High Performance Thin Film Composite Membranes for Post-Combustion Carbon Capture

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National Energy Technology Laboratory
Carbon Capture
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Project overview

Transformational Carbon Capture Field Work Proposal

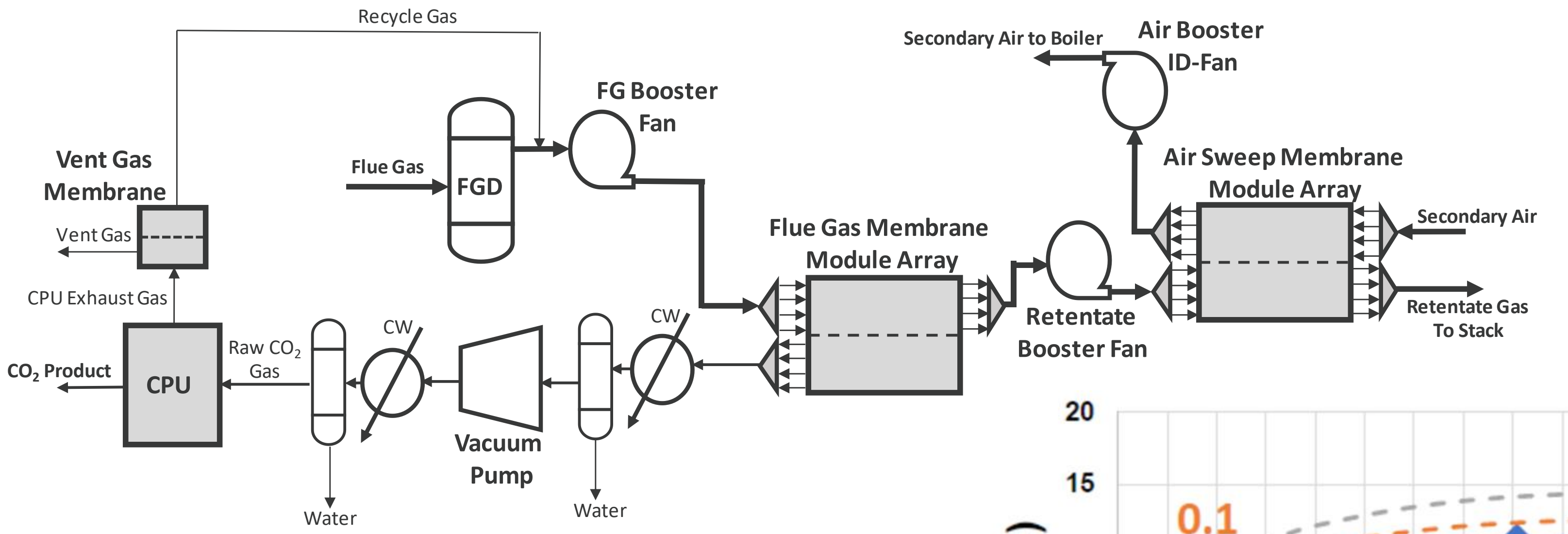
- EY20: 04/01/20 - 03/31/21
- Program area: post-combustion carbon capture
  - ❖ Advanced polymer membranes (Task 9)
  - ❖ Thin film composite design (Task 11.1)

Objective: In EY20, we aim to demonstrate a functioning, defect-free thin film composite (TFC) membrane with CO_2 permeance of >2,000 GPU and CO_2/N_2 selectivity >25. **[Completed]**

Project participants

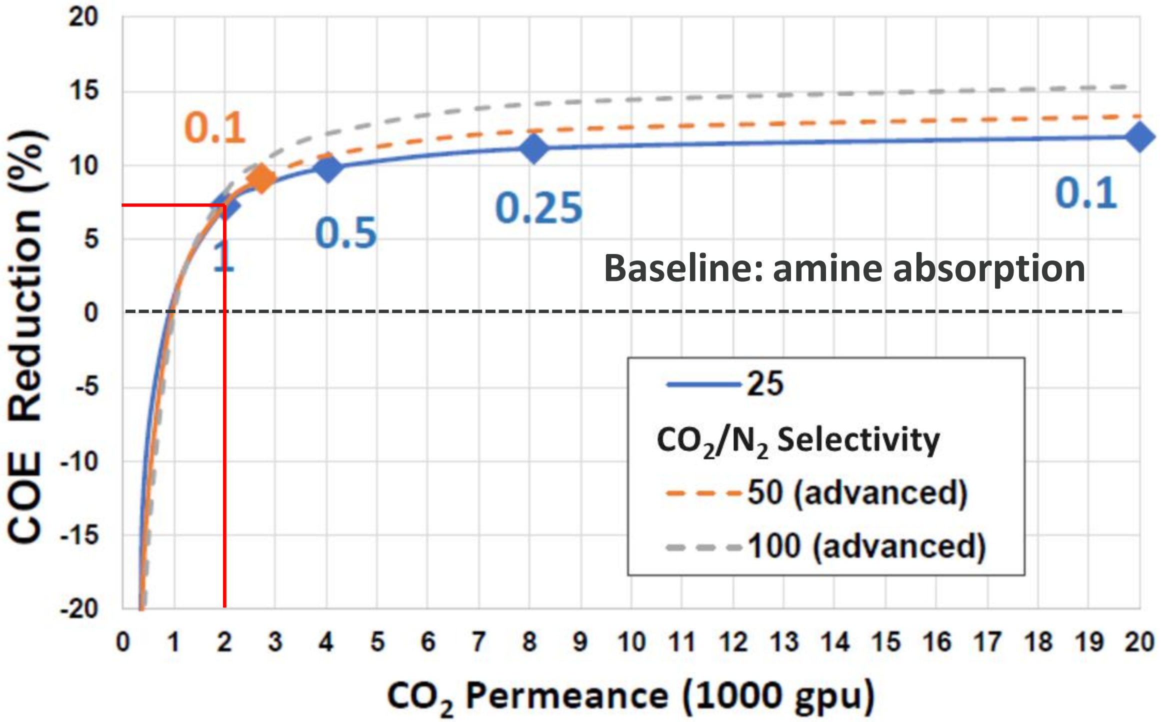
- NETL Research and Innovation Center (RIC)
- Idaho National Laboratory
- National Carbon Capture Center

Membrane tech. can reduce CO_2 capture cost in coal power plants



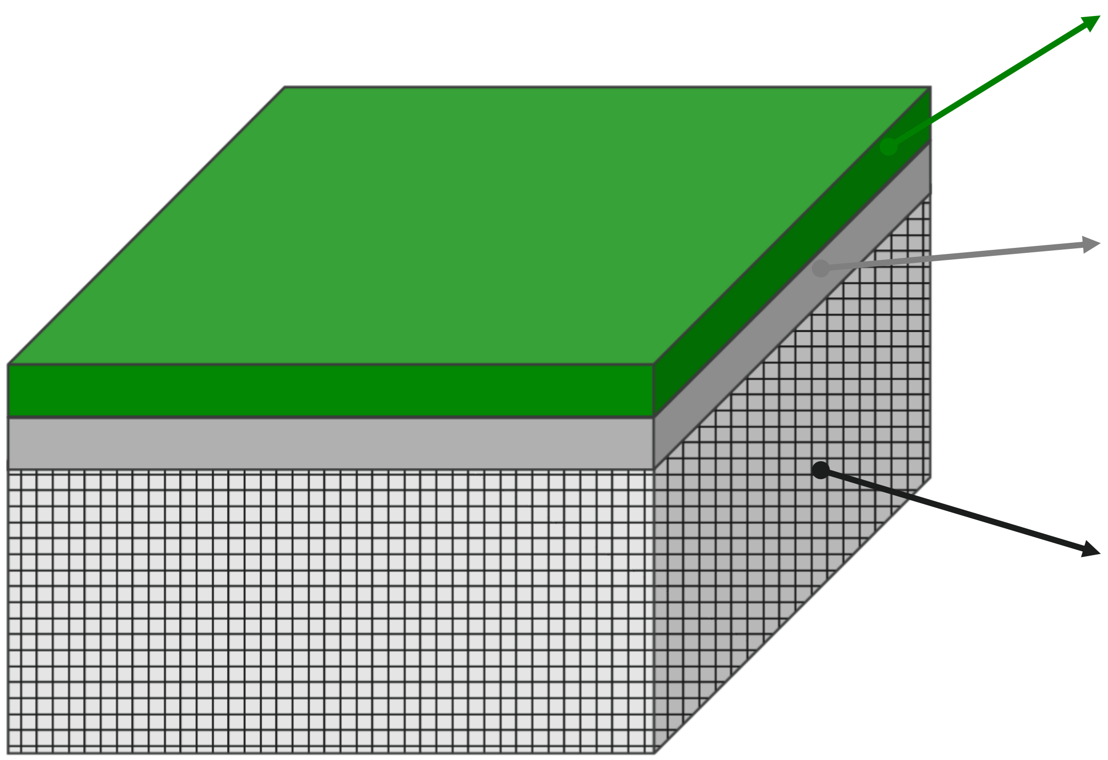
Two stage membrane process with air sweep

For a 7% reduction in cost of electricity (COE) over reference plant, CO_2 permeance of 2000 GPU and CO_2/N_2 selectivity of 25 is needed.



