Rational Development of Novel Metal-Organic Polyhedra-based Membranes for CO_2 Capture

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Haiqing Lin
University of Buffalo, SUNY

U.S. Department of Energy

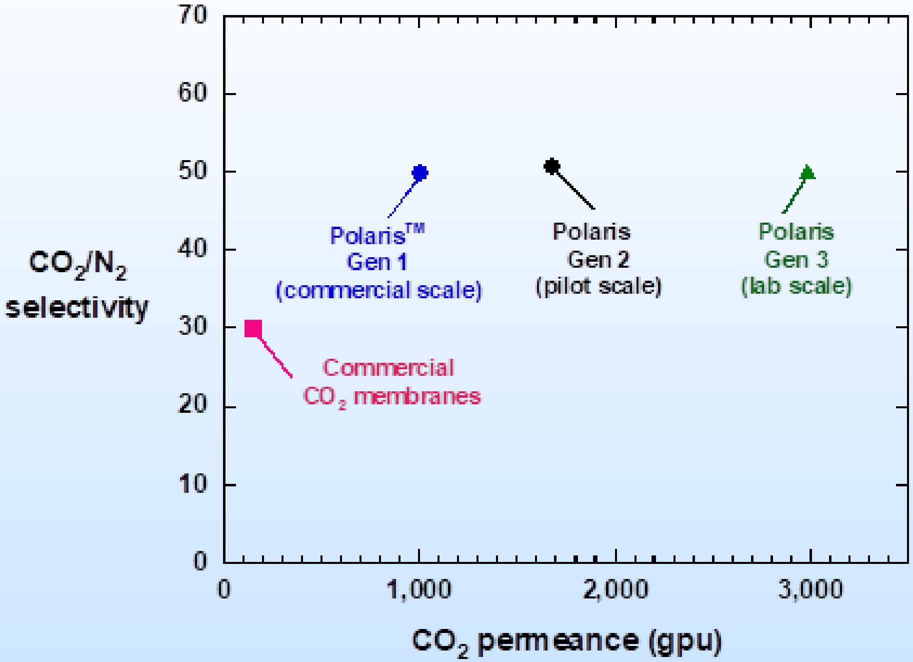
National Energy Technology Laboratory
Carbon Management Project Review Meeting
2:10-2:25pm; August 5 - 9, 2024

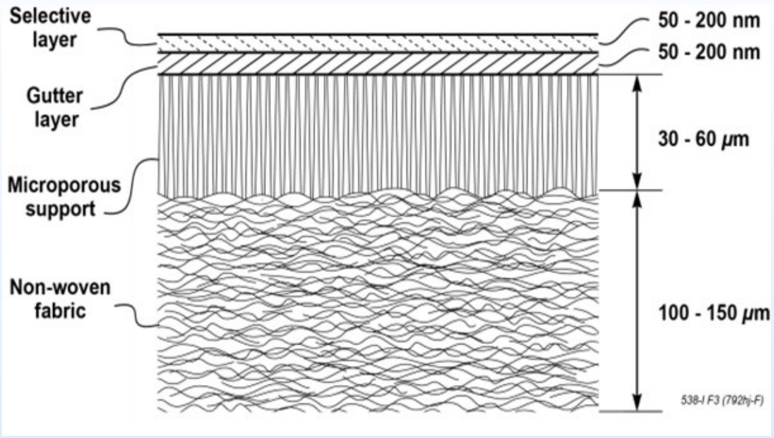
Project Overview

– Funding (DOE $2,857,896 and Cost Share $975,484)
– Overall Project: 7/1/2019 – 6/30/2024
– Project manager: Krista Hill
– Overall Project Objectives

- Rationally develop solubility-selective mixed matrix **materials** comprising polar rubbery polymers and metal organic polyhedra (MOPs);
- Develop thin film composite **membranes** achieving high CO_2 permeance (3000 GPU) and high CO_2/N_2 selectivity (50);
- ~~Demonstrate separation **performance** and stability with raw flue gas at NCCC; and~~
- ~~Perform **techno-economic analysis** on the membrane processes.~~

State-of-the-Art: MTR's Polaris Membranes





Pure-gas at 25 °C and 50 psig

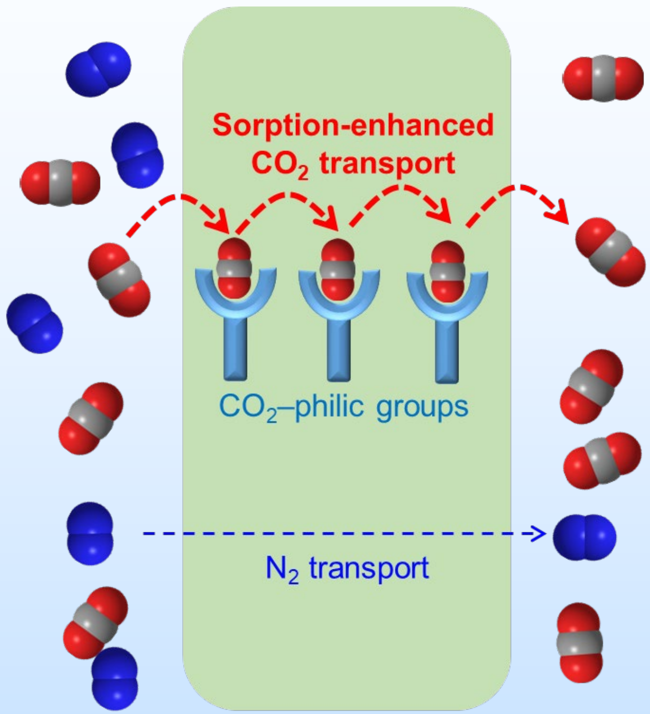
Membrane permeance (Q_A, GPU)

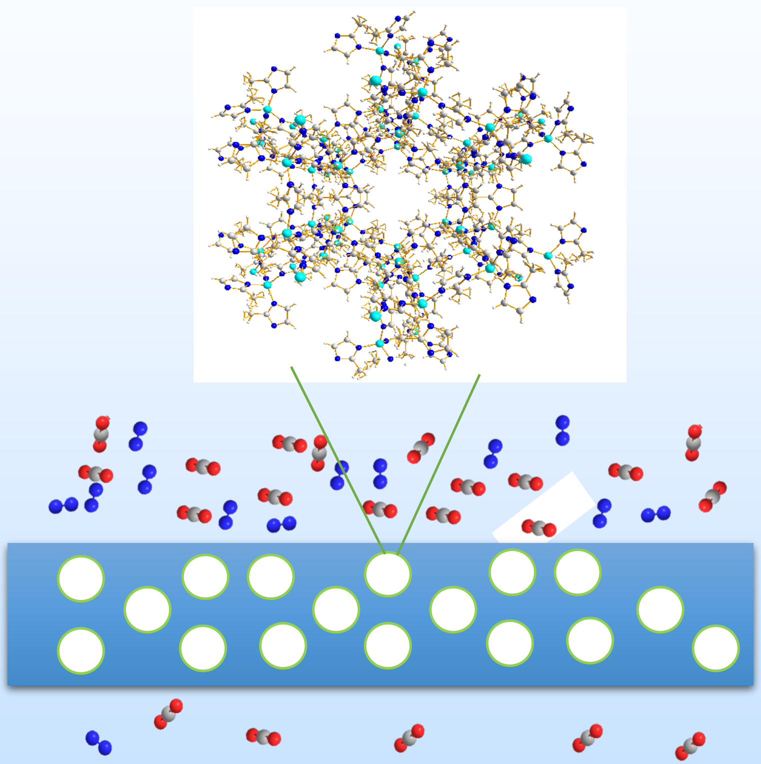
$$Q_A = P_A / l$$

Material permeability (P_A, Barrer)

