Mixed Matrix Membranes

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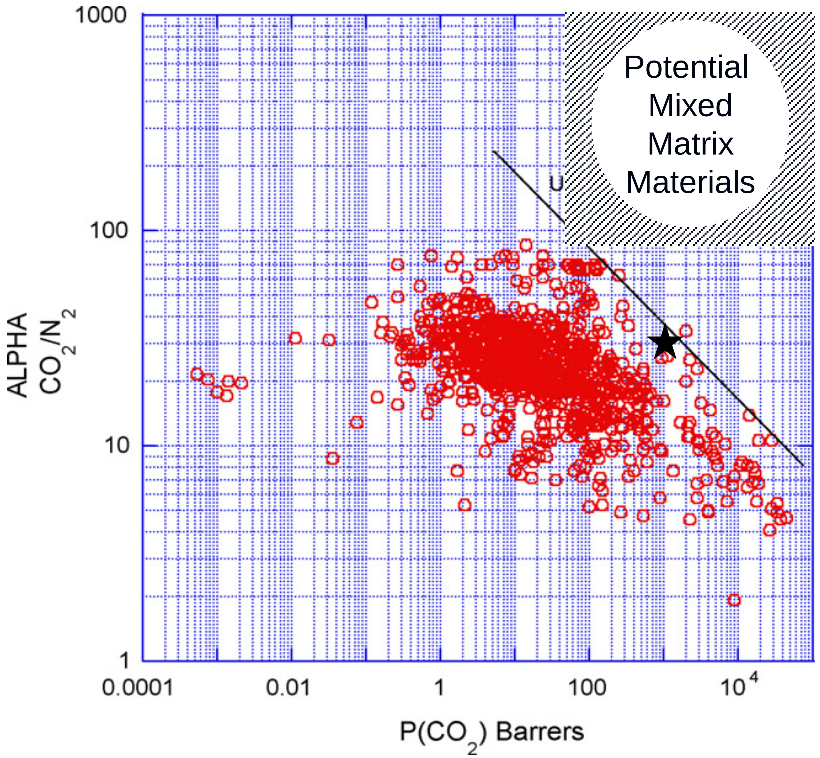
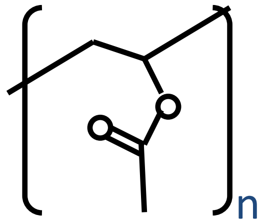
Carbon Capture Technology Meeting

Target - Mixed Matrix Membranes

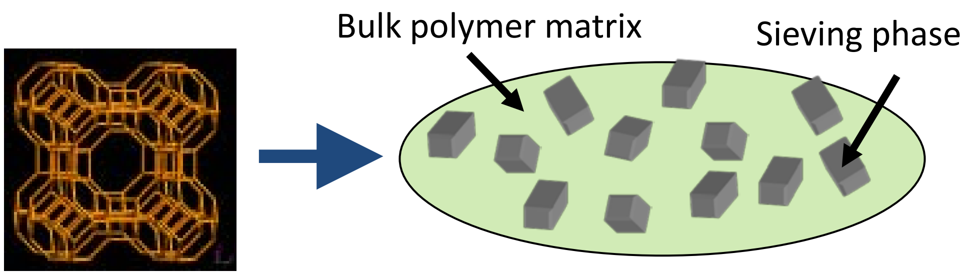
- **Membrane Performance Goals: Permeance >1000 GPU with >30 selectivity**
- **Trade-off exists between permeability and selectivity for the pure polymers**
- **MMMs have the potential to exceed the Robeson upper bound**
- **Combine the processability of polymer with superior gas separation of filler (sieves)**





