Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Carbon Capture (DE-FE0031596)

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DOE NETL CO2 Capture Technology Project Review Meeting
Pittsburgh, August 8, 2024

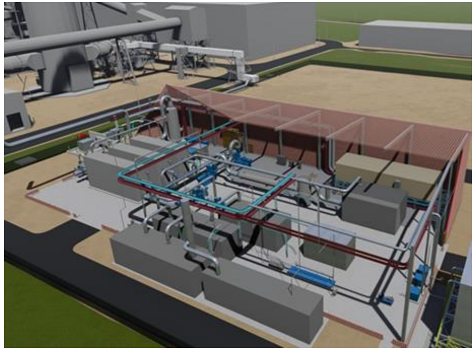
Project Details

- **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 **(Project period has ended)**
- **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, Prof. Haiqing Lin
  University of Texas at Austin, Prof. Nathaniel Lynd

This Project in Context

- MTR has been developing a membrane-based carbon capture process for over ten years
- Critical steps:
  - Membrane development
  - Module development
  - Process development
- These have to be optimized individually as well as optimized in integrated form

- Large Pilot Testing system is nearing completion at Dry Fork Station, Wyoming
- 150 TPD capacity



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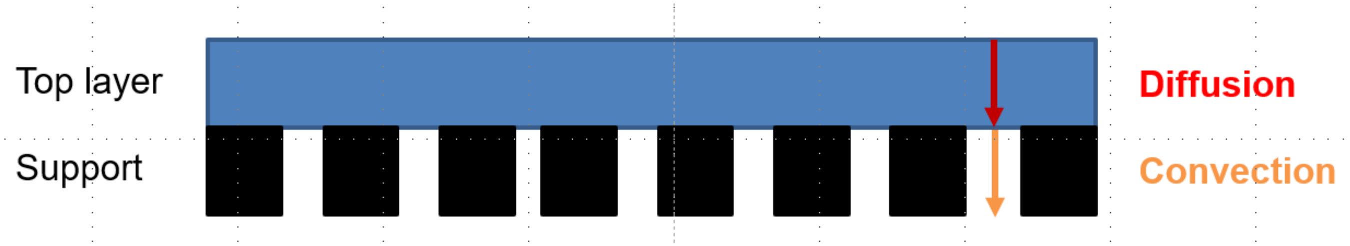
Support Membrane Background

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

- Experimental observation for highly 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



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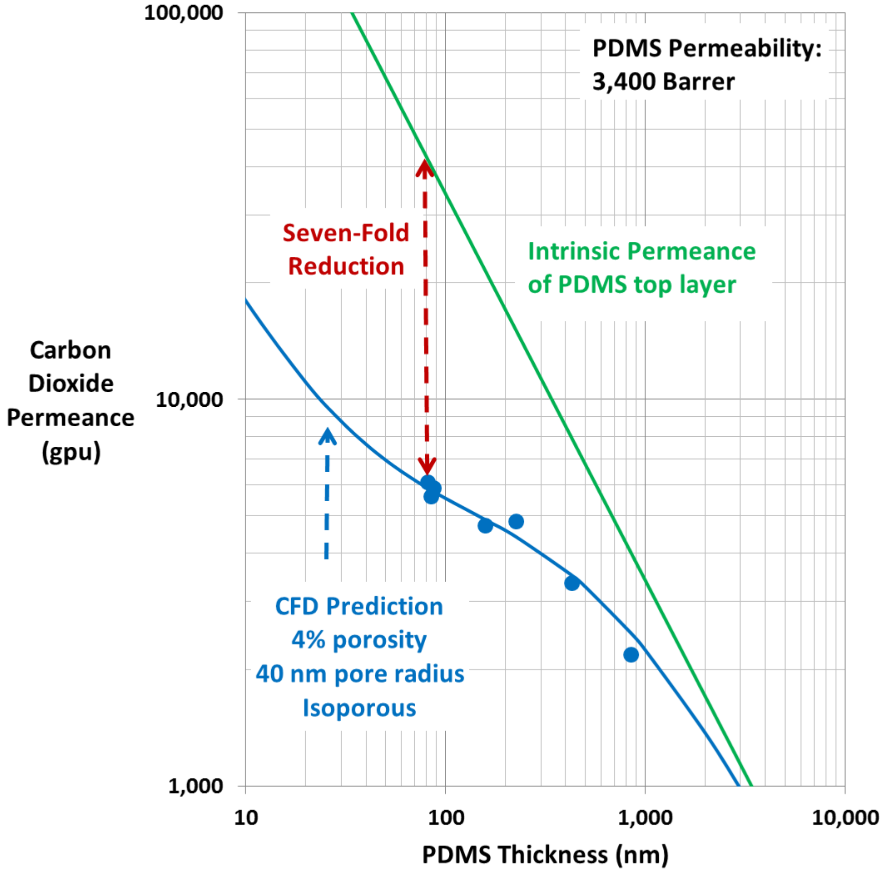
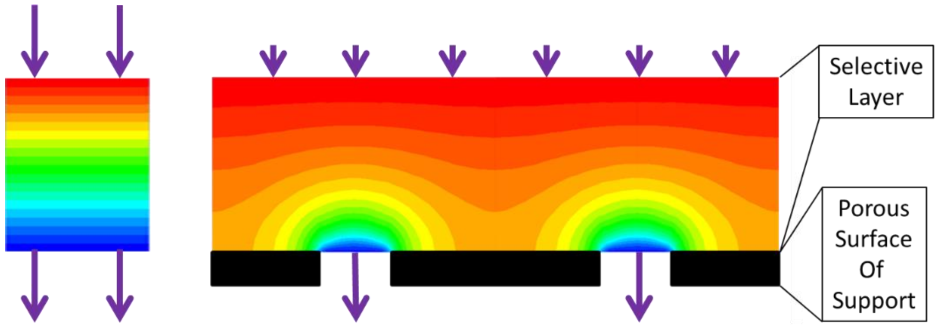
Support Effect is Significant



