MTR CARBON CAPTURE

Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Carbon Capture

(DE-FE0031596)

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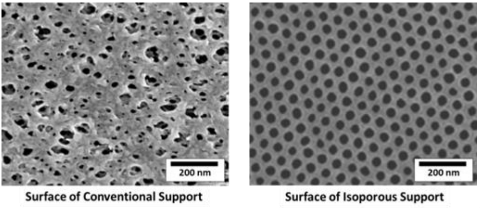
Project Details

- **Award Name:** Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture (DE-FE0031596)
- **Project Period:** June 1, 2018 – May 31, 2024
- **Funding:** $2,905,620 DOE; $726,805 cost share (MTR and University of Buffalo)
- **DOE Project Manager:** Carl Laird
- **Participants:** Membrane Technology and Research, Inc., University at Buffalo, University of Texas at Austin
- **Project Objectives:**
  1. Develop supports for composite membranes with highly regular surface pore structures that eliminate the restriction on diffusion in the selective layer that is present with current generation supports
  2. Develop improved selective materials with higher permeance and/or higher selectivity compared to the current generation Polaris material
- **Project Plan:**
  - **BP1:** Lab-scale support development, screening of novel selective materials
  - **BP2:** Lab-scale support development, scale up of selective materials, composite membrane optimization
  - **BP3:** Continue lab-scale composite membrane development; scale up optimized membrane

This Project in Context


Surface of Conventional Support

Surface of Isoporous Support

Self-Assembly Isoporous Supports, CA (DE-FE31596)

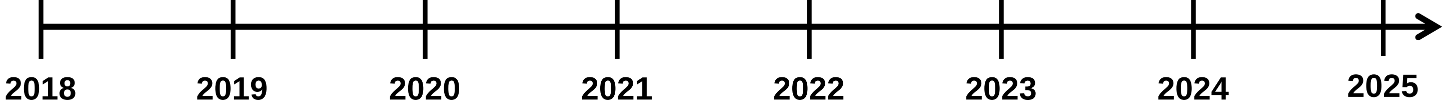
- Transformational new membrane (TRL 3 – 4)
- Reduces membrane area and energy use

Cement Engineering Study, TX (DE-FE0031949)

- Pre-FEED study at Cemex Balcones cement plant
- Cemex and Sargent & Lundy are project partners
- Use Gen2 Polaris and planar modules (TRL 6)

Large-Pilot Testing at WY ITC, WY (DE-FE31587)

- Phase I – Design 200 TPD pilot; secure host site
- Phase II – FEED and permitting
- Phase III – Fabricate, install and operate (TRL 7 – 8)

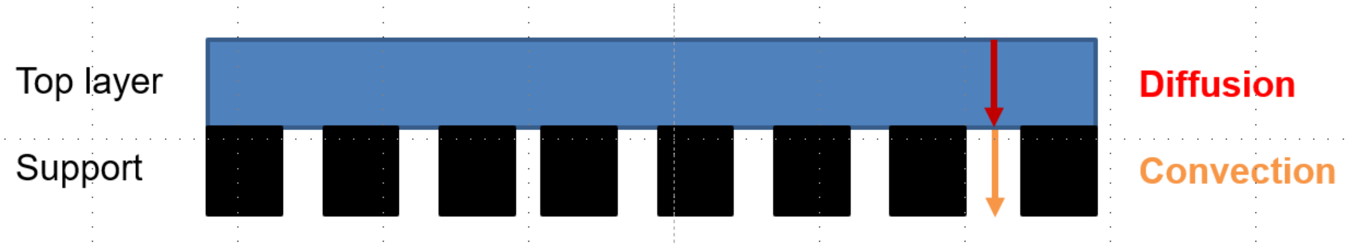


Support Membrane Background

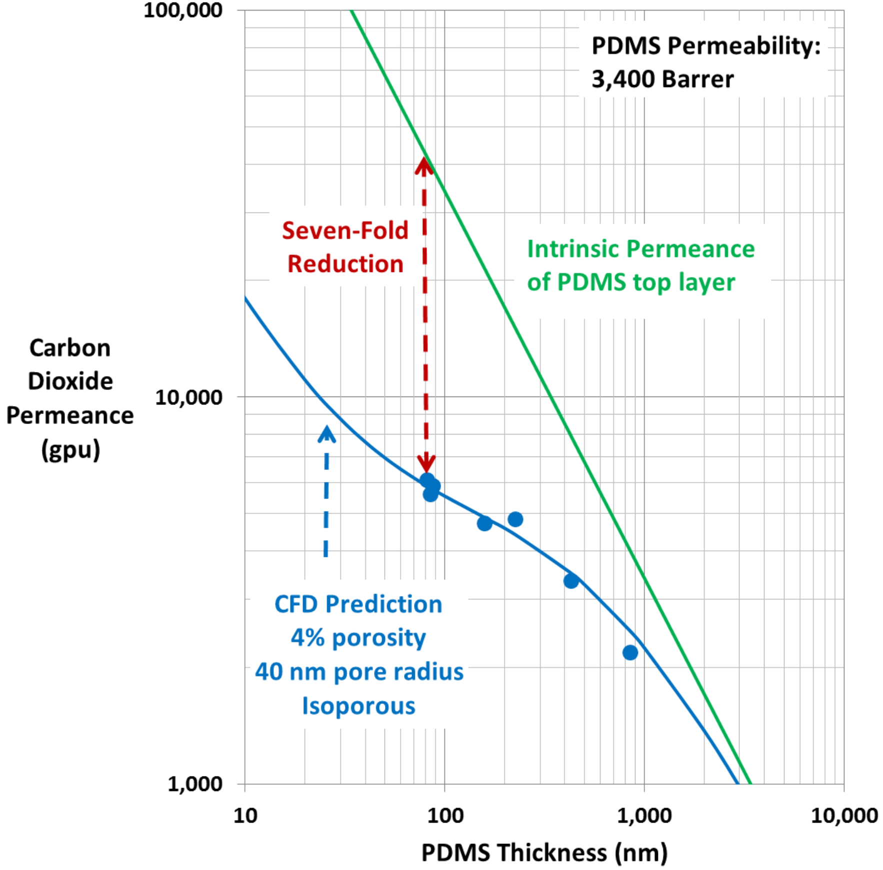
- Higher permeances are typically achieved by making composite membranes with thinner selective layers on top of a support membrane

- Experimental observation for super permeable membranes: Reducing the selective layer thickness by a factor of two **does not** double the permeance because of support resistance

- Earlier work at MTR has established that the surface pore structure of the support membrane is a limiting factor

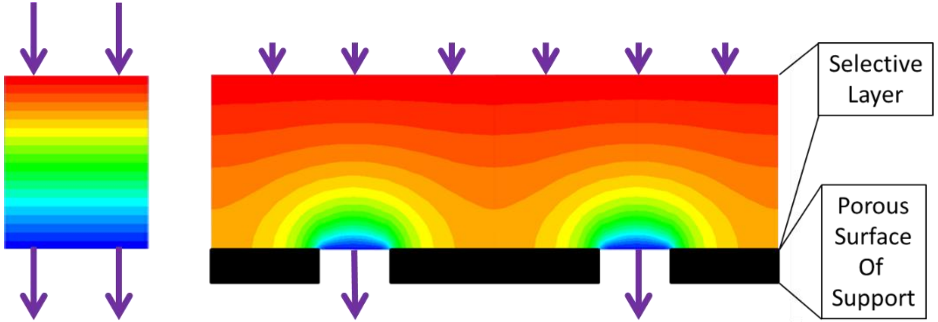


Support Resistance Data



Influence of the support is significant for highly permeable materials with coating thicknesses below 1 µm

Computational Fluid Dynamics

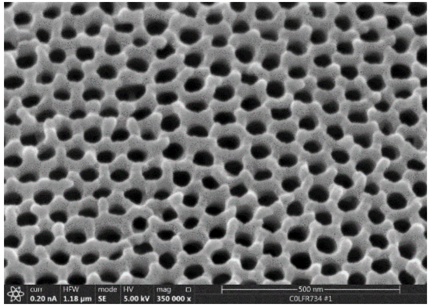


Wijmans and Hao, 2015; Ramon, et al. 2012

Conclusion from CFD analysis

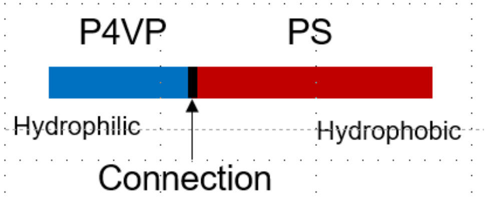
- High surface porosity and small pore radius are preferred
- Non-uniformity of pore size and/or non-uniformity of pore distribution on the surface both decrease membrane permeance