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

Technology background: gas separation uses polymer-based TFC membranes for their simplicity and processability.



Thin film composite (TFC) membrane

< 1 µm selective layer

- Separating gas molecules

100 - 500 nm gutter layer

- Preventing the selective layer pore penetration
- Smoothening the porous support surface

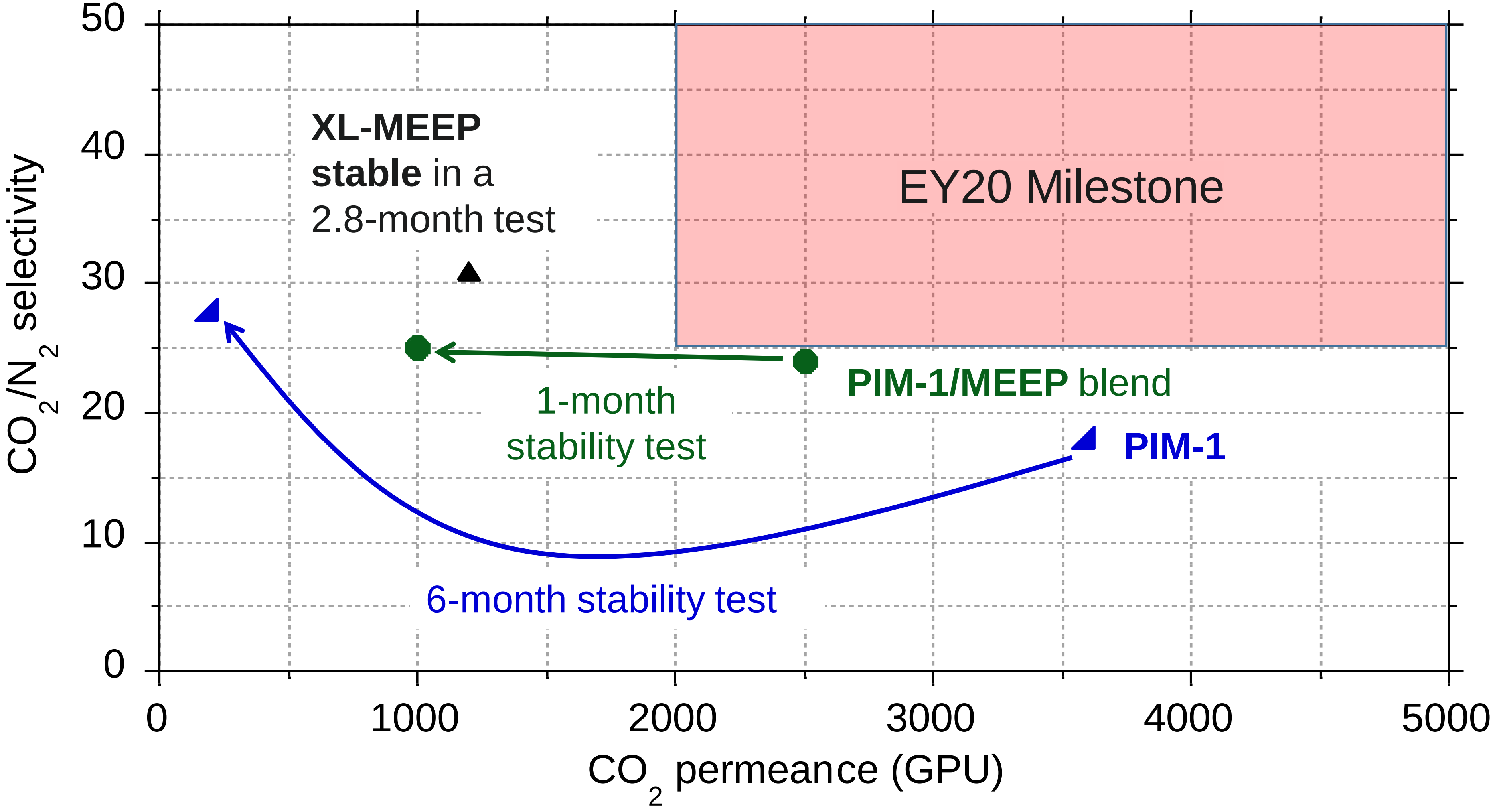
> 20 µm porous support

- Providing mechanical support
- Nanoporous, < 50 nm pores

NETL RIC's prior efforts in TFC membrane development

Sub-micron thin film studies in **EY18-19**:

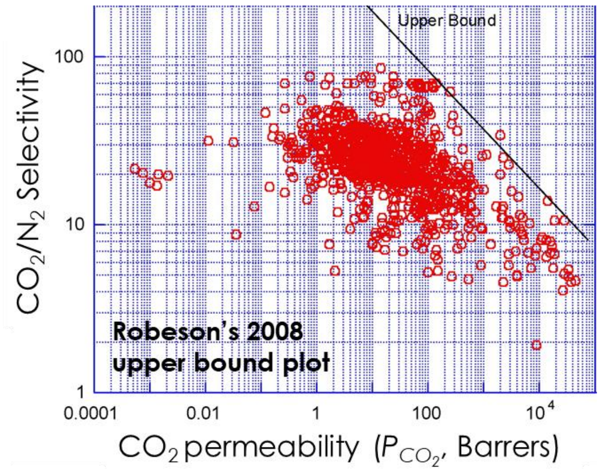
- Polymer of intrinsic microporosity **(PIM-1)**
- Cross-linked poly((methoxyethoxy) ethoxy)phosphazene **(XL-MEEP)**
- **PIM-1/MEEP** blend

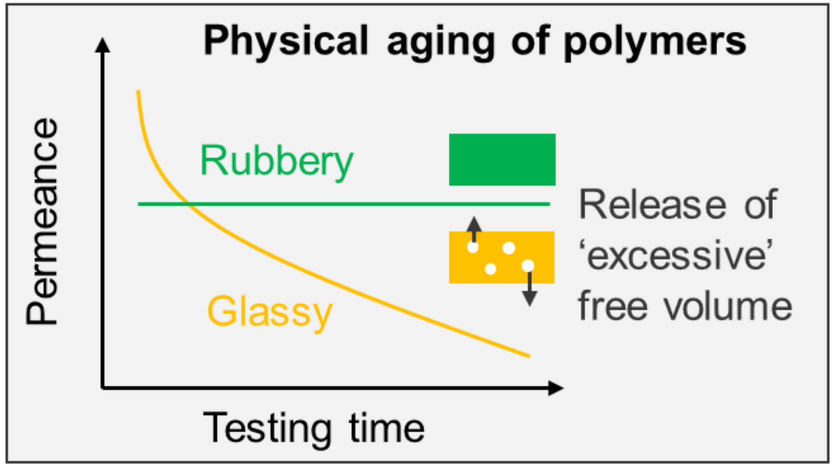


Zhu et al., *2019 AIChE Annual Meeting*, Orlando, FL; Zhu et al., *2019 NAMS 28th Annual Meeting*, Pittsburgh, PA
Kusuma et al. *ACS Appl. Mater. Interfaces* 2020, 12, 27, 30787–30795

