Polyphosphazene Based Membranes for Gas Separation

Dr. Hunaid Nulwala
Liquid Ion Solutions LLC
Pittsburgh, PA

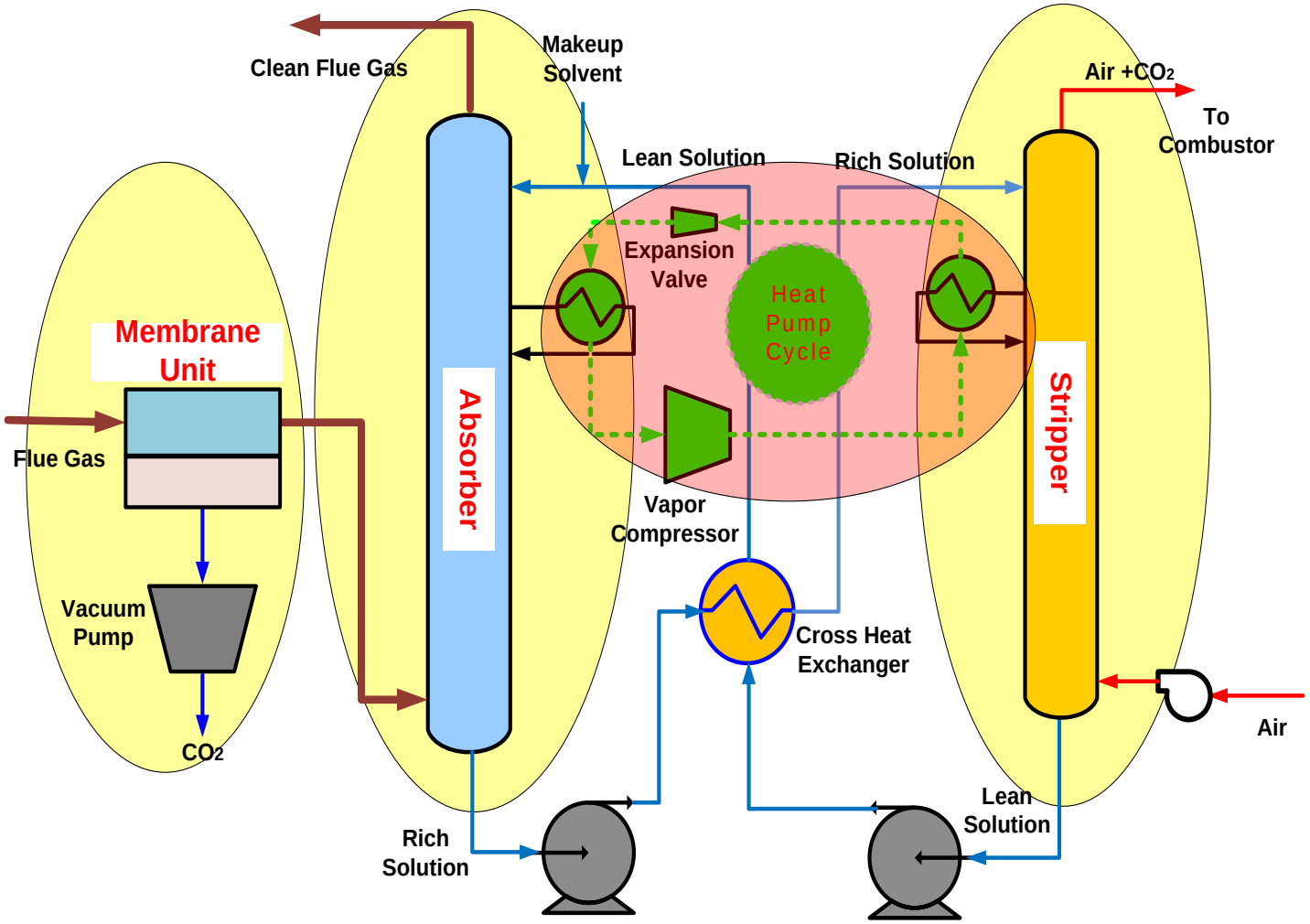
NATIONAL ENERGY TECHNOLOGY LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY · 1855 ·

CCS CARBON CAPTURE SCIENTIFIC LLC

Liquid Ion Solutions

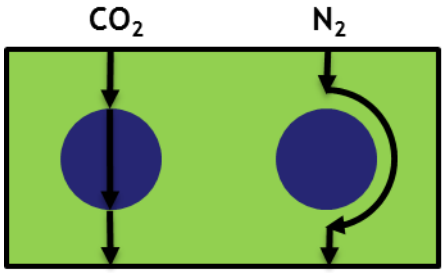
Membrane/Solvent Integrated Process



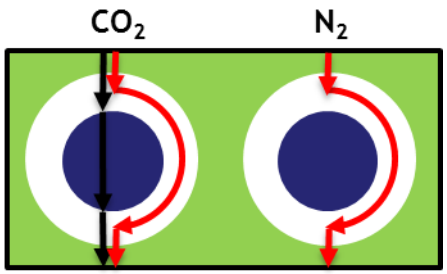
Membrane Needs

- Commercial membrane materials
  - Selectivity ≈ 40
  - Permeability ≈ 200
- Less conventional membrane needed to make substantial improvements
  - Supported liquids
  - Mixed matrix membranes
- Mixed matrix membranes
  - Better particles (Zeolites, MOFs)
  - Improved polymers
  - Controlled interaction of polymer with particles