If a material with 1,000 Barrer is made into a 0.33-μm selective layer, Q_A = 3,000 GPU

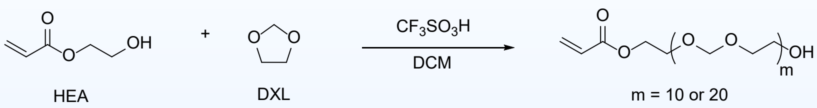
Our Approach: Sorption-Enhanced Mixed Matrix Membranes

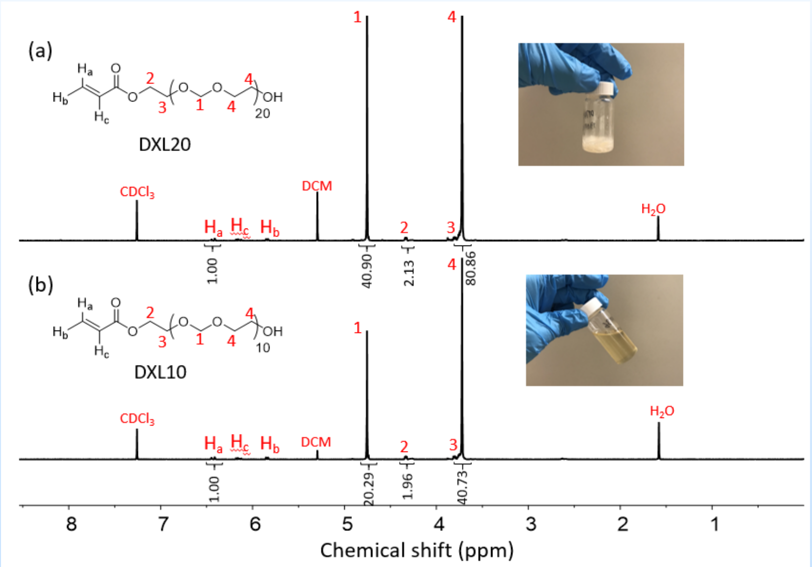


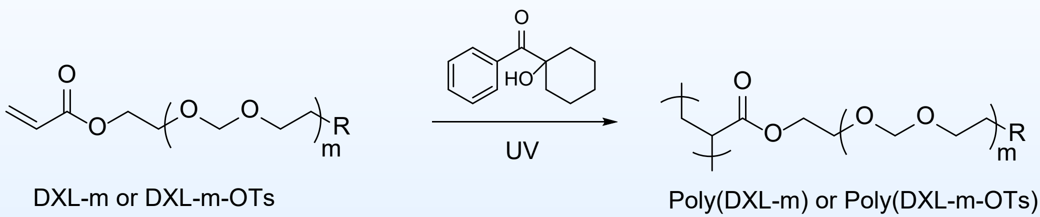


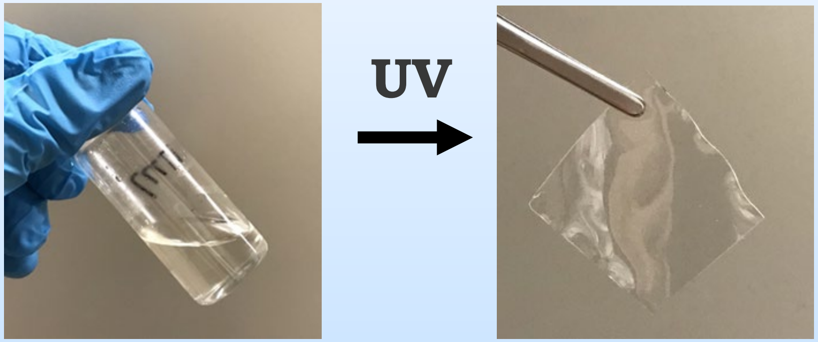
- **CO_2-philic rubbery polyethers**
- **Porous metal organic polyhedra (MOPs)**