Identified challenges and solutions

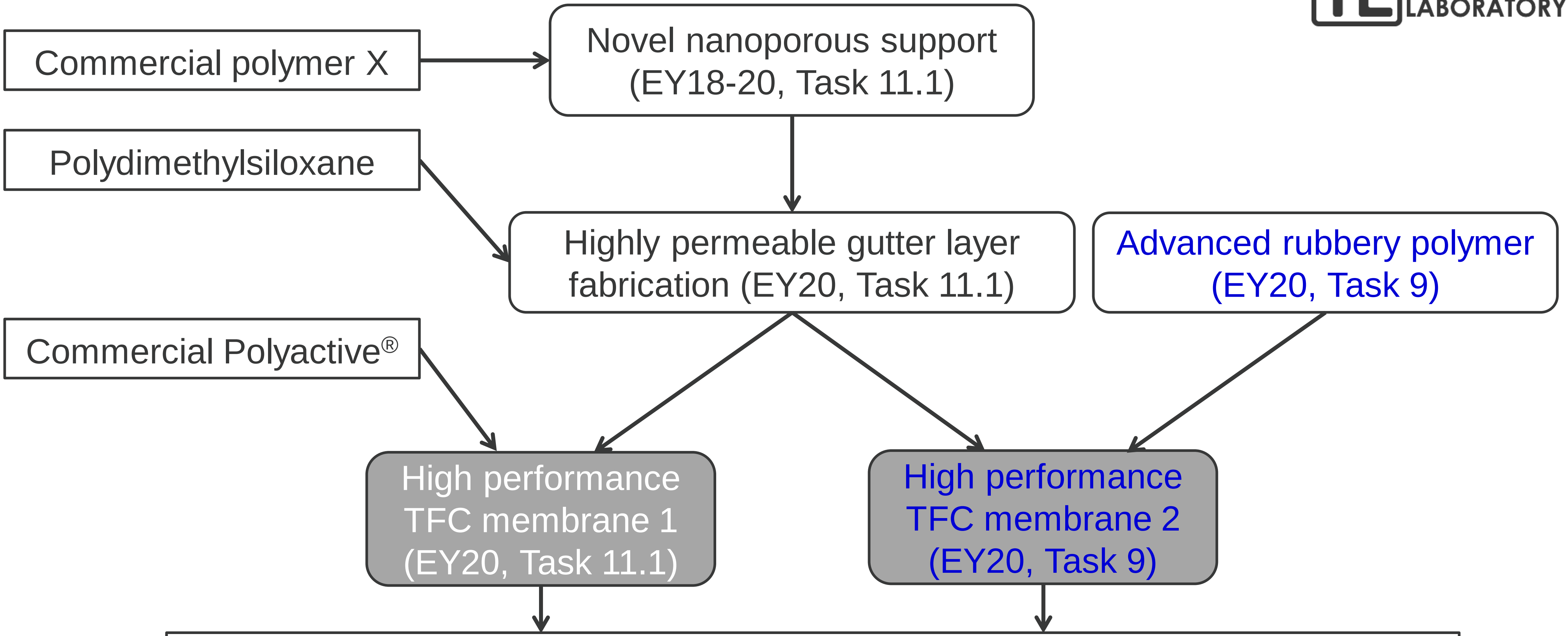
	Challenges	Technical solutions
Porous support	• Low gas permeance • Low surface porosity • Thermal/chemical stability issue	Novel nanoporous support
Gutter layer	• Low gas permeance	Highly permeable gutter layer
Selective layer	• Submicron, defect-free thin film formation • Polymer permeability/selectivity trade-off • (Accelerated) physical aging in thin films	Advanced rubbery polymer





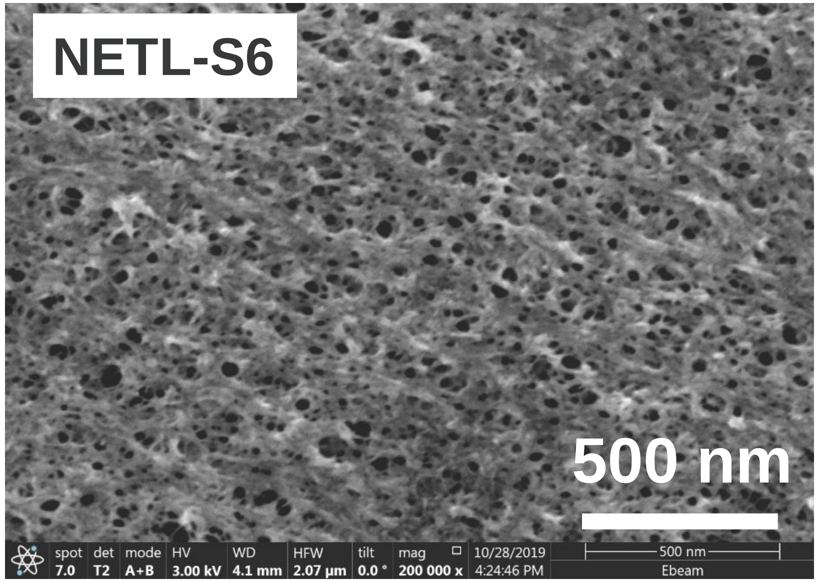
Robeson, *J. Membr. Sci.* 320, 390 (2008)

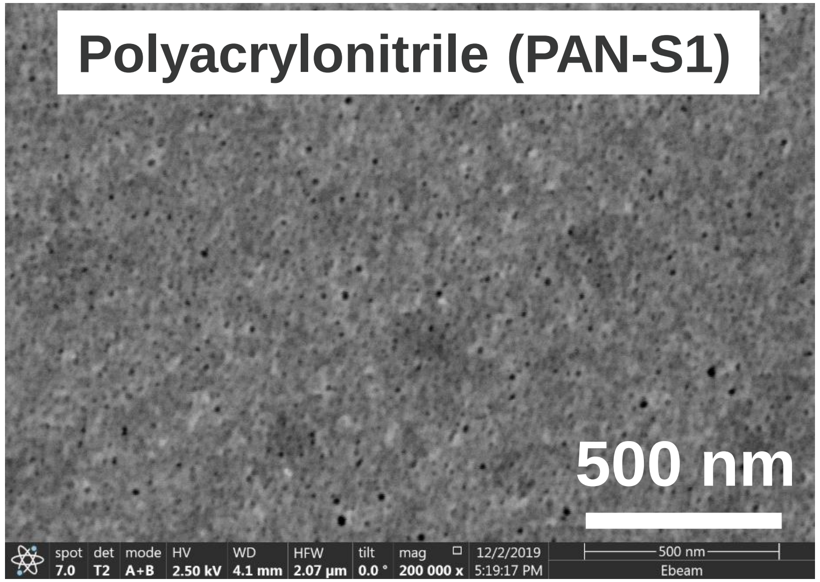
Project structure and technical approaches

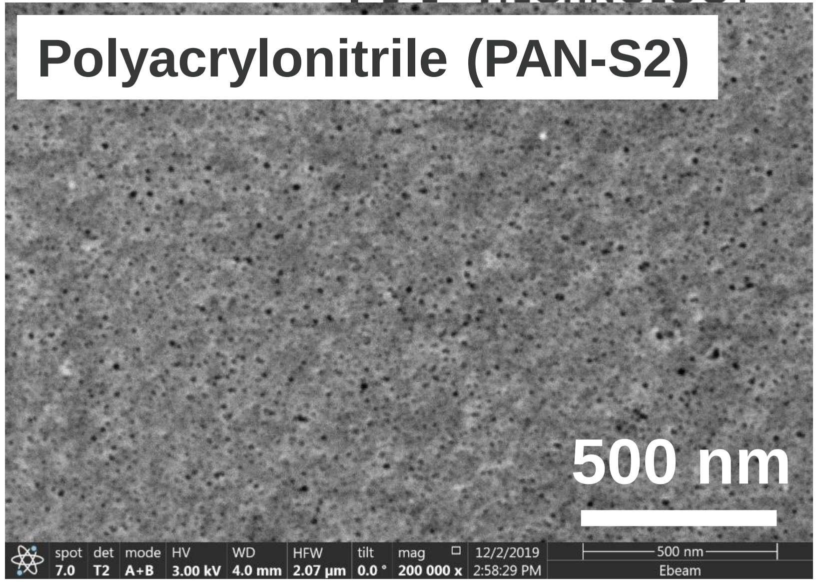


EY20 Milestone: demonstrate a functioning, defect-free TFC membrane with CO_2 permeance of >2,000 GPU and CO_2/N_2 selectivity >25.