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

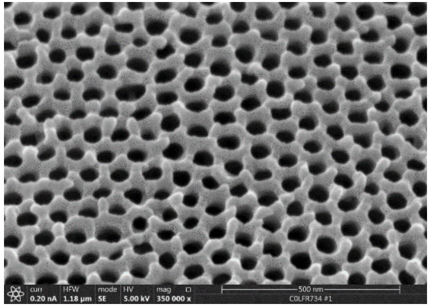
Computational Fluid Dynamics



Conclusion from CFD analysis

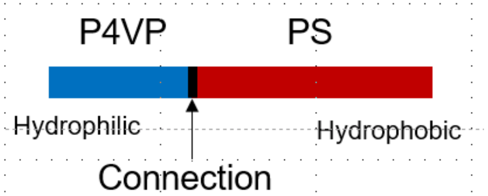
- High surface porosity and small pore radius are preferred
- Non-uniformity of pore size and/or non-uniformity of pore distribution on the surface both decrease membrane permeance

→ **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 very highly permeable membranes

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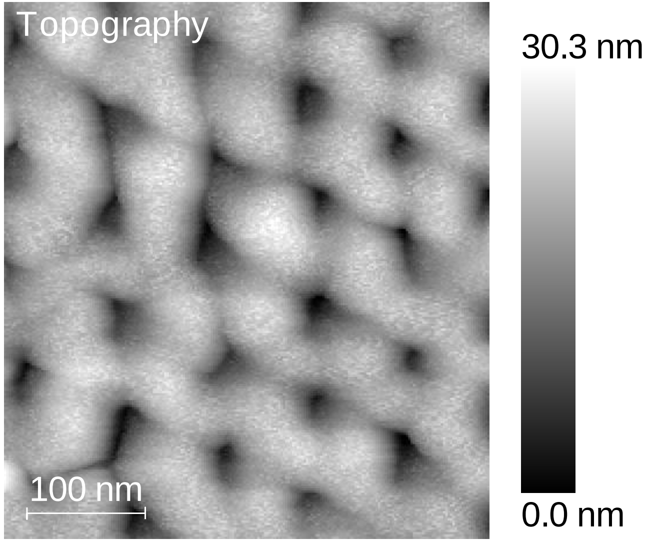
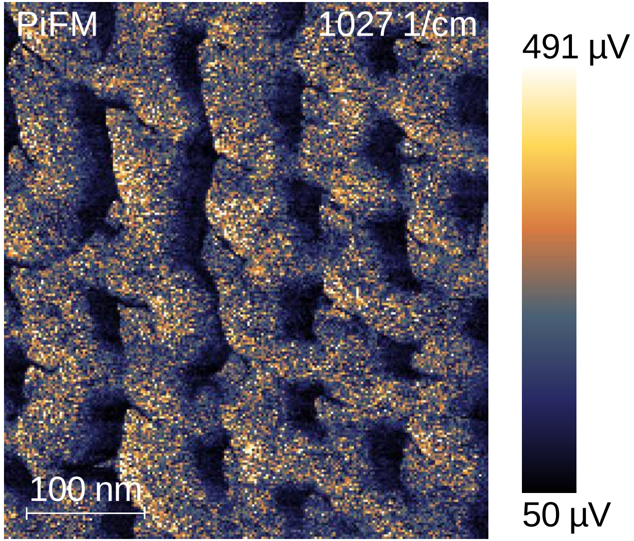
Distribution of copolymer blocks at the surface