Design and Synthesize Functional Polyethers



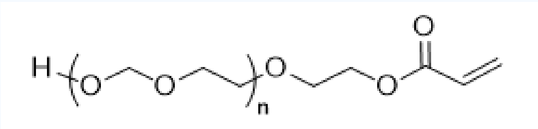




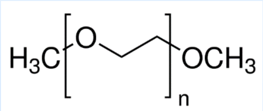


50 - 100 g/batch production demonstrated

Polymer Blends to Meet the Target



PDXLA8, n = 8



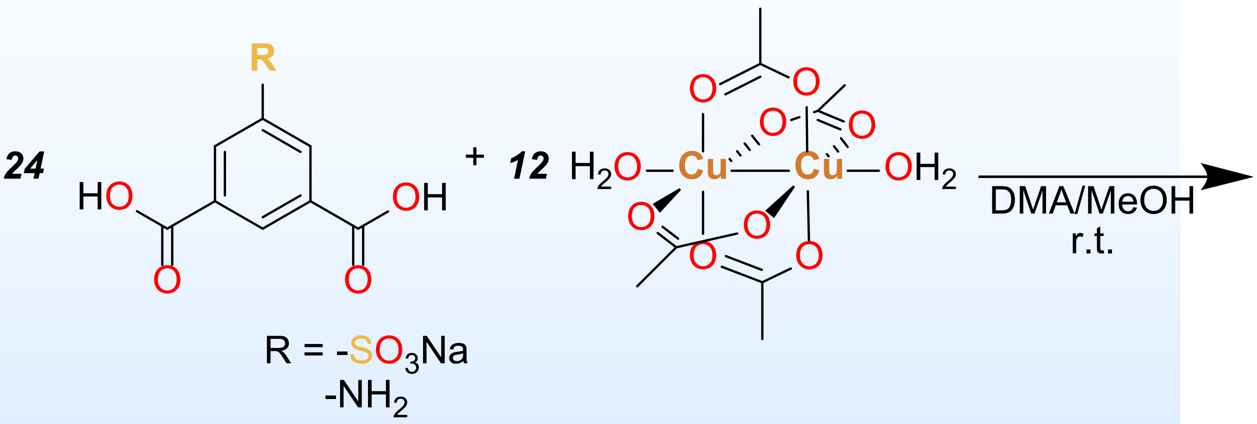
PEGDME
240 g/mol

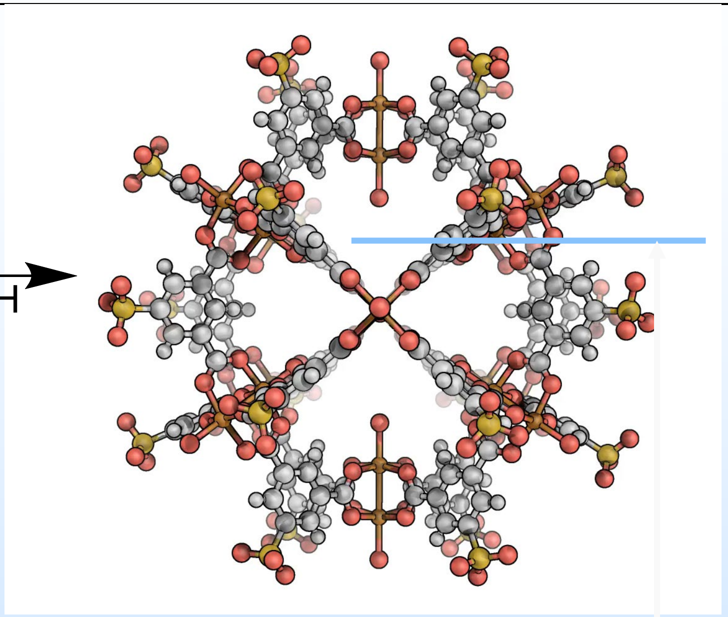
PDXLA8/PEGDME
Mixed gas: CO_2/N_2=15/85, 100-160 psig

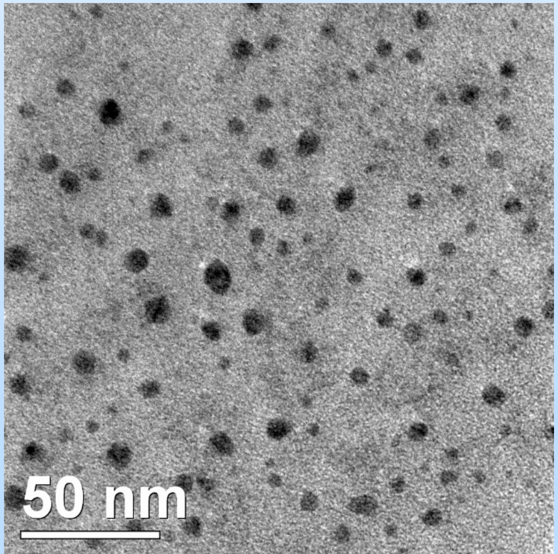
PEGDME (wt%)	T (°C)	Mixed-gas CO_2 (Barrer)	Mixed-gas CO_2/N_2 selectivity
45	35	1200	60
50	35	1450	62
50	**25**	**1290**	**79**

Meet the project target
CO_2: 1000 Barrer; CO_2/N_2: 75

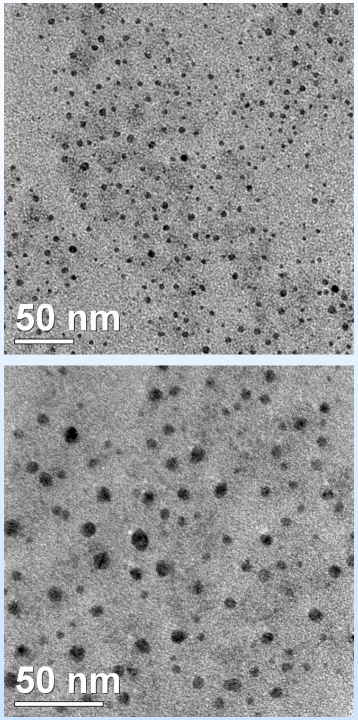
MOP Synthesis: 10 g/batch

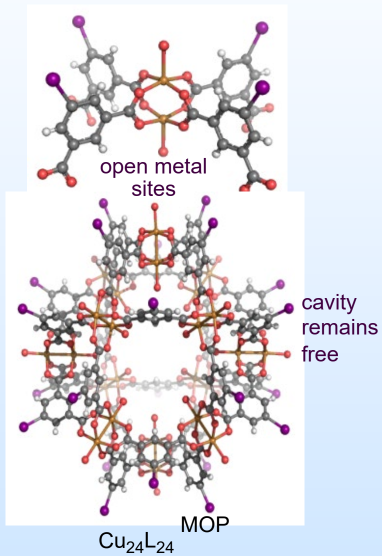






Mixed Matrix Materials (MMMs) to Meet the Target





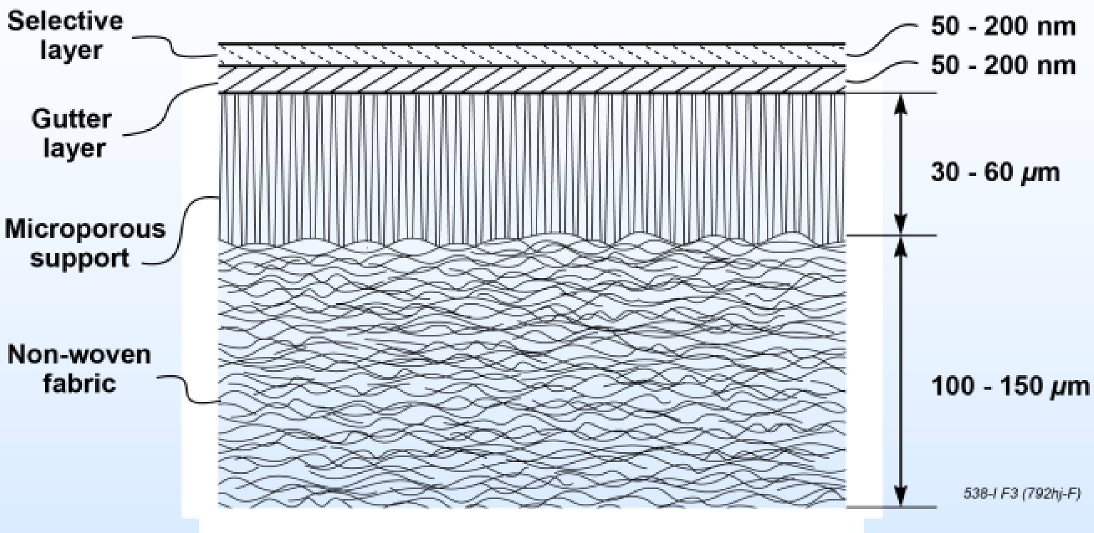
- 2 – 5 nm in size
- Soluble in solvents

