Highly Permeable Thin Film Composite Membranes of Rubbery Polymer Blends for CO_2 Capture

NATIONAL ENERGY TECHNOLOGY LABORATORY

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Point Source Capture — Lab, Bench, and Pilot-Scale Research
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U.S. DEPARTMENT OF ENERGY

Project overview

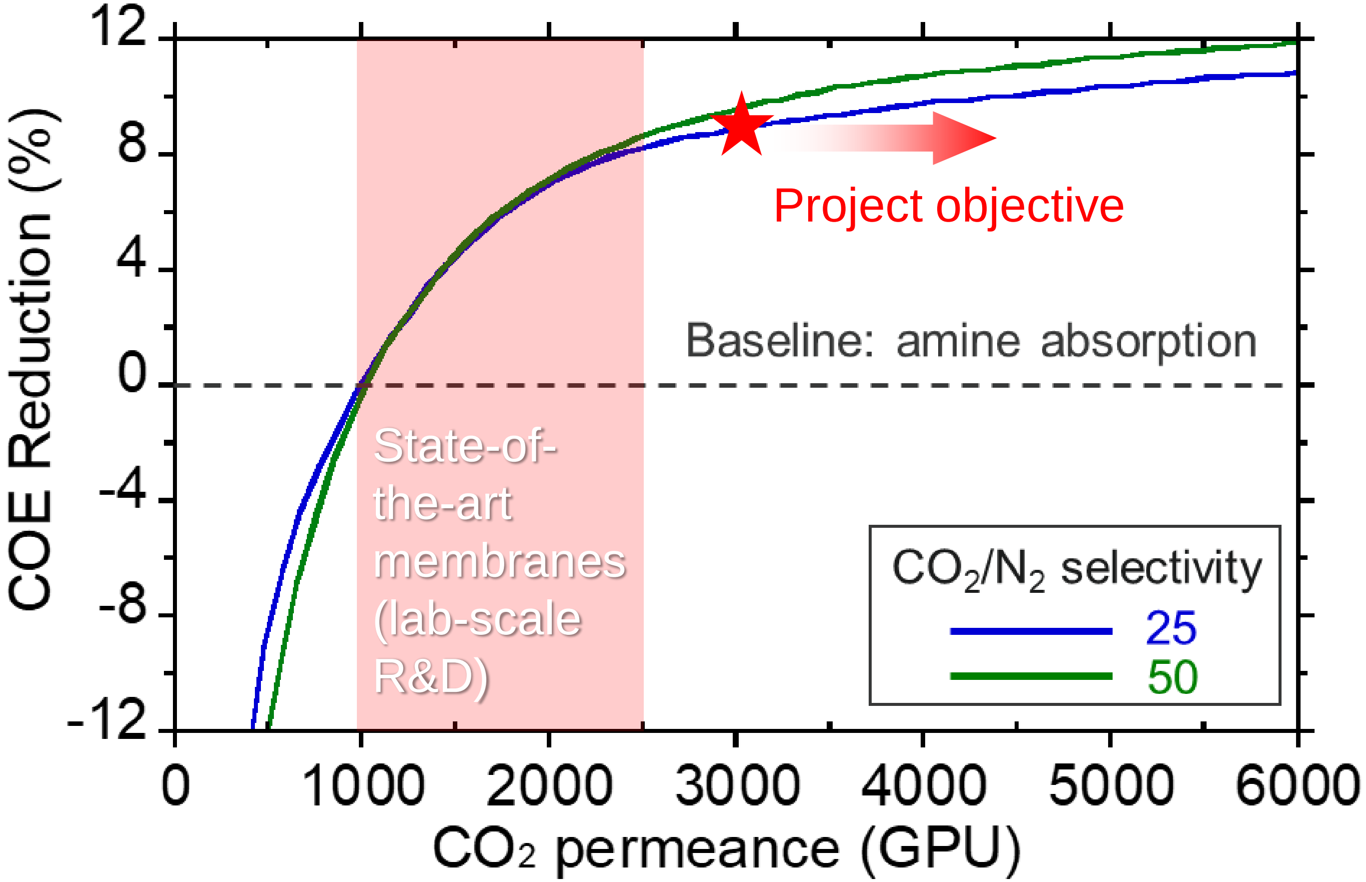
- **Project:** High Permeance Blended Rubbery Membranes
- **Funding source**: NETL-RIC Field Work Proposal - Transformational Carbon Capture - Task 21
- **Project period**: EY21 – EY23 (04/01/2021 – 03/31/2024)
- **Project Objectives: developing a scalable thin-film composite (TFC) membrane for industrial carbon capture that has a *CO_2 permeance >3,000 gas permeance unit (GPU)* and *CO_2/N_2 selectivity of >25*. Both the *membrane support* and *selective material* will be optimized for scalability, thermal and chemical stability, and anti-aging properties.**
- **Project participants:**

  NETL Research & Innovation Center (RIC)

  Idaho National Laboratory (INL)

  National Carbon Capture Center (NCCC)

Technology background: the importance of high-permeance membranes



COE: cost of electricity

- Coal flue gas decarbonization: membrane *vs* amine absorption
- Two-stage membrane process with air sweep (designed by MTR)
- 95% CO_2 purity at a high CO_2 recovery (capture rate) of 90%

For flue gas decarbonization, an increase in CO_2 permeance is more important than a further increase in CO_2/N_2 selectivity when the selectivity is above 25.