Nanoscale InfraRed Spectroscopy + Photo-induced Atomic Force Microscopy

AFM mode, no IR

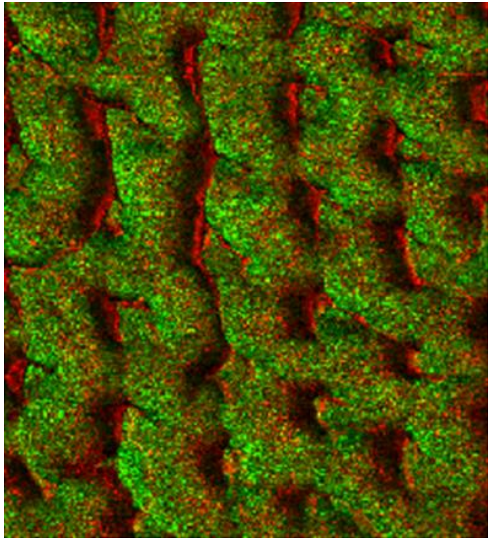


AFM plus IR at 1027 cm^{-1} (PS)



1027 cm^{-1} (PS)

AFM plus IR



1027 cm^{-1} (PS)

820 cm^{-1} (P4VP)

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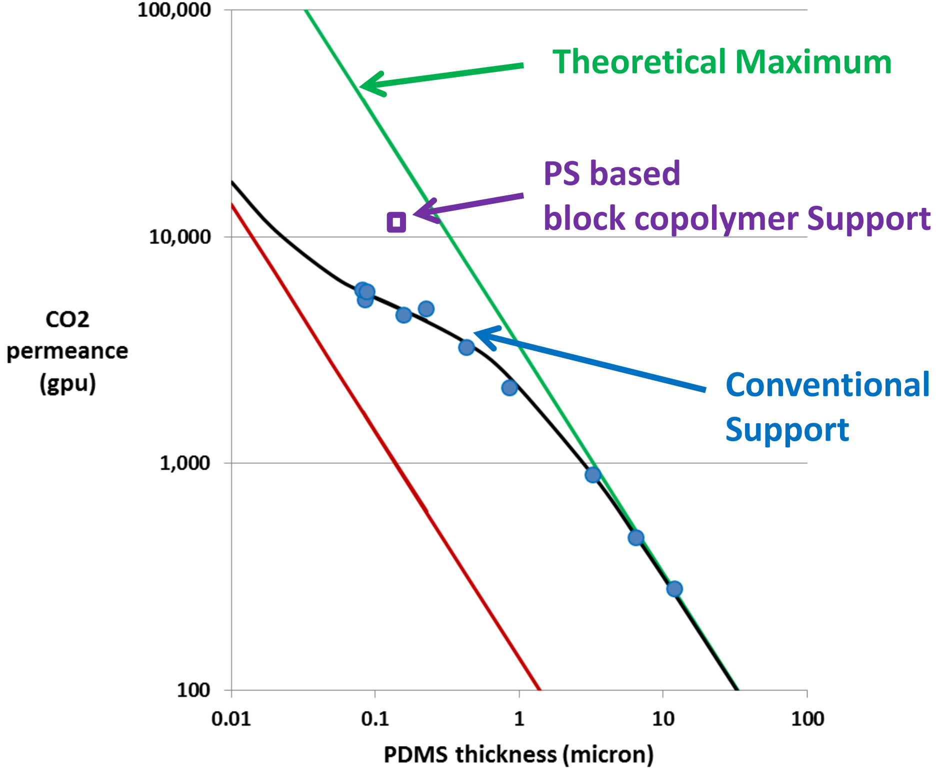
PS-b-P4VP block copolymer

