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DEVELOPMENT OF SELF-ASSEMBLY SUPPORTS ENABLING TRANSFORMATIONAL MEMBRANE PERFORMANCE FOR COST-EFFECTIVE CARBON CAPTURE

Final Project Report

by

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ABSTRACT

This final technical report describes work conducted by Membrane Technology and Research, Inc. (MTR) for the U.S. Department of Energy (DOE), National Energy Technology Lab (NETL) on the development of membranes with transformational performance for carbon capture under award number DE-FE0031596. The work was performed from June 1, 2018 through May 31, 2024. The results obtained fall into two categories: improved support membranes and improved selective layers.

Support membranes were prepared from a range of polymers, including commercially available block copolymers and a custom synthesized block copolymer alternative. The utility of these membranes as support for high-permeance composite membranes was determined by making single layer composite membranes and measuring their carbon dioxide permeance. The best support membranes developed in this project yielded single layer composite membranes with permeances that are two to three times higher (at the same selective layer thickness) compared to conventional support membranes.

The objective of the work on selective materials was to create a high-selectivity version of the Polaris™ membrane, as well as a high-permeance membrane version. A Technical and Economic Analysis (TEA) was performed for a carbon capture system that uses both advanced membrane types. The TEA shows the novel advanced membranes reduce the cost of capture by 10%, from \$63.32/tonne CO_2 to \$56.90/tonne CO_2.

EXECUTIVE SUMMARY

This final technical report describes work conducted by Membrane Technology and Research, Inc. (MTR) for the U.S. Department of Energy (DOE), National Energy Technology Lab (NETL) on the development of membranes with transformational performance for carbon capture under award number DE-FE0031596. The work was performed from June 1, 2018 through May 31, 2024.

For more than a decade, MTR has worked in partnership with DOE to develop an innovative membrane-based CO_2 capture process. This effort has included the first test of membrane modules with coal-fired flue gas at the Arizona Public Services (APS) Cholla plant in 2010; the accumulation of >11,000 hours of flue gas operation for Polaris modules on a bench-scale 1 tonne/day (TPD) system at the National Carbon Capture Center (NCCC); scale-up of first-generation (Gen-1) Polaris to a 20 TPD small pilot system, and successful operation of this system on a flue gas slipstream at NCCC and in integrated boiler testing at Babcock & Wilcox (B&W).

Through continued development efforts, a second-generation (Gen-2) version of the Polaris membrane has been scaled-up to pilot production. This membrane offers 70% higher CO_2 permeance with similar selectivity to the base case Polaris. MTR also developed planar modules designed specifically for the low-pressure, high-volumetric flow rate process conditions of flue gas operation. These new modules have significantly lower pressure-drop values compared to the type originally used (spiral-wound modules), which results in significant energy savings.

The goal of the work described in this report was to improve on the Polaris Gen-2 membrane with the ultimate aim to reduce the cost of carbon capture. The majority of the effort was to develop improved support membranes for the multi-layer composite structure of MTR's Polaris membrane. Earlier work at MTR had identified the support structure as limiting membrane permeances, not because the support itself represents a permeation resistance, but because the distribution of pores at the surface of the support imposes a geometric restriction to diffusion in the layers above it. Support membranes were prepared from a range of polymers, including commercially available block copolymers and a custom synthesized block copolymer alternative. The best support membranes developed in this project reduced the geometric restriction by a factor of two to three. These supports then were used to produce Polaris composite membranes with improved permeances.

The second topic was to create a high-selectivity version of the Polaris membrane. The high-selectivity version uses a novel selective polymeric material and high selectivities were confirmed in experiments at MTR. The material is not easily made into very thin films. Consequently, the permeances are significantly lower than the Polaris Gen-2 membrane. The utility of this membrane is therefore limited to the carbon dioxide purification step that produces liquid CO_2.

A Technical and Economic Analysis (TEA) was performed for a carbon capture system that uses both advanced membrane types. The TEA shows the novel advanced membranes reduce the cost of capture by 10%, from \$63.32/tonne CO_2 to \$56.90/tonne CO_2 (2022 USD).

Most of the development work was carried out with laboratory-scale casting and coating equipment. A number, but not all, of the improvements identified have been implemented on commercial-scale manufacturing equipment. The focus of future work at MTR is to incorporate the advancements made into the Polaris membrane manufacturing process.

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1. INTRODUCTION

1.1 Background and Approach

Over the past decade, DOE has invested in a large research effort to develop low-cost technologies to capture CO_2 from large point-source emitters. Coal-fired power plants have been a particular focus for CO_2 capture efforts because of the large installed base of these plants, which produce almost 40% of U.S. anthropogenic CO_2 emissions. Increasingly, capture from gas-fired power plants and industrial sources is also becoming a focus of efforts to meet decarbonization targets.

Currently, CO_2 capture using amine absorption is the most common technology for post-combustion CO_2 capture. Current estimates indicate that the cost of 90% CO_2 capture from coal flue gas with first-generation amines will be >$60/tonne CO_2. As a result, DOE is funding development of a suite of improved capture technologies based on advanced solvents, sorbents and membranes, with the ultimate goal of reducing this capture cost to $30/tonne or less.

Among the new capture technologies being developed are a number of membrane approaches. Membrane processes offer significant advantages when applied to post-combustion CO_2 capture, including no hazardous chemical storage, handling, disposal or emissions issues, simple passive operation, tolerance to high SO_x and NO_x content, a reduced plant footprint, recovery of flue gas water, and – because only electric power is used – no modifications to the existing power plant steam cycle are needed.

The main challenge for post-combustion capture membranes is the low partial pressure of CO_2 in flue gas, which results in a large membrane area being required because of the small driving force for separation. Working with DOE over the past 15 years, MTR has made several key innovations to yield a cost-effective membrane-based CO_2 capture process. This prior work has included the first test of membrane modules with coal-fired flue gas at the APS Cholla plant in 2010; the accumulation of >11,000 hours of flue gas operation for Polaris™ modules on a 1 tonne per day (TPD) bench-scale system at NCCC; and field validation of air sweep module performance. As a result of these successes, the technology was scaled-up to a 20 TPD (1 MW_e) small pilot system that was operated in slipstream tests at NCCC. These tests were completed on time and within budget. Later, this same system – operating in an integrated fashion with the Babcock and Wilcox (B&W) small boiler simulator (SBS)-II coal research boiler – was used to test the complete MTR capture process, including CO_2 recycle to the boiler. These activities show that MTR is experienced in bringing new membrane technology from concept to field demonstrations.

This prior work has also helped us identify key areas where additional cost reductions are possible, such as through the development of the transformational membranes that are the focus of the current project. Two separate approaches were taken. First, we developed improved support structures for the selective materials used in the MTR composite membranes. The improved supports have very uniform surface pores created through self-assembly of block copolymers. Second, in collaboration with the University of New York at Buffalo (NYUB), we developed improved selective materials that, in combination with the improved supports, yield composite membranes that are more permeable than the current Gen-2 MTR Polaris membrane, as well as more selective towards carbon dioxide.

1.1.1 Project Objectives

The overall objective of this project is to develop 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 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 current project consists of two parallel technology developments that address the support issue, as well as the development of more selective materials. These improvements will result in higher membrane permeances and higher selectivities, which reduce capital and operating costs, respectively.

The first development is to replace 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. The high surface porosity and uniformity in pore size and location of the isoporous supports reduce overall diffusion resistance and will allow fabrication of Polaris composite membranes with significantly increased CO_2 permeances.

The second technology development is to build on materials research carried out at NYUB by Professor Haiqing Lin, who was involved in the development of the Polaris selective material when he worked at MTR. Dr. Lin has identified related materials 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.

1.1.2 Membrane Criteria

The overall goal of this project is the development of composite membranes with transformational performance that will reduce the cost of carbon capture. The ambitious performance criteria for the project were:

- Composite membrane produced with dual-layer isoporous support and Polaris material has minimum mixed-gas performance values of CO_2 permeance = 4,000 gpu and CO_2/N_2 = 25.
- Composite membrane produced with dual-layer isoporous support and NYUB material has minimum mixed-gas performance values of CO_2 permeance = 3,000 gpu and CO_2/N_2 = 40.

