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

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Point Source Carbon Capture — Capture from Power Generation / Lab/Bench-Scale Research
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Project Overview

- **Project:** High Permeance Blended Rubbery Membranes
- **Project Period**: EY21 – EY24 (04/01/2021 – 03/31/2025)
- **Funding Source**: NETL-RIC Field Work Proposal: Transformational Carbon Capture - Task 21 (EY21)

  Point Source Capture Technology – Task 2 (EY22 – EY24)
- **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 non-aging properties.**
- **Project Participants:**

  NETL Research & Innovation Center (RIC)

  Idaho National Laboratory (INL)

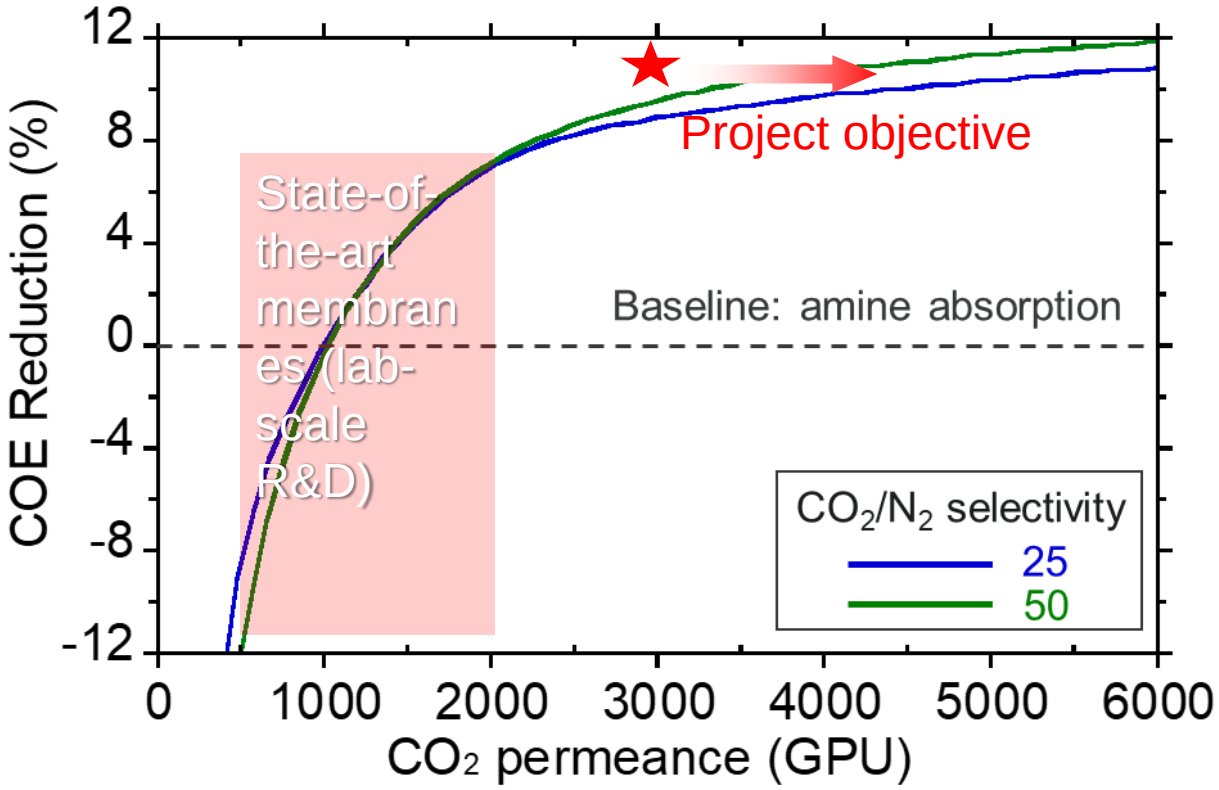
  National Carbon Capture Center (NCCC)

  and more are to join us…

Project Schedule and Milestones

Schedule	Milestones
EY21 (04/21-03/22)	Demonstrate a functioning 100 cm^2 TFC with CO_2 permeance of > 3,000 GPU and CO_2/N_2 selectivity of > 25, showing no significant aging for 1,000 hrs.
EY22 (04/22 – 03/23)	Demonstrate a bench-scale 100 cm^2 plate-and-frame module of the developed TFC membrane using simulated flue gas.
	Demonstrate a roll-to-roll fabrication of flat-sheet membrane supports.
EY23 (04/23 – 03/24)	Demonstrate a roll-to-roll fabrication of a TFC membrane at a size of 30 cm × 30 cm.
	Demonstrate a 30 × 30 cm plate-and-frame module using simulated flue gas.
EY24 (04/24 – 03/25)	Demonstrate a 30 × 30 cm plate-and-frame module of TFC membrane in a long-term field test at a commercial steel mill.

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

Background: Achieving High Permeance *via* Selective Material Optimization and TFC Fabrication

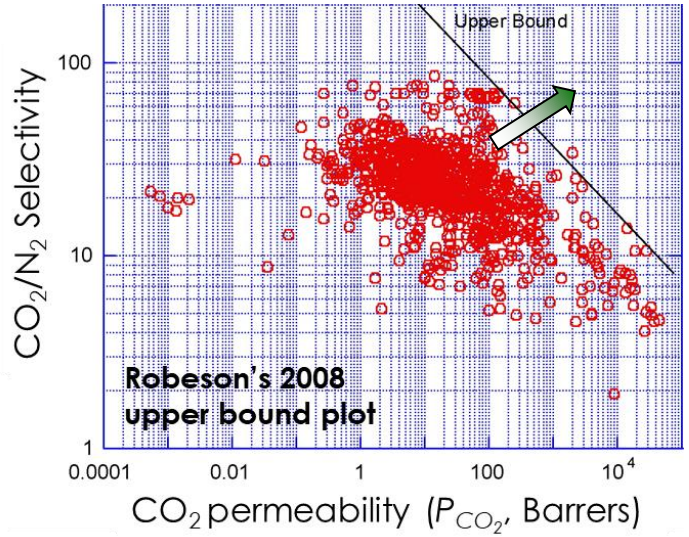
$$\uparrow \textbf{Permeance} = \frac{Permeability\ (P)\ of\ selective\ material \uparrow}{thickness\ of\ selective\ layer \downarrow}$$

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

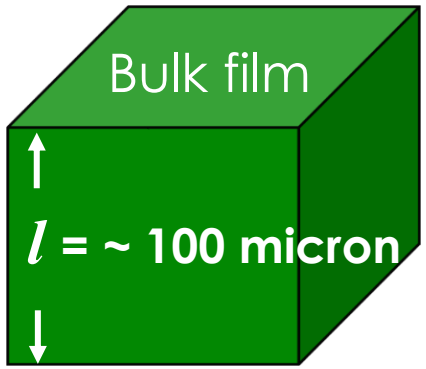
Permeance (in GPU) is pressure normalized flux. Permeability (in Barrer) is a material property independent of thickness.