Alex Zoelle *et al.*, Performance and Cost Sensitivities for Post-Combustion Membrane Systems, 2018 NETL CO_2 Capture Technology Project Review Meeting

Technology background: achieving high permeance *via* selective material optimization and thin-film composite (TFC) fabrication

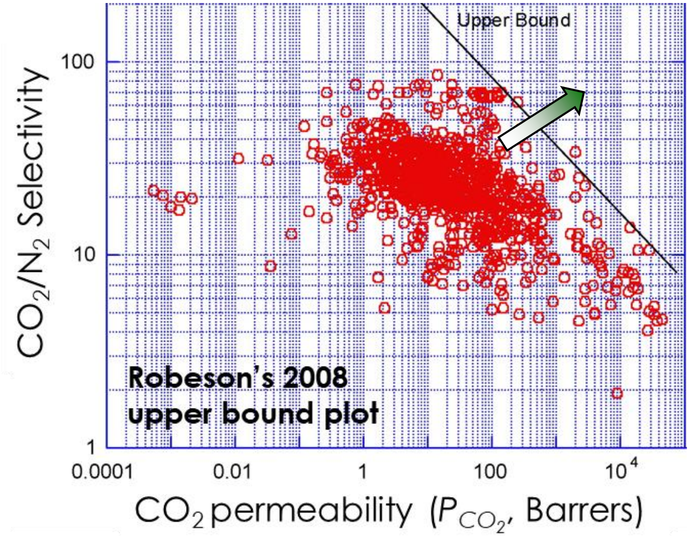
$$\uparrow \textbf{Permeance} = \frac{Permeability\ (P)\ of\ selective\ material \uparrow}{thickness\ of\ selective\ layer \downarrow}$$

$$\uparrow \textbf{Selectivity}\ (> 25) = P(CO_2)/P(N_2)$$

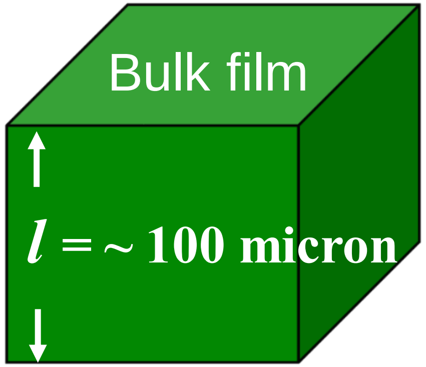
Permeance (in GPU) is pressure normalized flux. Permeability (in Barrer) is a material property independent of thickness.

1. Selective material optimization

Permeability/selectivity tradeoff

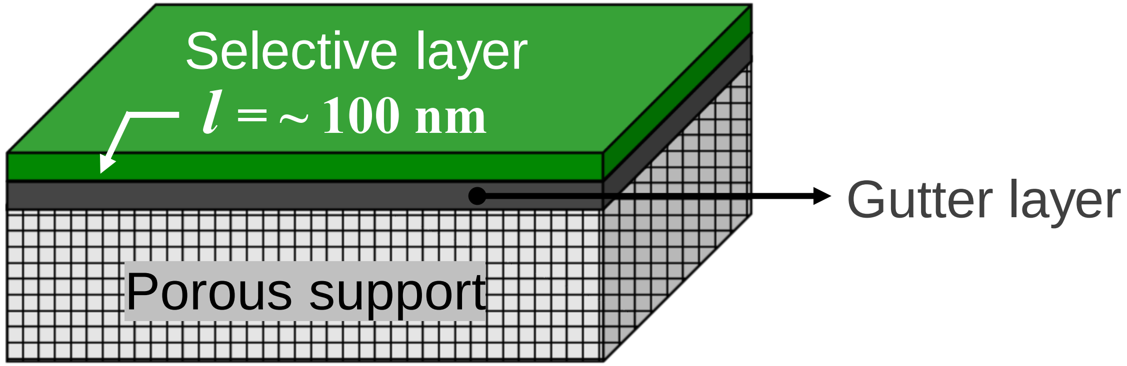


Robeson, *J. Membr. Sci.* 320 (2008) 390



Thickness reduction

2. TFC membrane fabrication



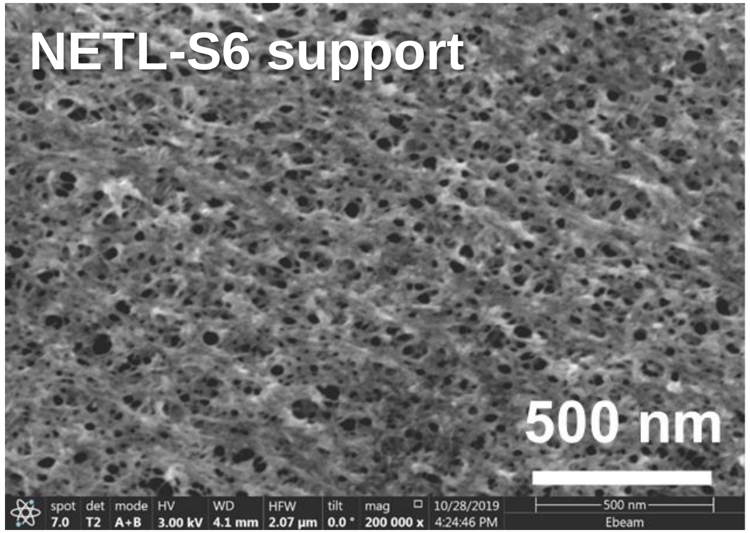
Selective layer (< <1 um): CO_2/N_2 separation