1.2 Composite Membrane Basics

The PolarCap carbon capture process developed by MTR uses the Polaris membrane to selectively permeate carbon dioxide over other gases, most importantly nitrogen and oxygen. The key component of the membrane is a selective material that is significantly more permeable to CO_2 than to N_2 and O_2. An important objective while developing a high-performance membrane is to form this material into a layer that is very thin, which maximizes the transport rate across the layer according to the basic membrane transport equation:

$$J_i = \frac{P_i}{\ell} \cdot \left(p_i^f - p_i^p \right)$$

where J_i is the transport rate of component *i*, P_i is the permeability coefficient, ℓ is the thickness of the layer and p_i^f and p_i^p are the partial pressures on respectively the feed (high-pressure) side and the permeate (low-pressure) side. The term P_i / ℓ is referred to as the permeance of component *i* in the membrane, and the term $\left(p_i^f - p_i^p \right)$ is the driving force for permeation of component *i* through the membrane.

MTR produces selective layers well below 1 micron thickness, which are not strong enough mechanically to withstand even small pressure differentials. The solution is to create a multi-layer membrane structure where additional layers provide the required mechanical strength. Figure 1 shows an example of the cross-section of such a structure, which is called a composite membrane. In addition to the selective layer, the composite membrane has a porous support and a gutter layer on the low-pressure side of the selective layer and optionally a protective layer on the high-pressure side of the selective layer.

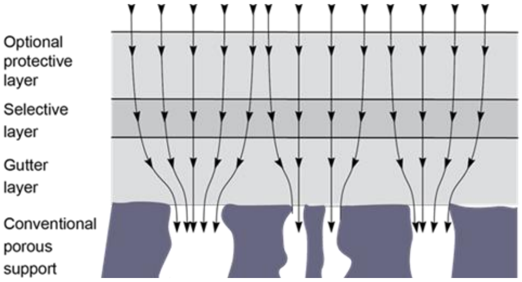


Figure 1. Schematic of a multi-layer composite membrane with flow lines indicating transport of the permeating molecules which can exit the gutter layer only through the openings of the pores in the support. Dimensions are not to actual scale.

The composite membrane structure requires careful optimization of the properties of the individual layers. The permeance of the composite membrane will be less than the intrinsic permeance of the selective layer because each additional layer represents an additional resistance to transport. The individual resistances are the inverse of the individual permeances and using the resistances-in-series model, we can write the following equation for the permeance of the composite membrane (the resistance of the porous support is very small and can be ignored):

$$\left(\frac{P_i}{\ell}\right)_{\text{composite}} = \left[\left(\frac{\ell}{P_i}\right)_{\text{top layer}} + \left(\frac{\ell}{P_i}\right)_{\text{selective layer}} + \left(\frac{\ell}{P_i}\right)_{\text{gutter layer}}\right]^{-1}$$

For the composite membrane to have selective permeation properties close to those of the selective layer, the dominant resistance to permeation has to be within the selective layer. This means the following conditions have to be met:

$$\left(\frac{P_i}{\ell}\right)_{\text{top layer}} >> \left(\frac{P_i}{\ell}\right)_{\text{selective layer}}$$

$$\left(\frac{P_i}{\ell}\right)_{\text{gutter layer}} >> \left(\frac{P_i}{\ell}\right)_{\text{selective layer}}$$

This can be achieved by selecting high permeability materials for the top and gutter layers and by making these two layers as thin as possible. However, as we were making the gutter layer thinner and thinner, we observed that the increase in gutter layer permeance did not follow the expected inverse relationship with thickness. There is a fundamental phenomenon that explains this observation, which will be discussed in detail in the next section. Insights into this phenomenon has led to strategies for improving membrane performance.

1.3 Support Membrane Influence

Figure 2(a) is a plot of the CO_2 permeance of a two-layer composite membrane which consists of a thin polydimethylsiloxane (PDMS) non-porous layer coated into a porous support membrane. The thickness of the PDMS layer varies from about 10 micron to less than 0.1 micron (100 nm). The thickness of the PDMS layer is measured using an ellipsometer, the CO_2 permeance is measured with pure-gas at a pressure difference of about 20 psid.

The permeance of the PDMS layer is defined as the permeability of PDMS divided by the thickness of the PDMS layer, so we expect permeance to increase proportionally with the inverse of the thickness. The experimental data in Figure 2(a) show a significant deviation from this behavior. The straight line in the figure is calculated using a CO_2 permeability of 3,400 Barrer and the data points are very close to this line for thicknesses greater than 5 microns. Below 5 micron thickness, the experimental data start to fall below the line and at 0.1 micron thickness the experimental permeance is seven times lower than predicted, which is a very significant difference. The support membrane has a very small resistance to transport; too small by orders of magnitude to be able to explain the observed reduction in permeance.

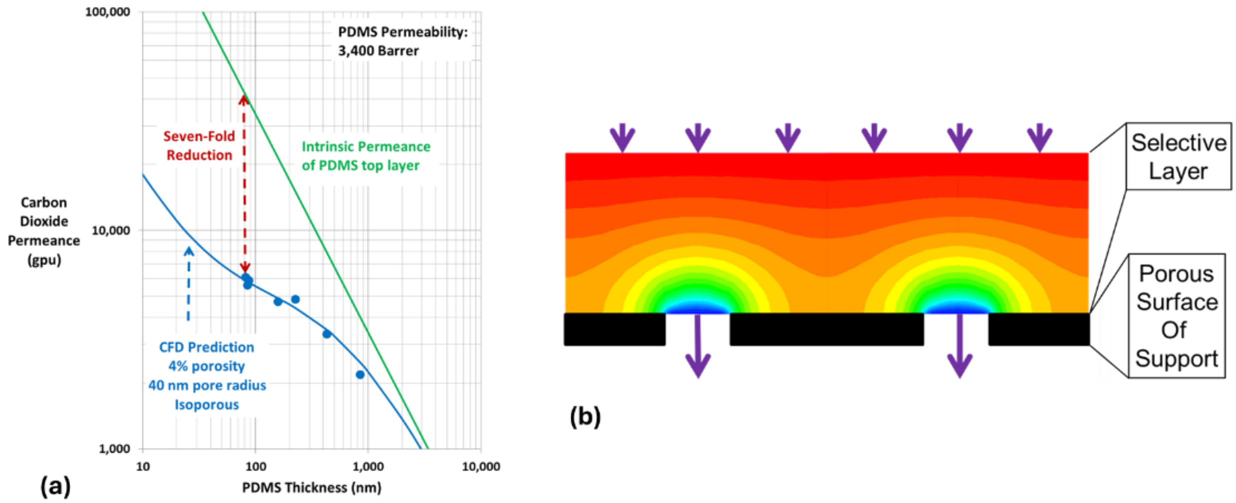


Figure 2. (a) CO_2 permeance of a PDMS composite membrane as function of PDMS thickness; plot illustrates the effect of the support membrane on permeance.

(b) CFD simulation of molecules diffusing through the selective layer. Diffusion rates are severely restricted at the pore openings, which reduces the permeance of the membrane.

