Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost-Effective Carbon Capture

primary project goal

Membrane Technology and Research, Inc. (MTR) is developing composite membranes with superior carbon capture performance using a novel transformational approach. Two membrane targets have been identified: (1) carbon dioxide (CO_2) permeance of 4,000 gas permeation units (GPU) with mixed-gas CO_2/nitrogen (N_2) selectivity of 25, and (2) CO_2 permeance of 3,000 GPU with mixed-gas selectivity of 50. The first type will be used in the CO_2 removal step and the second type will be used in the CO_2 sweep step, both of which are parts of MTR's innovative post-combustion CO_2 capture process.

technical goals

- Develop methods to produce isoporous supports, first manufacturing single-layer supports (14 inches wide) using the laboratory's continuous casting system and then manufacturing dual-layer supports (40 inches wide) using MTR's commercial-scale casting equipment.
- Synthesize and characterize polymers containing high ether-oxygen content for CO_2/N_2 separation, and down-select polymers with most promising CO_2/N_2 separation properties for scale-up and production of composite membranes.
- Prepare composite membranes by coating selective layers onto isoporous support, first using a laboratory-scale coating machine (12 inches wide) and then using MTR's commercial-scale coater (40 inches wide).
- Fabricate and test laboratory-scale spiral-wound and plate-and-frame modules, optimize the design to minimize pressure drop and produce prototype modules of both types for testing at the National Carbon Capture Center (NCCC).
- Design a bench-scale test skid for testing prototype membrane modules.
- Install and operate a test skid at NCCC for at least three months with actual coal-fired flue gas.
- Perform a techno-economic analysis (TEA) and sensitivity analysis of the process.

technical content

MTR is developing composite membranes with superior CO_2 capture performance using a novel transformational approach. Composite membranes consist of a selective polymer layer coated on a support that, ideally, does not hinder transport in the selective layer. MTR has conclusively demonstrated that this objective is not met for current supports when coated with very thin selective layers, leading to a reduction in permeance by a factor of two or larger. The proposed three-year project consists of two parallel technology developments that address the support issue, as well as the development of more selective materials.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Polymeric Membranes with Isoporous Supports

participant:
Membrane Technology and Research, Inc.

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FE0031596

predecessor projects:
N/A

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start date:
06.01.2018

percent complete:
60%

The first development is replacing the conventional porous supports used to fabricate composite membranes with novel isoporous supports. The remarkable pore structure of isoporous supports is created through self-assembly of block copolymers and is the ideal surface to support the nonporous layers that perform the separation in composite membranes. Work at MTR has shown that the surface pore structure of conventional supports restricts diffusion in the adjacent selective layers, and this geometrical effect significantly reduces the permeance of layers thinner than 1 micron. The high surface porosity and uniformity in pore size and pore location of the isoporous supports (Figure 1) eliminates this restriction and allows fabrication of Polaris™ composite membranes with significantly increased CO_2 permeances as high as 4,000 GPU. Building on extensive work on isoporous membranes reported in the open literature, the isoporous support preparation methods will be adapted to MTR's commercial membrane casting equipment.