→ **Uniform iso-porous surface would be an ideal support membrane**




Asymmetric superstructure formed in a block copolymer via phase separation

KLAUS-VIKTOR PEINEMANN, VOLKER ABETZ* AND PETER F. W. SIMON

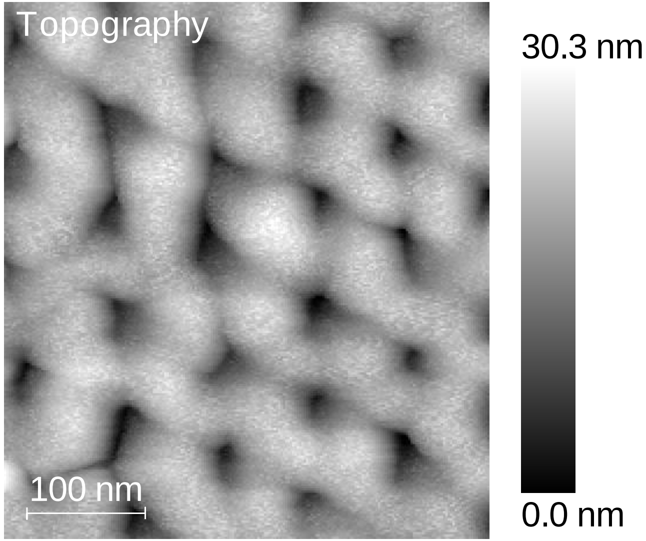


Could be an optimized substrate for super permeable membranes

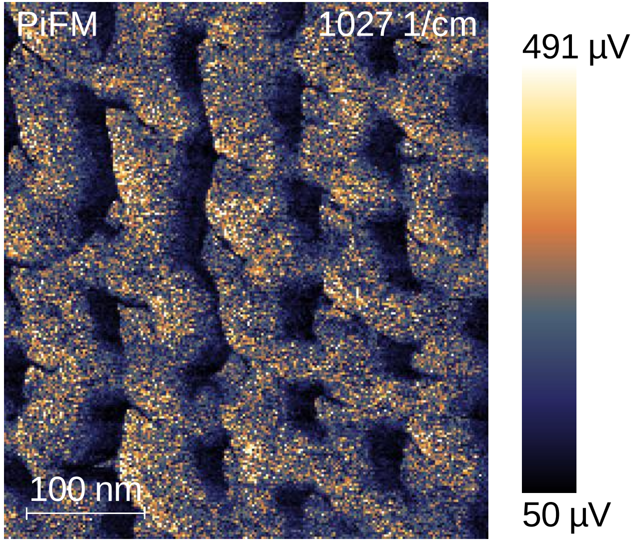
Distribution of copolymer blocks at the surface

Nanoscale InfraRed Spectroscopy + Photo-induced Atomic Force Microscopy

AFM mode, no IR

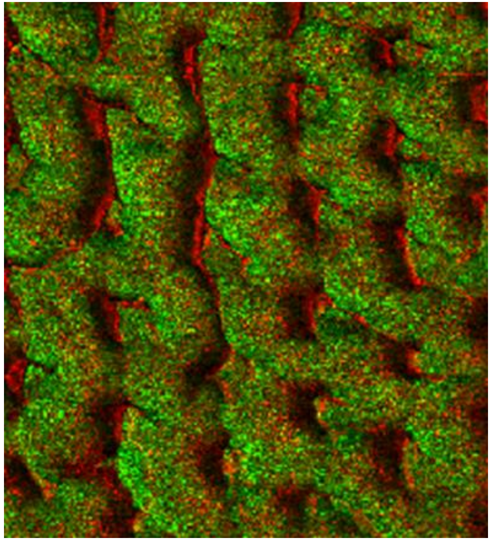


AFM plus IR at 1027 cm^{-1} (PS)



1027 cm^{-1} (PS)

AFM plus IR



🟩 1027 cm^{-1} (PS)

🟥 820 cm^{-1} (P4VP)

PS-b-P4VP block copolymer

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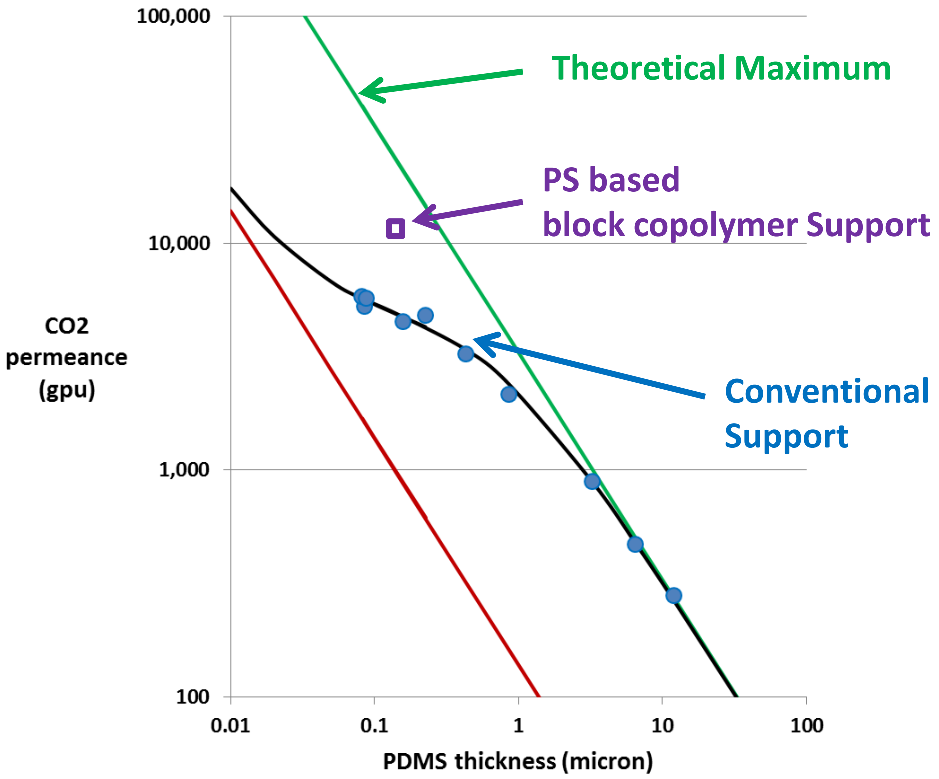
Support made from perfect block copolymer

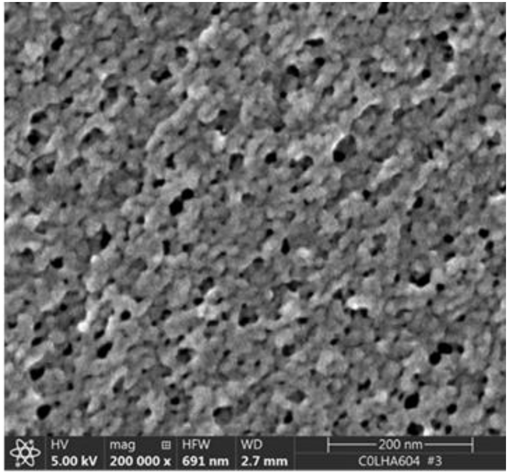
- Result confirms that a better surface results in an increase in permeance
- Permeance of uncoated support is 162,000 gpu; with pdms coating 11,800 gpu
- However, sample is too small to be coated with Polaris layer
- Also, fabrication of the iso-porous support from these materials is difficult to control and scale up



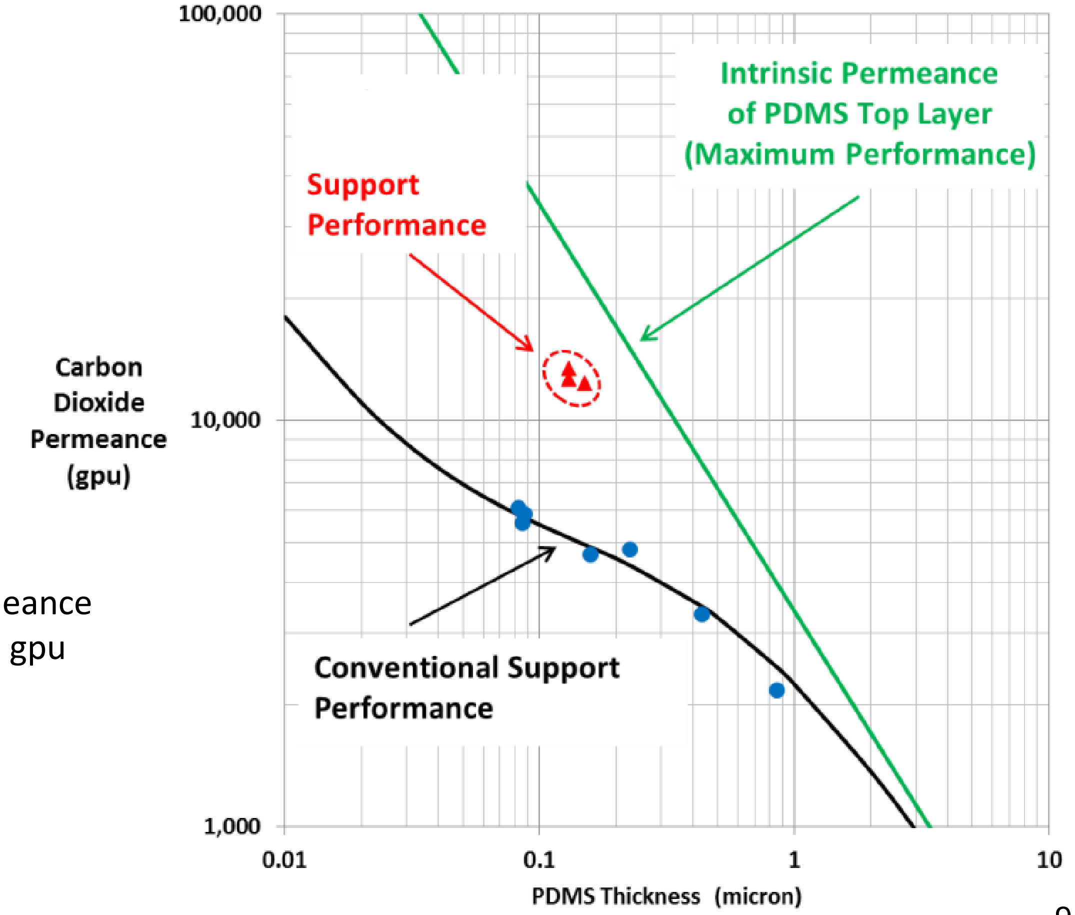
Support made from imperfect block copolymer