Earlier work at MTR has shown that the reduction in permeance can be explained by the influence of the pore structure of the support membrane on the diffusion rates in the selective layer [1,2]. Diffusion is affected because molecules entering the layer at the top can only exit the layer where the layer spans the pore openings. Figure 2(b) shows concentration profiles calculated using Computational Fluid Dynamics (CFD) simulations. The permeance calculated from these profiles is significantly reduced compared to an unsupported layer. A correlation has been established that accurately predicts the reduction in permeance [1]:

$$\frac{(P_i/\ell)_{\text{actual}}}{(P_i/\ell)_{\text{intrinsic}}} = \frac{\phi + 1.6\cdot\left(\frac{\phi}{1-\phi}\cdot\frac{h}{r}\right)^{1.1}}{1 + 1.6\cdot\left(\frac{\phi}{1-\phi}\cdot\frac{h}{r}\right)^{1.1}}$$

where ϕ and r are the surface porosity and pore radius of the support membrane and h is the thickness of the nonporous layer. This correlation is very useful as it avoids having to do CFD simulations for individual cases. The correlation predicts, as expected, that the negative effect of the support membrane surface structure becomes smaller when the porosity is high, when the pore size is small, and when the thickness of the nonporous layer is large. As shown in Figure 2(a), the correlation accurately reproduces the experimental data for a surface porosity of 4% and a pore radius of 0.04 micron (40 nm), which are typical values for the ultrafiltration membranes commonly used as support membranes.

Additional work [2] has shown that a uniform distribution of the pores across the support membrane surface combined with a uniform pore size is desired as well. In 2007, Peinemann et al [3] showed that these types of "perfect" porous surfaces can be made through the self-assembly properties of block copolymers using a process very similar to that currently used to commercially produce industrial membranes (see Figure 3). A major objective of the work described in this report was to investigate isoporous structures as support membranes for high-performance composite membranes, specifically for carbon capture applications.

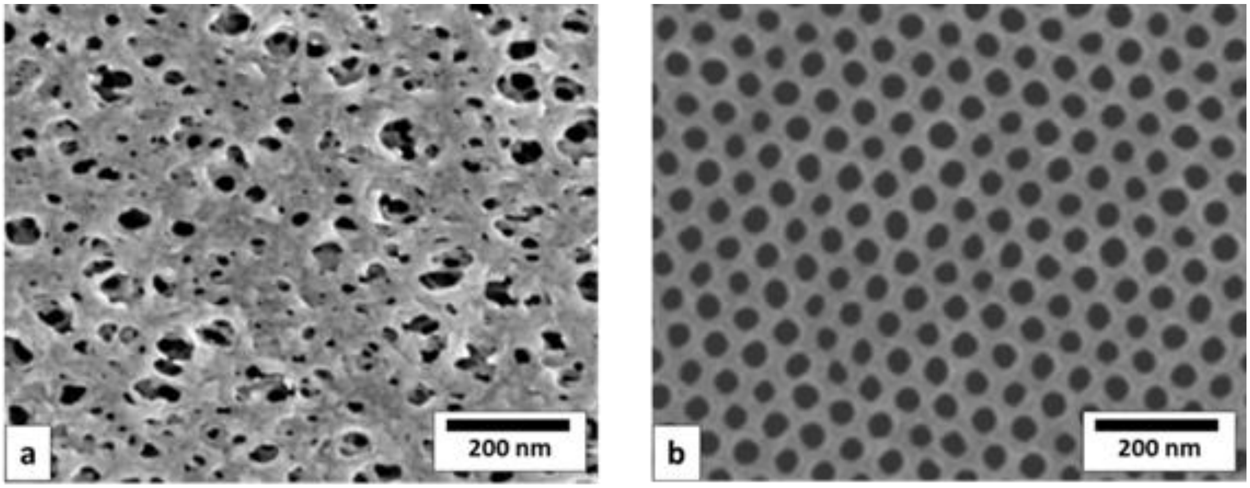


Figure 3. Surface pore structure of (a) a conventional porous support, and (b) an isoporous support. The high porosity, small pore size, uniform pore size and the uniform pore distribution of the isoporous surface makes this an ideally suited support membrane for high-performance composite membranes.

1.4 Self-Assembly of Block Copolymers

Block copolymers are a special set of polymers which consists of two separate polymer chains (two blocks): a hydrophobic block and a hydrophilic block. These two blocks normally are not compatible, but in a block copolymer they are linked to each other through a chemical bond. This results in complex thermodynamic behavior and it has been known for a long time that these block copolymers can self-assemble into intricate repeating patterns at the nanometer scale.

Peinemann and coworkers [3,4] first reported in 2007 that membranes with isoporous surfaces can be produced if a suitable block copolymer is used. Of great importance for the current project is that the techniques and the equipment used to make these membranes are the same as those used by MTR and other membrane manufacturers for conventional membranes. However, one significant drawback of block copolymers is that they are currently not produced at scale and are difficult to make. Consequently, they are orders of magnitude too expensive to be used at industrial scale. In this project we explored two different ways to overcome these issues:

- Use a dual slot die to produce two-layer support membranes, where more than 90% of the membrane consists of a standard polymer used for conventional membranes, and where a thin top layer of the support membrane consists of the block copolymer which creates the desired isoporous top surface, and
- Investigate alternatives to the “perfect” block copolymer that are easier to make in a cost-effective way, and which may not yield a “perfect” isoporous surface but produce a “better” porous surface.

1.5 Selective Materials

It is generally understood that the separation of CO_2 from N_2 and O_2 (as encountered in carbon capture applications) by membranes requires selective membrane materials that are different from those that have been used for decades for the separation of CO_2 from natural gas, where the main separation is CO_2 from methane. Hydrophilic rubbery polymers with a high oxygen to carbon ratio in their molecular structure are especially suited for carbon capture [5,6]. The research group of Professor Lin at SUNY Buffalo has significant expertise in the development of these materials and has published data on a number of materials with promising permeability properties. An example is given in Figure 4. Part of the work described in this report focused on converting these materials into high-performance composite membranes.

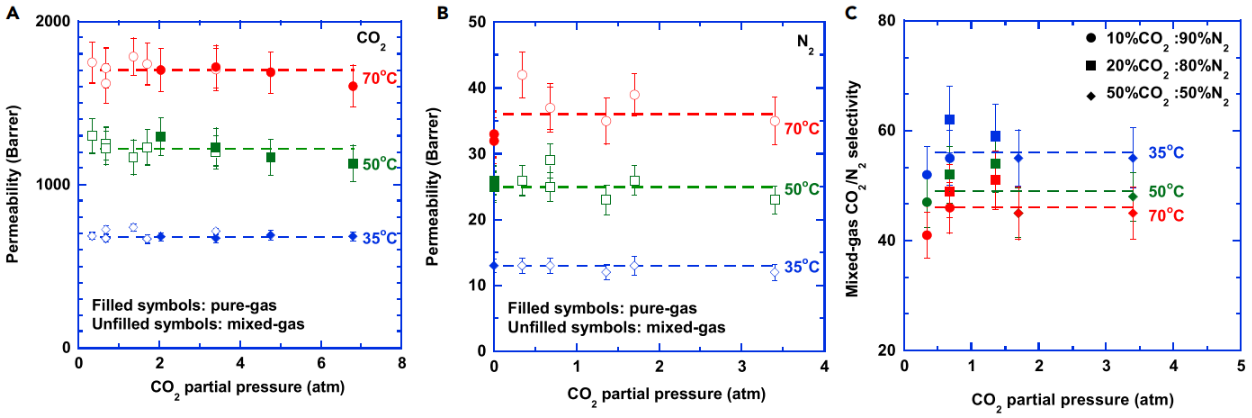


Figure 4. Effect of CO_2 partial pressure and temperature on the CO_2 permeability, the N_2 permeability and the CO_2/N_2 selectivity of films prepared from a PEO-based polymer. Figures taken from [6].

2. EXPERIMENTAL RESULTS

2.1 Support Membranes

During the project, a large number of different support membranes were prepared from a number of polymers using a range of different techniques. Two methods were used to characterize these support membranes in a way that is relevant for their use as a support membrane.

The first method is to measure the nitrogen permeance of the support membrane at different pressures and use the Dusty Gas model to calculate the average radius of the surface pores [7]. A small pore radius is desired, preferably below 50 nm. The small pore size has to be combined with a high nitrogen permeance; preferably larger than 50,000 gpu to be an effective support membrane.