Polymer

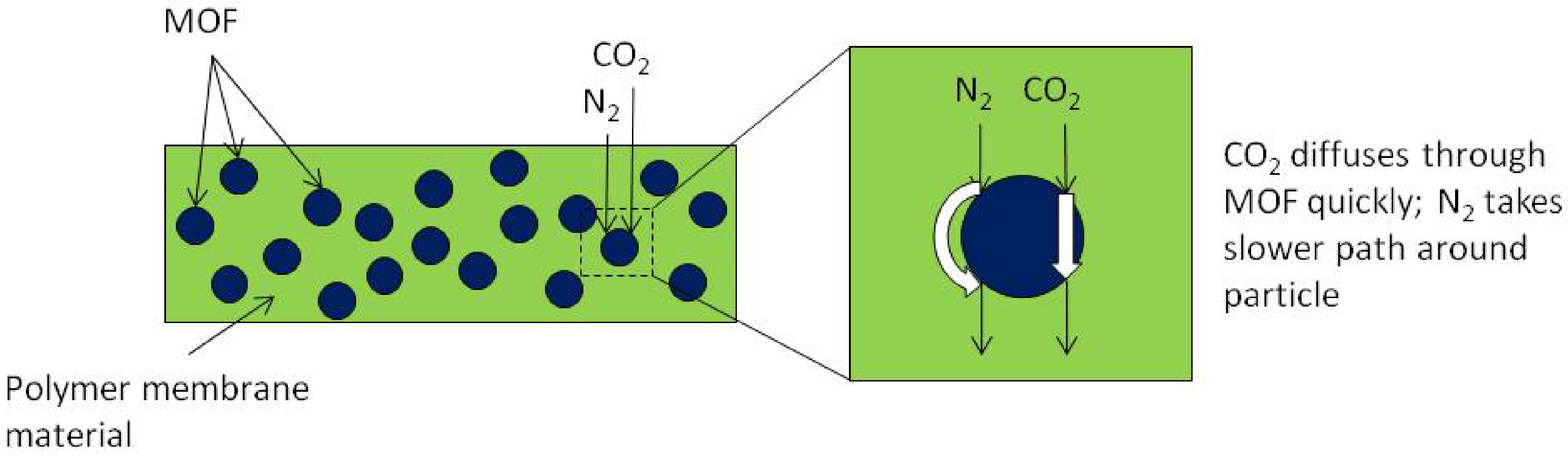
+



Inorganic Filler

Mixed Matrix Membrane

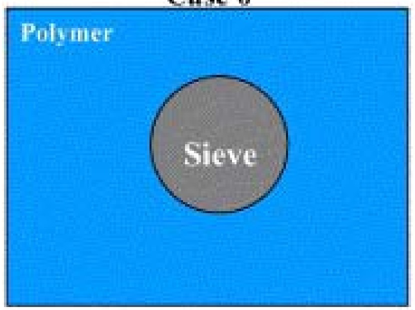
MOF-based Mixed Matrix Membranes



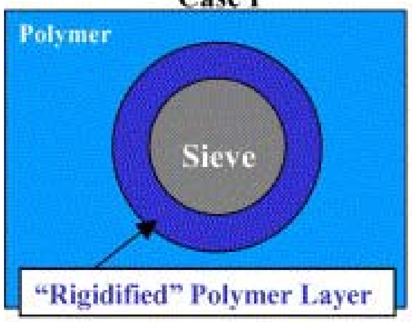
- **Appropriate for post-combustion carbon capture**
  - CO_2/N_2 separation.
- **MOF filler particles in a polymer matrix**
  - MOF Particles have shown promise as a CO_2 sorbent and the pore size can be tuned based on the linker.
- **The goal is to achieve separation properties like those of the filler rather than the polymer.**
- **Polymer membrane fabrication is potentially 10-fold less expensive than fabrication of membranes from crystalline materials like MOFs.**

Reasons for Decreased Performance

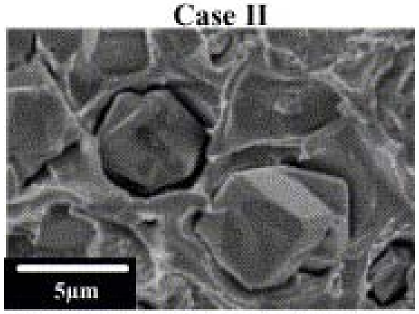
Case 0



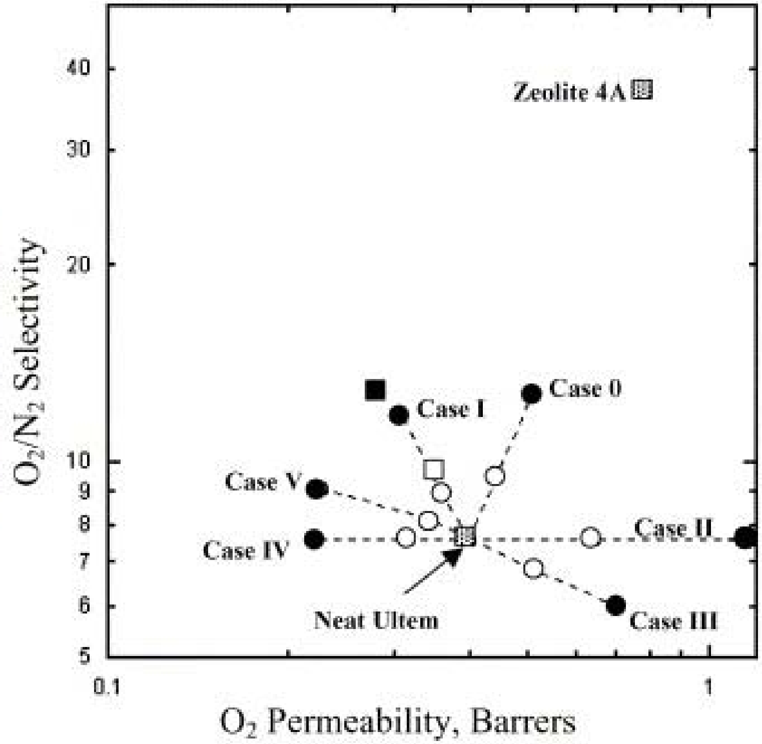
Case I



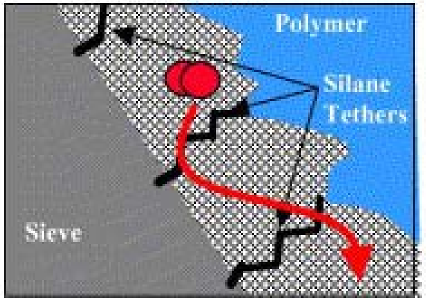
Case II



21 vol% Zeolite 4A in Udel® (Solvay Advanced Polymers; Alpharetta, GA)

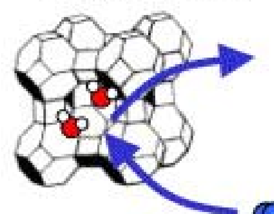


Case III

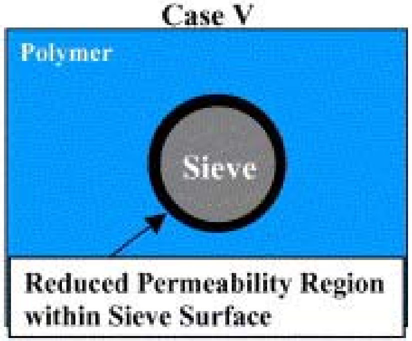


Case IV

"Clogged" Sieves



Case V



Optimizing the interfacial region is the focal point in the preparation of mixed matrix membranes.