1. Selective material optimization

Permeability/selectivity tradeoff

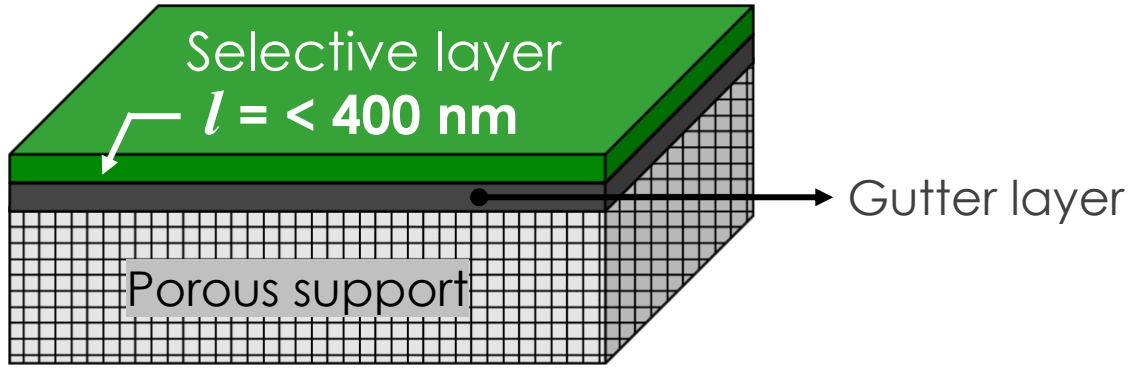


Robeson, *J. Membr. Sci.* 320 (2008) 390



Thickness reduction

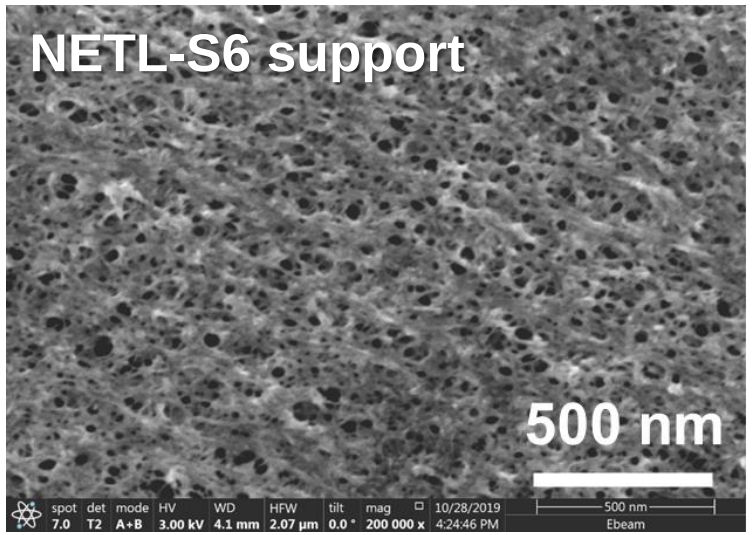
2. TFC membrane fabrication



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 Efforts

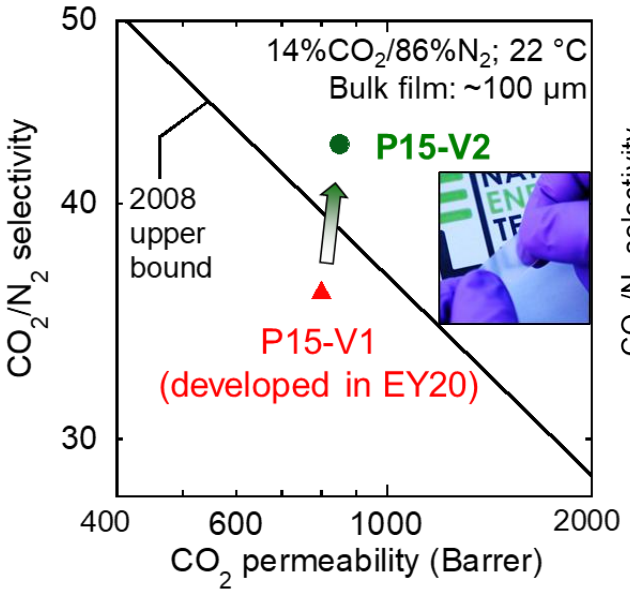
Novel nanoporous support
(EY18-20)



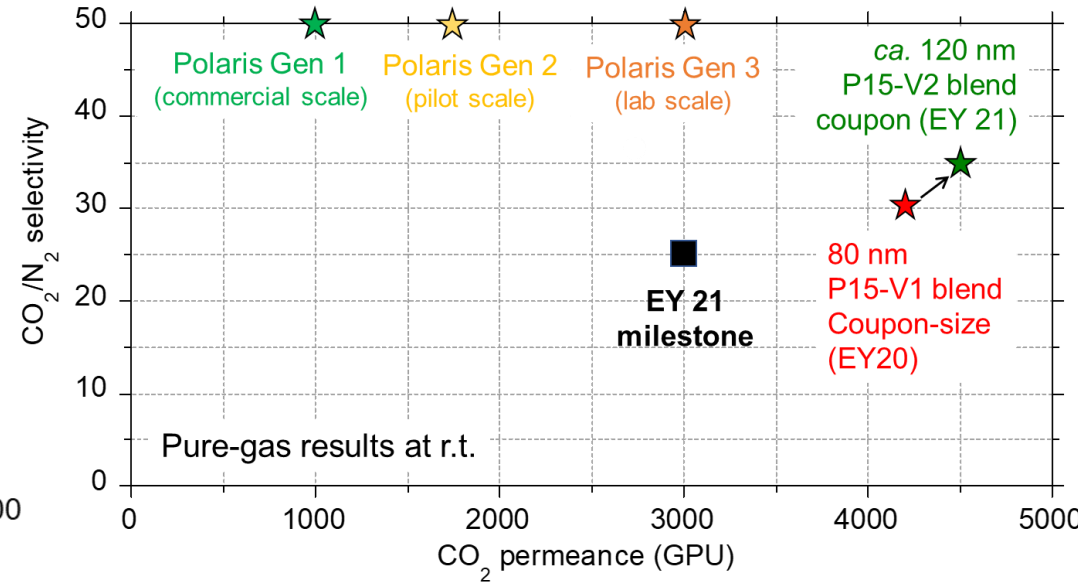
CO_2 perm.: 260,000 GPU
Pore size: 5 - 42 nm
Porosity: 20 ± 2%
Operation temp.: ≤ 200 °C
Solvent resistance to THF, chloroform, acetone, *etc.*
PDMS gutter layer: >12,000 GPU of CO_2 permeance

High-performance rubbery polymer blends
(EY20)

Bulk-film property



TFC performance

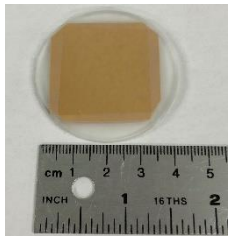


MTR Polaris membrane performance: Project FE0031591 Technology Sheet, https://netl.doe.gov/project-information?p=FE0031591