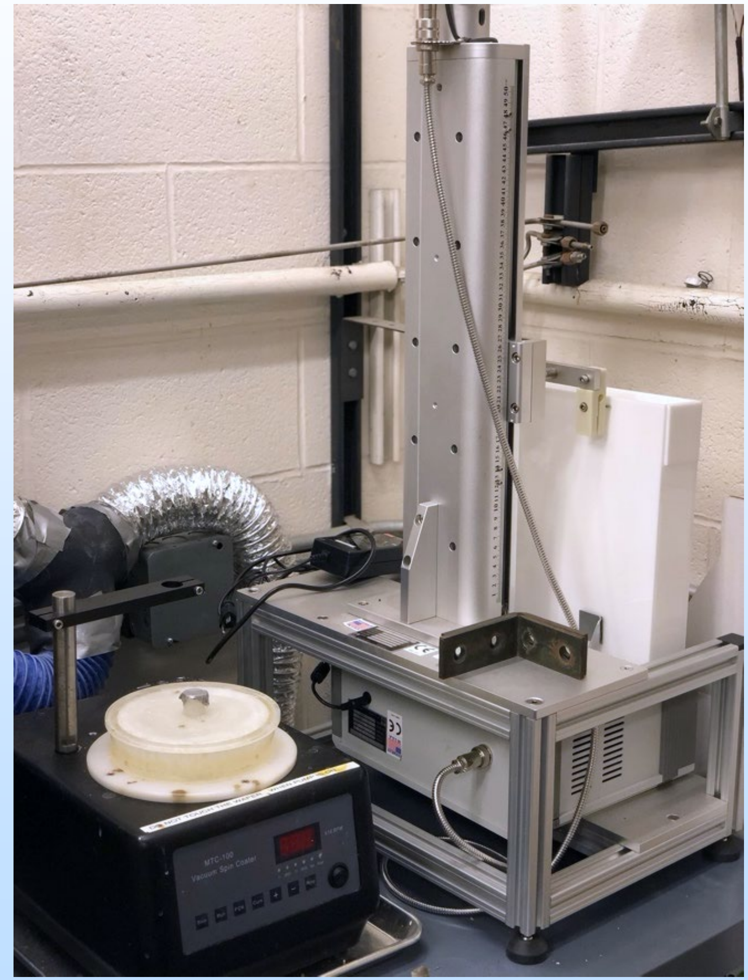
PDXLA8/PEGDME240 (50/50)

MOP-3 content (wt.%)	T (°C)	P_{CO2} (Barrer)	CO_2/N_2 selectivity	CO_2/O_2 selectivity
0	**25**	**1005**	**56**	**22**
1	25	662	48	25
3	25	1343	62	24
3	**21**	**1106**	**74**	**31**

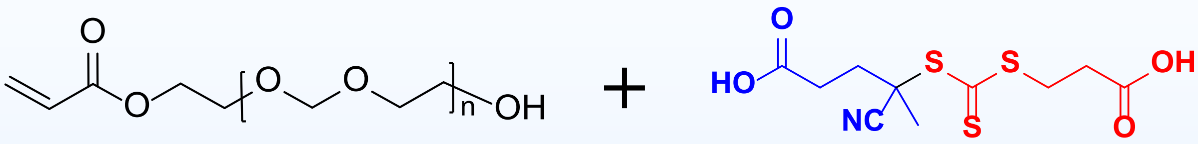
Pure-gas
Measurement uncertainty < 10%

Preparation of Thin Film Composite (TFC) Membranes at UB



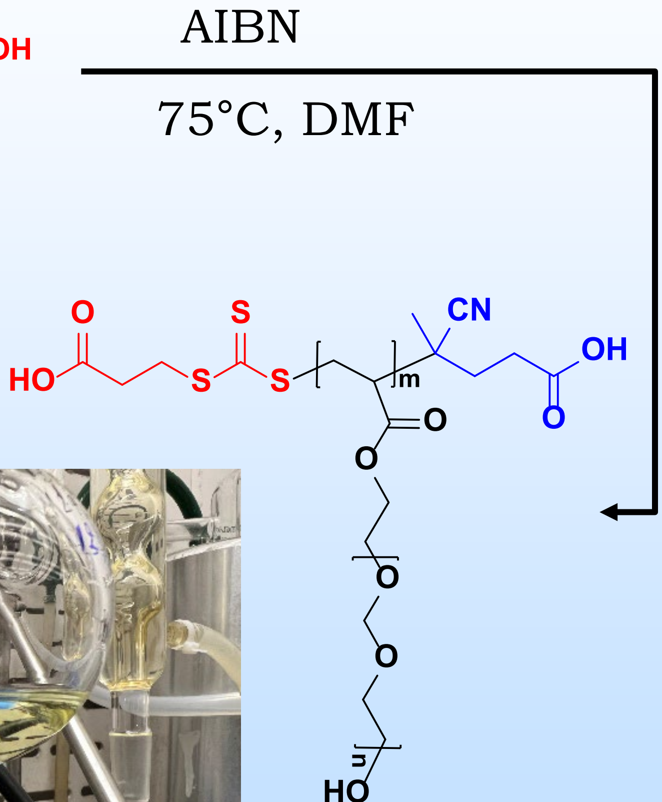


Synthesis of Soluble Polymers on a Large Scale



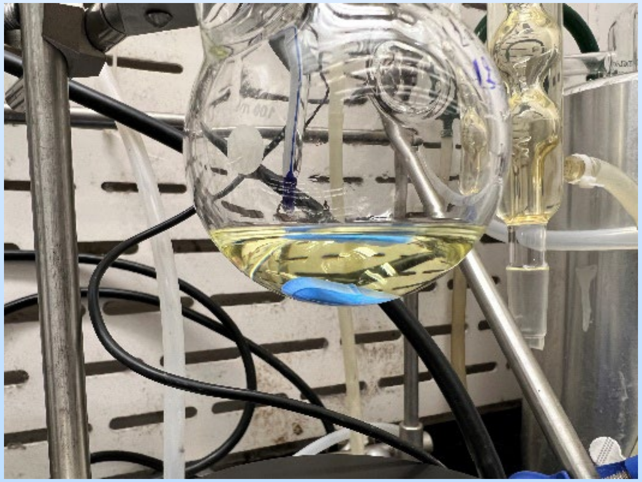
DXLA8 (J16)

BM1433
Chain transfer agent
(CTA)