The Trouble with Mixed Matrix Membranes

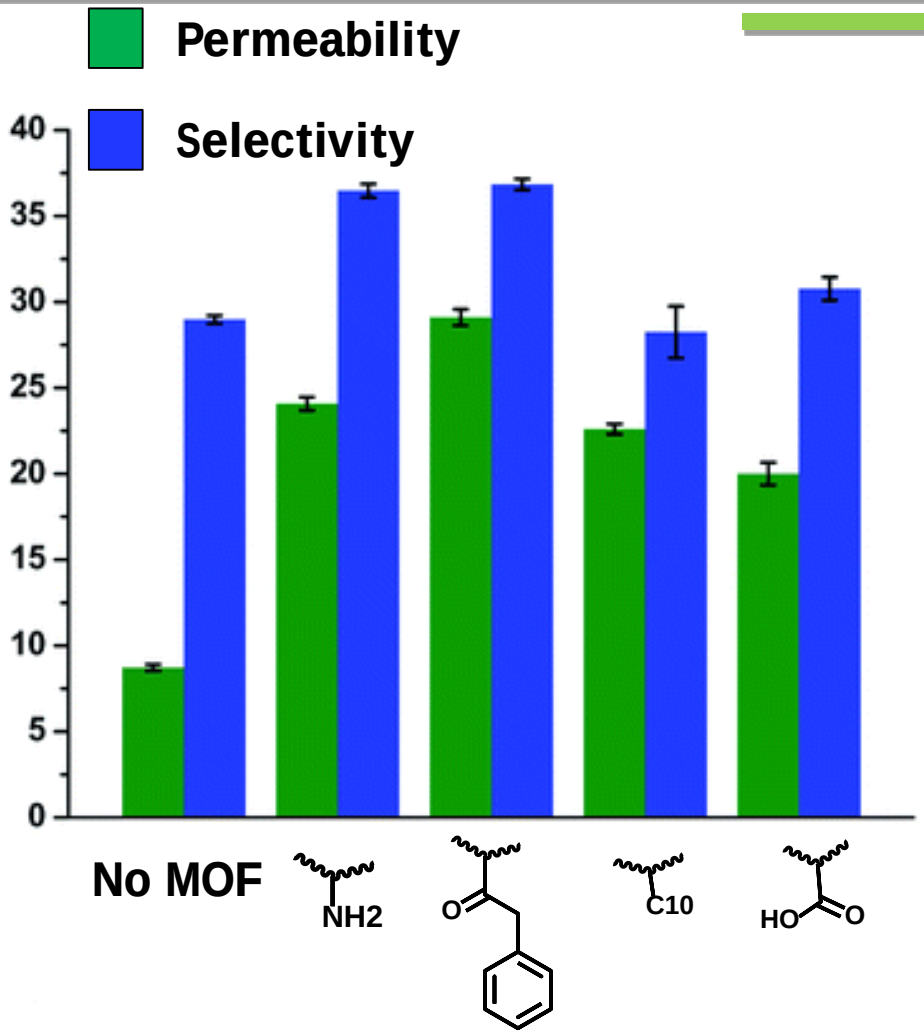


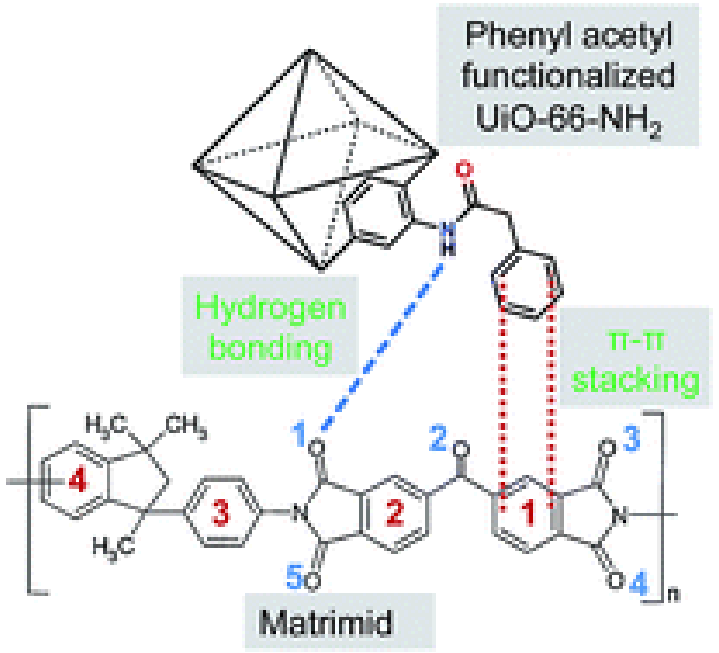
"True" MMM Transport



Particle Bypass

Insight

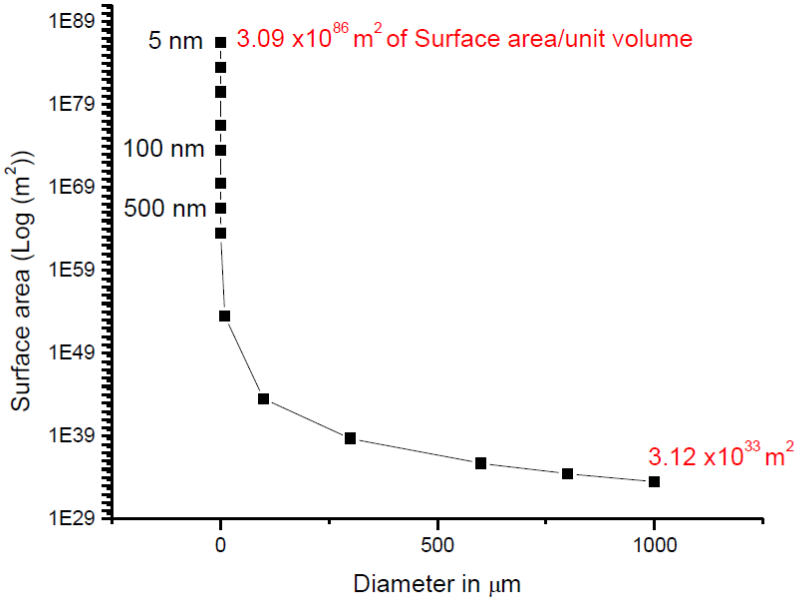


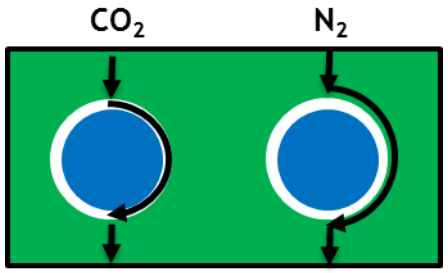


J. Mater. Chem. A, **2015**, *3*, 5014-5022
U.S. Patent Application number: 14/519,743

Interface

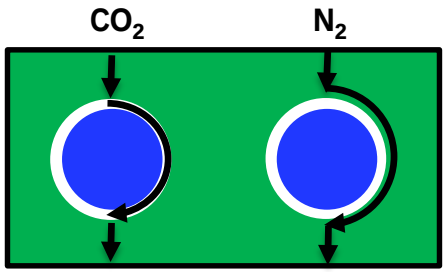
If you can't beat 'em, join 'em!