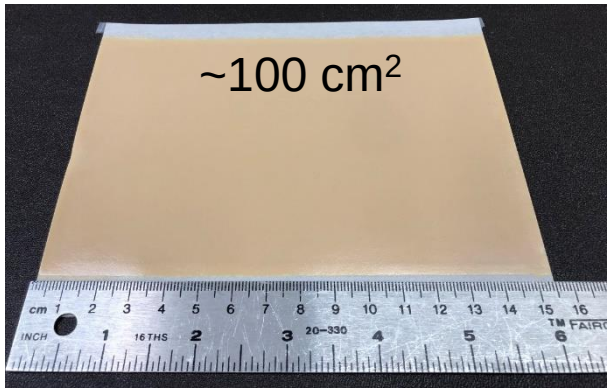
Highlights of EY21-22

TFC scale-up

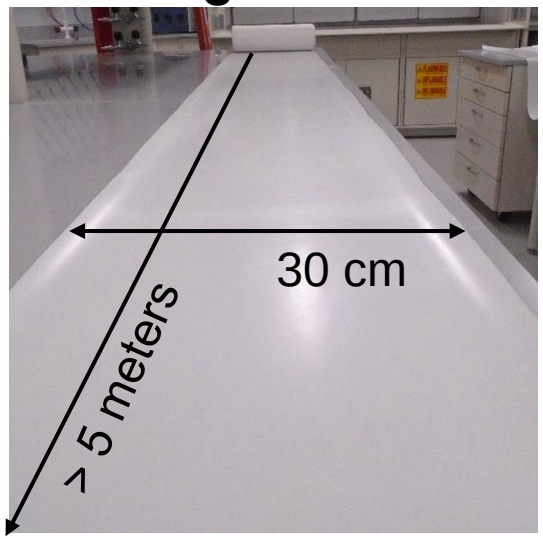
- **Lab-scale coating**



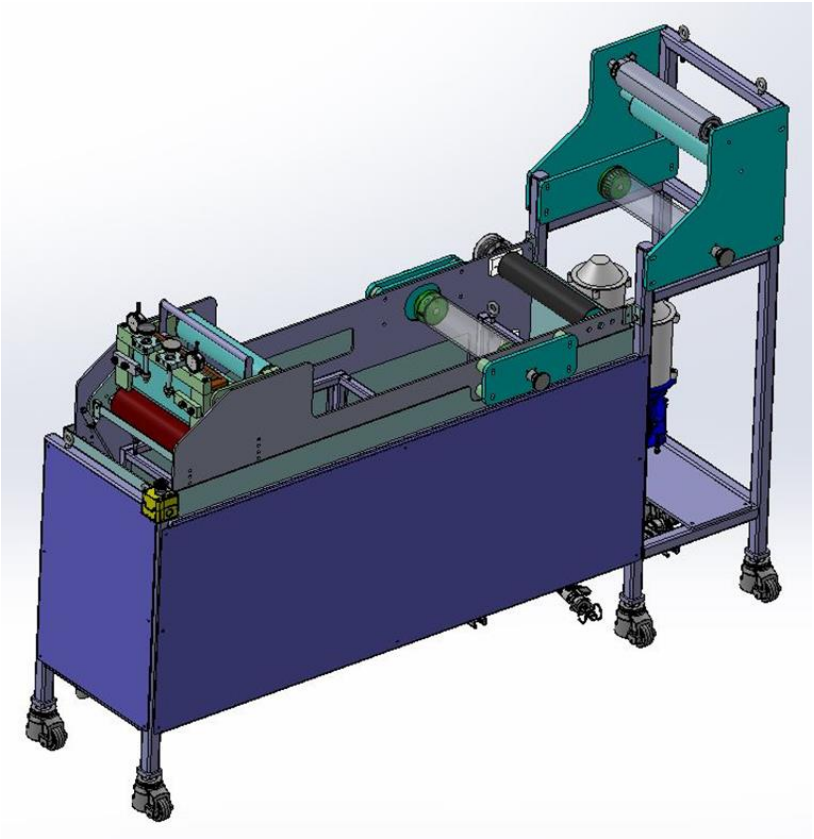
~10 cm^2



- **Roll-to-roll coating**

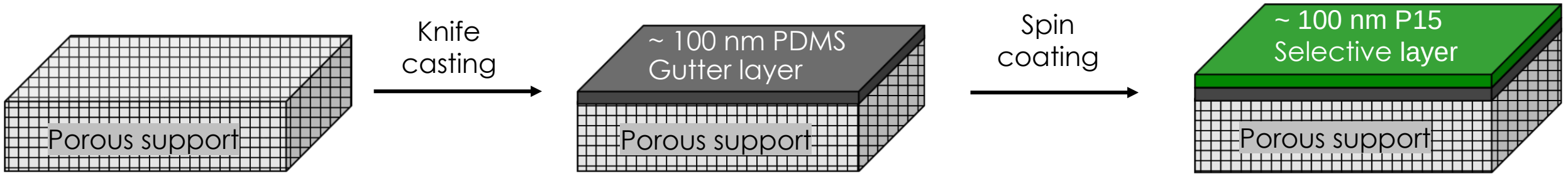


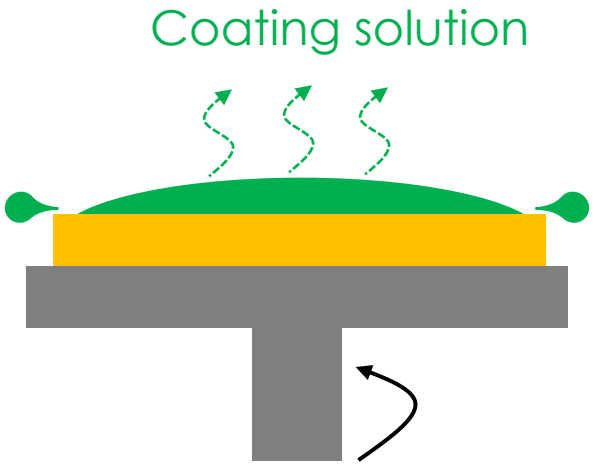
Porous support scale-up



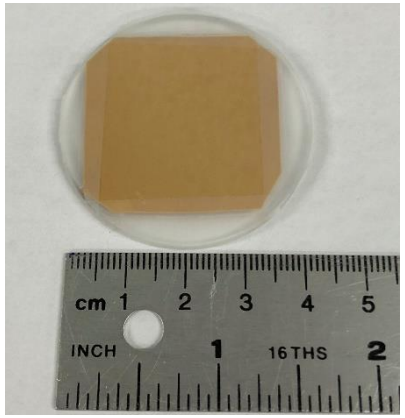
Progress Update on TFC Scale-Up

(~10 cm^2) Coupon-Size TFC Fabrication





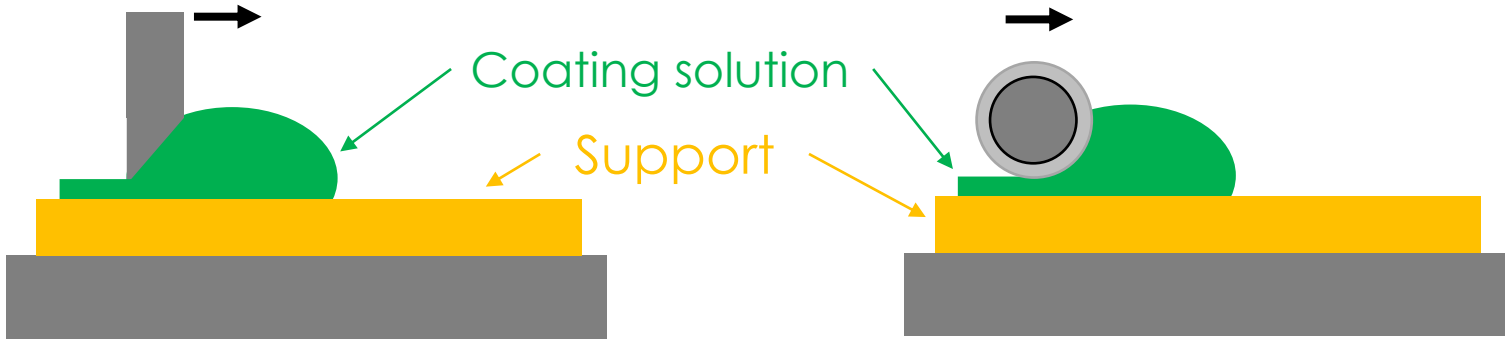
Spin coating



- High-permeance TFC: Pure-gas CO_2 permeance of 4,500 GPU & CO_2/N_2 selectivity of 34 at 22 °C
- However, spin coating is not suitable for scale-up fabrications