Accomplishment 1: novel nanoporous support



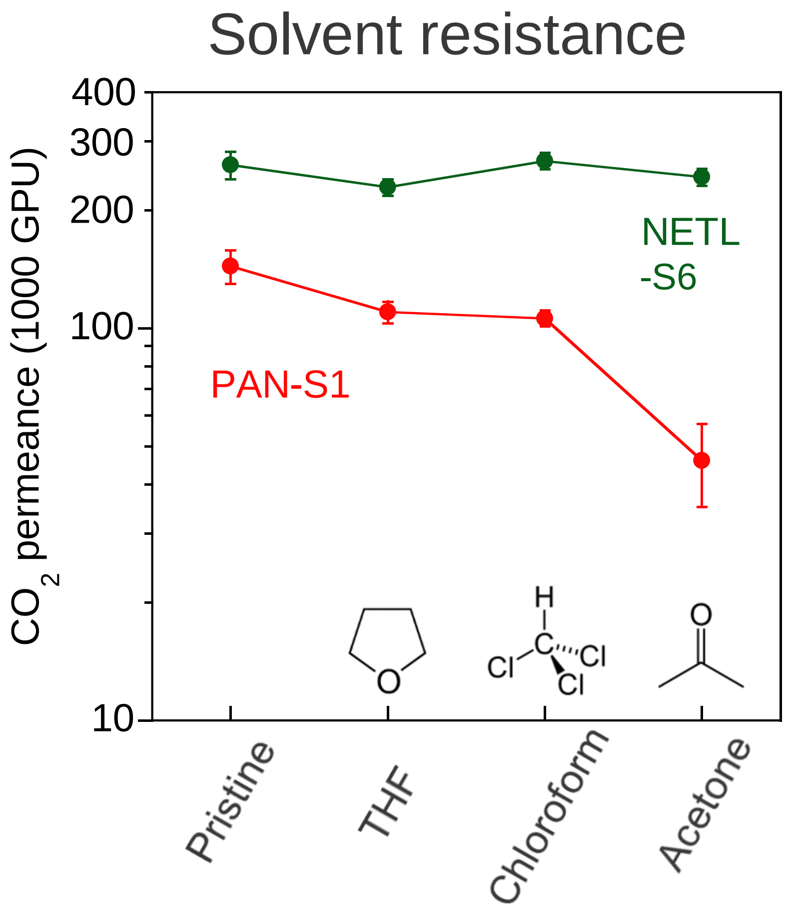


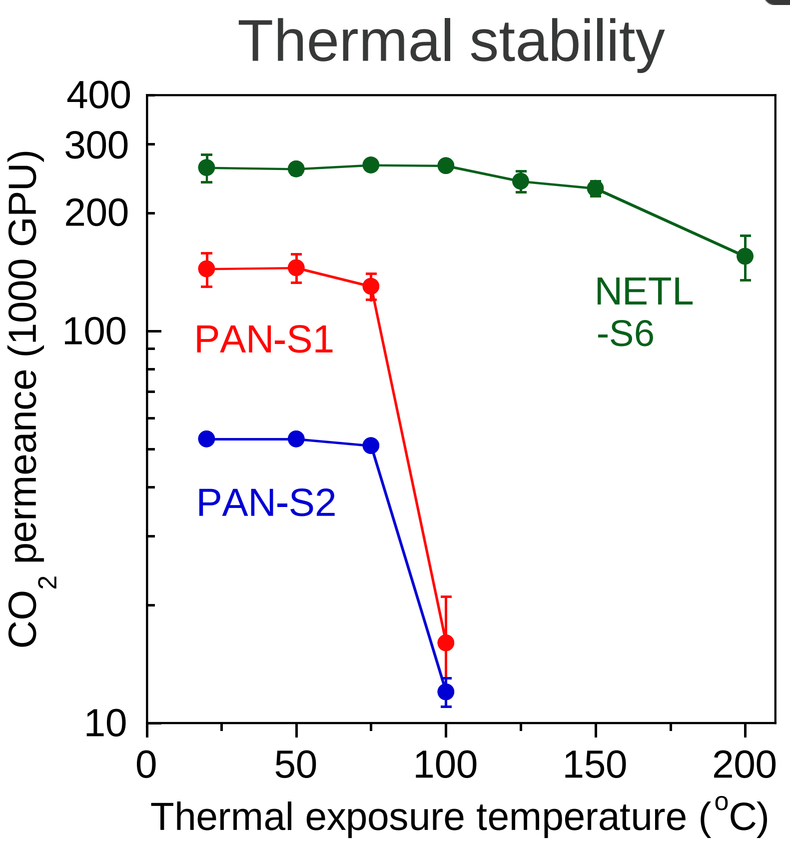


	NETL-S6	PAN-S1 (ULTURA™)	PAN-S2 (Synder®)
CO_2 permeance[1] (kGPU)	260 ± 20	138 ± 13	53 ± 1
Pore size (dia, nm)	10 - 40	≤ 20	≤ 22
Surface porosity (%)	20 ± 2	6 ± 1	8 ± 1
Operation temperature (°C)	≤ 200	≤ 75	≤ 75
Solvent resistance	Excellent[2]	Good[3]	Good[3]

1. Determined at a pressure drop of 1 bar & 22 °C. 2. Neither dissolved or swollen in common thin film coating solvents like acetone, tetrahydrofuran (THF), and chloroform. 3. Not dissolved but swollen in common solvents.

Accomplishment 1: novel nanoporous support





This high performance nanoporous support can be scaled up in a conventional phase-inversion/roll-to-roll fabrication technique.

Accomplishment 2: a highly permeable PDMS gutter layer with CO_2 permeance over 12,000 GPU

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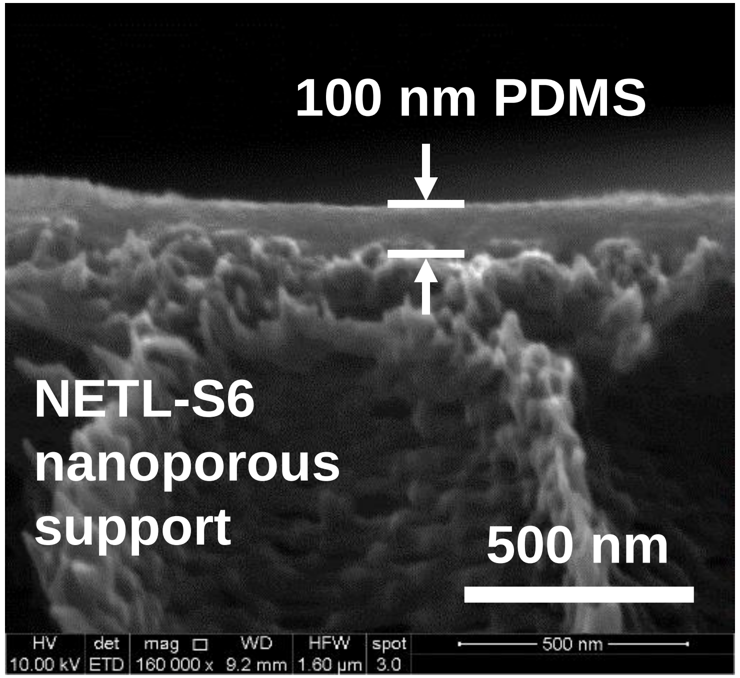
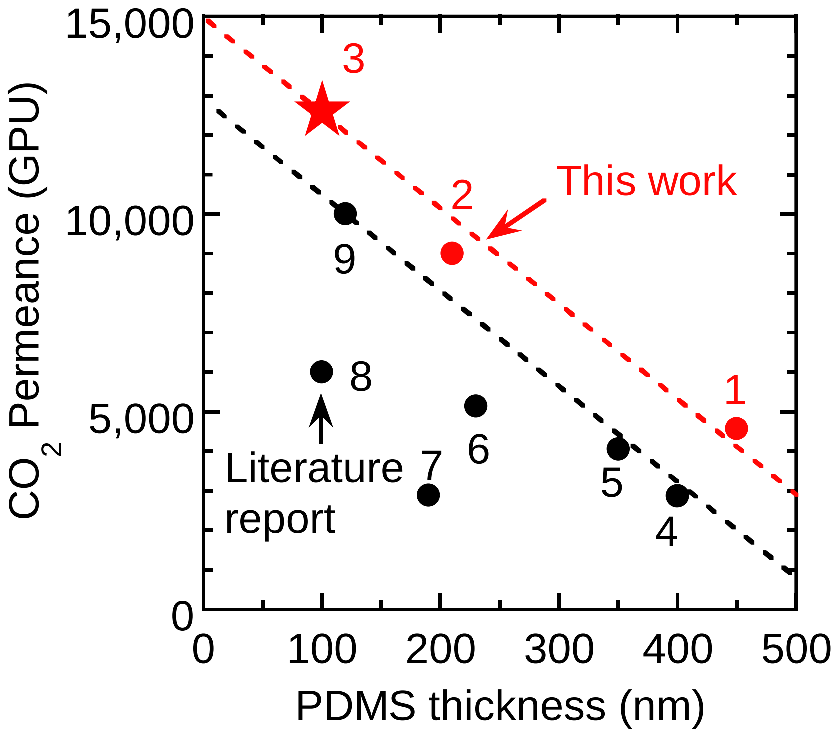