Gutter layer (< 500 nm): preventing pore penetration & smoothening porous support

Porous support (> 20 µm): mechanical reinforcement

Prior technology development efforts

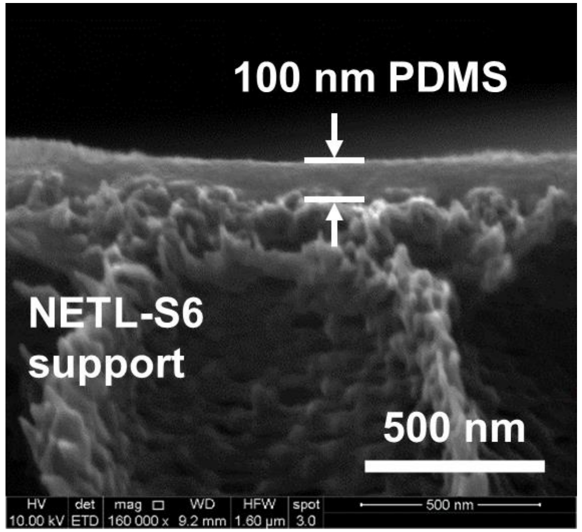
Novel nanoporous support
(EY 18-20)



CO_2 perm.: 260,000 GPU
Pore size: 5 - 42 nm
Porosity: 20 ± 2%
Operation temp.: ≤ 200 °C
Solvent resistance to alcohols, chloroform, THF, acetone, etc.

U.S. Patent Pending

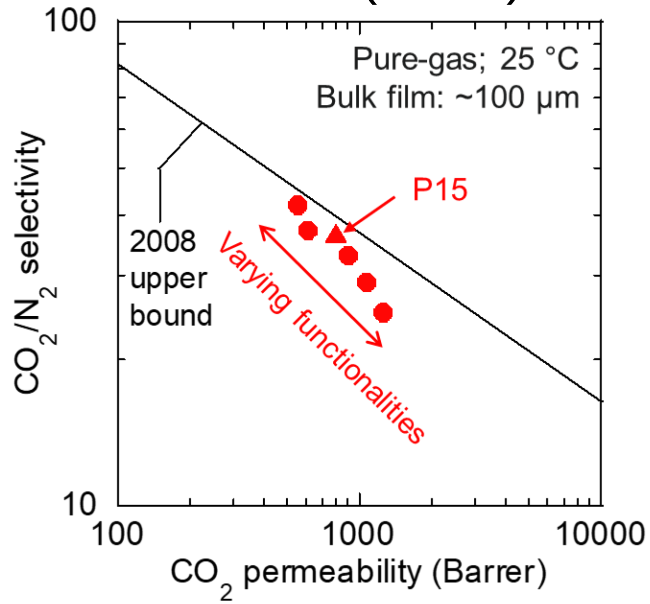
Gutter layer
(EY 20)

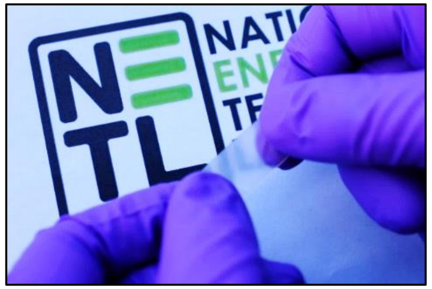


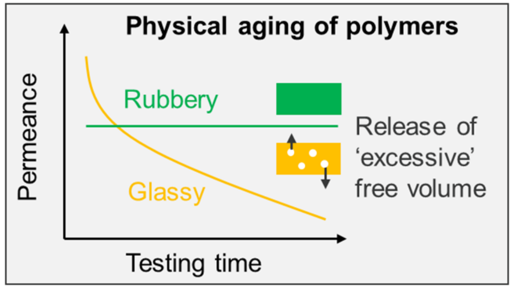
CO_2 perm.: 12,600 GPU
CO_2/N_2 selectivity: 11.5

Defect-free gutter layers with a record-breaking CO_2 permeance

Non-aging rubbery polymer blends (EY20)







Project structure & technical approaches

Polymer X → Novel nanoporous support NETL-RIC

Novel nanoporous support NETL-RIC → Nanoporous support scale-up NETL-RIC

Polydimethylsiloxane → Highly permeable gutter layer NETL-RIC

Rubbery polymer blends INL & NETL-RIC → High-permeance TFC membranes & lab test NETL-RIC → Small module development NETL-RIC

Membrane performance field test NCCC & NETL-RIC

Idaho National Laboratory

NATIONAL CARBON CAPTURE CENTER

Project objective (03/2024): demonstrating a TFC membrane module with CO_2 permeance of >3,000 GPU and CO_2/N_2 selectivity >25 in a long-term (>500 hrs) field test.