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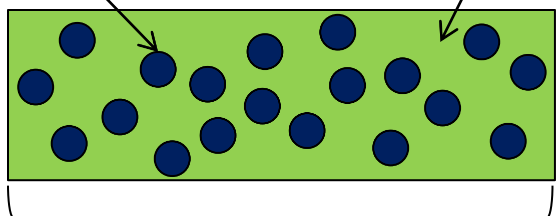
Scope of Work

MOF Selection and Synthesis
NETL, Pitt, CMU, WVU

MMM Polymer Selection and Synthesis
NETL, CMU



MMM

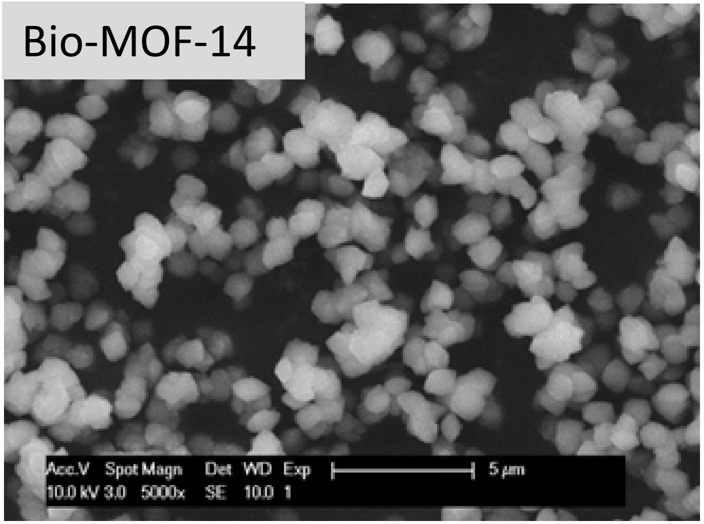
MMM Casting Development and MMM Fabrication
NETL, Pitt, CMU, WVU

High Throughput Membrane Testing
NETL, WVU

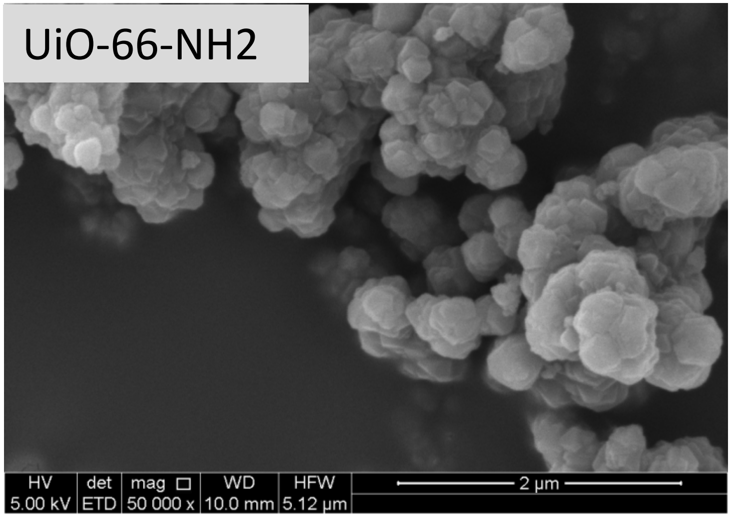
Systems and Techno-economic Analysis
NETL

MOF Selection and Synthesis

- Bio-MOF-14 crystallite
  - Good CO_2 uptake
  - Pore size <3-5Å
  - Synthesized in narrow size distribution around 1 micron



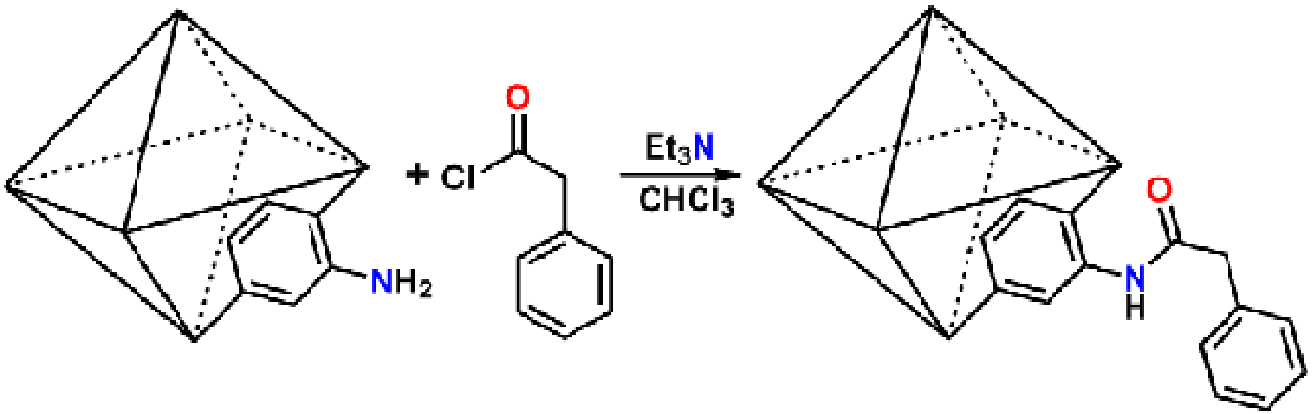
- UiO-66-NH2 crystallite
  - Good CO_2 uptake
  - Pore size 7-8Å
  - Particles synthesized were mostly below 1 micron



