

High-Performance Blended Rubbery Membranes

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is developing new, ultra-high-performance membranes and membrane modules for post-combustion carbon dioxide (CO₂) capture. NETL-RIC has performed key research to further develop a rubbery thin-film composite (TFC) membrane with proprietary membrane support.

technical goals

- Develop a scalable TFC membrane for industrial carbon capture that has a CO₂ permeance of at least 3,000 gas permeance units (GPU) and CO₂/nitrogen (N₂) selectivity of at least 25.
- Optimize both the membrane supports and the selective material for scalability, thermal and chemical stability, and anti-aging properties.
- Perform a long-term field test of the developed membranes for at least 500 hours.

technical content

Membrane technology poses an exciting option for large-scale gas separations due to the small footprint, simplicity of the device and process, ease of operation, modularity and bolt-on installation, and typically low parasitic energy requirements. Industrially, polymer-type membranes have a well-established role in gas separation technology, and are commonly used in applications such as separation of hydrogen from gas mixtures, purifying natural gas, etc. However, extremely high-permeance (or high-GPU) membranes are needed to make this technology an economically viable option for post-combustion CO₂ capture. As shown in Figure 1, a recent NETL techno-economic analysis (TEA) shows high-GPU membranes can greatly reduce the costs of CO₂ capture compared to conventional amine sorbents, and the capture cost reduction is extremely sensitive to CO₂ permeance enhancement at the range of 1,000–3,000 GPU when CO₂/N₂ selectivity is maintained above 25. For this project task, NETL-RIC is developing scalable CO₂-selective (CO₂/N₂ selectivity >25) TFC membranes with a CO₂ permeance greater than 3,000 GPU using a novel nanoporous membrane support, a blended rubbery polymer, and optimizing coating methods to integrate these two materials as TFCs.

As shown in Figure 2, NETL has developed a proprietary membrane support (NETL-S6) with high porosity (20%) and small pore sizes (<40 nm). This nanoporous NETL-S6 support provides much greater CO₂ permeance (260,000 GPU), surface porosity, and physicochemical stability than commercial polymer porous supports. NETL-RIC scaled up the NETL-S6 fabrication from 40 cm² per sheet in Execution Year (EY) 2020 to 200 cm² per sheet in EY 2021.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Rubbery Thin-film Composite Membrane

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

FWP-1022402 (Task 21)

predecessor project:

N/A

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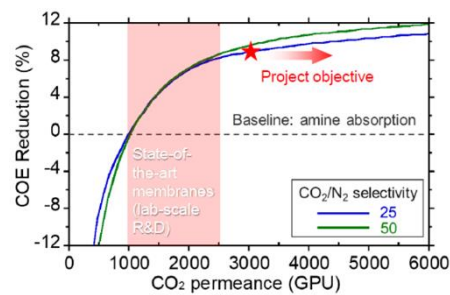


Figure 1: Cost of electricity (COE) reduction versus CO₂ permeance and CO₂/N₂ selectivity of membranes.

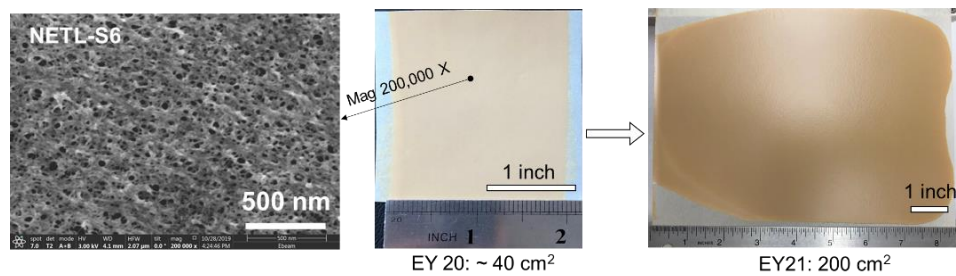


Figure 2: Surface micrograph of NETL-S6 membrane support and timeline of the evolving membrane support fabrication capabilities.

NETL-RIC has developed and optimized rubbery polymer blends (P15 polymers) having excellent CO₂/N₂ separation performance that exceeds Robeson's 2008 upper bound limit (Figure 3). This series of polymer blends are completely rubbery, so they are resistant to physical aging. More importantly, the blends presented excellent thin-film formation ability. Figure 3 also shows a general scheme of transforming a bulk material into a functioning TFC membrane via film thickness reduction. The TFC membranes consist of a top thin selective layer and a gutter layer made of polydimethylsiloxane (PDMS), which are both appended to the aforementioned NETL-S6 membrane support. As shown in Figure 4, small TFC membrane coupons (<10 cm²) have shown CO₂/N₂ separation performance beyond the project target.