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



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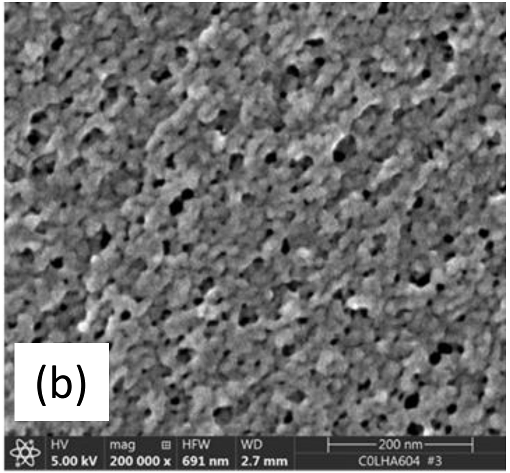
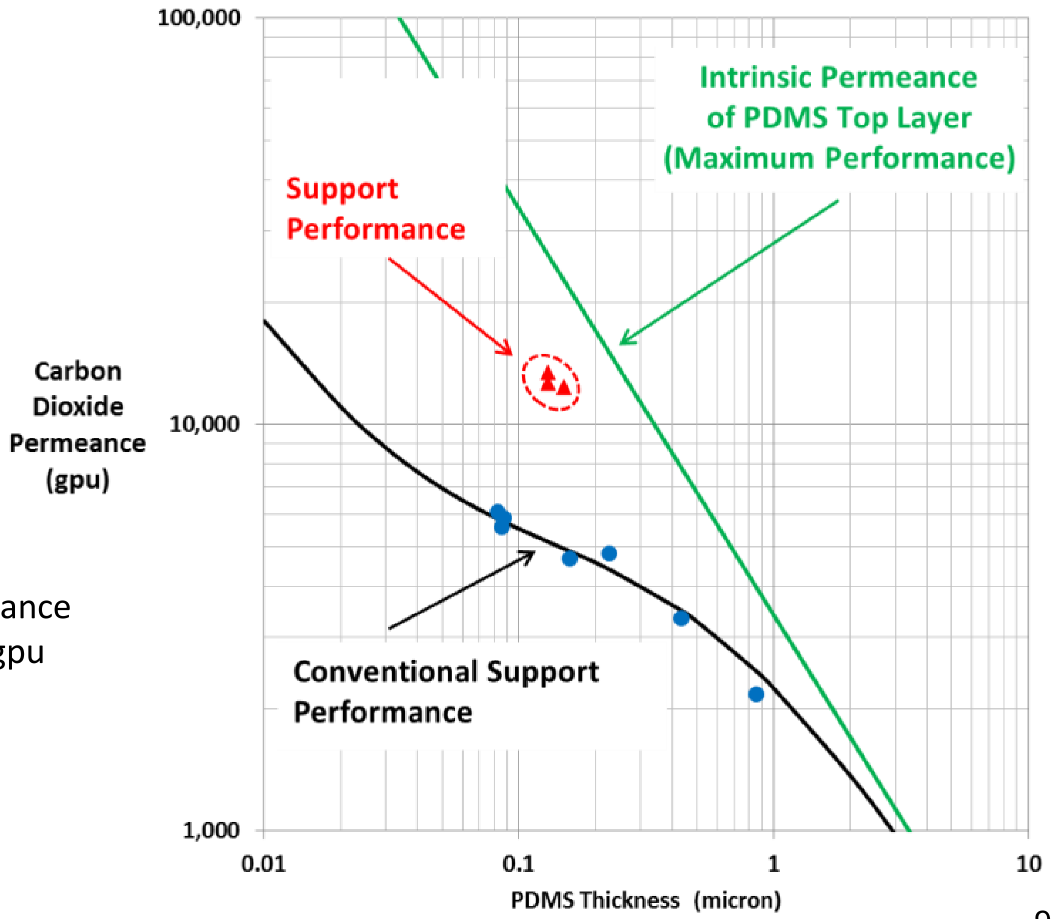
Support made from imperfect block copolymer

- 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:



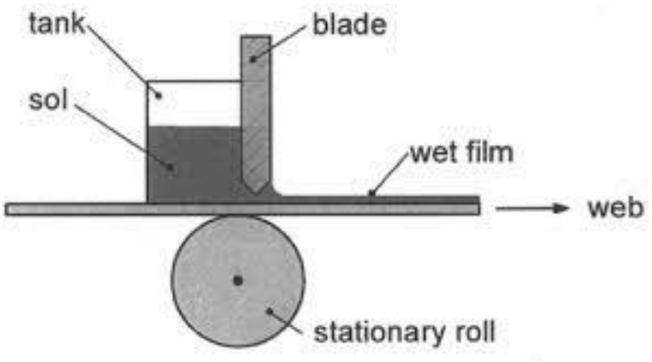
N2 permeance
= 95,000 gpu



Dual Slot Die Casting

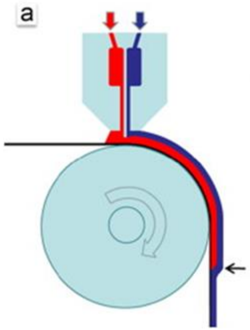
Blade Casting (traditional):

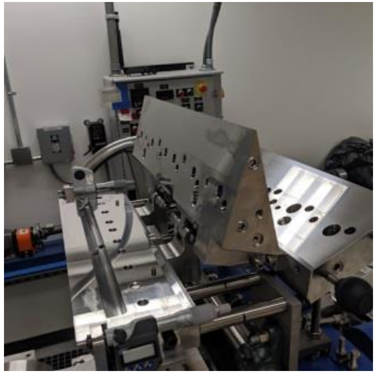
- Common method for membrane casting
- Simple equipment, simple operation
- Allows for deposition of only one layer

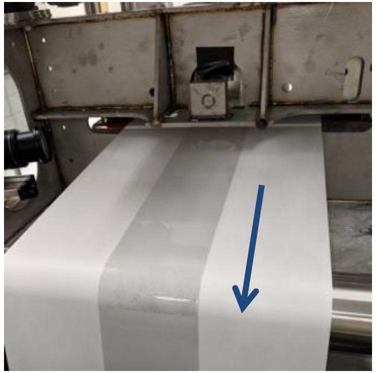


Slot Die Casting (this project):

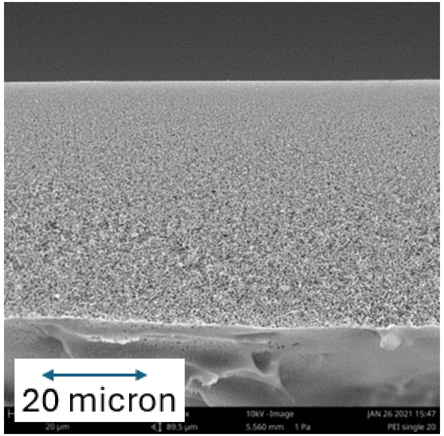
- Allows deposition of multiple layers
- Better control of thicknesses
- More complicated, but used on large scale in many industrial film operations



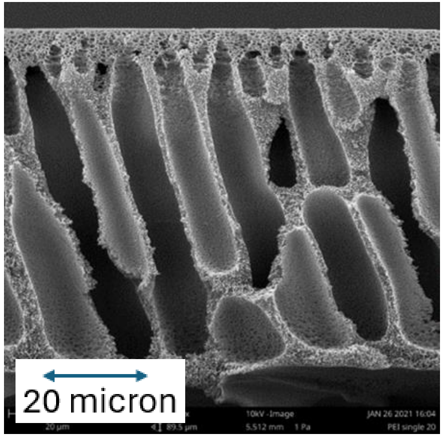




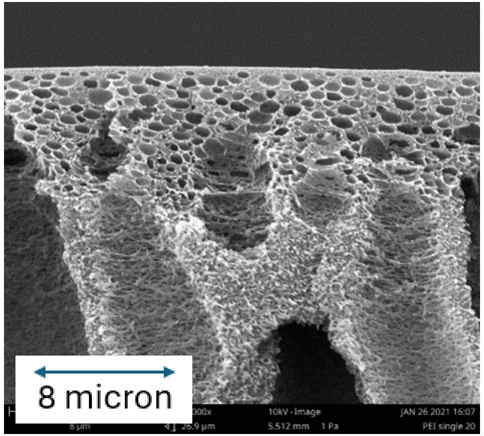
Dual Casting (R&D machine)



(a) Single Layer
Engineering Polymer



(b) Dual Layer
Top: Alternative block copolymer
Bottom: Engineering polymer



(c) Magnification of (b)