UiO-66-NH2 selected because of size, stability in the presence of water, and ease of functionalization

MOF Selection and Synthesis

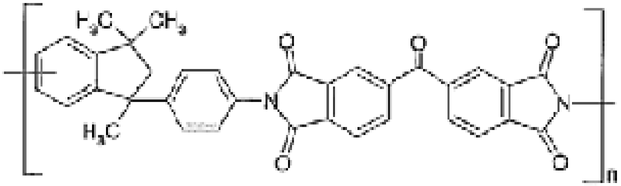
- How to improve adhesion between MOF and polymer
- Surface functionalize MOF to increase compatibility with polymer
- Phenyl acetyl group expected to give the best performance due to interactions between aromatic structures in the functional group and the polymer



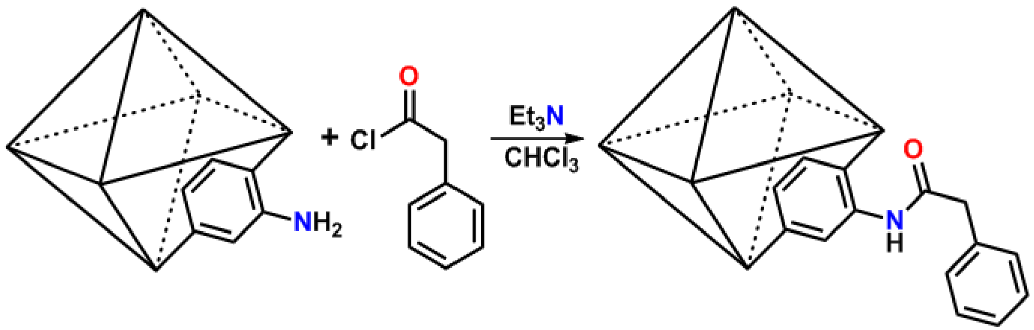
Functionalities tested:

1. C10 amide
2. Phenyl acetyl amide
3. Succinimide
4. Non-functionalized

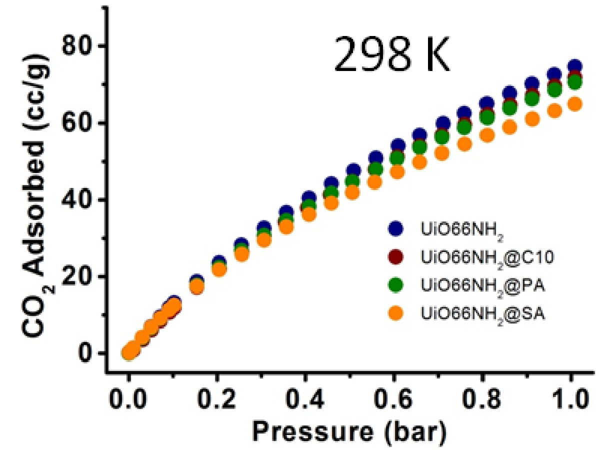
Commercial polymer selected – Matrimid

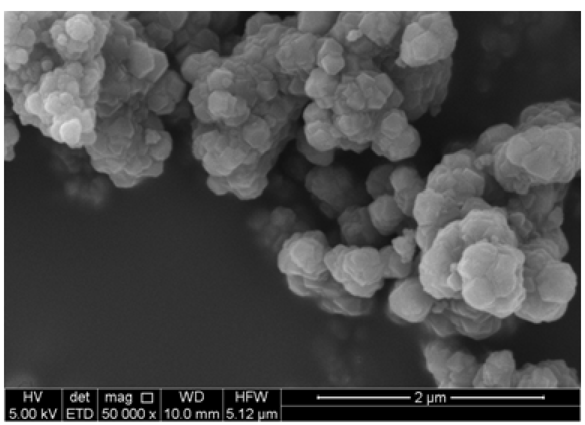


UiO-66 Properties

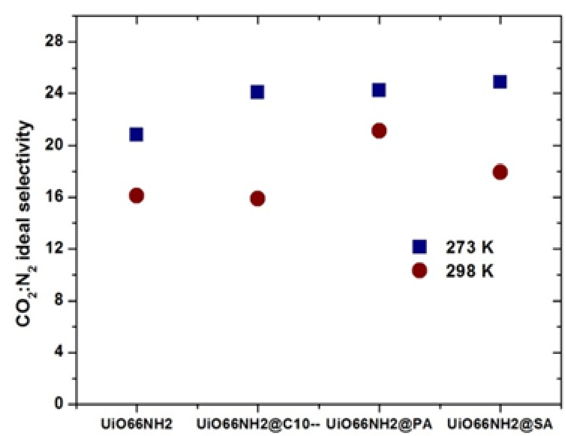


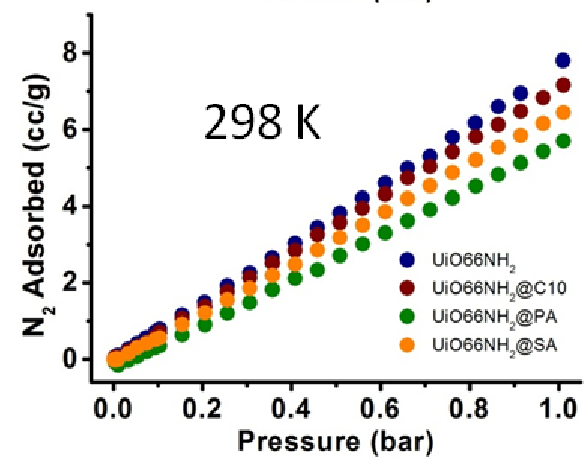
Functionalization of UiO-66-NH_2 with aromatic molecules