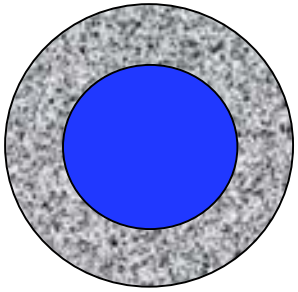




- Makes use of envelopment effects which have plagued mixed matrix membranes
- Diffusion phenomena determined by interactions with the particle and polymer surface
- Possibility of using simple nanoparticle fillers
- Advanced polymers allow an excellent starting point

Plan of Attack for Mixed Matrix Membranes



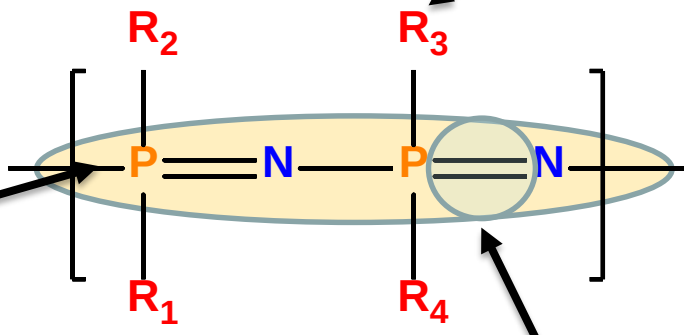


5-10 nm

- Use simple nanoparticle fillers
- Surface modify the particles to tune optimal interactions with CO_2 and the polymer
- Employ an advanced polymer with good compatibility and CO_2 transport properties
- Create a membrane in which diffusion phenomena are determined by interactions with the particle and polymer surface

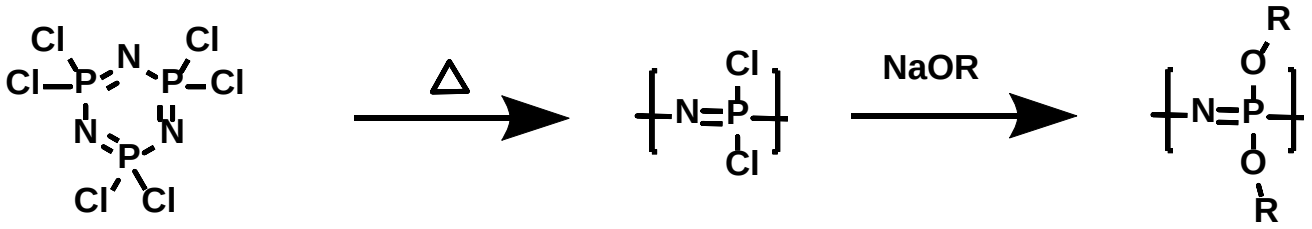
Polymer of Choice

Macromolecular substitution

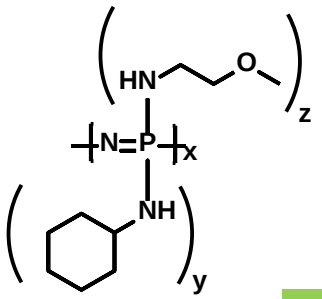


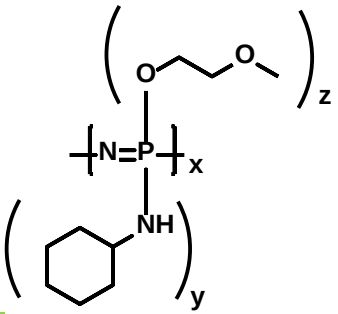
Ultra Flexible chains
High chain mobility
Improved gas solubility and diffusion

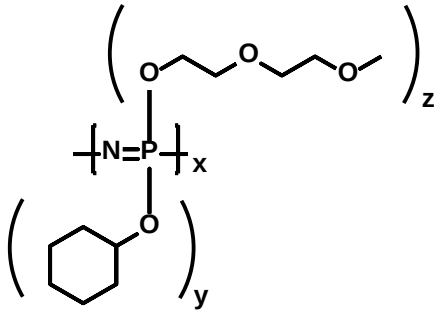
Excellent chemical and thermal stability
C-C =607Δ*Hf* kJ/mol vs.
P-N =617 Δ*Hf* kJ/mol