- Block copolymer made by UT Austin by attaching a hydrophilic block to a widely used hydrophobic polymer

- Excellent support membrane, even though the surface is not truly isoporous:



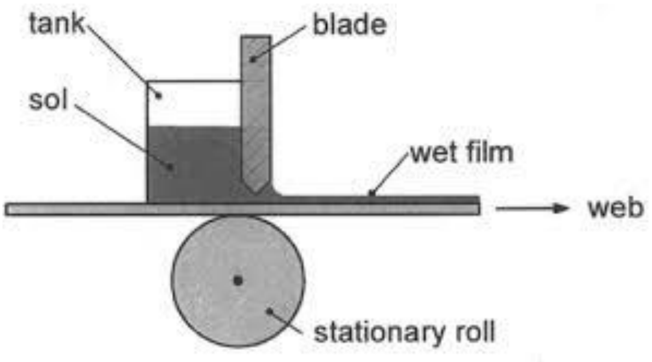
N2 permeance = 95,000 gpu



Dual Slot Die Casting

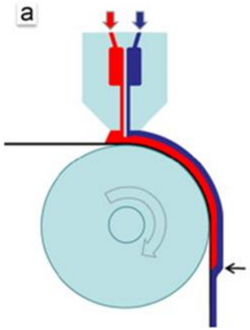
Blade Casting (traditional):

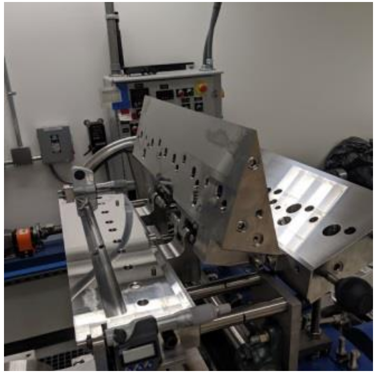
- Common method for membrane casting
- Simple equipment, simple operation
- Allows for deposition of only one layer

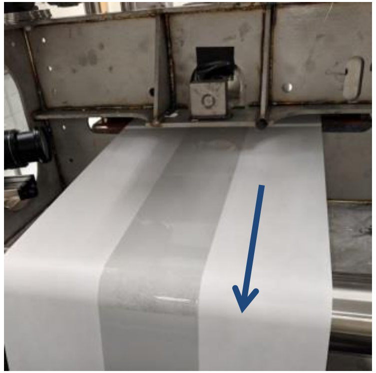


Slot Die Casting (this project):

- Allows deposition of multiple layers
- Better control of thicknesses
- More complicated, but used on large scale in many industrial film operations



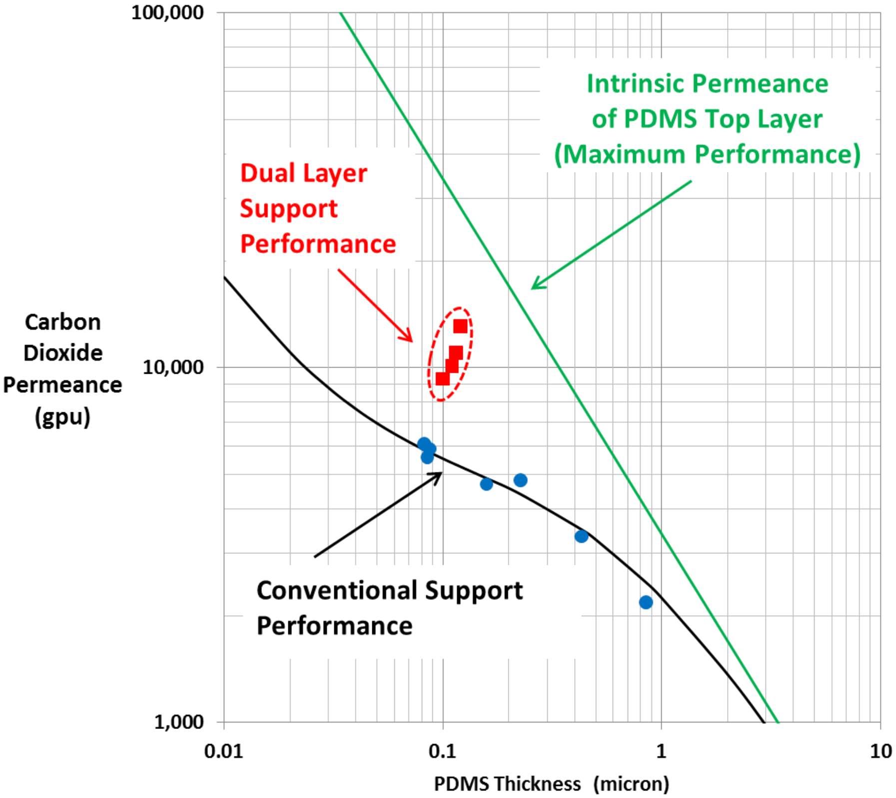




Support made with Dual Slot Die

- Advantage of Dual Slot Die is that the top and bottom layers can be made with different casting solution formulations
- This allows optimization of top layer for surface properties
- And allows optimization of the bottom layer for mechanical strength

- **Dual Slot Die produces a better support, even with conventional polymers**



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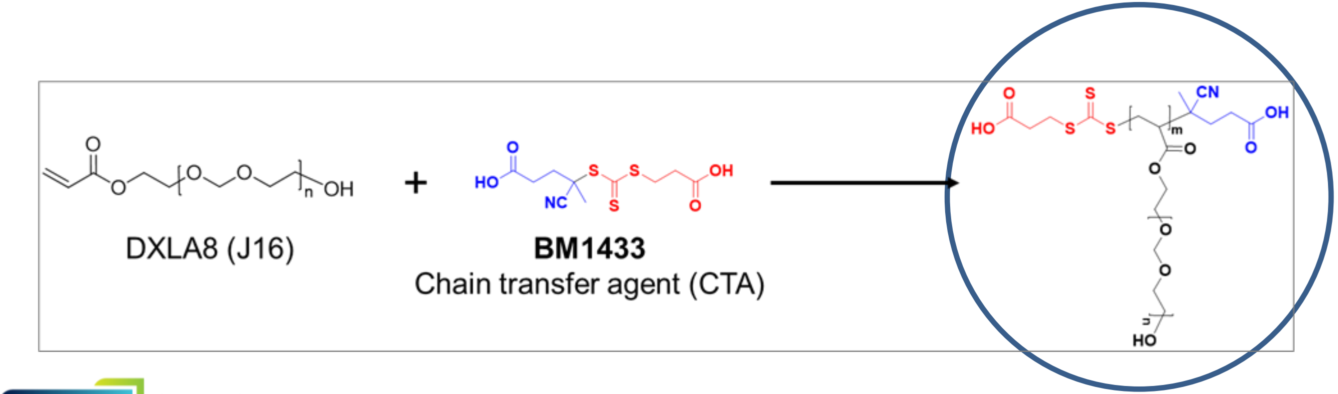
Novel Selective Layer Materials

- At the start of the project, the approach was based on earlier work at SUNY Buffalo
  - Buffalo makes a “macro-monomer”, then crosslinks the material as a film (100 micron thick)
  - MTR tried to develop coating solutions with these macromonomer to obtain composite membranes with selective layer thickness below 1 micron
  - This turned out to be very difficult: coating solutions not capable of producing defect-free thin films
- A joint effort of Buffalo and UT Austin led to the successful development of a polymerization procedure based on Reversible Addition Fragmentation Chain Transfer (RAFT).
- MTR was able to convert these materials into successful thin film composite membranes