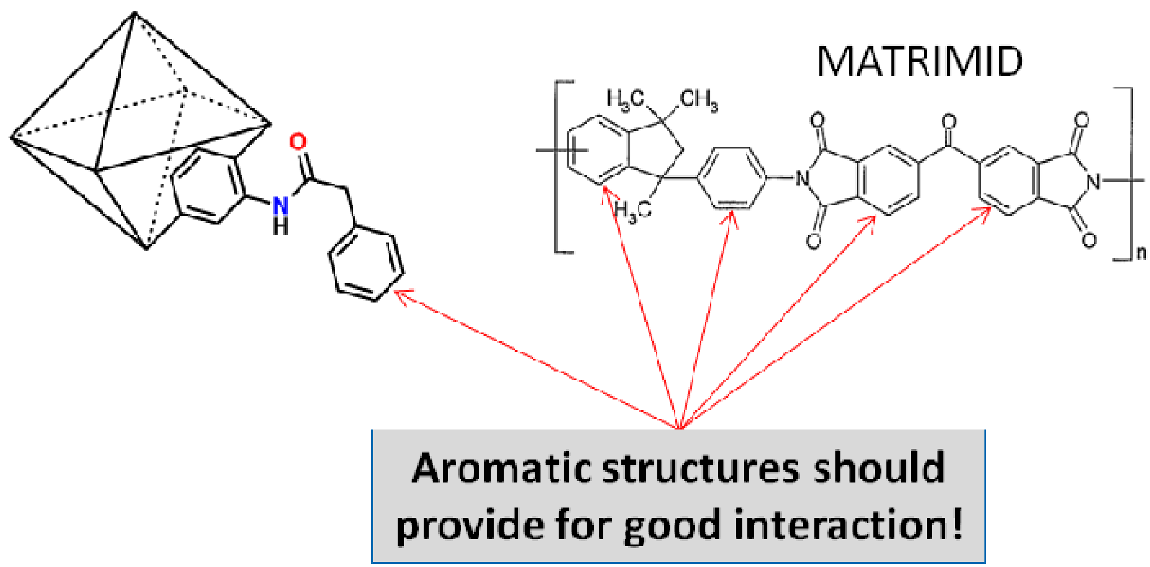
CO_2/N_2 ideal selectivity



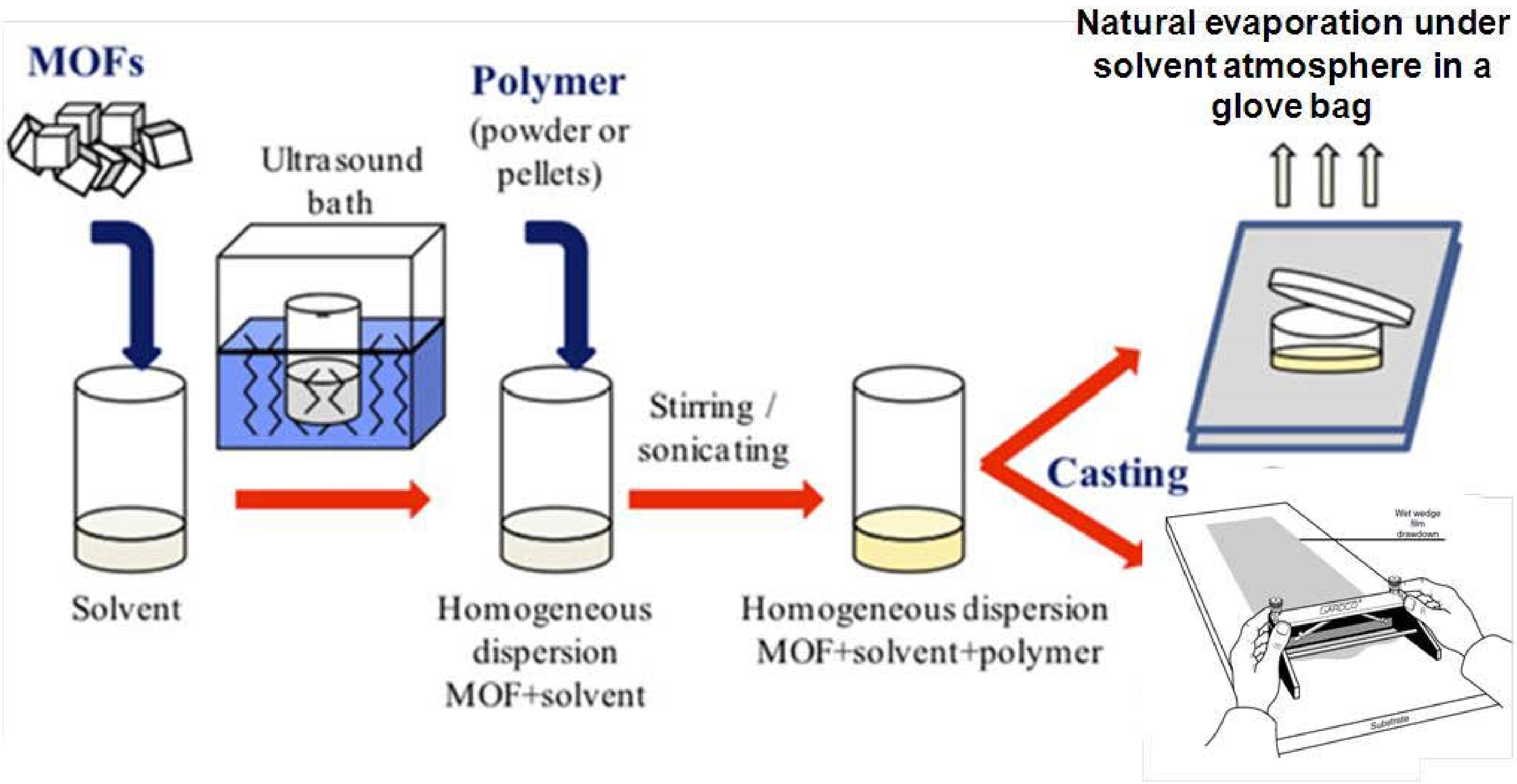


MMM Polymer Selection and Synthesis

- **Matrimid selected as commercial polymer for initial membrane fabrication**
  - Well studied and characterized in literature.
  - Glassy polymer – If we can make good MMMs with Matrimid, we should be able to do so with less glassy polymers.

