Rational Development of Novel Metal-Organic Polyhedra-Based Membranes for CO_2 Capture

primary project goal

The State University of New York (SUNY) at Buffalo, along with its partners, is developing solubility-selective mixed matrix membranes (MMMs) comprising highly polar rubbery polymers and soluble metal-organic polyhedra (MOPs) to achieve high carbon dioxide (CO_2) permeance (3,000 gas permeation units [GPU]), high CO_2/nitrogen (N_2) selectivity (75), and CO_2/oxygen (O_2) selectivity (30) at 60°C. Such membranes would outperform currently leading membranes by 50–100%, which can be implemented into Membrane Technology and Research Inc.'s (MTR's) membrane processes and may enable CO_2 capture at less than \$30/ton CO_2 from coal power plants.

technical goals

- Develop solubility-selective MMMs comprising polar rubbery polymers and MOPs.
- Develop thin-film composite (TFC) membranes achieving high CO_2 permeance (3,000 GPU) and high CO_2/N_2 selectivity (75) at 60°C.
- Demonstrate separation performance and stability with raw flue gas at the National Carbon Capture Center (NCCC).
- Perform techno-economic analysis (TEA) on the membrane processes.

technical content

The project team is developing transformative solubility-selective MMMs containing MOPs and rubbery polar polymers. These transformative MMMs are built upon three key unique approaches. First, rubbery polymers with CO_2-philicity (and N_2-phobicity) will be designed, in contrast with most of the literature approach in pursuing glassy polymers with strong size-sieving ability. Second, MOPs with strong CO_2 affinity will be designed and added to increase the CO_2/gas solubility selectivity. In contrast to the commonly pursued insoluble metal-organic frameworks (MOFs), these MOPs are discrete nano-cages and soluble in organic solutions, making it easier to prepare TFC membranes with selective layers as thin as 100 nm. Third, the structure of polymers and MOPs can be independently designed with enormous possibilities, which can be accelerated using computational simulation.

A consortium of six organizations with complementary capabilities was assembled to achieve these goals, including University at Buffalo (UB; SUNY–Buffalo), Rensselaer Polytechnic Institute (RPI), California Institute of Technology (Caltech), MTR, NCCC, and Trimeric Corporation (Trimeric). The UB team is conducting fundamental and industrial membrane development and MOP synthesis and application to develop the novel materials, performing laboratory parametric tests, and scaling-up the production. RPI is preparing functionalized polymers and scaling-up the production. Caltech is simulating gas permeation to guide the design of the MMMs. MTR is preparing TFC membranes and bench-

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Mixed Matrix Membranes for Coal-Derived Flue Gas

participant:
State University of New York–Buffalo

project number:
FE0031736

predecessor projects:
N/A

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partners:
Rensselaer Polytechnic Institute; California Institute of Technology; Membrane Technology and Research Inc.; National Carbon Capture Center; Trimeric Corporation

start date:
07.01.2019

percent complete:
55%

scale modules and performing field tests at NCCC. Trimeric is updating the membrane process design and economic analysis based on MTR's patented processes. The endpoint of this project is a field test of bench-scale membrane modules, and a TEA of the newly developed membranes elucidating their potential to meet U.S. Department of Energy's (DOE) goals for CO_2 capture. A graph of the selectivities of the two chosen macromonomers is shown in Figure 1, while a simplified visual perspective of the membrane process is shown in Figure 2. The parameters governing membrane operation are shown in Table 1.

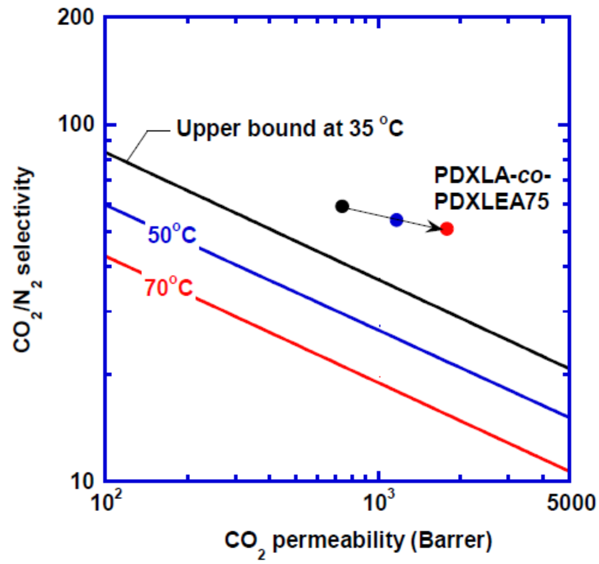

Figure 1: The "rubbery polymers": two macromonomers, poly(1,3-dioxolane) acrylate (PDXLA) and poly(1,3-dioxolane) ethyl ether acrylate (PDXLEA) are highly polar polymers that exhibit CO_2/N_2 separation properties above the upper bound in the Robeson's plot.