#	Support	CO_2/N_2	Test conditions
1	NETL-S6	11.7	1 bar/25 °C
2	NETL-S6	11.6	1 bar/25 °C
3	**NETL-S6**	**11.5**	**1 bar/25 °C**
4	PAN	9.0	3.5 bar/35 °C
5	PAN	9.0	3.5 bar/35 °C
6	PAN	10.6	2 bar/25 °C
7	PAN	10.0	3.4 bar/35 °C
8	PSF	8.0	1 bar/25 °C
9	PSF	10.5	0.2 bar/25 °C

PDMS:
the most used gutter layer material

Coating method:
Knife casting, a scalable technique

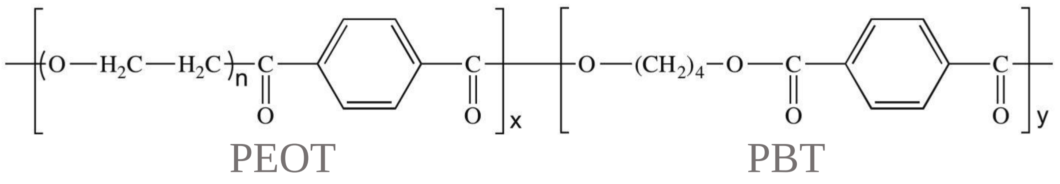
The defect-free (CO_2/N_2=11.5), 100-nm PDMS membrane exhibited a record-high CO_2 permeance of 12,600 GPU.

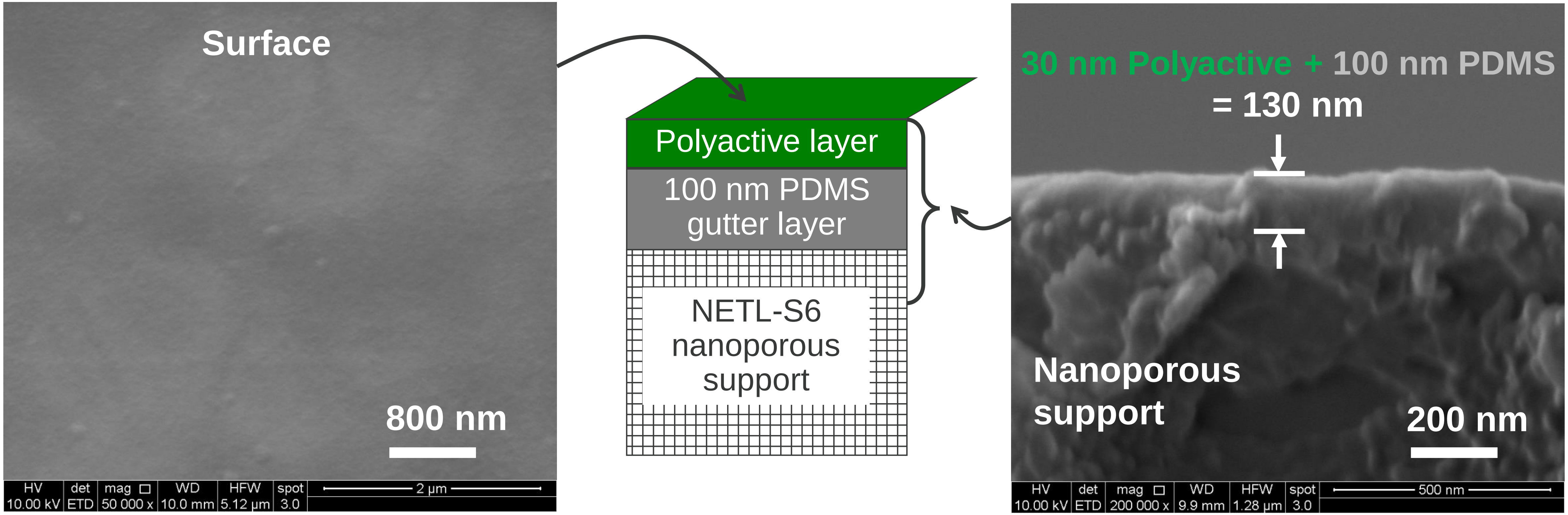
Refs: J Membr. Sci., 541 (2017) 367; J. Mater. Chem. A, 2 (2014) 17751; Energy Environ. Sci., 9 (2016) 434; Nanoscale, 8 (2016) 8312; J Membr. Sci., 499 (2016) 191; J Membr. Sci., (2019) in press

Accomplishment 3: Polyactive™-based ultrathin TFC membranes' performance exceeded the EY20 Milestone

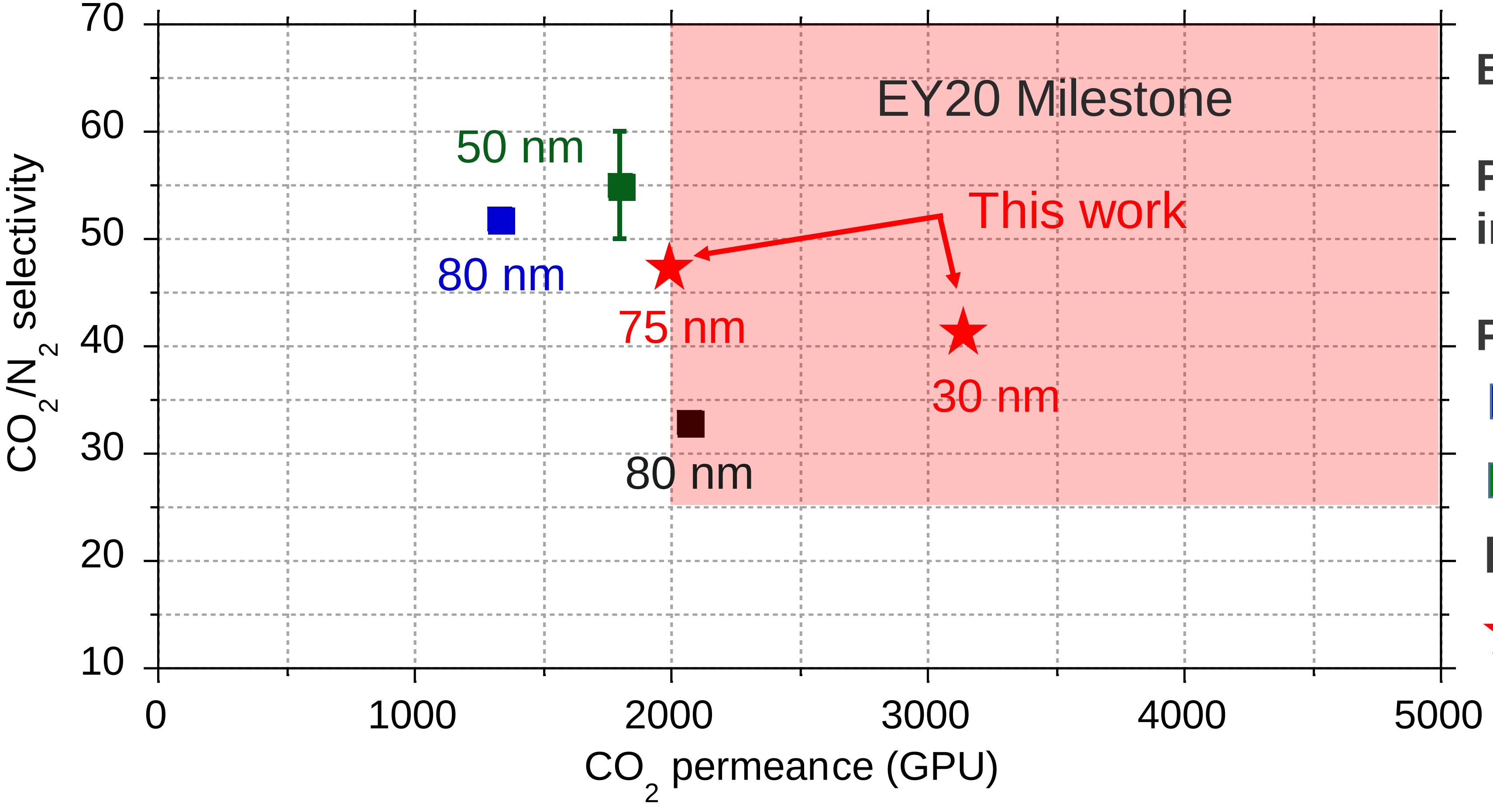
Polyactive™ 1500PEOT77PBT23 (**Poly1.5k**)

- Widely used for membrane CO_2/N_2 separation
- Commercially available from PolyVation BV, Netherlands





Accomplishment 3: Polyactive™-based ultrathin TFC membranes' performance exceeded the EY20 Milestone



Bench-scale, pure-gas study

Polyactive™ is the selective layer in all the membranes.