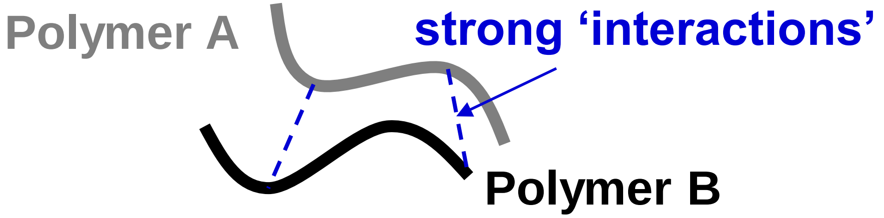
Project schedule and milestones

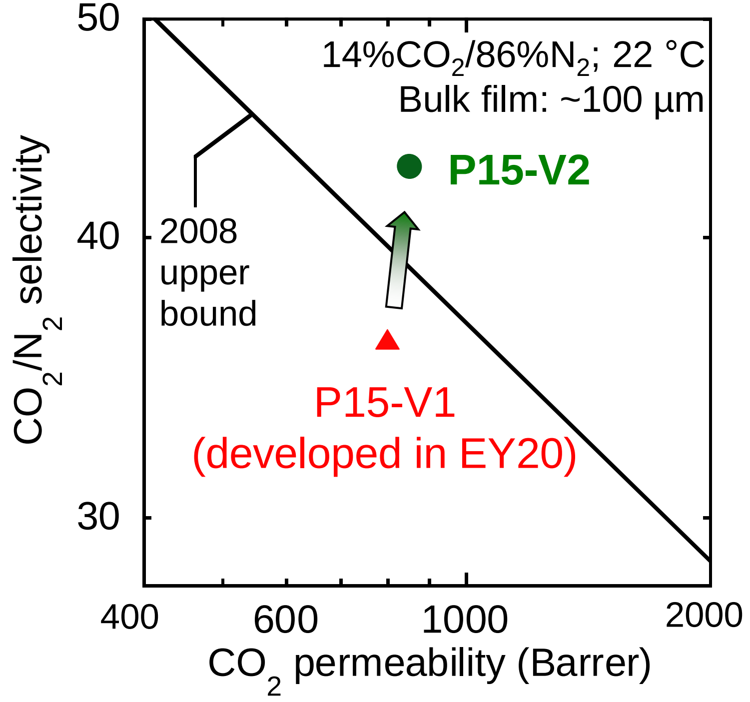
Schedule	Milestones
EY21: 04/01/2021 - 03/31/2022	Demonstrate a functioning 100 cm^2 TFC with CO_2 permeance of > 3,000 GPU and CO_2/N_2 selectivity of > 25 targeted for industrial flue gas and showing no significant aging for 1,000 hours.
EY22: 04/01/2022 - 03/31/2023	Demonstrate a bench-scale 100 cm^2 plate-and-frame module of TFC membranes with CO_2 permeance of > 3,000 GPU and CO_2/N_2 selectivity of > 25 using real or simulated flue gas.
EY22: 04/01/2022 - 03/31/2023	Demonstrate a roll-to-roll fabrication of flat-sheet membrane support at a size of 30 cm × 10 m.
EY23: 04/01/2023 - 03/29/2024	Demonstrate a TFC membrane module with CO_2 permeance of > 3,000 GPU and CO_2/N_2 selectivity of >25 in a long-term (> 500 hours) field test.

Progress & current status of project

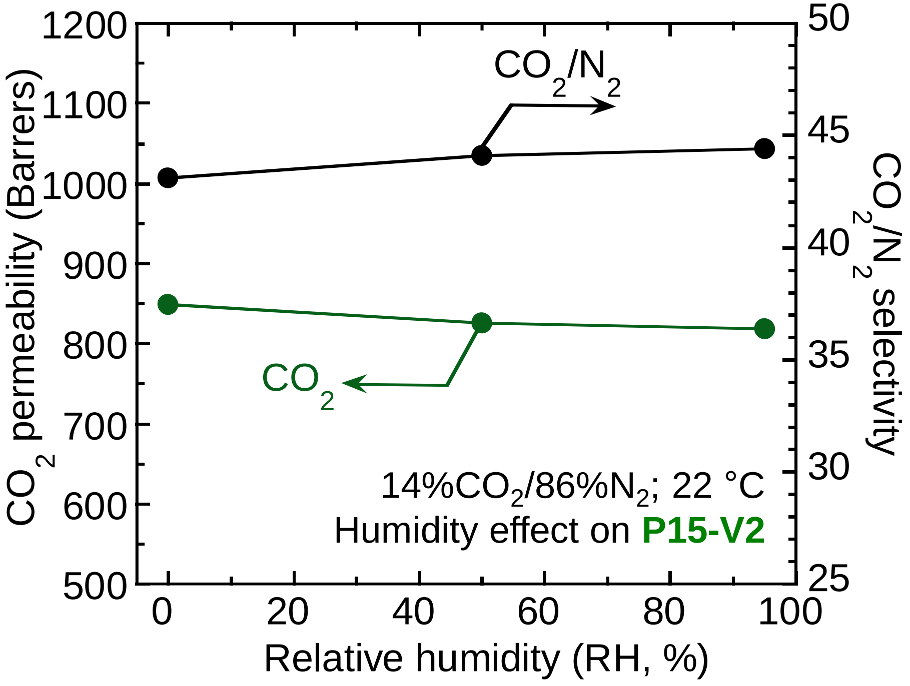
Polymer blend optimization

- Completely rubbery (T_g << -50 °C) → resistant to physical aging
- High molecular weight (M_w > 1 M Dalton) → excellent thin film formation
- Stable in the presence of water vapor