After completion of the first test, the support membrane is overcoated with a PDMS layer, using a specialized coating technique that avoids penetration of the PDMS into the pores. The thickness of the PDMS is around 0.1 micron (100 nm) and is measured with an ellipsometer. The CO_2 and the N_2 permeances are measured in pure-gas permeation experiments. A CO_2/N_2 selectivity of 12 indicates that the PDMS layer is free of defects. The CO_2 permeance/PDMS thickness datapoint is plotted in the graph first introduced in Figure 2(a) and shown here again as Figure 5. The quality of the support membrane can be judged on how close the data point is to the intrinsic permeance line and how far removed from the conventional support line.

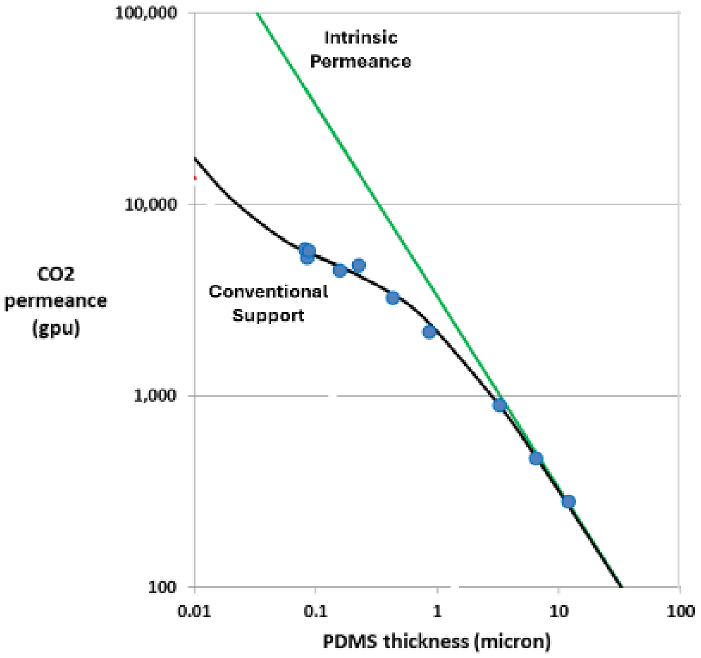


Figure 5. Plot of carbon dioxide permeance versus PDMS thickness for single-layer PDMS composite membranes.

2.1.1 *Block Copolymers*

The mechanism of formation of the isoporous membranes has been investigated by Nunes and coworkers [4] and is based on the presence of micelles in the starting block copolymer solution. The most extensive studies have been carried out by the group of Abetz [8,9] with poly(styrene)-block-poly(4-vinylpyridine) (PS-b-P4VP). Perfect isoporous membranes were prepared from 18 different PS-b-P4VP polymers, which are commercially available with different molecular weights of the PS and the P4VP blocks from Polymer Source. Specific and unique casting solution compositions had to be developed for each polymer to successfully achieve formation of the isoporous surfaces.

At the start of the project, we set out to reproduce the Abetz work using the recipes described in references 8 and 9 [8,9]. Eventually we succeeded, but we learned that producing these surfaces requires extreme control of the operating conditions. This makes it unlikely that reproducible manufacture of these membranes at large-scale is feasible.

Figure 6(a) is a high-resolution electron micrograph of the surface of an isoporous support produced at MTR. The pore radius is about 40 nm and the porosity is about 35%, which makes it an excellent support membrane. Figure 6(b) confirms this: at the same PDMS thickness the permeance is about four times what is achieved with a conventional support membrane. The restriction correlation discussed in the Background section predicts a permeance that is higher by about 25% than that measured, which suggests there is a minor amount of penetration by the PDMS into the pores.

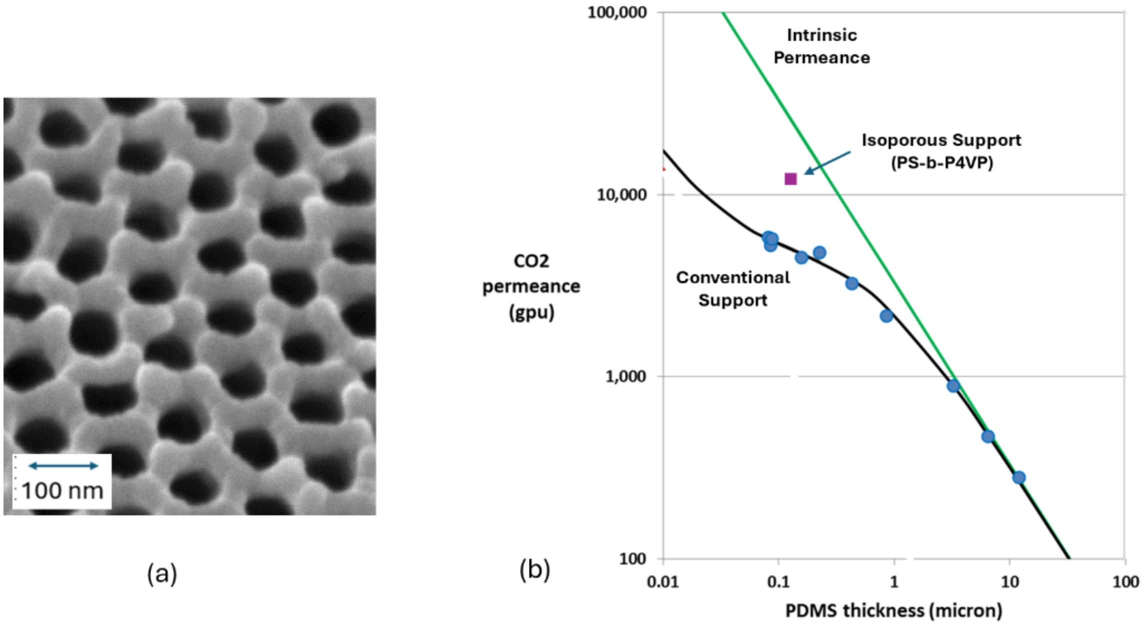


Figure 6. (a) Scanning electron microscope image of the top surface of an isoporous membrane prepared from PS-bP4VP. (b) CO_2 permeance of the support after overcoating with a thin layer of PDMS.

The electron micrograph shown in Figure 6 shows that the surface around the pores is not perfectly flat. This observation is in agreement with the mechanism of formation proposed by Nunes et al [4]. We analyzed the surface with an Atomic Force Microscope (AFM) and traced the perimeter around a pore, as shown in Figure 7. The left-hand figure is a Scanning Electron Micrograph (SEM) of the surface and shows the path around the pore that was traced by the AFM. The right-hand graph gives the height profile measured for that path. There are six maxima and six minima reflecting the six micelles that surround the pore, which are the reason the pores are distributed in a hexagonal pattern [4].

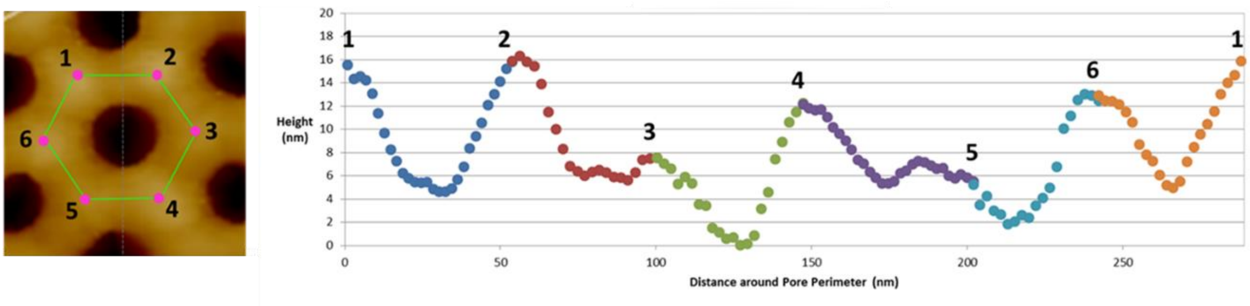


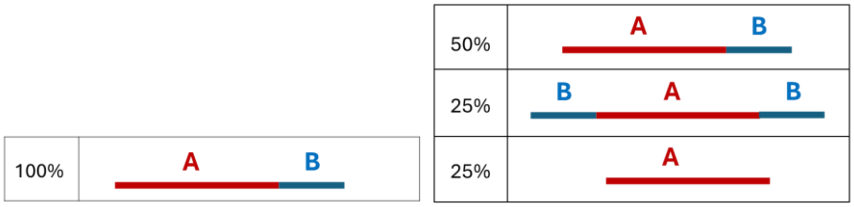
Figure 7. The left-hand figure is a SEM of the surface of an isoporous support and shows the path around the pore that was traced by the AFM. The right-hand graph gives the height profile measured for that path.