Porous support / gutter layer / Ref.

- Customized PAN / PDMS / #1
- Customized PAN / PDMS / #2
- Commercial PAN / MOF* / #3
- NETL-S6 / PDMS

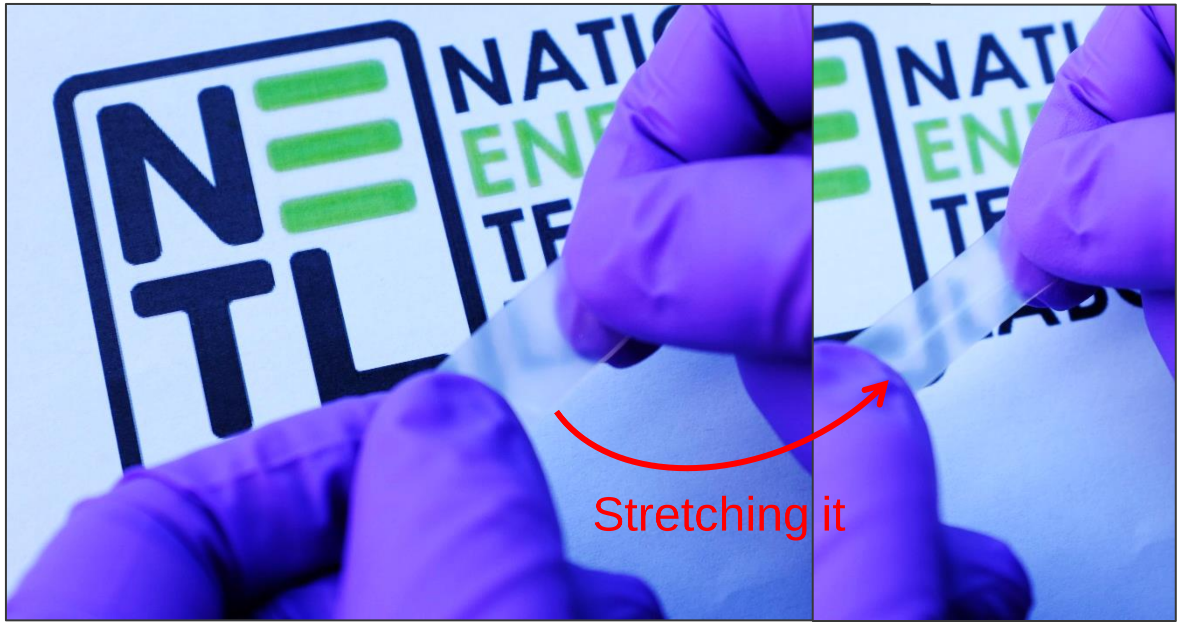
Refs: 1. Yave et al., *Nanotechnology* 21 (2010) 395301; 2. Yave et al., *Energy Environ. Sci.* 4 (2011) 4656; 3. Liu et al., *ACS Nano* 12 (2018) 11591.

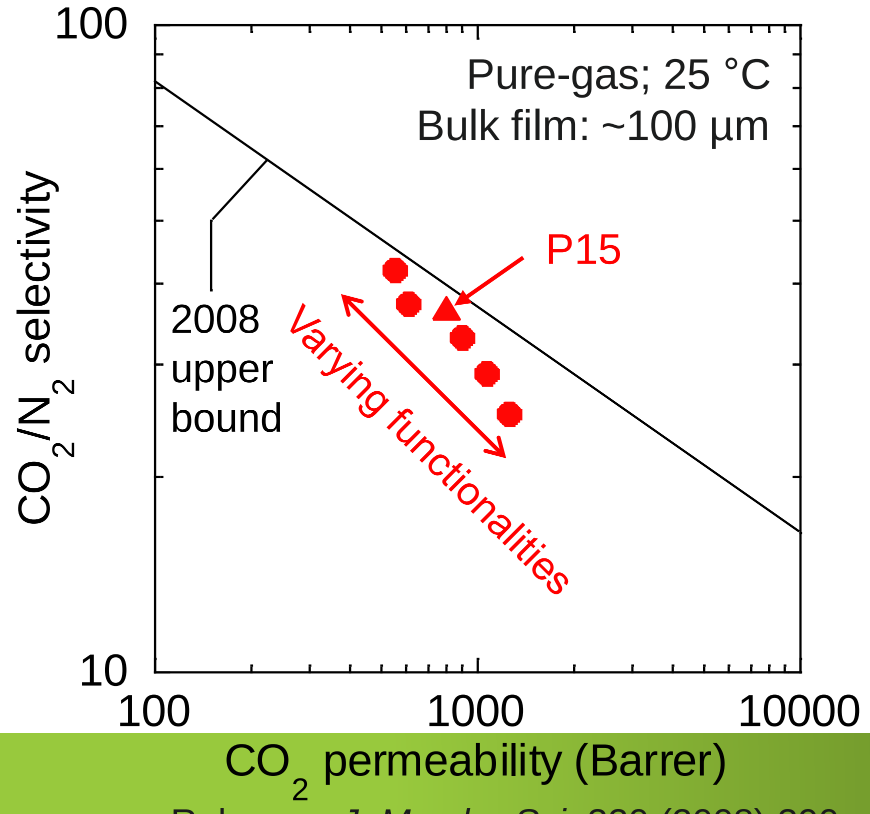
* The MOF (ZnTCPP) gutter layer is difficult to scale up.

Accomplishment 4: advanced rubbery polymer TFC membranes' performance exceeded the EY20 Milestone – *Polymer synthesis*

In EY20, a series of new polymers were synthesized in collaboration with Idaho National Laboratory.

- Completely rubbery (T_g < -73 °C) → resistant to physical aging
- High molecular weight (M_n > 400k) → excellent thin film forming ability
- Balanced CO_2 permeability and CO_2/N_2 selectivity (P15: 800 Barrers / 36-selectivity)
- Stable in liquid water or humid flue gas