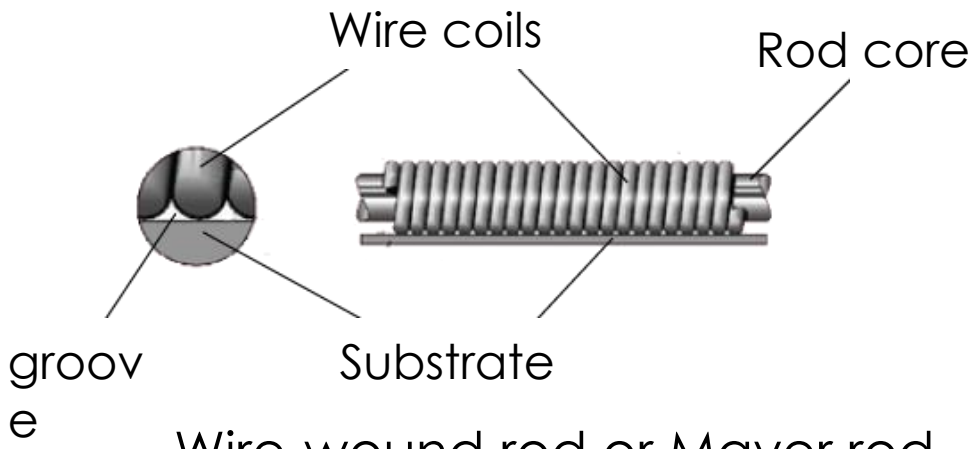
Progress Update on TFC Scale-Up

Selection of Scalable Coating Methods

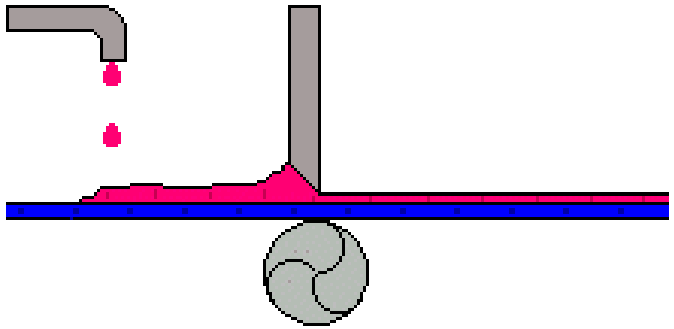


Knife casting

Mayer rod coating



Wire-wound rod or Mayer rod



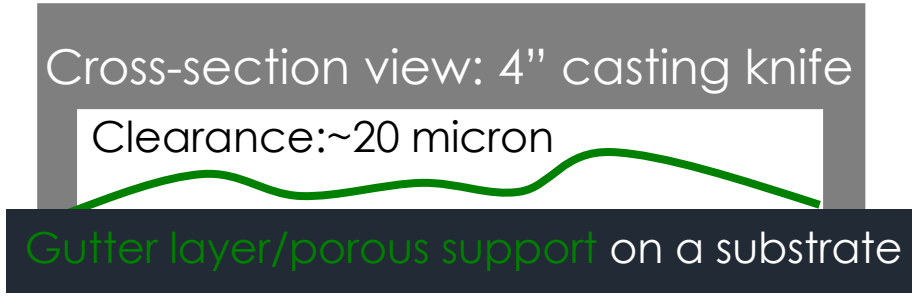
R2R continuous coating using a casting knife or a Mayer rod (*Courtesy of tciinc.com*)

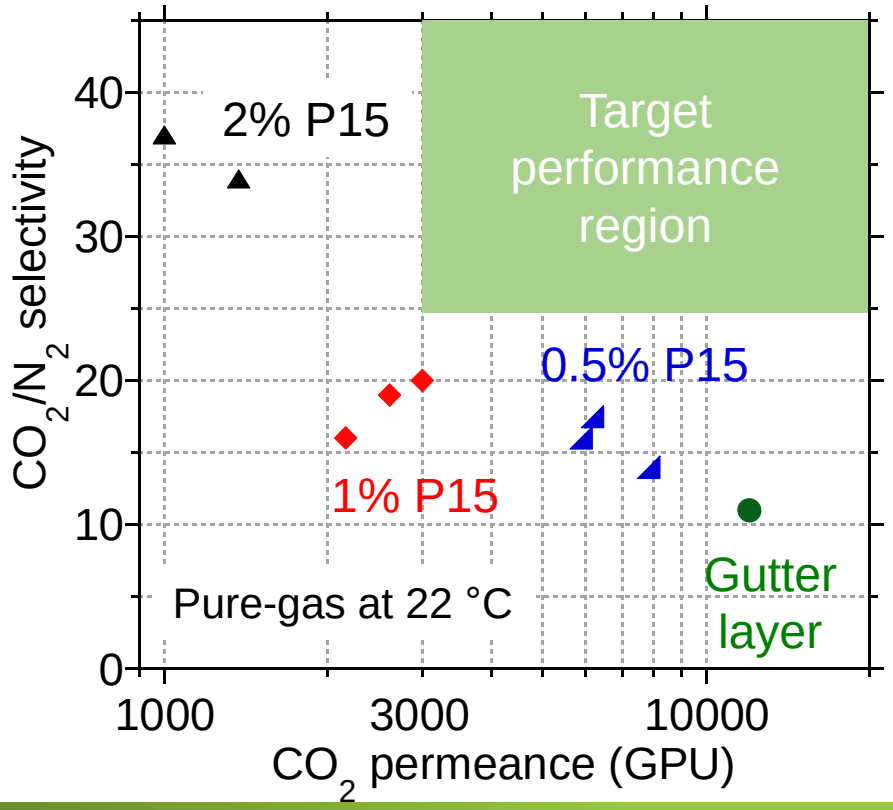
Progress Update on TFC Scale-Up

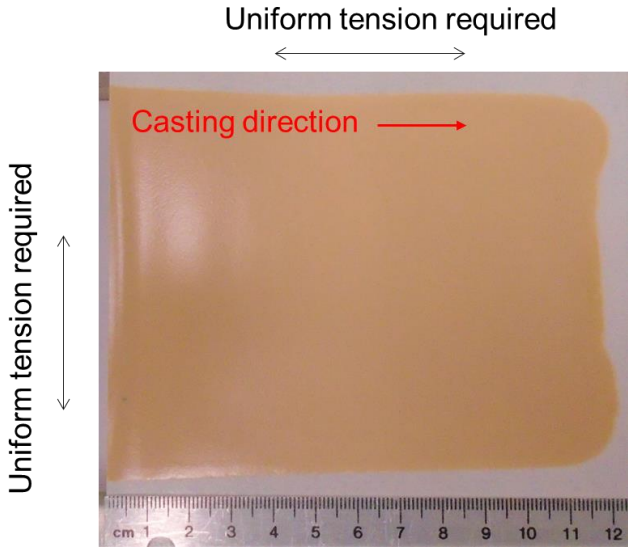
100 cm² TFC Fabrication *via* Knife Casting