2.1.2 Alternative Block Copolymer

Block copolymers (BCPs) are too expensive to be used as support membrane materials for large-scale carbon capture applications. In section 2.1.3 we will discuss the dual-layer casting technique that reduces the amount of block copolymer required. The current section focuses on an alternative approach for a low-cost block copolymer.

The alternative approach to producing BCPs was developed in the Polymer Chemistry group of Professor Lynd at UT Austin. As shown in Figure 8, a conventional “perfect” BCP consists of two monodisperse blocks A and B that are connected through one chemical bond. To create isoporous surfaces the desired ratio of hydrophilic block B to hydrophobic block A is approximately 0.1 to 0.4.

In the alternative approach, the hydrophobic block A is replaced with a commercially available engineering polymer which is not monodisperse but has a molecular weight distribution (polydisperse). The polymer is produced through polymerization of two monomers: each monomer has two identical reactive end groups. During polymerization the reactive groups form the linkage between the monomers. For each individual polymer chain there are three possible outcomes with respect to the chemical groups at the two ends of the chain: 50% of the chains will have one of each reactive group, 50% of the chains will have the same reactive group on each ends, 25% will have the reactive groups of one monomer on each end, and 25% will have the reactive groups of the other monomer on each end. The alternative block copolymer is formed by combining the engineering polymer with a hydrophilic block that is capable of reacting with one of the reactive groups present in the engineering polymer. As shown in Figure 8, the reaction product consists of a mixture of block copolymer AB (50%), block copolymer BAB (25%) and unreacted engineering polymer A.



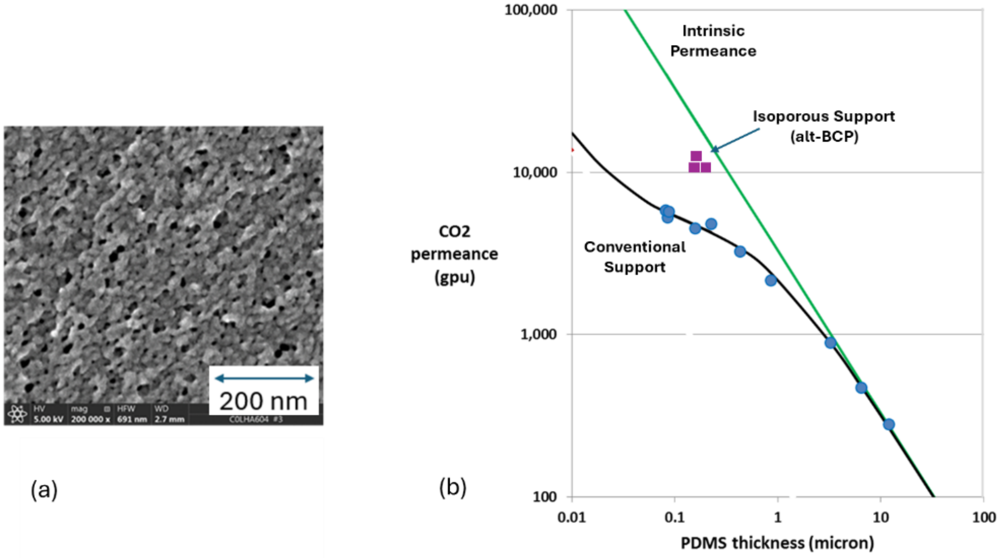
(a) Block Copolymer
A and B are monodisperse blocks

(b) Alternative Block Copolymer
A is a polydisperse engineering polymer
B is a monodisperse block

Figure 8. Block copolymer structures. (a) is a perfect block copolymer, consisting of two blocks joined together. (b) is a low-cost alternative block copolymer

A synthesis route for the alternative block copolymer was developed and high yields were obtained. Infrared spectra and Gel Permeation Chromatography (GPC) confirmed that the reaction runs to near completion and that the molecular weight of the engineering polymer has increased. The ratio of hydrophilic block to hydrophobic block is 0.33.

A support membrane was prepared with the alternative BCP after establishing a solvent mixture capable of dissolving the polymer. Figure 9(a) shows the SEM of the surface and Figure 9(b) shows that this support is nearly as good as the support made with the perfect BCP. The alternative BCP has a lower surface porosity but has much smaller pores, which compensates for the lower porosity. A smaller pore size is an advantage during the coating process and the high-nitrogen permeance of 95,000 gpu makes the alternative BCP an excellent low-cost replacement for the BCPs.



(a)

(b)

Figure 9. (a) SEM image of the top surface of a support membrane prepared from the alternative block copolymer synthesized at UT Austin. (b) CO_2 permeance of the support after overcoating with a thin layer of PDMS.

2.1.3 Dual-Layer Casting

Typical support membranes are produced in a casting step using a single polymer casting solution that is laid down on a base layer by either a casting knife or through a slot die. The casting solution then passes through a water bath where the porous structure of the support membrane is produced via a phase inversion process. In this case, the support membrane consists of one single polymer. It is possible to use a dual slot die, which offers the option to use two different casting solutions; the second solution is laid down on top of the first solution. The concept described in the proposal was for the second solution to contain the expensive block copolymer and to make this layer as thin as possible.

We purchased a 16” wide dual slot die and installed it on MTR’s lab-scale casting machine. Figure 10(a) shows a close-up picture of the dual slot die. The two taped-off ports shown are the inlet ports for the two separate slots. The height of each individual slot can be set independently by using shims of different thicknesses, which can be as thin as 0.5 mil (12.5 micron), resulting in a support membrane top layer of 2 to 5 microns.

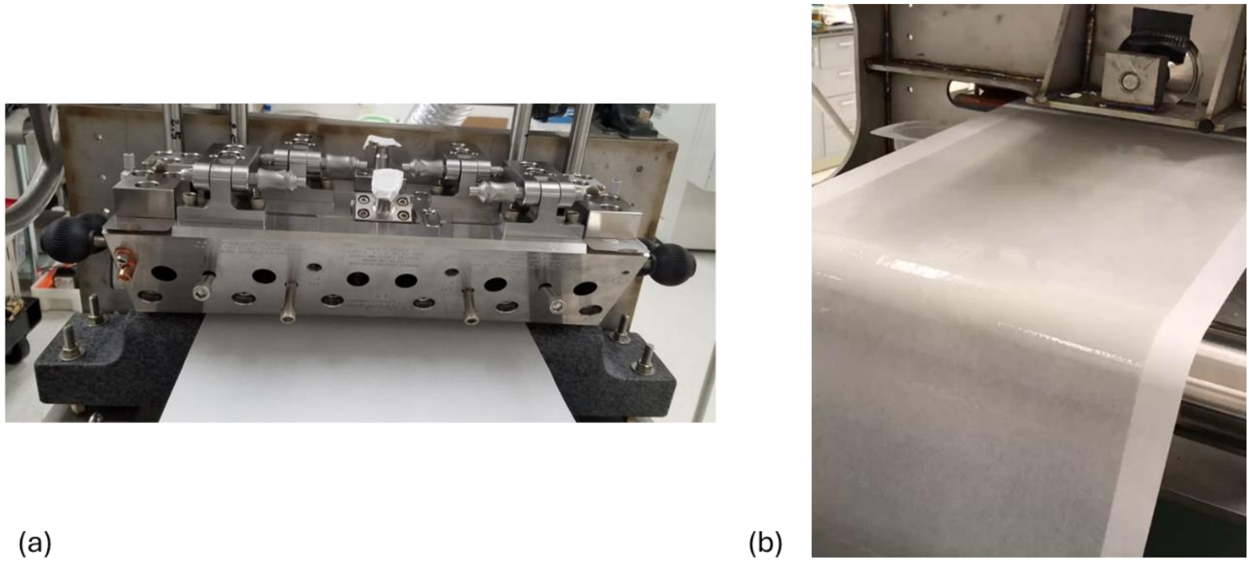


Figure 10. (a) Close-up of the dual slot die. (b) Dual slot die in operation.