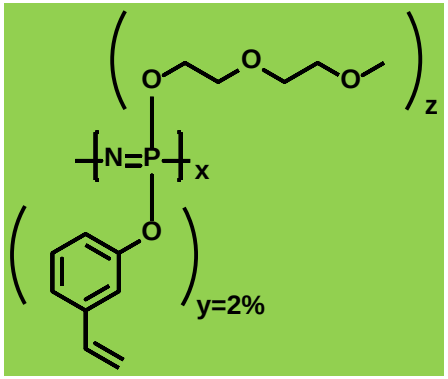


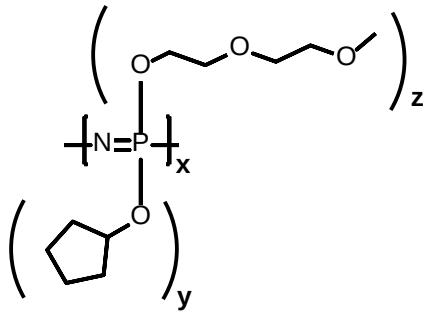
Polymer Screening



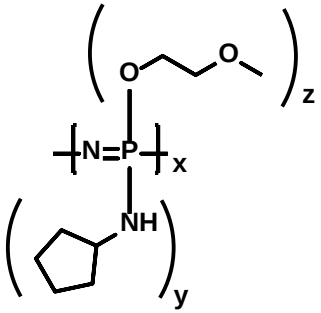


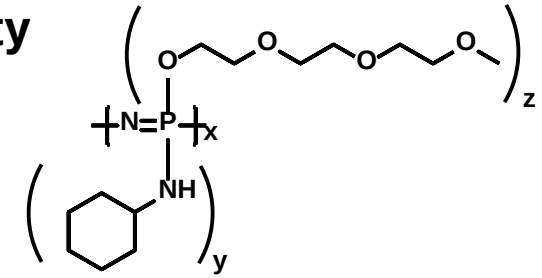






250 Barrers
62 selectivity



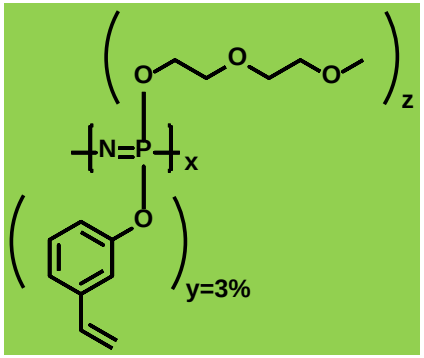


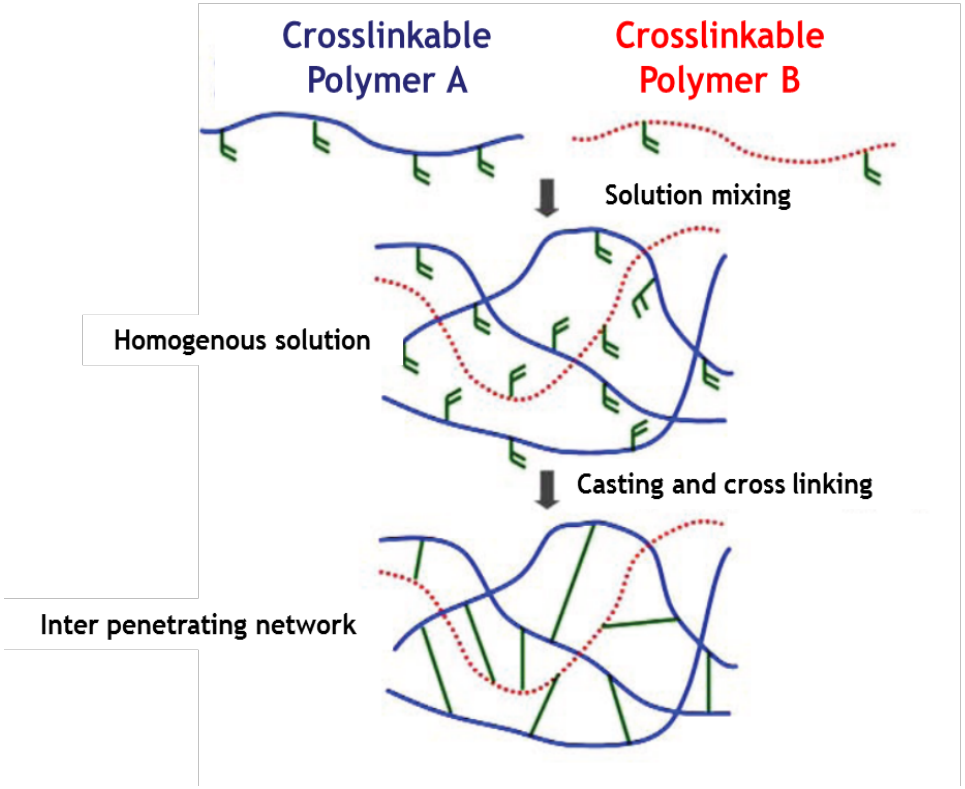
J. Mem. Sci., **2001**, *186*, 249-256

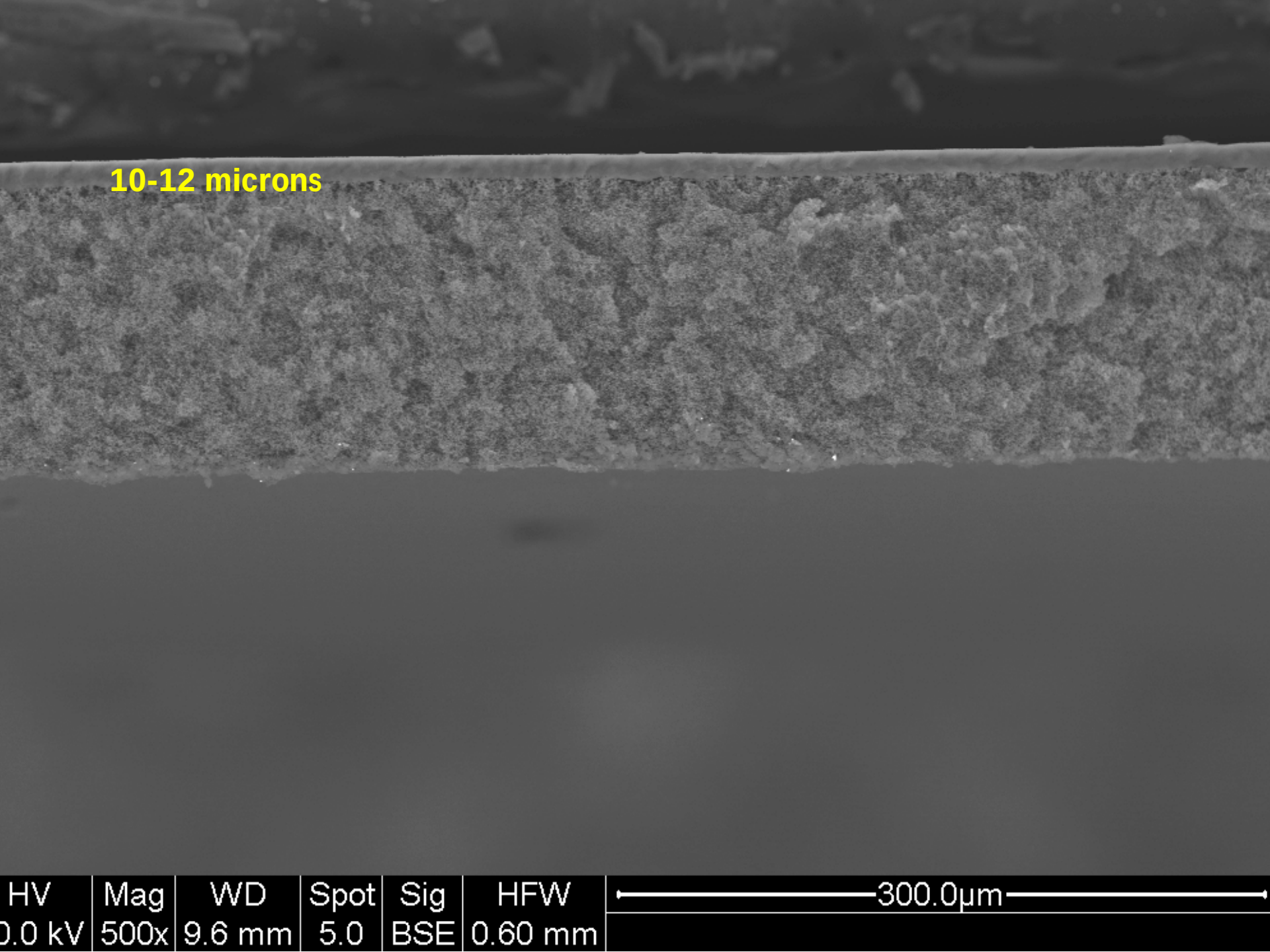