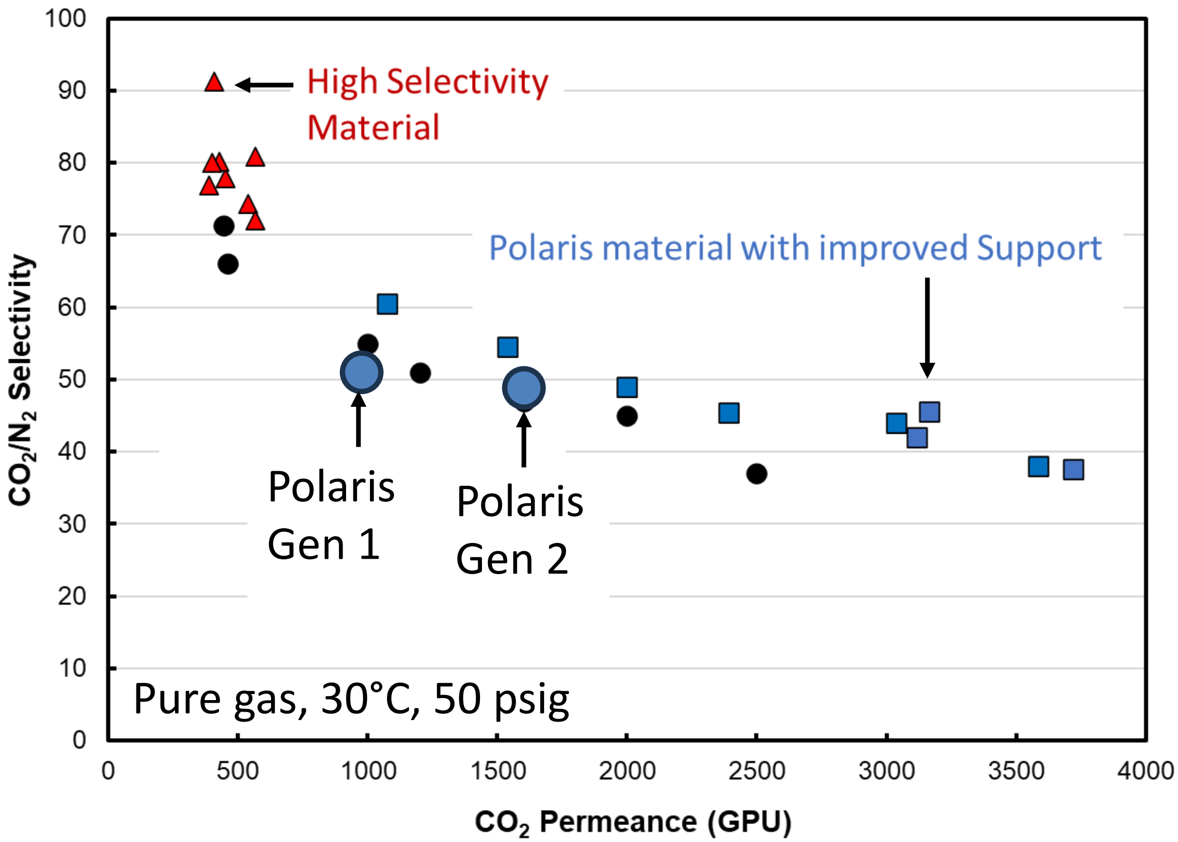


DXLA8 (J16)

BM1433
Chain transfer agent (CTA)

A highly branched polymer

Improved Polaris Membranes



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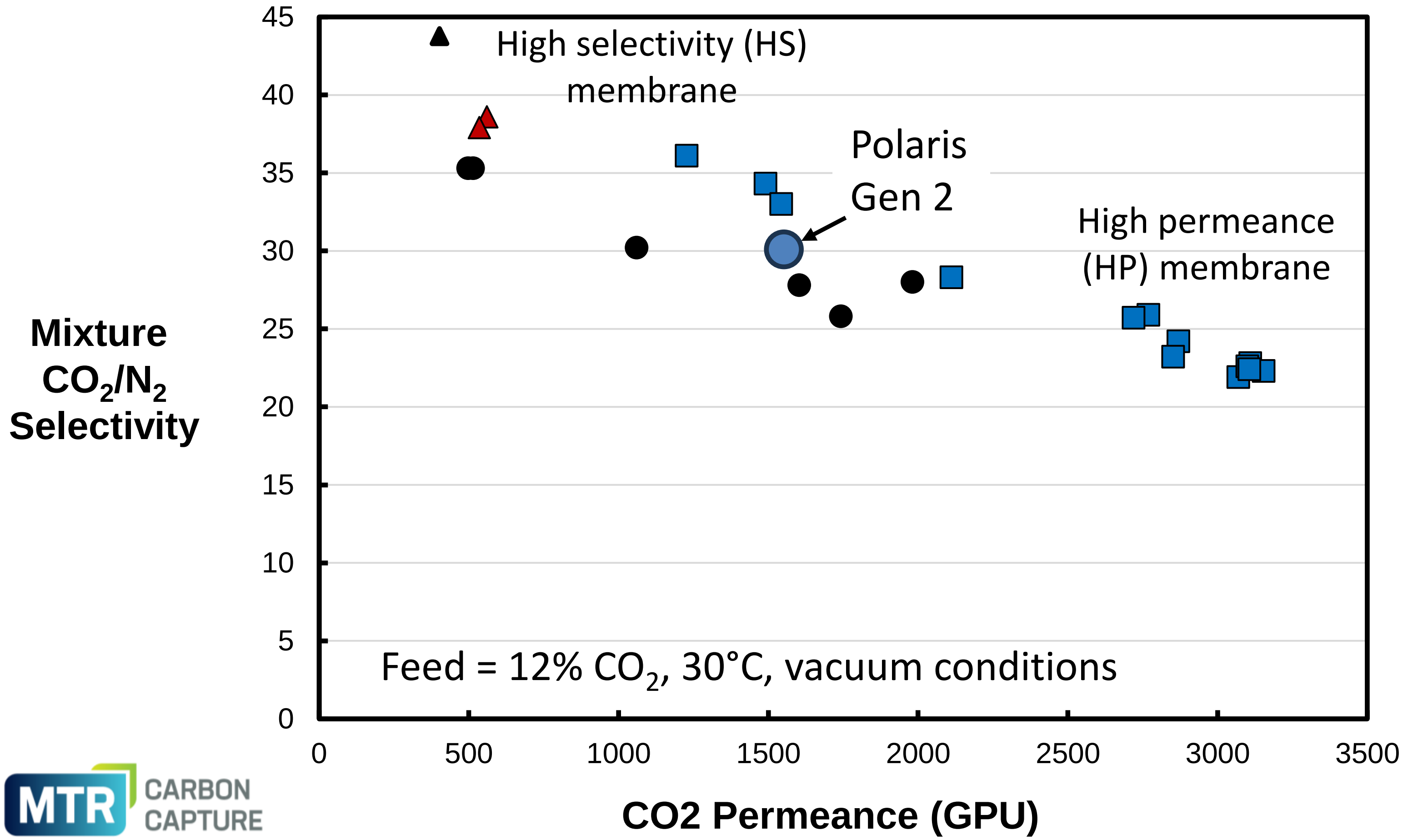
Improved Polaris Membranes (Mixed gas)



Preliminary Technoeconomic Analysis

Calculations performed for three different membranes:

Polaris version	CO2 Permeance (gpu)	CO2/N2 Selectivity (-)
A – Polaris Gen 2	1,500	30
B – Polaris Gen3 HP	2,500	25
C – Polaris Gen 3 HS	500	45

- 90% capture from a 12% CO_2 feed stream
- Equipment costs/performance based on Dry Fork Station FEED study (May 2022 $)
- Standard MTR capture process uses 2 stages of membranes; possible benefits of different membranes for different stages?