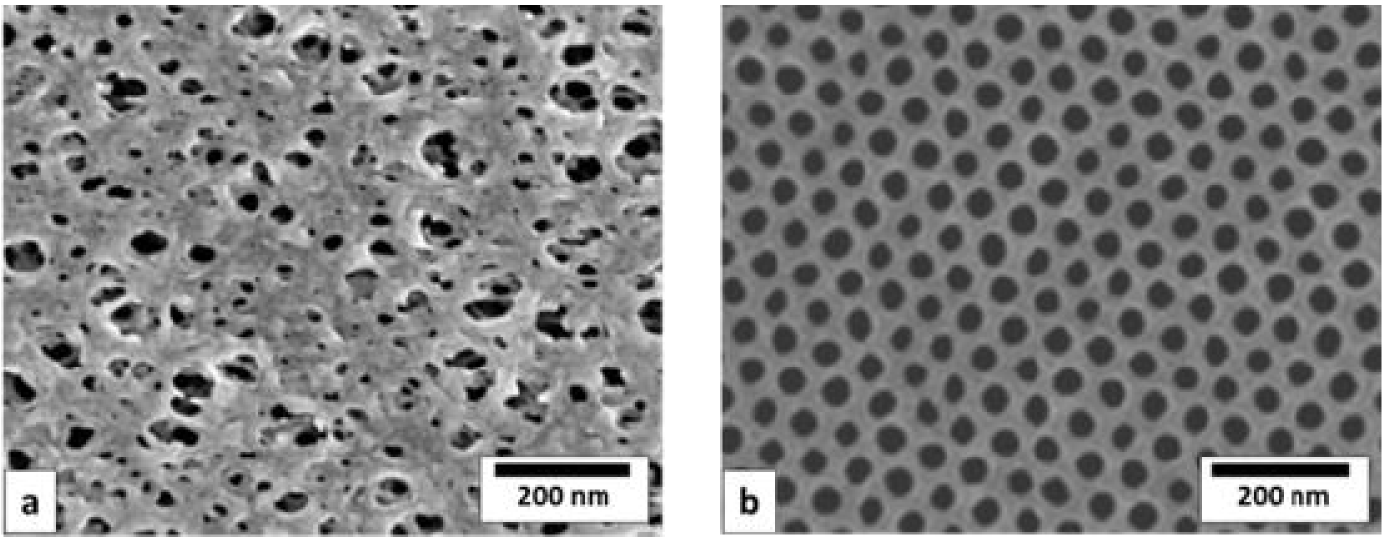

Figure 1: Surface pore structure of (a) a conventional porous support, and (b) an isoporous support.

The probability of successfully producing isoporous supports at commercial scale is high. The method to be used is very similar to existing methods for the manufacture of conventional supports. Moreover, the isoporous support, while of great importance, does not perform the actual separation, which means the occasional pore defects or misalignments are able to be tolerated. This is unlike the ultrafiltration and nanofiltration applications that are the traditional focus of isoporous membrane development.

The project team has prepared many support membranes using the Polystyrene-b-Poly-4-vinylpyridine (BCP1) polymer and has used scanning electron microscopes (SEMs) to evaluate the structures obtained. It is not easy to create the very perfect isoporous surfaces that are reported in the literature for these block copolymers. These surfaces likely represent a few out of many attempts, with the unsuccessful attempts not being reported. However, in the current work, perfect isoporous surfaces are not required; only surfaces that are an improvement over the conventional support membranes are needed. Figure 2 shows the top surface of a BCP1 support that by no means is perfectly isoporous but is expected to be a better support membrane than the conventional support made by MTR, of which a surface SEM is shown in the inset.

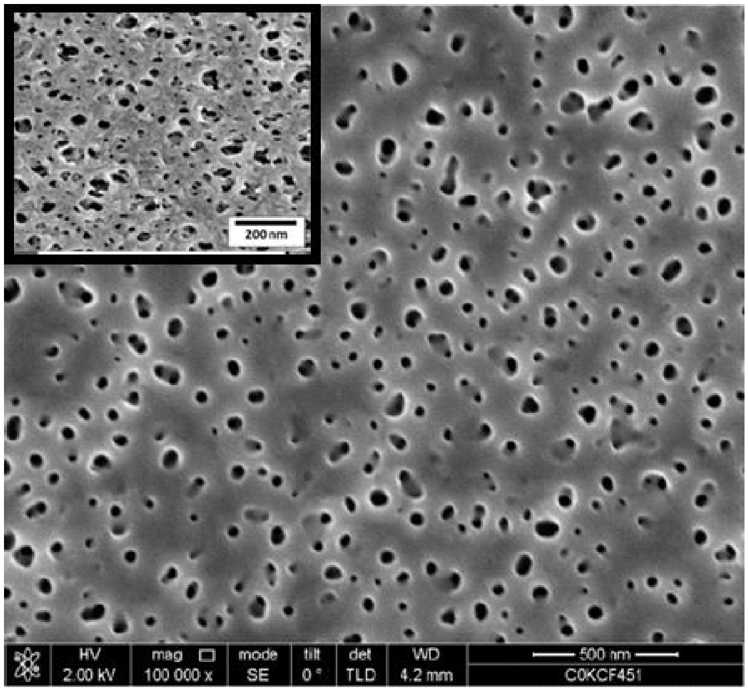

Figure 2: Top surface of a BCP1 support membrane. The inset is a conventional support.

The second development within this project is building on materials research carried out at the University of New York at Buffalo (NYUB), where materials have been identified that, in the form of films, have shown the potential to double the mixed-gas selectivity of the Polaris membrane, albeit at the expense of permeability. Variations of the materials will be synthesized at NYUB, and MTR will produce and test composite membranes using both conventional porous supports and the novel isoporous supports. It is expected that by using the isoporous supports, composite membranes can be produced that are significantly more selective than the current Polaris membrane without increasing the membrane area required.

Recently, the research group at NYUB has developed a new series of copolymers based on poly(1,3 dioxolane), which has the highest ether-oxygen (O)/carbon (C) ratio of any known chemical structure and significantly higher than polyethylene oxide (PEO) (O/C ratio of 0.67 versus 0.5 for PEO). Initial work has confirmed that the higher ether-oxygen content leads to superior CO_2/N_2 separation properties. In the proposed project, a series of PDXLA-co-PDXLEA materials will be thoroughly evaluated with simulated flue gas at various temperatures, pressures, and compositions.