Membrane Fabrication

Challenges

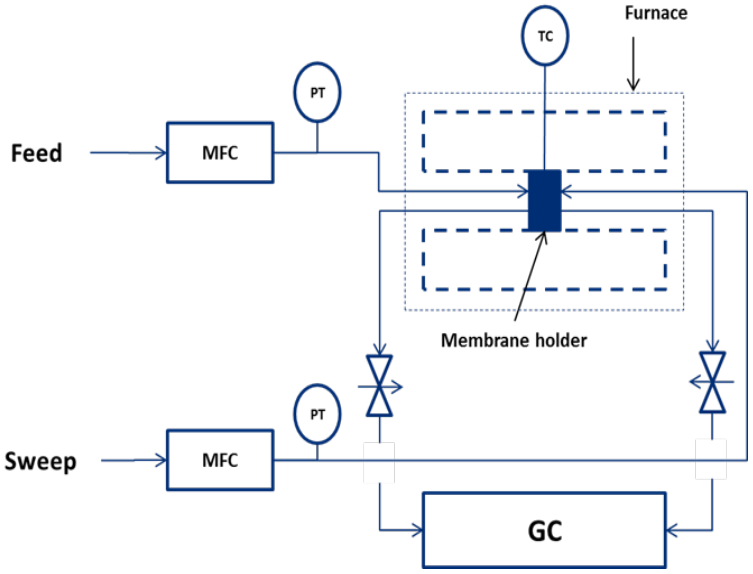
- Not a film former
- Sticky
- Does not have required mechanical properties

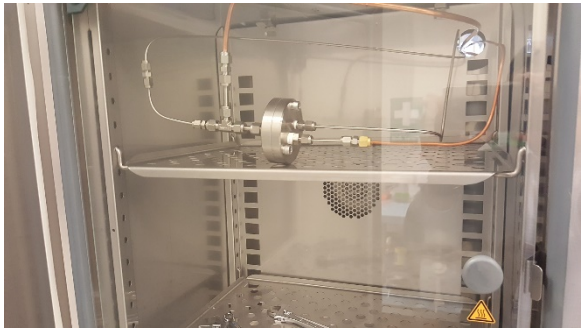





10-12 microns
HV
0.0 kV
Mag
500x
WD
9.6 mm
Spot
5.0
Sig
BSE
HFW
0.60 mm
300.0µm

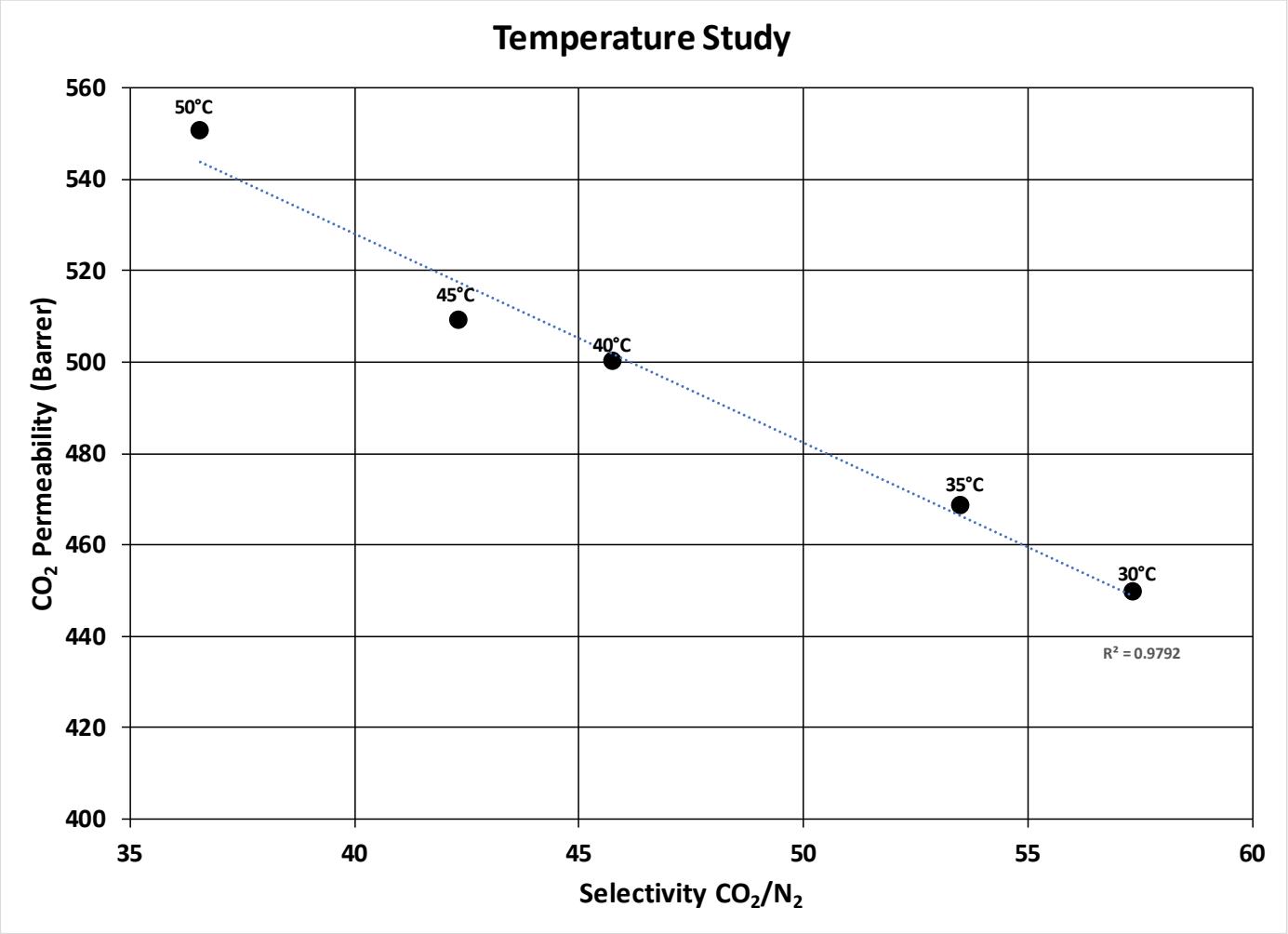
Gas Testing Systems and Performance Testing