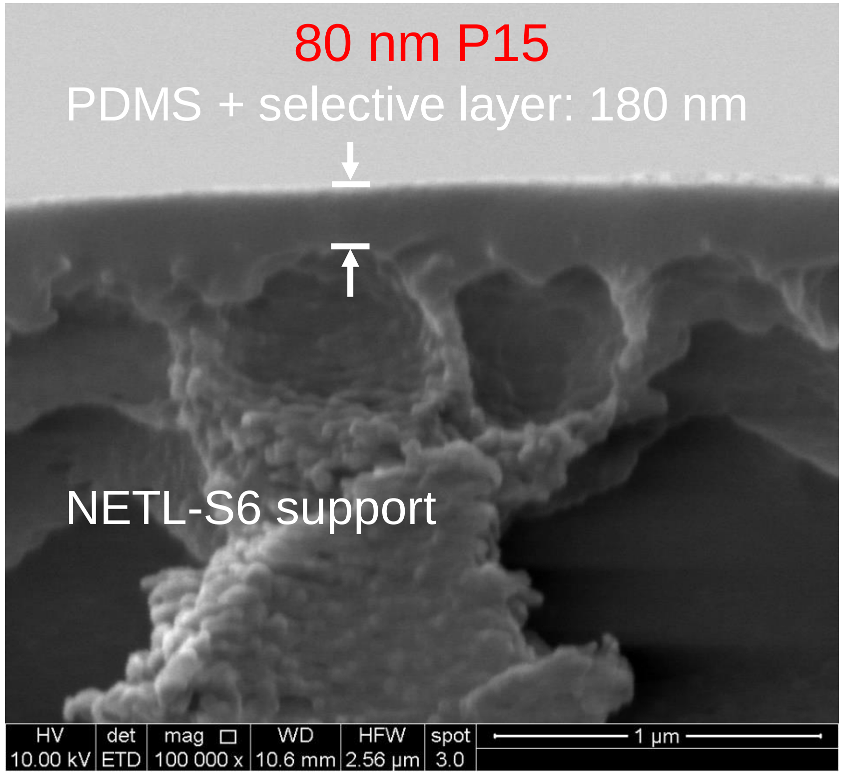


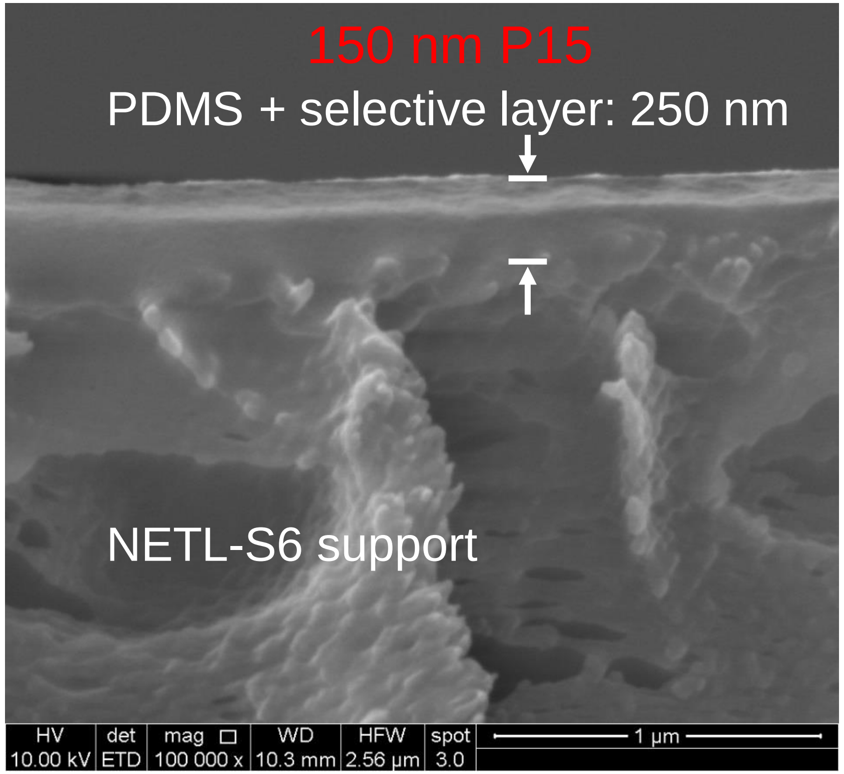


Robeson, *J. Membr. Sci.* 320 (2008) 390

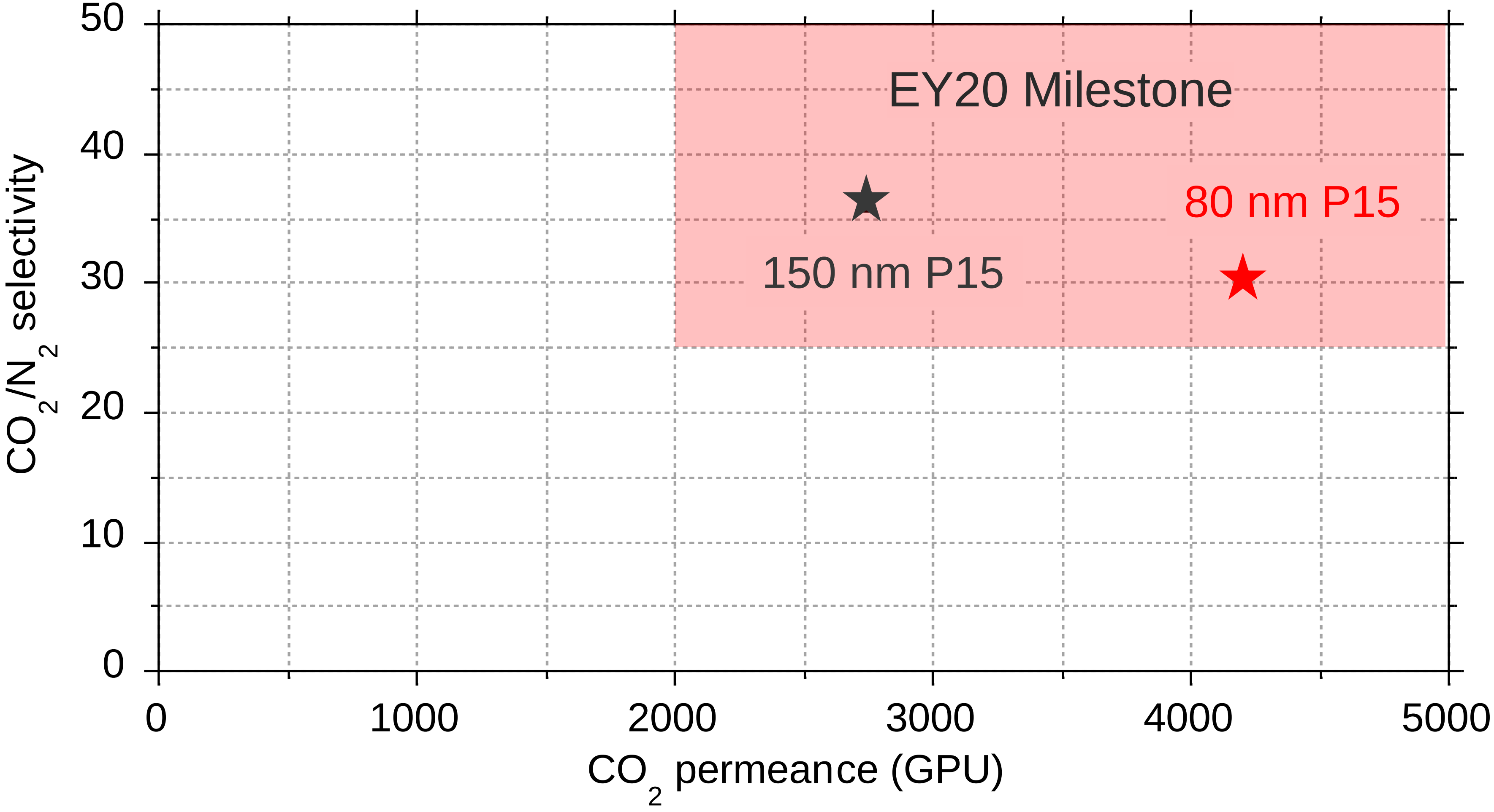
Accomplishment 4: advanced rubbery polymer TFC membranes' performance exceeded the EY20 Milestone – *TFC fabrication*

Selective layer: **NETL P15** (80 - 150 nm, spin coating)
Gutter layer: PDMS (100 nm, knife casting)
Porous support: NETL-S6