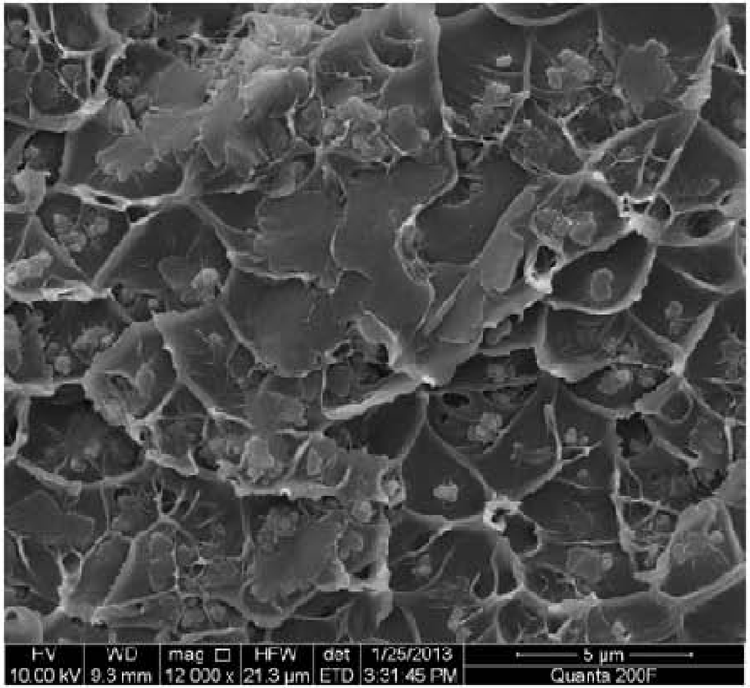


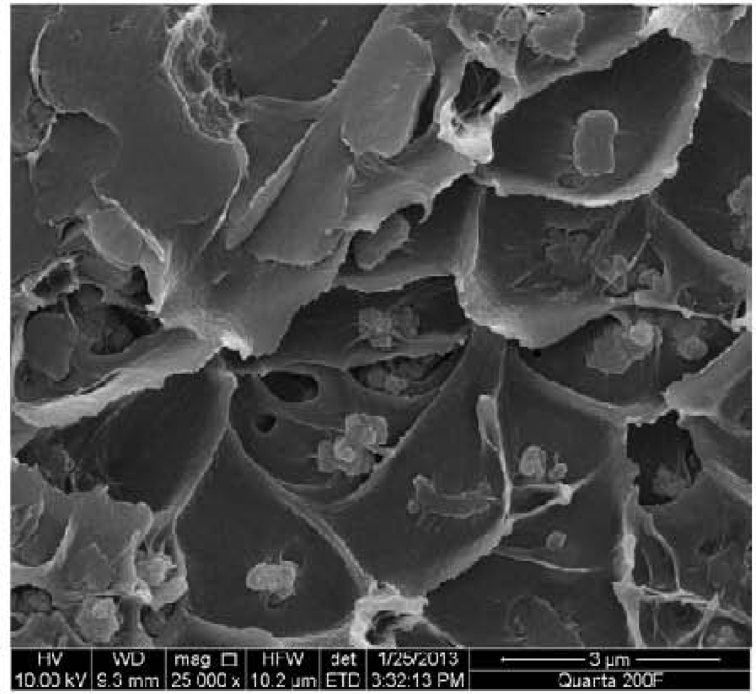
Dope Formulation and Membrane Casting

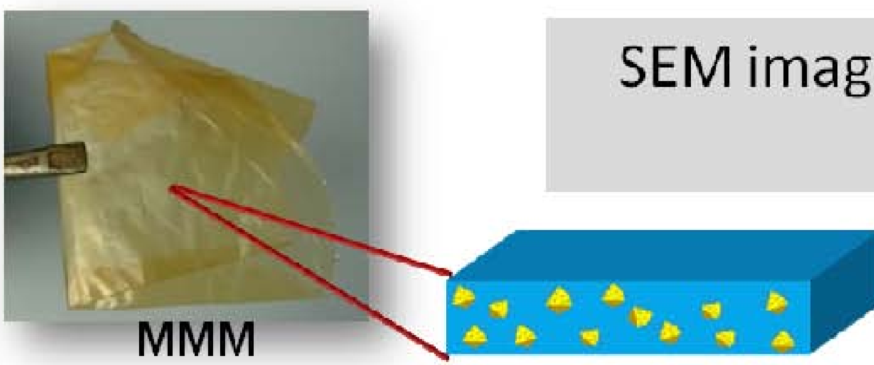


Matrimid membranes were prepared using 15 wt% matrimid in chloroform solution and mixed matrix membranes were prepared with MOF in Matrimid with 12 wt%, 23 wt% and 40 wt% loading