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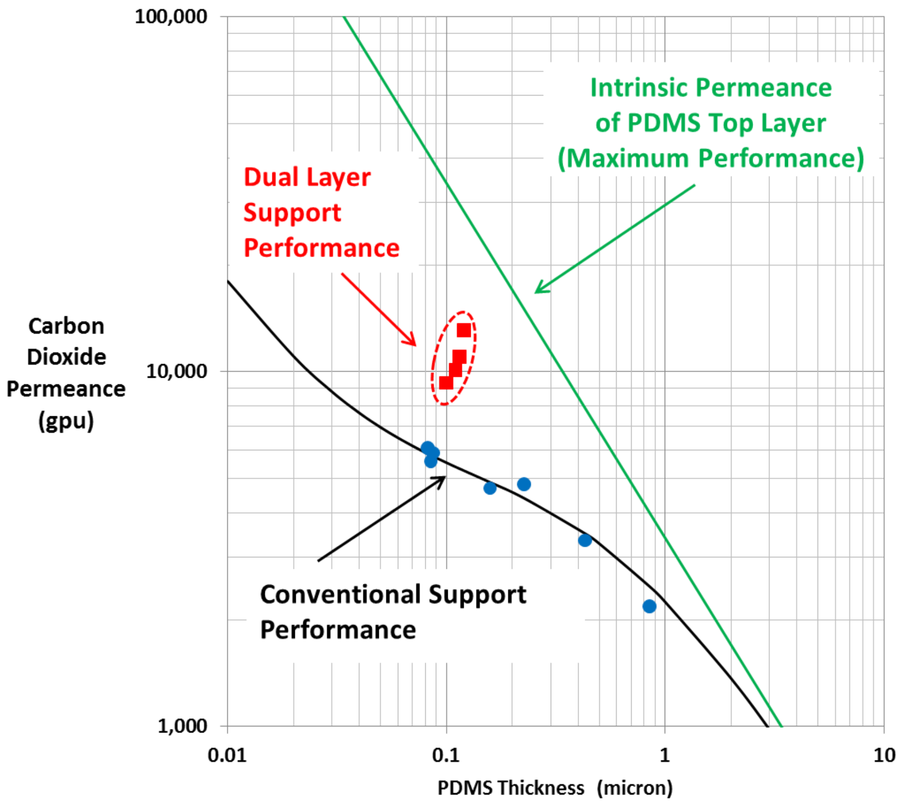
Support made with Dual Slot Die

- 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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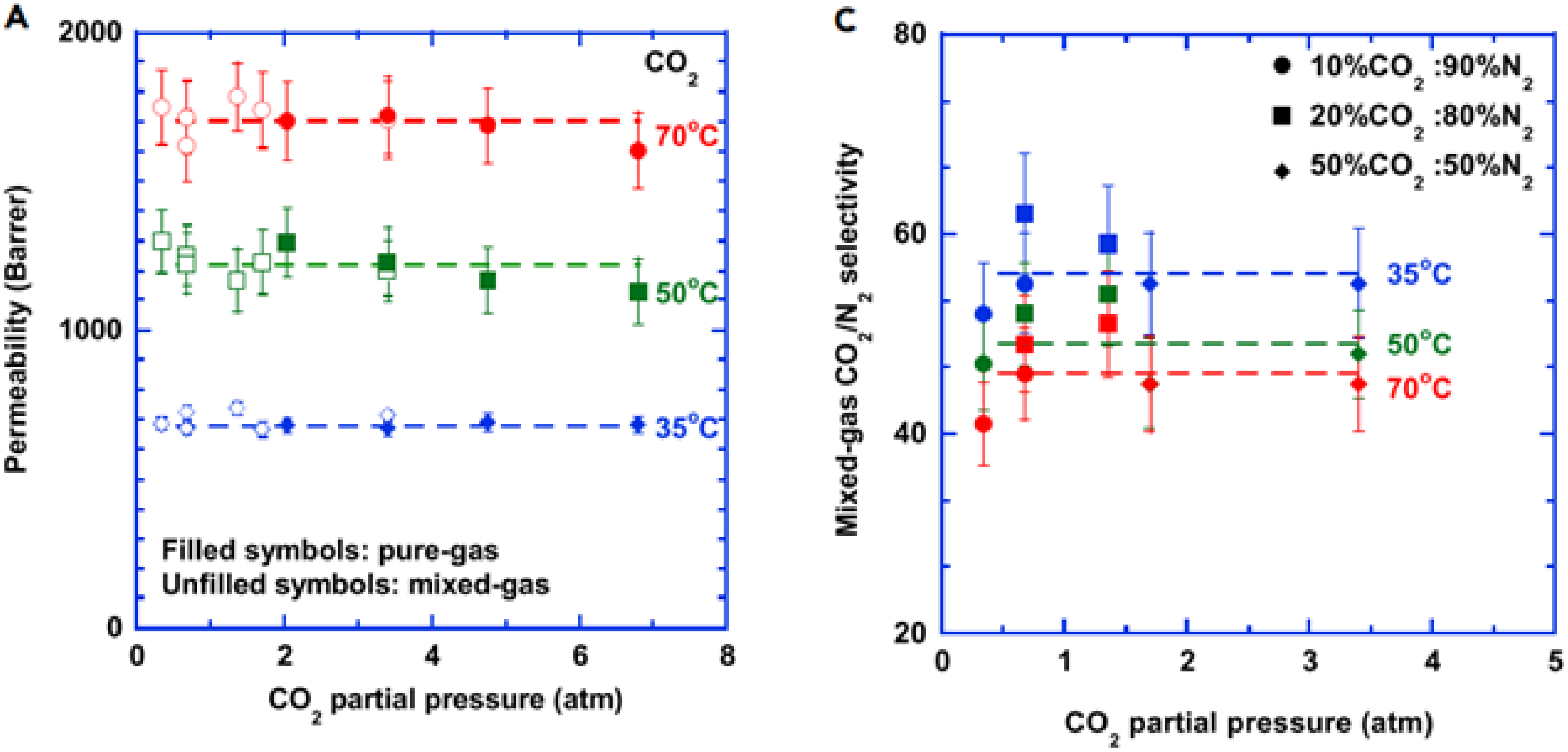
Novel Selective Materials