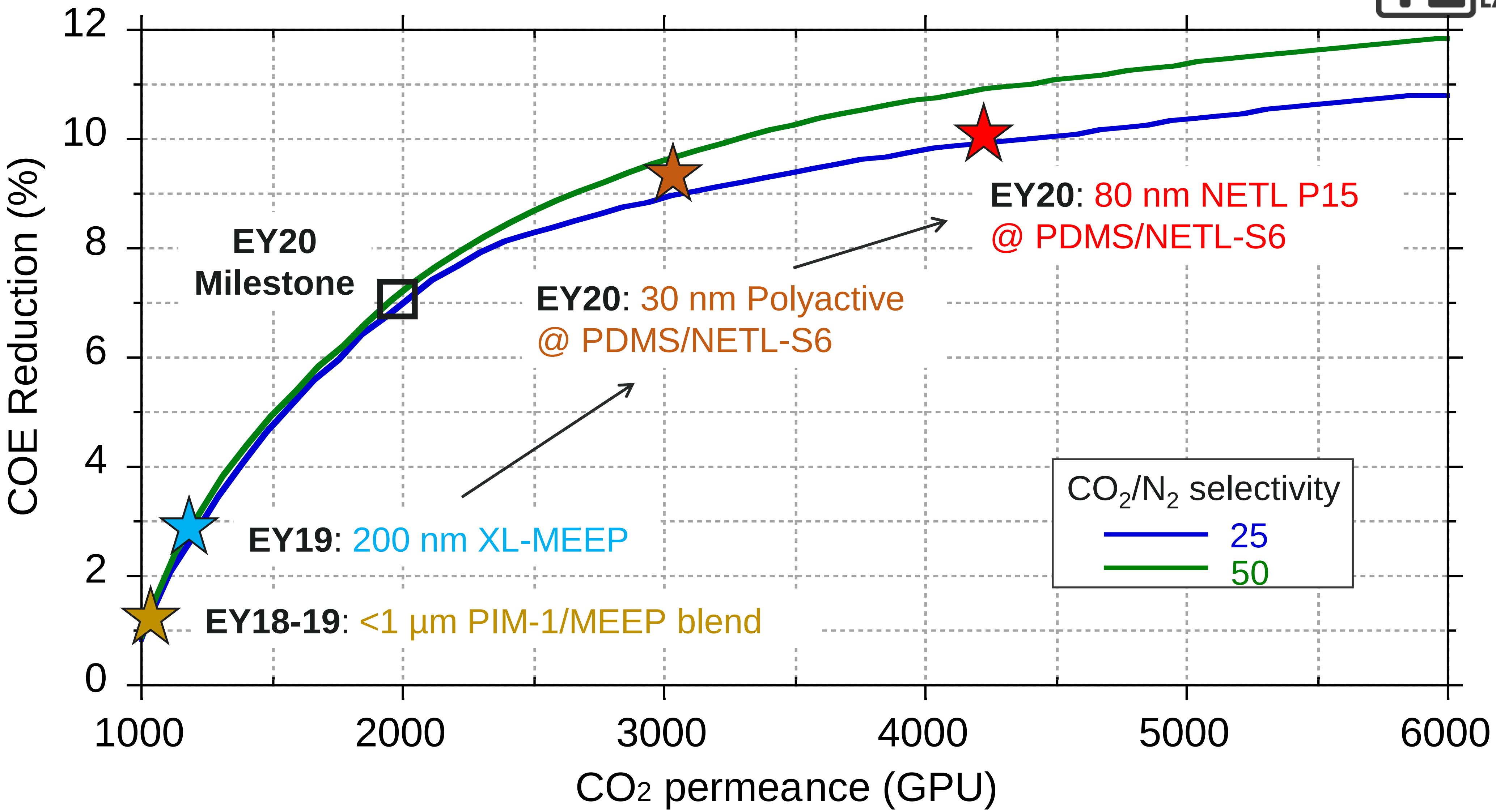


Accomplishment 4: advanced rubbery polymer TFC membranes' performance exceeded the EY20 Milestone – *TFC testing*



There is no physical aging observed in the thin films in a 500-hour stability test.

Performance-cost analysis on the fabricated TFC membranes



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

Future plans

Performance testing in the real flue gas at NCCC (EY20 – 21)

- Advanced rubbery polymer based-TFCs, down-selection via a simulated flue gas testing in the lab
- Bench-scale, 1-10 cm^2

TFC membrane scale-up (EY20 – 21)

- Bench-scale, from 1-10 cm^2 to 10 -100 cm^2

Nanoporous support scale-up (EY20 – 22)

- Design and construction of a continuous membrane fabrication machine
- Pilot-scale (30.5 cm × 10 m) fabrication of NETL-S6 support

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

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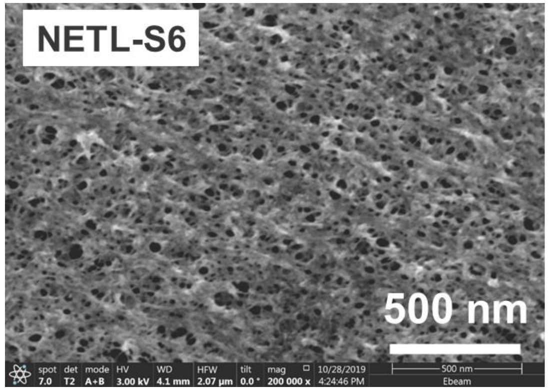
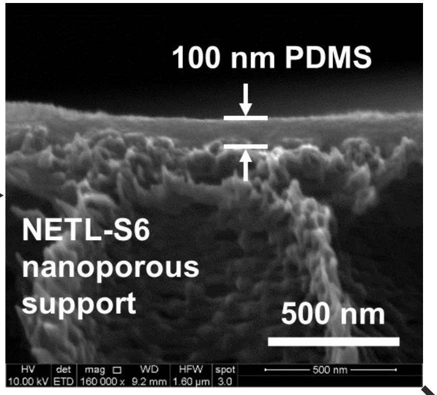
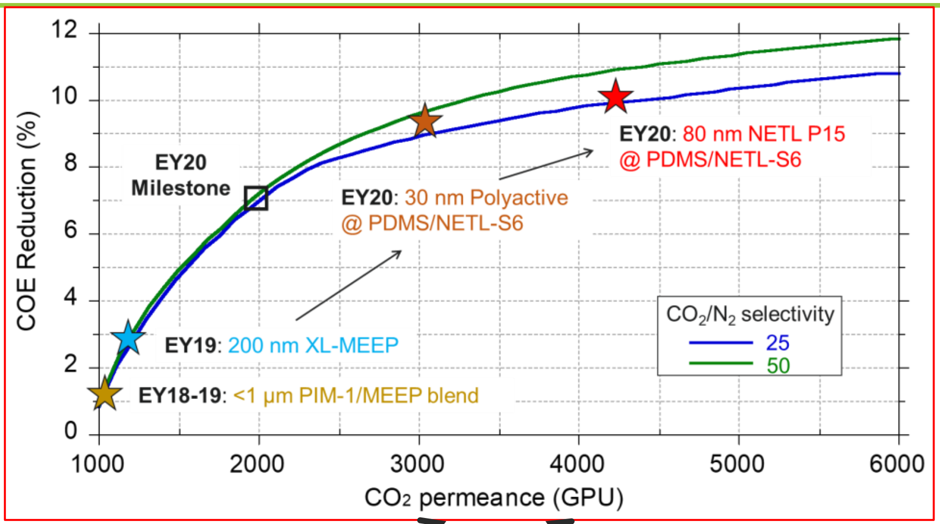
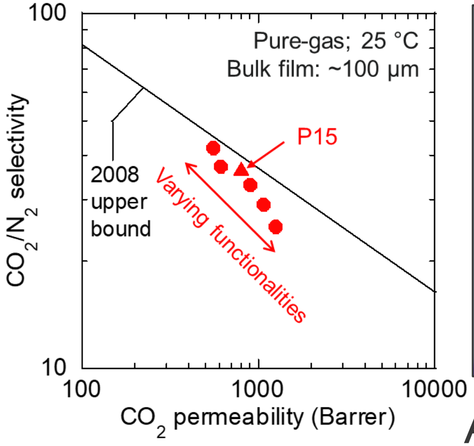


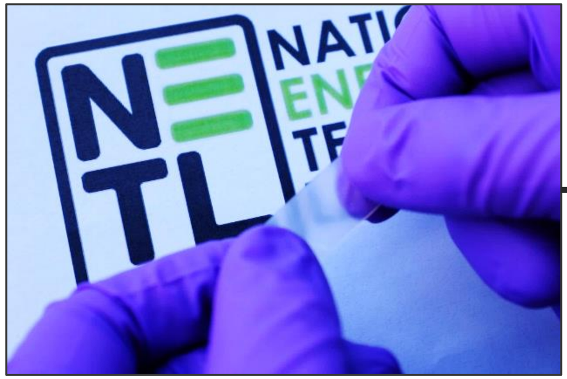
High performance nanoporous support



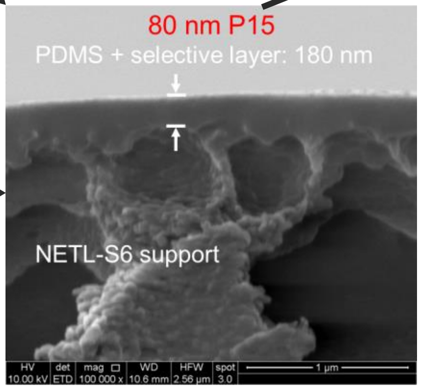
Highly permeable gutter layer

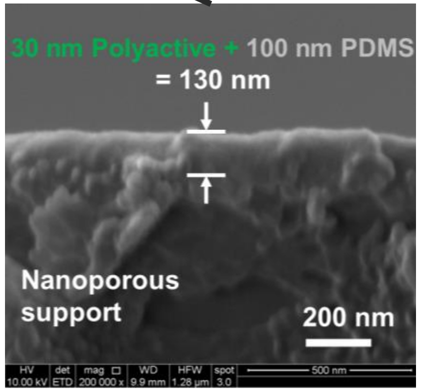






Advanced rubbery polymer





Ultrathin selective layer design and fabrication

Acknowledgements

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