Running the slot die with the PS-b-P4VP block copolymer is prohibitively expensive, so we hand-casted a dual-layer support using the casting block shown in Figure 11. The top-layer is made from the PS-b-P4VP block copolymer and a base layer from the homopolymer polystyrene (PS). The two layers are well-integrated and no delamination is observed.

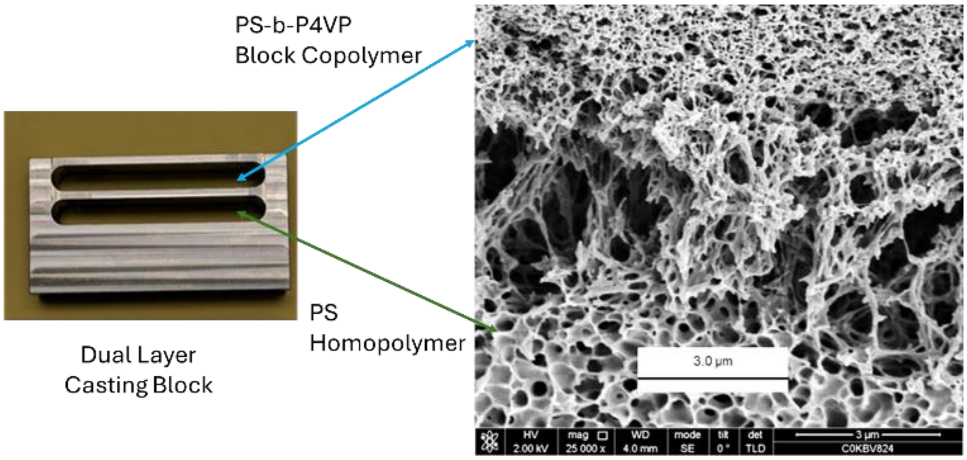
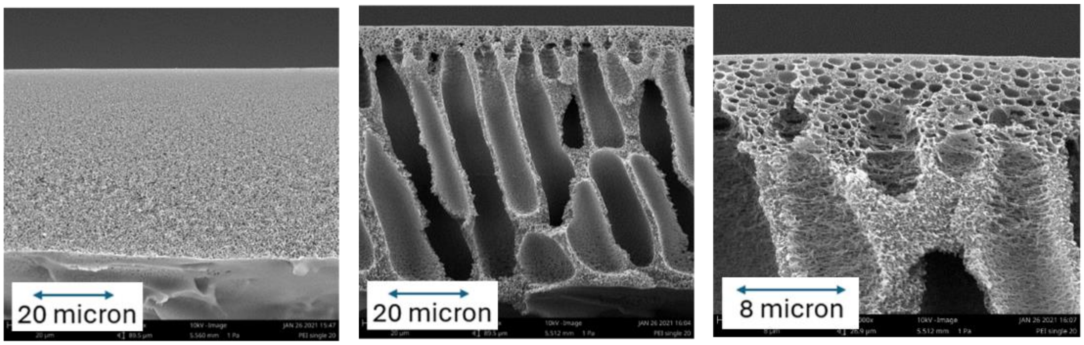


Figure 11. Casting block used to prepare a dual-layer support membrane, consisting of a top layer made from PS-b-P4VP block copolymer and a base layer of the homopolymer PS. The two layers are well-integrated and no delamination is observed.

UT Austin prepared sufficient quantity of the alternative block copolymer to support a run with the dual slot-die. The base layer of the support consisted of the engineering polymer used to make the alternative block copolymer and was 12” wide. The second slot of the dual slot-die laid down the alternative block copolymer at the center 4” of the membrane, which allowed us to compare the single-layer support and the dual-layer support. The nitrogen permeances of the uncoated membranes were very different: 38,000 gpu for the single-layer and 140,000 gpu for the dual-layer. Figure 12 shows that the structure of the two membranes also is very different. In the casting process, the contact area between the casting solution and the casting bath is at the top surface and the structure of the membrane forms from the top down. This explains why the thin layer on top influences the structure below. It is interesting to note that the dual-layer is thicker and yet has a significantly higher nitrogen permeance. This is a clear indication that the porosity of the dual-layer is much higher. Figure 12(c) shows that the thickness of the top layer is about 4 micron and that there is a smooth transition to the bottom layer.



(a) Single Layer
Engineering Polymer

(b) Dual Layer
Top: Alternative block copolymer
Bottom: Engineering polymer

(c) Magnification of (b)

Figure 12. Single- and dual-layer support membrane produced side-by-side in a single casting run.

Figure 13 shows that the dual-layer support after coating with PDMS has high CO_2 permeance. Performance is slightly below that of the pure PS-b-P4VP support, but lack of material prevented us from carrying out more than one run, so no optimization was possible.

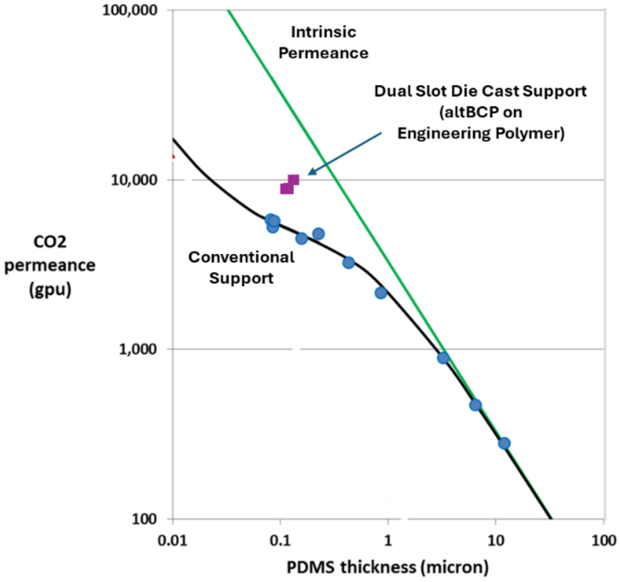


Figure 13. CO_2 permeance of the support shown in Figure 12(b) after overcoating with a thin layer of PDMS.

2.2 High-Selectivity Materials

Previous work by the group of Professor Lin at SUNY Buffalo has identified high oxygen/carbon ratio polymers with high CO_2/N_2 selectivities and high CO_2 permeabilities. They prepare films of these polymers by cross-linking the neat monomer (without solvents) in between glass plates using heat or ultraviolet light (UV). This method produces a film that is at least 100 micron thick, which can be used to measure gas permeabilities.

One of the objectives of the work described here was to turn these materials into high-performance composite membranes. This requires making the materials into layers that are less than 1 micron thick, which is achieved through a solution-based coating process. A number of different solvent systems was investigated with limited success. We found it difficult to produce coating solutions that would yield defect-free layers that are thinner than several microns, which was approximately ten times thicker than our goal.

Figure 14 shows a pure-gas CO_2/N_2 selectivity versus CO_2 permeance trade-off plot with many data points collected during the membrane optimization process. A surprising trend in this plot is that better membranes are prepared from lower molecular weight polymer in the range of 200 kDa to 50 kDa. This trend does not carry on indefinitely, however: at 30 kDa the properties are worse suggesting poor film forming ability for this low molecular weight material.