- [DXLA]:[BM1433]:[AIBN] = 100:1:0.1
- **[DXLA] = 0.5 M (25 wt.% DXLA in DMF)**

<u>Reaction time:</u>
3 h, 75°C



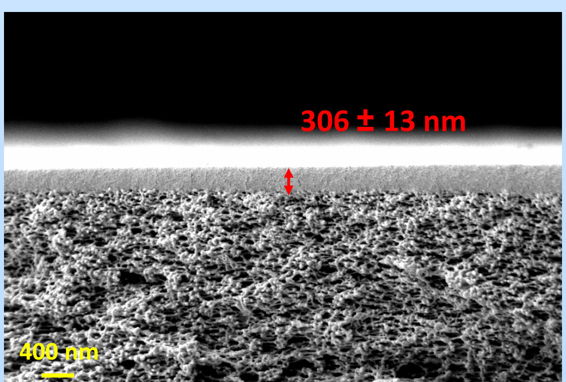
$M_{n,theo.} = 71.1\ kDa$

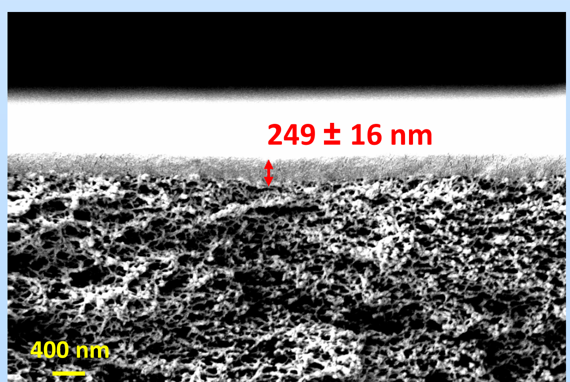
Representative TFC Membranes

Membranes	Polymer content (wt.%)	Temp. (°C)	CO_2 (GPU)	CO_2/N_2 selectivity
pDXLAc8	2	22	1563	47
pDXLAc12 (B2) (#1)	2	22	3690	42
pDXLAc12 (B2) (#2)	2	22	2684	57
		35	3722	38
pDXLAc12 (B2) (#3)	**1.5**	**22**	**3040**	**48**
		35	**4270**	**39**
pDXLAc12 (B2) (#3)	1.5	35	922	51
pDXLAc12 (B3) (#5)	1.5	35	1344	37

Lab-scale TFC Membranes at UB

Samples	Coating solutions		Gutter layer	CO_2 permeance (GPU)	CO_2/N_2 Selectivity
	Solvent	pDXLAc8 (wt.%)			
#1	Toluene	2.7	*d*PDMS/PAN	1021	55
#2	Toluene	1	*d*PDMS/PAN	**1682**	**45**
#3				**1674**	**44**
#4				1036	53
#5	IPA/H_2O	1.3	*d*PDMS/PSF	1235	39
#6				1627	30
			Average	**1380±320**	**44±9**



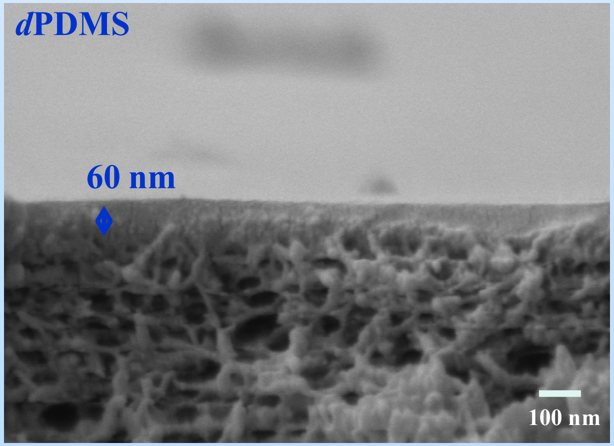


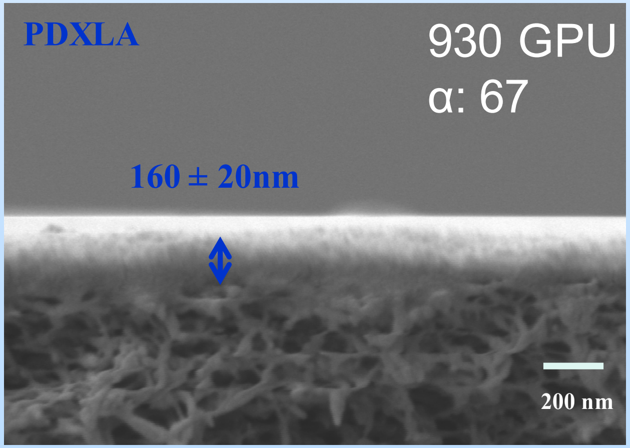
Pure-gas permeance at 25 ℃

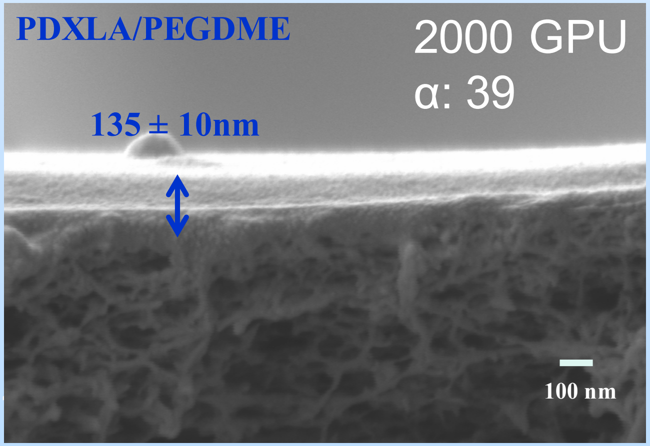
Gutter layer: ~150 nm
Selective layer: ~150 nm

Lab-scale TFC Membranes at UB: Effect of PEGDME

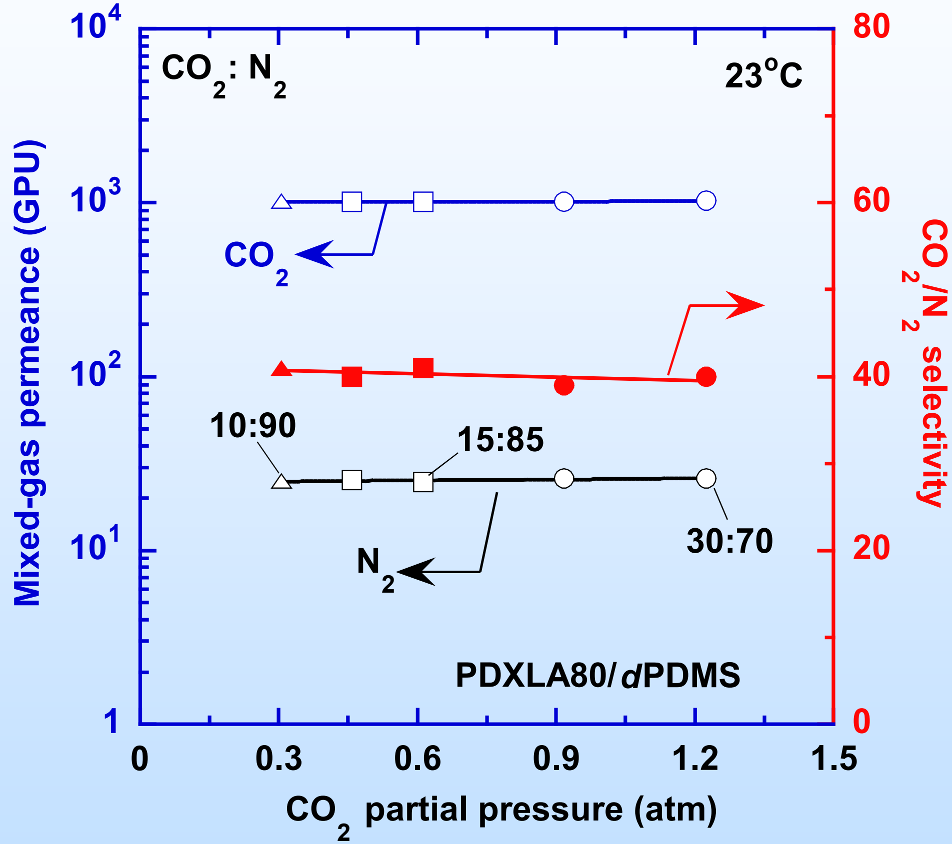
Samples	Coating solutions		PEGDME in selective layers (wt.%)	Temp. (°C)	CO_2 permeance (GPU)	CO_2/N_2 selectivity
	PDXLA (wt.%)	PEGDME (wt.%)				
#1	0.50	0	-	25	930±25	67±2
#2	0.40	0.10	20	25	2000	39
#3				**25**	**3500**	**41**
#3				**35**	**4600**	**28**