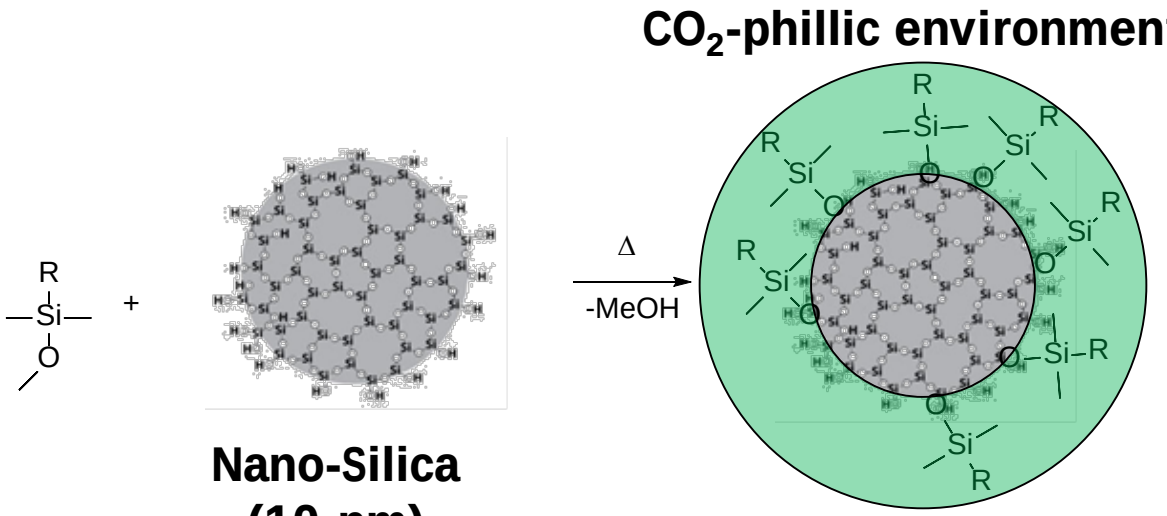


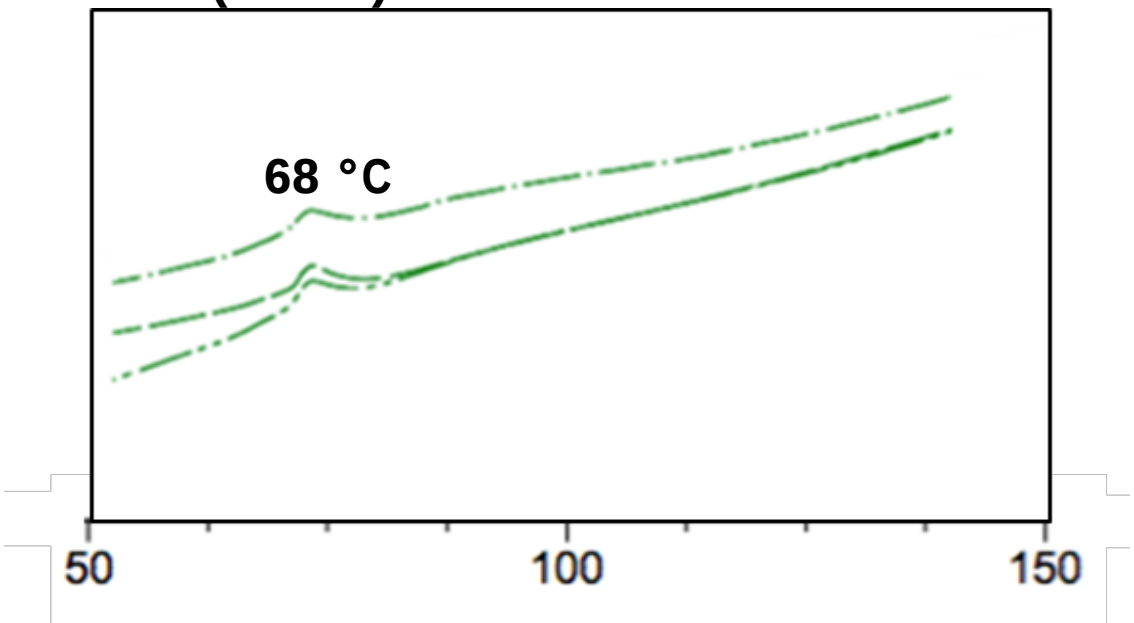
- **Mixed Gas Selectivities**
- **Testing in Presence of Moisture**
- **Testing in Presence of Contaminants**