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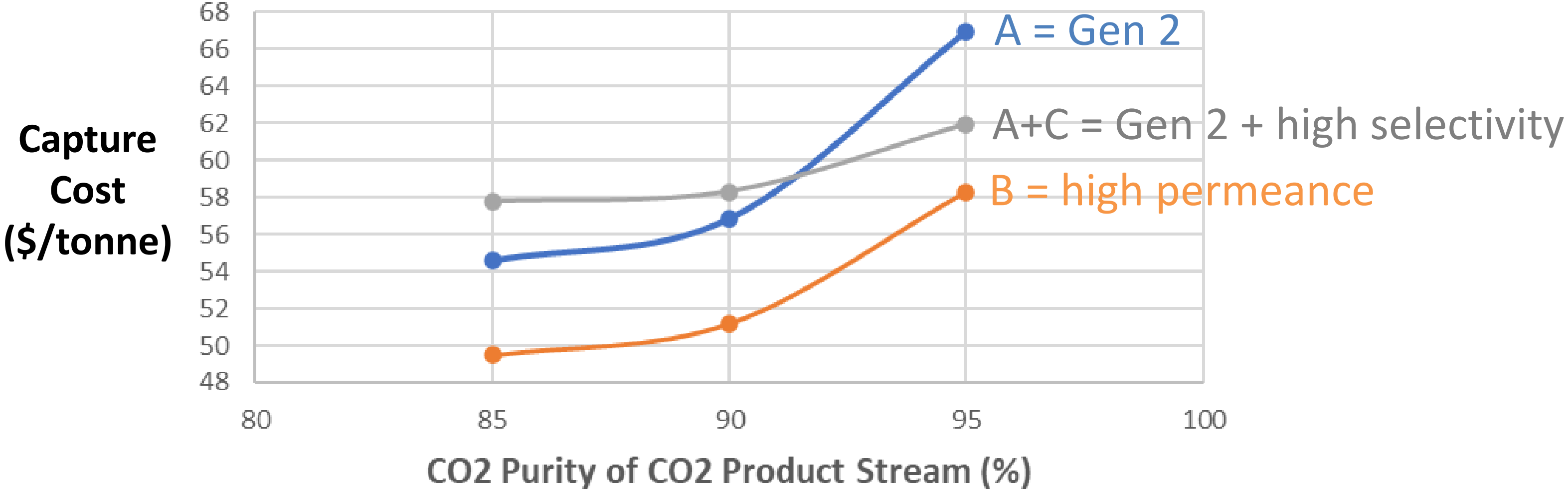
Impact of Membrane Properties on Cost



- Compared to the Polaris Gen2 membrane (A), the high permeance Gen 3 membrane (B) lowers capture cost by ~15%
- High selectivity Gen 3 membrane (C) can help slightly lower costs at high CO_2 purity; however, its benefit is limited by the lower permeance, which causes higher membrane area (capex)

Summary and Future BP3 Activities

- An improved support and new selective layer materials have been converted into high selectivity and high permeance composite membranes
- Design studies show that:
  - High selectivity membrane needs to reach at least 1000 gpu to be useful in the process second stage
  - Currently achieved high permeance membrane has significant cost reduction benefits (~15% vs Gen 2)
- Currently scaling high permeance membrane (Polaris Gen 3) to commercial roll-to-roll production equipment; permeance >3000 gpu appears attainable
- Remaining tasks: perform updated Techno-Economic Analysis, Technology Gap Analysis and EH&S Risk Analysis to include in final report

Acknowledgements

- U.S. Department of Energy

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  Carl Laird, Krista Hill

- University at Buffalo

  Haiqing Lin

- University of Texas at Austin

  Nathaniel Lynd

Thank You

Questions?

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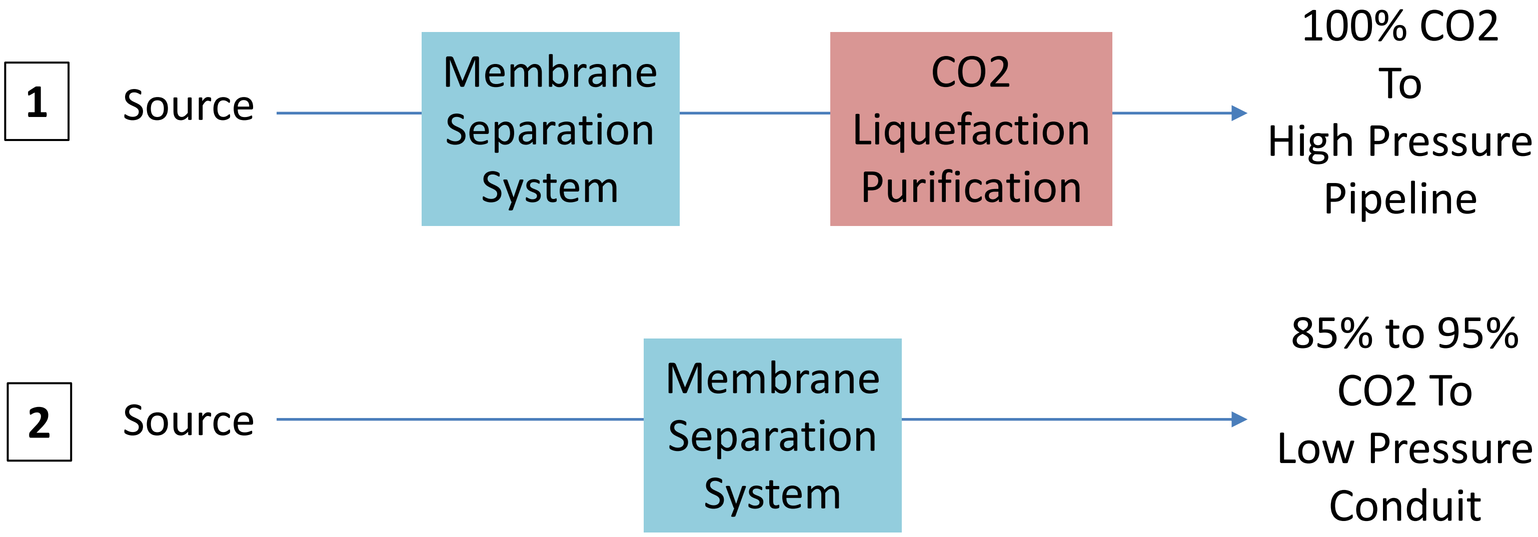
Extras/Old

Project Objectives

- Combine new advances in membrane substrates and selective layers to produce an advanced (Gen 3) Polaris membrane
  - BP3 success criteria: high-permeance composite membrane with CO2 = 4000 gpu and CO2/N2 = 25 (mixed gas) and,
  - High selectivity membrane with CO2 = 2000 gpu and CO2/N2 = 50 (mixed gas)
- Show how Gen 3 membrane could be incorporated into MTR's continuing technology scale up to reduce the cost of capture

Preliminary Technoeconomic Analysis



- The membrane system consists of multiple stages, which makes it possible to combine different membrane types in one system
- Option 2 is emerging as a viable option for capture systems that are co-located with a saline aquifer storage facility and do not require a CO2 pipeline

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Technical and Economic Analysis

Three different membrane performances:

	CO2 Permeance (gpu)	CO2/N2 Selectivity (-)
A	1,500	30
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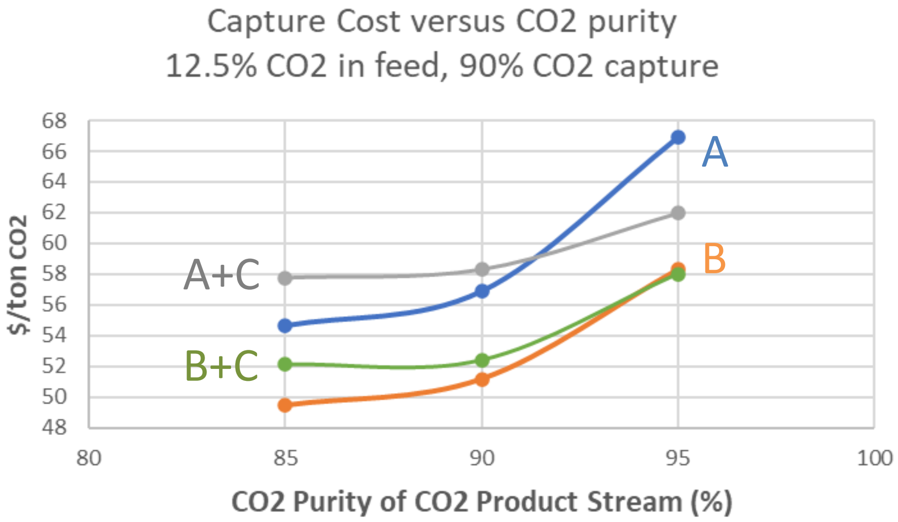

High selectivity membrane improves process at 95% purity CO2 product stream.

Improving CO2 permeance from 500 to 1,000 gpu will result in lower capture costs at product purities below 95%.