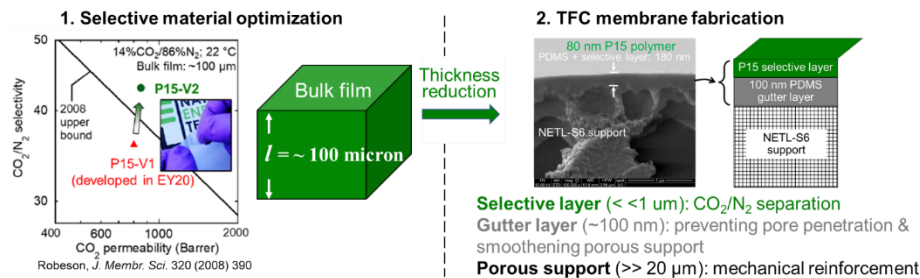


Figure 3: Selective layer material optimization and TFC development.

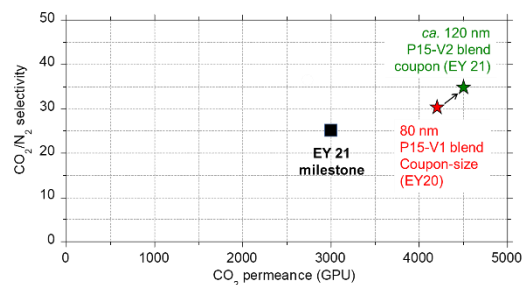


Figure 4: Comparison of CO₂/N₂ separation performance of the fabricated polymer blend TFC membranes with the target performance.

TABLE 1: MEMBRANE PROCESS PARAMETERS

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Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Proprietary polymer	
Materials of Fabrication for Support Layer	—	Proprietary polymer	
Nominal Thickness of Selective Layer	μm	0.1 – 0.4	0.1 – 0.4
Membrane Geometry	—	flat-sheet	flat-sheet
Max Trans-Membrane Pressure	bar	>4	>4
Hours Tested without Significant Degradation	—	N/A	500 hours
Manufacturing Cost for Membrane Material	\$/m ²	N/A	N/A
Membrane Performance			
Temperature	°C	20 – 60	20 – 60
CO ₂ Pressure Normalized Flux	GPU or equivalent	1,000 – 4,500	3,000
CO ₂ /H ₂ O Selectivity	—	N/A	N/A
CO ₂ /N ₂ Selectivity	—	20 –35	25
CO ₂ /SO ₂ Selectivity	—	N/A	N/A
Type of Measurement	—	Pure gas	Mixed gas
Proposed Module Design		(for equipment developers)	
Flow Arrangement	—	Crossflow and countercurrent in plate-and-frame	
Packing Density	m ² /m ³	1,000	
Shell-Side Fluid	—	vacuum permeate	
Flue Gas Flowrate	SLPM	6	
CO ₂ Recovery, Purity, and Pressure	%/%/bar	90%	>95% 140
Pressure Drops Shell/Tube Side	bar	feed: <0.05/m/permeate: <0.01/m	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	N/A	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10⁻⁶ cm³ (1 atm, 0°C)/cm²/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0°C)/cm²/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10⁻⁶ kg mol/m²-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO₂-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO₂ in CO₂-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
				vol%			ppmv	
14.7 psia	135°F	CO ₂	H ₂ O	N ₂	O ₂	Ar	SO _x	NO _x
		13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

- High-permeance TFC membranes.
- High-porosity membrane supports have negligible resistance to gas transport.
- Resistant to physical aging, providing performance stability.
- High molecular weight blended polymers lead to excellent thin film (~100 nm) formation.
- Stable under high humidity conditions.
- Low cost compared to conventional amine absorption.

R&D challenges

- Scaling up polymer synthesis of the selective layer materials.
- Fabricating ultra-thin, defect-free membranes in large areas.
- Maintaining robust performance in the long term under harsh operating conditions with high humidity, acid gases (sulfur oxide [SO_x] and nitrogen oxide [NO_x]), and other trace contaminants, such as flue ash, mercury (Hg), etc.

available reports/technical papers

Keairns, D.; Fout, T.; Hopkinson, D., 2022, "A cost and performance analysis of polymeric membrane-based post-combustion carbon capture," (in pre-publication and to be submitted to Journal of Membrane Science).

Zhu, L.; Kusuma, V.; Hopkinson, D., "Highly Permeable Thin Film Composite Membranes of Rubbery Polymer Blends for CO₂ Capture." 2021 DOE/NETL Carbon Management and Oil & Gas Research Project Review Meeting. Point Source Carbon Capture – Lab, Bench, and Pilot-Scale Research. August 2021.

https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Zhu.pdf.