Polymer Membrane Results

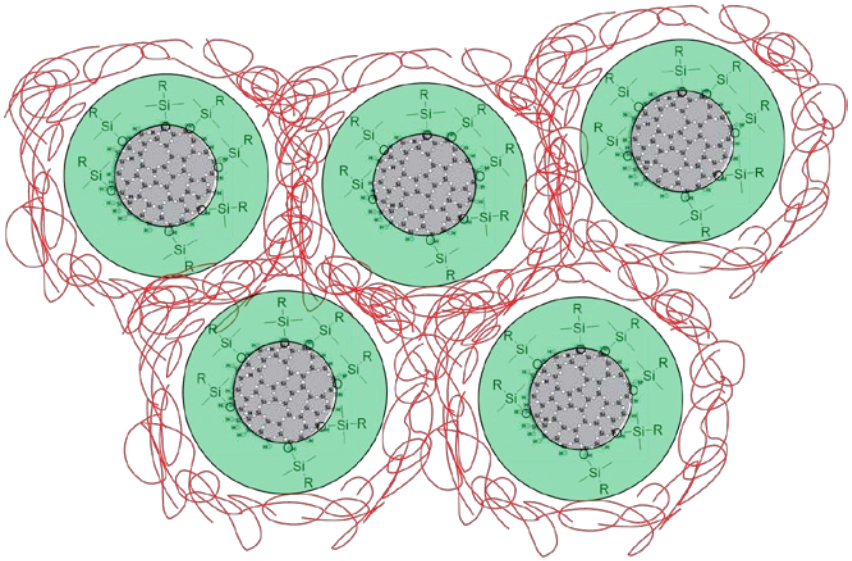


Surface Functionalized Nanoparticles

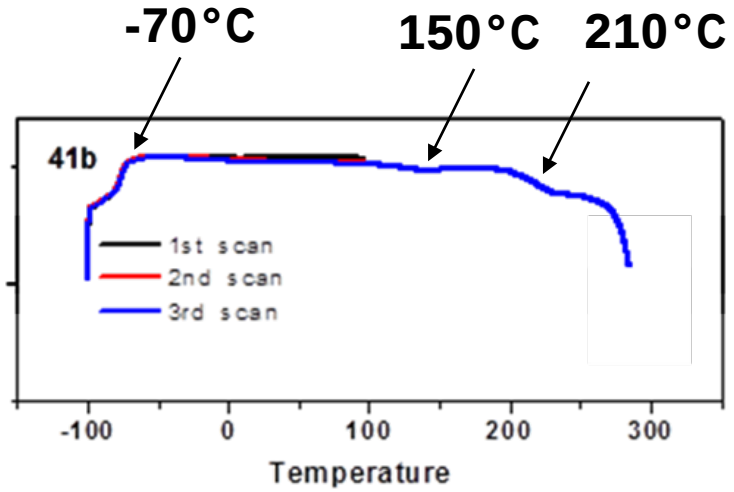


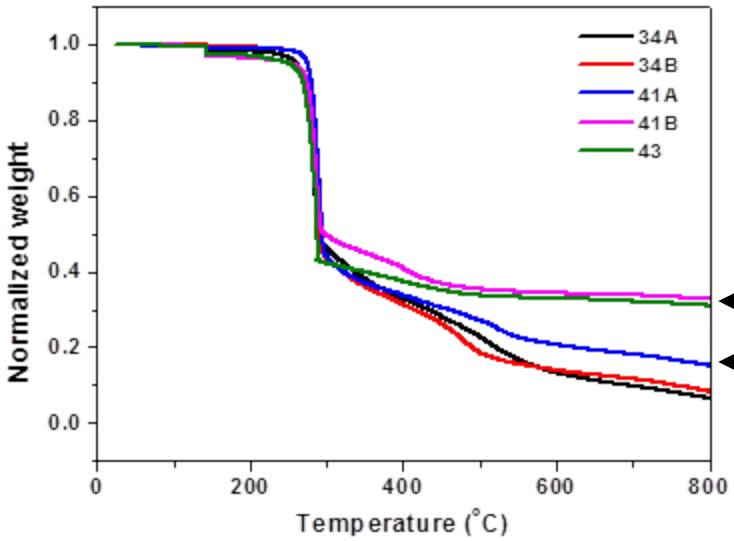


Interfacial Enveloped Composite Membranes



- **Multiple glass transition temperature**
- **Multiple regions**



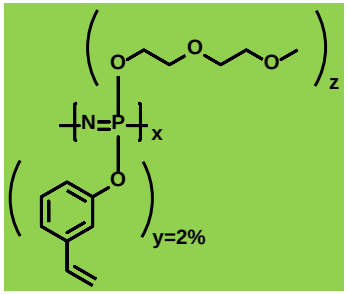


40% nano particles

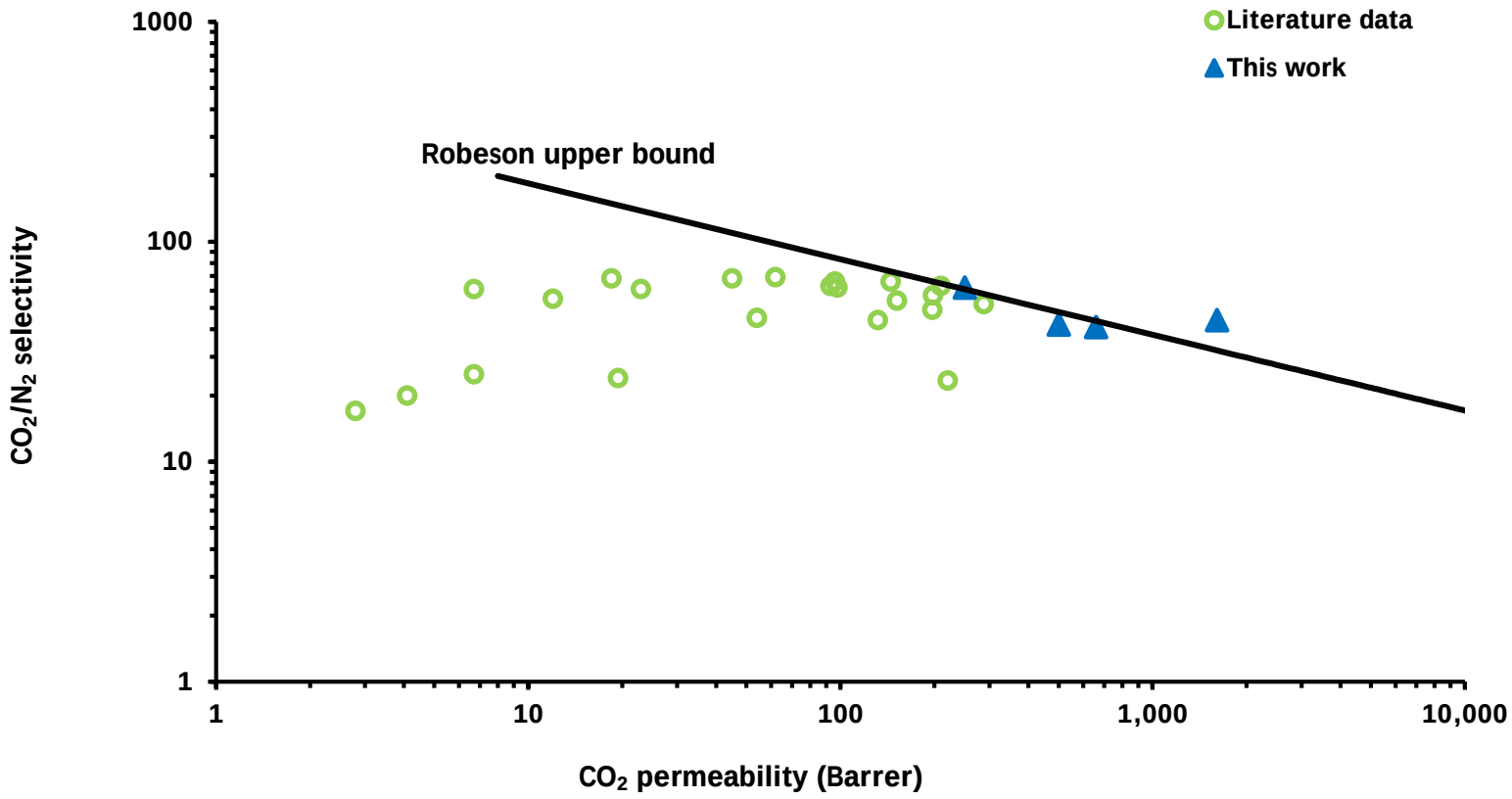
10% nano particles

Membrane performance

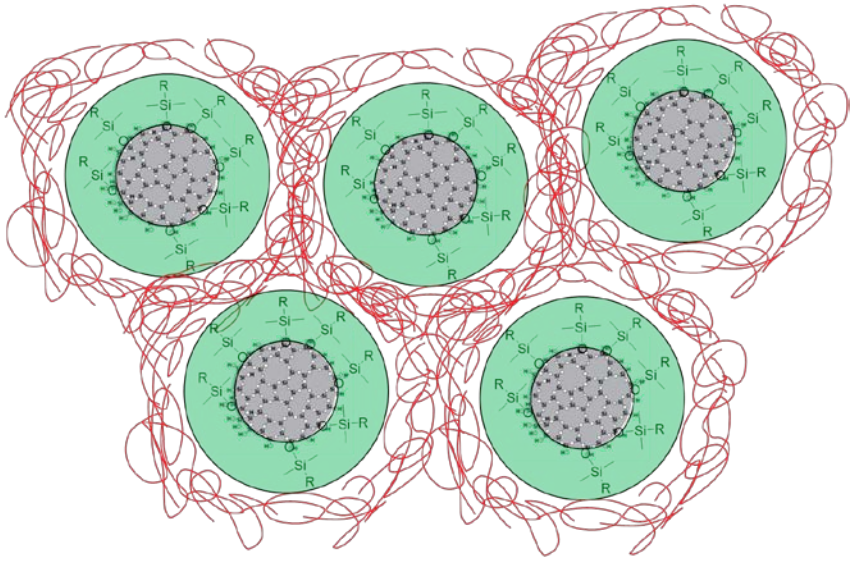
	Selectivity	Permeability (Barrer)
MEEP	62	250
MEEP-IPN	42	500
MEEP-IPN 10%	41	659
MEEP-IPN 40%	44	1609

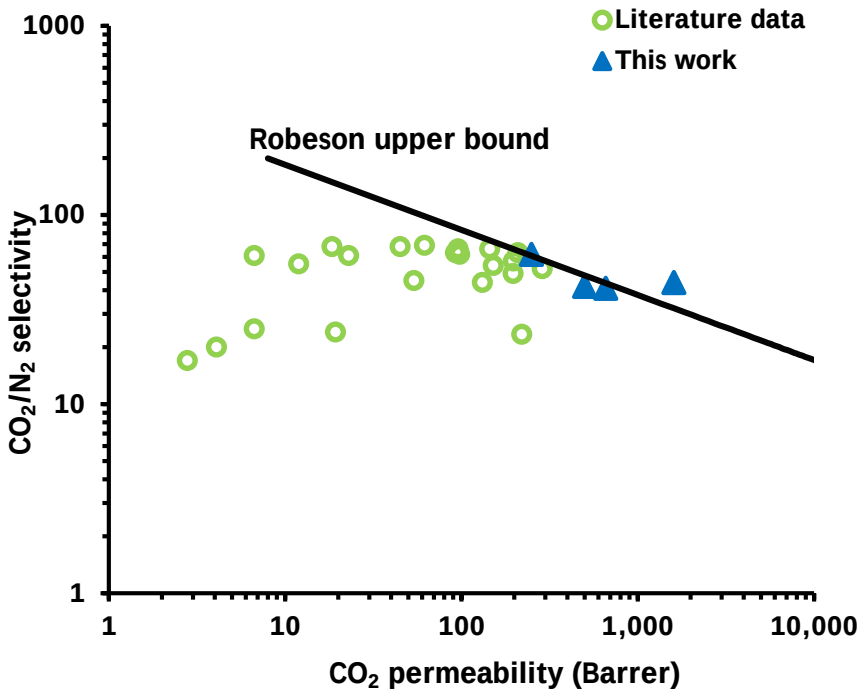


Membrane Performance



Cusp of a Major Breakthrough