Technical and Economic Analysis

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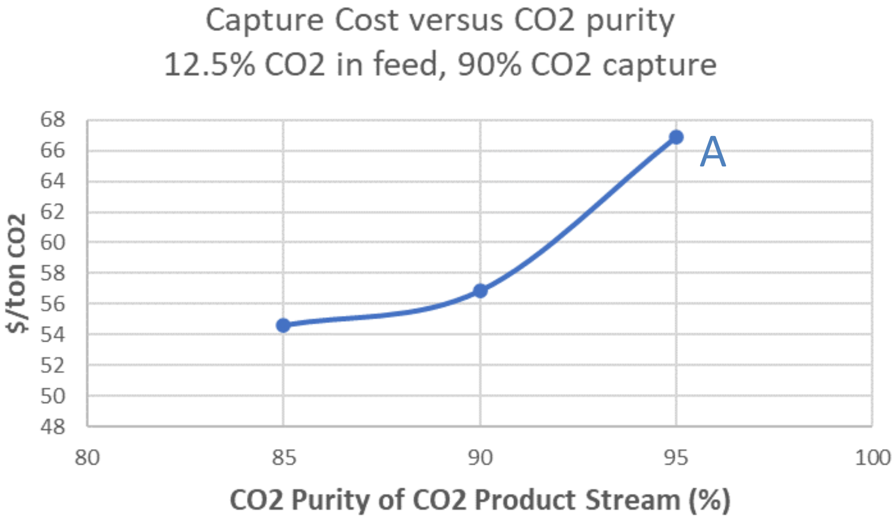
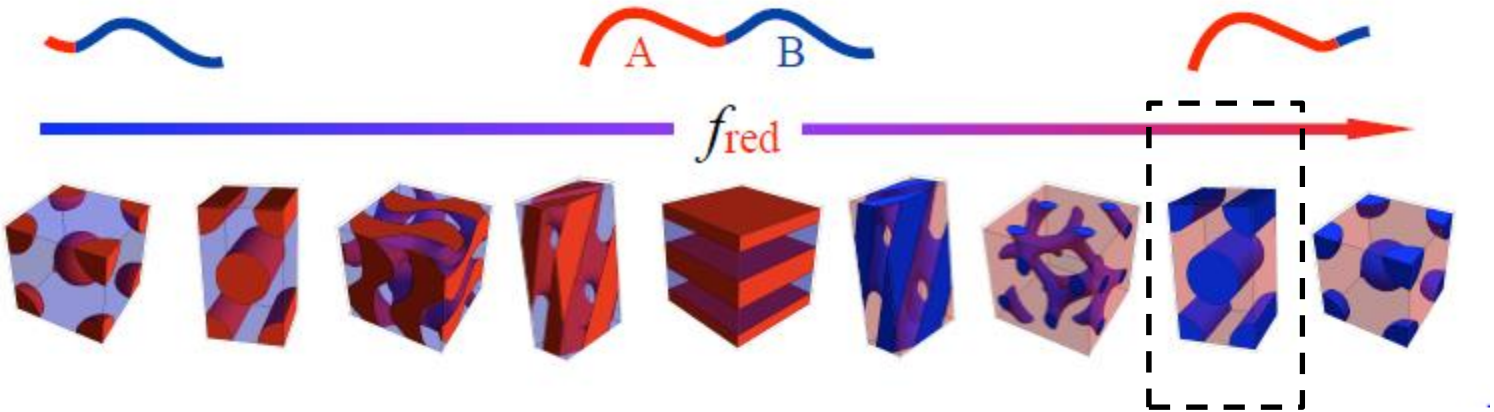


Self Assembly

Amphiphilic block copolymer: A is hydrophobic, B is hydrophilic.

Separately A and B are not compatible, but in the block copolymer they are connected.

This leads to assembly into a range of different morphologies, depending on composition.



Desired morphology

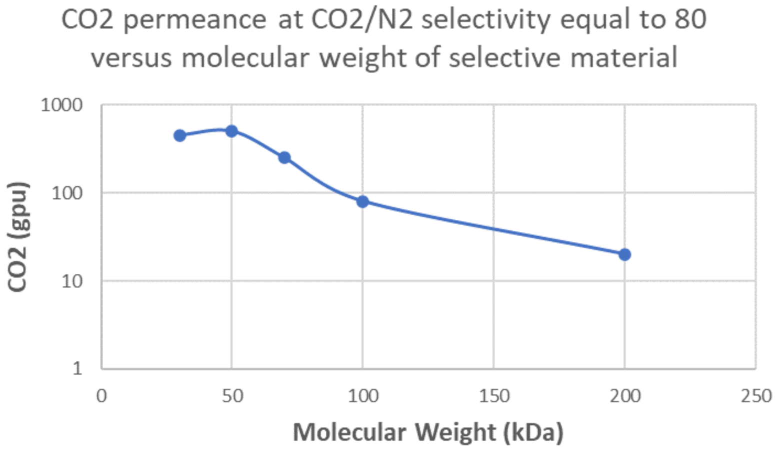
Novel Selective Materials: Composite Membranes

- Generally, a higher molecular weight polymer leads to higher quality coated layer
- However, for this branched polymer we found an optimum molecular weight of 50,000 Da

- Possible explanation: at the same coating concentration, the coating solution contains fewer (although larger) polymer spheres.

At 50,000 Da, the best mixed gas properties are:

CO2 permeance = 500 gpu
CO2/N2 selectivity = 45



Technical and Economic Analysis

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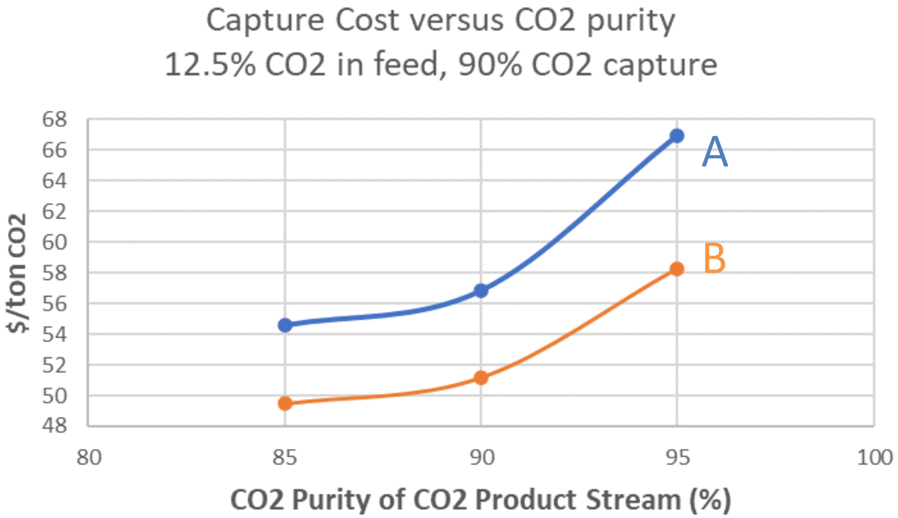
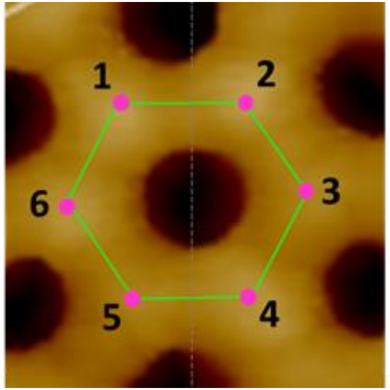
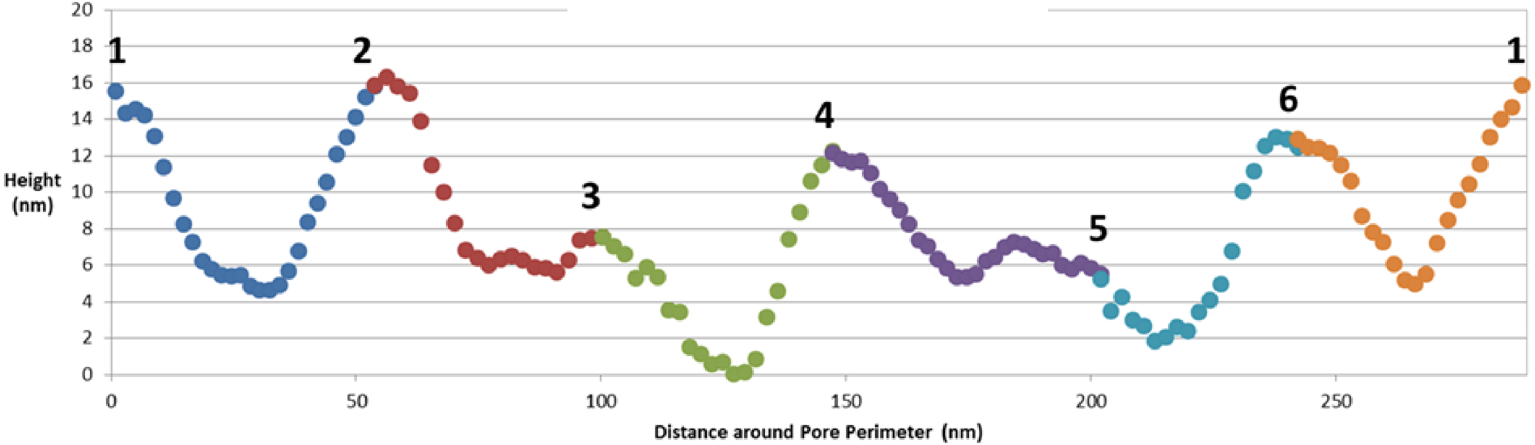


Height Profile around the Pore

- Confirms the hypothesis that a pore is created by assemblies of six spherical micelles
- The remnants of six micelles surround the pore at the surface and the profile reveals that the spheres have not been completely flattened