6% permeability enhancement &16% selectivity enhancement



Stable performance in the presence of humidity

Progress & current status of project

Influence of polymer blend optimization on TFC membranes

- Coupon-size TFC fabrication

Selective layer:

P15-V1 or P15-V2

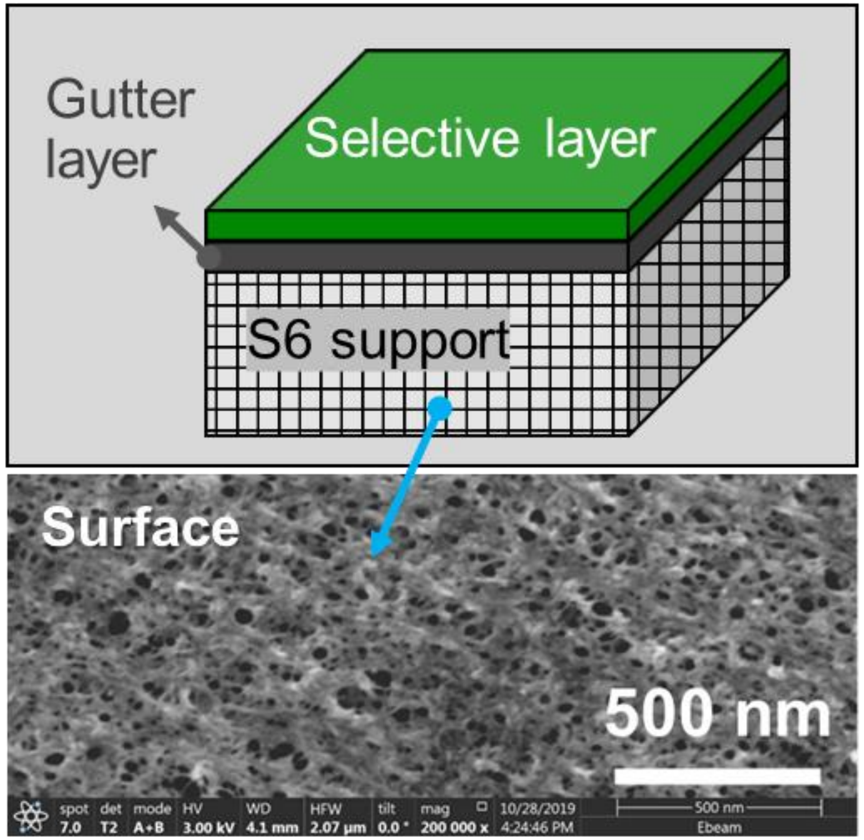
Gutter layer:

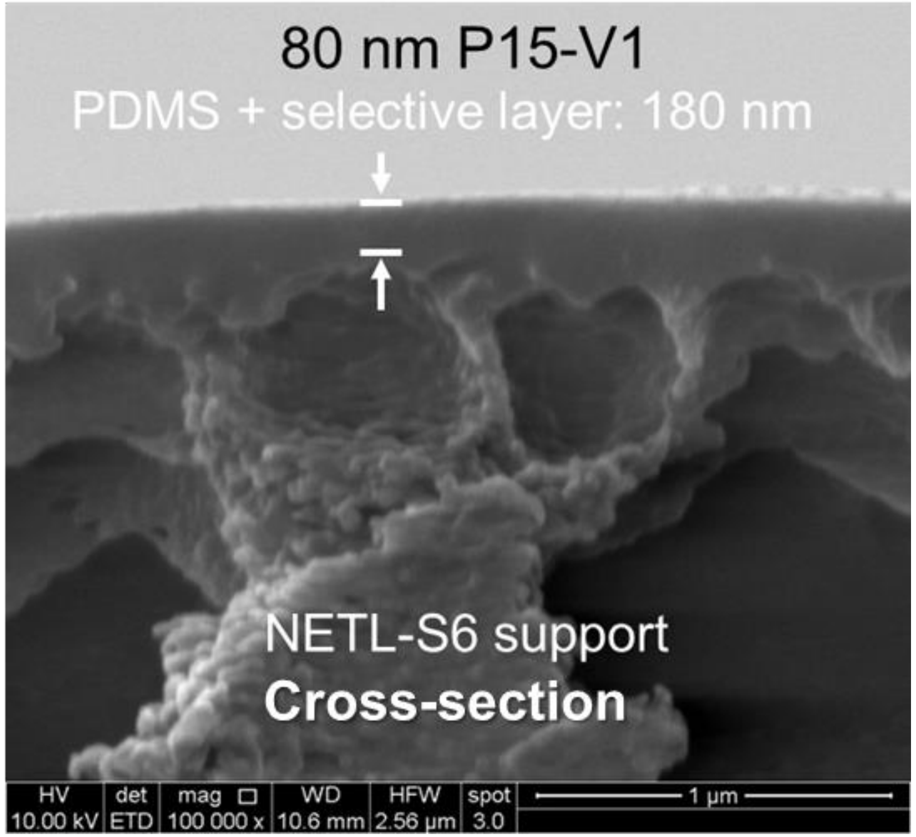
knife-cast 100 nm PDMS

Porous support:

NETL-S6

Fabrication technique:
Spin-coating;
< 10 cm^2 membrane





Progress & current status of project

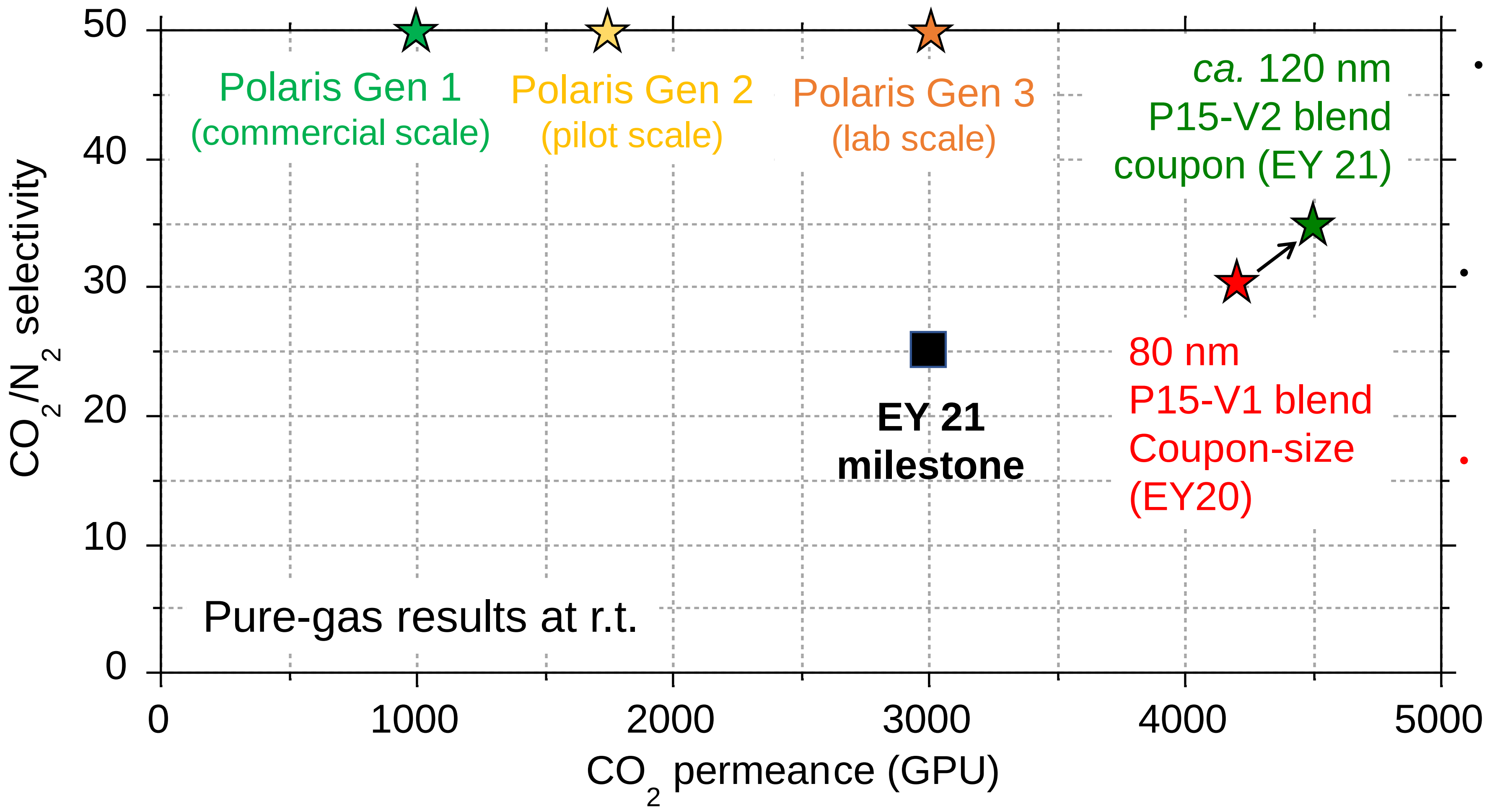
Influence of polymer blend optimization on TFC membranes

- TFC coupons' performance at 22 – 25 °C in pure-gas

Selective material	Selective layer thickness (nm)	CO_2 permeance (GPU)	CO_2/N_2 selectivity
P15-V1 (developed in EY20)	**80**	**4200**	**30**
P15-V2 (newly optimized)	**120 (est.)**	**4500** ↗ 7%	**34** ↗ 13%

- **Higher CO_2 permeance and selectivity in the P15-V2 TFC than the P15-V1 TFC though the P15-V2 layer is thicker.**
- **No permeance drop was observed on the P15-V2 TFC after aging for 300 hrs.**

Comparison of the polymer blend TFC membranes with the leading membranes for CO_2/N_2 separation



