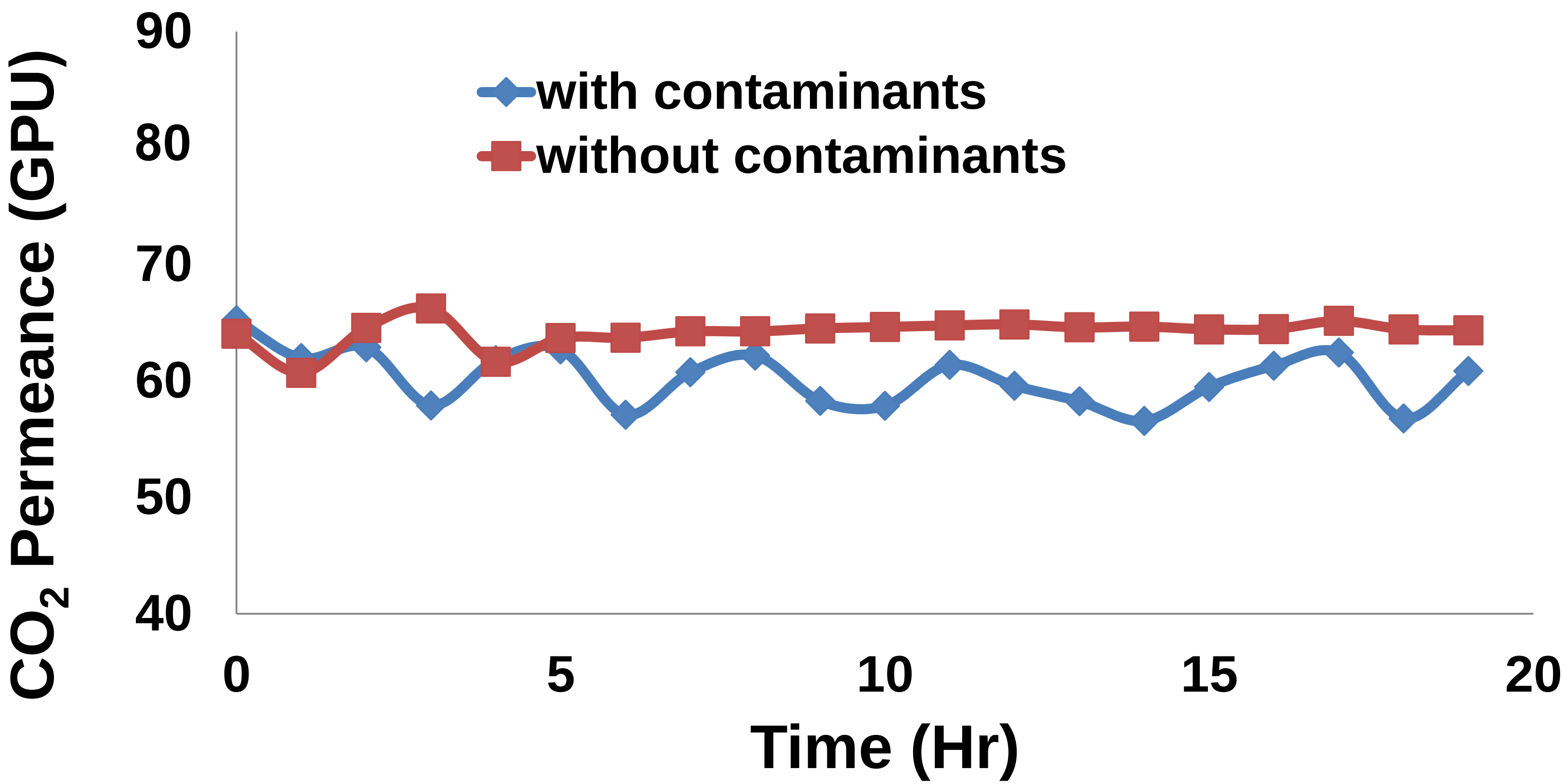


Details	CO_2 Permeance (GPU)	CO_2/N_2 Selectivity
Pure polymer	55.3	12.9
PZ-SIFSIX MMM	94.1	15.4

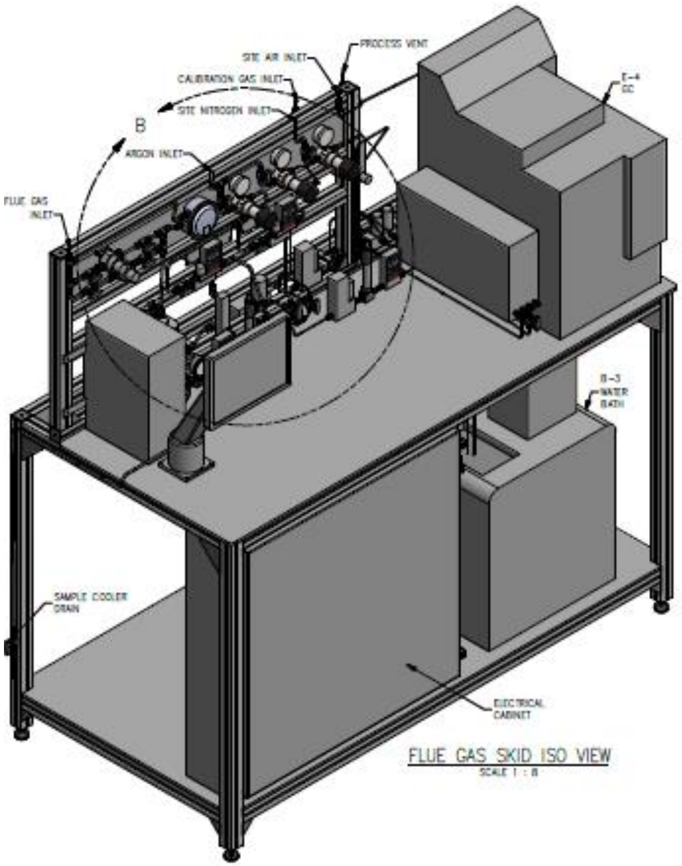
Performance testing with simulated flue gas