Data published by the group of Prof. Lin at SUNY Buffalo.

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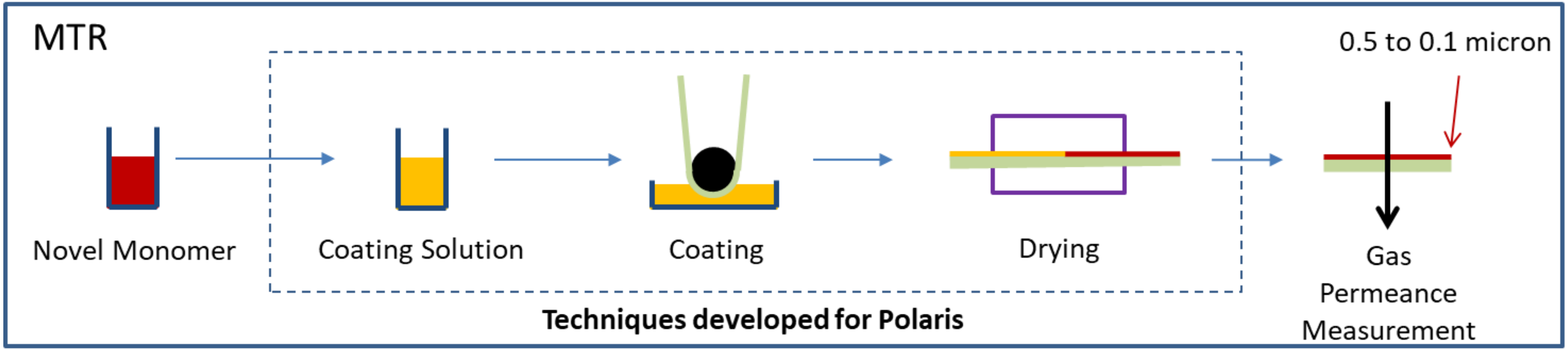
Novel Selective Layer Materials



- 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)
- 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 defect-free thin film composite membranes
  - Selectivities are up to 90, 30% higher than standard Polaris
  - Permeance is 500 gpu, which limits application range