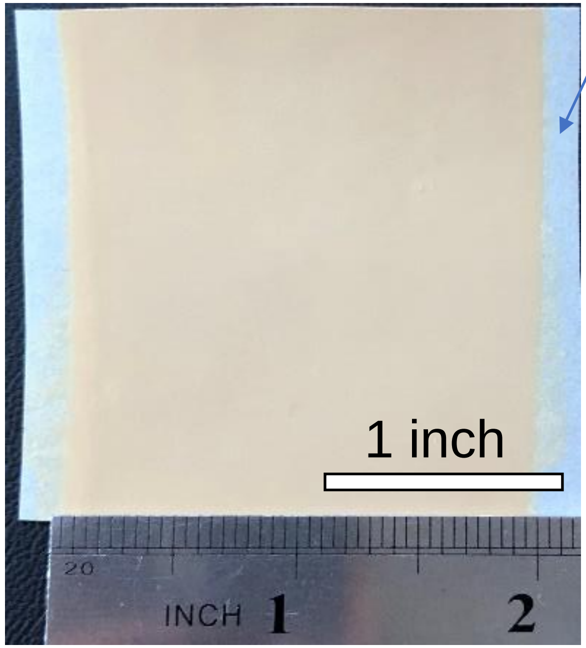
- MTR Polaris membrane performance: Project FE0031591 Technology Sheet, https://netl.doe.gov/project-information?p=FE0031591
- **Success criteria (EY21 milestone):** a 100 cm^2 TFC with CO_2 permeance > 3,000 GPU and CO_2/N_2 selectivity > 25 and showing no significant aging for 1,000 h.
- 100 cm^2 membranes have not yet been prepared, and our technical approach is to prepare the target size using knife-casting, instead of spin-coating that is only suitable for coupon-size preparation.

Progress & current status of project

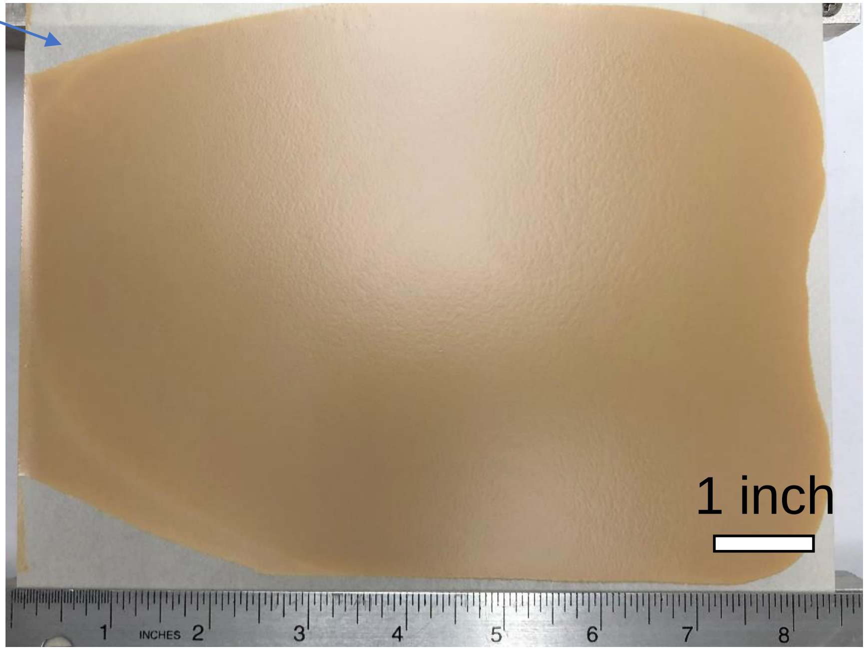
Scale-up activities on NETL-S6 support

to accommodate the P15-based TFC membrane scale-up (to 100 cm^2 in EY21)

Non-woven fabrics

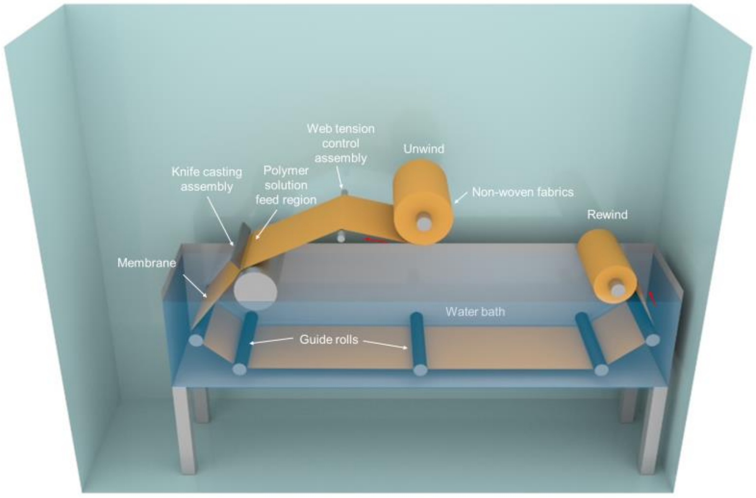


EY20: ~ 40 cm^2



Current: ~ 200 cm^2

Roll-to-roll fabrication



Machine customization in progress

A non-provisional patent application was filed on the NETL-S6 support fabrication in July 2021.

Future plans

TFC fabrication and lab test (the rest of EY21)

- Fabrication of 100 cm^2 P15-V2 based-TFC membranes;
- Dry/wet mixed-gas testing of P15-V2 based-TFC membranes using 10 – 30% CO_2 balanced with N_2 that simulates gas streams emitted from coal power plants (14% CO_2), cement plants (20-30% CO_2) or steel mills (20-30% CO_2).