In general, higher molecular weights correlate with better film forming properties. The exception seen here is likely caused by the physical structure of the polymer chains, which are highly branched as opposed to being long linear coils. A branched polymer chain more closely resembles a sphere or a "blob" and, at the same coating weight concentration, a lower molecular weight means a larger number of smaller polymer spheres, which produces a higher quality film.

The collection of data shown in Figure 14 indicates that a CO_2 permeance of 500 gpu can be achieved while maintaining the CO_2/N_2 selectivity close to the maximum value of 80. For comparison, this pure-gas selectivity is higher than a conventional Polaris membrane, which typically shows a CO_2/N_2 of 50-60, albeit with much higher CO_2 permeances up to 1,500 gpu.

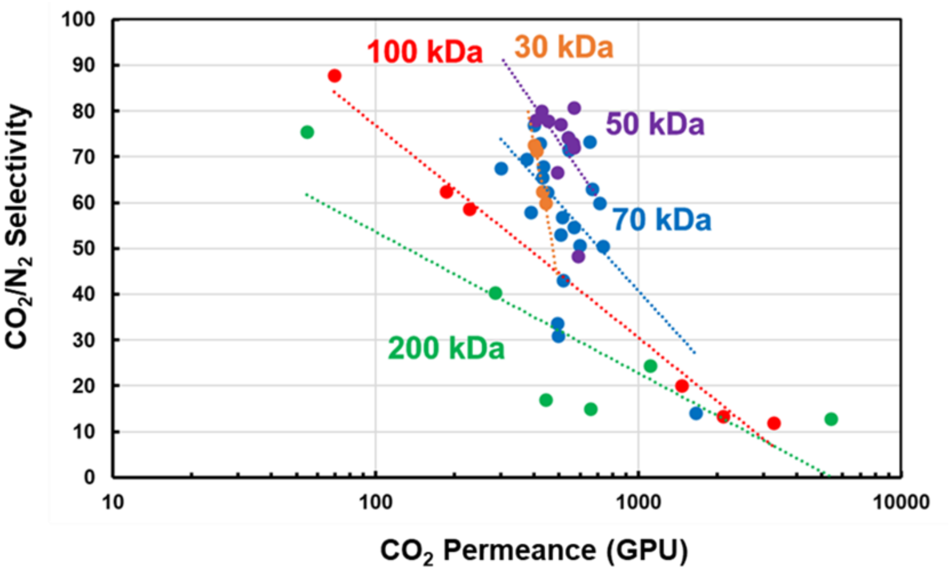


Figure 14. Selectivity – permeance trade-off plot for composite membranes prepared with a high CO_2/N_2 selectivity material.

2.3 Membrane Performance

Over the course of the project a large number of composite membrane samples were tested with pure-gases and with gas mixtures. Pure-gas tests were carried out at room temperature in a dead-end permeation cell using carbon dioxide, oxygen and nitrogen at 50 psig feed pressure. Selected membranes were tested with gas mixtures consisting of carbon dioxide in nitrogen; the carbon dioxide concentration ranged from 2 to 40%, with 15% as the standard. The permeation cell allows the feed gas to flow over the membrane surface and only a small fraction of the feed gas permeates through the membrane. Feed pressure was atmospheric, and a vacuum pump generated a permeate pressure in the range of 1.5 to 3 psia. Temperature ranged from 30 to 50°C, with 40°C as the standard. A gas chromatograph was used to obtain the gas composition of the feed, residue and permeate gas streams, which are used to calculate the permeances of carbon dioxide and nitrogen.

Figure 15 contains permeance and selectivity data for selected membranes obtained in pure-gas permeation experiments. The "Advanced Polaris" datapoints represent composite membranes prepared with the same selective material as the Polaris Gen-2 membranes, but with improved support membranes and with additional tweaks in the coating steps. The trade-off shown in the plot between permeance and selectivity is the result of variations in thickness of the various layers used to construct the composite membranes. The "High-selectivity Materials" datapoints represent composite membranes prepared with novel selective materials. The datapoints show that a selectivity as high as 90 can be achieved, but also that this level of selectivity only is obtained at relatively low-permeances.

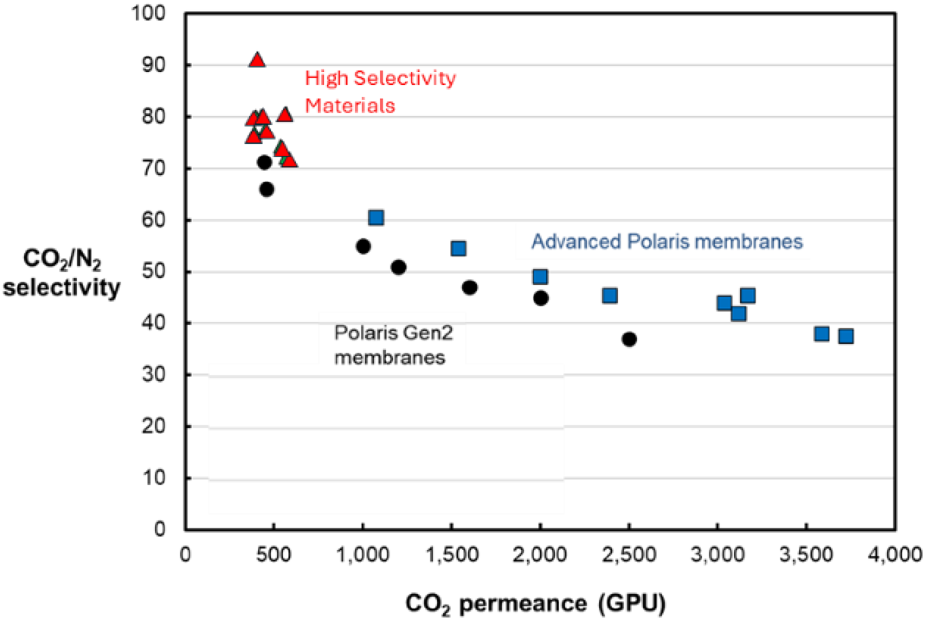


Figure 15. Permeance – selectivity trade-off plot for selected composite membranes. Permeances and selectivities obtained in pure-gas experiments at room temperature.

Figure 16 is similar to Figure 15 but contains gas mixture data, which are more relevant than the pure-gas data. The trends in the two figures are comparable, which means that pure-gas data are a good predictor of mixed-gas separation performance. At first sight, the Polaris Gen-2 and Advanced Polaris trade-off lines do not seem to be that different. However, closer inspection shows that at constant selectivity, the Advanced Polaris membrane offers a substantially higher permeance.

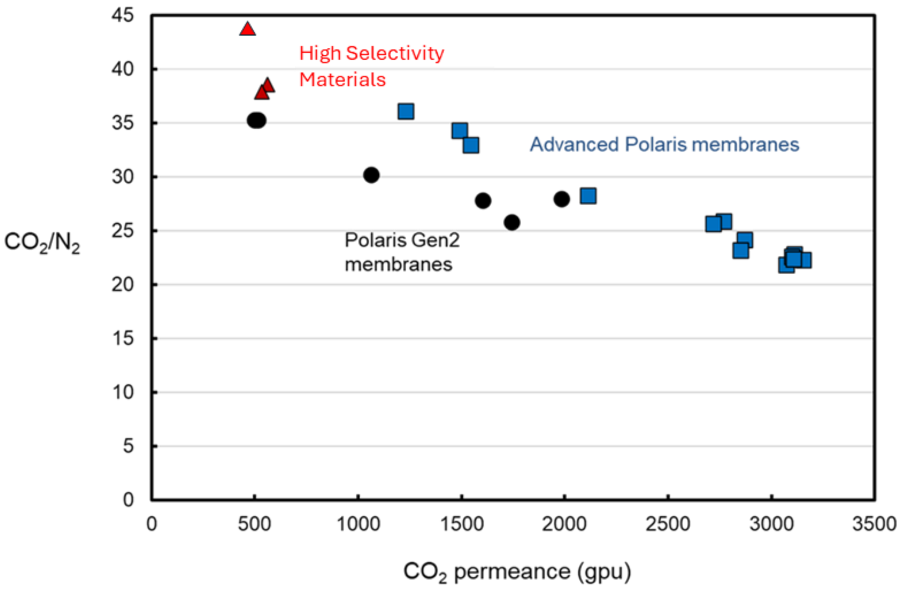


Figure 16. Permeance – selectivity trade-off plot for selected composite membranes. Permeances and selectivities obtained in mixed-gas experiments at 40°C and with a mixture of 15% CO_2 in nitrogen. Feed pressure is atmospheric, permeate pressure is 1.5 to 3 psia.