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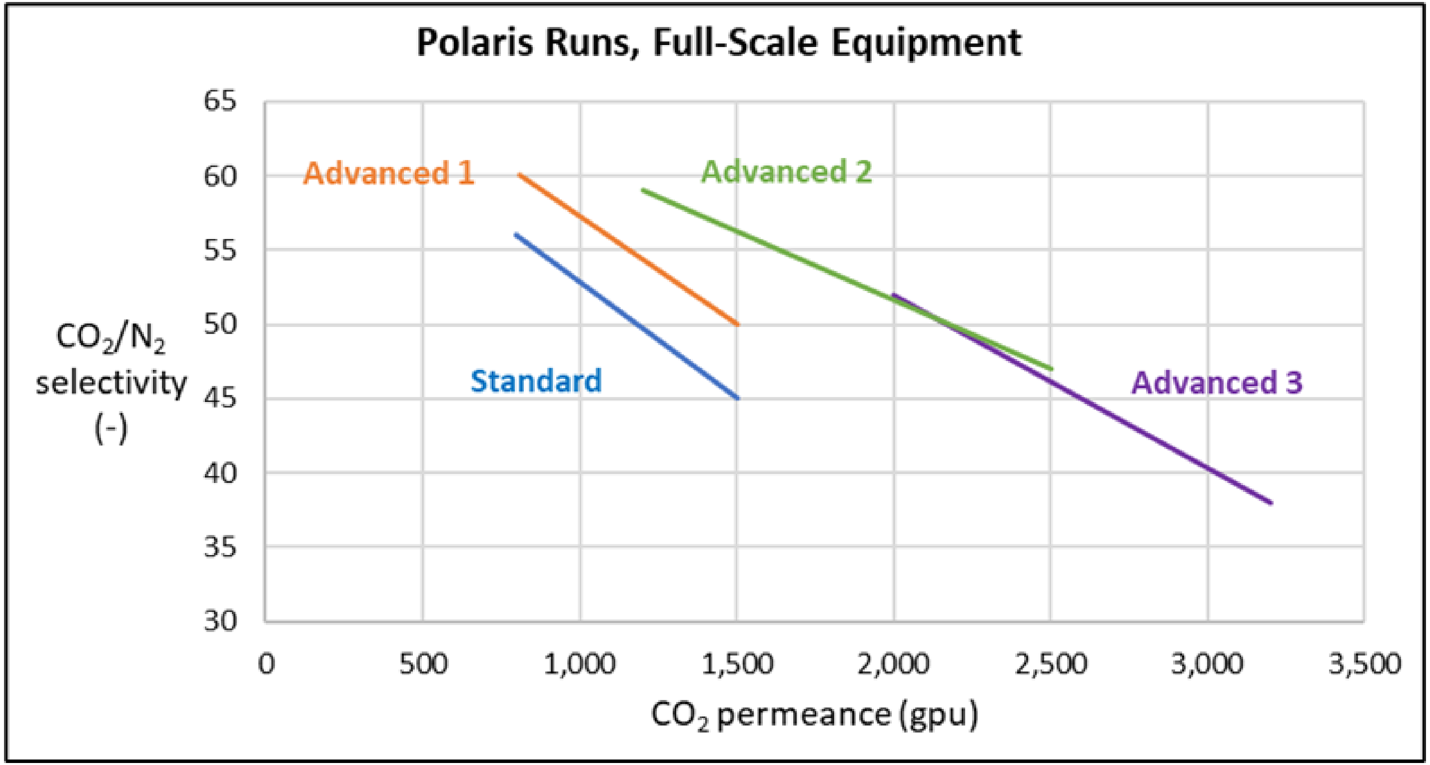
Commercial-scale Runs



Technical and Economic Analysis

- The technoeconomic analysis prepared for this project provides a comparison of the MTR CO_2 capture process using the advanced membranes developed in this project to the reference amine-based CO_2 capture process in Case B12B in the DOE baseline report.

- The cost of CO_2 capture for the MTR advanced membrane case was **\$56.90/tonne CO_2 captured**, which is a significant improvement of over 10% compared to the current standard membrane case of **\$63.32/tonne CO_2 captured**.

	Base Case Membrane Polaris Gen-2 (MEM1)		Advanced Membrane High Permeance (MEM2)		Advanced Membrane High Selectivity (MEM3)	
Permeant	Permeance (gpu)	Selectivity over N2	Permeance (gpu)	Selectivity over N2	Permeance (gpu)	Selectivity over N2
CO2	1,500	30	2,500	25	500	45
O2	120	12.5	230	10.9	28	17.9
N2	50	-	100	-	11.1	-

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Project Benefits to MTR

- Improved membrane supports

- Improved standard Polaris coating recipes
- New membrane version with high selectivity (lower permeance)

- Developed dual-slot die casting techniques
  - MTR's next generation commercial-scale casting machine will have dual-slot die capability
  - MTR's next generation coating machines will have multiple slot dies, in addition to dip coating

- Reduction in carbon capture costs by 10%

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Acknowledgements

- U.S. Department of Energy

  National Energy Technology Laboratory

  Carl Laird, Krista Hill

- University at Buffalo

  Haiqing Lin

- University of Texas at Austin

  Nathaniel Lynd

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