Acknowledgement

Liquid Ion Solutions, Carbon Capture Scientific and Penn State University gratefully acknowledge the support of the United States Department of Energy's National Energy Technology Laboratory under agreementDE-FE0026464, which is responsible for funding the work presented.

- Dr. Scott Chen
- Dr. Zijiang Pan
- Dr. Zhiwei Li

- Prof. Harry Allcock
- Dr. Zhongjing Li

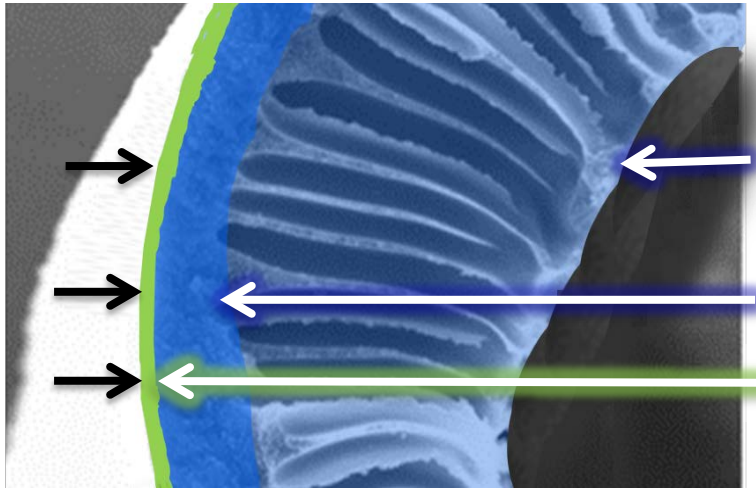
- Dr. David Luebke
- Brian Radka

NATIONAL ENERGY TECHNOLOGY LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY 1855

CCS CARBON CAPTURE SCIENTIFIC LLC

Permeability Vs. Permeance



Much Too Thick (~100 micron)

Still Too Thick (~10 micron)

Practical Membrane Thickness (~1 micron)