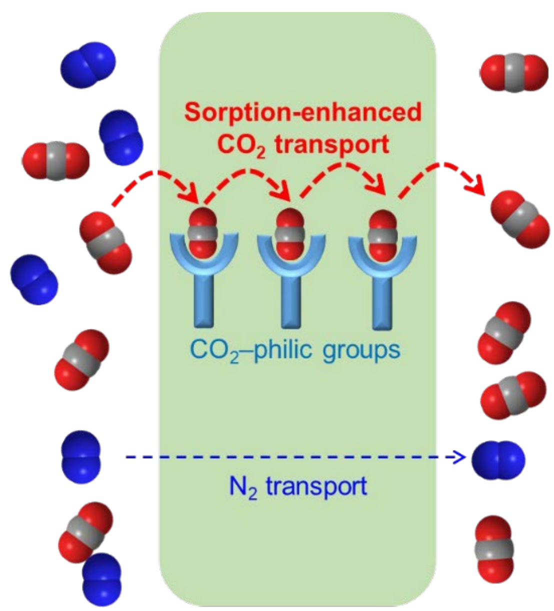

Figure 2: The highly branched amorphous polymers containing poly(1,3-dioxolane) (PDXL) in the branches interact favorably with CO_2, but not N_2, allowing for the design of solubility-selective membrane materials with superior performance for gas separations.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Mixed matrix materials of rubbery polymers and MOP	
Materials of Fabrication for Support Layer	—	Glassy polymers such as PAN, PSf	
Nominal Thickness of Selective Layer	nm	200–1,000	100–300
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	10	10
Hours Tested without Significant Degradation	—	120	500
Membrane Performance			
Temperature	°C	60°C	60°C
CO_2 Pressure Normalized Flux	GPU	1,500–2,000	3,000
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	75
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	Mixed gas	Mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Spiral-wound modules	
Packing Density	m^2/m^3	300–600	
Shell-Side Fluid	—	feed	
Flue Gas Flowrate	ft^3/min	–	
CO_2 Recovery, Purity, and Pressure	%/%/bar	–	
Pressure Drops Feed/Permeate Side	psi/m	–	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	–	

Definitions:

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

MOP – Metal-Organic Polyhedron (singular)/Polyhedra (plural); 2–5-nm-sized molecule with metal bonding sites for CO_2.

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} $cm^3/(cm^2 \cdot s \cdot cm$ mercury [Hg]) at 1 atmosphere (atm) and 0°C. For non-linear materials, the dimensional units reported shall be based on flux measured in $cm^3/(cm^2 \cdot s)$ (at 1 atm and 0°C) with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} $kgmol/(m^2 \cdot s \cdot kPa)$ (SI units).

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities shall 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 or retentate stream.

technology advantages

This membrane process builds upon innovative membrane process design using CO_2-selective membranes developed by MTR. If successfully developed, such membranes would outperform current leading membranes by at least 50%.

R&D challenges

This approach of solubility-selective MMMs based on soluble MOPs directly addresses the two key challenges for membranes for CO_2 capture: (a) transport phenomena in new membrane materials, and (b) fabrication and use of the novel membrane systems in effective process designs.

status

The DXL ring opening reactions have been optimized using methanol and ethanol as initiators. New ligands were synthesized to help improve self-assemblies at coordination sites. The synthesis of the PDXLA macromonomer was successfully scaled up to 90g/batch. Further optimization of the monomers continues with the development of new chain-end groups and new compatible MOPs. The PDXLA macromonomer was also successfully polymerized and fabricated into TFC membranes.

available reports/technical papers/presentations

Lin, H.; Cook, T.; Bae, C.; Wang, Z.; Merkel, T.; Morton, F.; Sexton, A., "Rational Development of Novel Metal Organic Polyhedra-based Membranes for CO_2 Capture (FE0031736)," presented by Haiqing Lin, University of Buffalo, The State University of New York, 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-UB-SUNY-Metalorganic-Membrane.pdf*.

Lin, H.; Cook, T.; Bae, C.; Wang, Z.; Merkel, T.; Morton, F.; Sexton, A., "Rational Development of Novel Metal Organic Polyhedra-based Membranes for CO_2 Capture (FE0031736)," presented by Haiqing Lin, University of Buffalo, The State University of New York, NETL Project Kickoff Meeting, Morgantown, WV, January 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10761&filename=Aoi+%5b1c%5d+Rational+Development+of+Novel+Metal-Organic+Polyhedra-Based+Membranes+for+CO2+Capture.pdf*