Some of the new materials developed at NYUB are 25 to 50% less permeable than the Polaris polymer but have shown mixed-gas selectivities for CO_2 over N_2 as high as 50 at temperatures between 50 and 60°C. This mixture selectivity is nearly double what Polaris would give at this temperature. Figure 3 compares the predicted performance of these materials coated directly on an isoporous support with Polaris performance. The data point on the PPDXLA curves represents the target performance for the new Polaris high selectivity (HS). This type of performance is well-suited for the sweep step in MTR’s patented process design.

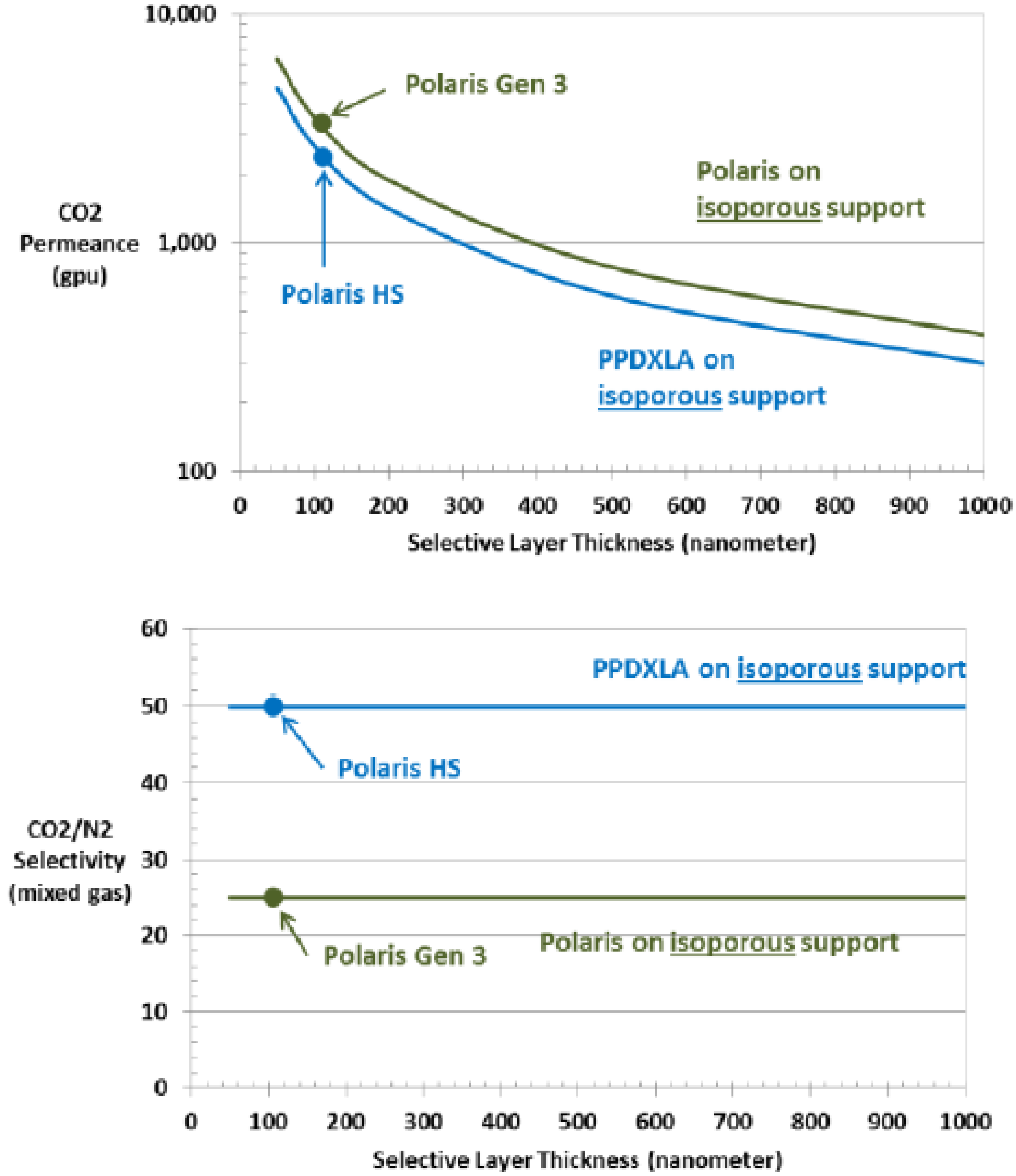

Figure 3: (a) Mixed-gas CO_2 permeance and (b) CO_2/N_2 selectivity as a function of selective layer thickness for Polaris™ and PPDXLA on an isoporous support.