Cross-section of the Mixed Matrix Membranes

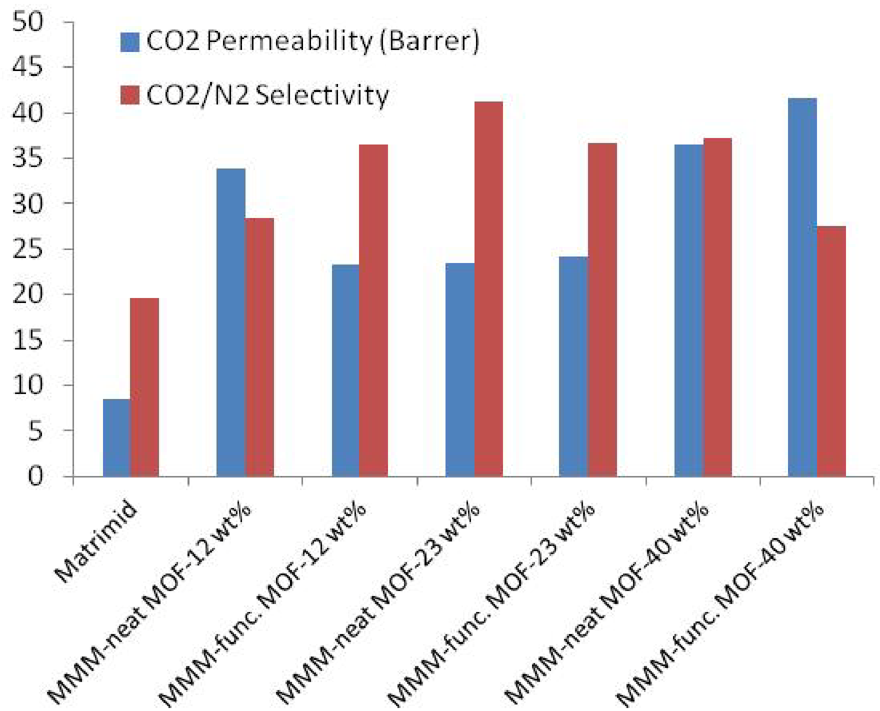


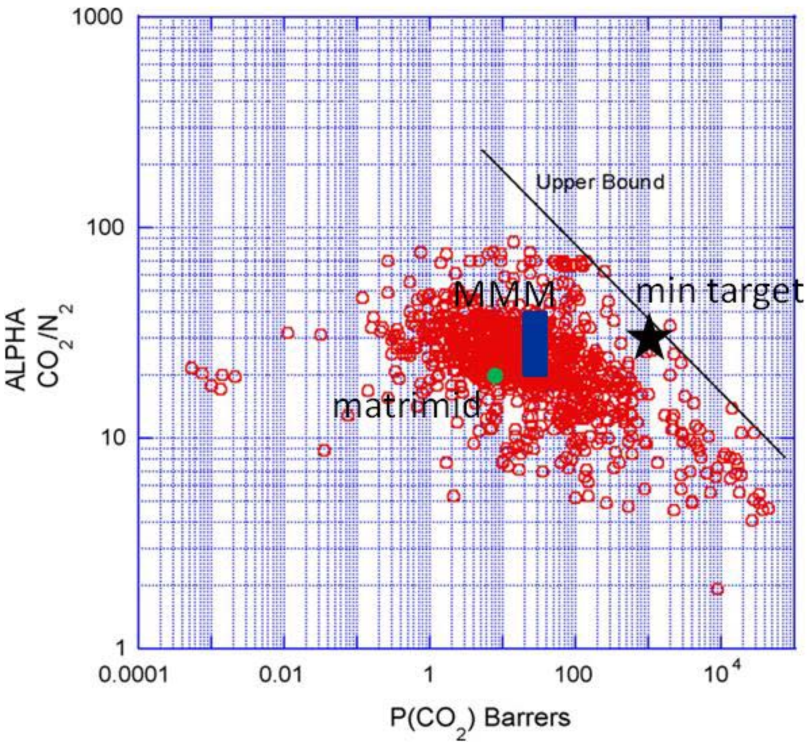




SEM images show good adhesion between polymer and MOF

MMM separation performance

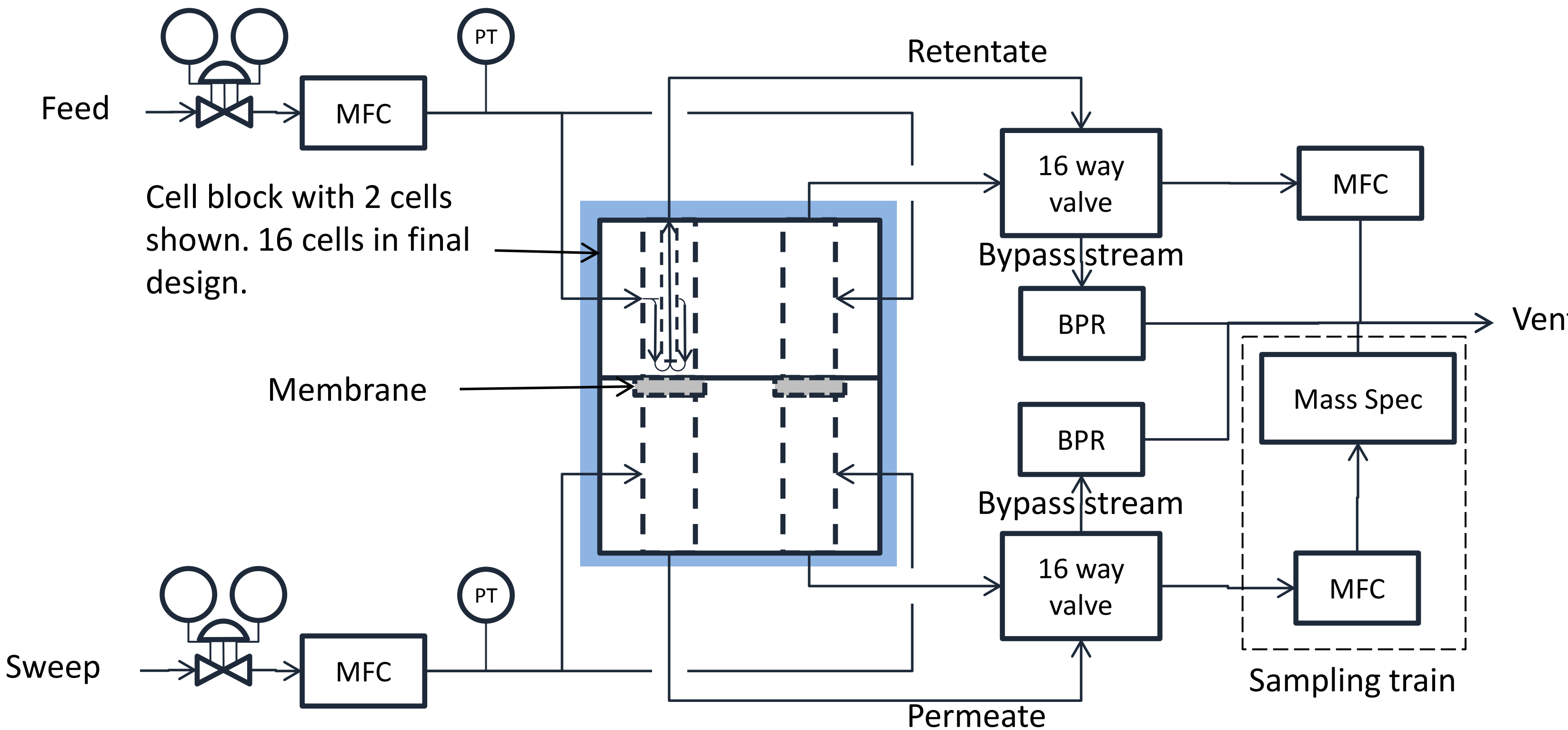




- Selectivity decreases above 23% loading
- Permeability increases above 23% loading
- Improved adhesion based on functional group

Possible Cause → Chain Rigidification
Interface Defects

High Throughput Membrane Testing



P range: 0-150 psig

T range: up to 250°C

16 membranes/test

- **<u>Capable of testing 16 membranes at once</u>**
- **Valves to isolate a cell if membrane rupture is detected.**
- **Mass Spec for rapid sampling.**
- **Easily automated.**

High Throughput Membrane Testing

Using MOF MMM as an example:

- MOF MMM variables include:
  - MOF material, crystal size, crystal loading.
  - Polymer support material.

1 MOF
5 crystal sizes
10 loadings

→ **50** membrane tests required

	Days/test	Membranes/ test	Membranes tested/day	Days to test 50 membranes
Single Cell System	3	1	0.33	150
HT System	4	16	4	12.5

Patent application has been submitted for the design and operation of the high throughput unit

Moving Forward

- **Continue development of Generation 2 materials**
  - Higher permeabilities
  - Custom polymer and MOF
- **Hollow fiber format**
  - Develop techniques to fabricate Generation 2 materials in high surface area hollow fiber format
- **Slipstream testing**
  - Most promising material to be tested at the NCCC
- **Seek industrial partners for licensing**

Conclusions

- UiO-66 MOF successfully synthesized and functionalized with different functional groups
- MMM successfully fabricated from MOF and Matrimid
  - Good interaction between the polymer and MOF
- CO_2/N_2 selectivity of about 30-40 with low permeability
  - Still a long way to reach the goal
- High throughput membrane testing system allows us to quickly optimize the MMM

Acknowledgments

- MOF Synthesis and Functionalization
  - Nat Rosi (Pitt)
  - Tao Li (Pitt)
  - Alex Spore (Pitt)
- Membrane Fabrication and Testing
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  - Surendar Venna (WVU)
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