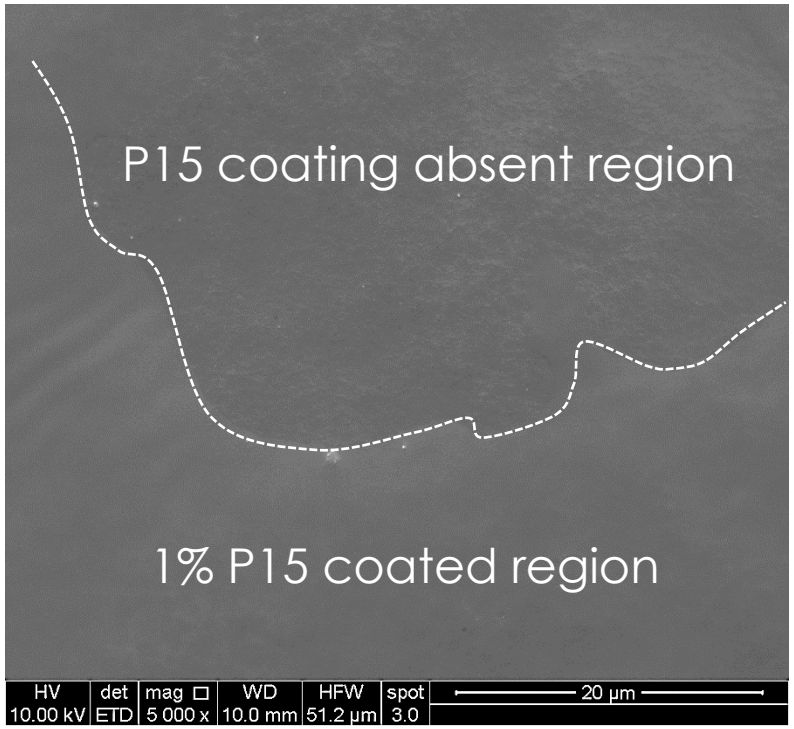
1st coating: gutter layer, ~100 nm PDMS

2nd coating: selective layer, 0.5 – 2.0 wt.% P15







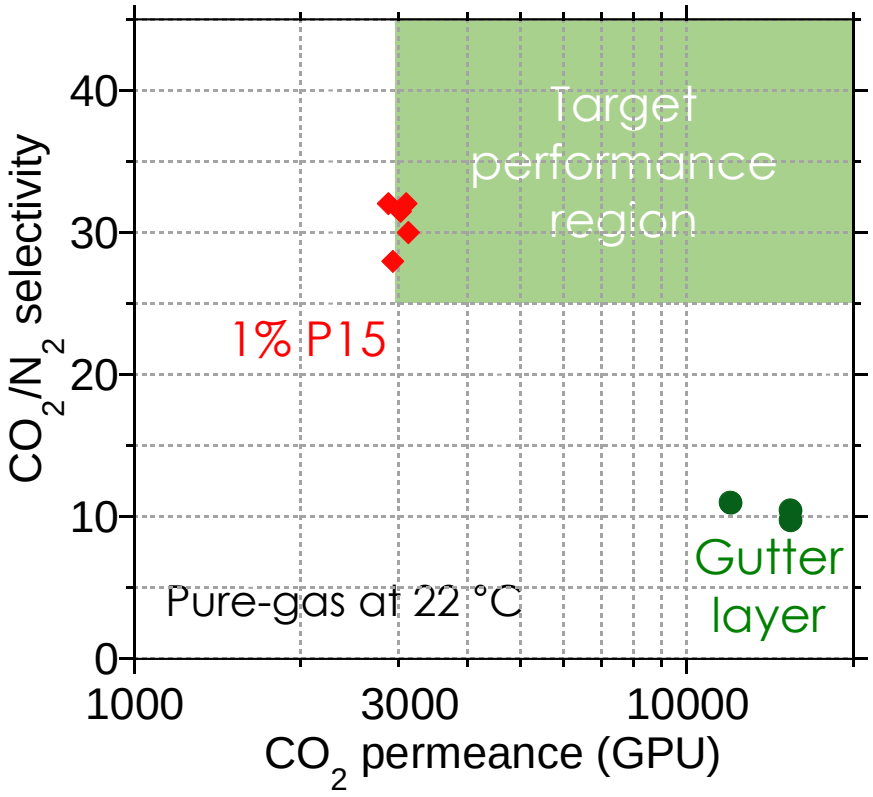


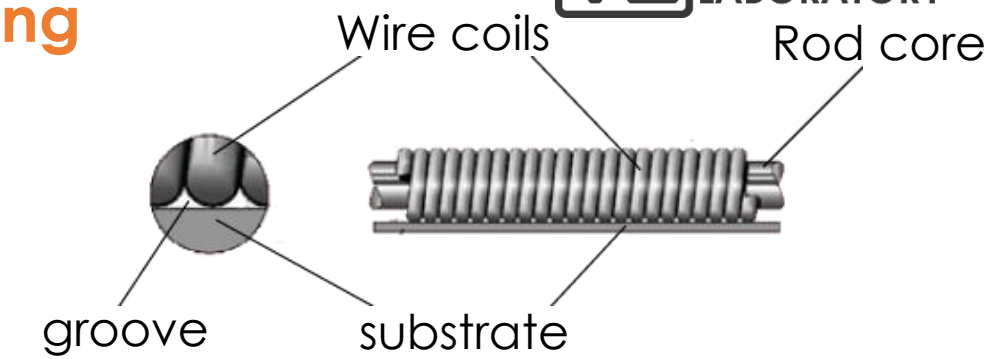
Progress Update on TFC Scale-Up

≥ 100 cm² TFC Fabrication *via* Mayer Rod Coating

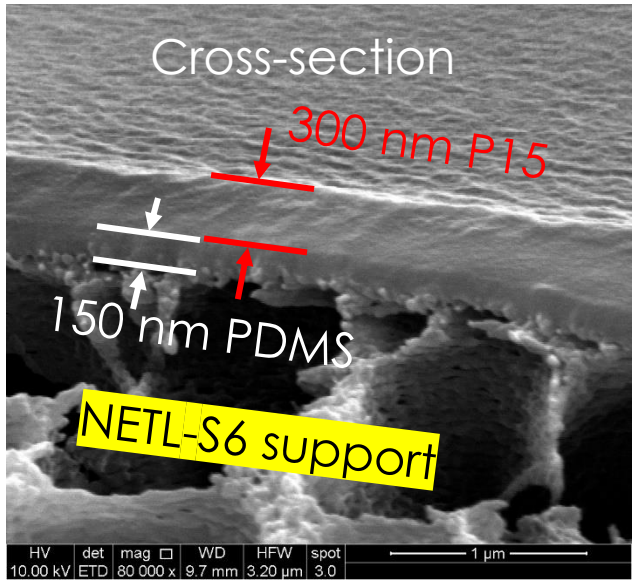