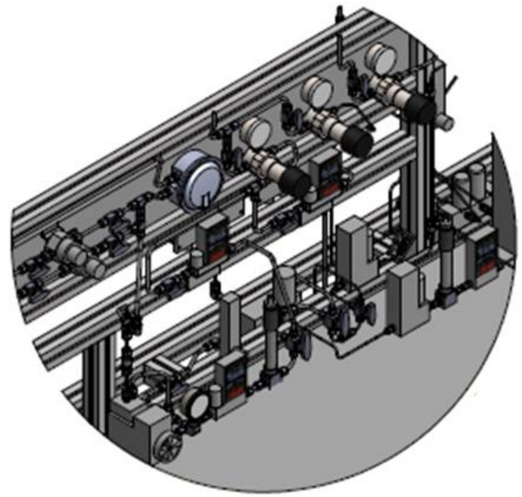
Testing Conditions:

Gas composition - CO_2 : O_2 : SO_2 : NO_2 : N_2 = 14 : 4 : 50PPM : 1PPM : BAL Humidity - 80%RH



Membrane testing at NCCC



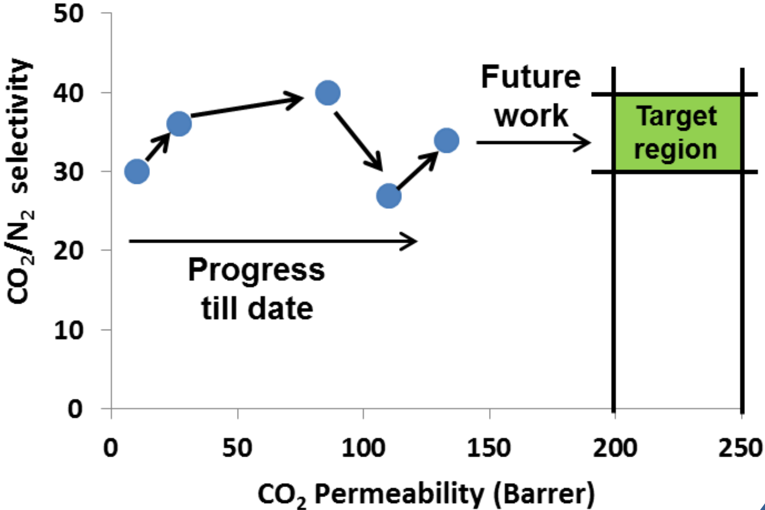


National Carbon Capture Center (NCCC), Alabama

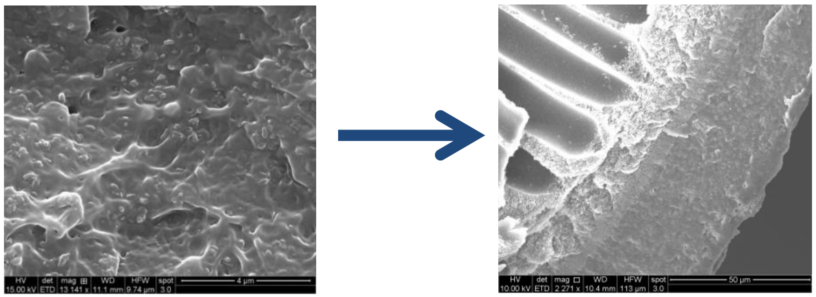
P&ID of the test skid is ready and construction is in progress. Will be ready for testing soon

Conclusions

Developed high performance Materials



Successfully transformed from Flat sheet to hollow fiber form



MMMs showed promising gas separation performance and stability under simulated flue gas conditions.

Key challenges and Future Plans

- Continue development of materials to increase permeance
- Synthesizing the smaller MOF particles
- Technique to coat thin films on the hollow fiber supports
- Testing long term stability of the membranes under realistic conditions

Acknowledgements

Membrane Fabrication and testing

- Erik Albenze, Victor Kusuma, Shan Wickramanayake, David Hopkinson

Polymer Synthesis

- Zhicheng Tian, Harry Allcock, Xu Zhou, Hunaid Nulwala

MOF synthesis and functionalization

- Anne Marti, Alex Spore, Nathaniel Rosi

Molecular simulations

- Jie Feng

System Analysis

- Olukayode Ajayi