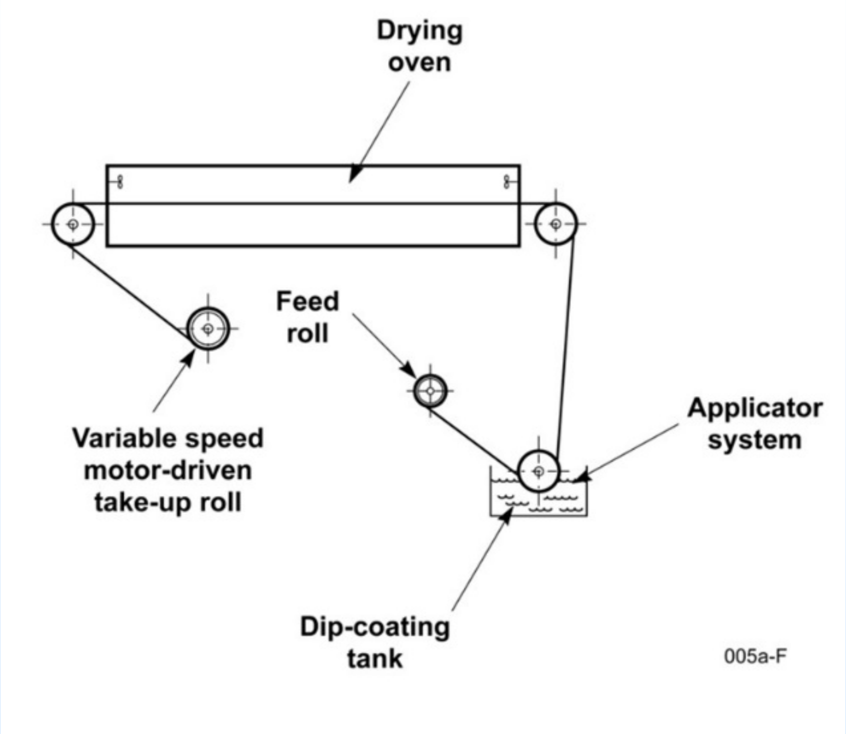


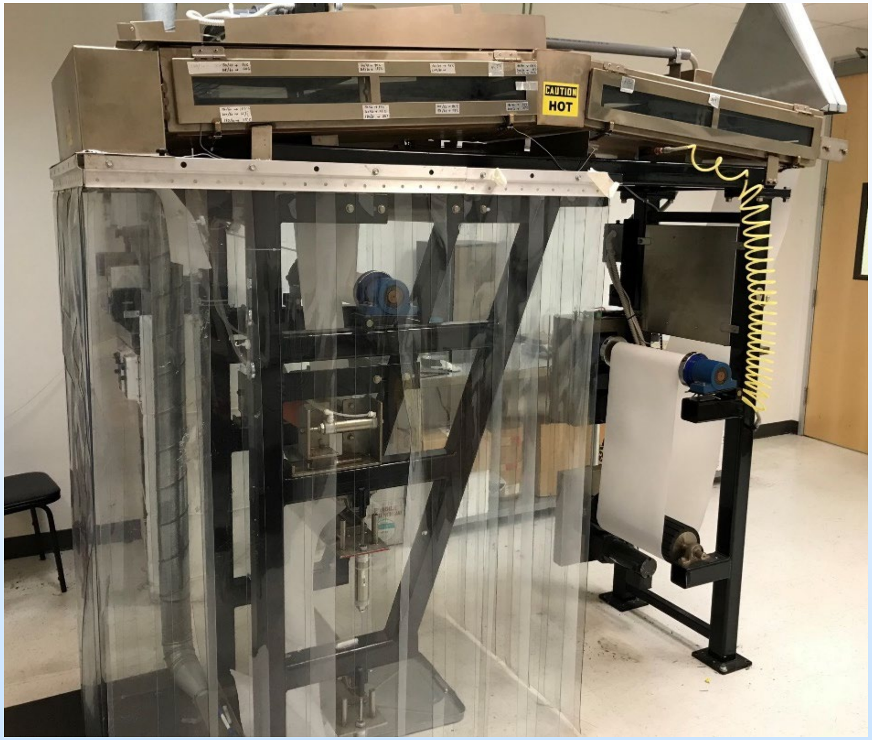
Mixed-Gas Performance of PDXLA/PEGDME (80/20)