Based on the data presented in Figure 16 we defined two different membrane configurations, MEM2 and MEM3, which are listed in Table1. They are compared to the Polaris Gen-2 (MEM1) configuration. The two advanced membranes represent a high-permeance alternative and a high-selectivity alternative to the Polaris Gen-2 membrane.

Table 1. MTR-Base (Polaris Gen-2) and transformative Advanced Membrane performance parameters used in the process simulations for the TEA.

Permeant	Base Case Membrane Polaris Gen-2 (MEM1)		Advanced Membrane High-Permeance (MEM2)		Advanced Membrane High-Selectivity (MEM3)	
	Permeance (gpu)	Selectivity over N2	Permeance (gpu)	Selectivity over N2	Permeance (gpu)	Selectivity over N2
CO2	1,500	30	2,500	25	500	45
O2	120	12.5	230	10.9	28	17.9
N2	50	-	100	-	11.1	-

3. TECHNO-ECONOMIC ANALYSIS (TEA) SUMMARY

A TEA of MTR's post-combustion CO_2 capture process was conducted to quantify the benefits of the improved Polaris membrane types developed in the work carried out under contract DE-FE0031596. In previous projects, MTR and Trimeric collaborated on a CO_2 capture process for a supercritical pulverized coal power plant consistent with the basis for Case B12B from the DOE/ NETL report entitled "Cost and Performance Baseline for Fossil Energy Plants, Volume 1a: Bituminous Coal (PC) and Natural Gas to Electricity", Revision 4. MTR developed the central membrane CO_2 capture unit while Trimeric developed supporting processes upstream (flue gas cooling, pre-treatment) and downstream (CO_2 purification and compression) of the capture unit.

The TEA that is the focus of this report provides a comparison of the MTR CO_2 capture process using the advanced Polaris membranes developed in this project with (1) the MTR process using the base case Gen-2 Polaris membrane, and (2) the reference amine-based CO_2 capture process in Case B12B in the DOE baseline report. Two cases of the MTR CO_2 capture process are presented in this report. The advanced membrane case utilized both the high-permeance and highly-selective transformative membranes developed in this project.

Key findings from the TEA are summarized below.

- The cost of CO_2 capture for the MTR advanced membrane case was \$56.90/tonne CO_2 captured, which is an improvement of more than 10% compared to the base membrane case (\$63.32/tonne CO_2 captured).
- For the membrane cases, the rotating equipment/compression used in the MTR process design represents ~39% of the purchased equipment costs (PEC). The membrane units (~35%) and CO_2 compression and purification unit (CPU) (~26%) are the other large components of the PEC.
- Compared to the reference Case B12B amine case, the membrane cases have a slightly higher cost of capture for 90% capture from coal flue gas (the difference is within the uncertainty in this cost estimate).
- From prior work, the cost of capture for a membrane process decreases significantly with increasing feed CO_2 content. We expect capture using the membranes developed in this project will look very attractive for relatively high CO_2 content industrial flue gas streams such as those found in cement, lime, steel, H_2 production, and refineries.

4. TECHNOLOGY GAP ANALYSIS (TGA) SUMMARY

The objective of the TGA is to review the current state of development of all major process components of MTR's post-combustion CO_2 capture process and to provide a realistic review of all research needs required to fully develop the technology to commercialization.

The details can be found in the full TGA report, the table below is a summary of the research gaps identified in the report.

Future R&D Focus	Benefit of R&D Effort
Large Pilot integrated demonstration of the total CO_2 capture process	Move the MTR CO_2 capture technology to TRL-7. MTR's current project (DE-FE0031587) is on track to commission a Large Pilot field test of the entire MTR CO_2 capture process at WITC by fall-2024.
Advanced Polaris membrane development with improved selectivity and permeance properties	Advanced Polaris membranes will reduce the required membrane area, system footprint, and energy use of the MTR CO_2 capture process. The current transformational capture project with DOE (DE-FE0031596) is focused on this membrane improvement and the membrane developed will reduce membrane area by a factor of 1.5, when implemented on full commercial-scale. In this project MTR used for the first time a dual-slot die method for membrane casting. Based on the results obtained we will implement this method in full-scale casting operations, which will increase line speed and thus reduce manufacturing costs. We also will implement this method in our full-scale coating operations, which will not only increase line speed, but will also reduce solvent usage per square meter of membrane by a factor of two to five, which is an environmental benefit and reduces the carbon footprint of the manufacturing operation.
Advanced vacuum and CO_2 compression equipment available at Large Pilot and demonstration scales	Advanced equipment would decrease the capital and operating expenses (CAPEX/OPEX) and possibly the complexity of any point-source CO_2 capture process.
Site-specific front-end engineering design (FEED) and TEA studies of the MTR membrane technology for large point source CO_2 capture at power and industrial plants	Rigorous evaluation of the MTR membrane CO_2 capture approach from various large point source emitters. MTR's proposal to the OCED full demo funding opportunity (DE-FOA-0002738) is one of the seven projects that has been chosen for award negotiation. Phase I will include a FEED study at DFS for integrate carbon capture, transport, and storage.

5. ENVIRONMENTAL HEALTH AND SAFETY RISK ASSESSMENT SUMMARY

The objective of this Environmental, Health, & Safety (EH&S) Risk Assessment is to review the environmental friendliness and safety of MTR's post-combustion CO_2 capture process and identify potential deficiencies that have the potential to cause environmental harms and damages. This study characterizes the general level of risk of the membrane system and identifies opportunities for remedies at a stage of development when corrective measures can be easily implemented.

The details can be found in the full EH&S report. The topics addressed in the report are summarized below.

1. Membrane and Module Production
    a. Chemical exposure of production workers
    b. Injury risks
    c. Air emissions
    d. Waste water discharge
    e. Sold and liquid chemical waste
2. Carbon Capture System
    a. Chemical exposure of operators
    b. Risks of process upsets
    c. Waste generation
        i. Membrane elements
        ii. Oil and oil filters
        iii. Water treatment, filters and sludge

6. TECHNOLOGY MATURATION PLAN (TMP) SUMMARY

The proposed improvement for MTR's PolarCap carbon capture process is through the development of unique new support structures for the Polaris composite membranes. These novel structures are expected to allow higher permeance membranes to be produced.

A related effort will be to develop jointly with New York University at Buffalo a new chemistry for the selective material.

Readiness level at the beginning of the project was Technology Readiness Level (TRL)-2 with no previous experimental work performed at MTR.

The steps taken in the project to reach the next TRL were:

Level	Project Activity	Task
TRL-3	Make isoporous structures using recipes reported in the literature as a starting point. The block copolymers used to date are not optimal for our purpose, so we will investigate alternatives.	Task 2
TRL-3	Prepare novel selective polymers that can be used in membrane coating operations.	Task 3
TRL-4	Make dual-layer isoporous structures, consisting of a standard engineering polymer bottom structure and a block copolymer at the surface. Objective is to reduce use of expensive block copolymers and to increase options for optimization.	Task 2 Task 4
TRL-4	Coat isoporous structures with current and newly developed selective layers. Demonstrate improved membrane performance.	Task 4

7. FUTURE WORK

Most of the development work was carried out with laboratory-scale casting and coating equipment. A number, but not all, of the improvements identified have been implemented on commercial-scale manufacturing equipment. The focus of future work at MTR is to incorporate the advancements made during this project into the Polaris membrane manufacturing process.

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