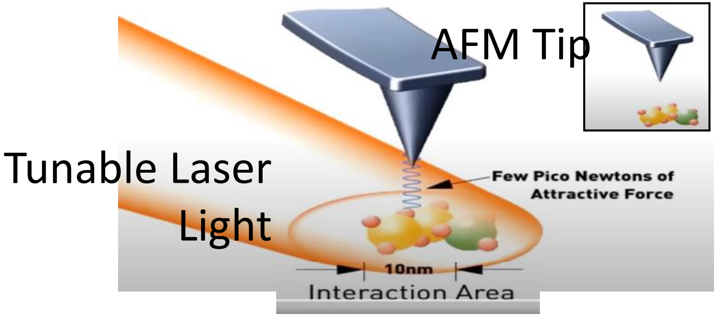


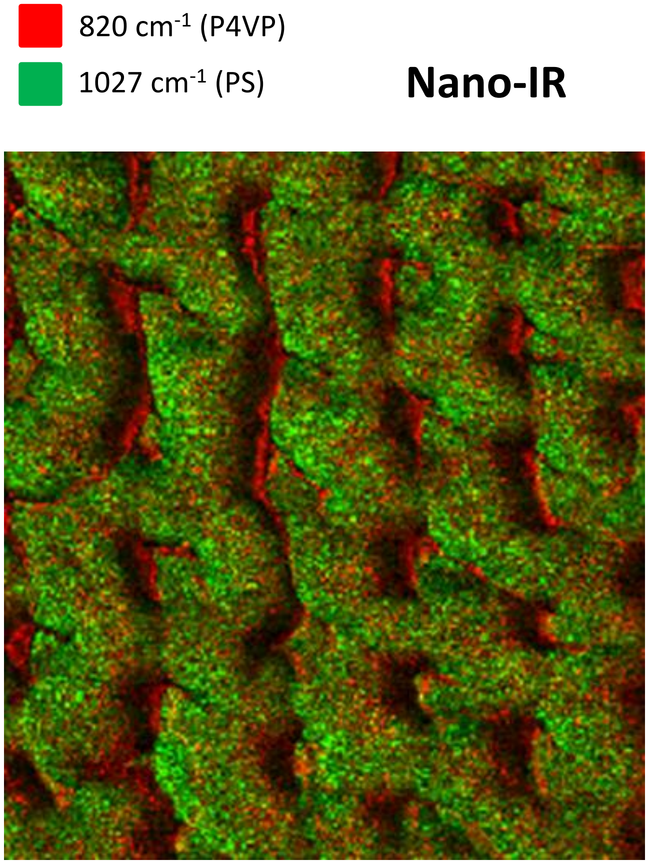
Atomic Force Microscope



Nano-IR + PiFM reveals distribution of the Blocks

- Polystyrene forms the bulk of the support
- Polyvinylpyridine lines the pores
- Top surface shows traces of polyvinylpyridine which is consistent with a top surface covered by a polyvinylpyridine layer of about 5 nm thickness (Nano-IR depth penetration is about 20 nm)





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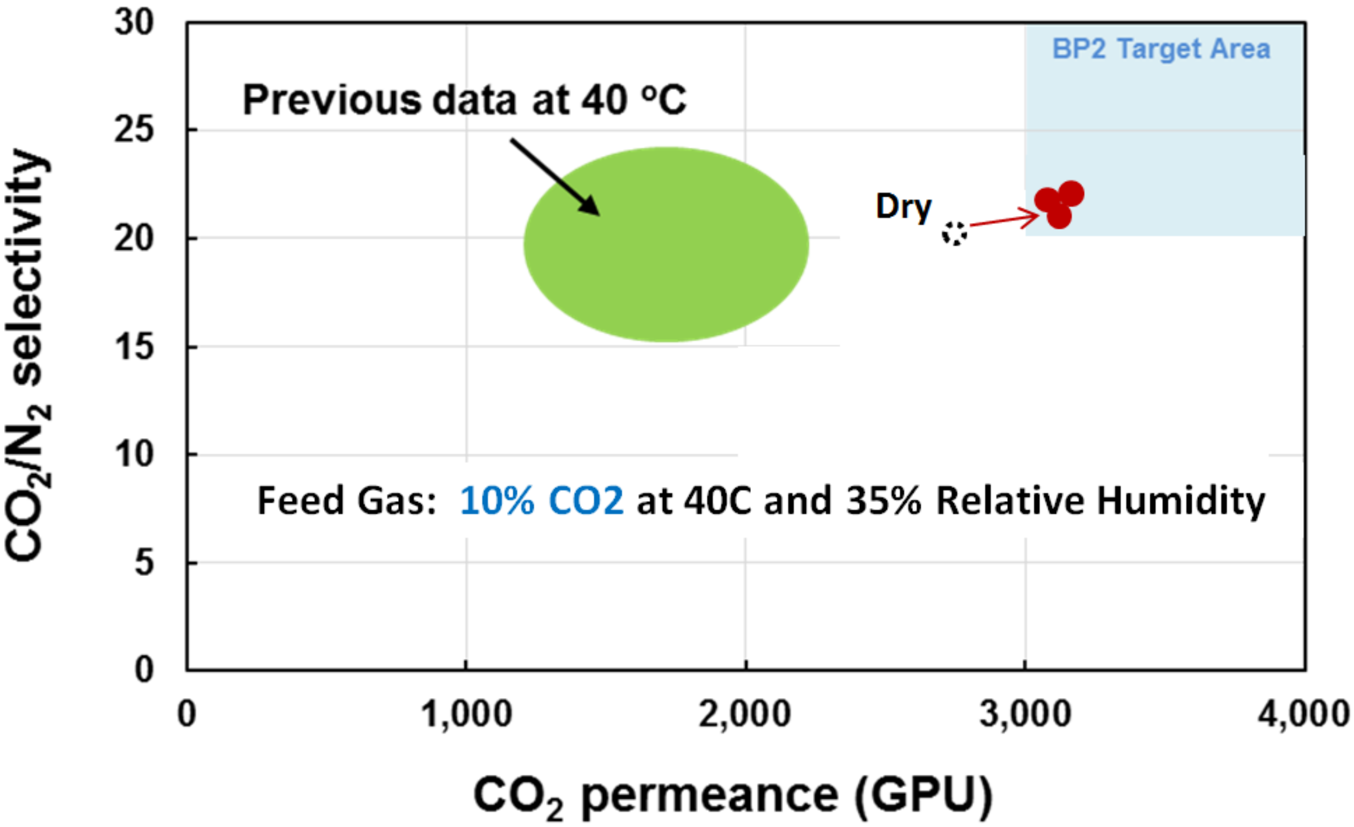
Current Best Polaris Membrane Performance



Feed Gas: 10% CO2 at 40C and 35% Relative Humidity

Selectivity and permeance increase with increasing CO2 concentration

Selectivity increases and permeance decreases with decreasing temperature

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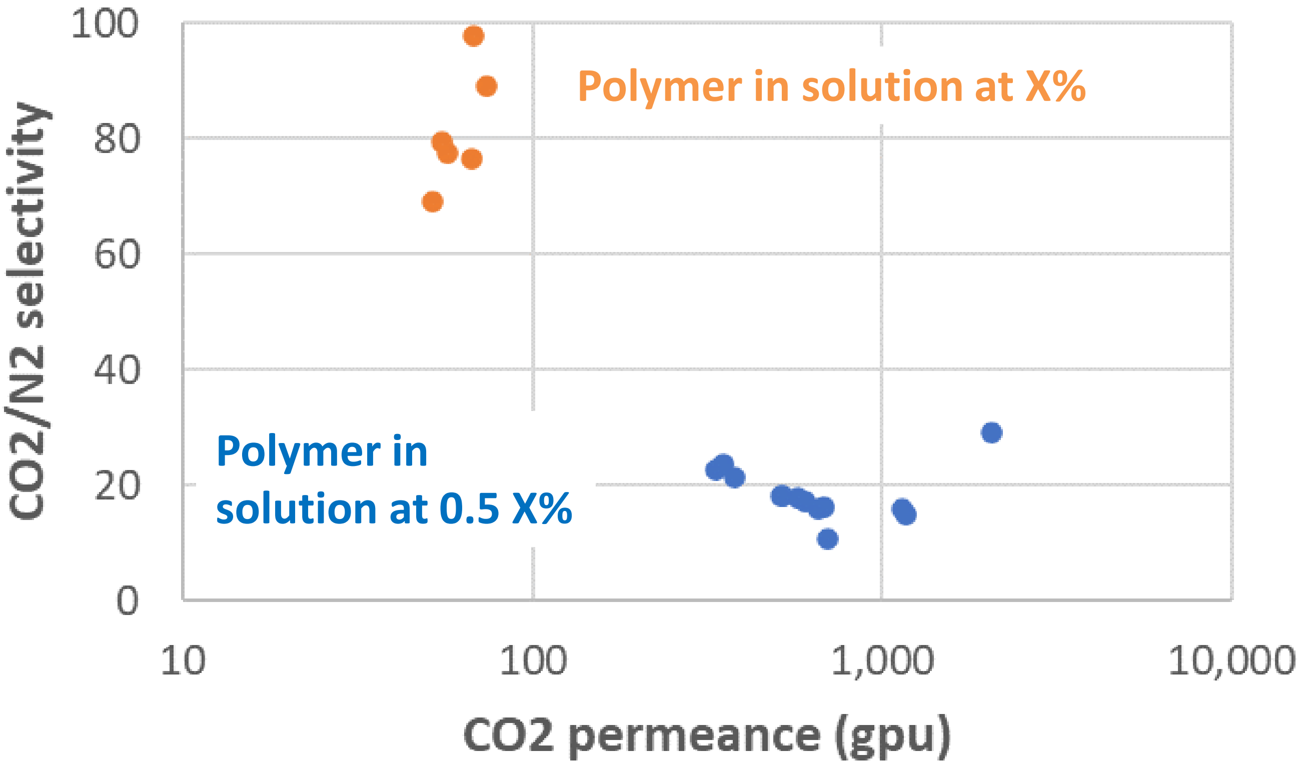
Novel Selective Materials