1st coating: gutter layer, ~150 nm PDMS

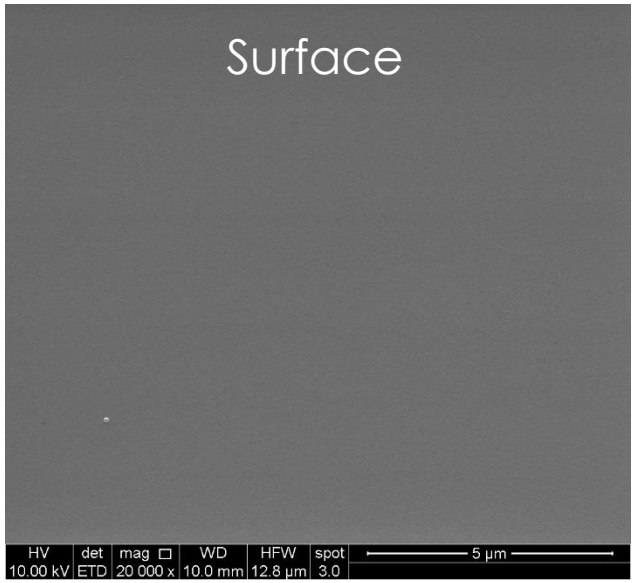
2nd coating: selective layer, 1 wt.% P15





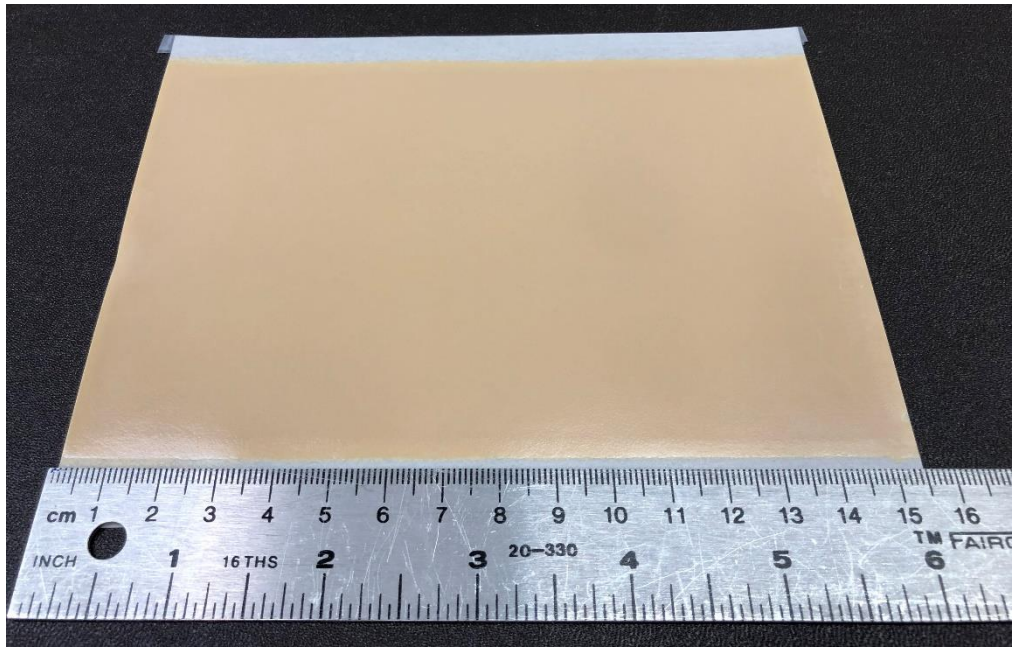
Coils can smoothen the membrane support during coating.





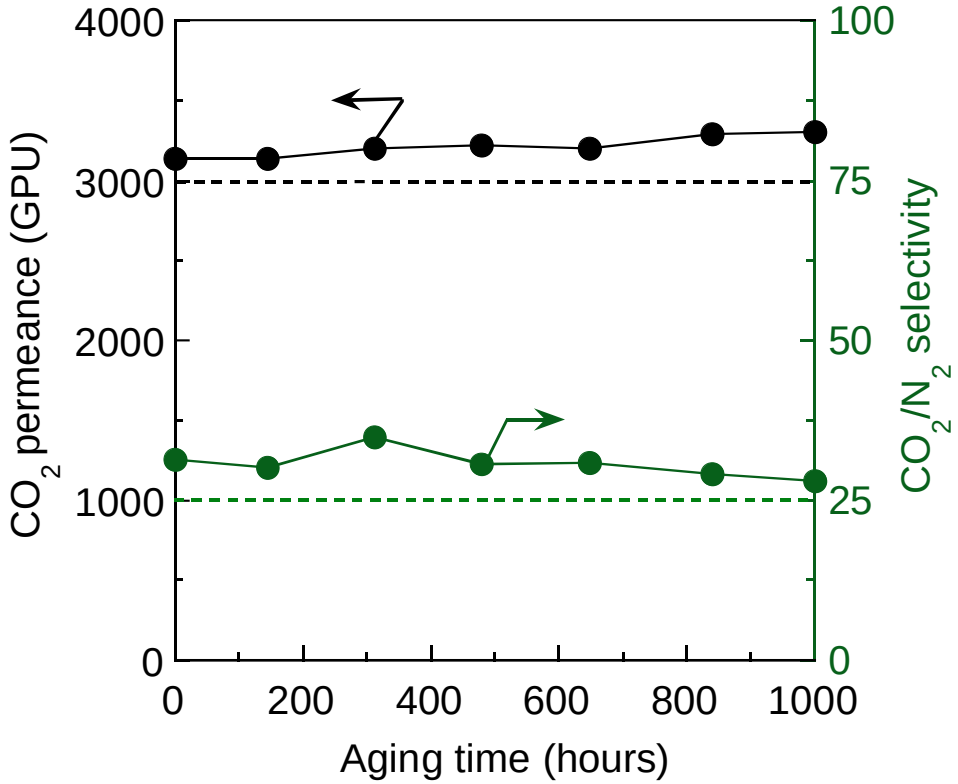
Progress Update on TFC Scale-Up

Non-Aging Behavior



~150 cm^2 multilayer TFC membrane:

300 nm P15 / 150 nm PDMS / NETL-S6 support



Test conditions: pure & dry gas, 22 °C

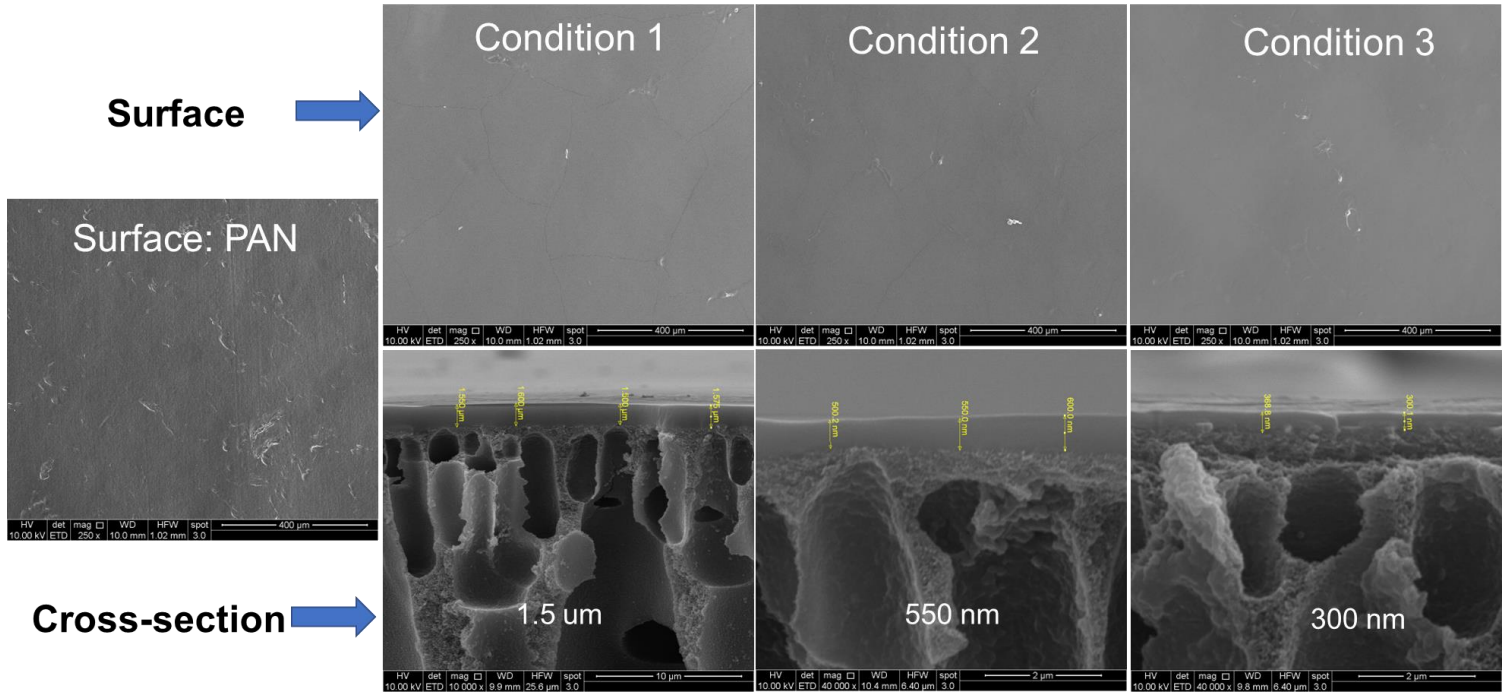
Progress Update on TFC Scale-Up

Further TFC Scale-Up: Roll-to-Roll Membrane Coating Machine

- Identified a suitable coating machine;
- Performed a membrane coating test run at the vendor's demo unit;
- Initiated the procurement of a custom coating machine.

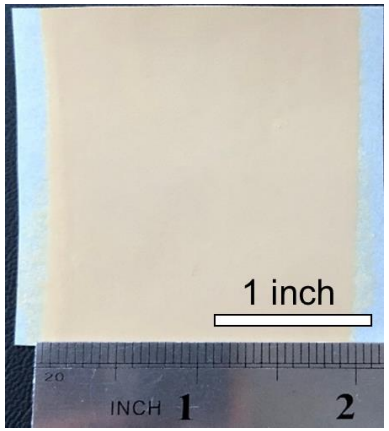
A test run performed in March 2022

- Coating material: a commercial polymer
- Porous support: polyacrylonitrile (PAN)
- Coating width: 30 cm
- 30 cm × 90 meters of TFCs prepared

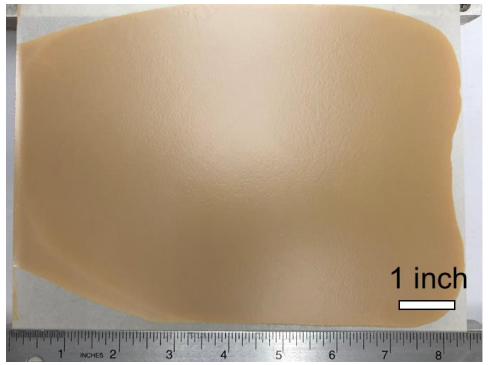


Progress Update on Membrane Support Scale-Up

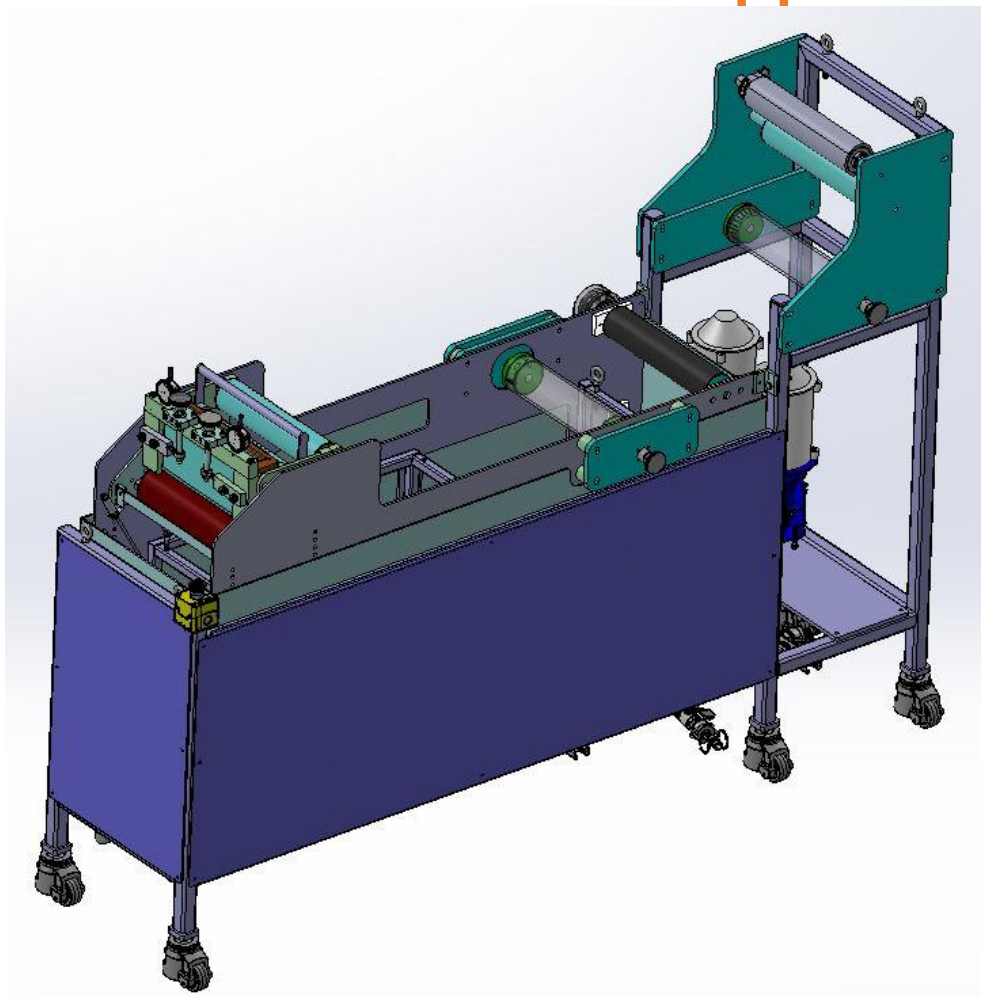
Scale-Up Activities on NETL-S6 Membrane Support