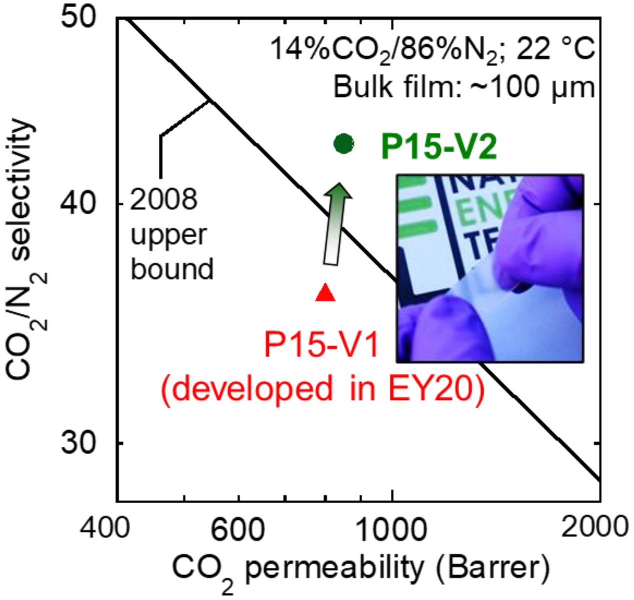
Membrane modulation and porous support scale-up (EY22)

- Small plate-and-frame membrane module fabrication and testing in lab and at NCCC;
- Procurement, installation, shakedown, and operational test of a roll-to-roll membrane fabrication machine. Pilot-scale (30 cm × 10 m) production of NETL-S6 support.

TFC scale-up and field test (EY23)

- TFC membrane scale-up, module optimization, and a long-term field test of the membrane modules

Summary: NETL has taken a well-designed and fruitful approach to high-permeance TFC membranes for low-cost CO_2 capture.



Selective material optimization

(U.S. patent application in preparation)

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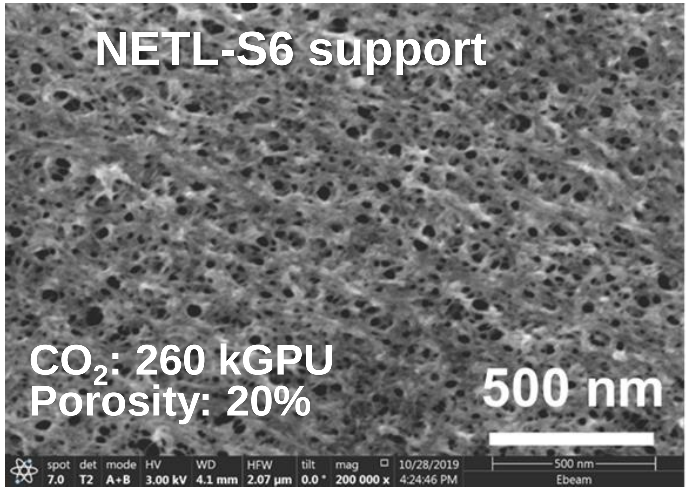

Novel porous membrane support

(U.S. patent pending)

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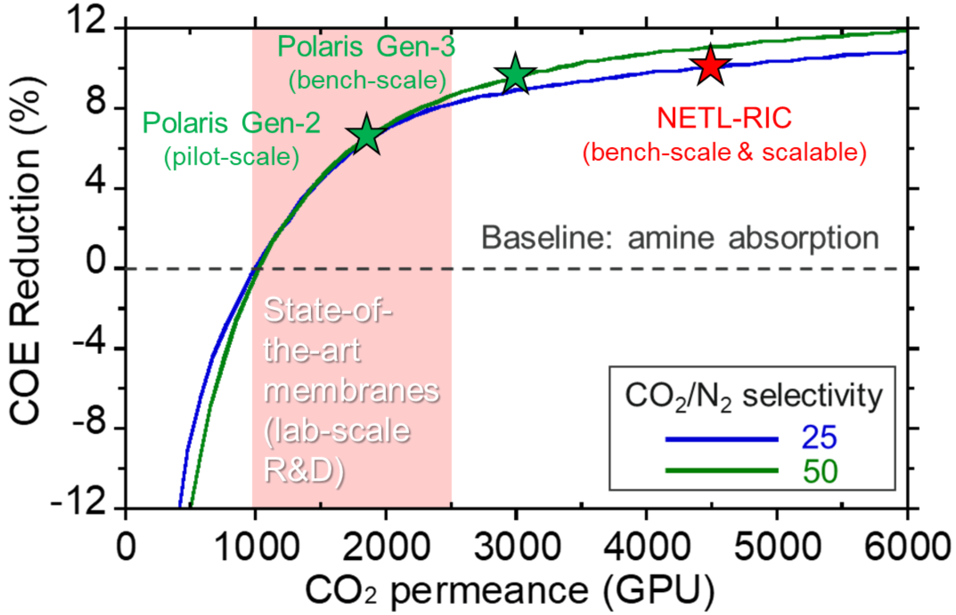

Lower-cost CO_2 capture (10% decrease) *vs.* amine absorption

1. Alex Zoelle *et al.*, *Performance and Cost Sensitivities for Post-Combustion Membrane Systems*, 2018 NETL CO_2 Capture Technology Project Review Meeting
2. MTR Polaris membrane performance: Project FE0031591 Technology Sheet, https://netl.doe.gov/project-information?p=FE0031591

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