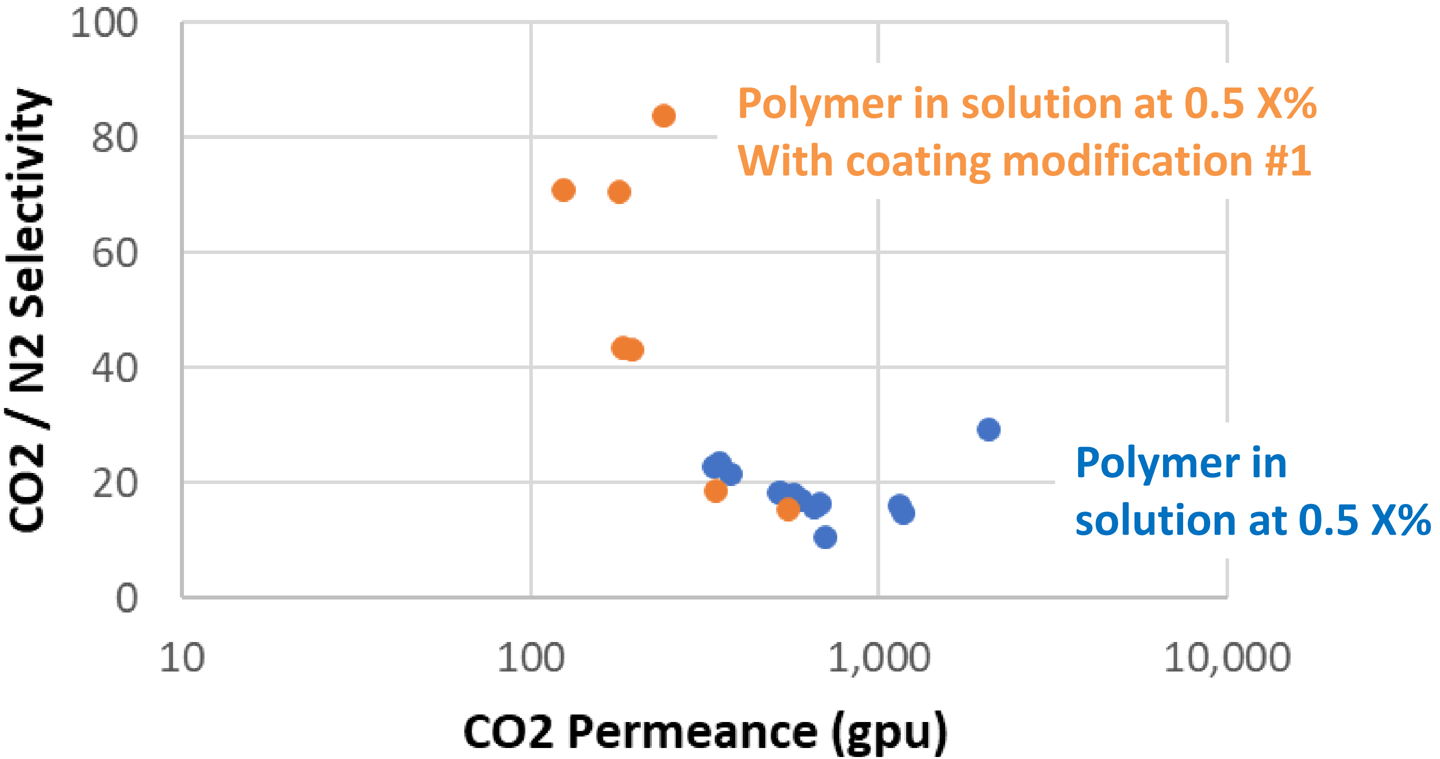
Party	Role
U Buffalo	Polymer preparation: Reversible addition−fragmentation chain-transfer polymerization (RAFT)
U Texas	Polymer preparation: Two different pathways to macro-monomers, followed by free radical polymerization
MTR	Preparation of support membranes Preparation of composite membranes Pure gas testing Gas mixture testing

In the first months of BP3, MTR has worked exclusively with polymers provided by the University at Buffalo.

Composite Membranes with Novel Material

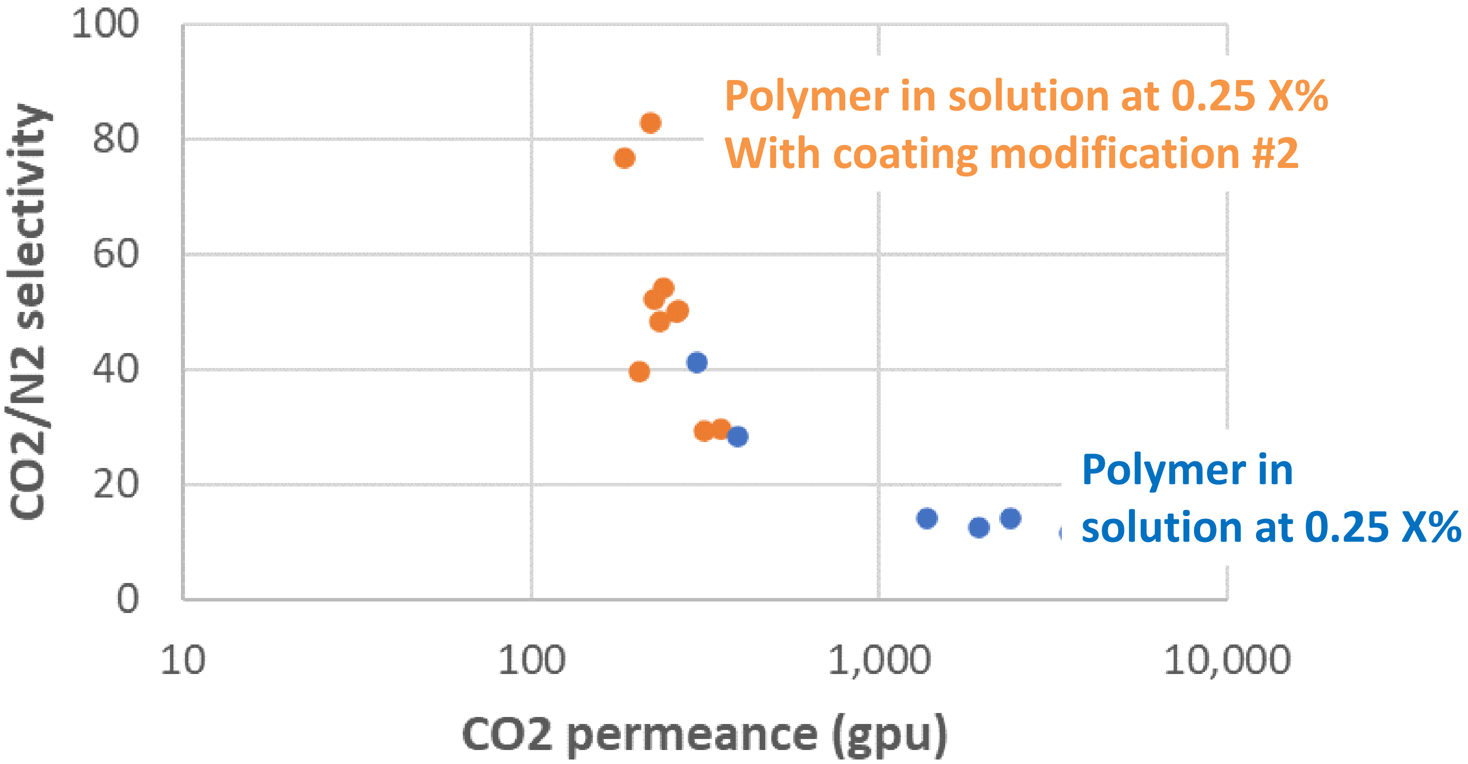


Coating Procedure Optimization



MTR CARBON CAPTURE

Coating Procedure Optimization



Polymer in solution at 0.25 X%
With coating modification #2

Polymer in solution at 0.25 X%

Topics

- Improved Support Membranes
- Higher Selectivity Membranes
- Improved Membranes with original Polaris materials
- Technical and Economic Analysis