EY20: ~ 40 cm^2



EY21: ~ 200 cm^2



EY21 & 22: Customization of a roll-to-roll membrane support casting machine

Kick-off: Dec. 2021

Est. delivery/shakedown test at NETL: Dec. 2022

Specifications:

Line speed: 0.6 – 4.8 m/min

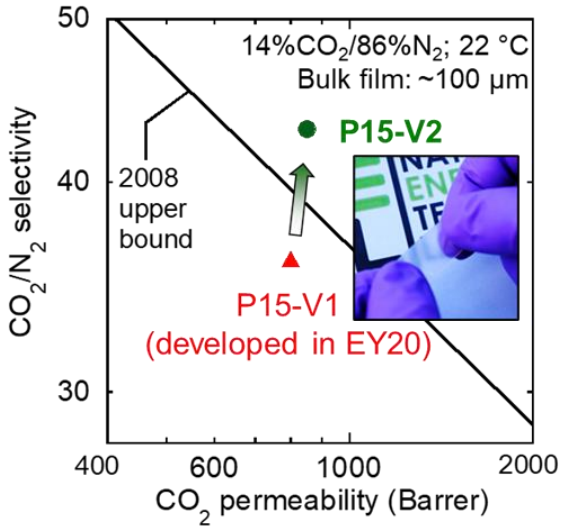
Membrane width: 30 cm

Project Status and Future Work

Schedule	Milestones	Status
EY21 (04/21-03/22)	Demonstrate a functioning 100 cm^2 TFC with CO_2 permeance of > 3,000 GPU and CO_2/N_2 selectivity of > 25, showing no significant aging for 1,000 hrs.	**Completed**
EY22 (04/22 – 03/23)	Demonstrate a bench-scale 100 cm^2 plate-and-frame module of the developed TFC membrane using simulated flue gas.	**On-track:** initiated module design and fabrication; studied membrane sealing methods
	Demonstrate a roll-to-roll fabrication of flat-sheet membrane supports.	**On-track:** machine shakedown expected in Dec. 2022
EY23 (04/23 – 03/24)	Demonstrate a roll-to-roll fabrication of a TFC membrane at a size of 30 cm × 30 cm.	Test run on a selected coating machine; the machine being acquired
	Demonstrate a 30 × 30 cm plate-and-frame module using simulated flue gas.	
EY24 (04/24 – 03/25)	Demonstrate a 30 × 30 cm plate-and-frame module of TFC membrane in a long-term field test at a commercial steel mill.	In talk with potential host site partners; a membrane test unit being designed

Summary: NETL's High-Permeance TFC Membranes for Low-Cost CO_2 Capture

High-performance materials



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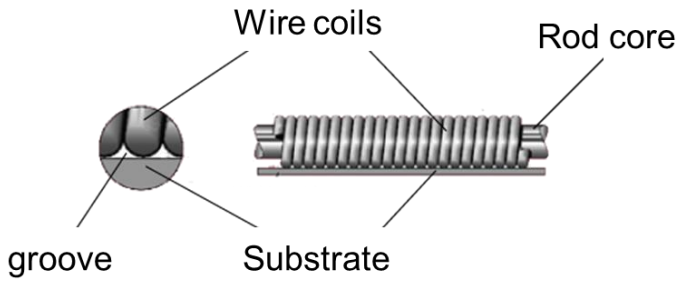
Suitable coating technique



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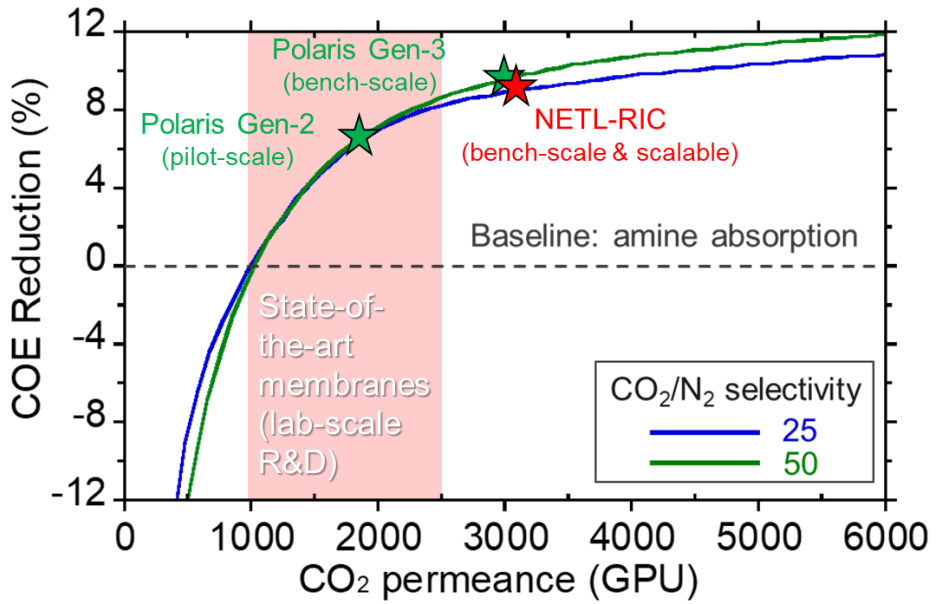

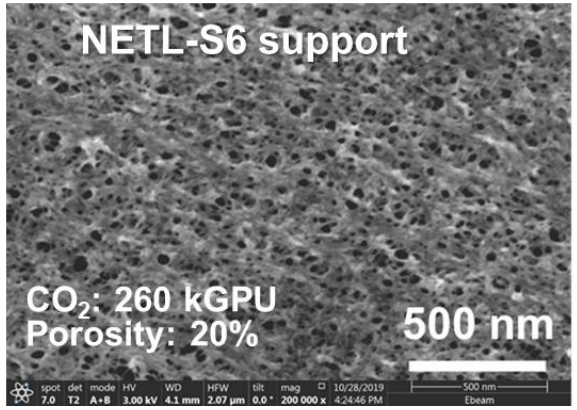

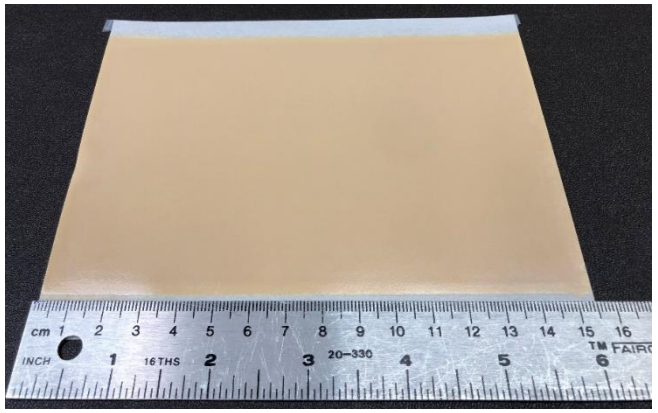

Lower-cost CO_2 capture *vs.* amine absorption

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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