CO_2 permeance and selectivity are independent of CO_2 partial pressure

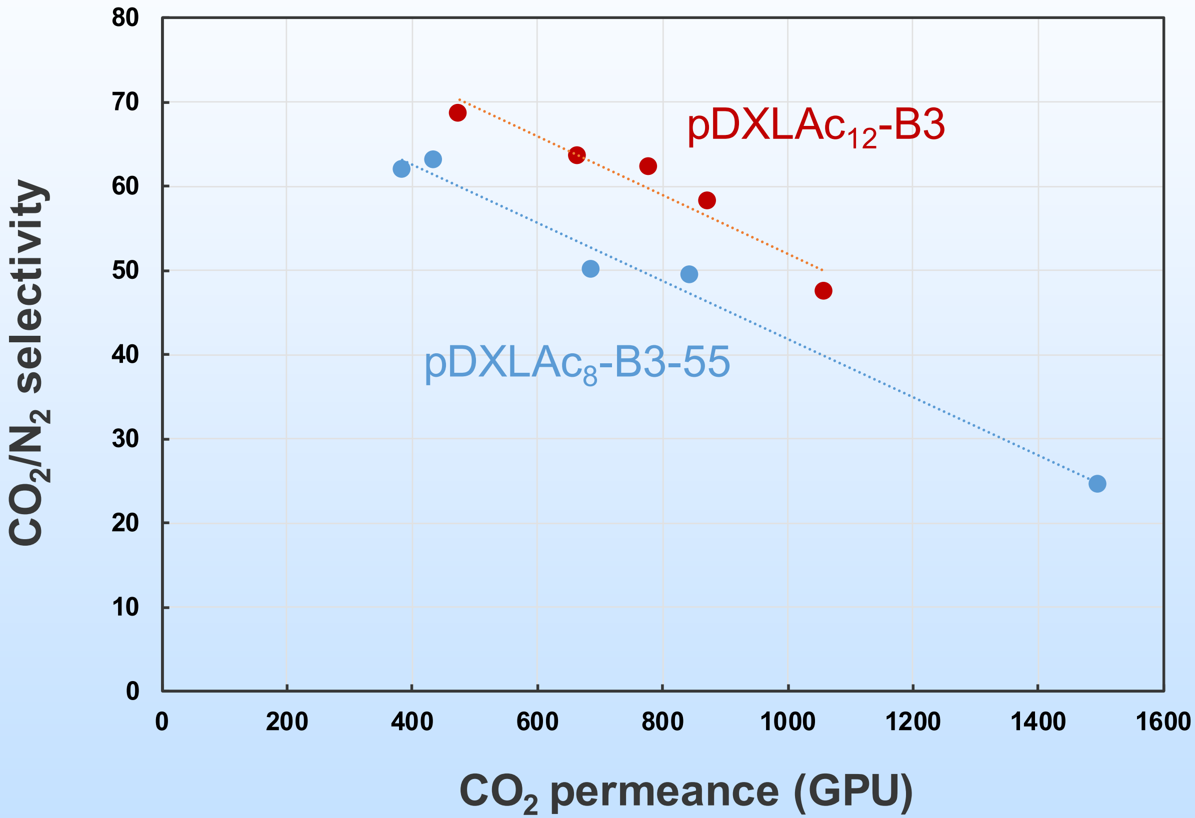
Development of Industrial Membranes at MTR





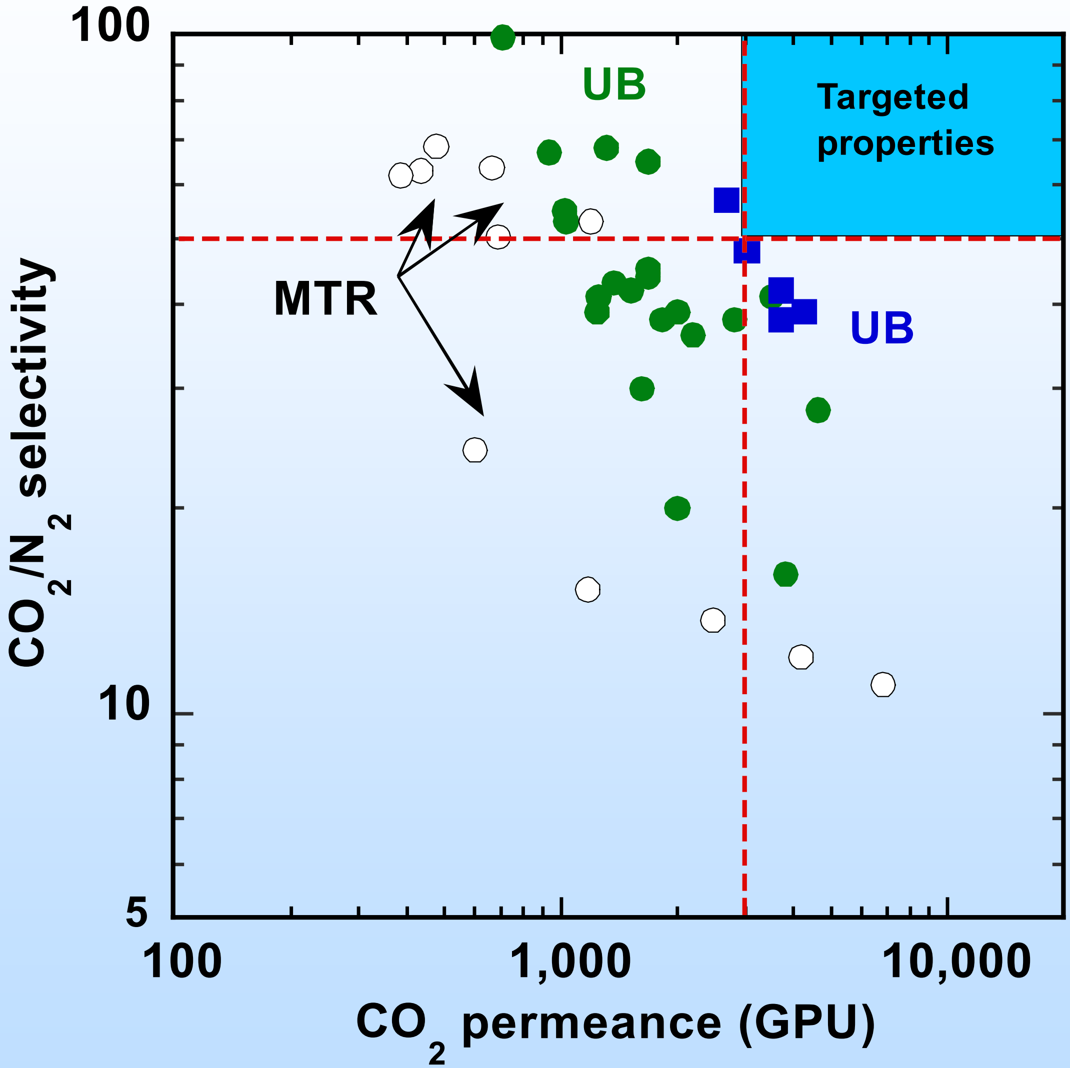
- MTR leads TFC membrane scale up activities
- Research-scale (12-inch width) roll-to-roll coating equipment has been used

Pure-gas Results of TFC Membranes



- PDXLAc composite membranes exhibit CO_2/N_2 values significantly higher than the project target of 50
- Best overall composite membrane has CO_2 permeance of 1,060 GPU and CO_2/N_2 of 47 at room temperature