The research group at NYUB is focused on the synthesis of polymers containing high ether-oxygen content for CO_2/N_2 separation. The production of polymers is optimized and scaled-up gradually. The polymers with the most promising properties are delivered to MTR for the production of thin-film composite membranes and then bench-scale membrane modules.

Composite membranes are prepared by coating selective layers onto the isoporous support produced. The selective materials are (1) MTR's Polaris formulation and (2) the selective materials to be developed by NYUB. Composite membranes are characterized first in pure-gas permeation experiments with CO_2 and N_2. Promising membranes are tested more extensively, including pure-gas permeation at different pressures and temperatures, and experiments with $CO_2/N_2/O_2$ mixtures representative of coal-derived flue gas. The coating step with Polaris is straightforward, as MTR has considerable experience with this material. More development and optimization work is required for the newly developed materials.

The very high permeance membranes under development require a redesign of the feed and permeate channels in the MTR planar membrane module. A few options to reduce pressure-drop in those channels are being developed. A summary of the target process parameters is shown in Table 1, while the capture economics data is shown in Table 2.

TABLE 1: MEMBRANE PROCESS PARAMETERS

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	<1	<1
Membrane Geometry	—	planar	planar
Max Trans-Membrane Pressure	bar	70	70
Hours Tested without Significant Degradation	—	10,000+ hrs (coal)	10,000+ hrs (coal)
Manufacturing Cost for Membrane Material	$\$/m^2$	50	10
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,700	Type 1: 4,000 Type 2: 3,000
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	60	Type 1: 25 Type 2: 50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	pure gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow and countercurrent	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	500	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >96%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.05	

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	54	43
Cost of Carbon Avoided	\$/tonne CO_2	97	80
Capital Expenditures	\$/MWhr	23.9	18.4
Operating Expenditures	\$/MWhr	25.9	22.2
Cost of Electricity	\$/MWhr	50	50

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} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-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 concurrent, countercurrent, crossflow 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 (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation of individual components through the Polaris membrane is driven by partial pressure differences across the membrane generated by a permeate vacuum.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, arsenic, etc., is unknown.

Flue Gas Pretreatment Requirements – Currently, pretreatment requirements are unknown.

Membrane Replacement Requirements – Membrane lifetime is estimated at three years.

Waste Streams Generated – The membrane process will recover greater than 95% of the H_2O in flue gas as liquid.

technology advantages

- The novel isoporous supports increases the CO_2 permeance (up to 4,000 GPU).
- The novel membrane selective layer material nearly doubles the CO_2/N_2 selectivity compared to membranes that use Polaris selective material.
- The two-stage capture process allows for high CO_2 capture rates and a high-purity product.
- The selective recycle of CO_2 to the boiler using the air sweep stream increases the CO_2 concentration in flue gas, reducing capital and operating expenditures.

R&D challenges

- Producing dual layer isoporous supports.
- Scale-up of polymer synthesis of improved selective layer materials.
- Tailoring the MTR coating techniques to the new NYUB materials.
- Producing defect-free top layers.

status

MTR continued to vary casting formulations and conditions to identify promising support membrane structures. Membranes prepared from new selective layer materials synthesized by NYUB show pure-gas CO_2/N_2 selectivity up to 89, which is considerably higher than conventional Polaris membranes (CO_2/N_2 selectivity = 50) and demonstrates the potential of this approach. Budget period two (BP2) tasks are nearly complete, and an initial TEA reveals that base CO_2 capture costs can be reduced by 14% with the selected BP2 membranes.

available reports/technical papers/presentations

Wijmans, H., et al. "Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture," Kickoff meeting presentation, Pittsburgh, PA, September 2018. *https://netl.doe.gov/projects/files/Development%20of%20Self-Assembly%20Isoporous%20Supports%20Enabling%20Transformational%20Membrane%20Performance%20for%20Cost%20Effective%20Carbon%20Capture.pdf*.

Wijmans, H., et al. "Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/projects/files/Development%20of%20Self-Assembly%20Isoporous%20Supports%20Enabling%20Transformational%20Membrane%20Performance%20for%20Cost%20Effective%20Carbon%20Capture.pdf*.

Wijmans, H., et al. "Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture," presented at the 2021 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/projects/files/Development%20of%20Self-Assembly%20Isoporous%20Supports%20Enabling%20Transformational%20Membrane%20Performance%20for%20Cost%20Effective%20Carbon%20Capture.pdf*.