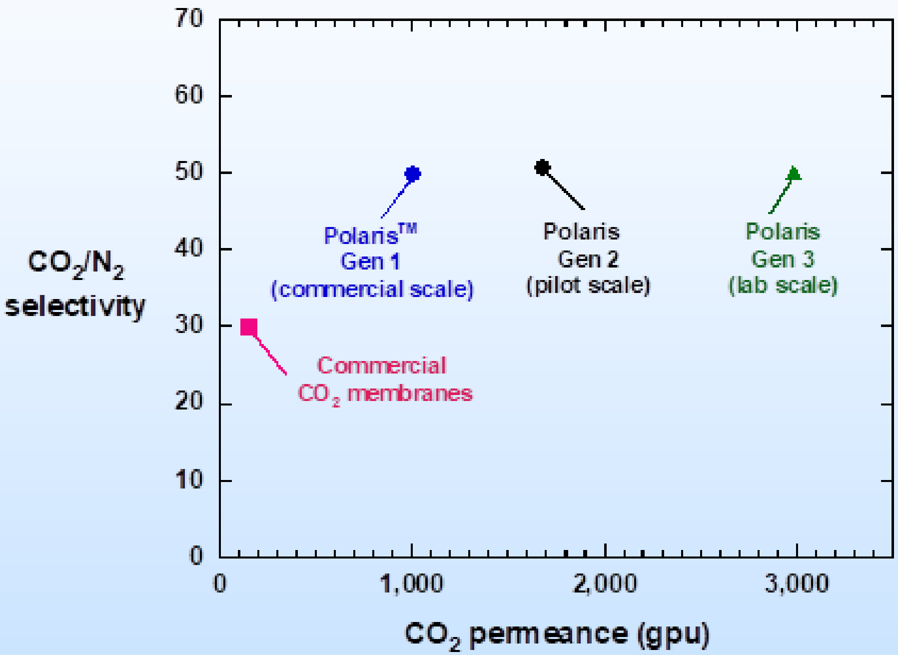
Summary of Membrane Data

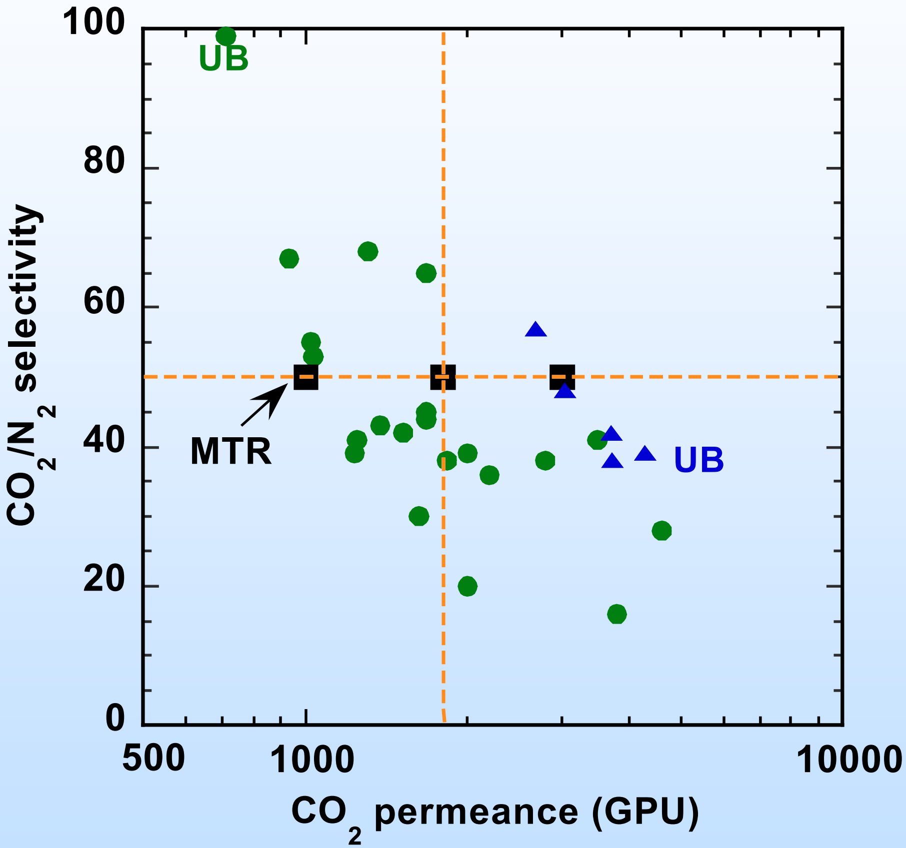


UB blue:
2/2023 – 4/2023

UB green:
5/2023 – 6/2024

Comparison with MTR's Polaris Membranes





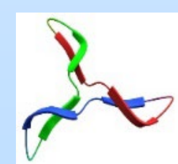
Pure-gas at 25 °C and 50 psig

Summary

- We have designed and synthesized materials that met CO_2/N_2 separation property targets
  - More than three formulations identified
  - Better than non-facilitated transport materials reported in the literature
- We can consistently make membranes that meet performance target at UB
- The transfer to industrial roll-to-roll coater is yet to be demonstrated.

Acknowledgement

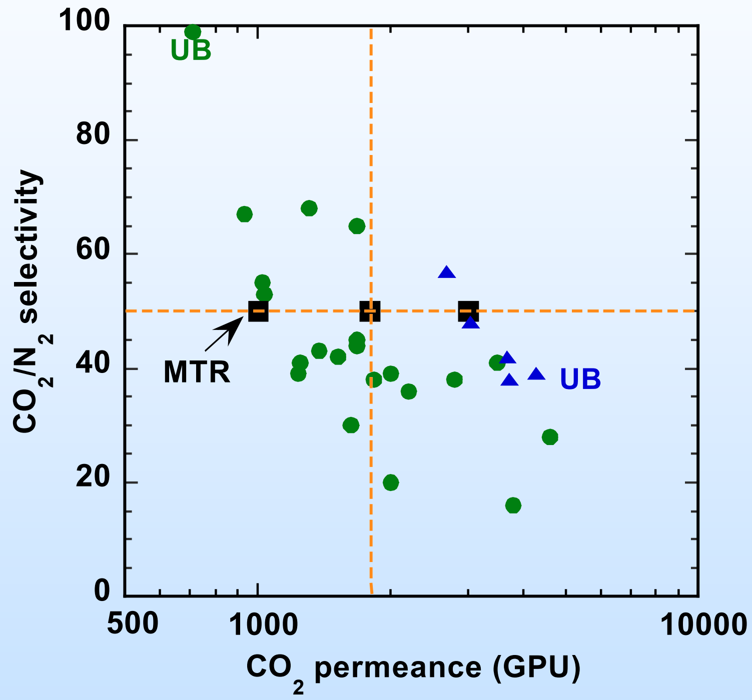
- Project manager: Krista Hill
- Funding from the NETL
- Costshare from NYSTAR, Caltech, RPI, and MTR



Challenges and Lessons Learned

Translation from materials to membranes by roll-to-roll manufacturing is challenging

- Solvent
- Compatibility with gutter layers
- Polymer quality
- Nanoparticle dispersion
- UB should have built a roll-to-roll dip coater



Risk management

- Pandemic
- Personnel approval
- Personnel changes
- UB should have had a more permanent staff during each BP.

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